\[ A = -kT \ln Q \]
Welcome 5
List of conferences and conference chairs 6
Awards and Prices in Thermodynamics conference series 7
Copenhagen overview 8
General information 10
Committees 12
Sponsors 13
Program 15
Invited lectures 31
Oral 43
Posters 131
List of participants 211
Author Index 219
Dear conference participants,

On behalf of the International Scientific Committee, we welcome you to the Thermodynamics 2015 Conference. It is a great pleasure and honor to organise the 24th meeting in the series of Thermodynamic Conferences for the first time in Copenhagen (and only the 4th outside the UK). This is indeed a historical conference series founded in 1964 by Harold Springall and championed early on by John Rowlinson and Max McGlashan.

The conference focuses on many aspects of theoretical and experimental thermodynamics and also includes a number of sessions on molecular simulation. The conference consists of invited lectures, oral and poster presentations as well as short oral talks for selected poster presentations.

Some of the highlights of the conference include the Lennard-Jones Prize and Lecture to be delivered by Professor Michael P. Allen (sponsored by Unilever and nominated by the Statistical Mechanics and Thermodynamics Group of the Royal Society of Chemistry), the Molecular Physics Lecture (sponsored by Taylor & Francis) which will be given by Professor Pablo G. Debenedetti, the Christopher Wormald Award for young scientists to Dr. Nathan A. Mahynski and, for the first time ever, the Guggenheim Medal of the Institute of Chemical Engineers which is awarded to Professor George Jackson. In addition, the conference will include over 60 oral and numerous poster presentations.

Following the tradition of the Thermodynamics Conference Series, a special issue of Molecular Physics with contributions from participants of works presented in the conference will be considered for publication, after review to the usual high standard. We encourage the conference participants to submit their contributions directly to the journal (http://mc.manuscriptcentral.com/tmph), selecting Thermodynamics 2015 Special Issue publication option. Professors Georgios Kontogeorgis and Ioannis Economou will assist the editor Professor George Jackson in the editorial process. Submissions will open on 1 September 2015 and close by 15 November 2015.

We would like to thank our sponsors for the generous funding of the conference, the International Scientific Committee for guidance during the preparation of the conference (including selection of the invited speakers and evaluations of the abstracts) and last but not least the local organising committee of the conference from CERE (Center of Energy Resources Engineering) at the Technical University of Denmark for their continuous help on all practical aspects related to the conference.

Finally, we would like to thank all of you for the participation to this conference and wish you an enjoyable stay in Copenhagen.

Best regards,

Georgios M. Kontogeorgis & Erling H. Stenby

Conference Chairmen,
Technical University of Denmark
# List of conferences and conference chairs

<table>
<thead>
<tr>
<th>Year</th>
<th>Venue</th>
<th>Conference Chairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1964</td>
<td>Keele</td>
<td>H. D. Springall</td>
</tr>
<tr>
<td>1966</td>
<td>Exeter</td>
<td>M. L. McGlashan</td>
</tr>
<tr>
<td>1968</td>
<td>Manchester</td>
<td>H. A. Skinner</td>
</tr>
<tr>
<td>1970</td>
<td>Royal Holloway</td>
<td>J. S. Rowlinson</td>
</tr>
<tr>
<td>1972</td>
<td>Lancaster</td>
<td>M. L. McGlashan</td>
</tr>
<tr>
<td>1974</td>
<td>Leeds</td>
<td>L. A. K. Staveley</td>
</tr>
<tr>
<td>1976</td>
<td>Bristol</td>
<td>J. D. Cox</td>
</tr>
<tr>
<td>1978</td>
<td>Surrey</td>
<td>J. D. Cox</td>
</tr>
<tr>
<td>1980</td>
<td>University College London</td>
<td>G. Pilcher</td>
</tr>
<tr>
<td>1984</td>
<td>Sheffield</td>
<td>I. A. McLure &amp; C. J. Wormald</td>
</tr>
<tr>
<td>1986</td>
<td>Reading</td>
<td>M. B. Ewing</td>
</tr>
<tr>
<td>1988</td>
<td>Leicester</td>
<td>R. J. Lindford</td>
</tr>
<tr>
<td>1993</td>
<td>Bristol</td>
<td>C. J. Wormald</td>
</tr>
<tr>
<td>1995</td>
<td>Reading</td>
<td>C. J. Wormald</td>
</tr>
<tr>
<td>1997</td>
<td>Surrey</td>
<td>C. J. Wormald</td>
</tr>
<tr>
<td>1999</td>
<td>Imperial College London</td>
<td>C. J. Wormald</td>
</tr>
<tr>
<td>2001</td>
<td>Bristol</td>
<td>M. P. Allen (J. P. M. Trusler)</td>
</tr>
<tr>
<td>2003</td>
<td>Cambridge</td>
<td>A. A. Louis (J. P. M. Trusler)</td>
</tr>
<tr>
<td>2005</td>
<td>Sesimbra</td>
<td>E. Filipe &amp; J. N. Canongia Lopes (J. P. M. Trusler)</td>
</tr>
<tr>
<td>2007</td>
<td>Paris</td>
<td>J.-C. de Hemptinne (G. Jackson)</td>
</tr>
<tr>
<td>2009</td>
<td>Imperial College London</td>
<td>E. A. Müller (G. Jackson)</td>
</tr>
<tr>
<td>2011</td>
<td>Athens</td>
<td>I. G. Economou (G. Jackson)</td>
</tr>
<tr>
<td>2013</td>
<td>Manchester</td>
<td>A. Masters</td>
</tr>
<tr>
<td>2015</td>
<td>Copenhagen</td>
<td>G. M. Kontogeorgis &amp; E. H. Stenby (G. Jackson)</td>
</tr>
</tbody>
</table>

Table 1. The Thermodynamic Conference Series; the TCS Committee Chair is indicated in brackets.
Awards and Prices in Thermodynamics conference series

Two prizes are currently awarded at the Thermodynamics Conference Series (TCS): the Lennard-Jones Lectureship and Prize in recognition of outstanding and enduring contributions to the field; and the Christopher Wormald Prize for the most meritorious postgraduate research as nominated by members of the community. The Lennard-Jones Prize has a long and illustrious history; it was originally awarded in alternate years by the Theoretical Chemistry Group (TCG) and the SMTG of the Royal Society of Chemistry (RSC), then biennially by the SMTG alone, and now by the TCS.

Nominations for the Lennard-Jones Prize are made by the SMTG Management Committee to the TCS during the Organization of the programme for the Thermodynamics Conference, at which the recipient of the prize gives a keynote presentation. The Lennard-Jones Prize is sponsored by Unilever.

In addition, Taylor and Francis sponsors the Molecular Physics Lecture lecture to be given at the conference.

The Guggenheim Medal of the Institution of Chemical Engineers (IChemE) will be awarded for the first time during Thermodynamics 2015. The Guggenheim Medal is awarded to one of more individuals who have made a significant recent contribution to research in thermodynamics and/or complex fluids.

<table>
<thead>
<tr>
<th>Year</th>
<th>Recipient</th>
<th>Awarded by</th>
</tr>
</thead>
<tbody>
<tr>
<td>1982</td>
<td>J. A. Pople</td>
<td>SMTG / TCG Joint</td>
</tr>
<tr>
<td>1983</td>
<td>L. A. K. Staveley</td>
<td>SMTG</td>
</tr>
<tr>
<td>1984</td>
<td>N. C. Handy</td>
<td>TCG</td>
</tr>
<tr>
<td>1985</td>
<td>J. S. Rowlinson</td>
<td>SMTG</td>
</tr>
<tr>
<td>1986</td>
<td>A. D. Buckingham</td>
<td>TCG</td>
</tr>
<tr>
<td>1987</td>
<td>J. M. Deutch &amp; I. Oppenheim</td>
<td>SMTG</td>
</tr>
<tr>
<td>1988</td>
<td>G. G. Hall</td>
<td>TCG</td>
</tr>
<tr>
<td>1989</td>
<td>P.-G. de Gennes</td>
<td>SMTG</td>
</tr>
<tr>
<td>1990</td>
<td>A. J. Stone</td>
<td>TCG</td>
</tr>
<tr>
<td>1991</td>
<td>W. Gelbart</td>
<td>SMTG</td>
</tr>
<tr>
<td>1992</td>
<td>B. T. Sutcliffe</td>
<td>TCG</td>
</tr>
<tr>
<td>1993</td>
<td>B. Widom</td>
<td>SMTG</td>
</tr>
<tr>
<td>1995</td>
<td>M. E. Fisher</td>
<td>SMTG</td>
</tr>
<tr>
<td>1997</td>
<td>D. Frenkel</td>
<td>SMTG</td>
</tr>
<tr>
<td>1999</td>
<td>E. Sackmann</td>
<td>SMTG</td>
</tr>
<tr>
<td>2001</td>
<td>D. Chandler</td>
<td>TCS</td>
</tr>
<tr>
<td>2003</td>
<td>J.-P. Hansen</td>
<td>TCS</td>
</tr>
<tr>
<td>2005</td>
<td>G. Schneider</td>
<td>TCS</td>
</tr>
<tr>
<td>2007</td>
<td>R. Evans</td>
<td>TCS</td>
</tr>
<tr>
<td>2009</td>
<td>K. Binder</td>
<td>TCS</td>
</tr>
<tr>
<td>2011</td>
<td>H. N. W. Lekkerkerker</td>
<td>TCS</td>
</tr>
<tr>
<td>2013</td>
<td>K. Gubbins</td>
<td>TCS</td>
</tr>
<tr>
<td>2015</td>
<td>M. P. Allen</td>
<td>TCS</td>
</tr>
</tbody>
</table>

Table 2. The Lennard-Jones Lectureship and Prize

<table>
<thead>
<tr>
<th>Year</th>
<th>Recipient</th>
<th>Awarded by</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>R. Allen</td>
<td>TCS</td>
</tr>
<tr>
<td>2005</td>
<td>J. Lachwa</td>
<td>TCS</td>
</tr>
<tr>
<td>2007</td>
<td>T. Lafitte &amp; E. E. Santiso</td>
<td>TCS</td>
</tr>
<tr>
<td>2009</td>
<td>F. Martinez-Veraocoechea</td>
<td>TCS</td>
</tr>
<tr>
<td>2011</td>
<td>A. Avlund</td>
<td>TCS</td>
</tr>
<tr>
<td>2013</td>
<td>E. Forte</td>
<td>TCS</td>
</tr>
<tr>
<td>2015</td>
<td>N. A. Mahynski</td>
<td>TCS</td>
</tr>
</tbody>
</table>

Table 3. The Christopher Wormald Prize for most recent conferences
Copenhagen overview

Copenhagen is a vibrant metropolis, the gateway to Scandinavia and amongst the safest and cleanest cities in the world. Copenhagen is very easy to get to and is, with an extremely efficient transportation system, also very easy to get around in. As the oldest monarchy in the world and one of the world’s greatest design capitals, the city offers a wide variety of cultural experiences and stunning architecture within its compact city centre.

1. Tivoli Hotel & Congress Center (conference venue)
2. Wake Up Copenhagen
3. Copenhagen City Hall (welcome reception)
4. Restaurant Grøften, Tivoli (conference dinner)
5. Main Station (train to/from the airport)
6. The Little Mermaid
7. Kastellet
8. Strøget (main shopping street)
9. Amalienborg (The Royal Couple’s winter residence)
10. Nyhavn (New Harbour)
11. The Opera House
12. Kings Garden
13. Copenhagen Street Food, Papirøen
14. Kødbyen (Meatpacking District, restaurant area)
15. Fisketorvet Shopping Center
General information

Venue
The Tivoli Hotel & Congress Center is located near Copenhagen Central Station, and it takes around 10 minutes by bus (bus line 30) to reach the conference venue from Copenhagen Central Station (15 minutes walking). The address is:

Tivoli Hotel & Congress Center
Arni Magnusons Gade 2-4
DK-1577 København V
Contact: (45) 44 87 00 00

Welcome Reception
All conference participants are invited to a welcome reception, which will take place in the “City Hall of Copenhagen” on Tuesday 15th September at 19:00. The City Hall opens its doors to all conference participants and offers its renowned “City Hall Pancakes” along with wine and soft drinks. You will receive your ticket for this event together with your nametag while registering. It must be shown at the entrance of the City Hall to join the reception. Please note that conference participants are responsible for arranging their own transportation to and from the City Hall. The City Hall doors will open at 18:30. Please be there in due time. The reception will take place at the second floor and we will be guided as a group to the Reception Hall. The City Hall is in the walking distance from the conference venue and the address is:
Rådhuspladsen 1, 1599 København V

Conference Dinner
The conference dinner will take place on Wednesday 16th September at Groften, a restaurant located inside the Tivoli Garden about 15 minutes walking distance from the conference venue. The exact address is: Vesterbrogade 3, 1620 København V. To get into Tivoli Garden you will need an entrance ticket which you will receive while registering for the conference together with your nametag and the conference material. This ticket will give you free access to Tivoli and not only to the conference dinner and will allow you to enjoy the garden the whole evening until it closes. Should you unfortunately loose this ticket, you will have to buy a new one at the entrance for 99 DKK. Groften is one of the oldest traditional restaurants established in Tivoli since 1874, where you will enjoy typical Danish food in a 4 courses menu, accompanied by Danish beer and snaps (or softdrinks, water or wine if you prefer). The restaurant will be aware about participants with special needs regarding the food, but those participants are also kindly requested to contact the waiters/waitresses serving their table.

Conference Lunch
Every day during the conference, lunch will be served in Tivoli Hotel & Congress Center. The lunch consists of a buffet including warm dishes, salad, cheese and cake. One soft drink per participant is served free of charge.

Special Requests
In case of special requests or questions, feel free to contact any of the conference organisation staff. The organisation staff are equipped with yellow coloured nametags.

Local Transportation
In general, the public transportation system in Copenhagen is reliable and efficient, and most areas are reachable using public transport. The most common ways of transportation are:

- S-Train, www.dsb.dk
- Metro (subway), www.m.dk
- Bus, www.movia.dk

Tickets can be bought from ticket machines in S-train stations and from the driver in the buses. The price of a ticket in a public transport
depends on how many zones the journey will cover. A 7-Eleven employee in the train stations should be able to assist with this information.

Also, journeys can be planned and price information can be obtained online at: www.rejseplanen.dk The rejseplanen is also available as an application on most mobile telephone platforms.

Taxi Services
Some of the most common taxi services in the area of Copenhagen are:
- Taxa4x35: (0045) 3535 3535
- DanTaxi: (0045) 7025 2525
- TaxiNord: (0045) 4848 4848

The taxi fares in Denmark are relatively high compared to public transportation.

Speaker Instructions
The presentation should be given to the conference organisation staff latest 15 minutes before the sessions start by USB. Please note that it is allowed to use the author’s own personal computer for the presentations (VGA output). Speaker preview is available for the presenters on request and should be done during the breaks. Our recommended and supported file formats are *.ppt, *.pptx and *.pdf. Please notify the organisation staff if you intend to use videos or audio in your presentation. It is important that these instructions are followed due to the tight programme. The total time allocated for presentations including Q&A are:
- Oral poster highlight presentation: 5 minutes
- Oral presentation: 20 minutes
- Oral invited presentation: 45 minutes

The invited talks are sponsored by: Carlsberg Foundation, CERE, Cowifonden, Molecular Physics, Otto Mønsteds Fond, Taylor & Francis, Unilever, VisitCopenhagen and Technical University of Denmark.

Poster Instructions
The poster session will take place on Thursday September 17 in the Hall next to the oral presentation rooms. The posters should be put on the stands in the morning and removed by the end of the day. The organising staff will provide the material for placing the posters on the stands. Note that posters not removed by the end of the day, will be taken down by the organising staff and discarded.

The guidelines for the oral highlights of the posters are that each speaker has a maximum of 5 minutes for their oral presentation and the presentation must be uploaded 15 minutes before the start of the session.
- Poster board size: 980 mm x 2400 mm
- Poster size: A0 (841 mm x 1189 mm)

Internet
The Tivoli Hotel & Congress Center offers free wireless internet in all areas. Choose the network Tivoli Hotel and use the password tivolihotel.

Emergency
The country code 0045 must be used before the emergency numbers in the different cases listed below.

<table>
<thead>
<tr>
<th></th>
<th>Police</th>
<th>Health</th>
<th>Fire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emergency</td>
<td>112</td>
<td>112</td>
<td>112</td>
</tr>
<tr>
<td>Acute</td>
<td>114</td>
<td>1813</td>
<td>112</td>
</tr>
</tbody>
</table>
### Committees

#### International Scientific Committee

<table>
<thead>
<tr>
<th>Name</th>
<th>Title</th>
<th>Company</th>
<th>Country</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Georgios Kontogeorgis</td>
<td>Professor</td>
<td>Technical University of Denmark</td>
<td>Denmark</td>
<td>Conference Acting Chair</td>
</tr>
<tr>
<td>Erling H. Stenby</td>
<td>Professor</td>
<td>Technical University of Denmark</td>
<td>Denmark</td>
<td>Conference Acting Chair</td>
</tr>
<tr>
<td>George Jackson</td>
<td>Professor</td>
<td>Imperial College, London</td>
<td>UK</td>
<td>Conference Treasurer</td>
</tr>
<tr>
<td>Amparo Galindo</td>
<td>Professor</td>
<td>Imperial College, London</td>
<td>UK</td>
<td></td>
</tr>
<tr>
<td>Stefano Brandani</td>
<td>Professor</td>
<td>University of Edinburgh</td>
<td>UK</td>
<td></td>
</tr>
<tr>
<td>Andrew J. Masters</td>
<td>Professor</td>
<td>University of Manchester</td>
<td>UK</td>
<td>Previous conference chair</td>
</tr>
<tr>
<td>Ioannis Economou</td>
<td>Professor</td>
<td>Texas A&amp;M University</td>
<td>Qatar</td>
<td></td>
</tr>
<tr>
<td>Nicolas von Solms</td>
<td>Assoc. Professor</td>
<td>Technical University of Denmark</td>
<td>Denmark</td>
<td></td>
</tr>
<tr>
<td>Kim Knudsen</td>
<td>Doctor</td>
<td>Haldor Topsoe</td>
<td>Denmark</td>
<td></td>
</tr>
<tr>
<td>Even Solbraa</td>
<td>Doctor</td>
<td>Statoil</td>
<td>Norway</td>
<td></td>
</tr>
<tr>
<td>Francois Montel</td>
<td>Doctor</td>
<td>Total</td>
<td>France</td>
<td></td>
</tr>
</tbody>
</table>

#### Local Organising Committee

<table>
<thead>
<tr>
<th>Name</th>
<th>Company</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Patricia Wagner</td>
<td>Technical University of Denmark</td>
<td>Denmark</td>
</tr>
<tr>
<td>Susana Almeida</td>
<td>Technical University of Denmark</td>
<td>Denmark</td>
</tr>
<tr>
<td>Christian Ove Carlsson</td>
<td>Technical University of Denmark</td>
<td>Denmark</td>
</tr>
<tr>
<td>Anne Louise Biede</td>
<td>Technical University of Denmark</td>
<td>Denmark</td>
</tr>
<tr>
<td>Farhad Varzandeh</td>
<td>Technical University of Denmark</td>
<td>Denmark</td>
</tr>
</tbody>
</table>
Sponsors

CERE
Center for Energy Resources Engineering

Technical University of Denmark

CARLSBERG FOUNDATION

COWI fonden

OTTO MØNSTEDS FOND

VISITCOPENHAGEN.COM

Taylor & Francis
Taylor & Francis Group

Unilever

Molecular Physics
Program
Tuesday 15 September

12:00 – 14:00
Registration

14:00 – 14:15
Welcome session
Georgios Kontogeorgis & Erling H. Stenby, Conference chairs

14:15 – 15:00
Pablo G. Debenedetti – Princeton University
Chair: George Jackson

15:00 – 15:45
Towards a coarse grained molecular representation valid both for static and transport properties
Guillaume Galliero – Université de Pau et des Pays de l’Adour
Chair: Andrew Masters

15:45 – 16:15
Coffee/ Tea break
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
<th>Speaker/Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:15-16:35</td>
<td>OP1</td>
<td>Comparison of absolute free energy calculation methods for fluids and solids</td>
<td>Martin B. Sweatman – University of Edinburgh</td>
</tr>
<tr>
<td>16:35-16:55</td>
<td>OP6</td>
<td>CO₂ Capture and Transport: Thermodynamic Investigation of Relevant Fluid Mixtures</td>
<td>Dimitra Aslanidou – Aristotle University of Thessaloniki</td>
</tr>
<tr>
<td>16:35-16:55</td>
<td>OP7</td>
<td>Surface Tension Calculations of Liquid Metals</td>
<td>Olivier Durand – CEA</td>
</tr>
<tr>
<td>16:55-17:15</td>
<td>OP7</td>
<td>Thermophysical Properties of Aqueous Amine Solutions for CO₂ Capture</td>
<td>Jiafei Zhang – Imperial College London</td>
</tr>
<tr>
<td>16:55-17:15</td>
<td>OP3</td>
<td>Calculating free energies of atmospherically relevant clusters using non-equilibrium molecular dynamics</td>
<td>Gabriel Lau – Imperial College London</td>
</tr>
<tr>
<td>17:15-17:35</td>
<td>OP8</td>
<td>MD Simulations of Low-Salinity Enhanced Oil Recovery. A molecular-level description of interactions between charged colloid particles, organic oil molecules and simple salt ions</td>
<td>Thomas Underwood – Durham University</td>
</tr>
<tr>
<td>17:15-17:35</td>
<td>OP4</td>
<td>The thermodynamics of low dimensional materials: Finding solvents for graphene, carbon nanotubes and their relatives</td>
<td>Henry Bock – Heriot Watt University</td>
</tr>
<tr>
<td>17:35-17:55</td>
<td>OP9</td>
<td>Liquid-Liquid Equilibrium of Aqueous Two-phase Systems for Protein Partitioning from goat milk whey in-nature</td>
<td>Camila G. Pereira – Federal University of Rio Grande do Norte</td>
</tr>
<tr>
<td>17:35-17:55</td>
<td>OP5</td>
<td>Mixtures of Hydrogenated and Fluorinated Alcohols: Thermodynamics, Spectroscopy and Simulation</td>
<td>Eduardo J. M. Filipe – Universidade de Lisboa</td>
</tr>
<tr>
<td>17:35-17:55</td>
<td>OP10</td>
<td>Modeling of the phase equilibrium and the thermodynamic properties of aqueous systems from an industrial point of view</td>
<td>Eirini K. Karakatsani – Haldor Topsoe A/S</td>
</tr>
<tr>
<td>19:00</td>
<td></td>
<td>Welcome reception - Copenhagen City Hall</td>
<td></td>
</tr>
</tbody>
</table>

**Parallel sessions**

16:15 - 18:00

**Simulation - 1**

Venue: Harlekin/ Columbine

Chair: Erich A. Müller

**Engineering applications**

Venue: Pjerrot

Chair: Kim Knudsen
<table>
<thead>
<tr>
<th>Time</th>
<th>Invited Talks</th>
</tr>
</thead>
</table>
| 9:00 – 9:45 | **Understanding the Self-Assembly and Phase Behavior of Skin Lipids**  
  Clare McCabe – Vanderbilt University |
| 9:45 – 10:30 | **Modelling at the appropriate lengthscale for industrial applications**  
  Massimo Noro – Unilever |
<p>| 10:30 – 11:00 | <strong>Coffee/ Tea break</strong>                                                          |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Topic</th>
<th>Presenter</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:00 – 11:20</td>
<td><strong>OP11</strong></td>
<td>Molecular simulation of ionic liquid solvents: Bulk properties and the effect of confinement</td>
<td>Niki Vergadou – Demokritos</td>
</tr>
<tr>
<td></td>
<td><strong>OP15</strong></td>
<td>Phase behaviour of the system (carbon dioxide + n-heptane + methylbenzene) and (carbon dioxide + methane + methylbenzene): A comparison between experimental data and SAFT-(\gamma)-Mie predictions</td>
<td>Saif. Z Al Ghafri – Qatar Carbonates and Carbon Storage Research Centre</td>
</tr>
<tr>
<td>11:20 – 11:40</td>
<td><strong>OP12</strong></td>
<td>Determining the Factors that Govern the Permeation of Ions into Graphene Oxide Membranes using Molecular Simulation</td>
<td>Christopher D. Williams – University of Manchester</td>
</tr>
<tr>
<td></td>
<td><strong>OP16</strong></td>
<td>A Comprehensive Investigation on (\text{CO}_2) Solubility and Kinetics in Tricyanomethanide-based Ionic Liquids: Experiments and ePC-SAFT Modeling</td>
<td>Lawien F. Zubeir – Eindhoven University of Technology</td>
</tr>
<tr>
<td>11:40 – 12:00</td>
<td><strong>OP13</strong></td>
<td>Non-equilibrium molecular dynamics simulations of water permeation through graphene-based membranes</td>
<td>Frederike Jaeger – Imperial College London</td>
</tr>
<tr>
<td></td>
<td><strong>OP17</strong></td>
<td>Multi-scale modelling of polyamide thin films</td>
<td>Jordan Muscatello – Imperial College London</td>
</tr>
<tr>
<td>12:00 – 12:20</td>
<td><strong>OP14</strong></td>
<td>Wetting on Grafted Thermo-responsive Polymer Brushes: A Molecular Dynamics Study</td>
<td>Debdip Bhandary – Indian Institute of Technology Kanpur</td>
</tr>
<tr>
<td></td>
<td><strong>OP18</strong></td>
<td>Modeling thermodynamic derivative properties of ionic liquids with ePC-SAFT</td>
<td>Xiaoyan Ji – Lulea University of Technology</td>
</tr>
<tr>
<td>12:30 – 13:30</td>
<td></td>
<td>Lunch, Brasseriet</td>
<td></td>
</tr>
</tbody>
</table>
Wednesday 16 September
– continued –

13:30–14:00
Christopher Wormald Award: Entropic Control over Nanoscale Colloidal Crystals
Nathan A. Mahynski – Princeton University
Chair: Georgios Kontogeorgis

14:00–14:30
Guggenheim Medal Award: The Legacy of Edward Guggenheim to Statistical Thermodynamics
George Jackson
Chair: Ioannis Economou

14:30–14:50
Modeling coarse grained linear alkanes and polymers using SAFT-\(\gamma\)-Mie using molecular dynamics simulations
Erich A. Müller – Imperial College London

14:50–15:10
Combining quantum chemistry and statistical mechanics for thermodynamic property prediction involving natural complex materials: Ligno-cellulosic biomass, kerogen, asphaltenes, clay minerals, and micro emulsions
Philippe Ungerer – Materials Design S.A.R.L.

15:10–15:30
Group Photo
Outside Main Entrance Hotel

15:30–16:00
Coffee/ Tea break
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
<th>Speaker/Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:00 – 16:20</td>
<td>OP21</td>
<td>Phase equilibria of methane and carbon dioxide hydrates using molecular dynamics simulations</td>
<td>Vasileios K. Michalis – Texas A&amp;M University at Qatar</td>
</tr>
<tr>
<td>16:00 – 16:20</td>
<td>OP27</td>
<td>Thermodynamic Modelling with SAFT of the properties of Aqueous Electrolyte solutions for Nuclear Waste Processing</td>
<td>Mark Bankhead – National Nuclear Laboratory</td>
</tr>
<tr>
<td>16:20 – 16:40</td>
<td>OP22</td>
<td>Multi-scale simulation of the early stages of zeolite nucleation</td>
<td>Carlos Nieto-Draghi – IFP Energies nouvelles</td>
</tr>
<tr>
<td>16:20 – 16:40</td>
<td>OP28</td>
<td>Evaluation of the quadrupolar CPA EoS for modeling multicomponent CO₂-mixtures</td>
<td>Martin G. Bjørner – Technical University of Denmark</td>
</tr>
<tr>
<td>16:40 – 17:00</td>
<td>OP23</td>
<td>Spatial resolution of thermal transport properties in simulated nanomaterials</td>
<td>Niall Jackson – Imperial College London</td>
</tr>
<tr>
<td>16:40 – 17:00</td>
<td>OP29</td>
<td>Predicting the formation of liquid-liquid phase splits from mixing rules thermodynamically correct in the limit of zero pressure</td>
<td>Stefano Brandani – University of Edinburgh</td>
</tr>
<tr>
<td>17:00 – 17:20</td>
<td>OP24</td>
<td>Taming Thermophoretic transport across nanopores: Novel approaches for nanofluidic analytical devices</td>
<td>Silvia Di Lecce – Imperial College London</td>
</tr>
<tr>
<td>17:00 – 17:20</td>
<td>OP30</td>
<td>Modelling electrolytes using a single-parameter molecular-based equation of state: Improving solvation energies</td>
<td>Daniel Kunisch Eriksen – Imperial College London</td>
</tr>
<tr>
<td>17:20 – 17:40</td>
<td>OP25</td>
<td>Hydrogen bonding in hybrid scale models</td>
<td>Richard J. Gowers – University of Manchester</td>
</tr>
<tr>
<td>17:20 – 17:40</td>
<td>OP31</td>
<td>Pressure-Driven Molecular Dynamics Simulations of an Electrolytes Solution through a polyamide membrane</td>
<td>Aziz Ghoufi – Université de Rennes</td>
</tr>
<tr>
<td>17:40 – 18:00</td>
<td>OP26</td>
<td>Self-Assembly of High-Symmetry Planar Rings</td>
<td>Carlos Avendano – University of Manchester</td>
</tr>
<tr>
<td>17:40 – 18:00</td>
<td>OP32</td>
<td>The complementing rôles of Coulombic forces and association in the thermodynamics of selected room-temperature ionic liquids</td>
<td>Fernando del Rio – Universidad Autónoma Metropolitana</td>
</tr>
<tr>
<td>19:00</td>
<td></td>
<td>Conference dinner (Grøften – Tivoli)</td>
<td></td>
</tr>
</tbody>
</table>
### Thursday 17 September

#### Lennard-Jones Prize and Lecture: Liquid crystal structure and dynamics: What can computer simulations tell us?

**Michael P. Allen – University of Warwick**

#### Plenary Lectures

**Venue: Harlekin/ Columbine**

**Chair: Andrew Masters**

<table>
<thead>
<tr>
<th>Time</th>
<th>Lecture</th>
<th>Speaker</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:00-9:45</td>
<td><strong>Lennard-Jones Prize and Lecture</strong></td>
<td><strong>Liquid crystal structure and dynamics: What can computer simulations tell us?</strong></td>
<td><strong>Michael P. Allen – University of Warwick</strong></td>
</tr>
<tr>
<td>9:45-10:05</td>
<td><strong>Simulations of mean ionic activity coefficients and solubilities in aqueous electrolyte solutions</strong></td>
<td><strong>Athanassios Panagiotopoulos</strong></td>
<td><strong>Princeton University</strong></td>
</tr>
<tr>
<td>10:05-10:25</td>
<td><strong>Atomistic Molecular Dynamics Simulations of Transport Properties for the H$_2$O+CO$_2$+NaCl mixture at conditions relevant to CCS processes</strong></td>
<td><strong>Ioannis G. Economou</strong></td>
<td><strong>Texas A&amp;M University at Qatar</strong></td>
</tr>
<tr>
<td>10:25-10:45</td>
<td><strong>Molecular simulation of polarizable models of electrolytes: Concentration dependence of the chemical potentials, density and solubility</strong></td>
<td><strong>Ivo Nezbeda</strong></td>
<td><strong>J.E. Purkinje University</strong></td>
</tr>
<tr>
<td>10:45-11:00</td>
<td><strong>Coffee/ Tea break</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
<td>Venue</td>
<td>Chair</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------------</td>
<td>------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>11:00 – 11:20</td>
<td>Nanoparticle thermophoresis under thermal gradients: Thermophobic or thermophilic, ... and why?</td>
<td>Harlekin/Columbine</td>
<td>Athanassios Panagiotopoulos</td>
</tr>
<tr>
<td>11:20 – 11:40</td>
<td>Coarse graining of polymer systems employing SAFT</td>
<td>Harlekin/Columbine</td>
<td>Kai Langenbach</td>
</tr>
<tr>
<td>11:40 – 12:00</td>
<td>The molecular segregation of tri-butyl phosphate in an organic diluent and its relevance to nuclear extraction processes</td>
<td>Harlekin/Columbine</td>
<td>Kai Langenbach</td>
</tr>
<tr>
<td>12:00 – 12:20</td>
<td>Computer-Based Discovery of Surfactants</td>
<td>Harlekin/Columbine</td>
<td>Kai Langenbach</td>
</tr>
<tr>
<td>12:20 – 12:40</td>
<td>Developing Peptoid Simulation Models</td>
<td>Harlekin/Columbine</td>
<td>Kai Langenbach</td>
</tr>
<tr>
<td>12:40 – 13:00</td>
<td>Mixing rules for modelling asymmetric systems with water</td>
<td>Harlekin/Columbine</td>
<td>Kai Langenbach</td>
</tr>
<tr>
<td>13:00 – 13:20</td>
<td>Computer Simulation of chromonic materials: The influence of molecular structure on self-assembly</td>
<td>Harlekin/Columbine</td>
<td>Kai Langenbach</td>
</tr>
<tr>
<td>13:20 – 13:40</td>
<td>Prediction of the phase behaviour of hydrocarbon and water mixtures with the SAFT-γ-Mie group-contribution equation of state: properties at infinite dilution</td>
<td>Harlekin/Columbine</td>
<td>Kai Langenbach</td>
</tr>
<tr>
<td>12:30 – 13:30</td>
<td>Lunch, Brasseriet</td>
<td>Tivoli Hotel &amp; Congress Center</td>
<td></td>
</tr>
</tbody>
</table>

**OP36**
Nanoparticle thermophoresis under thermal gradients: Thermophobic or thermophilic, ... and why?
Irene Iriarte-Carretero – Imperial College London

**OP40**
Coarse graining of polymer systems employing SAFT
Jos Tasche – Durham University

**OP37**
The molecular segregation of tri-butyl phosphate in an organic diluent and its relevance to nuclear extraction processes
Junju Mu – University of Manchester

**OP41**
Computer-Based Discovery of Surfactants
Mariah Ritz – North Carolina State University

**OP38**
Developing Peptoid Simulation Models
Laura J. Weiser – North Carolina State University

**OP42**
Mixing rules for modelling asymmetric systems with water
Duncan Paterson – Technical University of Denmark

**OP39**
Computer Simulation of chromonic materials: The influence of molecular structure on self-assembly
Mark R. Wilson – Durham University

**OP43**
Prediction of the phase behaviour of hydrocarbon and water mixtures with the SAFT-γ-Mie group-contribution equation of state: properties at infinite dilution
Panatpong Hutacharoen – Imperial College London
### Interfaces

**Venue:** Harlekin/Columbine  
**Chair:** Jadran Vrabec

<table>
<thead>
<tr>
<th>Time</th>
<th>Session Code</th>
<th>Title</th>
<th>Speaker/Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>13:30</td>
<td>OP44</td>
<td>Molecular modelling of interfacial properties by multi-criteria optimization</td>
<td>Martin Horsch – University of Kaiserslautern</td>
</tr>
<tr>
<td>13:30</td>
<td>OP50</td>
<td>Solubility and diffusion of small molecules in polymers</td>
<td>Peter Ahlström – University of Borås</td>
</tr>
<tr>
<td>13:45</td>
<td>OP45</td>
<td>First Principles Prediction of Liquid/Liquid Interfacial Tension</td>
<td>Martin P. Andersson – University of Copenhagen</td>
</tr>
<tr>
<td>13:30</td>
<td>OP46</td>
<td>Phase behaviour and interfacial properties of ternary system (\text{CO}_2 + \text{n-butane} + \text{n-decane}:) Coarse-Grained theoretical modelling and Molecular Simulations</td>
<td>Andrés Mejía – Universidad de Concepción</td>
</tr>
<tr>
<td>13:50</td>
<td>OP52</td>
<td>Thermodynamic properties of inverse patchy colloids</td>
<td>Gerhard Kahl – Technische Universität Wien</td>
</tr>
<tr>
<td>14:00</td>
<td>OP47</td>
<td>Molecular Modelling and Simulation of Wetting on Solid Surfaces</td>
<td>Maximilian Kohns – University of Kaiserslautern</td>
</tr>
<tr>
<td>14:00</td>
<td>OP53</td>
<td>Surface photografting of acrylic acid on poly(dimethysiloxane). Experimental and dissipative particle dynamics studies</td>
<td>Carlos Nieto-Draghi – IFP Energies nouvelles</td>
</tr>
<tr>
<td>14:10</td>
<td>OP48</td>
<td>Thermodynamics and statistical mechanics of wetting transitions: Fluid phase behavior in prototypical nanostructured substrates</td>
<td>P. Yatsyshin – Imperial College London</td>
</tr>
<tr>
<td>14:10</td>
<td>OP54</td>
<td>Application of Lattice Cluster Theory to Solid-Liquid-Liquid Equilibria of Semi-crystalline Polymer Solutions</td>
<td>Kai Langenbach – Technical University of Berlin</td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
<td>Title</td>
<td>Speaker</td>
</tr>
<tr>
<td>----------</td>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>15:10 – 15:30</td>
<td>OP49</td>
<td>Prediction of Interfacial Properties of Industrially Relevant Fluid Mixtures by Molecular Simulation and Density Gradient Theory + PC-SAFT</td>
<td>Stephan Werth – University of Kaiserslautern</td>
</tr>
<tr>
<td>15:30 – 16:00</td>
<td>OP55</td>
<td>Solubility predictions for active pharmaceutical ingredients using the SAFT-γ-Mie approach</td>
<td>Simon Dufal – Imperial College London</td>
</tr>
<tr>
<td>15:30 – 16:00</td>
<td></td>
<td>Coffee/ Tea break</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
<td>Title</td>
<td>Speaker/Institution</td>
</tr>
<tr>
<td>------------</td>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>16:00 - 16:05</td>
<td>PP1</td>
<td>Comparison of GERG-2008 and Soave-BWR for modeling of natural gas mixtures</td>
<td>Farhad Varzandeh – Technical University of Denmark</td>
</tr>
<tr>
<td>16:05 - 16:10</td>
<td>PP10</td>
<td>A predictive square-gradient route to the interfacial tension of fluids</td>
<td>Daniel Kunisch Eriksen – Imperial College London</td>
</tr>
<tr>
<td>16:10 - 16:15</td>
<td>PP2</td>
<td>High pressure phase equilibrium measurement of methane + n-decane</td>
<td>Teresa Regueira – Technical University of Denmark</td>
</tr>
<tr>
<td>16:15 - 16:20</td>
<td>PP11</td>
<td>Coarse-Grained SAFT-(\gamma)-Mie for Understanding Wax Deposition in Crude Oil</td>
<td>Sara Shahrudin – Imperial College London</td>
</tr>
<tr>
<td>16:20 - 16:25</td>
<td>PP3</td>
<td>Water structure effects of anions and their volumes</td>
<td>Yizhak Marcus – Hebrew University of Jerusalem</td>
</tr>
<tr>
<td>16:25 - 16:30</td>
<td>PP4</td>
<td>Prediction of Self Diffusion Coefficients from Chapman-Enskog-Theory in Combination with PC-SAFT or LCT-EOS</td>
<td>Hendryk Rudolph – TU Berlin</td>
</tr>
<tr>
<td>16:30 - 16:35</td>
<td>PP12</td>
<td>Experimental study of phase equilibria of systems involved in CH₄ hydrate production coupled with CO₂ sequestration</td>
<td>Ludovic Legoix – IFREMER</td>
</tr>
<tr>
<td>16:40 - 16:45</td>
<td>PP5</td>
<td>Thermodynamic Equilibrium</td>
<td>Richard M. Gibbons</td>
</tr>
<tr>
<td>16:45 - 16:50</td>
<td>PP13</td>
<td>Development of Predictive Association Models for the Description of Multifunctional Molecules with the CPA EoS</td>
<td>André M. Palma – University of Aveiro</td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
<td>Title</td>
<td>Speaker/Institution</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td>----------------------------------------------------------------------</td>
<td>---------------------------------------------------------</td>
</tr>
<tr>
<td>16:25 – 16:30</td>
<td>PP6</td>
<td>Thermodynamic investigation of ternary electrolyte system NiCl₂ + Triton X-100 + H₂O at T = 298.15 K</td>
<td>Mohammad.A. Bagherinia – Islamic Azad University</td>
</tr>
<tr>
<td>16:30 – 16:35</td>
<td>PP15</td>
<td>Applications of The Virial Expansion</td>
<td>Tom Bourne – University of Manchester</td>
</tr>
<tr>
<td>16:30 – 16:35</td>
<td>PP7</td>
<td>Parameterization and Evaluation of the Electrolyte CPA Equation of State</td>
<td>Anders Schlaikjer – Technical University of Denmark</td>
</tr>
<tr>
<td>16:35 – 16:40</td>
<td>PP16</td>
<td>Universal scaling behavior of short flexible Mie n-6 chains: A simple and accurate correlation for the influence parameters</td>
<td>José Matías Garrido – Universidad de Concepción</td>
</tr>
<tr>
<td>16:40 – 16:45</td>
<td>PP8</td>
<td>Interfacial Supermittivity of Confined Water at the Nanoscale</td>
<td>Aziz Ghoufi – Université de Rennes</td>
</tr>
<tr>
<td>16:40 – 16:45</td>
<td>PP17</td>
<td>Asphaltene aggregation process analyzed by scattering experiments and molecular simulation</td>
<td>Carlos Nieto-Drighi – IFP Energies Nouvelles</td>
</tr>
<tr>
<td>16:45 – 17:00</td>
<td>PP9</td>
<td>The effect of accounting for the contribution of the heat capacity in solubility predictions</td>
<td>Sara Febra – Imperial College London</td>
</tr>
<tr>
<td>17:00 – 19:00</td>
<td>PP18</td>
<td>Volumetric and ultrasonic study of mixtures of Benzyl alcohol with 1-propanol, 2-propanol, and 1, 2-propanediol, 1, 3-propanediol and t-butanol at T=(298.15-323.15) K and atmospheric pressure: Measurement and prediction</td>
<td>Mohammad M. Alavianmehr – Shiraz University of Technology</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Poster session with refreshments</td>
<td></td>
</tr>
</tbody>
</table>
## Friday 18 September

### Parallel sessions
9:00 - 10:30

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
<th>Speaker(s)</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 - 09:20</td>
<td>OP56</td>
<td>Temperature-dependent sublimation enthalpy for molecular crystals obtained from high-level quantum chemistry calculations</td>
<td>Ctirad Červinka</td>
<td>Institute of Chemical Technology Prague</td>
</tr>
<tr>
<td>09:20 - 09:40</td>
<td>OP60</td>
<td>Transport of Gases in Polymers for Offshore Applications</td>
<td>Susana Almeida</td>
<td>Technical University of Denmark</td>
</tr>
<tr>
<td>09:40 - 10:00</td>
<td>OP57</td>
<td>Structure of water confined in nanopores</td>
<td>Malgorzata Sliwinska-Bartkowiak</td>
<td>North Carolina State University</td>
</tr>
<tr>
<td>10:00 - 10:20</td>
<td>OP58</td>
<td>Confinement Effect on Chemical Reaction Yield: The Nitric Oxide Dimer Reaction</td>
<td>Deepti Srivastava</td>
<td>North Carolina State University</td>
</tr>
<tr>
<td>09:40 - 10:00</td>
<td>OP61</td>
<td>Clay suspensions in and out of equilibrium</td>
<td>Jeroen S. van Duijneveldt</td>
<td>University of Bristol</td>
</tr>
<tr>
<td>10:00 - 10:20</td>
<td>OP59</td>
<td>Optimisation of Interactions and Pathways for Self Assembly</td>
<td>Mark A. Miller</td>
<td>Durham University</td>
</tr>
<tr>
<td>10:00 - 10:20</td>
<td>OP62</td>
<td>Modelling the self-assembly of polyphilic molecules via coarse-grained simulations</td>
<td>Maziar Fayaz-Torshizi</td>
<td>Imperial College London</td>
</tr>
</tbody>
</table>

### Coffee/ Tea break
10:30 - 11:00
The Role of Interfacial Water on Water Desalination, Hydrates Management, and Oil & Gas Production
Alberto Striolo – University College London

Presentation of Thermodynamics 2017
Martin Sweatman

Closing Thermodynamics 2015

Lunch, Brasserie
Invited lectures

Thermodynamics
The physical properties of supercooled water have been a source of continued interest since the pioneering work of Speedy and Angell, who reported sharp increases in the response functions upon isobaric cooling [1]. One intriguing hypothesis that has been formulated to explain this behavior is the existence of a metastable liquid-liquid transition at deeply supercooled conditions [2]. The preponderance of experimental evidence is consistent with this hypothesis (e.g., [3], [4]), although no definitive proof exists to date. Computational studies have played an important role in this area [2], [5]-[13]. State-of-the-art free energy techniques provide clear evidence of a liquid-liquid transition in the ST2 model [14] of water [15], including the identification of three phases at the same, deeply supercooled thermodynamic conditions: two metastable liquids in equilibrium, and a stable crystal [15]. Recent calculations on tunable tetrahedral models support this key conclusion of the free energy results [16].

A coarse-grained implementation of the forward-flux sampling technique [17] allows the direct calculation of the rate of homogeneous ice nucleation in the TIP4P/Ice molecular model of water [18] and provides new insights into the mechanism of ice formation at deeply supercooled conditions. The early stages of nucleation are characterized by a competition between cubic and hexagonal ice polymorphs. Transition states are rich in cubic ice, rather than in the thermodynamically stable hexagonal ice.

Modern computational methods provide important insights into the thermodynamics and kinetics of deeply supercooled water, complementing ongoing experimental studies.

References
Towards a coarse grained molecular representation valid both for static and transport properties

Guillaume Gallier

Laboratoire des Fluides Complexes et leurs Réservoirs (UMR-5150 with CNRS and TOTAL), Université de Pau et des Pays de l'Adour, BP 1155, F-64013 Pau Cedex, FRANCE

Corresponding author e-mail: guillaume.galliero@univ-pau.fr

1. Introduction

For the time being, there exist two main philosophies to estimate fluid thermophysical (equilibrium, interfacial and transport) properties under typical petroleum reservoir conditions:

- Precise molecular representations combined with extensive molecular simulations (accurate but time consuming, dozens of parameters per species, not widely used in the industry)
- Macroscopic correlations, which are property-dependent and designed for purpose (fast but inadequate when extrapolated to new systems, three to four parameters per species, widely used in the industry)

In this work, we are looking for the best of these worlds and we therefore propose a compromise between these approaches. To do so, we are developing a scheme based on a coarse-grained molecular model that will require a limited number of “microscopic” parameters to describe each species, yet providing accurate description of all “macroscopic” thermophysical properties simultaneously.

2. Towards a coarse grained representation

As an initial coarse grained molecular model we have employed the flexible Lennard-Jones Chain (LJC) model. It has been already largely studied by molecular simulations and accurate equation of states/correlation have been developed to describe its thermophysical properties [1-3]. Furthermore, as this model is fully defined by three “molecular” parameters, a simple link of these parameters with some macroscopic quantities such as critical point location and acentric factor can be established.

As shown in Figure 1, the LJC model is sufficient to provide a reasonable description of the equilibrium properties of some normal-alkanes. Unfortunately, this three parameters model is insufficient to provide accurately the liquid viscosity of long chains at low temperature with the same “molecular” parameters [4].

As we will show during the conference there exist some possibilities to improve these results while keeping a simple coarse grained molecular model (in figure 1 the example of the Mie chain fluid is shown). In addition, we will show that, to ensure the uniqueness of the set of “molecular” parameters associated to the coarse grained model, one has to take into account not only equilibrium properties but also transport properties.
3. Conclusion

In this work a heuristic scheme is proposed to define the simplest coarse grained molecular model able to provide simultaneously equilibrium, interfacial and transport properties of simple fluids. One interest of such an approach is that the so defined coarse grained model can be combined with modern molecular thermodynamics to deduce its fluid thermophysical properties without molecular simulations [5-7].

References
Understanding the Self-Assembly and Phase Behavior of Skin Lipids

Clare McCabe

Department of Chemical & Biomolecular Engineering and Department of Chemistry, Vanderbilt University, Nashville TN 37235-1604

Corresponding author e-mail: c.mccabe@vanderbilt.edu

The outermost layer of the skin (the stratum corneum) consists of skin cells embedded in a rich lipid matrix, whose primary role is to provide a barrier to foreign agents entering the body and to water leaving the body. This lipid system is unique in biological membranes in that it is composed of ceramides, cholesterol, and free fatty acids, with phospholipids, which are the major components of most biological membranes, being completely absent. This unique composition enables the lipids of the stratum corneum form highly organized lamellae, which in turn are believed to control barrier function. While much is known about the nature of the skin lipids from extensive experimental studies, a clear understanding of how and why these molecules assemble into the structures observed through microscopy and biophysical measurements does not yet exist. In order to probe lipid phase behavior and molecular level arrangement, we are performing molecular simulations with both atomistic and coarse-grained models of key stratum corneum lipids and water. The development and validation of the coarse-grained models will be discussed alongside the results of simulation studies for simple mixed lipid systems that provide insight into the lamellar organization and enable us to validate the models developed while working towards the study of more complex stratum corneum systems.
Modelling at the appropriate lengthscale for industrial applications

Massimo Noro

Strategic Science Group, Unilever R&D Port Sunlight (UK)

Corresponding author e-mail: Massimo.Noro@Unilever.com

A large portion of the European manufacturing sector is based on complex liquid formulations, for example, in the area of home care and personal care products. Many of them are underpinned by similar liquid mesostructures. We need to choose the appropriate length-scale tools for the appropriate product mesostructure application [1]. Coarse-grained mesoscale calculations insights to be gained, for example, on the mechanism of structure formation and on the interactions with surfaces of interest.

Dissipative Particle Dynamics is a core mesoscale capability that has been used to calculate the structure of typical products like laundry liquids, containing, often, complex mixtures of surfactants, polymers and a range of other ingredients. The challenge is to develop and employ appropriate force field parameters that accurately reproduce the essential thermodynamic questions of interest [2]. The issue becomes especially important when dealing appropriately with charged and partially dissociated surfactant ingredients [3].

Reproducing and predicting the self-assembly behaviour at the low concentration regime is not trivial. We have studied complex surfactant/polymer mixtures [4] and developed rapid phase-diagram calculation approaches that shed light on transient structures as well. Recent extensions make these approaches more palatable for industrial applications. The shape, symmetry and size of complex aggregates can be detected automatically thanks to modern computational methodologies.

References
Entropic Control over Nanoscale Colloidal Crystals

Nathan A. Mahynski\textsuperscript{1}, Sanat K. Kumar\textsuperscript{2}, Athanassios Z. Panagiotopoulos\textsuperscript{1}

\textsuperscript{1}Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544,  
\textsuperscript{2}Department of Chemical Engineering, Columbia University, New York, NY 10027

Corresponding author e-mail: mahynski@princeton.edu

Globally ordered colloidal lattices have broad utility in a wide range of novel optical and catalytic devices, for example, as photonic bandgap materials. However, the self-assembly of stereospecific structures is often confounded by defects created by, for instance, polymorphism. Weak free energy differences and complex hierarchical length scales often characterize ensembles of these structures, making it difficult to produce a single morphology at will. Current techniques to handle this problem adopt one of two approaches: that of the “top-down”, or “bottom-up” methodology whereby structures are engineered starting from the largest, or smallest relevant length scales, respectively. The ubiquitous design strategy in such approaches is energy minimization; many colloids have been computationally engineered with anisotropic pairwise interactions to achieve morphological control in theory. However, the complexity of these designs often makes experimental realization difficult. In this talk I will discuss how extensive computer simulations show that the introduction of polymeric co-solutes into crystallizing colloidal suspensions can be used to intelligently direct the resulting nano- and mesoscale colloidal structures by relying upon the polymer’s entropic interactions alone \cite{1-3}. These entropic interactions result entirely from the interplay between the polymer’s internal degrees of freedom and the void structure of a material. This represents a novel third design paradigm that has the potential to significantly simplify control over colloidal polymorphism. I will elaborate on how to rationally design the co-solute structure to thermodynamically stabilize a single desired polymorph in a binary mixture, and the consequences that thermal perturbations have on this effect \cite{2}. I will then offer insights into how to design temperature-dependent co-solute “switches” that allow the stability of a polymorph to be controlled via experimentally accessible parameters \cite{3}. As a whole, this work represents a novel entropic route to polymorphic control that has not yet been explored.

References

\cite{1} Mahynski, Panagiotopoulos, Meng, and Kumar, \textit{Nature Communications} 5, 4472 (2014).
\cite{3} Mahynski, Kumar, and Panagiotopoulos, \textit{(submitted)}. 
Liquid crystal structure and dynamics: what can computer simulations tell us?

Michael P. Allen

Department of Physics, University of Warwick, Coventry CV4 7AL, U. K. and H. H. Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, U. K.

Corresponding author e-mail: m.p.allen@warwick.ac.uk and m.p.allen@bristol.ac.uk

1. Introduction

The description of liquid crystals [1] at the mesoscopic level is standard material in textbooks [2,3]. However, the link with molecular properties is still an active area of experimental and theoretical research. Molecular simulation is a rather mature field, but the modelling of liquid crystals at the atomic level is still challenging, due to the length- and time-scales involved. Consequently, the study of simple, coarse-grained, molecular models continues to be of interest.

2. Elasticity, Viscosity, and Defects

The structure and dynamics of nematic liquid crystals are dominated by three general factors: the orientational elastic constants, the various viscosity coefficients, and the disclination defects. In this talk, following a general introduction, I shall give examples where Monte Carlo and molecular dynamics simulations help us to understand each of these three key areas. Following the first determination of the Frank elastic constants [4], by studying orientational fluctuations as a function of wave-vector, the ability to study larger and larger system sizes has made it possible to significantly improve the precision of such measurements [5]. This in turn has allowed detailed comparisons to be made with both theory and experiment [6,7]. The study of the time correlation functions associated with these fluctuations, and their coupling with momentum flow, has revealed modes which propagate (oscillate), contrary to...
the beliefs of the last forty years [8]. This behaviour is linked to the values of the various viscosity coefficients, which appear in the nematodynamic equations. Finally, molecular simulation allows us to study the cores of the disclination line defects, which characterize the nematic phase, and are especially important when they surround and entangle suspended particles [9,10]. I hope to conclude the talk with a brief discussion of the prospects for using simulation to study the topological rearrangements of such defect lines.

References

The Role of Interfacial Water on Water Desalination, Hydrates Management, and Oil & Gas Production

Alberto Striolo

University College London, Department of Chemical Engineering, London, United Kingdom

Corresponding author e-mail: a.striolo@ucl.ac.uk

The molecular structure of interfacial water, and in particular of the electric double layer, is known to determine the outcome of a number of physical processes, including the dissolution of minerals, corrosion, and perhaps even the biological activity of enzymes. Our research group has employed massive molecular simulation studies to quantify how interfaces, in particular wet ones, determine the outcome of processes of vast societal importance. In this presentation we will explore how water adsorption within clays can affect the transport of natural gas through shale formations, how water and CO2 affect the mobility of hydrocarbons through silicates, how designing appropriately carbon-based electrodes could lead to new processes for water desalination, and finally how hydrates particles assemble within hydrocarbon systems. We will discuss how experimental information, obtained via appropriate collaborations, could be used to validate our predictions and perhaps lead to advancements in all the processes just discussed.
Comparison of absolute free energy calculation methods for fluids and solids

Martin B. Sweatman

Institute of Materials and Processes, School of Engineering, Kings Buildings, University of Edinburgh, Edinburgh, UK, EH9 3FB

Corresponding author e-mail: martin.sweatman@ed.ac.uk

1. Introduction

Several established and very general methods for calculating the absolute Helmholtz free energy from Monte Carlo simulations are compared; namely the method of Schilling and Schmid [1], Speedy’s method [2], the Self-referential method of Sweatman et.al. [3], and an approach inspired by the phase-switch method of Wilding et.al [4]. It is shown [5] how they are all closely related, in that they all calculate the free energy difference between a pinned configuration, for which the free energy can be calculated analytically, and the state of interest. A novel scheme is devised based on analysis of the advantages and problems with each method. Performance tests with hard sphere fluid and face-centred-cubic crystalline states demonstrate that the novel scheme described is the most straightforward, efficient and robust method of those tested. The Method of Schilling and Schmid requires sampling of rare events and cannot be recommended for high density states. Speedy’s method is less efficient than the novel scheme proposed here, while a path sampling approach inspired by the phase-switch method is more complex and less efficient in general. However, for free energy difference calculations involving states that are structurally very similar, a phase switch method might still be the most efficient method of those tested.

2. Conclusion

Of all general and exact methods for computing the absolute free energy from Monte Carlo simulations, the new method described here [5] appears to be the most straightforward, efficient and robust, certainly of those tested. It is expected to be useful for bulk and confined solids and fluids, as well as host-guest systems, for both lattice and off-lattice simulations. Future work will aim to explore its application to interfacial situations, and to combine it with a phase switch approach for comparison of structurally similar phases.

References
Surface Tension Calculations of Liquid Metals

Emeric Bourasseau, Olivier Durand, Gaëlle Filippini

CEA, DAM, DIF, F-91297 Arpajon, France

Correspond author e-mail: emeric.bourasseau@cea.fr

When a shock-wave goes through a free surface presenting microscopic defaults, it produces ejecta that will finally fragment and form microscopic spherical aggregates. With the help of large scale molecular dynamics simulations performed to study and to model the ejecta [1], we have shown that the modelling of such phenomena using hydrodynamic codes will imply the understanding of the physics occurring at the surface of the liquid fragments. Thus, it appears that surface tension is one of the overriding properties to be taken into account in the hydrodynamic codes. As a consequence, we report here Monte Carlo calculations of surface tension of liquid metals using both mechanical (Irving-Kirkwood method) and thermodynamic (Test Area method) approaches [2]. Metals are described using EAM and MEAM potentials. We also report a study of the surface tension in regards with the thickness of the liquid phase, and we try to explain in which conditions a sheet of liquid metal can break. It appears that the study of a single liquid metal interface is sufficient to know at which thickness a liquid sheet of a given metal will break. Surface tension calculations of liquid metal in cylindrical and spherical geometries will also be reported.

References
Calculating free energies of atmospherically relevant clusters using non-equilibrium molecular dynamics

Gabriel Lau1, Ian Ford2, Patricia Hunt3, Erich A. Müller1, George Jackson1,

1Department of Chemical Engineering, Imperial College London, 2Department of Physics and Astronomy, University College London, 3Department of Chemistry, Imperial College London

Corresponding author e-mail: gabriel.lau07@imperial.ac.uk

1. Introduction

Atmospheric aerosols play a key role in affecting climate, pollution and human health by influencing the properties and lifetimes of clouds and precipitation. There is therefore great motivation to understand the underlying molecular mechanisms involved in the nucleation rates of aerosol liquid droplets. One important quantity in nucleation studies is the excess free energy. In this work, we extract this free energy for atmospherically relevant clusters using a novel disassembly method (Hoi and Ford [1]) based on non-equilibrium molecular dynamics and the Jarzynski relation [2].

2. Disassembly of water and sulphuric acid-water clusters

We initially investigate clusters of pure water (using the TIP4P/2005 model [3]). The free energy of splitting a $2N$ water cluster into two $N$ sub-clusters is first evaluated to obtain the curvature-dependent surface tension and the results are compared to other values reported in the literature. We then simulate the complete disassembly of water clusters to extract the excess free energy curve, which was established to be in good agreement with internally consistent classical theory (ICCT) [4] at 300 K. Furthermore, the nucleation rate is calculated using the classical Becker-Döring equations and compared to the experimental values by Brus et al. [5-6]. It was found that our values lie within two orders of magnitude of the experimental data within the range of supersaturation studied at 300 K. Finally, a preliminary investigation into the excess free energy surface of sulphuric acid-water clusters is made using a newly developed potential model based on empirical valence bond (EVB) theory [7].

3. Conclusion

The excess free energies were obtained for pure water clusters and sulphuric acid-water clusters using non-equilibrium molecular dynamics. For pure water, the excess free energy curve was found to be consistent with ICCT at 300 K and the resultant nucleation rates based on classical kinetic equations were consistent to within two orders of magnitude of the experimental values.

References
The thermodynamics of low dimensional materials: Finding solvents for graphene, carbon nanotubes and their relatives

Adam Hardy and Henry Bock

Institute of Chemical Sciences, Heriot Watt University, UK

Corresponding author e-mail: h.bock@hw.ac.uk

The development of solvents for the vast range of interesting one- and two-D materials has been hampered by a lack of understanding of the underlying thermodynamics of these systems. We fill this gap by developing equations for the thermodynamic potentials of solutions of low dimensional materials in order to determine their thermodynamic stability.

Our work reveals that there is a computational approach that easier and more efficient than the traditional potential of mean-force method. We use this new approach to design new solvents for the two most prominent examples of one- and two-D materials, i.e. carbon nanotubes and graphene.

Due to its simplicity the method can be used in connection with any computer simulation approach and for any low dimensional material. It may even be possible to use it to determine the thermodynamic stability of solutions of stiff chain molecules such as cellulose. We are currently adapting the method to develop green cellulose solvents.
Mixtures of Hydrogenated and Fluorinated Alcohols: Thermodynamics, Spectroscopy and Simulation

Ana Rosa Garcia, Pedro Morgado, Martim Anastácio, João Marcos, Miguel Teixeira, Luís F. G. Martins, Laura Ilharco and Eduardo J. M. Filipe

1Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av Rovisco Pais, 1049-001 Lisboa, Portugal, 2Centro de Química-Física Molecular, Instituto Superior Técnico, 1049-001 Lisboa, Portugal, 3Centro de Química de Évora, University of Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal

Corresponding author e-mail: efilipe@ist.utl.pt

Highly fluorinated compounds have become key fluids in a wide range of fields due to their chemical inertness, biocompatibility and peculiar physical properties. Some of their most significant applications involve its use in liquid ventilation formulations, as oxygen carriers in blood substitutes or as solvents for biphasic synthesis and lubricants.

Perfluorinated chains (\(-\text{CF}_2\text{CF}_2\text{CF}_2\)-) are not only highly hydrophobic, but also lyophobic, i.e. they segregate hydrogenated chains. In fact, mixtures of alkanes and perfluoroalkanes are known to be highly non-ideal systems, exhibiting large regions of liquid–liquid immiscibility and large positive excess properties.

This work is part of a project in which mixtures of hydrogenated and fluorinated alcohols are being investigated, hoping to clarify the effect of the combined presence of hydrogen bonding between molecules with mutually phobic segments (hydrogenated and perfluorinated) and how this affects the properties of the liquid mixture and induces organization [1].

Bulk and interfacial properties of several mixtures of hydrogenated and fluorinated short-chain alcohols (n=2 to 4) have been studied: surface tensions as a function of composition and densities as a function of composition, temperature and pressure have been experimentally measured.

Additionally, infrared spectra of the pure alcohols and mixtures have been recorded and molecular dynamics simulations have been performed in order to gain a better understanding of the intermolecular interactions in these systems.

The organization of the liquids seems to be the result of a delicate balance between the unfavourable unlike dispersion interactions and the preferred unlike hydrogen bonding. Important conformational changes have also been identified in the mixtures. At the surface, geometrical constraints may play an important role in the structure of the interface.

Understanding these phenomena at the molecular level will ultimately allow the prediction and fine-tuning of the structure of molecular films of the long-chain hydrogenated and fluorinated alcohols, which are known to form patterned structures at the nanometer scale.

References
CO₂ Capture and Transport: Thermodynamic Investigation of Relevant Fluid Mixtures

Ioannis Tsivintzelis¹, Dimitra Aslanidou¹, Alexandra Tsali¹, Costas Panayiotou¹ and Georgios K. Kontogeorgis²

¹ Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece, ² Department of Chemical and Biochemical Engineering, Center for Energy Resources Engineering, Technical University of Denmark

Corresponding author e-mail: tioannis@cheng.auth.gr

Abstract

Carbon capture and storage (CCS) technology could become a reliable solution for reducing CO₂ atmospheric emissions in order to hinder global warming. Many processes for CO₂ capture have been suggested [1,2], which, among others, include chemical and physical absorption. Such broad categories include commercialized methods (mainly developed for treating natural gas), and newer concepts like absorption using novel tailored made solvents, such as ionic liquids, which present room for improvement and need to be tested beyond the setting of a laboratory [1-4]. Regarding CO₂ transport through pipelines and depending on the fossil fuel, the combustion method and the capture process, the CO₂ rich mixture to be transport may also contain water, residual solvents and a wide range of other compounds [5], which may range up to 10%. The temperature/pressure ranges of interest are rather extended up to 300 bar and between -25 and 60 °C.

In this study, the phase behavior of CO₂ mixtures with both traditional and novel CCS solvent systems is experimentally investigated using a high pressure variable volume view cell and the corresponding data are reported. Furthermore, high pressure densities of saturated phases for CO₂ binary mixtures relevant to transport process were measured using vibrational tube densitometers and the relevant data are reported. In a second step, two thermodynamic equation of state models, namely the Non Random Hydrogen Bonding (NRHB) and the Cubic plus Association (CPA) equations of state, are applied in modeling thermodynamic properties of CO₂ mixtures relevant to CCS.

References

Thermophysical Properties of Aqueous Amine Solutions for CO₂ Capture

Jiafei Zhang, Paul S. Fennell, J.P. Martin Trusler*

Department of Chemical Engineering, Imperial College London, South Kensington Campus, Exhibition Road, London SW7 2AZ, United Kingdom

*Corresponding author e-mail: m.trusler@imperial.ac.uk

Keywords: Vapour-liquid equilibrium, density, viscosity, heat capacity, amine solution, CO₂ loading

1. Introduction

The amine scrubbing process is one of the most mature technologies for acid gas treatment and recently has been adapted for CO₂ capture from exhaust gases to mitigate global warming [1]. Various conventional alkanolamines, including monoethanolamine (MEA), diethanolamine (DEA) and N-methyl diethanolamine (MDEA) as benchmark solvents, and a wide range of blended or specialty absorbents have been proposed for post-combustion carbon capture (PCC). The key challenge lies in process economics, i.e. solvent degradation and energy consumption [2], with such considerations varying with different processes. It is therefore necessary to develop and characterise new solvents such as tertiary amine 2-diethylaminoethanol (DEAE), sterically hindered amine 2-amino-2-methyl-1-propanol (AMP) and diamine piperazine (PZ) for PCC. These amines exhibit good chemical stability, moderate energy requirement and high CO₂ capacity and so are potential absorbents for future advanced PCC technologies. To optimise the solvent recipe and improve the absorption/regeneration performance, blended amine solvents e.g. DEAE+PZ are recommended for separating dilute CO₂ from flue gases as efficiently and effectively as possible.

Knowledge of thermophysical properties is important for the further implementation of CO₂ capture in modelling or process simulation, pilot plant operation, and process commercialisation. Vapour-liquid equilibrium (VLE) of CO₂ and amine solutions represents key information on CO₂ loading (α) at both the absorption and regeneration conditions. A solvent with high cyclic al CO₂ capacity not only requires a lower solvent circulation rate and process energy demand, but also reduces the ab-/desorption column size. Knowledge of density and viscosity is essential for engineering design, especially in the calculation of fluid dynamics and the estimation of mass transfer resistance. Understanding of heat capacity is also helpful for assessing the energy requirement in terms of sensible heat, which contributes approx. 25% of total energy consumption.

2. Research activities

A static-analytic apparatus was employed to conduct accurate VLE measurements on CO₂-amine-H₂O systems. The experiments were carried out in a 100 ml stainless steel vessel at temperatures from (313 to 393) K and total pressures up to 1 MPa. Both the gas and liquid phases were analysed by a Perkin-Elmer Clarus 500 gas chromatograph (GC) to determine the coexisting-phase compositions. The apparatus was validated in earlier work [3] but the gas sampling system was improved in this study. As seen in Figure 1, solutions of 2-dimethylaminoethanol (DMAE) and DEAE exhibit higher cyclical CO₂ loading than the benchmark MEA system. We also find that, by adding PZ as an activator to the DMAE- or DEAE-based solution, the absorption kinetics can be accelerated without suppressing the net CO₂ capacity.

An Anton Paar DMA 5000 M vibrating-tube densimeter and a certified U-tube capillary viscometer (PSL) were used for density and viscosity measurements, respectively, on partially carbonated aqueous amine solutions at temperatures from (298 to 353) K. Extensive studies on the density and viscosity of aqueous amine systems were found in the literature, but only very few have reported the influence of CO₂ loading. This study is therefore of particular interest to understanding of
the effect of CO₂ dissolution in aqueous amine solutions. Correlations for density and viscosity as a function of temperature, amine concentration and CO₂ loading were regressed with a satisfactory agreement between calculated and measured data.

The heat capacity was measured with an isobaric flow calorimeter at temperatures between (313 and 373) K and ambient pressure. The principle of this apparatus was described by Segovia et al. [4]. A set of measurements have been carried out for several amine solutions with various concentrations and CO₂ loading. As illustrated in Figure 2, dissolution of CO₂ was observed to increase the isobaric specific heat capacity (Cₚ) but to increase the isobaric heat capacity per unit volume (ρCₚ).

**3. Conclusions**

VLE data for CO₂ and aqueous amine solutions were obtained in this work to assist in the design of absorption and stripping columns for CO₂ capture. The selected amine solvents e.g. DEAE and its blended solutions exhibit a good cyclic CO₂ capacity for operation at flue gas conditions. To facilitate fluid dynamics calculations and the estimation of energy requirements, the density, viscosity and heat capacity of the partially carbonated aqueous amine solutions were measured and correlated by means of empirical equations as functions of temperature, amine concentration and CO₂ loading.

**Acknowledgment**

The authors appreciate the financial support from the EPSRC granted Gas - Future Advanced Capture Technology Systems (Gas-FACTS) project EP/J020788/1 as part of the RCUK Energy Program.

**References**

MD Simulations of Low-Salinity Enhanced Oil Recovery. A molecular-level description of interactions between charged colloid particles, organic oil molecules and simple salt ions.

Thomas Underwood, Valentina Erastova, Pablo Cubillas, H. Chris Greenwell

Department of Earth Sciences, Durham University

Corresponding author e-mail: thomas.underwood@durham.ac.uk

1. Introduction
In an age of increasing energy demand it is clear that we must utilise our energy resources as efficiently as possible. Current oil extraction methods only recover in the region of a third of the oil in a reservoir. Presently oil is recovered through primary methods (pressure differentials) and secondary methods (water flooding). However, it has been shown that incremental oil recovery beyond secondary methods can be achieved via using water floods of decreased salinity [1]. The aim of this research is to bring clarity to the fundamental mechanisms behind low salinity enhanced oil recovery (EOR), a technique where sea water, partially desalinated, is used to push increasing amounts of crude oil from existing, and future, oil reservoirs, increasing the reservoir lifetime and overall production.

2. Background Theory
The phenomenon of low-salinity enhanced oil recovery is thought to be due to the complex interactions between the organic oil compounds, inorganic colloid clay particles and the simple salt ions within the reservoir. Many theories have been hypothesised to describe the phenomenon, from the electric double layer expansion of charged clay particles [2], to divalent cation bridging between clay and organic [2], and pH effects of the local system surrounding the clay [3].

2. Methodology
It is difficult to observe the molecular effects of low salinity enhanced oil recovery experimentally, however computational simulations are perfectly suited to study such problems. Here, a comprehensive set of classical molecular dynamic simulations has been used to examine the interactions between various clays and organic oil molecules at multiple brine strengths.

Figure 1: A snapshot presenting the interaction between an initially oil-wet Montmorillonite clay particle, charged decanoate organics, and a salt concentration of 5 parts NaCl per thousand water molecules (water molecules not represented).
3. Conclusions

Using large-scale classical molecular simulations this study shows that it is neither the effect of double layer expansion nor divalent cation bridging that explains the phenomenon of low-salinity enhanced oil recovery. Rather, the results show that it is the pH level surrounding the clay, and thus it is the altered charge of the organic molecules that is the determining factor driving the titular effect.

References

Liquid-Liquid Equilibrium of Aqueous Two-phase Systems for Protein Partitioning from goat milk whey in-nature

Luziany A.C. Freire, Camila G. Pereira

Department of Chemical Engineering, Federal University of Rio Grande do Norte, Av. Senador Salgado Filho, CEP 59072-970, Natal - RN, Brazil

Corresponding author e-mail: camila@eq.ufrn.

1. Introduction

The whey corresponds to the aqueous fraction which remains after milk coagulation during cheese production or in casein production; it retains about 55% of milk nutrient [1]. The goat milk whey has a greater protein amount (1.3%) compared with the bovine milk whey (0.85%) [2]. Among whey proteins the α-lactoalbumin (α-La) and β-lactoglobulin (β-Lg) are those which are present in large quantities (more than 50%) [3]. Due to the bioactive activity of these molecules, the separation process choice is a critical step, since it is desired obtaining functional compounds of quality.

Most protein purification processes involve several steps and solvent consumption. Aqueous two-phase systems have been applied with success in the recovery of biomolecules from natural products. The simplicity, the low cost and efficiency of phase forming allow this method for large-scale purification. Two aqueous phases consists of two hydrophilic polymers or a polymer and an inorganic salt.

The partition α-La and β-Lg utilizing aqueous two-phase systems has been presented in the literature [4-6], however, the studies were performed using protein in its pure form. Studies using milk whey in-nature and goat milk whey have not been found yet. In this sense, the aim of this study was to evaluate the liquid liquid equilibrium of aqueous two-phase systems in the partition of α-La and β-Lg from goat milk whey in-nature. The aqueous two-phase systems were formed by polyethylene glycol, potassium phosphate and water. All systems were maintained at 298 K and pH 7.0. The partition coefficient, selectivity, process yield and purity of α-La e β-Lg proteins were determined. The amount of the goat milk whey in-nature necessary for the separation was also evaluated.

2. Results and Discussion

The phase diagram for the system polyethylene glycol, potassium phosphate and water is presented in Figure 1. Table 1 shows the partition coefficient, process yield and purity of α-La and β-Lg proteins.

According to Table 1, the system formed by 1 mL of goat milk whey in-nature presented better partition coefficient, yield and high purity. This occurred due to it low amount of water. The increase of goat milk whey quantity in the aqueous two-phase systems promoted the increased of water in the global system, changing the equilibrium. This occurrence prevented the separation of proteins in the systems using higher amount of goat milk whey.

The results also demonstrated the efficiency of aqueous two-phase systems in the separation of these proteins, since 85% of β-Lg was recovery in the lower phase, and 92% of α-La in the upper phase.
Figure 1: Ternary diagram for the system polyethylene glycol, potassium phosphate and water at 298 K, and 101.3 kPa.

Table 1: Partition coefficients, selectivity, yield and purity for of the $\alpha$-La e $\beta$-Lg proteins partitioned in aqueous two-phase systems.

<table>
<thead>
<tr>
<th>Goat milk whey amount (mL)</th>
<th>$K_{\alpha-La}$</th>
<th>$K_{\beta-Lg}$</th>
<th>Selectivity</th>
<th>Yield (%) $\alpha$-La$_{F\ up}$</th>
<th>Yield (%) $\beta$-Lg$_{F\ up}$</th>
<th>Yields (%) $\alpha$-La$_{F\ up}$</th>
<th>Purity (%) $\beta$-Lg$_{F\ up}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.78</td>
<td>0.09</td>
<td>63.71</td>
<td>78.61</td>
<td>94.54</td>
<td>77.08</td>
<td>94.99</td>
</tr>
<tr>
<td>5</td>
<td>2.25</td>
<td>0.05</td>
<td>45.57</td>
<td>58.91</td>
<td>96.95</td>
<td>81.84</td>
<td>91.00</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* up= upper phase, lp= lower phase

It is important to emphasize that the partition coefficient of these proteins were coherent with studies of literature that also applied polyethylene glycol, potassium phosphate and water at the same operational conditions, however using pure $\alpha$-La e $\beta$-Lg proteins [7-8]. This indicates the success of application of the aqueous two-phase in the real systems.

3. Conclusions

The results demonstrate that the phase diagram provided information about best condition to be applied in the recovery of whey protein in the two-phases. The amount of goat milk whey in-nature needs to be considered in order to promote the best separation of the proteins. The partition coefficients was coherent with literature and the values of selectivity, yield and purity were satisfactory for the separation of the $\alpha$-La e $\beta$-Lg proteins from goat milk whey in-nature. The results showed that the aqueous two-phase systems is applicable, indicating high efficiency in the whey proteins recovery from real systems.

References

Modeling of the phase equilibrium and the thermodynamic properties of aqueous systems from an industrial point of view

Eirini K. Karakatsani\textsuperscript{1}, Kim Aasberg-Petersen\textsuperscript{1}, Lars J. Christiansen\textsuperscript{1}

\textsuperscript{1}R&D Chemicals Process Department, Haldor Topsoe A/S – Nymøllevej 55 – 2800 Kgs. Lyngby - Denmark

Corresponding author e-mail: eika@topsoe.dk

1. Introduction

Knowledge of the phase behavior and thermodynamic properties of pure water and of several aqueous mixtures is essential for the development and design of the synthesis gas catalytic processes, Topsoe is involved in. In the simulation of such processes, water/steam properties and phase behaviour calculations are currently being performed using ordinary thermodynamic methods, but with proprietary parameters. However, there are still many challenges to overcome, especially related to new processes under development.

2. Examples

The current internationally agreed upon equations for industrial calculations of thermophysical properties of water and steam, IAPWS-IF97 \cite{1} are used in our calculations. A question though arises when thermodynamic properties of mixtures including steam or water must be calculated, at the moment through inter- and extra-polations between steam/water formulas and EoS properties. The necessity to combine phase equilibrium with chemical reaction equilibrium, with reactions in the liquid aqueous phase, is another example of a challenge. This requires a significant number of adjustable parameters, making the models highly empirical (see f.ex. ref.\cite{2} on the NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O system).

3. Conclusion

There are many hidden inconsistencies even when using the “most accurate” pure water / steam properties in mixture calculations, which are probably more severe in case of highly complex systems, such as systems with multiple azeotropes or with combined chemical and phase equilibrium. An effort to quantify them and –if possible- eliminate them would be of paramount importance.

References

Molecular simulation of ionic liquid solvents: bulk properties and the effect of confinement

Niki Vergadou¹, Georgios Kritikos¹, Eleni Androulaki¹ and Ioannis G. Economou¹,²

¹National Center for Scientific Research “Demokritos”, Institute of Nanoscience and Nanotechnology, Molecular Thermodynamics and Modelling of Materials Laboratory, GR-153 10, Aghia Paraskevi Attikis, Greece, ²Texas A&M University at Qatar, Chemical Engineering Program, Education City, PO Box 23874, Doha, Qatar

1. Introduction

Ionic liquids (ILs) are organic salts with melting points usually near room temperature (RTILs). ILs exhibit a unique combination of properties such as extremely low vapor pressures, thermal stability, chemical tunability, good electrolytic and solvation properties, non-flammability and easy recycling. The combination of these properties renders them ideal for use in a number of industrial applications [1] such as solvents and catalysts in synthesis, as lubricants, as electrolytes in electrochemistry and in gas storage and CO₂ capture and separation applications. Molecular simulation methods are proven to be extremely valuable in the direction of screening the most promising systems by reliable property prediction strategies as well as by revealing the underlying mechanisms [2,3] that are responsible for the macroscopic behavior of ILs aiming at the molecular design of solvents with controlled properties.

2. Methodology

The present work focuses on the molecular simulation of imidazolium-based [TCM⁻] ionic liquids using an optimized classical atomistic force field. Long molecular dynamics (MD) simulations of the [Cₙmim⁺][TCM⁻] ILs family have been performed at various temperatures and at atmospheric pressure in order to calculate the thermodynamic, structural and transport properties of the pure ILs, exploring, simultaneously, the intrinsic characteristics and mechanisms of the systems under study at the atomistic level. Additional simulations have been performed for the study of the behaviour of the IL systems inside pores [4]. The effect of confinement in the structure and dynamic properties has been investigated in a wide temperature range and the influence of the inter-wall distance and the cation’s alkyl tail length on the above properties has been thoroughly studied.

3. Conclusion

Molecular simulation has been applied for the study of imidazolium-based tricyanomethanide ILs and a wide range of properties has been calculated. Predictions on density, ionic diffusivity, viscosity and gas permeability are in good agreement with experimental data for the pure ILs. A wealth of microscopic information has been extracted on the spatial organization and dynamics of the bulk and confined systems.

References
Determining the Factors that Govern the Permeation of Ions into Graphene Oxide Membranes using Molecular Simulation

Christopher D. Williams, Paola Carbone, Flor R. Siperstein

School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, M13 9PL, UK.

Corresponding author e-mail: christopher.williams-2@manchester.ac.uk

1. Introduction

Despite being completely impermeable to gases and some organic liquids, the intercalated layers of graphene oxide (GO) can be wetted by water [1]. Regions of oxygenated functionalities (eg. hydroxy and epoxy groups) are believed to play a crucial role as spacers, separating individual layers and generating a porous material that allows fast water transport over the hydrophobic unoxidised regions of the graphene surface. Combining results obtained from simulation and experiment, a recent study carried out at the University of Manchester [2] showed that at high humidity the graphene pores expand, increasing the interlayer spacing between GO sheets and allowing the entry of water molecules which organise themselves in single or multi-layers. Under these conditions GO pores can act as selective sieves that only permit the transport of certain ionic species based on the relative sizes of the GO pore and the ion’s hydrated radius. Since the interlayer spacing in GO can be carefully controlled by adding appropriate spacer groups this material shows great promise for the desalination of water.

2. Ion Selectivity in GO Membranes

One very promising application of GO pores is the remediation of land contaminated by the nuclear industry. The removal of some radioactive anions (such as TcO$_4^-$ and I$^-$) from groundwater has proven to be extremely challenging [3], in part due to the presence of environmentally ubiquitous competing ions.

In this work, the factors that control the uptake of TcO$_4^-$, I$^-$ and competing ions into GO pores were investigated using realistic atomistic models and molecular dynamics simulations. The thermodynamic integration technique was used to validate the models by determining ionic hydration free energies. Potentials of mean force (PMFs) for ions entering the GO pore were obtained from umbrella sampling simulations. The selectivity of the pore for ions was deduced from the free energy barriers observed along the PMF profiles and rationalised by calculating separate enthalpic and entropic contributions for the process, in the context of the changes in the structure of the hydration shells around each ion (dehydration). The affinity of ions for the pore was found to depend on their hydration free energies and hydrated radii, and the selectivity was simply modified by adjusting the pore diameter. Finally, polarisation effects were incorporated into the graphene force field [3] and these appear to be especially important when calculating PMFs for the highly polarisable TcO$_4^-$ and I$^-$ ions.

3. Conclusion

Since their pore diameters can be finely tuned GO membranes are potentially useful for the selective removal of ionic radioactive contaminants from water. The selectivity is dependent on the hydrated properties of the ions and our results have wider implications for the properties of ionic solutions under confinement.

References

Non-equilibrium molecular dynamics simulations of water permeation through graphene-based membranes

Frederike Jaeger\textsuperscript{1,2}, Jordan Muscatello\textsuperscript{1}, Omar Matar\textsuperscript{1}, Erich A. Müller.\textsuperscript{1}

\textsuperscript{1}Department of Chemical Engineering, Imperial College London, \textsuperscript{2}Department of Physics, Imperial College London.

Corresponding author e-mail: fj13@ic.ac.uk

1. Introduction

With an ever-increasing population, the need for clean fresh water becomes greater, not only for direct consumption but also for application in agriculture and sanitation systems. Developing novel membranes with faster water transport and better sieving properties to be used for water purification is hence a focus in the engineering community. In this study the transport properties of water through graphene sheets with slits are investigated.

2. Effect of slit geometry on permeation

Graphene-based membranes, along with carbon nanotubes, have recently been the focus in the research community due to their hydrophobic nature, leading to exceptional transport properties.\textsuperscript{[1-3]} During our molecular dynamics simulations a force is applied to a region of the water, leading to a density gradient inducing steady state flow (see Fig. 1). This allows for a flux and consequently a transport coefficient to be calculated. We consider both single sheet and multiple sheet set-ups. Both the slit width and the spacing between the sheets are varied.

It is found that increasing either the slit width or the spacing between sheets increases flow whereas the addition of sheets decreases it. Further, charged functional groups at the sheet edges inhibit flow due to electrostatic effects of the functional group with the partial charges of water.

Both one sheet and two sheet systems display layering in both the direction of flow and within the slit. The number of layers increased with increasing slit width or spacing, with a maximum of four layers observed. Both confinement effects, as well as the hydrophobic nature of the graphene sheets, cause these density variations.

It has been suggested that fast transport through multiple sheet graphene-based membranes is caused by super diffusion through nanochannels between the sheets.\textsuperscript{[3]} However, we have shown that water molecules on average spend more time inbetween the sheets than in the bulk. This suggests that the energy cost of passing through the slit is high.

Figure 1: Simulation set-up and corresponding density gradient.
3. Conclusion

The effect of system geometry on the flow of water through graphene sheets is analysed. It is found that confinement effects are notable for small enough slits and sheet spacing, mostly in the form of non-uniform density distributions. Theories suggesting that super-diffusion between the sheets is responsible for good transport properties could so far not be confirmed.

References

Wetting on Grafted Thermo-responsive Polymer Brushes: A Molecular Dynamics Study

Debdip Bhandary¹, Zuzana Benková²,³, M. Natália D. S. Cordeiro², Jayant K Singh¹

¹Department of Chemical Engineering, Indian Institute of Technology Kanpur, UP, India – 208016, ²REQUIMTE, Department of Chemistry and Biochemistry, University of Porto, 4169-007 Portugal, ³Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

Keywords: Thermo-responsive polymer brushes, Water contact angle, LCST, Hydrogen bonding

Poly-N-isopropylacrylamide (pNIPAAm) is a thermo-responsive polymer that switches its behaviour from being hydrophobic to hydrophilic with temperature. pNIPAAm is widely used in various pharmaceutical applications as well as for controlling surface properties such as wetting, adhesion etc. Due to change in its structure, they are able to switch its property under external stimuli, such as electric field, pH, surfactants etc. In this work, we have studied the effect of temperature on the contact angle of water (WCA) on the grafted pNIPAAm brushes and investigated the change of structural properties using molecular dynamics simulation. In particular, we address the role of hydration on the wetting transition on grafted pNIPAAm brushes. We have used united atom model with explicit model of amide group (CONH) for pNIPAAm and SPC model for water [1]. The transition temperature of hydrated pNIPAAm chains is 32 °C (305K), which is the lower critical solution temperature (LCST) of the polymer. Polymer chains of 30-monomer units are grafted on silica surface with grafting density of 114.19 Å²/chain [2] to see swelling and deswelling behaviour of the brushes. We have calculated the contact angle (CA) of cylindrical water droplet in the temperature range of 270-350 K. The contact angle increases with increase in temperature from 300 to 310 K on the hydrated grafted pNIPAAm brushes. The average monomer height of the chains decreases as the temperature increases. On the other hand, dry brush layer shows opposite behaviour i.e. WCA water droplet on the dry polymer brushes starts spreading on the brush layer and the reverse transition have been observed. The CA at 270 K is higher for dry brushes than the hydrated system. On the other hand, the CA is lower for dry brushes and higher for hydrated brushes at 320 K. The behaviour is explained using hydrogen-bonding analysis. We observed that the hydrogen bonding as well as the presence of isopropyl group is playing an important role in deciding the behaviour of CA on both dry and hydrated brushes.

Reference:

Phase behaviour of the system (carbon dioxide + \textit{n}-heptane + methylbenzene) and (carbon dioxide + methane + methylbenzene): a comparison between experimental data and SAFT-\(\gamma\)-Mie predictions

\textit{Saif. Z Al Ghafri\textsuperscript{1}, Simon Dufal\textsuperscript{2}, Amparo Galindo\textsuperscript{1,2}, George Jackson\textsuperscript{1,2}, Geoffrey C. Maitland\textsuperscript{1}, and J. P. Martin Trusler\textsuperscript{1}}

\textsuperscript{1}Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), \textsuperscript{2}Molecular Systems Engineering, Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ

Corresponding author: Saif. Z. Al Ghafri. E-mail: saif.al-ghafri06@imperial.ac.uk

\textbf{Keywords:} SAFT-\(\gamma\)-Mie, CO\textsubscript{2}, Hydrocarbon

1. Introduction

Carbon dioxide may be injected into petroleum reservoirs for purposes of enhanced oil recovery and/or carbon storage. In order to model these processes quantitatively, it is necessary to know the phase behaviour and physical properties of the mixtures formed between CO\textsubscript{2} and reservoir fluids under the conditions prevailing in the reservoir and, for this purpose, compositional thermodynamic models are required. Traditional equation of state models contain large numbers of adjustable binary parameters which require for their determination not only a compositional analysis but also experimental phase equilibrium data. In this work, we explore the capabilities of the SAFT-\(\gamma\)-Mie approach to model the phase behaviour of (CO\textsubscript{2} + hydrocarbon) mixtures by comparing the model predictions with new experimental data.

2. Experimental

In this work, a new experimental apparatus was designed and constructed to measure the phase equilibria in systems containing CO\textsubscript{2} and hydrocarbons at reservoir temperatures and pressures. The apparatus involved a high-pressure high-temperature variable-volume view cell driven by a computer-controlled servo motor system. The maximum operating pressure and temperature were 40 MPa and 473.15 K, respectively. The apparatus was calibrated and validated by comparison with published isothermal vapour-liquid equilibrium data for the different binary systems. The vapour-liquid phase behaviour of the mixture (CO\textsubscript{2} + \textit{n}-heptane + methylbenzene) was measured over the temperature range (298 and 473) K and pressures up to 16 MPa. The molar ratio between \textit{n}-heptane and methylbenzene in the ternary system was fixed at different values, and the bubble-curve and part of the dew-curve was measured under carbon dioxide addition along five isotherms. The ternary mixture (CO\textsubscript{2} + methane + methylbenzene) was measured over the temperature range (323 and 473) K and pressures up to 36 MPa. The molar ratio between CO\textsubscript{2} and methane in the ternary system was fixed at different values (0, 0.25, 0.5, 0.75 and 1), and the bubble-curve and part of the dew-curve was measured under carbon dioxide addition along four isotherms.

3. Modelling

In this work, we explore the predictive capability of SAFT-\(\gamma\)-Mie [1] to model the phase equilibria of the ternary mixtures. The Statistical Associating Fluid Theory, stemming from the first order perturbation theory of Wertheim [2], was implemented in this work with a group contribution approach and the generalized Mie potential to represent segment-segment interactions. In the resulting SAFT-\(\gamma\)-Mie, complex molecules are represented by fused segments representing the functional groups from which the molecule may be assembled. All
interactions, both like and unlike, as implemented in this work were determined from experimental data of systems comprising the constituent groups.

4. Comparison and Conclusions

The experimental data for the different values of molar ratios were compared at different isotherms with the predictions of the SAFT-\(\gamma\)-Mie approach. The agreement, while not perfect, is very good, especially on the bubble curve. The results suggest that there is merit in the approach of combining, within a SAFT approach, the Mie potential with a group-contribution scheme for the interaction parameters based on pure component data alone. The comparison proves the predictive capability of SAFT-\(\gamma\)-Mie approach.

References


Acknowledgment

We gratefully acknowledge the funding of QCCSRC provided jointly by Qatar Petroleum, Shell, and the Qatar Science and Technology Park, and their permission to publish this research.
A Comprehensive Investigation on CO₂ Solubility and Kinetics in Tricyanomethanide-based Ionic Liquids: Experiments and ePC-SAFT Modeling

Lawien F. Zubeir*, Theodora Spyriouni#, Maaike C. Kroon#

*Separation Technology, Eindhoven University of Technology, Den Dolech 2, 5612AZ Eindhoven, The Netherlands, #Scienomics, 16 rue de l’Arcade 75008 Paris, France

*Corresponding author: Lawien F. Zubeir, L.F.Zubeir@tue.nl

Keywords: Tricyanomethanide-based Ionic Liquids, Carbon Capture, ePC-SAFT

1. Introduction
As the attention to climate debate is growing, reduction of the anthropogenic carbon dioxide (CO₂) emissions produced from combustion of fossil fuels in an efficient and cost-effective way has become an urgent topic. Carbon capture and storage (CCS) technologies are a promising route to reduce these emissions. The capture stage accounts for ~80% of the overall costs of the CCS activity. Besides, current capturing techniques and the subsequent compressing of CO₂ increase the parasitic energy requirements by 25-40% of the power plant output. Thus, improvements in the efficiency of the capturing step have the highest impact on cost reduction and the environment.

Using a solvent for CO₂ absorption is accepted as the most compatible technology. In recent years, ionic liquids (ILs) have shown to be good candidates for CO₂ capture. They exhibit major advantages over amine-based systems. Their negligible vapor pressure, high thermal and chemical stability and tunability outweigh the disadvantages of lower absorptive capacity and kinetics.

To design IL-based absorption processes, knowledge of the solubilities and diffusivities is needed. Besides, the thermophysical properties of the novel solvents have to be characterized, since limited information is available in literature. Moreover, experimental measurements of gas solubilities are time-consuming and expensive. Preferably, the thermodynamic phase behavior is described using a well-defined model that rigorously relates thermodynamic properties to physical intermolecular forces between the solute and the solvent.

2. Experimental
In this work a comprehensive study of the thermophysical properties of the ILs [emim]-, [bmim]-, [hmim]- and [omim]-tricyanomethanide [TCM] has been carried out. These ILs belong to the group of non-fluorinated and low-viscous ILs. The thermodynamics (i.e., absorptive capacity and Henry’s law coefficient) and kinetics (i.e., diffusion coefficient) at several temperatures and pressures have been studied using a magnetic suspension balance.

3. Modeling
The electrolyte Perturbed-Chain Statistical Association Theory (ePC-SAFT) was used in this work for modeling the phase behaviour of ILs + CO₂ systems. ePC-SAFT is a physically based model that explicitly accounts for electrostatic interactions. The ILs were modeled by fitting the parameters of the cations and the anion to density data of the pure ILs. Good agreement with the experiment was observed even without the use of binary interaction parameter kij, showing the great predictive ability of the thermodynamic model.
4. Conclusion

It will be shown at the conference that TCM-based ILs are promising sorbents for pre-combustion CO₂ capture due to their high (physical) absorptive capacity, their low regeneration energy consumption (low heat of absorption) and improved kinetics (high diffusivity due to the low viscosity of the ILs) compared to the conventional ILs.

The modeling results for the ILs-CO₂ phase equilibria show good agreement with the experimental data even without the use of adjustable parameters. This is very encouraging for the use of this theoretical tool for calculating the solubility of gases in ILs.
Multi-scale modelling of polyamide thin films

*Jordan Muscatello*, *Arash Mostofi*, *Erich Müller* and *Adrian Sutton*

1Department of Chemical Engineering, Imperial College London, 2Department of Physics, Imperial College London

Corresponding author e-mail: jlm105@ic.ac.uk

1. Introduction

Interfacial polymerization is a common technique to generate thin films for commercial applications, such as the fabrication of membranes for purification of water through reverse osmosis. In this work we propose the generation of atomistic polyamide reverse osmosis membrane configurations via mimetic simulation of the interfacial polymerisation process in conjunction with a coarse-grained (CG) molecular model for the monomer species. We perform an implicit solvent Brownian dynamics of a CG model of both monomeric species involved in the polymerization process and allow the system to artificially bond and cross-link during the simulation. Since the CG model respects the molecular geometry of the cross-linked polyamide network, it allows us to superimpose a fully atomistic description once the self-assembly has concluded. We analyse and compare the structures resulting from different stoichiometric ratios of reactants in terms of their static properties (free volumes, densities, bond linkage) and study the transport and rejection properties of the membrane via fully atomistic non-equilibrium molecular simulation.
Modeling thermodynamic derivative properties of ionic liquids with ePC-SAFT

Gulou Shen\textsuperscript{1,2}, Christoph Held\textsuperscript{3}, Xiaohua Lu\textsuperscript{2}, Xiaoyan Ji\textsuperscript{1}

\textsuperscript{1} Division of Energy Science/Energy Engineering, Lulea University of Technology, 97187 Lulea, Sweden, \textsuperscript{2} State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, PR China, \textsuperscript{3} Laboratory of Thermodynamics, Department of Biochemical and Chemical Engineering, TU Dortmund, Emil-Figge-Str. 70, 44227 Dortmund, Germany

Corresponding authors’ e-mails: gulou.shen@ltu.se, xiaoyan.ji@ltu.se

1. Introduction

CO\textsubscript{2} separation plays an important role in CO\textsubscript{2} emission mitigation, biofuel production and biogas upgrading. In general, the CO\textsubscript{2} separation requires a lot of energy, and exploring low-cost CO\textsubscript{2}-separation technologies is still a hot research topic. Recent research reveals that ionic liquids (ILs) are promising liquid sorbents for CO\textsubscript{2} separation. Research work has been conducted mainly on the density of ILs and the gas solubility in ILs experimentally and theoretically. Second order derivative properties are important, however, modelling of the second order derivative property for systems containing ILs is still a challenge task.

In this work, ePC-SAFT was extended to predict the second order thermodynamic derivative properties of pure ILs, such as isothermal and isentropic compressibility coefficients, thermal pressure coefficient, heat capacities, speed of sound, thermal expansion coefficient and internal pressure. The imidazolium-based IL was chosen as the focus to verify the performance of the model prediction by comparing with the available experimental data. The model parameters for the cations of [C\textsubscript{2}mim]\textsuperscript{+}, [C\textsubscript{4}mim]\textsuperscript{+}, [C\textsubscript{6}mim]\textsuperscript{+} and [C\textsubscript{8}mim]\textsuperscript{+} were taken from our previous work, and the model parameters for the cations of [C\textsubscript{3}mim]\textsuperscript{+}, [C\textsubscript{5}mim]\textsuperscript{+}, [C\textsubscript{7}mim]\textsuperscript{+} and [C\textsubscript{10}mim]\textsuperscript{+} were predicted based on the linear molecular-weight-dependent equations proposed in our previous work. The new predicted model parameters were verified with the predicted density of ILs and CO\textsubscript{2} solubility in ILs. The model with the available and predicted model parameters was used to predict the thermodynamic derivative properties and compared with the available experimental data. The comparison shows that the model prediction on the derivative properties is reliable in a wide temperature and pressure range.
Modeling coarse grained linear alkanes and polymers using SAFT-\(\gamma\) Mie using molecular dynamics simulations

Sadia Rahman, Olga Lobanova, Carlos Braga, Vasileios Raptis, Erich A. Müller, George Jackson and Amparo Galindo

Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, United Kingdom

Corresponding author e-mail: a.galindo@imperial.ac.uk

1. Introduction

Alkanes are key in many industries such as oil and gas, and as intermediates for synthesis of drugs, pesticides etc. In this work we use a coarse graining methodology previously proposed by our group [1-4] which is based on the Statistical Associating Fluid Theory (SAFT)-\(\gamma\) Mie approach [5]. A transferable coarse grained force field is developed for \(n\)-alkanes to be used in molecular dynamics simulations.

2. Alkanes and polymer study

A combination of a top-down and a bottom-up approach was used to implement both the role of inter- and intra-molecular interactions in the force field. The coarse grained model for \(n\)-alkanes groups three consecutive backbone carbon atoms together. A distinction in made between beads that contain the CH\(_3\) end group, giving two different types of beads for a heteronuclear model.

The intermolecular interactions are characterized by taking advantage of the accuracy of the SAFT-\(\gamma\) Mie equation of state. The SAFT-\(\gamma\) Mie is a group contribution EOS, which allows the development of a force field where the parameters characterized can be transferable to different molecules, in this case longer alkanes such as C\(_{60}\)H\(_{122}\) and polyethylene.

SAFT models do not take into account the structure and flexibility of molecular systems. Uniquely, in these models, the intra-molecular interactions are explicitly considered. The inclusion of intra-molecular interactions in the coarse grained models was developed by using atomic simulations and allows not only an improved description of thermodynamic properties such as vapour-liquid equilibria, but also of the structural and transport properties. The surface tension, self-diffusion coefficients and viscosity are properties which in spite of not being employed in the development of the force field, are however predicted in good agreement to experiment with the proposed coarse grained force field.

3. Conclusion

A transferable coarse grained model has been developed for \(n\)-alkanes that includes both inter- and intra-molecular potentials. The model can now be used either on its own or as part of group-contribution models for more complex molecules such as semi-fluorinated alkanes, polyethylene oligomers, branched hydrocarbons and/or surfactants.

References

Combining quantum chemistry and statistical mechanics for thermodynamic property prediction involving natural complex materials: ligno-cellulosic biomass, kerogen, asphaltenes, clay minerals, and micro emulsions.

Philippe Ungerer¹, Marianna Yiannourakou¹, Julien Collell², Paul Saxe³

¹Materials Design S.A.R.L., Montrouge, France, ²LFCR, University of Pau, UMR with CNRS and Total SA, ³Materials Design Inc., Angelfire, USA

Corresponding author e-mail: pungerer@materialsdesign.com

Complex materials represent three types of challenges for molecular modeling: i) they present heterogeneities at different scales, ii) their detailed structure is ill-defined because they are not synthesized in controlled laboratory processes iii) their modelling requires efficient software and large computing resources. The purpose of the presentation is to illustrate recent applications in this field motivated by industrial processes (oil and gas production, production of chemicals by biomass hydrogenation, among others).

The properties computed from molecular modeling have been validated with experimental data on known compounds and materials. Quantum chemistry provides total electronic energies, material structure and standard thermodynamic data in the ideal gas state. Molecular Dynamics predict materials properties including the density, thermal expansivity, and diffusivity. Monte Carlo techniques allow the investigation of phase equilibria and sorption in micropores. The commercially supported MedeA software environment allows the use of these tools in a time-saving mode. For instance, ideal gas properties are computed at the quantum level and the residual properties by molecular dynamics on the same macromolecular system. Most calculations are performed on workstations of 128 parallel processors. This makes the cost per CPU hour very interesting compared with large supercomputers.

In the area of ligno-cellulosic biomass combustion or conversion, a current challenge is the cost of drying green waste and improving the energy balance of fuel-, biogas, chemicals or power production from biomass. Molecular quantum chemistry is applied to the reliable prediction of thermochemical properties of relevant macromolecules (cellulose, lignin). Forcefield-based methods are applicable to sample conformations and modelling solvent effects. We discuss the energy balance of drying and of hydrogenation processes of lignin.

In the area of oil and gas exploration and production, we use elemental analysis and NMR data to construct explicit models of kerogen, the organic matter from which oil and gas are generated. Computed density and heat capacity variations of kerogen with elemental analysis agree well with experimental data. Molecular modeling has proved extremely useful to understand the preferred retention of polyaromatics in organic-rich shales during petroleum expulsion and during production of shale oil liquids. Using atomistic interface models we describe the interactions of clay minerals with reservoir fluids, the nanoaggregation of asphaltenes, and the role of anionic surfactants for Enhanced Oil Recovery.

We conclude that this type of simulations provides improved coverage, systematic property data as well as understanding thus reaching beyond state of the art correlation methods.
Phase equilibria of methane and carbon dioxide hydrates using molecular dynamics simulations

Vasileios K. Michalis¹, Joseph Costandy¹, Ioannis N. Tsimpanogiannis¹,², Athanassios K. Stubos², Ioannis G. Economou¹,*

¹ Chemical Engineering Program, Texas A&M University at Qatar, PO Box 23847, Doha, Qatar,
² Environmental Research Laboratory, National Center for Scientific Research NCSR “Demokritos”,
GR-15310 Aghia Paraskevi, Attiki, Greece

*Corresponding author e-mail: ioannis.economou@qatar.tamu.edu

1. Introduction

Clathrate hydrates [1] are solid solutions of water molecules with small “guest” molecules such as methane, ethane, propane, iso-butane, carbon dioxide, hydrogen sulfide, nitrogen and hydrogen and others. The water molecules through hydrogen bonding form a three-dimensional crystal lattice with well-defined cages, occupied by the guest molecules. These structures remain stable under relatively low temperatures and high pressures. The interest in clathrate hydrates is vivid due to their central role in a number of existing or future potentially-important technological areas, such as flow assurance issues in the gas and oil industry, gas transport and mixture separation processes and the existence of large natural gas hydrate deposits.

The present work refers to the study of clathrate hydrates through molecular dynamics simulations. We examine two important hydrates, namely the methane and carbon dioxide hydrates. The three-phase coexistence curve of these systems is calculated using the direct phase coexistence method [2], where solid, liquid and gas phases of the constituents are brought in contact and the time evolution of the system provides information on its stability (Figure 1).

![Figure 1. Snapshots of methane hydrate molecular dynamics simulation runs. Left: initial configuration, upper right: hydrate dissociation, bottom right: hydrate formation.](image)

2. Results

For the case of methane hydrates the three-phase coexistence temperature is calculated covering a wide range of coexistence conditions. Taking into consideration the stochastic nature of the process and avoiding bubble formation phenomena, statistical averaging over a large number of long (1000-4000 ns) independent simulations results in predictions that are in very good agreement with experimental results [3]. For the case of the carbon dioxide hydrate, following a similar approach and additionally correcting the predictions of the used forcefield for the solubility of carbon dioxide in
water, through a modification of the energy cross interaction parameter, an equally consistent agreement with the experimental results is achieved.

**Acknowledgements**

This study was made possible by NPRP grant number 6-1547-2-632 from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of the authors.

**References**


Multi-scale simulation of the early stages of zeolite nucleation

M. Ciantar\textsuperscript{1}, Thuat T. Trinh\textsuperscript{2,3}, C. Nieto-Draghi\textsuperscript{1}, C. Mellot-Draznieks\textsuperscript{4}, P. Sautet\textsuperscript{3},

\textsuperscript{1}IFP Energies nouvelles 1-4 avenue de Bois-Préau 92852 Rueil-Malmaison France, \textsuperscript{2}Department of Chemistry, Norwegian University of Science and Technology, Trondheim, Norway, \textsuperscript{3}Université de Lyon, CNRS, Laboratoire de Chimie, École Normale Supérieure de Lyon France, \textsuperscript{4}Laboratoire de Chimie des Processus Biologiques, UMR 8229, Collège de France, Paris, France

Corresponding author e-mail: marine.ciantar@ifpen.fr

1. Introduction

Nucleation is one of the first steps in the process of crystallization of porous materials like zeolites which is hardly accessible from experiments. Understanding the role played by reactant concentrations, pH, organic templates, etc., on the resulting structures is a real challenge that can be addressed by means of multi-scale molecular simulations. In the present work we provide a combined approach of DFT and kinetic Monte Carlo (kMC) simulations\textsuperscript{[1]} to model the influence of synthesis variables on the concentration profile of key species (rings, tetramers, etc. ranging from monomer to hexamers) during early stages of oligomerization.

2. Methods and results

In previous studies\textsuperscript{[2,3]}, two mechanisms for zeolite oligomerization have been proposed including negatively charged or neutral oligomers\textsuperscript{[4]}. We focus our study under optimal pH conditions (between 10-11)\textsuperscript{[5]} for anionic species\textsuperscript{[2]}. Activation free energies (Eact) were calculated by using DFT calculations using a continuum solvation method (CPCM) for the solvent using B97D/6-311+g(d,p) functional (dispersion correction included) as implemented in GAUSSIAN 09. The reaction pathway was extended by building Brønsted–Evans–Polanyi (BEP) models for branched and linear species. Our chemical model contains 21 reaction paths each one including two transition states and one intermediate specie to form the finale product. The rates for each elementary reaction were calculated according to the Eyring equation from Gibbs free energies and introduced into the kMC simulations (using a modified version of the SPPARKS code). We can see in the Figure 1 the stabilisation of branched tetramer with respect to linear trimer during time according to the Gibbs free energy profile presented in Figure 2.

![Figure 1](image1.png)

**Figure 1**: Linear dimer, trimer and branched tetramer during time at pH=11 and T=350 K.

![Figure 2](image2.png)

**Figure 2**: Gibbs free energy profile for branched tetramer.

The influence of the pH and template type on the steady state concentration (ssc) of trimer is presented in Figure 3. We observe an important role played by the pH (by an optimum between 10 and 11) on the ssc whereas templates have a limited impact on small species contrary to what is observed on larger species, particularly 5-ring and 6-ring.
Figure 3: Trimer ssc with the pH and template type at 350 K (TMA: tetramethylammonium, TEA: tetraethylammonium, TPA: tetrapropylammonium)

At low initial concentrations the formation of branched and cyclic species is favored (with TEA and TMA) while linear species are observed at high concentrations (with TPA).

3. Conclusion

We have performed a complete analysis by combining DFT and kMC multi-scale simulations. We have seen an optimal pH range (between 10 and 11) for the global nucleation process, while initial reactant concentrations produce different species yielding (branched vs linear). One of main contributions of this study is the inclusion of organic templates, which plays an important role on the formation of large oligomers.

References

Spatial resolution of thermal transport properties in simulated nanomaterials

Niall Jackson¹, Fernando Bresme¹

¹Department of Chemistry, Imperial College London

Corresponding author e-mail: npj12@imperial.ac.uk

Keywords: heat transport, nanomaterials, non-equilibrium molecular dynamics, thermal interfacial resistance, thermal conductivity

There is currently great interest in the ability to accurately determine thermal properties of materials. As technological devices become increasingly small, efficient heat management becomes increasingly difficult. Nanofluids have shown promise as highly efficient coolants due to their potentially extremely high thermal conductivity [1]. From a biological perspective, magnetic and plasmonic nanoparticles are investigated as potential novel drug delivery mechanisms [2]. It may even be possible to directly kill tumours by local heating of such particles by laser of magnetic fields [3]. Temperature gradients may also be used to enhance the transport of biomolecules through small pores used in biosensing applications [4], and simulation studies have been performed on thermal nanopumps – pore-based devices which use thermodiffusion to sort mixtures of particles [5]. To exploit these devices for maximum benefit, and to design new ones effectively, we must understand their thermal properties. The two principal quantities are the thermal conductivity, which relates the magnitude of a temperature gradient to the size of the resultant heat flux, and the thermal interfacial resistance (Kapitza resistance), which quantifies the discontinuous change in temperature across an interface [6].

Non-equilibrium molecular dynamics simulations are extremely well suited to the task of quantifying heat transport at the nanoscale. Various algorithms for heating and cooling different parts of a simulation are available which allow a range of experimental situations to be replicated. Furthermore, there is a long established microscopic definition of the heat flux [7] which can be evaluated in small volumes of the system to determine thermal conductivities and resistances with high spatial and temporal resolution. This expression naturally separates into ballistic and collisional terms, allowing the relative importance of different mechanisms of heat transfer in different regions of the material to be compared.

In this work, we demonstrate that the microscopic definitions of both temperature and heat flux may be used “locally” in computer simulations to quantify and spatially resolve the thermal conductivity and interfacial thermal resistance of nanomaterials of technological importance, such as functionalized nanoparticles (polymer coated iron oxide or thiol coated gold nanoparticles, for example). We demonstrate that in such materials, which involve both chemical and spatial heterogeneities, the heat flux may be highly anisotropic, with certain parts of the system dominating the heat transport. This lays the microscopic basis for the design of materials able to conduct heat in a highly efficient and localised manner.

References
Taming Thermophoretic transport across nanopores: novel approaches for nanofluidic analytical devices

Silvia Di Lecce¹, Tim Albrecht¹, Fernando Bresme¹

¹Department of Chemistry, Imperial College London, London, SW7 2AZ, United Kingdom

Corresponding author e-mail: silvia.di-lecce12@imperial.ac.uk

1. Introduction

External gradients, pressure, chemical, electrostatic or thermal, can be used to induce mass fluxes. The interplay of these gradients gives rise to a number of interesting coupling phenomena, such as the Ludwig-Soret effect [1, 2] in which a thermal gradient induces mass diffusion. Another coupling phenomena of particular relevance to us is the Seebeck effect, whereby the thermal gradient couples to a electrostatic potential.

Thermophoresis, [3, 4] the motion of solute particles in suspensions, and thermodiffusion, [5-7] which involves the separation of mixtures, are attracting significant interest. It has been found that the thermophoretic response of aqueous solutions is extremely sensitive to the solutions composition. The strength of the thermophoretic effect can be quantified by the Soret coefficient. A negative/positive value indicates migration of the solute from the cold/hot to the hot/cold region (thermophilic/thermophobic). Several studies have reported a wide range of values for the Soret coefficient of aqueous solutions. The magnitude depends on the type and concentration of electrolyte [8], and on the solute properties (size, shape, solvent-solute interactions) and charge [7, 9]. This subtle dependence of the Soret coefficient with the solution composition can be exploited to design thermophoretic analytical devices [9].

We are interested in combining electric and thermal fields to design electro-thermophoretic device with applications in energy conversion and analytical devices. As a first step to achieve this objective we investigate using Non-Equilibrium Molecular Dynamics (NEMD) simulations, nanopore structures that furnish a “gate” for transport and recognition of solutes (e.g. DNA translocation). Our system consists of a nanopore made of silica and an electrolyte solution containing alkali halides ([Li⁺, Na⁺, K⁺] Cl⁻, Na⁺ [Cl⁻, F⁻]).

The response of the alkali halide solutions in bulk and in the confined region is investigated as a function of the thermal gradient and an external electric field, in order to quantify the coupling phenomena between both external fields. We find that the Soret coefficient increases with the temperature, being of the order of ~10⁻³ K⁻¹, in good agreement with available experiments in bulk solutions [5, 6, 8]. We further analyse the impact of confinement on the transfer of ions across the silica nanopore.

Our NEMD methodology provides information on the temperature distribution around the nanopore. We compare this with results obtained from Finite Elements (FE) approach, hence providing a benchmark to test the reliability of FE method to nanoscale systems.
Taming Thermophoretic transport across nanopores: novel approaches for nanofluidic analytical devices

Silvia Di Lecce1, Tim Albrecht1, Fernando Bresme 1

1Department of Chemistry, Imperial College London, London, SW7 2AZ, United Kingdom
Corresponding author  e-mail: silvia.di-lecce12@imperial.ac.uk

1. Introduction
External gradients, pressure, chemical, electrostatic or thermal, can be used to induce mass fluxes. The interplay of these gradients gives rise to a number of interesting coupling phenomena, such as the Ludwig-Soret effect [1, 2] in which a thermal gradient induces mass diffusion. Another coupling phenomena of particular relevance to us is the Seebeck effect, whereby the thermal gradient couples to a electrostatic potential.

Thermophoresis, [3, 4], the motion of solute particles in suspensions, and thermodiffusion, [5 -7], which involves the separation of mixtures, are attracting significant interest. It has been found that the thermophoretic response of aqueous solutions is extremely sensitive to the solutions composition. The strength of the thermophoretic effect can be quantified by the Soret coefficient. A negative/positive value indicates migration of the solute from the cold/hot to the hot/cold region (thermophilic/thermophobic). Several studies have reported a wide range of values for the Soret coefficient of aqueous solutions. The magnitude depends on the type and concentration of electrolyte [8], and on the solute properties (size, shape, solvent-solute interactions) and charge [7, 9]. This subtle dependence of the Soret coefficient with the solution composition can be exploited to design thermophoretic analytical devices [9].

We are interested in combining electric and thermal fields to design electro- thermophoretic device with applications in energy conversion and analytical devices. As a first step to achieve this objective we investigate using Non -Equilibrium Molecular Dynamics (NEMD) simulations, nanopore structures that furnish a “gate” for transport and recognition of solutes (e.g. DNA translocation). Our system consists of a nanopore made of silica and an electrolyte solution containing alkali halides ([Li +, Na+, K+] Cl-, Na+[Cl-, F-]).

The response of the alkali halide solutions in bulk and in the confined region is investigated as a function of the thermal gradient and an external electric field, in order to quantify the coupling phenomena between both external fields. We find that the Soret coefficient increases with the temperature, being of the order of ~10 -3 K-1, in good agreement with available experiments in bulk solutions [5, 6, 8]. We further analyse the impact of confinement on the transfer of ions across the silica nanopore.

Our NEMD methodology provides information on the temperature distribution around the nanopore. We compare this with results obtained from Finite Elements (FE) approach, hence providing a benchmark to test the reliability of FE method to nanoscale systems.

References
Hydrogen bonding in hybrid scale models

Richard J. Gowers¹, Paola Carbone¹

¹School of Chemical Engineering and Analytical Science, University of Manchester, UK
Corresponding author e-mail: richard.gowers@postgrad.manchester.ac.uk

1. Introduction

In the field of Molecular Dynamics (MD) simulations, the use of coarse-graining (CG) techniques to create models which can sample the behaviour of systems much faster than conventional atomistic models is a commonly used practice. These coarse-grained models have discarded degrees of freedom from within the model to decrease the computational workload by an order of magnitude, allowing these simulations to reach mesoscopic time and length scales. This has made MD a powerful tool for investigating the behaviour of polymers.

However in some applications, such as modelling polymers which feature hydrogen bonding or other such fine details, degrees of freedom from the atomistic level cannot be discarded without fundamentally and irreparably changing the behaviour of the model. To address this shortcoming of CG models, hybrid scale models which simultaneously feature both fine and coarse levels of detail have been devised.[1] These allow a combination of CG and atomistic force fields to be used to model systems which feature important small scale details, but also require observation at long length and time scales to properly capture their behaviour.

2. Hybrid scale polyamide

In this contribution we present the latest developments in our methodology for constructing hybrid scale models[2] as well as results from our novel hybrid scale model for the polymer polyamide 6-6 (PA66)[3]. PA66 features a strong hydrogen bonding network, the modelling of which is crucial to understanding its behaviour, and therefore represents a strong challenge for our hybrid scale methodology.

The ability of our model to recreate both the large scale properties of the polymer chains as well as the inherently atomistic hydrogen bonding network is demonstrated and the thermodynamics of these bonds is explored. Finally the dynamics of our model is examined and contrasted with both the atomistic and CG model.

This work opens up new possibilities in creating computationally cheap models for MD which feature selective areas of detail. These will in turn allow the study of materials and systems which were previously out of reach.

References

Self-Assembly of High-Symmetry Planar Rings

Carlos Avendano 1, George Jackson 2, Erich A. Müller 2, and Fernando A. Escobedo 3

1School of Chemical Engineering and Analytical Science, The University of Manchester, Sackville Street, Manchester M13 9PL, UK, 2Department of Chemical Engineering, Centre for Process Systems Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K, 3School of Chemical and Biomolecular Engineering, 120 Olin Hall, Cornell University, Ithaca, New York 14853, USA.

Corresponding author email: carlos.avendano@manchester.ac.uk

In this work, we report a molecular dynamics study of the phase behavior of several models of non-convex colloidal rings. The rings are rigid and planar and, starting from a circular shape as the basis, two types of shape variations are investigated: ellipsoidal and polygonal rings. As we will show, both non-convexity and particle symmetry effects, i.e. the number of in-plane (2D) order of discrete rotational symmetry of the rings, determine the type of liquid crystalline (LC) order (or lack thereof) that can be attained. In our model, the particles are described as a collection of Nb tangent spheres of diameter D interacting via a WCA potential forming a planar ring. It is found that smectic phases are formed when the shapes of the particles are such that their in-plane rotational symmetry is large (favoring layer thickness uniformity) and that their inner cavity is large enough to allow particles to interlock (favoring efficient particle packing within smectic layers. The effect of particle symmetry and cavity size is further analyzed by reducing or increasing the size of the polygons, showing that only polygons having a small degree of interlocking can form stable liquid crystalline phases.

FIG. 1. Particle model for colloidal rings with (a) circular Nb = 28, (b) ellipsoidal Nb = 28, (c) hexagonal Nb = 30, (d) pentagonal Nb = 30, (e) square Nb = 32, and (f) triangular Nb = 34 shapes. Ellipsoidal rings (b) are characterized by the ratio of the major a to minor axes b.

FIG. 2. Representative configuration of the liquid crystalline smectic-A phase formed by circular colloidal rings.
Thermodynamic Modelling with SAFT of the properties of Aqueous Electrolyte solutions for Nuclear Waste Processing

Mark Bankhead1, Martin Whittle2, Karl Travis2, Ester Forte3, Amparo Galindo3

1National Nuclear Laboratory, 2University of Sheffield, 3Imperial College London

Corresponding author e-mail: mark.bankhead@nnl.co.uk

1. Introduction

The nuclear industry requires the accurate prediction of thermodynamic properties to support the development of flow-sheets for a number of applications including the treatment of aqueous legacy nuclear wastes [1], recycling of spent nuclear fuel which faces considerable challenges [2] and nuclear fuel manufacture. Thermodynamic modelling is an important tool for process optimisation and design. The choice of the method is dependent on the following factors: Its theoretical robustness in the region of the phase diagram of interest; the accuracy or precision required for each particular stage of the design flow sheet; the availability and ease of use of software to apply the method; and the availability of data to validate the approach.

Statistical Associating Fluid Theory is generating wide interest in academia and within the nuclear industry. There are several potential benefits with respect to the current challenges. SAFT is being actively developed in academia, providing a route for technical underpinning and peer review. It has been developed for complex multi-phase fluids including organic and salts mixtures, relevant to nuclear industry waste streams. It is a complete method for the phase behaviour of these mixtures, and can be used to compute properties including densities, vapour liquid equilibrium and solubility. This is theoretically superior to many of the industries standard methods where there is not a single self-consistent approach to computing such a broad range of physical properties from a single model.

2. Description of the Research

This talk describes the collaboration between academia and industry to develop a SAFT model for nuclear waste materials. The main advantages of SAFT over other methods include the treatment of temperature and complex mixtures, including potentially organic components. With respect to the established methods being applied within the nuclear Industry (Debye-Hückle, SIT and Pitzer all implemented within PHREEQC [3]) the SAFT method represents a significant potential improvement, particularly with respect to modelling temperature dependence of solubility and VLE.

3. Conclusion

The development of a SAFT model for modelling the VLE of nitric acid solutions will be presented. The nuclear industrial requirements are for model verification by rigorously understanding the model and its implementation in software from a theoretical perspective, to model validation against both experimental and plant trial data. Further results will be presented on the development of software codes for SAFT modelling. Commercial software does exist for including SAFT computed parameters within process engineering models. These codes are robust and allow rapid development of models for a specific application. However, commercial software is limited by the closed approach and limited ability for including competing methods from the academic literature.

References

Evaluation of the quadrupolar CPA EoS for modeling multicomponent CO₂-mixtures

Martin G. Bjørner¹, Georgios M. Kontogeorgis¹

¹Center for Energy Resources Engineering, Department of Chemical and Biochemical Engineering Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark.

Corresponding author e-mail: mgabj@kt.dtu.dk

1. Introduction

Despite the importance of CO₂-containing mixtures, most commonly used equations of state (EoS) cannot satisfactorily predict the phase equilibrium of such mixtures [1]. A reason for this may be that traditional approaches such as the Soave-Redlich-Kwong (SRK) EoS and even the more advanced Statistical Association Fluid Theory (SAFT) treat CO₂ as an inert. The continued use of such procedures may be attributed to the fact that the mixture behavior is mostly captured when the model is adjusted with an interaction parameter.

2. A quadrupolar contribution to CPA

The cubic plus association (CPA) combines the simplicity of the SRK with the association term of Wertheim. This procedure has been quite successful, making the CPA capable of modeling the phase equilibria of complex associating mixtures. Pragmatic approaches to improve CO₂ predictions with the CPA tend to treat CO₂ as a self-associating or solvating molecule, such procedures often works well resulting in somewhat improved predictions [1]. Rigorously, however, CO₂ has a large quadrupole moment which is unaccounted for in traditional approaches. The quadrupole is believed to be the reason for the unusual phase behavior of mixtures of CO₂. The large quadrupole moment is, for instance, believed to be the reason for the liquid-liquid equilibrium between CO₂ and heavy hydrocarbons.

During the last decade several quadrupolar (and polar) extensions have been suggested, primarily within the framework of SAFT [2-4]. Recently de Villiers et al. extended the CPA to include various dipolar terms by modifying terms employed within some polar SAFT versions [5].

Inspired by the advances within SAFT and CPA we have recently extended the CPA to also include a quadrupolar term which is similar to that employed by Karakatsani et al. [7]. The model has previously been evaluated in terms of pure compound derivative properties and for a range of binary mixtures. In this work we evaluate further the applicability of the quadrupolar CPA for the prediction of multicomponent equilibrium for mixtures containing CO₂. Moreover the new quadrupolar equation of state will be incorporated in a van der Waals-Platteuw model for describing mixtures of CO₂ and gas hydrates.

3. Conclusion

The applicability of the recently proposed quadrupolar CPA for predicting multicomponent equilibria as well as hydrate equilibria of CO₂-containing mixtures is evaluated. The results will be compared to those of the CPA.

References

Predicting the formation of liquid-liquid phase splits from mixing rules thermodynamically correct in the limit of zero pressure

Stefano Brandani¹, Federico Brandani² and Pietro Brandani¹

¹School of Engineering, The University of Edinburgh, Edinburgh UK, ²Centre de Recherche Claude-Delorme, Air Liquide, Jouy-en-Josas, France

Corresponding author e-mail: s.brandani@ed.ac.uk

Keywords: Equations of state; mixing rules; liquid-liquid phase split

1. Introduction

The accurate prediction of phase equilibria in process simulators can be achieved by combining equations of state (EOS) with advanced mixing rules [1]. The most flexible and accurate mixing rules currently available are those based on combining excess Gibbs energy models at a set pressure or reduced density of the system [2]. By matching the excess Gibbs energy model and the EOS in the limit of zero pressure one has the advantage of being able to use the mixture parameters obtained from the regression of low pressure data [3-4]. This approach does not allow to include the thermodynamically correct limit at zero pressure, i.e. imposing the mixing rule for the second virial coefficients, which can be recovered if one uses a fixed reduced density [5-6] or the limit of infinite pressure [7]. This second approach has been shown in some cases [8] to lead to predictions which include liquid-liquid phase splits even when excess Gibbs energy models which cannot predict the formation of vapour-liquid-liquid equilibria are used.

In this contribution we investigate in detail the effect that the mixture parameter from the second virial coefficient has on the formation of two liquid phases. The aim is to arrive at simple relationships which can be used to identify when this may become an issue in process simulations.

2. Theory

The general methodology to establish the existence of multiple liquid phases in phase equilibria calculations is based on the tangent plane method [9]. While this is applicable to both low and high pressures it does not lead to simple analytical equations that can be used to identify the incipient formation of the additional liquid phase. The approach we follow is the reverse of trying to match the EOS to the excess Gibbs energy model. We derive the equivalent activity coefficient model from the EOS and the thermodynamically correct mixing rule based on second virial coefficients.

\[ G_E^{EOS} = \sum x_i \ln \left( \frac{\phi_i^M}{\phi_i} \right) \]  

(1)

where \( \phi \) are the fugacity coefficients in the liquid phase of the mixture and of the pure component at the same temperature and pressure of the mixture. The Gibbs energy of mixing can then be obtained from

\[ \Delta G_{mix}^{EOS} = \sum x_i \ln \left( \frac{\phi_i^M}{\phi_i} \right) + \sum x_i x_i \ln x_i , \]  

(2)

but for any EOS

\[ \sum x_i \ln \left( \frac{\phi_i^M}{\phi_i} \right) = \sum x_i (z_M - z_i) + \tilde{A}_{E}^{rep} + \tilde{A}_{E}^{attr} - \sum x_i \ln \left( \frac{z_M}{z_i} \right) \]  

(3)

The first term on the RHS of eq. 3 is simply

\[ \sum x_i (z_M - z_i) = \frac{P}{RT} v_E \]  

(4)
which can be neglected at low pressure. Therefore
\[ \Delta G_{\text{mix}}^{\text{EOS}} \approx \bar{A}_{E}^{\text{rep}} + \bar{A}_{E}^{\text{attr}} - \sum x_i \ln(z_M / z_i) + \sum x_i \ln x_i \] (5)

and a the reference reduced density one obtains
\[ \Delta G_{\text{mix}}^{\text{EOS}} \approx \bar{A}_{E}^{\text{attr}} - \sum x_i \ln(b_M / b_i) + \sum x_i \ln x_i \] (6)

where \( b \) are the volume parameters of the EOS. Substituting the mixing rule valid at zero pressure
\[ \Delta G_{\text{mix}}^{\text{EOS}} \approx G_{E}^{\text{ACM}} - \sum x_i \ln(b_M / b_i) + \sum x_i \ln x_i \] (7)

This equation can be used to map where the condition for incipient formation of two liquid phases in a binary mixture is fulfilled by imposing [10]
\[ \frac{d^2 \Delta G_{\text{mix}}^{\text{EOS}}}{dx_i^2} = 0 \] (8)

Direct comparisons with full phase equilibria calculations show that this approach is very accurate at low to medium pressures and provides good guiding values at higher pressures. To illustrate in a simple way the importance of the result, consider the special case for which one selects an ideal liquid phase, \( G_{E}^{\text{ACM}} = 0 \), and a pseudo binary mixture with two identical components, \( b_1 = b_2 \) and \( \varepsilon_1 = \varepsilon_2 \), where \( \varepsilon \) is the energy parameter of the EOS, then
\[ \Delta G_{\text{mix}}^{\text{EOS}} \approx 0 - \ln(1 - 2x_i x_j (1 - k_{12})) + \sum x_i \ln x_i \] (9)

for which the remarkably simple result is derived that \( k_{12} = 2/3 \) for the incipient formation of two liquid phases if the second virial coefficient mixing rule is imposed.

3. Conclusion
We have developed a methodology to derive the equivalent excess Gibbs energy model for EOS mixing rules that include the thermodynamically correct mixing rule for second virial coefficients valid in the limit of zero pressure. An analytical expression is derived that allows to map the regions where two liquid phases are predicted without the need to apply the full tangent plane approach.

Dedication
This contribution is dedicated to the memory of our father, the late Professor Vincenzo Brandani who was the Professor of Chemical Engineering Thermodynamics at the University of L’Aquila for 40 years. He would have been 75 this year.

References
Modelling electrolytes using a single-parameter molecular-based equation of state: improving solvation energies

Daniel Kunisch Eriksen¹, Georgia Lazarou², Simon Dufal², Amparo Galindo¹,², Andrew J. Haslam¹ and George Jackson¹,²

¹: Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, United Kingdom; ²: Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, United Kingdom

Corresponding author e-mail: daniel.kunisch-eriksen10@imperial.ac.uk

Keywords: Electrolyte systems, EOS, solvation energy, SAFT-VRE Mie

Thermodynamic modelling of electrolyte solutions is industrially relevant for applications as diverse as pipeline flow, subsurface CO₂ injection and solvent design. The problem associated with such modelling is that one is required to account for many different types of molecular interaction. Molecular-based equations of state represent an ideal platform to tackle such problems. We employ SAFT-VRE Mie, a thermodynamic perturbation theory tailor made to incorporate the different forces of interaction between molecules in such diverse applications.

SAFT-VRE Mie is an extension for electrolytes of the SAFT-VR Mie [1] equation of state (EOS). Coulombic interactions are accounted for using Debye-Hückel [2] theory or the MSA [3]. Ion potential parameters are obtained from well-known physical quantities, so that only a single model parameter is obtained from fluid-mixture experimental data, thereby simplifying the parameter space of the EOS. Solvation energies are improved by explicitly incorporating solvation diameters from the literature.

Our single-parameter approach retains almost equivalent performance to the more-common three-parameter schemes in relation to commonly studied electrolyte properties, while allowing for quantitative prediction of solvation energies.

References


DKE and AJH gratefully acknowledge funding from the Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), provided jointly by Qatar Petroleum, Shell, and Qatar Science & Technology Park; GL acknowledges financial support from Pfizer, Inc.
Pressure-Driven Molecular Dynamics Simulations of an Electrolytes Solution through a polyamide membrane

Aziz Ghoufi¹, Anthony Szymczyk², M. Ding¹,²

¹Institut de Physique de Rennes, CNRS, UMR 6251, Université de Rennes 1, Rennes, France ²Institut des Sciences Chimiques de Rennes, CNRS, UMR 6226, Université de Rennes 1, Rennes, France

Corresponding author e-mail: aziz.ghoufi@univ-rennes1.fr

In this work we carried out equilibrium and pressure driven molecular dynamics simulations to model water and ions transport through a polyamide membrane. For that we used a general method developed in our previous work to construct an atomistic model of a highly cross-linked polyamide RO membrane. The so-obtained water permeability and the salt rejection are in fair agreement with experiments. A local increase in the local density close to the inlet of the polyamide membrane was found. That was imputed to the very dense structure of the membrane which limits dramatically mass transfer. Regarding ion transport we observed a partial dehydration of both sodium and chloride ions inside the membrane, accompanied by decrease in the number of hydrogen bonds between water molecules.

Figure 1: Illustration of hydrated polyamide with both electrolytic solutions
The complementing rôles of Coulombic forces and association in the thermodynamics of selected room-temperature ionic liquids

Fernando del Río¹, Alejandro Gil-Villegas⁵, Orlando Guzmán¹ and J Eloy Ramos³

¹ Universidad Autónoma Metropolitana- Iztapalapa, Mexico DF, Mexico, ²Universidad de Guanajuato, León, Guanajuato, Mexico, ³Universidad Autónoma de la Ciudad de México, Mexico DF, Mexico

Corresponding author e-mail: fdr@xanum.uam.mx

Keywords: room-temperature ionic liquid, SAFT-VRE, mean spherical approximation, Coulombic forces, ionic pairing

1. Introduction

Thermodynamic properties of room-temperature ionic liquids, RTIL, have been modelled by variations of the Statistically Associating Fluid Theory, SAFT, such as those of Andreu and Vega [1,2], Ji and Adidharma [3], and Ji, Held and Sadowski [4,5]. These works focus mainly on the prediction of liquid densities and solubilities of various gases, and perform successfully. It is worth noticing that Andreu and Vega assume full association of the ion pairs, whereas Ji et al. introduce a purely Coulombic force.

2. Aim of this work

The objective of this work is to explore the complementarity between explicit ionic forces and different models for ionic association. To do so, we consider a theory for pure RTIL, based on the SAFT-VRE theory developed by Gil-Villegas, Galindo and Jackson [6], to model a wide range of properties: densities, liquid-vapour equilibrium, critical coordinates, heats and entropies of vaporization, thermodynamic coefficients and surface tension. The study is carried out for three families of imidazolium-based ionic liquids, for which the literature contains results of all-atom molecular simulations.

The SAFT-VRE theory, which treats the Coulombic force at the level of the mean spherical approximation, MSA, is complemented with the binding MSA, as introduced by Bernard and Blum [7]. Special emphasis is made in analysing the rôles played by Coulombic forces and ionic-pair formation. The Coulombic interaction is kept fixed for each series of RTIL and the dependence of the properties on the strength of the dispersion forces is analysed. The properties predicted are compared with experiment and results of molecular simulations, in particular those of Rai and Maginn [8], and Rane and Errington [9].

3. Conclusions

The theory accounts correctly for the properties and RTIL selected. It is shown that, in order to account for a variety of pure RTIL thermodynamic properties, it is necessary to introduce the Coulombic force explicitly and at a level beyond the MSA.

References


Acknowledgements. We acknowledge support of CONACYT (Mexico) Project 2008-105843.
Simulations of mean ionic activity coefficients and solubilities in aqueous electrolyte solutions

Zoltan Mester and Athanassios Z. Panagiotopoulos

Department of Chemical and Biological Engineering, Princeton University, Princeton NJ 08544, U.S.A.

Corresponding author e-mail: azp@princeton.edu

1. Introduction

Aqueous electrolyte solutions play an important role in industrial and biological applications, and the study of geothermal brines. Thermodynamic descriptions of aqueous electrolytes typically rely on the Debye-Hückel limiting law or empirical models, which rely on parameters fitted to experimental results. In order to overcome the limitations of phenomenological descriptions, there is significant interest in developing methods and models to predict accurately the properties of aqueous electrolyte solutions via molecular simulations. Because of the difficulties in sampling for explicit-solvent models, there have been relatively few prior atomistic simulation studies of solubilities and chemical potentials of salts in water [1-4]. The mean ionic activity coefficients quantify the deviation of salt chemical potential from Henry's law (ideal solution) behavior; experimental measurements are available for many salts over broad ranges of concentration and temperature. The focus of the present work is on determination of activity coefficients for atomistic models of aqueous electrolytes, which require high precision measurements of chemical potential differences and have not been previously available from simulations.

2. Methods and Results

We devised a method for obtaining mean ionic activity coefficients of aqueous electrolyte solutions from molecular dynamics simulations by gradually inserting ion pairs into the solution. The method is based on slow growth of the non-Coulombic part of the interactions first, followed by the Coulombic part. The infinite-dilution (reference) chemical potential of the salt is obtained by matching the simulation results at very low concentrations to the Debye-Hückel limiting law. Several common non-polarizable water and ion models were used to obtain the mean ionic activity coefficients of NaCl, KF, LiCl, LiBr, and CaCl₂ solutions at several concentrations at a temperature of 298.15 K and pressure of 1 bar. Gibbs-Duhem equation calculations of the thermodynamic activity of water were used to confirm thermodynamic consistency of the calculations. We also tested the effect of the temperature on the predictions for the mean ionic activity coefficients.

3. Conclusions

Deviations at high concentrations of the simulated mean ionic activity coefficients from experiment and the inaccuracies in solubility predictions necessitate the use of more sophisticated models. To this end, we are presently testing the accuracy of several polarizable ion and water models with respect to the solubility and activity coefficient predictions.

References

Atomistic Molecular Dynamics Simulations of Transport Properties for the H$_2$O+CO$_2$+NaCl mixture at conditions relevant to CCS processes

Othonas A. Moultos$^1$, Hao Jiang$^2$, Ioannis N. Tsimpanogiannis$^3$, Athanassios Z. Panagiotopoulos$^2$ and Ioannis G. Economou$^{1,*}$

$^1$Chemical Engineering Program, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar
$^2$Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States
$^*$Corresponding author e-mail: ioannis.economou@qatar.tamu.edu

1. Introduction

Emissions of long-lived greenhouse gases (GHGs) are believed to be a major driver of climate change. CO$_2$ is the most important greenhouse gas, according to latest available studies and one of the most prominent strategies to lower its emissions is carbon capture and sequestration (CCS) [1]. CO$_2$ can be stored in geological repositories, such as hydrocarbon reservoirs in which sodium chloride (NaCl) is the most common dissolved salt. For the optimum design of any CCS process, accurate experimental data and computational models that can provide reliable prediction of transport properties are necessary. This study focuses on validating the performance of various existing molecular-based models and methodologies to allow for reliable prediction of the transport properties of H$_2$O + CO$_2$ + NaCl mixture and its binary constituents over a broad range of temperatures and pressures relevant to geological storage.

2. Results and Discussion

Atomistic molecular dynamics (MD) simulations were employed for the prediction of densities and mutual diffusion coefficients of the H$_2$O + CO$_2$ system [2] and the densities, viscosities and interfacial tension of H$_2$O + NaCl mixture [3]. The predictive abilities of several combinations of existing H$_2$O, CO$_2$ and NaCl models [2,3], with either Lennard-Jones 12-6 or Buckingham exponential-6 (Exp-6) functional forms, were assessed and useful comparisons with the available experimental data [4-7] were performed. The MD results are in very good agreement with the available experimental data. Overall, the combinations TIP4P/2005 – EPM2, TIP4P/2005 – TraPPE and Exp-6 – Exp-6 with optimized cross interactions [8] are found to be the most accurate for the calculation of diffusivities of the H$_2$O + CO$_2$ mixture and the SPC/E – SD for the prediction of viscosities in the H$_2$O + NaCl mixture. For the interfacial tension and densities the most accurate combination is found to be the semiflex SPC/E – JC.

Acknowledgements

This study was made possible by NPRP grant number 6-1157-2-471 from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of the authors.

References

Molecular simulation of polarizable models of electrolytes: Concentration dependence of the chemical potentials, density and solubility

Filip Moucka¹, Ivo Nezbeda¹,², William R. Smith³

¹Faculty of Science, J. E. Purkinje University, Usti n. L., Czech Rep, ²Institute of Chem. Process Fund., Acad. Sci., Prague, Czech Rep., ³Univ. of Ontario Inst. of Technology, Oshawa, Ontario, Canada

Corresponding author e-mail: IvoNez@icpf.cas.cz

Aqueous electrolytes are ubiquitous in environmental, biological, and industrial systems. In addition to experimental data on their properties it has become common nowadays to study and predict their behavior by molecular simulations using various force fields (FF), i.e., intermolecular interaction models with specific parameters obtained by fitting the selected properties to experimental data. Among the most important properties of solutions of electrolytes are the chemical potential and electrolyte solubility.

Typically, infinite dilution electrolyte chemical potentials and the density have been used to determine the FFs parameters. Attempts to predict chemical potentials at finite concentrations and the electrolyte solubility have been rare for two simple reasons. First, such calculations are both very computationally intensive and technically challenging. Second, chemical potentials are a very sensitive test of a FF, i.e., different FFs may produce significantly different results. Furthermore, since the electrolyte chemical potential curve flattens at higher concentrations, the predicted solubility value is also very sensitive to the details of the simulation procedure used.

There are two aspects associated with the chemical potential determination from simulations. Concerning the FFs, there has been gathered enough evidence that the pairwise models have exhausted their potential and non-additive effects, typically via polarization, must be accounted for. Concerning the technical aspects of simulations, the Monte Carlo (MC) techniques used to calculate chemical potential are limited to pairwise interaction models. Furthermore, the common way to determine solubility by calculating the chemical potential over a range of concentrations is rather cumbersome.

In order to overcome the above mentioned obstacles, we have recently developed (i) a Multi-Particle-Move MC (MPM-MC) which makes it possible to efficiently use the MC methodology even for polarizable models, and (ii) the osmotic ensemble (OEMC) method making it possible to determine the solubility at one MC run. Both techniques have been used to compute the chemical potential and concentration dependence of density of the NaCl electrolyte along with the solubility for two polarizable models, Lamoureux and Roux SWM4—DP model and Baranyai-Kiss BK3 model. In addition to a brief account of the used methodology, results of these simulations will be reported and discussed along with the comparison with those produced by commonly used non-polarizable models and experimental data. It is shown that the BK3 model yields the results in the quantitative agreement with experiment. Recommendations for future work will also be discussed.
Nanoparticle thermophoresis under thermal gradients: thermophobic or thermophilic, … and why?

Irene Iriarte-Carretero1 and Fernando Bresme1

1Department of Chemistry, Imperial College London, SW7 2AZ, London, UK

Corresponding author e-mail: irene.iriarte-carretero08@imperial.ac.uk

1. Introduction

Thermal gradients are responsible for thermophoretic and thermodiffusive processes, in which the heat flux induces particle motion and mass separation, respectively [1]. The Soret coefficient quantifies the strength of the effect and it depends on many different factors such as particle size and mass of the components involved [2], or the nature of intermolecular interactions [3]. Despite considerable experimental studies there is not, however, a complete theoretical explanation to the thermophoretic effect.

Many Soret experiments have considered thermodiffusion and thermophoresis in aqueous solutions, as water is the most important solvent in chemistry and biology. The complexity of water thermophoretic response is highlighted by the thermal orientation effect in water [4], a coupling phenomenon whereby water is polarized by a thermal gradient. Experimental studies have further shown that aqueous suspensions and aqueous solutions feature inversion temperatures. Above this temperature the solute or solution is thermophobic, which means the solutes such as DNA [1], proteins [5] or salt [6] move towards the cold region. Below this temperature, however, they are normally found to be thermophilic. These puzzling observations are still not well understood, but it has been suggested that the thermophoretic response of aqueous solutions/suspensions can be traced back to the solvation entropies [7]. For particles smaller than the range of the solute-solvent interaction, it has been proposed that the sign is defined by the enthalpy of solvation [8]. An understanding of the thermophoretic response of aqueous solutions can help us to rationalize the behaviour of many biological systems and suspensions under thermal gradients, as well as the solvation thermodynamics of a wide range of colloidal suspensions.

In the present work we employ Non-Equilibrium Molecular Dynamics simulations to examine the thermophoretic response of hydrophobic and hydrophilic nanoparticles in TIP4P/2005 water. The single particle thermodiffusion algorithm (SPTA) [9] is used to perform a systematic study of the dependence of the thermophoretic force with the size of the solute and the average temperature of the system at infinite dilution. In the SPTA, a temperature gradient is applied to the solution, which consists of water and a single nanoparticle. This solute is tethered to a point in the simulation box through a harmonic potential, which allows the calculation of the thermophoretic force on the solute. Our results show an inversion in the sign of the Soret coefficient in the temperature range studied (250-425K). Interestingly, the hydrophobic nanoparticles migrate towards the hot region at high temperature, unlike the behaviour observed in many DNA, alkali halide salt and protein solutions.

We have computed the free energy of solvation of model nanoparticles and resolved its entropic and enthalpic contributions. We establish in this way an unequivocal correlation between the change of sign of the entropy of solvation and the inversion of sign of the Soret coefficient, making it possible to address the accuracy of current theories. [7,8] Interestingly, the role of the entropy in determining the inversion temperature can be modulated by tuning the attractive solute-solvent interactions. We investigate the water solvation structure around the solute to propose a microscopic explanation to the observed temperature inversion effect.
Irene Iriarte-Carretero1 and Fernando Bresme 1
1Department of Chemistry, Imperial College London, SW7 2AZ, London, UK
Corresponding author e-mail: irene.iriarte-carretero08@imperial.ac.uk

1. Introduction
Thermal gradients are responsible for thermophoretic and thermodiffusive processes, in which the heat flux induces particle motion and mass separation, respectively [1]. The Soret coefficient quantifies the strength of the effect and it depends on many different factors such as particle size and mass of the components involved [2], or the nature of intermolecular interactions [3]. Despite considerable experimental studies there is not, however, a complete theoretical explanation to the thermophoretic effect.

Many Soret experiments have considered thermodiffusion and thermophoresis in aqueous solutions, as water is the most important solvent in chemistry and biology. The complexity of water thermophoretic response is highlighted by the thermal orientation effect in water [4], a coupling phenomenon whereby water is polarized by a thermal gradient. Experimental studies have further shown that aqueous suspensions and aqueous solutions feature inversion temperatures. Above this temperature the solute or solution is thermophobic, which means the solutes such as DNA [1], proteins [5] or salt [6] move towards the cold region. Below this temperature, however, they are normally found to be thermophilic. These puzzling observations are still not well understood, but it has been suggested that the thermophoretic response of aqueous solutions/suspensions can be traced back to the solvation entropies [7]. For particles smaller than the range of the solute-solvent interaction, it has been proposed that the sign is defined by the enthalpy of solvation [8]. An understanding of the thermophoretic response of aqueous solutions can help us to rationalize the behaviour of many biological systems and suspensions under thermal gradients, as well as the solvation thermodynamics of a wide range of colloidal suspensions.

In the present work we employ Non-Equilibrium Molecular Dynamics simulations to examine the thermophoretic response of hydrophobic and hydrophilic nanoparticles in TIP4P/2005 water. The single particle thermodiffusion algorithm (SPTA) [9] is used to perform a systematic study of the dependence of the thermophoretic force with the size of the solute and the average temperature of the system at infinite dilution. In the SPTA, a temperature gradient is applied to the solution, which consists of water and a single nanoparticle. This solute is tethered to a point in the simulation box through a harmonic potential, which allows the calculation of the thermophoretic force on the solute. Our results show an inversion in the sign of the Soret coefficient in the temperature range studied (250-425K). Interestingly, the hydrophobic nanoparticles migrate towards the hot region at high temperature, unlike the behaviour observed in many DNA, alkali halide salt and protein solutions.

We have computed the free energy of solvation of model nanoparticles and resolved its entropic and enthalpic contributions. We establish in this way an unequivocal correlation between the change of sign of the entropy of solvation and the inversion of sign of the Soret coefficient, making it possible to address the accuracy of current theories. [7,8] Interestingly, the role of the entropy in determining the inversion temperature can be modulated by tuning the attractive solute-solvent interactions. We investigate the water solvation structure around the solute to propose a microscopic explanation to the observed temperature inversion effect.

References
The molecular segregation of tri-butyl phosphate in an organic diluent and its relevance to nuclear extraction processes.

Junju Mu and Andrew J. Masters

School of Chemical Engineering & Analytical Science, University of Manchester, Manchester M13 9PL, UK

Corresponding author e-mail: andrew.masters@manchester.ac.uk

1. Introduction

Tri-butyl phosphate (TBP) is used as a complexing agent in the PUREX liquid-liquid phase extraction process [1] for recovering uranium and plutonium from spent nuclear reactor fuel. After the nuclear reaction has finished, the waste material is dissolved in nitric acid. To this is added TBP and an organic diluent, usually odourless kerosene. The TBP complexes selectively with uranyl and plutonium nitrate, and these metal nitrates move into the organic phase, thus achieving the desired separation. Conventional activity models, however, have difficulty in predicting the thermodynamics of this phase separation with good accuracy. One likely reason for this is that the organic phase is not a conventional solution, as assumed in standard process models, but is instead a structured fluid. A number of experimental and simulation studies have shown this to be highly likely [2].

Rather than tackling this system in its full complexity, we first use simulation to study a binary TBP/hydrocarbon system. Previous work by Leay et al. indicated that the polar TBP molecules stacked into filaments [3]. On the other hand, recent simulations by Cui et al. showed considerably less TBP aggregation [4]. These simulations indicated that the system resembled a normal homogeneous solution. The difference between the simulations lies in the use of different partial charges on the TBP molecules. Before proceeding to the study of the organic phase in all its complexity, it is necessary to get a reliable TBP model.

The experimental techniques most appropriate for revealing TBP-aggregation are X-ray or neutron scattering. Motakawa et al. have such data for TBP/octane systems [5]. Neither the Leay nor the Cui force-fields predict the experimental low wavelength forms of the scattering functions. We have therefore re-parameterised the TBP partial charges so as regain agreement with these experiments.

2. Conclusion

We present the results of these new simulations and discuss the degree of TBP aggregation. We then show what happens when water and nitric acid are added to the TBP/hydrocarbon phase, focusing on the types of structures that form.

In parallel to this, we have developed a hybrid coarse-grained/atomistic model of the TBP/hydrocarbon system. This allows us to simulate large systems over long time scales. We present evidence of liquid-liquid demixing in the organic phase, corresponding to the “third phase” that appears in the PUREX process at high metal loadings.

References

Developing Peptoid Simulation Models

Laura J. Weiser1, Erik E. Santiso1

1Dept. of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, USA

Corresponding author email: eesantis@ncsu.edu

1. Introduction

Peptoids (poly-n-substituted glycines) are peptide-like macromolecules composed of modified glycine units which have side chains attached to the nitrogen atoms [1]. Peptoids are biocompatible and resistant to protease degradation [2] and peptoid sequences can be synthesized using more than 300 commercially available amines [1], [3], making peptoids versatile and appealing compounds for combinatorial materials design.

Simulation models of peptoids are desirable in order to predict the folded structures of previously uncharacterized peptoid chains. The large number of potential peptoid side chains makes experimental synthesis and characterization of all possible peptoid sequences impossible. Therefore, predictive simulations may provide a way to search parameter space and guide experimental focus toward peptoid chains with useful properties. In this work, we show the simulation models that we have developed and compare their predictions to newly obtained experimental data.

2. Work Presented

We present our newly developed simulation models of peptoids. All-atom molecular dynamics simulations are performed using the Generalized CHARMM force field with new parameters fit specifically for peptoids via \textit{ab initio} simulations. Using these new force-field parameters, we explore the conformational preferences of the peptoid backbone using enhanced sampling techniques, including the adaptive biasing force method. We also study how backbone length and the choice of peptoid end groups affect these structures. These results are compared with existing experimental data.

Additionally, we present newly fitted Generalized CHARMM parameters for several peptoid side chains. Using molecular dynamics simulations, we characterize the effects of these peptoid side chains on the peptoid backbone conformation. We also study how these side chains can be sequenced to create ordered secondary structures in peptoid polymers. The results of these simulation studies are compared with experimental characterizations performed via NMR and circular dichroism.

3. Conclusion

We present here the first steps toward developing predictive simulation models of peptoid folding. This work benefits from the framework of peptide simulation studies; however, the wealth of possible peptoid side-chains and dearth of experimentally defined peptoid structures presents a challenge to model development. To that end, our simulation studies are aided by new experimental characterizations of peptoid side chains. These simulation studies will serve as the foundation of future work to develop simulation models capable of predicting the conformations of novel peptoid chains.

References


Computer Simulation of chromonic materials: the influence of molecular structure on self-assembly

Mark R. Wilson1, Martin Walker1

1Department of Chemistry, Durham University, Durham, UK.

Corresponding author e-mail: mark.wilson@durham.ac.uk

1. Introduction

Chromonic molecules are non-conventional amphiphiles. Common molecular features of a chromonic mesogen are a rigid, often aromatic, molecular core functionalised with multiple solubilising groups. In solution, chromonic mesogens self-assemble into larger aggregates, which orient into a nematic (or other) ordered phase at higher concentrations. The self-assembly process is unlike that observed for many conventional amphiphiles; it typically has a strong enthalpic component to aggregation and occurs without a critical micelle concentration [1].

2. Simulations of aggregation in aqueous solution

Recently, atomistic computer simulations have been shown to be effective in predicting the structures of chromonic aggregates [2,3]. We show here that atomistic simulations can be used to understand aggregation in a series of non-ionic chromonic molecules (figure 1). Simulations demonstrate spontaneous self-assembly in aqueous solution and predict the preferred structures of aggregates. For the molecules in figure 1, we explore how changes in molecular structure influence aggregation and hence chromonic phase formation. We also carry out potential of mean force (PMF) calculations of binding events (involved in aggregate growth). The PMF allows estimates of aggregate size distributions at different temperatures.

3. Conclusion

Atomistic simulations have been used to understand aggregate structure and strength of binding in three related nonionic chromatogens.

References

Coarse graining of polymer systems employing SAFT

Jos Tasche\(^1\), Mark R. Wilson\(^1\)

\(^1\)Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Corresponding author e-mail: jos.tasche@durham.ac.uk

1. Introduction

Molecular simulations of polymers using readily-available atomistic or united atom force fields are often too expensive to predict slow processes, particularly in highly-viscous polymers. One way forward is to use coarse-grained models to extend time (and length) scales. Use of atomistic reference simulations for systematic parameterisation of coarse-grained models often use structural properties, such as radial distribution functions, within an iterative Boltzmann inversion (IBI) approach. However, thermodynamic properties obtained via this approach are sometimes less than optimal. In this paper we aim to systematically develop coarse-grained force fields for the prediction of thermodynamic properties, such as free energies of mixing and partition coefficients, for polymer systems and polymer/small molecule mixtures.

2. Coarse-grained approach

We employ a combination of the Statistical Association Fluid Theory (SAFT) and molecular simulations to develop coarse-grained force fields for polymer systems (Figure 1).

The non-bonded potentials of the force field are parameterised employing recent SAFT incarnations (SAFT-VR Mie and SAFT-γ Mie) [1, 2]. The non-bonded potentials are fitted within SAFT to experimental thermophysical data for the accurate description of thermodynamic properties. The bonded potentials are obtained with direct and iterative Boltzmann inversion of simulations with higher-resolution force fields. The bonded potentials account for the configurational restrictions of the chains, which are expected to improve the prediction of thermodynamic properties of polymer mixtures. We find this methodology to be significantly faster than employing iterative Boltzmann inversion for all force-field potentials.
3. Conclusion

Predictions of solubilities and partition coefficients for model systems of oligomers and polymers are presented based on a combined SAFT/IBI approach.

References


Computer-Based Discovery of Surfactants

Mariah Ritz¹, Erik Santiso¹, Nathan Duff¹

¹Department Of Chemical and Biomolecular Engineering, North Carolina State University
Corresponding author e-mail: eesantis@ncsu.edu

1. Introduction

Surfactants are amphiphilic substances that alter the interfacial properties between liquids, solids, and gases. They are used in industry, agriculture, and medicine as dispersion agents, detergents, and antiseptics. Many conventional surfactants have been shown to have negative effects on the environment. Notorious examples include perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and nonylphenol ethoxylates (NPEs), traditionally used in the synthesis of non-stick coatings, in stain-repellent coatings, and as industrial detergents. Perfluorinated surfactants are persistent pollutants and have been implicated in endocrine disruption in seawater species as well as carcinogenesis in mammals [1]. Most people (>98%) in the United States have detectable levels of PFOA/PFOS in their blood, and PFOA has been associated with increased risks of chronic kidney disease, kidney cancer, testicular cancer, hypercholesterolemia, and pregnancy-induced hypertension in humans. NPEs have also been implicated in endocrine disruption and are being phased out due to environmental concerns. It would thus be desirable to find surfactants with similar physicochemical properties without the deleterious effects.

2. Background and Computational Methods

Recent studies have found that increasing the degree of branching of the tail group allows for improved performance with lower fluorine content (Figure 1). However, there is no comprehensive study on the relation between tail group topology and surfactant performance. Furthermore, there is no general theory connecting topological features to the ability to reduce surface tension. Without such a theory, it is difficult to devise candidate surfactants to test experimentally, as the space of possible topologies is large. In this work we seek to gain fundamental understanding of how different topological motifs affect the surfactant’s performance by using molecular simulation.

We present results of molecular dynamics (MD) simulations of water/vacuum/surfactant using coarse-grained interaction potentials based on the SAFT-γ Mie approach. Water is modeled using a Mie potential parameterized to reproduce experimental vapor-liquid equilibrium properties and surface tensions. Surfactant molecules are built from chains of coarse-grained segments interacting via Mie potentials. We use two types of segments: (1) A head-group segment parameterized to interact strongly with water; and (2) An alkane-like segment parameterized to reproduce properties of compounds from the alkyl series. Our results suggest that, for small to medium tail group sizes, the best-performing surfactants have tail group topologies that match those used in experimental studies [2].

Figure 1. Compatibility of surfactant/ CO₂ versus branching/fluorocarbon content
3. Conclusion

As a first step toward understanding the features that lead to better behaviour and lower toxicity, we present results of coarse-grained simulations exploring the connection between surfactant topology and physical properties. This approach will be integrated in the future with automatic search tools [3] in order to predict optimal surfactant topologies and chemistries to replace toxic surfactants in current applications.

References
Mixing rules for modelling asymmetric systems with water

Duncan Paterson, Wei Yan*, Erling H. Stenby, Michael L. Michelsen

Technical University of Denmark, Department of Chemistry, Building 206,
DK2800 Lyngby, Denmark

*Corresponding author e-mail: weya@kemi.dtu.dk

1. Introduction

This work will present a comparison of mixing rules for the modelling of asymmetric systems and systems containing water with large hydrocarbons at elevated temperatures and pressures. The models investigated will be the traditional vdW mixing rules, the advanced excess Gibbs energy mixing rules and the SAFT-like CPA equation.

The motivation for this work is to improve the modelling of heavy oil production using steam and solvent within reservoir simulators. Heavy oil and bitumen are increasingly being viewed as alternatives to conventional oil reserves. However their extraction involves very complex phase behaviour with up to four fluid phases coexisting [1].

2. Modelling

The van der Waals equations are known to not accurately represent water with hydrocarbons, as they are unable to accurately represent the aqueous phase and hydrocarbon phases simultaneously. The more advanced excess Gibbs energy mixing rules which incorporate an activity coefficient model (in this work NRTL was used) are capable of accurately representing both phases with a suitable set of binary interaction parameters. The CPA[2] model was designed to accurately represent hydrocarbons with associating components. The reason that these equations have not traditionally been implemented is due to their increased computational cost.

To compare these models a range of data for asymmetric hydrocarbons and hydrocarbons with water was collected and used to regress the applicable binary interaction parameters. Using the regressed parameters the phase diagrams have been recreated and compared.

Figure 1: PXY diagram for water/n-decane at 593.2K with CPA ($k_i=0.066$)
Figure 1 illustrates the PXY diagram for water/n-decane. This shows that at the elevated temperatures and pressures encountered in heavy oil extraction there can be complex phase equilibrium, this is made more complex as more components are introduced.

3. Conclusion
In this work we investigate the modelling of asymmetric systems and systems containing hydrocarbon with water. We illustrate the strengths and weaknesses of each model with a wide range of systems. The CPA model has been proven to be sufficient for modelling of the systems while the excess Gibbs energy models have been found to require precise fitting parameters before they give accurate results – requiring a large range of experimental data.

References
Prediction of the phase behaviour of hydrocarbon and water mixtures with the SAFT-\(\gamma\) Mie group-contribution equation of state: properties at infinite dilution

Panatpong Hutacharoen\(^1\), Vasileios Papaioannou\(^1\), Simon Dufal\(^1\), Ravi M. Shanker\(^2\), Amparo Galindo\(^1\), George Jackson\(^1\), Claire S. Adjiman\(^1\)

\(^1\)Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, United Kingdom, \(^2\)Pfizer Inc, Pharmaceutical Sciences, Worldwide R&D, Groton, CT, 06340, USA

Corresponding author e-mail: a.galindo@imperial.ac.uk

**Keywords:** group contribution, SAFT-\(\gamma\) Mie, VLLE, partition coefficient

Thermodynamic modeling of aqueous solutions of hydrocarbons is of great interest in many industrial applications ranging from the petrochemical to biological processes. The modeling of such systems is particularly challenging due to the highly non-ideal behaviour exhibited over a wide range of thermodynamic conditions. Here, the SAFT-\(\gamma\) Mie equation [1, 2] is used to model the extreme nature of the phase behaviour of hydrocarbon-water mixtures, in which the respective solubilities of the two liquid phases differ by many orders of magnitude.

The SAFT-\(\gamma\) Mie approach is a fused heteronuclear group contribution formulation of the SAFT-VR [3] equation of state. In SAFT-\(\gamma\) Mie, molecules are broken down into different types of monomeric segments and modeled as comprising segments that interact via Mie (generalized Lennard-Jonesium) potentials of variable repulsive and attractive range. Our hydrocarbon-water model within the SAFT-\(\gamma\) Mie approach can accurately describe the solubility of the hydrocarbons in the aqueous phase as a function of alkane length without any adjustable parameters. This model serves as a firm basis for more complex systems containing alkyl-water interactions.

The thermodynamic properties of hydrocarbons at infinite dilution are examined. The properties of interest include the Henry’s law constant, the infinite dilution activity coefficient and the octanol-water partition coefficient. The SAFT-\(\gamma\) Mie predictions are in good agreement with experimental data, validating the quality of the parameters.

**References**

Molecular modelling of interfacial properties by multi-criteria optimization

Martin Horsch¹, Katrin Stöbener¹,², Stephan Werth¹, Peter Klein², Hans Hasse¹

¹Laboratory of Engineering Thermodynamics, University of Kaiserslautern, Germany, ²Fraunhofer Institute for Industrial Mathematics, Kaiserslautern, Germany

Corresponding author e-mail: martin.horsch@mv.uni-kl.de

Multi-criteria optimization, based on the Pareto optimality criterion [1], is employed to assess the capacity of molecular models to reproduce both bulk and interfacial properties accurately. Furthermore, literature models, which were adjusted to bulk properties only, are validated by comparing model predictions with the vapour-liquid surface tension of real fluids. In most cases, these models overestimate the surface tension. On this basis, it is evaluated how the agreement with the surface tension can be improved by reparameterization [2].

The surface tension is computed from molecular simulations of heterogeneous systems, containing a vapour-liquid interface, by evaluating the difference between the normal and the tangential pressure. The density contrast between the coexisting phases makes it necessary to apply an asymmetric long-range correction which contributes both to the potential energy and the intermolecular forces. For this purpose, a novel correction scheme is introduced, which can be combined with a centre-of-mass cutoff for multi-site models. This long-range correction remains valid even for extremely small cutoff radii, of the order of 1 nm [3].

The present work concerns 2CLJQ models, which contain two Lennard-Jones sites and a point quadrupole. This model class has four parameters, which were adjusted to bulk properties of a variety of real fluids in the literature. The properties which were thereby considered include the saturated vapour pressure, the enthalpy of vaporization, and the liquid density at saturation. Interfacial properties, however, were not taken into account. The predicted surface tension, which is computed here to validate the literature models, is found to overestimate the surface tension of real fluids by 20% on average [2].

The simultaneous quantitative agreement with various properties can be improved by considering the respective experimental data, e.g. for the vapour-liquid surface tension, during the parameterization of the force field. It is shown here that multi-criteria optimization based on the concept of Pareto fronts provides a suitable and versatile framework to realize this in practice: A model is defined to be Pareto-optimal if a further improvement in one objective can only be achieved at the expense of a decline in at least one other objective. By navigating on the Pareto front, which contains the Pareto-optimal models, the parameterization can be fine-tuned to the requirements of a particular application [1, 2].

References
First Principles Prediction of Liquid/Liquid Interfacial Tension

Martin P. Andersson¹, Martin V. Bennetzen², Andreas Klamt³, ⁴, Susan L.S. Stipp¹

¹Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, Copenhagen Ø, DK-2100, Denmark, ²Maersk Oil Research and Technology Centre, Doha, Qatar, ³COSMOlogic GmbH&CoKG, Imbacher Weg 46, D-51379 Leverkusen, Germany, ⁴Institute of Physical and Theoretical Chemistry, Universität Regensburg, Germany

Corresponding author e-mail: ma@nano.ku.dk

1. Introduction

Interfacial tension is an important factor for two-phase liquid behaviour in a variety of systems ranging from water flooding in oil recovery processes to drug delivery and other industrial processes such as corrosion inhibition. Normally, theoretical prediction of interfacial tension relies on empirical relationships or time-consuming molecular dynamics calculations.

2. Results

We present a model for predicting interfacial tension based on first principles calculations using density functional theory (DFT) combined with the COSMO-RS implicit solvent model [1],[2]. COSMO-RS allows for molecules to be solvated at a liquid/liquid interface interacting with both liquids simultaneously (Figure 1). For each different type of molecule, the free energy of transfer from the bulk phases to the interface as well as the cross-sectional area at the interface can be computed and combined to predict the interfacial tension of the system. Our model requires no experimental input and can be used for liquid/liquid systems of arbitrary compositions, in contrast to most empirical relationships. The consistency of our predictions with experimental data is very good for binary, ternary and multicomponent water/organic compound systems (Figure 1), and includes the effect of temperature. The mean absolute deviation for a set of 40 binary water/organic solvent systems is less than 3 mN/m. The good results for ternary systems offers confidence in using the model to predict behaviour of a water/organic interface in the presence of surface-active compounds.

Figure 1. Comparison between predicted and experimental IFT for binary (left) and a ternary system (middle). The COSMO surfaces for the most probable configurations of aniline and water at an aniline-water interface are shown (right) with the interface marked in grey (aniline = light grey, water = dark grey).
3. Conclusion

We have developed a method for predicting liquid/liquid interfacial tension using density functional theory and the COSMO-RS implicit solvent model that is very fast and robust. The model requires no experimental input and can treat multicomponent systems at any given temperature. Our model can be employed as a screening technique as well as to extend experimental data into conditions where measurements are technically too difficult, time consuming or impossible.

References


Phase behaviour and interfacial properties of ternary system \( \text{CO}_2 + n\text{-butane} + n\text{-decane} \): Coarse-Grained theoretical modelling and Molecular Simulations.

Harry Cárdenas¹, Andrés Mejía¹, Hugo Segura¹, Erich A. Müller²

¹Departamento de Ingeniería Química, Universidad de Concepción POB 160 – C, Correo 3, Concepción, Chile, ²Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

Corresponding author e-mail: amejia@udec.cl

1. Introduction

The continuous accumulation of greenhouse gases in the atmosphere has been considered as a high priority environmental issue. In order to reduce its concentration, several alternatives have been proposed, but none of them are massive to generate a real impact in their reduction. For the case of the carbon dioxide, some mitigation solutions may be the large-scale geological carbon capture and sequestration (CCS) and the use of carbon dioxide (\( \text{CO}_2 \)) in petroleum extraction process.[1] In the latter application, the \( \text{CO}_2 \) is used as injected gas in the ternary oil recovery. For an efficiency enhanced oil recovery (EOR), an adequate thermophysical characterization, specially the phase equilibrium and interfacial properties, of \( \text{CO}_2 + \text{hydrocarbons} \) mixtures is needed. However, the appropriate characterization of these thermophysical properties is a not easy task. Indeed, it needs a crafty combination of experimental determinations, theoretical predictions and molecular simulations, as we demonstrated for binary mixtures in previous work [2].

In this work, we illustrate the application of this three-party approach for the case of ternary mixtures. Specifically, we employ a coarse-grained force field for both theoretical predictions and molecular simulation of the bulk phase equilibrium and interfacial properties of ternary system \( \text{CO}_2 + n\text{-butane} + n\text{-decane} \), and its corresponding binary sub-systems.

2. Theoretical Modelling and Molecular Simulations.

Theoretical predictions are based on the van der Waals Square Gradient Theory (SGT), where the homogeneous contribution of the Helmholtz energy density is described by the Statistical Associated Fluid Theory (SAFT–VR–Mie) equation of state (EoS) [3]. This combination provides a unique route for simultaneous predictions of bulk phase equilibrium and interfacial properties in multicomponent systems. In fact, the need parameters can be found from the pure components and binary interactions. In addition, the SAFT–VR–Mie formulation allows the use of the same intermolecular force field (Mie potential) in both theoretical prediction and molecular simulations.

Molecular Dynamics (MD) simulations were performed in the canonical ensemble using a coarse-grained (CG) model [4,5] where molecules are represented by a “super”-united-atoms model. Within this CG approach, \( \text{CO}_2 \) is represented by one single sphere without electrostatic interactions, and \( n\text{-butane} \) is described as a single sphere, whereas \( n\text{-decane} \) is modelled as three tangent spheres.

In order to evaluate the performance of this cooperative and predictive approach for ternary mixtures, the \( \text{CO}_2 + n\text{-butane} + n\text{-decane} \) ternary mixture has been selected as a test case. This selection is based on the available experimental data of bulk phase equilibrium densities and interfacial tension for pure fluids and binary systems, as well as the ternary mixture.

Figures 1 and 2 shows the corresponding results for bulk phase equilibrium and interfacial tensions for the three binary mixtures at 344.3 K. These Figures include the available experimental data, the theoretical calculations and the MD results. From these results, it is possible to observe a very good agreement each other for all the binary mixtures. Comparing the theoretical results to previous works, it is possible to conclude that SAFT–VR–Mie EoS not only display similar results than cubic EoS but also provide a molecular level predictions.
Figures 3 and 4 display the phase equilibrium and interfacial tension for the ternary mixture at 344.3K. Similar than the binary mixtures, Fig. 3 and 4, include the available experimental data, the theoretical calculations and the MD results. It is important to remark that the results include in these Figures are obtained by only using pure fluids parameters and binary interactions.

3. Conclusion

Results on phase equilibrium and interfacial tension in liquid-vapour equilibrium for both binary and ternary mixtures show a very good agreement between theory, experiments and molecular simulations. It is important to remark that the results for both phase equilibrium and interfacial tensions in the ternary mixture as well as the interfacial tensions in the binary mixtures are fully predictive results due to these are based on pure fluids parameters and binary interactions, which are fitted from phase equilibrium data. In complement to the displayed integral properties, the theory and MD are capability to describe other microscopic interfacial properties, such as concentration profiles along the interfacial region, surface activities, and relative Gibbs adsorption isotherms at the interfaces. Preliminary results show a quantitative agreement between SGT+ SAFT– γ predictions and MD calculations.

References

1. Introduction

Wetting of solids is important for many processes. Molecular simulations are useful for investigating wetting and yield insight with atomistic resolution. The results solely depend on the choice of the force fields that are used for describing the intermolecular interactions. The simulations yield a consistent description of wetting and adsorption. They enable systematic studies of the influence of the molecular interactions and the surface structural properties on wetting.

2. Results and Discussion

In the present study, wetting phenomena are studied by molecular dynamics (MD) simulations with the massively parallel simulation code *ls1 mardyn* [1] on the basis of classical force fields. Droplets resting on a solid substrate are simulated in a model system interacting via the truncated and shifted Lennard-Jones potential. The contact angles are obtained by evaluation of the density profile. The temperature is varied over a wide range of the vapour-liquid coexistence of the fluid. The dispersive fluid-solid potential strength is varied and the entire range between complete wetting (θ = 0°) and dewetting (θ = 180°) is observed. A correlation is given that reproduces the results quantitatively: The cosine of the contact angle varies linearly with the reduced fluid-solid potential strength and a power law term accounts for the temperature dependence. The study is extended for different models of the wall and the expected strong impact of the solid density on the contact angle is found and characterized. A variation of the droplet size shows a decreasing solid liquid surface tension for very small droplets which is due to the perturbation of the liquid in vicinity to the wall.

The pinning of the three phase contact line is examined by MD simulations of droplets of different radii resting on pillars of different shapes (see Figure 1). The transition from pinning to depinning is found to be continuous on the molecular scale. Atomistically, the three phase contact is not a line but has a width of a few nanometers. The precursor layer has an important influence on the line pinning. It brings about the full development of the solid-gas interfacial tension.

![Density Profile of the Fluid](image)

**Figure 1:** Density Profile of the fluid: A liquid drop is resting on a solid pillar (black). The precursor layer extending beyond the drop can be discerned.
3. Conclusion

A universal correlation for contact angles in systems with solely dispersive interaction is presented. The relevance of the three phase contact region for the establishment of the solid-fluid interfacial tension is studied.

References

Thermodynamics and statistical mechanics of wetting transitions: fluid phase behavior in prototypical nanostructured substrates

P. Yatsyshin¹, N. Savva¹, ² and S. Kalliadasis¹

¹Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, UK ²School of Mathematics, Cardiff University, Cardiff, CF24 4AG, UK

Corresponding author e-mail: p.yatsyshin@imperial.ac.uk

Keywords: wetting, capillarity, phase transitions, density functional theory

1. Introduction

Studies of nano-confined fluids are motivated by fundamental as well as applied interest. From a theoretical point of view, a fluid confined inside a small pore is a statistical-mechanical system with a potentially rich phase behaviour since the parameters of the fluid-substrate potential and the characteristic dimensions of the pore act as thermodynamic degrees of freedom. In applications, enhancing our understanding of adsorption in confined geometry, e.g. small pores, is essential in new and rapidly developing branches of engineering and science, such as micro- and nano-fluidics, biomimetics, colloidal science and design and operation of lab-on-a-chip devices. We undertake a detailed investigation of wetting in prototypical nanostructured substrates and uncover new phenomena, such as continuous capillary condensation and prewetting, and will also provide the foundation for understanding adsorption on patterned substrates and the phenomenon of superhydrophobicity.

2. A systematic computational framework for investigating fluid phase behavior

Density functional theory (DFT) for fluids is a classical statistical mechanical approach, where starting with molecular fluid-fluid and fluid-substrate potentials, one constructs an approximation for the fluid free energy as a functional of the one-body fluid density. An unconstrained minimization then provides the fluid equilibrium density profile, along with interfaces, microscopic contact angles and interfacial tensions. Analysis of the free energy surface provides a systematic way to obtain the boundaries of stability of various fluid phases via a method similar to van der Waals loops. The fact that a DFT calculation typically takes up a fraction of the cost of a simulation of the same system, along with the high accuracy provided by the latest DFT approximations, makes DFT an attractive tool for thermodynamic analysis. In the present talk we consider several cases of spatially and chemically heterogeneous substrates, e.g. wedge- and groove-like pores and chemically heterogeneous planar walls, which lead to largely unexpected and intriguing phase behaviours of the confined fluid. In particular, we show how such transitions as prewetting and capillary condensation can change order and become continuous [1-3]. Our findings should have important ramifications in experimental investigations of wetting and technological processes and devices that exploit fluids in confinement.

References

Prediction of Interfacial Properties of Industrially Relevant Fluid Mixtures by Molecular Simulation and Density Gradient Theory + PC-SAFT

Stephan Werth, Kai Langenbach, Martin Horsch, Hans Hasse

Laboratory of Engineering Thermodynamics, University of Kaiserslautern, Erwin-Schrödinger-Straße 44, 67663 Kaiserslautern, Germany

Corresponding author: Kai.Langenbach@mv.uni-kl.de

At interfaces in fluid mixtures important enrichment effects may occur. It is assumed that they are the reason for unexpected behaviour observed in mass transfer studies [1]. Unfortunately, the interfacial enrichment cannot be studied directly by experiment. Therefore, theoretical methods are needed, with which the interfacial effects can be investigated and which, thereby, contribute to the understanding of unusual values of the transport coefficients. The interfacial adsorption is investigated here by two independent methods: 1) The density functional theory in the square gradient approximation, often denoted as density gradient theory (DGT), combined with the PC-SAFT [2] equation of state, and 2) molecular dynamics (MD) simulation based on force fields.

From a molecular point of view, there exists no sharp interface. The partial densities of the components change smoothly from their liquid bulk value to the gas bulk value through the interfacial region. In the case of mixtures, however, these density profiles need not be monotonously increasing or decreasing as could be expected, i.e. enrichment or depletion may occur. Both density gradient theory as well as molecular simulation can describe this. Comparisons between both methods, cf. Mejía et al. [3], have only been conducted for Lennard-Jones systems so far. In the present work, results from both methods for the interfacial density profiles are compared for models describing several real binary mixtures. Only the recent advances in equations of state and molecular modeling and simulation with force fields make such an attempt viable, as good models of the real fluids and their mixtures as well as the necessary simulation techniques are now available for both methods.

In this contribution, force fields from previous work of our group [4,5] are used to investigate different mixtures of carbon dioxide, hydrogen chloride and toluene using molecular dynamics simulations. The DGT + PC-SAFT results are based on models from the literature for carbon dioxide and toluene and a new model for hydrogen chloride developed in the present work. In a first step, the results of both methods for the studied pure fluids are compared and very good agreement between both methods, as well as with experimental data is found. The surface tension of the pure components, which was not included in the model development for MD simulations, is slightly overestimated by this method over the entire temperature range. Using DGT + PC-SAFT, the gradient expansion coefficient is fit to one experimental surface tension. The results are mostly within the experimental error bar, except for the critical region. Bulk properties in vapour-liquid equilibria of the binary mixtures agree well with experimental data for both methods. Unlike interaction parameters are fitted to one experimental data point, where necessary.

In the second step, interfacial properties of the mixtures are predicted. Density profiles, the interfacial adsorption and the interfacial tension are studied. The interfacial tension predicted by both methods is compared to each other and to experimental data, where available, and shown to be in good agreement. Carbon dioxide and hydrogen chloride show a strong enrichment at the interface in mixtures with toluene. This enrichment is shown to rise with rising vapour pressure. Furthermore results for the ternary system CO2 + HCl + toluene are shown, in which both carbon dioxide and hydrogen chloride are found to adsorb at the interface.
References

Solubility and diffusion of small molecules in polymers

Martin Bohlén¹, Edvin Erdtman¹,², Peter Ahlström¹, Mikael Berlin³, Thorbjörn Andersson³, Thomas Gkourmpis⁴, Kim Bolton¹


Corresponding author e-mail: peter.ahlstrom@hb.se

1. Introduction

The solubility and diffusion of water and oxygen in industrially relevant polymers have been studied using molecular simulation methods. The solubility and diffusion through polyethylene (PE) have been studied using a combination of Gibbs ensemble Monte Carlo (GEMC) and molecular dynamics (MD) simulation methods.

The PE molecules were modelled using the Amber force field [1], water was modelled using a modified TIP3P [2] model and the oxygen molecule was modelled using the model by Fischer and Lago [3].

The solubility coefficients of oxygen and water were calculated from GEMC simulations where the polymer was in equilibrium with liquid water or gaseous oxygen. The diffusion coefficients were calculated from the slopes of the water/oxygen mean square displacements over time in the polymer matrix as obtained from MD simulations. The permeability coefficients were then calculated as the products of the solubility and the diffusion coefficients.

2. Results

In PE, the calculated permeation of oxygen is 5 to 6 orders of magnitude larger than that of water, which is similar to experimental results [4]. Also, the obtained trends regarding solubility and diffusion are similar to experimental results. The large diversity in experimental data hinders, however, a detailed comparison with the simulated data.

Permeation properties in polymer nanocomposites consisting of PE and graphene or carbon nanotubes have also been studied. The solubility of water decreases with the inclusion of either graphene or carbon nanotubes compared to amorphous PE while the effect on the solubility of oxygen is dependent on the type of additive. The solubility of oxygen in PE decreases with the addition of carbon nanotubes while the addition of graphene does not significantly alter the solubility compared to amorphous PE. The diffusion of water and oxygen in the PE nanocomposites, and in the direction parallel to the additive surface, is not significantly altered compared to pure amorphous PE. However, the diffusion rate increases with the distance to the additive.

3. Conclusion

In summary we have been able to model the essential properties of penetration of water and oxygen in polyethylene. The effect of carbonaceous nanostructure addition is due to both induced structural effects and binding to the filler material.

References

Impact of Ions on the Vitamin C Uptake and Release Using Hydrogels

Daniel Althans, Sabine Enders

TU Berlin, Chair of Thermodynamics and Thermal Separation Science, Ernst-Reuter-Platz 1, 10587 Berlin, Germany

Corresponding author e-mail: sabine.enders@tu-berlin.de

1. Introduction

Hydrogels which undergo volume change in response to clinically relevant stimuli, e.g. temperature, have high potential for use as drug delivery systems [e.g. 1,2]. PNIPAAm Hydrogels gels collapse in polar solutions in response to the temperature and kind and concentration of substances in the environment. The volume phase transition corresponds to a lower critical solution temperature (LCST) of the linear PNIPAAm in aqueous solution. The swelling behavior of PNIPAAm hydrogels in water, in solvent mixtures [e.g. 3,4,5,6] and in salt solutions [e.g. 7,8] in a low concentration or temperature range were studied in literature before. The development of a drug delivery system for a given drug require the knowledge about the swelling, uptake and release behavior as function of the gel character, temperatures, kind and concentration of substances and drugs in the coexisting and gel phase. The swelling of PNIPAAm hydrogels in aqueous solution containing vitamin C, the uptake of vitamin C and the release were studied recently [9]. However, all this quantities depend also on the presence of other substances in the biological environment, especially salts. This contribution is focused on the experimental investigation of the swelling degree, uptake and release in aqueous salty/vitamin C (vit C) systems as function of the solute concentrations at different temperatures. Because of the time intensive experiments a method for estimation of the degree of swelling only on basis of the binary degree of swelling and differential scanning calorimetry measurements (DSC) are developed [8].

2. Experimental Investigations

The gravimetrical degree of swelling in aqueous NaCl, KCl, NaBr, KI, MgSO4, CaCl2 solution without the model drug vit C was measured at different salt concentrations and temperatures. In addition, also the quaternary system NaCl/vit C was investigated. The obtained phase transition temperatures at a given ionic strength, which is strongly related to the maximum drug uptake, were compared with DSC results. The drug release experiments were performed in a reactor at different temperatures, volumes and stirring rates.

3. Conclusion

Generally, the degree of swelling decreases with ionic strength in aqueous salt solutions, independently of the kind of salt. For these solutions a linear relationship between the transition temperature and the ionic strength could be established. In the quaternary system which made from polymer, vit C, NaCl, and water the gravimetrical degree of swelling decreases with increasing concentration of vit C and/or salt and temperature. The transition from a swollen in a shrunken state shifts to lower vit C concentration with decreasing ionic strength of NaCl. The uptake passes through a maximum, which is located close to the transition point. Per contra to the uptake of vit C only a small amount of NaCl can be detected in the gel phase. Nonetheless, this low concentration leads to a high shift of the swelling transition point. In comparison of the impact of the different salts, the anions determine significant the transition. The release of NaCl decreases linear with the temperature until transition occurs.

Reference

Impact of Ions on the Vitamin C Uptake and Release Using Hydrogels

Daniel Althans, Sabine Enders
TU Berlin, Chair of Thermodynamics and Thermal Separation Science, Ernst-Reuter-Platz 1, 10587 Berlin, Germany
Corresponding author e-mail: sabine.enders@tu-berlin.de

1. Introduction
Hydrogels which undergo volume change in response to clinically relevant stimuli, e.g. temperature, have high potential for use as drug delivery systems [e.g. 1,2]. PNIPAAm Hydrogels gels collapse in polar solutions in response to the temperature and kind and concentration of substances in the environment. The volume phase transition corresponds to a lower critical solution temperature (LCST) of the linear PNIPAAm in aqueous solution. The swelling behavior of PNIPAAm hydrogels in water, in solvent mixtures [e.g. 3,4,5,6] and in salt solutions [e.g. 7,8] in a low concentration or temperature range were studied in literature before. The development of a drug delivery system for a given drug require the knowledge about the swelling, uptake and release behavior as function of the gel character, temperatures, kind and concentration of substances and drugs in the coexisting and gel phase. The swelling of PNIPAAm hydrogels in aqueous solution containing vitamin C, the uptake of vitamin C and the release were studied recently [9]. However, all this quantities depend also on the presence of other substances in the biological environment, especially salts. This contribution is focused on the experimental investigation of the swelling degree, uptake and release in aqueous salty/vitamin C (vit C) systems as function of the solute concentration at different temperatures. Because of the time intensive experiments a method for estimation of the degree of swelling only on basis of the binary degree of swelling and differential scanning calorimetry measurements (DSC) are developed [8].

2. Experimental Investigations
The gravimetrical degree of swelling in aqueous NaCl, KCl, NaBr, KI, MgSO 4, CaCl 2 solution without the model drug vit C was measured at different salt concentrations and temperatures. In addition, also the quaternary system NaCl/vit C was investigated. The obtained phase transition temperatures at a given ionic strength, which is strongly related to the maximum drug uptake, were compared with DSC results. The drug release experiments were performed in a reactor at different temperatures, volumes and stirring rates.

3. Conclusion
Generally, the degree of swelling decreases with ionic strength in aqueous salt solutions, independently of the kind of salt. For these solutions a linear relationship between the transition temperature and the ionic strength could be established. In the quaternary system which made from polymer, vit C, NaCl, and water the gravimetrical degree of swelling decreases with increasing concentration of vit C and/or salt and temperature. The transition from a swollen in a shrunken state shifts to lower vit C concentration with decreasing ionic strength of NaCl. The uptake passes through a maximum, which is located close to the transition point. Per contra to the uptake of vit C only a small amount of NaCl can be detected in the gel phase. Nonetheless, this low concentration leads to a high shift of the swelling transition point. In comparison of the impact of the different salts, the anions determine significant the transition. The release of NaCl decreases linear with the temperature until transition occurs.

Reference
Thermodynamic properties of inverse patchy colloids

Monika Stipsitz¹, Emanuela Bianchi¹, Eva G. Noya², Silvano Ferrari¹, and Gerhard Kahl¹

¹Institut für Theoretische Physik, Technische Universität Wien, Wien, Austria, ²Instituto de Química Física Rocasolano, CSIC, Madrid, Spain

Corresponding author e-mail: gerhard.kahl@tuwien.ac.at

Keywords: thermodynamic properties, patchy colloids, self-assembly

1. Introduction

During the past years there has been a tremendous increase in investigations of the properties of particles with anisotropic interactions. This development is due to the fact that such particles have become very promising building entities of novel self-assembled, functionalized materials with specific symmetries and targeted physical properties. In this contribution we will focus on a particular subclass of these particles, namely so-called inverse patchy colloids (IPC) [1]. These particles are mutually repulsive; in addition they are decorated on their surface by well-defined regions (so-called patches) that repel each other while they attract those regions of the colloidal surface that are free of patches (see Figure 1). As a consequence, the ensuing interparticle potentials are characterized by a highly complex interplay of attractive and repulsive directional interactions [1]. It is therefore not surprising that the determination of the thermodynamic properties of the ordered and disordered phases of such IPC systems (for an example see simulation snapshots in Figure 2) is a very delicate and rather complex computational challenge: so far, only simulation based methods [2] have been applied successfully [3] to solve this problem; however, the required computational effort is extremely expensive.

Figure 1: Schematic representation of a two-patch IPC. The colloidal particle is shown in grey while the two (polar) patches are shown in yellow.

Figure 2: Simulation snapshots of an IPC system close to coexistence conditions of a disordered and an ordered (layered) structure (from [3]).
2. Our method

In an effort to reduce the computational effort in calculating the thermodynamic properties of the ordered phases of our IPCs to a justifiable amount, we propose - as an alternative to the simulations - a theoretical approach, whose basic ideas go back to the self-consistent phonon (SCP) approach proposed by Fixman [4] for spherical particles. This framework, recently extended to Janus particles by Shin and Schweizer [5], is based on a reference harmonic potential that parameterizes the vibrations and rotations of the particles in their equilibrium positions; the related “spring constants” are calculated within a self-consistent scheme. With this information at hand, the thermodynamic properties of an arbitrary ordered arrangement of the particles can be calculated; this information provides the basis for the determination of the phase diagram in a subsequent step.

In this contribution we have generalized the SCP approach to IPCs, considering different patch decorations, considering up to three patches. In addition, our modifications allow to characterize the vibrations of the particles in different spatial directions.

3. Conclusion

We have applied our generalized version of the SCP approach to differently decorated IPCs, varying, in addition, the width and the interaction range of the patches. In parallel we have calculated the thermodynamic properties of these systems via simulation-based thermodynamic integration schemes [2]. The comparison of the two sets of data for the thermodynamic properties (i.e., SCP vs. simulation results) over a broad range of decorations and/or system parameters allows us a critical assessment of the applicability of our approach. Further, the frequencies of the rotational and spatial particle displacements obtained within the SCP framework have been compared with corresponding data extracted from molecular dynamics simulations.

References

Surface photografting of acrylic acid on poly(dimethylsiloxane).
Experimental and dissipative particle dynamics studies

David Ramírez-Gutiérrez,1,2 Carlos Nieto-Draghi1 Nicolas Pannacci,1 Laura V. Castro,3 Fernando Álvarez-Ramírez,2 Benoit Creton1

1 IFP Energies nouvelles, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison, France, 2 Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730, México City, México, 3 Escuela Superior de Ingeniería Química e Industrias Extractivas, Instituto Politécnico Nacional, Unidad Profesional "Adolfo López Mateos", Zacatenco, 07738, México City, México

Corresponding author e-mail: carlos.nieto@ifpen.fr

1. Introduction

There has been an extensive research on the control of wetting behaviour of materials exhibiting strong hydrophilic and hydrophobic surfaces. Potential applications include biomaterials, microelectronics, surface coatings, wetting phenomena in oil/surfactant/water systems and the fabrication of microfluidic devices.[1] Selection of polymer-based substrates in microfluidic devices is critical to reproduce the wetting behaviour of the target application which is controlled by chemical structure and surface roughness of surface motif. In this work, we propose a general method to study contact angle variations applied to systems containing water droplets in various media upon poly(dimethylsiloxane) (PDMS) modified by photografting acrylic acid (AA), using both experiments and dissipative particle dynamics (DPD) simulation.

2. Experimental/simulation protocols and main results

A surface elastomeric PDMS was prepared and cut into parallelepipeds followed by a photografting polymerization procedure using a photoinitiator (benzophenone dissolved in a 35:65 % weight ratio solution of acetone/water) and a solution containing AA monomers. This whole ensemble is exposed to Ultra-Violet (UV) radiations at different exposure times and intensities to change the amount of AA surface grafted. Identical contact angle definition has been used both in experiments and simulations to describe the wetting capability (hydrophobic/hydrophilic character) [2] of a liquid (water droplet in silicon oil) to a solid (PDMS grafted with different degrees of AA),[3] as can be seen in Figure 1.a.

Repulsion parameters for DPD simulations were computed from the Flory-Huggins approximation using solubility parameters extracted from atomistic simulations (using the COMPASS force field [4]). Starting from the molecular structures of the different species present in the system (AA, PDMS, Silicon oil and water) two methods are used: Cohesive Energy Density (CED) at 298 K and Blends module as available in Materials Studio 7.0.[5] A schematic representation of the DPD simulation box can be observed in Figure 1.b, where standard dimensionless units were used ($\rho^*=3, T^*=1$).

Figure 1.c contains the comparison between the experimental and simulation results for the variation of the contact angle of water droplet in silicon oil as a function of the concentration of grafted AA on the PDMS surface (this comparison is based on the fact that no additional coating and contact angle variation is observed for the surface beyond 300 s of UV exposure time).[6] We obtain a good agreement between both approaches, showing the validity of both the experimental approach and DPD model parameterisation (it is important to notice that results obtained with the two parameterisation approaches used in DPD simulations lead to the same results).
3. Conclusion

Using a two-step photografting polymerization procedure (photoinitiator absorption and UV irradiation) to modify a PDMS surface with a hydrophilic monomer (AA), we are able to change wetting properties of the surface, tuning from hydrophobic to hydrophilic behaviour. A good agreement was observed between experimental contact angles and those from DPD simulations. In this context the method proposed here can be generalised and applied to different coated surfaces or to study the surface adsorption phenomena of molecules in different applications.

References

Application of Lattice Cluster Theory to Solid-Liquid-Liquid Equilibria of Semi-crystalline Polymer Solutions

Michael Fischlschweiger¹, Kai Langenbach¹,², Sabine Enders¹

¹Chair of Thermodynamics, Technical University of Berlin, Germany, ²Laboratory of Engineering Thermodynamics, University of Kaiserslautern, Germany

Corresponding author e-mail: "Kai.Langenbach@mv.uni-kl.de

1. Introduction

When crystallizing high polymers, part of the resulting solid remains amorphous. The fraction of this material, \( \lambda \), can be accessed using experimental techniques such as X-ray measurements. The onset temperature of crystallization out of a solvent depends on the polymers architecture, as well as the degree of crystallinity and of course also on the used solvent. Depending on the solvent, there may also be a liquid-liquid demixing region above the solid-liquid equilibrium leading to a fundamentally different crystallization process. The theoretical description needs a versatile thermodynamic tool, since it has to describe polymer architecture, molar mass, degree of crystallinity and the mixing behaviour of solvent and polymer. In this contribution Lattice Cluster Theory (LCT) is used to describe the polymer architecture, as well as the mixing behaviour. LCT has been proven before to accurately account for molecular architecture in fluid phase equilibria [1], as well as solid-liquid equilibria [2]. In order to describe semi-crystallinity, an idea of Flory [3] is used, which has previously been applied to describe solid-liquid equilibria in conjunction with LCT.

2. Theory

LCT, originally developed by Freed and co-workers [4] is a formal series expansion around the mean field. It includes contributions due to architecture, which enter theory as combinatorial numbers directly calculable from the molecular structure. As LCT does not account for semi-crystallinity, the configurational entropy derived by Flory [3] is incorporated into the framework. The theory describes the entropy arising from the placement of crystal regions and amorphous regions onto the lattice. In case of solid-liquid equilibria, several pure compound parameters need to be known before the binary phase diagram can be calculated. These are taken from independent experimental data, like differential scanning calorimetry and X-ray. The binary interaction parameter is fit to the liquid-liquid equilibrium of the linear polymer only and branching is handled predictive.

3. Conclusion

LCT in conjunction with Flory’s theory describing semi-crystallinity is used to describe solid-liquid-liquid equilibria. The theoretical influence of branching, interaction energy and semi-crystallinity is discussed over a broad range of possible combinations. As an example, the system poly-ethylene + diphenyl ether is used, in which such equilibria occur. Predictions of the theory for the binary phase diagram compare favourably to experimental data [5], where available. It is shown that both branching and semi-crystallinity have a tremendous impact on the shape and location of the respective equilibria.

References
**Solubility predictions for active pharmaceutical ingredients using the SAFT-γ Mie approach**

S. Dufal\(^1\), V. Papaioannou\(^1\), G. Lazarou\(^1\), H. Panatpong\(^1\), T. Pogiatzis\(^1\), M. Sadeqzadeh\(^1\), R. Shanker\(^2\), A. Galindo\(^1\), G. Jackson\(^1\), C. S. Adjiman\(^1\)

\(^1\)Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK, \(^2\)Pfizer Inc., 558 Eastern Point Rd, Groton, Connecticut 06340, U.S.A.

Corresponding author e-mail: c.adjiman@imperial.ac.uk

**Keywords:** SAFT, Solubility, API

The solubility of active pharmaceutical ingredients (APIs) in different organic solvents as well as water influences many aspects of the synthesis of drugs and formulation of drug products. An accurate prediction of solubility can replace expensive and time-consuming experimental measurements as well as eliminate solvent compositions where the desired range of solubility cannot be attained and is thus a very desirable capability.

The SAFT-γ Mie approach [1] can readily predict the properties of complex organic molecules such as APIs. The rigorous physical basis of the SAFT-γ Mie approach ensures an accurate treatment of hydrogen-bonding effects, which are ubiquitous in most APIs and in the solvents commonly used in the pharmaceutical industry.

The heteronuclear model and group-contribution formalism of SAFT-γ Mie eliminate the need for direct parameter estimation based on properties of the molecules, instead relevant group parameters are estimated using simpler molecules for which data are easily available. Thus, the framework to predict solubility for complex molecular structures of APIs starts with the development of the different group interactions using small, simple molecules. Once these interactions have been validated by examining a range of different properties (vapour-liquid and liquid-liquid equilibrium, excess heat and volume of mixing, single phase second derivative properties) and systems the solubility of APIs is then predicted. In particular we present results for drug molecules such as lovastatin, ibuprofen and ketoprofen in solvents with H-bond interactions such as esters and 1-alkanols. The predicted results were found to be in good agreement with experimental data obtained from the literature.

**References**

Temperature-dependent sublimation enthalpy for molecular crystals obtained from high-level quantum chemistry calculations

Ctirad Červinka¹, Ralf Peter Stoffel², Richard Dronskowski², Michal Fulem¹

¹Department of Physical Chemistry, Faculty of Chemical Engineering, Institute of Chemical Technology Prague, Technická 5, Praha 6, CZ-16628, Czech Republic; ²Institute of Inorganic Chemistry, RWTH Aachen University, D-52056 Aachen, Germany

Corresponding author e-mail: ctirad.cervinka@vscht.cz

Keywords: DFT, phonon DOS, quasi-harmonic approximation, cohesive energy, heat capacity, sublimation enthalpy, molecular crystals

1. Introduction

The sublimation enthalpy represents an important thermodynamic quantity describing the sublimation equilibrium. Its accurate description for molecular crystals by quantum chemistry has remained a challenging task over last decades due to the important effect of the dispersion forces. A study carried out for a set of 20 rather small molecules is presented, and temperature-dependent $\Delta_{\text{sub}}H$ are computed along with other thermodynamic data for the crystalline and ideal-gas phases.

2. Methodology

To evaluate the cohesive energy, a fragment-based approach [1] using ab-initio methods up to the CCSD(T)/CBS level [2] is used and compared to periodic DFT calculations [3] with empirical corrections for dispersion [4], which are also used for calculation of phonon properties. A quasi-harmonic approximation [5] is used to obtain properties of the crystalline phase while the rigid rotor – harmonic oscillator model, corrected for internal rotations [6, 7] is applied for the gas phase.

3. Conclusion

The CCSD(T)-based cohesive energies represent a n accurate starting point for $\Delta_{\text{sub}}H$ evaluation. The quasi-harmonic model accounts for a significant part of anharmonicity of the crystal vibrations. Generation of thermodynamic data for the ideal gas is relatively straightforward and feasible with high accuracy. Combining these techniques leads to high-quality temperature-dependent $\Delta_{\text{sub}}H$.

Figure 1. a) Unit cell of $\alpha$-N₂; b) Calculated phonon DOS for $\alpha$-N₂; c) Helmholtz energy for $\alpha$-N₂ as a function of $V$ and $T$; d) Calculated and experimental heat capacities of $\alpha$-N₂.

References

Structure of water confined in nanopores

M.Sliwinska-Bartkowiak1*, K.Domin1, M.Jazdzewska1 Y.Long2 and K.E.Gubbins2

1 Faculty of Physics, A.Mickiewicz University, Poznan, Poland, 2Department of Chemical Engineering, North Carolina State University, Raleigh, USA

Corresponding author e-mail: msb@amu.edu.pl

1. Introduction

Phenomena that occur only at very high pressures in the bulk phase are often observed to occur in the confined phase at normal pressures (the pressure of the bulk phase in equilibrium with the confined phase). Abundant experimental evidence suggests that adsorbates confined in nanoporous materials exhibit high pressures, such as high pressure crystal structures, high pressure chemical reactions, and the deformation of pore walls due to the adsorbate. Also molecular simulation studies of the pressure tensor for simple adsorbates in carbon nanopores of slit, cylindrical and spherical geometries show that for modest bulk phase pressures, the pressures parallel to the pore walls (tangential pressure) is of the order of GPa, while the pressure normal to the wall is of the order of about hundreds of MPa, and can be positive or negative depending on the pore size [1]. The ice structures experimentally observed in nanopores are typical for high pressures ice.

2. Experiment

We report X-ray diffraction studies of water and carbon tetrachloride adsorbed in nanoporous activated carbon fibres (ACFs). The fibres are built of turbostratic nanoparticles separated by quasi two-dimensional voids, forming narrow slit-shaped pores. In order to determine the structure of water within the pores and its influence on the fibres’ structure, mean interatomic and intermolecular distances have been estimated from the positions of the maxima of the normalized angular distribution functions obtained by X-ray diffraction [1]. We observe a cluster arrangement of the water molecules, as well as significant changes in the interlayer distance of the carbon nanoparticles. The results suggest that very high pressures arise within the pores, about a few hundreds MPa, as has been observed in molecular simulations [1,2]. Such a result is confirmed by observation of high pressure forms of ice in cylindrical nanocarbons, using neutron diffraction method. [3] For water in cylindrical nanocarbons (CMK-3) we observe the existence of cubic ice, tetragonal: ice VIII and ice IX nanocrystal forms, while we find cubic ice in the case of multiwalled carbon nanotubes (MWCN) and CMK-3 mesopores. For water confined in silica pores KIT-6 the existence of cubic ice was also observed. These crystal forms, which occur in bulk water only at temperatures below 180 K in the case of cubic ice, and at pressures of hundreds or thousands of MPa in the case of ice VIII and IX, are stabilized by the confinement.

3. Conclusion

Our observation of deformation of pore walls due to the adsorbate of water and carbon tetrachloride in ACF allow us to estimate experimentally the pressure normal to the pore walls as 377 MPa (for water) and 345 MPa for carbon tetrachloride. The crystal forms of ice, observed in cylindrical nanocarbons and silica pores are typical for ice at pressures of hundreds or thousands of MPa.

References

Confinement Effect on Chemical Reaction Yield: The Nitric Oxide Dimer Reaction

Deepti Srivastava\(^1\), C. Heath Turner\(^2\) and Keith E. Gubbins\(^1\)

\(^1\)Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, USA, \(^2\)Department of Chemical & Biological Engineering, University of Alabama, Tuscaloosa, AL 35487

Corresponding author e-mail: dsrivas@ncsu.edu

1. Introduction

It is well established that confinement within a nano-porous material, such as an activated carbon, carbon nanotube, or porous oxide can affect reaction yield, reaction rate and even the mechanism of the reaction [1,2,3,4]. These effects arise from the strong intermolecular forces between the various reacting species, including the activated state, and the pore walls, but are poorly understood. Understanding from experiment alone is difficult to achieve due to many competing effects, but complementary experimental and molecular simulation studies may help.

2. Motivation and Background

In this study, we report a molecular simulation study of the effects of confinement within a nanoporous carbon material on the equilibrium yield of the nitric oxide dimerization reaction, \(2\text{NO} = (\text{NO})_2\). This reaction is chosen for study both because of its importance in atmospheric chemistry and biology, and because experimental data is available for the effect of confinement within carbon materials. Thus Kaneko and coworkers [3] have used magnetic susceptibility measurements to determine the equilibrium yield of the dimer in activated carbon fibers having slit-shaped pores of 0.8 nm width, while Yates and coworkers [5] have used FTIR spectra to find the yield in single-walled carbon nanotubes of diameter 1.35 nm. At the experimental conditions the yield of dimer in the gas phase in equilibrium with the pore phase was less than 1 mol %, whereas the yield within the pores was 100 mol % within the accuracy of the experiment. Monte Carlo simulations reported [6] in 2001 found a large increase in the yield within slit-shaped pores due to the confinement, but the calculated yield was well below the experimental value.

3. Conclusion

In this work, we report a Reactive Monte Carlo study of this reaction in slit-shaped carbon pores of various widths and over a range of temperatures. We examine several approximations made in earlier molecular simulation studies, in particular the dimensionalities of the molecular partition functions and the force fields used, and show that the latter have a large effect on the calculated yield.

References

Modelling the self-assembly of polyphilic molecules via coarse-grained simulations

Maziar Fayaz-Torshizi, Carmelo Herdes, Erich A. Müller

Department of Chemical Engineering, Imperial College London, U.K.

Corresponding author e-mail: mf2810@imperial.ac.uk

1. Introduction

With improving force fields and computational capacity, molecular simulation has become a viable procedure to investigate intricate self-assembly behaviour of complex molecules. To access the challenging time and size scales needed, appropriate coarse graining of the molecular interactions is a pre-requisite (Glotzer, 2015). In this work, the self-assembly of polyphilic molecules will be investigated following previous strategies (Crane & Muller, 2011).

2. Polyphilic Molecules

Coarse-grained (CG) simulations of polyphilic molecules in solvents are presented, with each molecule consisting of up to four different functional groups, which include aliphatic, aromatic, fluorinated and polar oligomers. The functional groups’ chain length and polarity, as well as overall molecular structure (e.g. T-shaped molecule) are used as variables to analyse the overall patterns of self-assembly of molecules in different model solvents, each corresponding to the different groups of the polyphilic molecule.

Coarse-graining is carried out by simplifying molecules via combining multiple chains into single beads, thus reducing the degrees of freedom of the system. The link to experimental observations is provided by implementing the SAFT-$\gamma$ Mie CG force fields (Müller & Jackson, 2014). Different beads are made for different groups of molecules, such as CH₂CH₃ and CH₂CH₂, and each group of beads have different parameters for the force fields.

Examples are shown for molecular configurations of an amphiphilic molecule made from non-polar moieties that self-assembles into essentially infinite length worm-like entities in an organic solvent. The global phase diagram for these molecules in terms of the solvent type and concentration are presented.

3. Conclusion

The phase behaviour of worm-like self-assembling molecules consisting of mutually repulsive functional groups are presented, showing the overall phase behaviour of these molecules at different solvent concentrations and other variables such as chain length and polarity of the functional groups. The methodology will be further expanded to more complex molecules, such as those with very long and self-attracting chains.

References

Transport of Gases in Polymers for Offshore Applications

Susana Almeida¹, Luis González Martos¹, Jordi Brull Costa¹, Rasmus Lundsgaard¹, Georgios Kontogeorgis¹, Jacob Sonne², Christian Wang², Adam Rubin², Nicolas von Solms¹

¹Center for Energy Resources Engineering, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, 2800 Kgs. Lyngby, Denmark, ²NOV Flexibles, Priorparken 480, 2605 Brøndby, Denmark

Corresponding author e-mail: nvs@kt.dtu.dk

1. Introduction
Carbon dioxide (CO₂) has a crucial role in the oil and gas industry, but one of the main problematics, that is frequently forgotten in comparison with its capture and storage, is transportation [1]. National Oilwell Varco (NOV) is a specialist in the manufacture of flexible pipes to transport gases at extreme conditions (e.g. supercritical stage) from offshore locations. The design of flexible pipes encloses several layers, being the so-called inner polymer liner the barrier to the egress of the gas being transported [2]. In order to, safely, transport supercritical gases in these pipelines, it is necessary to measure and understand several thermodynamic and transport properties of the polymer/gas system at different pressures and temperatures. The purpose of this work is to determine these key properties (solubility, permeability and swelling), for the development of flexible pipeline systems, under the direct collaboration with an industrial partner: NOV.

2. Experimental Set-up and Conditions
Operation may be at rather extreme conditions and thus high pressure (up to 650 bar) and temperature (up to 110 °C) measurements were carried out in two different apparatus for the determination of gas solubility (Magnetic Suspension Balance) and gas permeation (2-D permeation cell) properties, Figure 1.

(a)
Three different polymers, PVDF, XLPE and PA11 were studied with pure CO$_2$ and methane mixture (90/10). Not only these data provides a qualitative description of the gas/polymer system operation range, it also provides an input for the development of predictive models.

3. Conclusion

A predictive mass transport model is being developed, based in the experimental data of both solubility and permeability. Solubility has been successfully modeled while using a complex equation of state for polymeric systems (sPC-SAFT) [3]. It was found that new parameters were required for modeling CO$_2$ far beyond the critical pressure (ultrasupercritical CO$_2$).

References
Clay suspensions in and out of equilibrium

William J. Ganley¹, Phillip Woolston¹, Jeroen S. van Duijneveldt¹

¹School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom

Corresponding author e-mail: J.S.van-Duijneveldt@bristol.ac.uk

1. Introduction

Clay mineral particles have high aspect ratios and form suspensions which present a wealth of phase behaviour, ranging from fluids to liquid crystals and glassy or gelled states. Such systems are ubiquitous in industrial formulations as a means of controlling the flow properties of liquids and soft solids, stabilising emulsions and providing additional microstructure to composite materials and are also used as model systems for the study of flow in non-spherical particle suspensions. Here mixtures of such particles are studied displaying a range of equilibrium and non-equilibrium behaviour.

2. Modifying montmorillonite platelets

Montmorillonite consists of thin platelets with a typical aspect ratio of 1:300. Their suspensions in water form gels at concentrations of a few weight percent. Here we extend recent work [1] on these systems by taking two molecules that adsorb to different faces of the platelet surface. We find that these molecules alter behaviour in different regions of the rheological phase diagrams. The weight fraction required for a solid-fluid transition in the glassy regime is increased by the adsorption of an amine terminated amphiphilic polymer to the particle face and in the gelled regime it is increased by adsorption of multivalent pyrophosphate anions to the particle edges.

Structural signatures in the fluid phase accompanying these differences are only found at length scales above a micron where colloidal clusters and elongated assemblies are observed in small angle light scattering. Such clusters are common in systems with competing attractive and repulsive interactions. The two adsorbing molecules studied here do not interact with each other and act in different regions of the phase diagram hence have the potential to control rheology across a large range of ionic strengths.

3. Rod-plate mixtures

Sepiolite clay rods can be dispersed in water using sodium polyacrylate, resulting in formation of a nematic phase at low salt [2]. Here such rods are mixed with montmorillonite plates and a range of new behaviour is found, including what appears to be formation of an isotropic – gel – nematic three-phase coexistence. The samples display a remarkable time-dependence where the initial phase separation occurs within a few days; then sudden, dramatic reorganisation takes place on a time scale of days to weeks, possibly as a result of the middle phase being a gel rather than an equilibrium fluid.

4. Conclusion

Clay suspensions show a rich and complex phase behaviour. Suspensions of rodlike particles, discussed here, show equilibrium phase separation, whereas montmorillonite platelets tend to arrest in a gel phase. Their binary mixtures combine the hallmarks of both phenomena, with rods still tending towards what looks like an equilibrium phase separation whereas the platelets are expelled into a middle gel phase.

References
Anisotropic interactions constitute one necessary ingredient for molecular or colloidal building blocks to self-assemble reliably into well-defined target structures. The present study probes the limits of reliability and the complexity of the target that can be reached by decorating building blocks with patchy interactions [1].

To investigate these matters systematically, we introduce a highly idealised model of cubic building blocks that have patterns of attractive patches on their faces. In the simplest case, all patches are identical, and self-assembly must be controlled by the pattern of patches on the faces of the particles. Additional flexibility can be introduced by using an “alphabet” of interaction types, mimicking the matrix of interactions between amino acids [2] or the specificity of DNA strands [3].

We compare different strategic routes to the self-assembly of small discrete targets, considering sequential and hierarchical pathways [4], and schemes in which each particle in the structure can be addressed individually, as in DNA bricks [3]. The pattern of patches on the building blocks are allowed to evolve via genetic algorithms in order to optimise the assembly of a target structure under given conditions of temperature and density.

We have devised a hybrid Monte Carlo algorithm to simulate dynamics-like trajectories of our model building blocks. The method builds on the Virtual Move Monte Carlo algorithm of Whitelam and coworkers [5], which effectively incorporates gradients of the potential to propose realistic cluster moves. Our hybrid scheme provides a smooth crossover between single-particle moves, internal relaxation of clusters, and bulk diffusion of clusters with rates governed by Stokes’s law.

The model can readily be extended to incorporate further refinements, such as internal degrees of freedom and allosteric coupling.

References
Posters
Comparison of GERG-2008 and Soave-BWR for modeling of natural gas mixtures

Farhad Varzandeh¹, Wie Yan¹*, Erling H. Stenby¹

¹ Center for Energy Resources Engineering (CERE), Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

* Corresponding author e-mail: weya@kemi.dtu.dk

1. Introduction

Accurate description of thermodynamic properties of natural gas systems is of great importance in the oil and gas industry. For this application, non-cubic equations of state (EoSs) are advantageous due to their better density description. Among these non-cubic models, GERG-2008 [1] is a new wide-range EoS for natural gases and other mixtures of 21 natural gas components. It is considered as a standard reference equation suitable for natural gas applications where highly accurate thermodynamic properties are required.

Soave’s modification of Benedict-Webb-Rubin (Soave-BWR) EoS [2] is another model that also presents accurate density results even around the critical point. It is much simpler than GERG-2008 and easier to handle and generalize.

2. Comprehensive comparison between GERG-2008 and Soave-BWR

This study presents a comprehensive comparison between GERG-2008 and Soave-BWR in description of pure component densities in a wide temperature and pressure range, calculation of binary Vapor-Liquid-Equilibria (VLE), and prediction of multicomponent phase envelopes. In addition, the two models are compared in modeling Joule-Thomson coefficients for both pure components and mixtures and the results are compared with available experimental data in the literature. Special focus has been given to the reverse Joule-Thomson effects at high pressure conditions.

3. Conclusion

It is found that Soave-BWR is largely comparable to GERG-2008, although not as good, in density description. The two models are very similar in phase equilibrium calculation whereas Soave-BWR has some challenges in highly asymmetric systems. The comparison shows the potential of Soave-BWR as a light-weight alternative to GERG-2008 although further development of Soave-BWR, e.g., modification of its mixing rules, seems to be needed.

References
High pressure phase equilibrium measurement of methane + n-decane

Teresa Regueira, Erling H. Stenby, Wei Yan

Department of Chemistry, Center for Energy Resources Engineering (CERE), Technical University of Denmark, DK-2800 Lyngby, Denmark

Corresponding author e-mail: weya@kemi.dtu.dk

1. Introduction

The depletion of conventional oil and gas resources along with the current increasing oil demand has led to the exploration of deeper formations at higher pressures and temperatures. The reservoirs with pressures higher than 69 MPa and temperatures higher than 422 K are classified as HPHT (high pressure-high temperature) reservoirs. They are risky to develop and there is an urgent need for thermophysical data of reservoir fluids under these extreme conditions. These data could allow a safer exploitation of the reservoir as well as a more accurate reservoir engineering calculation including compositional reservoir simulation.

We have recently implemented in our laboratory a PVT unit with full visibility that can perform measurements up to 473.15 K and 150 MPa. Reliable phase equilibrium data for hydrocarbon mixtures related to reservoir fluids can be obtained through this apparatus. We have validated our experimental technique used for this unit by studying the phase equilibrium of the binary system methane + n-decane.

2. Experimental method and results

Phase equilibrium of the system methane + n-decane has been studied from 293.15 K to 423.15 K and pressures up to 35 MPa in this full visibility PVT unit. The temperature control is performed within ±0.1 K by means of an electric heating system together with a circulating oil thermostat, whereas pressure transducer was calibrated with an accuracy of ±0.1 MPa. Homogenization of the system is achieved through a rotating stirrer mounted on the top of the piston with retractable blades.

The studied binary mixtures were prepared in the PVT unit by transferring a certain volume of the pure compounds to the PVT cell at 10 MPa and ambient temperature through a high pressure pump. Bubble points were visually determined by slowly decreasing the pressure at constant temperature from single phase until the appearance of a vapour phase.

Experimental results show a good agreement with bubble point data reported by Reamer et al. [1], Sage et al. [2] and Rijkers et al. [3]. As an example, results for the binary mixture with methane molar fraction around 0.6 are shown in Figure 1. The measurement also provides the densities of the mixture at various temperature and pressure conditions.

Fig.1. $p$-$T$ diagram for the system methane (1) + n-decane (2). (●) $x_1=0.582$ [1], (▲) $x_1=0.5908$ [1], (+) $x_1=0.5997$ [2], (○) $x_1=0.6021$ (this work), (□) $x_1=0.6111$ [1], (×) $x_1=0.6124$ [1], (*) $x_1=0.6168$ [1].
3. Conclusion

The visual technique for phase envelope determination was validated for the new PVT unit by use of the methane + n-decane system. The results are in agreement with those previously reported in literature [1-3]. The study opens the possibility for accurate phase equilibrium measurement of other synthetic and real fluid mixtures of interest to HPHT reservoir development.

References

Water structure effects of anions and their volumes

Yizhak Marcus

The Hebrew University of Jerusalem

Corresponding author e-mail: ymarcus@vms.huji.ac.il

1. Introduction

The structure of aqueous solutions in terms of the hydrogen bonding taking place in them has been studied experimentally (e.g., [1]) and by computer simulations (e.g., [2]). One common measure of the effects of ions on the water structure is the viscosity $B$-coefficient [3], which is additive with respect to the ions. Ionic $B_i$ values can be derived on the assumption that $B(Rb^{+},aq) = B(Br^{-},aq)$ [4]. Water structure is enhanced for solutes with $B_i > 0$ and disrupted for those with $B_i < 0$ [5].

2. Anion sizes and water structure effects

Cavities for ions to move into are on the average $(V_W - V_{vdW})/N_A = 0.0094 \text{ nm}^3$, and the sizes of the solute particles relative to this are determinative for their effect on the water structure. Too large ions must disrupt some of the hydrogen bonding on moving. There are two measures of the sizes of anions: their microscopic volumes $v_i$ [6] and their standard partial molar volumes $V_i^{\infty}$ [7]. Both correlate well linearly with the $B_i$ values of the anions:

$$B_i/\text{dm}^3\text{mol}^{-1} = 0.095 |z_i|^{5/3} - 2.76 |z_i|^{-2/3} v_i/\text{nm}^3 \text{ ion}^{-1} = 0.118 |z_i|^{4/3} - 0.00385 |z_i|^{-1/3} V_i^{\infty}/\text{cm}^3 \text{ mol}^{-1}$$

These correlations were established for some 50 anions with charge numbers $z_i$ from $-1$ to $-3$. The breaking point between structure making and breaking is $v_i \sim 0.02 |z_i|^{3} \text{ nm}^3 \text{ ion}^{-1}$ or $V_i^{\infty} \sim 40 |z_i|^{4/3} \text{ cm}^3 \text{ mol}^{-1}$. However, no correlation was found at finite concentrations with the deviations from the limiting law of standard partial molar volumes [8].

3. Conclusions

Both the microscopic and thermodynamic measures of the sizes of the anions permit prediction of whether an anion would be water structure breaker or maker. This may be applied to complex anions [6] for which neither direct data of the viscosity $B_i$ nor quantities linearly related to it (e.g., NMR longitudinal relaxation rate [9]) are available for judging their effects on the water structure surrounding them.

References

Prediction of Self Diffusion Coefficients from Chapman-Enskog-Theory in Combination with PC-SAFT or LCT-EOS

Christoph Walowski, Hendryk Rudolph, Sabine Enders

Chair of Thermodynamics and Thermal Separation Science, TU Berlin Ernst-Reuter-Platz 1, D-10587 Berlin, BH 7-1

Corresponding author e-mail: sabine.enders@tu-berlin.de

1. Introduction

The modelling of several technical processes (e.g. air drying, gas purification and rectification) is depending heavily on the correct calculation of both the phase equilibrium and the inherent transport processes. For the latter, knowledge of the diffusion coefficients and their dependencies on temperature and concentration is of particular importance. Since the experimental estimation of the diffusion coefficients is laborious and difficult, a theoretical model for their calculation is highly desirable.

2. Calculation of the diffusion coefficients

The foundation for the calculations presented in this work is the theory for diffusion coefficients by Chapman [1], following the works of Enskog. The theory links the diffusion coefficients in the gas phase to the radial distribution function and therefore to the molecule diameters and phase densities. The calculation of these required properties were on the one hand made using the Perturbed Chain-Self Associating Fluid Theory (PC-SAFT) Equation of State (EOS) as developed by Gross and Sadowski [2]. On the other hand the Lattice-Cluster-Theory (LCT)-EOS, developed by Langenbach et al. [3] and based on the work of Freed and Dudowicz [4], was applied.

With the application of the PC-SAFT-EOS, it was possible to calculate several polar and non-polar substances. To also account for systems containing larger or even branched molecules, the LCT-EOS was applied. In both cases, the required EOS parameters were fitted to PVT data and the calculation of the diffusion coefficients was carried out as a pure prediction.

Since the diffusion process is highly linked to the shape of the molecule, and as the treatment of this property is reduced to the molecule diameter within the Chapman-Enskog-Theory, the considerations are restricted to systems containing spherical or nearly spherical molecules.

3. Conclusion

It was shown that with the application of the Chapman-Enskog-Theory in combination with the PC-SAFT and the LCT-EOS, the calculated gas-phase diffusion coefficients of systems with nearly sphere-shaped molecules are in good agreement with the experimental data for both polar and non-polar substances. The variation of the diffusion with temperature and concentration was reproduced correctly. Exemplarily performed calculations for aspherical molecules show the limitations of the theory as deviations to experimental data increase. With the application of this model, it is possible to give a good prediction of the diffusion coefficients and to therefore avoid time-consuming experiments. The theory, however, is to be expanded to also account for non-spherical molecules.

References

Thermodynamic Equilibrium

R M Gibbons

Corresponding author e-mail: richandhelen@gibbons.entadsl.com

Keywords: Thermodynamics, equilibrium, statistical mechanics

1 Introduction
The arguments in this paper lead to a new definition of thermodynamic equilibrium that remedies the deficiencies of the current versions. This definition relates thermodynamic equilibrium to its physical causes and accounts for all factors that determine it for all types of equilibrium. Standard definitions of thermodynamic equilibrium are incomplete. They do not take account of all factors that determine such equilibriums, discuss the impediments which may prevent them being reached or relate the properties that define equilibriums to the physical reasons that determine them when impediments are present.

2 The Causes of Thermodynamics and Thermodynamic Equilibrium
The laws of thermodynamics determine the requirements for equilibrium. These laws arise from the behaviour of the molecules in molecular systems and are consequences of the conservation of energy, the energies of molecules, statistics, Newton’s laws of motion, and the equi-partition of energy.

3 Conclusion
The standard definition of thermodynamic equilibrium correctly defines equilibrium whenever impediments are not factors. The discussion demonstrates how impediments arise, accounts for their role in defining equilibrium and how they relate to the energies of molecules at the conditions of the system. The new definition accounts for the effects of impediments and molecular energies in determining equilibrium and applies to all types of equilibrium for all molecular systems.
Thermodynamic investigation of ternary electrolyte system NiCl$_2$ + Triton X-100 + H$_2$O) at T = 298.15 K

M.A. Bagherinia$^{*a}$, S. Yosefnia$^a$

$^a$Department of Chemistry, Faculty of Science, Lahijan Branch, Islamic Azad University, Lahijan, Iran.

Corresponding author e-mail: mabagherinia@yahoo.com

1. Introduction

Recently, there has been an increasing amount of work concerning the measurement of thermodynamic properties of electrolytes in mixtures of solvents [1–2]. The investigation on the interactions between inorganic salts and organic compounds is a subject of current interest in chemistry and biology [3]. In the last decades, a series of ion-interaction models for electrolyte solution have been proposed to predict activity coefficient of each solute and osmotic coefficient of the aqueous systems. One of the most famous and useful models is that proposed by Pitzer [4]. In this work, the resulting values of the mean activity coefficients of NiCl$_2$ in H$_2$O- triton X-100 as a mixed solvent solution were determined using potentiometric model.

2. Experimental

2.1. Potentiometric measurements

The cell arrangement for studying the NiCl$_2$ + triton X-100 + water system was described as follows:

\[ \text{Ag|AgCl | NiCl}_2(\text{m}), \text{triton X-100 (wt.%), H}_2\text{O (100–wt.%)} | \text{Ni}^{2+} - \text{ISE} \] (A)

where wt. is the mass fraction of triton in the mixed solvent. The emf measurements of the galvanic cell (A) were made by using standard addition procedure. Then the mean activity coefficients for NiCl$_2$ in the solvents were determined from the emf measurements in according to Nernst equation. Figure 1 presents the variation of the NiCl$_2$ mean activity coefficients versus the ionic strength in water, and different mass fractions of triton in mixed solvents at T = 298.15 K. The Pitzer ion interaction parameters were determined by an iteration minimization procedure employing the Microsoft MATLAB program.

Fig. 1. Natural logarithm mean activity coefficients of NiCl$_2$ versus total ionic strength.
2.2. Calculation of thermodynamic properties

The Pitzer parameters obtained were used to predict the thermodynamic properties of under investigation system by the Pitzer model. The osmotic coefficients ($\phi$) and the excess Gibbs free energy for all of the under investigation series can be calculated by utilizing Pitzer equations. Figures 2 and 3 show the plot of osmotic coefficients ($\phi$), the excess Gibbs free energy ($G_E$) versus the ionic strength, respectively.

![Fig 2. Osmotic coefficient versus total ionic strength.](image)

![Fig 3. Excess Gibbs energy versus total ionic strength.](image)

3. Conclusions

The mean activity coefficients of NiCl$_2$ in the NiCl$_2$/Triton X-100/water system were determined by a potentiometric method using a solvent polymeric ion-selective membrane electrode and Ag–AgCl electrodes at T = 298.15 K. These mean activity coefficients were correlated with the Pitzer ion-interaction model to get the Pitzer adjustable parameters ($\beta^0$, $\beta^1$ and $C^\phi$). Then the Pitzer adjustable parameters obtained used to determination the other thermodynamic properties such as the osmotic coefficients ($\phi$) and excess Gibbs free energy ($G_E$). It can be concluded that the Pitzer ion-interaction model satisfactorily describes the system under investigated.

References
Parameterization and Evaluation of the Electrolyte CPA Equation of State

Anders Schlaikjer1, Kaj Thomsen1, Georgios Kontogeorgis1

1Center for Energy Resources Engineering, Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Corresponding author e-mail: andsh@kt.dtu.dk

1. Introduction

Electrolytes have a significant effect in many industrial processes in both the petroleum and the Chemical Industry. Electrolytes have proved to enhance the inhibitory effect of methanol and glycols on the formation of gas hydrates, but also to promote corrosion and scale formation in both pipelines and heat exchangers. Also electrolytes are key components in fertilizer production, and several separation processes [1].

While electrolyte equations of state historically have received less attention than for instance association models, several electrolyte equations of state have been proposed over the years, where the most recent almost all are extensions of Association models, like SAFT or CPA [2-5]. Relatively many of the electrolyte models have, however, only been utilized at 25 °C and/or only for a very limited range for salts. Where practically all the proposed model is parameterized to excess Gibbs energy properties in form of activity and osmotic coefficients, and some to density, very few are using equilibrium data in the parameter estimation [6]. Solubility is a key property of salts, but correlation or prediction of solubility specifically is only investigated with a few of the existing models, and only briefly where it has been included. Furthermore a thorough investigation of solubility for a wider range of salts has not been found in literature for any equation of state, including investigation of standard states.

2. Electrolyte CPA Equation of State

An electrolyte extension to the CPA Equation of State has been development at the Technical University of Denmark (DTU), by including the full Debye-Hückel and the Born term [6,7]. The framework also includes a new model for the static permittivity, that accounts for association and electrolytes [8,9].

In this work this electrolyte-CPA equation of state is parameterized, for a range of salts over an extended temperature range, under different assumptions. Parameters are estimated with special emphasize on the description of salt solubility while still having accurate description of osmotic and mean ionic activity coefficients, and these are compared with parameters estimated only to osmotic and mean ionic activity coefficients.

Describing solubility with an equation of state requires the use of standard states, e.g. the Gibbs energy and enthalpy of formation, as well as the heat capacity, for the solid. Such can be found experimentally, and are available for most pure salts, however for hydrates salts the properties has to be estimated through data fitting.

The model will be utilized for correlation and prediction of mixed salt properties including solid-liquid-equilibrium and the results will compared to an established electrolyte activity coefficient model.

3. Conclusion

Several extensions to Association models like SAFT and CPA for electrolytes have been proposed in recent years, however only few have investigate the correlation or prediction of salt solubility. In this work the electrolyte CPA equation of state is parameterized with special emphasize on the salt solubility.
References

Interfacial Supermittivity of Confined Water at the Nanoscale

Aziz Ghoufi1, Anthony Szymczyk2, R. Renou1,2

1Institut de Physique de Rennes, CNRS, UMR 6251, Université de Rennes 1, Rennes, France 2Institut des Sciences Chimiques de Rennes, CNRS, UMR 6226, Université de Rennes 1, Rennes, France

Corresponding author e-mail: aziz.ghoufi@univ-rennes1.fr

Nowadays it well established that the physical properties of confined liquids strongly differ from those in bulk phase. While dynamical and structural properties were strongly explored, dielectric properties are poorly studied despite their importance in the understanding and the modeling of molecular mechanism in a number of nano-applications such as nanofluidics, nanofiltration and nanomedicine. Among them, the dielectric permittivity is probably one of the most important. The lack of knowledge about it strongly limits our ability to model fluid-material interactions and more generally our understanding of the behavior of confined fluids. Recently, the dielectric permittivity of confined water in silica, MOFs and graphene materials was found to be slightly higher than the permittivity of water in bulk phase. In this work, the permittivity of water in carbon nanotubes was predicted by means of Molecular Dynamics simulations and its value was interpreted by means of a microscopic point of view.
The effect of accounting for the contribution of the heat capacity in solubility predictions

Sara Febra1, Simon Dufal1, Vasileios Papaioannou1, Amparo Galindo1, Claire Adjiman1, George Jackson1

1Department of Chemical Engineering, Centre for Process Systems Engineering, Imperial College London, London, SW7 2AZ, United Kingdom

Corresponding author e-mail: a.galindo@imperial.ac.uk

Keywords: SAFT-γ Mie, solubility prediction, HCD contribution

1. Introduction

Industry, and in particular the chemical sector, is faced with the need of characterization, design and optimization of materials and processes of increasing complexity. The development of computational tools, with the capability to accurately predict both physical properties and optimal fluid system composition and process conditions, is, thus, of great interest. Solvent selection procedures, for which solubility data is key, are typically part of such efforts.

The Statistical Associating Fluid Theory, SAFT [1], constitutes one of the most successful and versatile molecular-based theories for the determination of thermodynamic and phase equilibrium properties relevant to the chemical and pharmaceutical industry. This is achieved through the combination of a detailed molecular model in conjunction with a realistic partition of the free energy between association- and dispersive-forces, and the monomer and molecular contributions.

In this work, we assess the accuracy of predictive solubility calculations of carboxylic acids, based on a SAFT approach.

2. Solubility calculation procedure

We employ SAFT-γ Mie [2], a group contribution approach for heterogeneous molecular models of fused spherical segments interacting through Mie potentials, together with the thermodynamics of solid-liquid equilibrium (SLE) to predict the solubility of solutions of carboxylic acids in different solvents. Three levels of approximation are assessed for the term in the SLE working equation that accounts for the heat capacity differential (HCD) contribution, given by the difference between the pure subcooled liquid and solid heat capacities. The three levels are: the full description with a temperature dependent HCD; a first level approximation which neglects the dependence of the HCD on temperature; and a second level approximation that neglects HCD contribution altogether.

The application of the full description for solubility is limited by the paucity of HCD experimental data as well as the inaccuracy of the heat capacity values for subcooled liquid carboxylic acids as predicted by SAFT-γ Mie. The solubility values obtained with the second level approximation, most commonly used in practical applications [3], are satisfactory. However, the first approximation is found to provide the better accuracy, when the HCD term is given by the difference between the extrapolations of the experimental heat capacities to the melting point.

3. Conclusion

Including the HCD term in the solubility calculation is found to improve the accuracy of the solubility prediction for carboxylic acids, provided that good experimental data for both solid and liquid heat capacities near the melting point are available.
1. Introduction

Industry, and in particular the chemical sector, is faced with the need of characterization, design and optimization of materials and processes of increasing complexity. The development of computational tools, with the capability to accurately predict both physical properties and optimal fluid system composition and process conditions, is, thus, of great interest. Solvent selection procedures, for which solubility data is key, are typically part of such efforts.

The Statistical Associating Fluid Theory, SAFT [1], constitutes one of the most successful and versatile molecular-based theories for the determination of thermodynamic and phase equilibrium properties relevant to the chemical and pharmaceutical industry. This is achieved through the combination of a detailed molecular model in conjunction with a realistic partition of the free energy between association- and dispersive-forces, and the monomer and molecular contributions.

In this work, we assess the accuracy of predictive solubility calculations of carboxylic acids, based on a SAFT approach.

2. Solubility calculation procedure

We employ SAFT-$\gamma$Mie [2], a group contribution approach for heterogeneous molecular models of fused spherical segments interacting through Mie potentials, together with the thermodynamics of solid-liquid equilibrium (SLE) to predict the solubility of solutions of carboxylic acids in different solvents. Three levels of approximation are assessed for the term in the SLE working equation that accounts for the heat capacity differential (HCD) contribution, given by the difference between the pure subcooled liquid and solid heat capacities. The three levels are: the full description with a temperature dependent HCD; a first level approximation which neglects the dependence of the HCD on temperature; and a second level approximation that neglects HCD contribution altogether.

The application of the full description for solubility is limited by the paucity of HCD experimental data as well as the inaccuracy of the heat capacity values for subcooled liquid carboxylic acids as predicted by SAFT-$\gamma$Mie. The solubility values obtained with the second level approximation, most commonly used in practical applications [3], are satisfactory. However, the first approximation is found to provide the better accuracy, when the HCD term is given by the difference between the extrapolations of the experimental heat capacities to the melting point.

3. Conclusion

Including the HCD term in the solubility calculation is found to improve the accuracy of the solubility prediction for carboxylic acids, provided that good experimental data for both solid and liquid heat capacities near the melting point are available.

References


A predictive square-gradient route to the interfacial tension of fluids

Daniel Kunisch Eriksen¹, Amparo Galindo¹, Andrew J. Haslam¹ and George Jackson¹

¹Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, United Kingdom

Corresponding author e-mail: daniel.kunisch-eriksen10@imperial.ac.uk

Keywords: Interfaces, SGT, Square Gradient Theory, Interfacial tension

Existing approaches to modelling the fluid-fluid interfacial tension (IFT) require a compromise between computationally expensive predictive techniques such as density functional theory, and more-straightforward, non-predictive approaches such as the square gradient theory [1] (SGT), which remain tractable for the study of complex mixtures. In this work we leverage the molecular model underlying SAFT-VR Mie [2] to bridge the gap between these extremes, developing a predictive yet computationally much less expensive route to the IFT.

We employ an SGT approach, proposing a simple approximation for the influence parameter. We obtain a predictive formalism by means of an effective mapping in state variables through the potential parameters; the mapping is calibrated for a range of Mie potentials using IFT data from molecular simulations of Mie spheres. Extension of the approach to multi-segment chains, and to mixtures, is straightforward.

We test our approach by predicting the IFT of Mie fluids not included in the calibration, and further demonstrate its predictive power by comparison with experimentally determined IFTs.

References

Acknowledgements
DKE and AJH gratefully acknowledge funding from the Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), provided jointly by Qatar Petroleum, Shell, and Qatar Science & Technology Park.
Coarse-Grained SAFT-γ Mie for Understanding Wax Deposition in Crude Oil

Sara Shahrudin, Sadia Rahman, Maria G. Jimenez Serratos, Omar Matar, Erich A. Muller

Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, United Kingdom

Corresponding author e-mail: e.muller@imperial.ac.uk

1. Introduction
Inherent presence of alkanes in the crude oil can precipitate as wax deposits on oil pipelines and processing equipment due to a change in equilibrium conditions. The wax are formed when the system temperature falls below the Wax Appearance Temperature (WAT), promoting the deposits to grow and subsequently limiting the flow \cite{1}. Wax deposition causes significant economic impact through the cost of remediation, reduced or deferred oil production and replacement of pipelines and equipment.

2. Investigation of wax precipitation
It has been shown conclusively from previous studies that long linear alkanes are the key components in the crude oil responsible for wax depositions \cite{2}–\cite{6}. To further understand and better predict the formation of wax precipitation, a well-defined wax model system is essential to gain reliable end results. A hetero-group coarse grained \cite{7} models of linear alkanes recently proposed by our group shown in Figure 1 was used in this study. The model consists of three consecutive backbone carbon atoms together with differentiation on the beads containing the CH$_3$ end group, giving two different types of beads for a heteronuclear model. This distinct feature makes a better representation of alkanes presence in the crude oil as it is transferrable from shorter to longer chain alkanes. Statistical Associating Fluid Theory (SAFT)-γ Mie \cite{8}–\cite{11} was employed to describe the precipitation boundaries and predict the thermodynamic properties of the model system at various conditions, particularly at lower temperature to simulate the state of freezing process.

![Figure 1: CG strategy for nonane, grouping three backbone carbon atoms into single beads. The green end-bead (CH$_3$-CH$_2$-CH$_2$-) differs from the blue mid-bead (-CH$_2$-CH$_2$-CH$_2$-) as it contains the CH$_3$ terminal group.](image)

3. Conclusion
The precipitation boundaries and thermodynamic properties of wax containing crude oil has been investigated using hetero-group coarse grained SAFT-γ Mie approach. The findings confirms temperature as the governing factor for solid-liquid phase separation. The calculated thermodynamic properties obtained are in agreement with the available experimental data for the systems studied, demonstrating the reliability and accuracy of this approach.
References


Extension of SAFT-VRE to reacting systems by application to aqueous solutions of weak electrolytes

Georgia Lazarou\textsuperscript{1}, Esther Forte\textsuperscript{1}, Simon Dufal\textsuperscript{1}, Claire S. J. Adjiman\textsuperscript{1}, Amparo Galindo\textsuperscript{1}, George Jackson\textsuperscript{1}, Ravi M. Shanker\textsuperscript{2}

\textsuperscript{1} Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, UK, \textsuperscript{2} Pfizer Inc., Groton Laboratories, Groton, Connecticut 06340, USA

Corresponding author e-mail: a.galindo@imperial.ac.uk

Keywords: SAFT, electrolytes, pH

Aqueous solutions of weak electrolytes are widely encountered in the pharmaceutical industry, since active pharmaceutical ingredients (APIs) are often weak acids or weak bases which partially ionize in water. The solubility of such APIs is sensitive to the variations of pH in the physiological environment, therefore the ability to predict the pH-dependent aqueous solubility of weak electrolytes carries significant value.

The thermodynamic treatment of electrolytes is often formulated with ion-specific model parameters, which tends to confine their application to fully dissociated strong electrolytes. The SAFT-VRE \cite{1} equation of state (EoS) has been used in this way to successfully model the phase behavior of aqueous solutions of strong electrolytes, thus providing a platform for developing a theoretic framework for weak electrolytes. In order to describe the partial dissociation of weak electrolytes, the reaction equilibria which govern their extent of dissociation must also be considered alongside the physical model. In this work, we employ SAFT-VRE Mie \cite{2} – which is an electrolyte extension of the SAFT-VR Mie \cite{3} EoS – to model both the unionized weak electrolyte and the corresponding ions in solution. The relevant reaction equilibria governing the extent of ionization are taken into account by means of a minimization of the Gibbs free energy, which also incorporates a consideration of the solid-liquid phase equilibrium.

The resulting methodology is aimed at predicting the solubility of weak electrolytes in multicomponent solutions. We apply the methodology to calculate the aqueous solubility of typical pharmaceutical compounds including weak acids and weak bases at different conditions of pH and temperature, in order to demonstrate the predictive potential of our proposed approach.

References

\cite{1} J. M.A. Schreckenberg et al., \textit{Mol. Phys.}, 112, 2339-2364 (2014)

\cite{2} S. Dufal, Ph.D. Thesis, Imperial College London (2014)

\cite{3} T. Lafitte et al., \textit{J. Chem. Phys.}, 139, 154504 (2013)
Experimental study of phase equilibria of systems involved in CH$_4$ hydrate production coupled with CO$_2$ sequestration

Ludovic Legoix$^1$, Livio Ruffine$^1$, Jean-Pierre Donval$^1$, Matthias Haeckel$^2$

$^1$IFREMER, Centre de Bretagne, Département REM, Unité des Géosciences Marines, BP70 - 29280 Plouzané France, $^2$IFM GEOMAR, Helmholtz Centre for Ocean Research Kiel Wischhofstr. 1-3 D-24148 Kiel Germany

Corresponding author e-mail: ludovic.legoix@ifremer.fr

Keywords: gas hydrates, methane production, CO$_2$ sequestration, phase equilibria, Water-CH$_4$-CO$_2$ system.

Natural methane hydrates are crystalline structures formed from water and methane under high pressure and low temperature conditions. They are widely encountered in oceanic sediments on the continental margins, and in the permafrost. Oceanic methane hydrates accumulate within sedimentary intervals where the thermal regime condition is favorable for their formation. Thus, they form shallow natural-gas reservoirs, and are being considered as a potential energy resources. Moreover, the exploitation of such resources may also contribute to the mitigation of greenhouse gas as carbon-dioxide hydrates are more stable than their methane homologues. Thus, methane production coupled with CO$_2$ sequestration is one of the process which is under intense investigation in the view of methane hydrate exploitation [1].

However the development of such a process necessary involves a good description of the phase equilibria of systems containing water (brine)-CH$_4$-CO$_2$-(N$_2$) [2]. Amongst the thermodynamic issues which need to be solve for the development of that process, methane solubility in CO$_2$ as well as water solubility in liquid CO$_2$ [3] are key. They are needed to provide a fair estimation of the lost of CH$_4$ during production and to assess the CO$_2$ injectivity, respectively. The understanding of the CH$_4$-CO$_2$ exchange also deserves detailed investigations.

A high-pressure apparatus has been modified to investigation on such systems [4]. At the conference we will present data of hydrate-involving phase equilibria and solubility measurements for systems containing CH$_4$-CO$_2$-N$_2$-water. These data will be discussed with the aims to describe the formation mechanism of complex mixed-hydrate during methane production coupled with CO$_2$ sequestration.

References


Development of Predictive Association Models for the Description of Multifunctional Molecules with the CPA EoS

André M. Palma¹, Mariana B. Oliveira¹, António J. Queimada², João A. P. Coutinho*¹

¹Ciceco, Chemistry Department, Aveiro University, 3810-193 Aveiro, Portugal, ²Infochem, KBC Process Technology, 42-50 Hersham Road, Walton on Thames, Surrey KT12 1RZ, United Kingdom

*Corresponding author e-mail: jcoutinho@ua.pt

Keywords: CPA; Phase Equilibria; Multifunctional molecules

Design and optimization of processes using multifunctional molecules is of great importance to the chemical, petrochemical, pharmaceutical, cosmetics, food and energy industries.

The CPA EoS has already demonstrated to be a general and accurate thermodynamic model to deal with different associating molecules. As an example, it is widely used in the oil and gas industry to simulate systems with water and hydrocarbon components and is a well-respected model to simulate hydrate formation and inhibition.

Currently, CPA parameters are obtained by fitting to pure component vapor pressure and liquid density data. But the lack of such data, or the impossibility to measure them (as some of these compounds do not exist as pure liquids) hampers its use. As a result, its use in process simulators is limited, as there are no pure component parameters for every component we might be interested in. Also, process engineers who want to use the model are not interested in having to fit every set of CPA parameters for each new component. Thus, predictive methods to generate CPA parameters are needed.

In this work a new approach will be made to the development and application of the Cubic-Plus-Association of State (CPA EoS) for the description of thermophysical properties and phase equilibria of multifunctional molecules and their mixtures with hydrocarbons, water and other polar solvents.
Applications Of The Virial Expansion

Tom Bourne¹, Andrew Masters²

¹,²School of Chemical Engineering & Analytical Science, University Of Manchester, Oxford Road, Manchester M13 9PL, UK

Corresponding author email: thomas.bourne@postgrad.manchester.ac.uk

1. Introduction

The virial expansion is a systematic method for calculating the thermodynamic properties of a bulk fluid. It is expressed as an equation of state in terms of the virial coefficients $B_n$ as follows [1]:

$$\beta P = \rho + \sum_{n=2} B_n(T) \rho^n,$$

where $\rho$ is the number density and all other symbols take their usual meanings. The virial coefficients depend on both the temperature and the form of the intermolecular potential, allowing equation (1) to link macroscopic thermodynamic properties to microscopic particle behaviour.

Virial coefficients may be written as sums of cluster integrals of the Mayer function [2]. Increasing the order results in an increased dimensionality of the integrals, meaning that solutions for the virial coefficients become increasingly difficult to obtain. Because of this, relatively few coefficients have been calculated. The most successful methods developed so far are based on a ‘Mayer Sampling Monte Carlo’ technique (MSMC) [3, 4].

This work seeks to investigate the behaviour of the virial expansion in three different situations: a fluid described by an integrable pair-potential potential which undergoes a gas-liquid phase transition; a description of the structure of a Lennard-Jones (LJ) fluid; the properties of a hard-sphere crystal.

2. Improving the convergence of the virial expansion for a DPD potential

The virial expansion converges slowly, if at all, for dense fluids [5]. If one has extra information about how the equation of state behaves at high density, however, the virial series may be resummed to yield rapidly convergent results [6]. Integrable pair potentials, such as those used in dissipative particle dynamics (DPD) simulations, are finite for overlapping particles and have been shown to obey a quadratic equation of state at high density. We have calculated virial coefficients to 6th order by MSMC and have applied this resummation methodology. This leads to a very accurate equation of state which shows promise for predicting the vapour-liquid transition.

3. Investigating the structure of an L-J fluid using the virial expansion

Below the critical temperature, the virial expansion of the LJ fluid appears only to be convergent below the vapour density at vapour-liquid co-existence [7]. This means the expansion cannot describe the phase transition. To better understand why, the direct correlation function of an L-J fluid is calculated using MSMC and is used to describe the structure of the fluid through the radial distribution function. A comparison of these data with the corresponding data for a reference, repulsive potential gives insight into how the attractive regions of the LJ potential affect the convergence properties of the virial series. By taking advantage of the high temperature approximation, that works well for dense liquids, we indicate how this knowledge allows us to greatly improve the range of utility of the virial series and predict liquid structure as well as thermodynamic properties.
permits the calculation of the properties of a hard sphere crystal and the liquid-solid transition. While it is known that the virial expansion for the hard sphere fluid appears to be convergent up to the freezing transition, this work provides evidence that the virial series also converges in the solid phase.

5. Conclusion

We present findings showing several examples of how virials may be used to provide information about the structure and thermodynamic properties of both fluids and solids.

References

Universal scaling behavior of short flexible Mie n-6 chains: A simple and accurate correlation for the influence parameters

José Matías Garrido¹, Hugo Segura¹, Manuel M. Piñeiro², Felipe J. Blas¹, Erich A. Müller⁴, Andrés Mejía¹

¹Departamento de Ingeniería Química, Universidad de Concepción, Chile, ²Departamento de Física Aplicada, Universidade de Vigo, España, ³Departamento de Física Aplicada, Universidad de Huelva, España, ⁴Department of Chemical Engineering, Imperial College London, United Kingdom

Corresponding author e-mail: amejia@udec.cl

1. Introduction

The Square Gradient Theory (SGT) was originally developed by van der Waals in 1893 [1] and rediscovery more than sixty year latter by Cahn and Hilliard [2]. In this approach, the interfacial region is described as a diffusive model where the inhomogeneous Helmholtz energy density continuously varies from the vapor bulk phase to the liquid bulk phase. In order to apply the SGT, it is necessary to provide two key inputs: the Helmholtz energy density of the homogeneous fluid and the so-called influence parameter of the inhomogeneous fluid. The homogeneous Helmholtz energy density can be obtained from any (empirical, cubic, molecular based) equation of state (EoS) that consistently predicts the bulk phase equilibrium. The influence parameter can be theoretically computed from its molecular definition, i.e. integration of the direct correlation function of the homogeneous fluid. However, the available approximate results still exhibit a poor performance when they are compared to experimental or molecular dynamic results. In order to overcome this problem, Carey [3] in 1976 proposed to calculate this parameter by using experimental data of interfacial tension and SGT. The results of this combination provide a route to compute the influence parameter, and correlated it in terms of the chemical family of the pure fluids and the EoS parameters. This semi-empirical approach has been broadly used in SGT and nowadays more refined correlations are available. (see Breure and Peters [4] and references therein). However, the main limitations of these correlations are their universality and transferable use.

In this work, we propose a universal correlation for the influence parameter for pure fluids. This correlation can be used for short flexible Mie n-6 pure chain fluids, composed from one to six tangential segments.

2. Theoretical modeling and Molecular Simulations.

In this work, we combine the SGT to the VR Mie Statistical Associated Fluid Theory (SAFT) EoS [5] and canonical Molecular Dynamics simulations to develop a universal correlation for the influence parameter for pure fluids. In this work, we consider short (m = 1 to 6) flexible Mie n-6 (n = 8, 10, 12, 20) pure fluids.

Figures 1 show the results for the case of short (m = 1 to 6) flexible Mie 12-6 (aka Lennard – Jones) pure fluids. Specifically, Fig. 1 (a) shows a lineal behavior of MD and SGT results, which allow concluding that the interfacial tension Mie 12-6 chains fluid follows a quasi-perfect universal behavior. Similar results have been obtained for other Mie n-6 cases (n = 8 and 10).
Figure 1. (a) Universal behavior and (b) interfacial tensions calculated by MD of Mie 12-6 chains fluid. (▬) SGT + SAFT-VR Mie with our expression for the influence parameters, (− • −) LJ-Chains+GT using the expression proposed by Duque et al. [4]. Mie 12-6 chains formed from $m_s = 1$ (●), $m_s = 2$ (■), $m_s = 3$ (◆), $m_s = 4$ (▲), $m_s = 5$ (▼), $m_s = 6$ (▲) segments.

Figure 1 (b) suggests an excellent capability of the SGT+SAFT-VR Mie EoS approach to simultaneously represent the interfacial tensions obtained from MD results and those given by Duque et al [4].

3. Conclusion

Results show that the mathematical features on expression obtained in this work can be expressed in a conformal manner. In other words, the final expression of the influence parameter is described in terms to a length scale, $\sigma$, an energy scale, $\varepsilon$, the range or functional form of the Mie n-6 potential defined in this work, $\alpha_{vdW}$, while the elongation of a molecule can be appropriately described by the chain length, $m_s$.

References

Asphaltene aggregation process analyzed by scattering experiments and molecular simulation

Julio Jover\textsuperscript{1,2}, Joëlle Eyssautier\textsuperscript{2}, George Jackson\textsuperscript{1}, Erich A. Müller\textsuperscript{1}, Carlos Nieto-Draghi\textsuperscript{2}, Loïc Barré\textsuperscript{2}, Pierre Levitz\textsuperscript{3}

\textsuperscript{1}Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K., \textsuperscript{2}IFP Energies Nouvelles, 1 et 4, Avenue de Bois-Préau, 92852 Rueil-Malmaison, France, \textsuperscript{3}Université Pierre et Marie Curie, Laboratoire PHENIX, UMR 8234, Paris France.

Corresponding author e-mail: carlos.nieto@ifpen.fr

1. Introduction

Asphaltenes have been studied for well over 50 years \cite{1}, yet remain one of the least-understood components of crude oil. They are formally defined as a solubility class \cite{2}; specifically they are classified as soluble in toluene but insoluble in n-heptane (although in some cases they are defined instead with reference to insolubility in n-hexane or n-pentane). Our aim is to combine SAXS experimental analysis on asphaltene aggregation to extract mean topological and dimensional features and, to compare this information with molecular simulation on the same process using simple molecular models starting with basic building blocks. The idea is to capture the main characteristics of real asphaltene precipitation that can be explained without atomic-level molecular detail…

2. Methods and results

Complementary SAXS and SANS experiments (figure 1.a and 1.b) were used to characterize the supramolecular asphaltene aggregates formed in Toluene solutions. Neutron contrast variation allowed to select a realistic core-shell form factor. Nano-aggregates were found to be described by a disk of total radius 32 Å and a height of 6.7 Å (figure 1.c). Composition and density calculations show that the core is a dense and aromatic structure whereas the shell is highly aliphatic \cite{4}.

![Figure 1. Experimental (symbol) and modelling (line) X-ray and neutron form factors of asphaltene nanoparticles in various mixtures of hydrogenated and deuterated toluene. The geometry and dimension of core-shell disc are explicated.](image)

Molecular Dynamics (MD) simulation of models of asphaltene molecules in explicit organic solvents were performed using a coarse grained approach that captures the behaviour of molecular aggregation under good-bad-solvent environment while reducing the computational load \cite{3}. Coarse grained models of molecules, corresponding to plausible continental-type morphologies (with a core of 12.5 Å and a shell of 6 Å and a molecular weight of 1616.7 g/mol) were constructed by joining together constitutive building blocks representing core conjugated aromatic rings, aliphatic chains,
aliphatic and aromatic solvents. Additionally, in order to assess the effect of the side aliphatic chains on the process of asphaltene aggregation we have also considered a second model where we have deliberately removed half of the aliphatic chains (with a molecular weight of 1316.06 g/mol) as represented in Figure 3.ab

![Figure 2. Hemi-asphaltene model (a) and results for the MD cluster analysis of hemi-asphaltenes in (b) toluene at 473k.](image)

The process of aggregation on the hemi-asphaltene system in toluene at 473 K is sketched in Figure 2.b. The aggregation does not lead to a full phase segregation of molecules in toluene but rather to a stable equilibrium of isolated clusters of 2 (40%), 3 and 4 (~10%) molecules with at least 20% of isolated molecules. This feature is in close agreement with the height of nano-disks measured using scattering experiments where stacking thickness of 2-3 molecules are observed. The aggregation in the case of hemi-asphaltenes seem to be more important than in the case of the "complete" model of asphaltene (not shown). It is important to notice the fact that experiments show a disk-like nano-aggregate of about 32 Å in radius which is not far from the one observed in simulations ranging between 18.5 Å to 27Å. Finally, A free energy difference ($\Delta F$), calculated using a potential of mean force for the process of aggregation is estimated to be -10.0 and -12.0 (in $k_B T$ units) for the fully branched asphaltene and the hemi-asphaltene respectively at 473 K in toluene.

3. Conclusion

A combination of SAXS and SANS experiments allow us to extract a plausible disk-like model of nano-aggregate of asphaltene molecules in toluene having 2-3 molecular diameters in thickness. Complementary molecular dynamics simulation on a coarse-grained model of continental-like asphaltenes roughly reproduces the size and shape of this aggregates in toluene. Further analysis on both techniques are required to better understand the internal arrangement of asphaltene molecules inside of the observed nano-aggregates.

References
1. Introduction

Thermodynamic properties for pure and mixtures of liquids especially alcohols have both practical and theoretical interest. They have to be known to design industrial processes properly. They can be used to develop models that allow us to predict other properties [1, 2].

In the present work, densities and speeds of sound for four binary mixtures of benzyl alcohol with 1, 3-propandiol, 1-propanol, 2-propanol, 1,2-propandiol and phenylethnol were measured over the entire range of composition and at five temperatures from 298.15K to 318.15K at 5K interval and atmospheric pressure using a vibrating u-tube densimeter (DSA 5000) [3]. Besides, the densities for pure compounds in the above-mentioned temperature range were measured. The experimental densities and speeds of sound were used to calculate other thermodynamic properties of mixtures including the excess molar volumes, $V^E$, the excess isentropic compressibility, $k^E$, the excess thermal expansion coefficients, $\alpha^E$, and the excess partial molar volumes at infinite dilution, $\bar{V}^E_i$, $\infty$.

The results have been used to discuss the nature and strength of intermolecular interactions in aforementioned mixtures. The calculated excess and deviations quantities are correlated with a third-order Redlich–Kister equation [4] which takes into account the dependence on composition and temperature simultaneously. Furthermore, Modeling of densities, sound speeds, and excess volumes have been performed with the Tao-Mason [5] and Peng-Robinson EOSs [6], being the accuracy of Tao-Mason remarkable and always better than the one from the PR EOS.

2. Conclusion

All the systems under study showed non-ideal behavior. This non-ideality can be explained by two factors: intermolecular forces in the mixture and enhanced rigidity. The main source of intermolecular interactions comes from hydrogen bonding between the components and also interaction between electrons of benzene ring and proton of alkanols.

References

Self-Assembly of Directionally Interacting Spheres and Rods

Nathan A. Mahynski 1, Wenyan Liu 2, Oleg Gang 2, Athanassios Z. Panagiotopoulos 1, Sanat K. Kumar 3

1Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, 2Center for Functional Nanomaterials, Brookhaven National Laboratories, Upton, NY 11973, 3Department of Chemical Engineering, Columbia University, New York, NY 10027

Corresponding author e-mail: mahynski@princeton.edu

There has been considerable recent interest in understanding the self-assembly of mixtures of differently shaped objects. Non-directional entropic and energetic effects are known in the specific case of rods mixed with spheres to exclusively yield layered phases. [1,2] However, here we use computer simulations and theory to demonstrate that the introduction of directional energetic attractions, between pairs of rod ends and between rod ends and isotropically interacting spherical nanoparticles (NPs), can be used to intelligently stabilize specific crystal morphologies through the interplay of energetic and entropic effects. To illustrate, we rationally design rods and spheres to obtain either face-centered cubic (FCC) or hexagonal close-packed (HCP) NP crystals at will. By tuning the relative size of the rods and spheres we control the interaction between non-nearest neighbor NPs in these crystals allowing us to control their relative stability with respect to each other, and with respect to an amorphous phase. Experiments with mixtures of gold spheres isotropically decorated with single stranded DNA (ssDNA) and rods with complementary ssDNA ends, unequivocally verify this behavior. We therefore propose that directionally specific attractions, which reflect only some features of the building block anisotropies, offer an entrée into completely different classes of self-assembly behavior.

References
From stripe to slab confinement for DNA linearization in nanochannels

Zuzana Benková, Pavol Námer and Peter Cifra

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

Corresponding author e-mail: cifra@savba.sk

We investigate recently suggested advantageous analysis in the chain linearization experiments with macromolecules confined in a stripe-like channel [1] using Monte Carlo simulations. The enhanced chain extension in a stripe that is due to significant excluded volume interactions between monomers in two dimensions is weakened considerably on transition to experimentally feasible slit-like channel. Based on the chain extension-confinement strength dependence and the structure factor behavior for the chain in stripe we infer the excluded volume regime (de Gennes regime) typical for two-dimensional systems. On widening of the stripe in direction perpendicular to the stripe plane, that is on transition to the slab geometry, the advantageous chain extension decreases and the Gaussian regime is observed for not very long semiflexible chains. The evidence for pseudo-ideality in confined chains is based on four indicators: the extension curves, variation of the extension with the persistence length, estimated limits for the regimes in investigated systems and the structure factor behavior. The slab behavior is observed when the two-dimensional stripe (originally of monomer thickness) reaches the thickness larger than approximately 10nm in the third dimension. This maximum height of the slab to retain the advantage of the stripe is very low and have implications for recent DNA linearization experiments. The presented analysis, however, has a broader relevance for confined polymers.

References
Nitrogen + Oxygen Solubility in Liquids for Bulk or Solution

Polymerization of Styrene

Tomota Tsuji, Koh-hei Ohya, Taka-aki Hoshina

College of Industrial Technology, Nihon University, Japan

Corresponding author e-mail: tsuji.tomoya@nihon-u.ac.jp

1. Introduction

Oxygen has been well known for an inhibitor in radical polymerization, because oxygen reacts with vinyl monomers or polymer radicals at the propagation reactions, and stabilized to be peroxide radicals. Then, the monomer solution, saturated with gaseous nitrogen, is often used to avoid the oxygen inhibition. On the contrary, oxygen is sometimes fed into the solution to inhibit an unexpected radical reaction in the reservoir, and to interrupt an uncontrollable reaction. However, the precise gas solubility data are not available in the literature. Then, in our previous paper, nitrogen or oxygen solubility in benzene, styrene, and divinylbenzene was measured at room temperature, 298, 303, and 313 K. Successively, gas mixture, nitrogen + oxygen, solubility was measured in the component of the polymerization solution, benzene, and styrene at the same temperature.

2. Experimental Results and Discussion

Gas mixture of nitrogen + oxygen was purchased from Taiyo Nippon Sanso Co., Tokyo. The mole ratio was set to be nitrogen: oxygen = 50.0 : 50.0. For the solubility measurements, a synthetic type apparatus was employed. The detail equipment, and the procedures have been already described [1]. The panoramic view cell employed was made of Pyrex glass, and its inner volume about 37 cm³. The cell was specially designed, and its safe pressure up to 7.5 MPa. A magnetic stirrer tip was used to agitate the sample in the cell. The volume of the cell has been calibrated within the accuracy of 2% by use of pressurized nitrogen. The mole of nitrogen or nitrogen + oxygen were evaluated by assuming the ideal gas state. Then, the temperature, and the pressure were measured by an absolute pressure sensor with the resolution of 0.01 kPa, and a thermistor thermometer with the resolution of 0.01 K. The experimental temperature was set to be around 293, 303, and 313 K, and the pressure up to 4.000 MPa. To check the reliability of the data, the nitrogen solubility in benzene was measured at 303.22 K. The data agreed well with those of Jabloniec et al. [2], and they showed a linear pressure dependence following the Henry's law. The gas solubilities were slightly increased with the temperature for the two systems. Especially, the Henry constants seemed to be an averaged value for the two pure gases, nitrogen, and oxygen, at given temperature. The Henry constants were correlated by Peng-Robinson equation of state combined with van der Waals one fluid model mixing rule. The calculations showed good reproducibilities for all systems.

References

Thermodynamic Equilibrium of Mixtures of Combustible Gases and Air

R M Gibbons

Corresponding author e-mail: richandhelen@gibbons.entadsl.com

Keyword: thermodynamics, equilibrium, statistical mechanics

1. Introduction

Standard treatments of thermodynamic equilibrium are incomplete. They do not take account of all factors determining equilibrium, cannot explain why many systems do not reach equilibrium and do not discuss the questions of reaching and maintaining equilibrium.

2. A New Definition of thermodynamic Equilibrium

The arguments presented here provide a single physical definition of thermodynamic equilibrium that accounts for all factors determining thermodynamic equilibrium for mixtures of combustible gases and air. Based on the standard definition of thermodynamic equilibrium, the Maxwell Boltzmann Distribution and a simple molecular model it leads to three possible types of equilibrium. The regions of temperature pressure and composition for each type of equilibrium for these molecular systems are defined by the measured values of ignition temperatures and the explosive and flammability limits.

3. Conclusion

Analysis of the wealth of data for ignition temperatures, explosive limits and flammability limits confirms the validity of the simple molecular model and its essential role in defining thermodynamic equilibrium for these molecular systems. How this definition of thermodynamic equilibrium can be extended to the definition of thermodynamic equilibrium for all molecular systems is discussed in the following paper.
Characterization of electrical conductivity and rheological properties of ionic liquids

Carlos Topette-Reyes, Andrés Estrada-Alexanders, Pedro Díaz-Leyva, & Fernando del Río

Departamento de Física, Universidad Autónoma Metropolitana – Iztapalapa, Mexico

Corresponding author e-mail: afea@xanum.uam.mx

Ionic Liquids (IL) are salts in liquid state at pressure and temperature close to room conditions. While ordinary liquids such as water are composed predominantly by electrically neutral molecules, IL are composed by charged ions [1]. Some characteristics of these materials make them very attractive for applications; in fact, they are currently used in industry as powerful solvents and electrically conducting fluids [2].

It has been seen that IL exhibit a rather high electric conductivity because their natural conformation. However, in aqueous solutions, this electrical conductivity depends on the concentration of IL and on the nature of the compound. Furthermore, the appearance of aggregates affects seriously this electrical conductivity.

In this work we study the electrical conductivity of the following pure IL:
- Tri-isobuthylmethyl-phosphonium-tosylate,
- 1-Buthyl-3-methylimidazolium-hexafluoromethyl-phosphate,
- Tributhyltetradecyl-phosphonium dodecylbenzene-sulfonate,
- Methyltrioctyl-ammonium bis (trifluorometylsulfonil) imide,

and aqueous solutions at several concentrations in a temperature range of 20 to 50 ºC.

On the other hand, rheological properties such as shear viscosity have been characterized for several pure IL at the above temperatures and also for aqueous solutions. The rheological characterization has been carried out performing rotational viscosimetry. Studying flow curves, a phenomenon of shear thinning has been observed on pure IL.

References
Synthesis of TiO2-ZnO nanopowders doped with Fe via sol-gel method and photochemical degradation on anionic surfactant

M. Giahi¹, M. Meskinfam²

¹,²Department of Chemistry, Lahijan Branch, Islamic Azad University, Lahijan, Iran

Corresponding author e-mail: giahi_m@yahoo.com

1. Introduction

One of the most intriguing application areas of TiO2 is photocatalytic activity for environmental protection, since it can decompose a large number of organic and inorganic pollutants. However, Pure TiO2 exhibits low photocatalytic property due to rapid charge carrier recombination. Numerous efforts have been attempted to improve the photoexcited charge separation and to enhance the photocatalytic activity by modifying the surface or bulk properties of a photocatalyst, such as deposition of metals, doping, surface chelation, and coupling of two Semiconductors [2]. Among the coupled semiconductors, many efforts have been devoted to combine TiO2 with other metal oxides such as ZnO, SnO2, Fe2O3, ZrO2, Cu2O, etc. Recently TM (transition metal)-doped II–VI and III–V compound semiconductors have been extensively studied (such as Fe, Co, Ni, Mn, etc.) [3]. In this study, the nano-scale Fe doped ZnO/TiO2 coupled oxide photocatalyst has been synthesized by the sol-gel method. The synthesized powders was characterized by XRD and photocatalytic activity was determined by means of degradation of anionic surfactant under UV light irradiation. The degradation was studied under different conditions.

2. Methods

Fe-doped ZnO-TiO2 nanopowders containing 0.05 mol% Fe ion dopant were synthesized via a sol–gel technique. Titanium (IV) isopropoxide (TTIP), Zinc nitrate and copper sulphate powders are chosen as starting materials. Two solutions were prepared by dissolving separately measured amount of zinc nitrate and citric acid into 25mL ethylene glycol and deionized water. After 10 min TTIP was dissolved in zinc nitrate solution. After complete dissolution of the precursors, citric acid solution was added to zinc nitrate solution and then chelated in with magnetic stirring at 80 °C. The dopant stoichiometry was controlled by adding the Iron sulphate in to solution after 30 min. The concentration of the as prepared solutions was chosen to be 0.4 M. The Fe/Zn and Fe/Ti molar ratio in solution was 0.05 mol%. The obtained mixture was stirred at 80 °C for 4 h to yield a clear and homogeneous solution. Afterwards sols were slowly cooled in air down to room temperature and then aged for 24 h in that situation. Following this, the samples put into a tube furnace and annealed in air at 700 °C for 2 h. Prepared Fe-doped ZnO-TiO2 nanoparticles were characterized by X-ray diffraction. Photodegradation experiments were performed with a photocatalytic reactor system under the irradiation of a UV lamp.

3. Results and discussion

The crystal structures of Fe-doped ZnO and ZnO were characterized using XRD. Fig. 1 shows the XRD pattern of 0.05 mol% Fe doped ZnO-TiO2 nanopowder. It can be seen that the sample exhibit a three phase with TiO2, ZnTiO3 and ZnFe2O4 structure. The successful doping of the Fe element into the ZnO host was evident by XRD lines.

The crystallite size of the samples was estimated from the Scherrer's equation. The average crystallite size is about 16.62nm. Results obtained from Photodegradation experiments revealed that Fe-doped ZnO-TiO2 showed high activity for UV-photocatalytic degradation of linear alkyl benzene sulfonate (LABS). The best conditions for the photocatalytic degradation of LABS were obtained. The optimal degradation conditions of LABS are: 5mg catalyst, pH 6.0, 1mM K2S2O8 and concentration of LABS 20mg/L.
4. Conclusions

Fe-doped ZnO-TiO$_2$ photocatalyst was prepared by the sol-gel method. XRD pattern exhibit a three phase with TiO$_2$, ZnTiO$_3$ and ZnFe$_2$O$_4$ structure and 0.05% Fe/Ti molar ratio was the optimum doping ratio for Sodium alkyl benzene sulfonate. Under optimal degradation conditions of surfactant, the photodegradation percent of LABS was 92% when the solution was irradiated by the 400W high pressure mercury vapor lamp for 4h.

Reference

Estimation of Pitzer interaction parameters from heat capacity and osmotic coefficient for the NaOH-H₂O system at temperatures from 0 to 150°C and concentrations up to NaOH(s) saturation

Lach Adeline¹,², André Laurent¹, Lassin Arnault¹, Azaroual Mohamed¹, Cézac Pierre², Serin Jean-Paul²

¹BRGM, Water Environment and Ecotechnologies Direction (Orléans, France), ²LaTEP, UPPA (Pau, France)

Corresponding author e-mail: A.Lach@brgm.fr

Keywords: Pitzer interaction model, NaOH electrolyte system, heat capacity, high saline solutions

1. Introduction

The aim of this study is to determine new Pitzer interaction parameters for the NaOH-H₂O binary system from heat capacity and osmotic coefficient data between 0 and 150°C and up to NaOH solid salt saturation. As shown in Fig. 1, from the excess Gibbs free energy ($G^\text{ex}$) we can access to several properties [1]: the osmotic coefficient ($\phi$), the apparent relative molar enthalpy ($L_{\phi}$) and the apparent molar heat capacity ($C_p,\phi$). With the last property, we can calculate heat capacity ($C_p$) of an electrolyte solution.

As shown in our previous work [2] the interpretation of osmotic coefficient data needs taking into account the partial dissociation of NaOH. In this case, the interaction parameters used are $\beta_0^{\text{Na}+/\text{OH}^-}$, $\beta_1^{\text{Na}+/\text{OH}^-}$, $C_\phi^{\text{Na}+/\text{OH}^-}$, $\zeta^{\text{Na}+/\text{OH}^-/\text{NaOH}}$ and $\lambda^{\text{NaOH}/\text{NaOH}}$ with the following temperature dependence [3]:

$$Y(T)=a_1+a_2T+a_3T^2+a_4T+a_5\ln(T)+a_6(T-263)+a_7(680-T)+a_8(T-227) \quad (Eq. 1)$$

The $C_p,\phi$ expression depends on the $Y^j$ parameters which are a combination of the first and second temperature derivatives of $Eq. 1$. The partial molar heat capacity of the solute at infinite dilution ($C_p^\text{°}$) is determined from the HKF equation of state for aqueous species given in Johnson et al. [4].

These equations were implemented in the geochemical code Phreeqc V3 [5]. Coupling with optimization software (PEST), new interaction parameters have been determined using simultaneously the heat capacity and osmotic coefficient data.

2. Results

In Fig. 2 we plotted the calculated (dotted lines) and experimental (open symbols) osmotic coefficient as a function of the molar fraction of total NaOH molality. For convenience of representation, the curves were shifted 1.2 for 0°C, 1 for 25°C and so on. In Fig. 3, we plotted the calculated (dotted
lines) and experimental (open symbols) heat capacity as a function of NaOH molality. The results are obtained at saturated water vapour pressure.

Fig. 2: Osmotic coefficient, \( \varphi \), for the NaOH-H_2O binary system at several temperatures.

Fig. 3: Heat capacity, \( C_p \), for the NaOH-H_2O binary system at a) 25°C and b) 148.89°C.

3. Conclusion

In this study, we proposed a new Pitzer parameterization able to reproduce the osmotic coefficient and the heat capacity data of NaOH-H_2O complex solutions up to solid salt (NaOH(s)) saturation from 0 and 150 °C. The developed methodology can be applied to many other electrolyte systems, if sufficient experimental data are available to fully parameterize the systems.

References
Interfacial Mass Transfer in Liquid-Liquid Systems

Tim Zeiner

1Laboratory of Fluid Separations, Department of Biochemical and Chemical Engineering, TU Dortmund University, Emil-Figge-Straße 70, 44227 Dortmund, Germany

Corresponding author e-mail: tim.zeiner@bci.tu-dortmund.de

Keywords: Demixing liquids, Cahn-Hilliard, Interfacial mass transfer

1. Introduction

In chemical engineering extraction plays a crucial role for the purification of products ranging from bulk products to biopharmaceuticals. For the extraction the mass transfer of the target product across the interface is essential as it determines the residence time and so the dimensions of the extraction unit. The nature of the interface between two fluids has been the subject of science since Young, Laplace and Gauss in the 1800. All three have the assumption of an interface between two fluids as a surface of zero thickness. On this surface there would be unsteadiness in all physical properties. Later Poisson, Maxwell and Gibbs recognized that the interface actually represented a rapid but smooth transition of physical quantities between the bulk fluid values. The idea of an interface with a non-zero thickness was developed in detail by Lord Rayleigh and van der Waals proposing gradient theories for the interface based on thermodynamic principles [1]. Based on the ideas of the gradient theory by Van der Waals, Cahn and Hilliard developed the spinodal decomposition [2]. In contrast to other mass transfer models, the thermodynamics can be directly considered by the inclusion of the Helmholtz free energy in the Cahn-Hilliard theory. Up to now, relative simple thermodynamic models were used which cannot represent experimental data.

2. Theoretical Background

The aim of this work is to close this gap in the modelling of mass transfer across the interface using the Cahn Hilliard theory. For this reason, different systems will be investigated. These systems contain polymer blend or polymer solutions. In the scope of this work is the impact of different functional groups of polymers and the structure of polymers on the mass transfer. This influence can be regarded by the Lattice Cluster theory (LCT) combined with an association model [3, 4]. The LCT, developed by Dudowicz and Freed [4], allows the calculation of the thermodynamic properties of a molecule having an arbitrary structure. But the LCT cannot consider the influence of functional groups. For this reason the LCT is combined with association model [3]. For this investigation two phenomena will be regarded: On the one hand the dissolution of drops and the demixing of liquids.

3. Conclusion

In contrast to other works [5], this contribution shows the influence of functional groups and molecular architecture on the mass transfer of polymers for the first time.

References

Surface thermodynamics of planar, cylindrical and spherical vapour-liquid interfaces of water

Gabriel Lau¹, Ian Ford², Patricia Hunt³, Erich A. Müller¹, George Jackson¹,

¹Department of Chemical Engineering, Imperial College London, ²Department of Physics and Astronomy, University College London, ³Department of Chemistry, Imperial College London

Corresponding author e-mail: gabriel.lau07@imperial.ac.uk

1. Introduction

The test-area (TA) perturbation approach [1] has been gaining popularity as a methodology for the direct computation of the interfacial tension in molecular simulation. In this work, we provide a new geometric analysis of the TA method and employ the technique to determine the vapour-liquid interfacial tension of TIP4P/2005 water [2] for planar, cylindrical, and spherical geometries [3].

2. Analysis and application to different geometries of TIP4P/2005 water

By expressing the change in configurational energy of a molecular configuration as a Taylor expansion in the distortion parameter, compact relations are derived for the interfacial tension and its energetic and entropic components for three different geometries: planar, cylindrical, and spherical fluid interfaces. We show that a greater statistical uncertainty is to be expected when calculating the thermodynamic properties of a spherical interface than for the planar and cylindrical cases, and the evaluation of the separate entropic and energetic contributions poses a greater computational challenge than the tension itself.

We apply the TA method on planar, cylindrical and spherical geometries of TIP4P/2005 water. A weak peak in the curvature dependence of the tension is observed in the case of cylindrical threads of condensed liquid at a radius of about 8 Å, below which the tension is found to decrease again. In the case of spherical drops a marked decrease in the tension from the planar limit is found for radii below 15 Å; there is no indication of a maximum in the tension with increasing curvature. The vapour-liquid interfacial tension tends towards the planar limit for large system sizes for both the cylindrical and spherical cases. Estimates of the entropic and energetic contributions are also evaluated for the planar and cylindrical geometries and their magnitudes are in line with the expectations of our simple analysis.

3. Conclusion

We provide an interpretation of the TA method taking the view that it corresponds to the change in free energy under a transformation of the spatial metric and derive relations for the tension and its energetic and entropic components for three different geometries. As an application, we investigate different geometries of condensed structures formed by water represented with the TIP4P/2005 model. The tension (and where relevant, its size dependence) was obtained for all geometries and the entropic components were also calculated for planar and cylindrical interfaces.

References
Formation of structures made of ionic liquids in diluted aqueous solutions

Eduardo Plácido-Flores, Pedro Díaz-Levy, Andrés Estrada-Alexanders & Fernando del Río

Departamento de Física, Universidad Autónoma Metropolitana – Iztapalapa, Mexico

Corresponding author e-mail: pdleyva@xanum.uam.mx

Ionic Liquids (IL) are salts in liquid state at pressure and temperature close to room conditions. While ordinary liquids such as water are composed predominantly by electrically neutral molecules, IL are composed by charged ions [1]. Some characteristics of these materials make them very attractive for applications; in fact, they are currently used in industry as powerful solvents and electrically conducting fluids [2].

IL have a high thermal expansion coefficient, a high viscosity and a high electric conductivity. On the other hand they have a very low melting point and a very low vapour pressure. Some of them build amorphous solids at low temperatures and other ones form liquid crystals.

In this work we study the dynamics of formation and the morphology of microscaled structures made of aggregated IL in water at diluted regime (around 10^{-5} in volume) at room temperature.

We worked with the following substances:
- 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
- 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
- 1-Butyl-3-methylimidazolium hexafluorophosphate
- 1-Butyl-3-methylimidazolium tetrafluoroborate
- Triisobutylmethylphosphonium tosylate
- 1-Butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide
- 1-Methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide
- Tributyltetradecylphosphonium dodecylbenzenesulfonate
- Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide
- Tributylmethylammonium bis(trifluoromethylsulfonyl)imide

The aggregation kinetics has been studied by time resolved Dynamic Light Scattering (DLS). To resolve the structural conformation of the aggregates Small Angle X-Ray Scattering (SAXS) has been used.

Measuring the hydrodynamic radii $r_H$, DLS reports growing structures, sized from tents of nanometers up to few micrometer, following an specific grow law. The form factor $P(q)$ has been measured by SAXS. It is observed that kinetics of aggregation and structural conformation depends on the concentration and on the nature of the compound. We also report the dynamical evolution of these structures.

Acknowledgements

Authors thank to CONACyT (Mexico) under grant 2008-105843.

References

Computer simulations of an anionic chromonic dye: spontaneous symmetry breaking to form chiral aggregates and the formation of a novel smectic phase

Romnik Thind¹, Mark R. Wilson¹

¹Department of Chemistry, Durham University, Durham, DH1 3LE, UK

Corresponding author e-mail: romnik.thind@durham.ac.uk

1. Introduction

Controlling self-assembly of nanostructured soft matter in aqueous solution is of considerable interest in the formation of thin organic films and in future organic electronics applications. A rare “self-assembled” motif, named the double-width column structure has been proposed to interpret experimental findings for the anionic chromonic dye (figure 1). High concentrations of dye in water are proposed to form a “smectic chromonic”. However, the vast majority of chromonic mesogens favour a direct face-to-face aromatic stacking arrangement, causing some controversy as to whether either of these proposed models is energetically feasible.

Figure 1: Structure of an anionic chromonic dye

2. Simulation studies

Molecular dynamics simulations at a fully atomistic level are able to provide a “picture” of the preferred stacking structure within chromonic aggregates in aqueous solution [1]. Results for low concentrations of the anionic dye (figure 1) show spontaneous symmetry breaking, wherein chiral aggregates (figure 2) form as the energetically most stable species, despite the presence of strictly achiral dye molecules. This provides a new interpretation of experimental results.

Results for higher concentrations show the alignment of several aggregates to form a novel biaxial-smectic layer structure, with the inherent loss of chirality as a result of this new molecular environment. The formation of the novel layer structure, which is stabilized by interactions of surface charged groups explains key experimental findings.

Figure 2: Chiral aggregates of an anionic dye

3. Conclusion

Atomistic molecular dynamics simulations have provided evidence for i) chiral aggregates, which arise from spontaneous self-assembly of achiral molecules in solution, ii) a novel biaxial-smectic chromonic phase not seen previously.

References


DPD simulations to predict the phase behaviour of nonionic chromonics

*Martin Walker*¹ and *Mark Wilson*¹

¹Department of Chemistry, University of Durham, UK.

Corresponding author e-mail: martin.walker2@durham.ac.uk

1. Introduction

Dissipative particle dynamics (DPD) simulations are a powerful tool to rapidly explore the phase behaviour of coarse grained systems. We use DPD studies to explore the effects of subtle changes in interactions for a series of related models of self-assembling-nonionic-chromonic mesogens.

![Figure 1: A DPD model for a nonionic chromonic mesogen](image)

2. DPD studies

Results are presented from DPD studies of the model shown in figure 1, based on the chromonic molecule TP6EO2M [1,2], and several related systems. Here, we study the phase behaviour as a function of concentration, and explore the influence of the shape of the core, length and hydrophilicity of the solubilizing arms, and the effect of the DPD solubility parameter ($a_{ij}$). The simulations are shown to reproduce experimental behaviour for TP6EO2M: i.e. the formation of single molecule stacks in solution at low concentration and the alignment of molecular stacks into a nematic phase at higher concentrations. Similarly, the DPD model reproduces the trend in the binding energy of growing an aggregate, when the $a_{ij}$ parameters are fine-tuned to match experiment.

3. Conclusion

A DPD model is used to provide predictions for the structure of aggregates in solution, and the structure of chromonic mesophases for a series of related nonionic chromonic molecules.

References

Using DPD simulation to study the phase behaviour of complex polymer-surfactant mixtures

Sarah Gray\textsuperscript{1}, Mark Wilson\textsuperscript{1}

\textsuperscript{1}Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Corresponding author e-mail: s.j.gray@durham.ac.uk

1. Introduction

Dissipative particle dynamics (DPD) has developed as a powerful predictive tool over the past two decades \cite{1-3}. In this study, we use DPD to analyse the phase behaviour of polymer-surfactant mixtures, in particular focussing on the sometimes surprising effects that small amounts of additives (for example perfumes and colourants) can have on phase stability.

2. Parameterization and testing of representative DPD models

Parameterization of DPD models using the traditional Groot-Warren approach has shown promising results in relation to experiment (both qualitatively and quantitatively) in various studies \cite{2-5}. The traditional method of generating DPD parameters requires separate tuning calculations for any change in the simulation system and suffers from a lack of transferability. To avoid this pitfall we investigate a combination of parameterization techniques, including:

- studying partitioning of species between different phases to establish free energies of mixing,
- drawing parallels between the DPD equation of state and regular solution theory, as outlined by Travis et. al. \cite{6},
- matching experimental solubilities,

These techniques ensure our coarse grained DPD model provides a good representation of the desired systems. Having developed a “reasonably” representative and transferable DPD model, we hope to make quantitative predictions as to which features in additive molecules have the greatest impact on the phase stability of mixtures.

3. Conclusion

In our work we aim to establish a parameterization scheme for DPD models, such that it can reproduce phase behaviour across a desired range of temperatures and concentrations. We apply this method to simulating complex surfactant/polymer/additive mixtures, in order to predict phase behaviour and study the impact of additive concentrations on stability.

References

\cite{3} R. D. Groot and K. L. Rabone, Biophys. J., 81, 725-736 (2001)
Combustion calorimetry of hydrocortisone acetate and analysis of the thermodynamic functions of steroids

A.S. Shipilova, A.V. Knyazev, E.V. Gusarova

Chemistry Department, Lobachevsky State University of Nizhni Novgorod Gagarin Av. 23/2, 603950
Nizhni Novgorod, Russia

Corresponding author e-mail: 28_stasy@bk.ru

Keywords: Hydrocortisone acetate; Hormone; Combustion calorimetry; Thermodynamic functions

Hydrocortisone acetate is a corticosteroid with anti-inflammatory properties. Hydrocortisone acetate may stimulate superoxide dismutase production as well as release release antioxidants [1]. Hydrocortisone acetate can be used for biochemical research. As a sugar cortical hormone drug, it can anti-allergic, antitoxin, resistance to shock action.

This work is a continuation of systematic studies of bioactive compounds. Earlier in the articles [2-4], we have investigated the thermodynamic properties of vitamins.

Hydrocortisone acetate was purchased from Fluka. According to the certificate of Fluka the content of impurities (0.1 wt %) led us to conclude that the hydrocortisone acetate sample studied was an individual crystalline compound.

The energy of combustion, \( \Delta_cU \), of hydrocortisone acetate was measured in a calorimeter (V-08) with a static bomb and an isothermal shield.

As a result, the energies and enthalpies of combustion of hydrocortisone acetate at \( T = 298.15\text{K} \) and standard pressure were determined. The values are for the reaction:

\[
\text{C}_{23}\text{H}_{32}\text{O}_6(\text{cr}) + 28\text{O}_2(\text{g}) \rightarrow 23\text{CO}_2(\text{g}) + 16\text{H}_2\text{O}(\text{l})
\]

In brackets are given the physical states of reagents: (cr), crystalline; (g), gaseous; (l), liquid. The pressure in the oxygen bomb for the combustion of samples was 3.0 MPa. Transfer the high pressure to the standard state (\( p = 0.1\text{MPa} \)) was performed similarly the work [5].

The data on the enthalpy of combustion of the crystalline hydrocortisone acetate was used to estimate enthalpy of combustion and formation at \( T = 298.15\text{K} \) and \( p = 0.1\text{MPa} \).

\[ \Delta_H^\circ (\text{C}_{23}\text{H}_{32}\text{O}_6, \text{cr}) = -1307.0 \pm 11.6 \text{kJ} \cdot \text{mol}^{-1}. \]

The values conform to the following process:

\[
23\text{C(gr)} + 16\text{H}_2(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{C}_{23}\text{H}_{32}\text{O}_6(\text{cr})
\]

where in the brackets are indicated the physical states of reagents: (gr), graphite; (g), gaseous; (cr), crystalline. Correlation analysis showed that the dependence of the enthalpy of formation of steroids on the molecular weight is described by a linear equation (Fig.1). Our results are in good agreement with the available statistics.
Was carried a thermochemical analysis acylation reaction of hydrocortisone. Hydrocortisone and acetic acid under the condition of azabenzene can be used to manufacture hydrocortisone acetate. The standard enthalpy of the acylation reaction of hydrocortisone into hydrocortisone acetate was calculated.

\[ C_{21}H_{30}O_5(cr) + CH_3COOH(l) \rightarrow C_{23}H_{32}O_6(cr) + H_2O \]  \hspace{1cm} (3)

\[ \Delta H^\circ (298.15) = -39 \pm 32 \text{ kJ mol}^{-1}. \]

The reaction is exothermic and deeper thermodynamic analysis will be possible if the entropy of the reaction will be determined.

References


Study of the properties of some oxygen-containing compounds of thorium

M.E.Manyakina, A.V. Knyazev, I.A. Savushkin, A.Alahmad

Chemistry Department, Lobachevsky State University of Nizhni Novgorod Gagarin Av.
23/2,603950 Nizhni Novgorod, Russia

Corresponding author e-mail: mmanyakina@yandex.ru

Keywords: Thorium; Thermodynamic functions; Adiabatic vacuum calorimetry;

At the present time, decision radiochemical problems are impossible without fundamental information about the oxygen-containing compounds of thorium. The knowing of dependences “composition-structure-properties” is of great importance. One of the most widespread minerals of thorium are phosphates and silicates. This work is a continuation of systematic studies of these compounds.

Double thorium phosphates $M_k\text{Th}_{3-k}(PO_4)_{4-k}$ ($M^I =$ Li, Na, Ag, K, Rb, Tl, Cs; $M^{II} =$ Cd, Ca, Sr, Pb) crystallize in the monoclinic system (space group C2/c for $M^I\text{Th}_2(PO_4)_3$ and P21/n for $M^{II}\text{Th}(PO_4)_2$) [1]. Several stoichiometric composition are known today for thorium-containing silicates: $\text{ThSiO}_4$ (Th : Si = 1 : 1), $\text{MM'}\text{CaTh(SiO}_4\text{)}_6\text{O}_2$ (Th : Si = 2 : 3), $\text{Na}_{12}\text{Th}_3(\text{Si}_{8}\text{O}_{19})_4\cdot18\text{H}_2\text{O}$ (Th : Si = 3 : 32) [2]. Among the mineral containing Th and Si, the most diverse are minerals with the general formula $\text{MM'}\text{CaTh(SiO}_2\text{O}_2\text{)}$ (M - □, Li, Na, K, Rb, Cs; M' – Na, Ca). In ekanite (space group I422), the M' positions are occupied by Ca ions. In turkestanite minerals (space group P4/mcc), the M positions are occupied by Na and K atoms.

The temperature dependence of heat capacity of $K\text{Th}_2(PO_4)_3$ [3] and $K\text{NaCaTh(Si}_2\text{O}_3\text{)}$ has been measured for the first time in the range from 5.5 to 350 K by precision adiabatic vacuum calorimetry. The experimental data were used to calculate standard thermodynamic functions, namely the heat capacity, enthalpy, entropy and Gibbs function for the range from T $\rightarrow$ 0 to 350 K. The value of the fractal dimension D in the function of multifractal generalization of Debye’s theory of the heat capacity of solids was estimated and the character of heterodynamics of structure was detected. To calculate the standard thermodynamic functions of the $K\text{NaCaTh(Si}_2\text{O}_3\text{)}$ and $K\text{Th}_2(PO_4)_3$, its values were extrapolated from the temperature of the measurement beginning at approximately 5.5 K to 0 K by graphic method. The absolute entropies of these compounds and the corresponding simple substances were used to calculate the standard entropy of formation of the compound under study at 298.15 K.

The experimental values of the molar heat capacity of $K\text{NaCaTh(Si}_2\text{O}_3\text{)}$ (fig.) over the range from 5.5 to 350 K. The heat capacity of this substance in interval from 10 to 350 K gradually increases with rising temperature and does not show any peculiarities.
Thermal analysis of the compounds $\text{M}_x\text{Th}_{3-x}(\text{PO}_4)_{4.4}$ showed that they are stable up to 1723 K, except for $\text{CsTh}_2(\text{PO}_4)_3$ whose thermogram exhibits an endothermic effect at 1588 K. This compound irreversibly decomposes without melting. A study of the thermal stability of $\text{MM'}\text{CaTh}(\text{Si}_8\text{O}_{20})$ showed that $\text{Ca}_2\text{Th}(\text{Si}_8\text{O}_{20})$ is stable up to 1723 K, whereas turkestanite group compound incongruently melts at 1494 K. The reaction scheme can be presented as follows: $\text{MNaCaTh}(\text{Si}_8\text{O}_{20})$ (cr) $\rightarrow \text{ThSiO}_4$ (cr, huttonite) + $\text{SiO}_2$(cr) + 0.5$\text{M}_2\text{O}$.0.5$\text{Na}_2\text{O}$.CaO.6SiO$_2$ (melt).

References
Simultaneous description of phase equilibria and derivative properties for testing the accuracy of the soft-SAFT parameterization

Mariana B. Oliveira1, André Palma1, Felix Llovell2, Lourdes F. Vega2,3, João A. P. Coutinho1

1 CICECO, Chemistry Department, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal, 2 MATGAS Research Center, Campus de la UAB, 09193 Bellaterra, Barcelona, 3 Carburos Metálicos/Air Products Group, C/Aragón 300, 08009 Barcelona

Corresponding author e-mail: jcoutinho@ua.pt

Keywords: soft-SAFT, parameterization, VLE, derivative properties

Although it is of common practice to remark the theoretical background of statistical mechanics based equations of state (EoS), such as the family of SAFT EoSs, these approaches are not always used in a systematic and predictive manner becoming, in some occasions, to behave similarly to any correlation. The ability to describe polar and hydrogen bonding systems in wide ranges of thermodynamic conditions is undoubtedly a step forward in the thermodynamic modelling for industrial applications, but unfortunately most studies are limited to phase equilibria calculations. The so-called predictability and transferability of the SAFT molecular parameters should be given by the ability to describe other properties, such as heat capacity, isothermal compressibility and speed of sound. In some cases, different sets of molecular parameters offer a similar description of the phase envelope, while having a very different performance when studying derivative properties.

In this work, we propose to test the soft-SAFT EoS to describe the phase equilibria and derivative properties of a series of systems, including alkanes, alcohols, carboxylic acids and ionic liquids. Apart from the classical parameters optimization method, where only density and vapor pressure data are used, a new method for determining the soft-SAFT [1] compound parameters, including derivative properties data, is investigated and developed. A discussion about the most relevant thermodynamic properties to be included in the parameters fitting, their weight in the regression procedure and the influence of the association molecular parameters in the families where short-range interactions are present will be carried out.

Since advanced association EoSs generally derive from the same theoretical background, the methods and conclusions developed can be easily transferred to other SAFT models.

References

Acknowledgements
M.B. Oliveira acknowledges for her Post-Doctoral grant (SFRH/BPD/71200/2010) and F. Llovell for a TALENT contract from the Catalan Government and MATGAS. This work is financed by FEDER funds through Programa Operacional Factores de Competitividade – COMPETE and by Nacionais funds through FCT – Fundação para a Ciência e Tecnologia through project CICECO - FCOMP-01-0124-FEDER-037271 (Ref. FCT PEst-C/CTM/LA0011/2013). This work has also been partially financed by the Catalan government (project 2014SGR1582), and from Carburos Metálicos, Air Products Group.
soft-SAFT EoS for the vapor-liquid equilibria and water activities of aqueous ionic liquids

Mariana B. Oliveira¹, André Palma¹, Emanuel Crespo¹, Felix Llovell², Lourdes F. Vega²,³, João A. P. Coutinho¹

¹ CICECO, Chemistry Department, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal, ² MATGAS Research Center, Campus de la UAB, 09193 Bellaterra, Barcelona, ³ Carburos Metálicos/Air Products Group, C/Aragón 300, 08009 Barcelona

jcoutinho@ua.pt

Keywords: soft-SAFT, VLE, Water, Ionic liquids

The unique physical properties of ionic liquids (ILs) make them valuable alternatives to traditional compounds for different applications. Aqueous ILs systems are of particular interest for different applications such as in absorption refrigeration and in separation and purification processes through the use of aqueous biphasic systems [1]. The precise description of thermodynamic properties and phase equilibria of aqueous ionic liquid solutions is fundamental for a correct design and application of these processes. In this work, the soft-SAFT equation of state (EoS) [2], a successful approach able to accurately describe the thermophysical properties and phase behavior of ILs and their mixtures, will be used to describe water activities and the vapor-liquid equilibrium (VLE) of a wide range of water + IL systems covering different families of ILs. The correct description of these properties provides new insights about aqueous ILs ideal behavior and solute-solvent interactions, and allows further model application to predict the behavior of other aqueous ILs. The information obtained will be used to discriminate among different sets of molecular soft-SART parameters for the ILs which have never been modeled using soft-SAFT.

References

Acknowledgements
M.B. Oliveira acknowledges for her Post-Doctoral grant (SFRH/BPD/71200/2010) and F. Llovell for a TALENT contract from the Catalan Government and MATGAS. This work is financed by FEDER funds through Programa Operacional Factores de Competitividade – COMPETE and by Nacionais funds through FCT – Fundação para a Ciência e Tecnologia through project CICECO - FCOMP-01-0124-FEDER-037271 (Refª. FCT PEst-C/CTM/LA0011/2013). This work has also been partially financed by the Catalan government (project 2014SGR1582), and from Carburos Metálicos, Air Products Group.
Semiclassical DFT-SAFT approach to model confined quantum fluids

Susana Figueroa-Gerstenmaier\textsuperscript{1}, José R. Pérez-Mendoza\textsuperscript{1} and Alejandro Gil-Villegas\textsuperscript{1}

\textsuperscript{1}Sciences and Engineering Division, University of Guanajuato, León, México.

Corresponding author e-mail: sfigueroa@fisica.ugto.mx

1. Introduction
Structural and thermodynamic properties of confined quantum fluids have been modelled using the Statistical Associating Fluid Theory (SAFT) and a Fundamental Measure Density Functional Theory [1], based on a semiclassical approach for fluids like molecular hydrogen [2,3]. Results are compared with computer simulations for a first-order Wigner effective potential [4].

2. SAFT-DFT Semiclassical Theory
The thermodynamic and structural properties of inhomogeneous quantum fluids has been used to describe the adsorption of Lennard-Jones particles in cylindrical pores using the Fundamental Measure Density Functional Theory [1], introducing quantum effects via a first-order Wigner effective potential [4]. The effect of the pore size in the adsorption isotherms is studied as a function of the de Broglie thermal wave-length. Results are compared with Monte Carlo simulations for classical and quantum fluids. This study complements a previous thermodynamic approach that has been applied for the adsorption of molecular hydrogen onto different substrates, including graphene [3].

3. Conclusion
The theory presented can be used to predict adsorption isotherms of confined quantum fluids in a semiclassical regime, determining specific information like the role of the de Broglie wave-length versus pore-size, in order to assess the importance of introducing a quantum description in SAFT-DFT-like approaches.

References
Coexistence of polymer-colloid mixtures under slit confinement

Susana Figueroa-Gerstenmaier1, Arturo Moncho-Jordá2, Gerardo Odriozola3

1Departamento de Ingenierías Química, Electrónica y Biomédica, División de Ciencias e Ingenierías, Universidad de Guanajuato, Campus León, Loma del Bosque 103, 37150, León Gto., Mexico, 2Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Granada, Campus Fuente-Nueva S/N, 18071, Granada, Spain, 3Instituto Mexicano del Petróleo, Eje Central Lázaro-Cárdenas 152, 07730 México, DF, Mexico.

Corresponding author e-mail: godriozo@imp.mx

1. Introduction

Depletion forces are frequently involved in the physics of colloidal systems [1, 2]. The depletion effect pushes colloidal particles into contact and, for sufficiently large polymer coil concentrations, yields phase separation of colloids into a concentrated liquid-like phase and a diluted vapor-like phase. Due to the fact that the effective attraction of the colloidal particles increases with the polymer coil density, the liquid-like colloidal phase turns denser meanwhile the vapor becomes sparser. Conversely, density differences between the liquid-like and vapor-like phases tend to vanish when the polymer concentration is decreased. The coexistence ends at a critical polymer density below which a single homogeneous phase is found. Therefore, the polymer density plays the role of the inverse of temperature for a typical one-component liquid-vapor coexistence. It is thus interesting to find out how this coexistence is affected by confinement. Confinement can strongly affect phase diagrams [3].

In this work we are using the so called Asakura-Oosawa model [5], where polymers can interpenetrate each other but they cannot overlap with the colloidal particles, to study the coexistence behaviour of a mixture of colloids and polymer coils under confinement. This is done as a function of the colloid-polymer coil relative size, confinement strength, and wall-colloid/wall-polymer interactions.
2. Simulation methods

We carried out molecular dynamics simulations using the Gromacs package [6]. We have considered a NPT system (using a velocity rescale algorithm as thermostat) containing both, the vapor and liquid phases. The system contains a couple of vapor-liquid interfaces making possible their characterization. A large box side is used for the direction perpendicular to the interfaces to get fully developed bulk properties on the vapor and the liquid phases. This implementation allows accessing the structure of the menisci. The diameter of the colloidal particle is $\sigma_c$ and the diameter of the polymer coil is $\sigma_p$. A system snapshot having slit geometry with a wall-wall separation of $10\sigma_c$, $\sigma_c = \sigma_p$, and densities large enough to produce phase separation (for both colloidal and polymer particles) is shown in figure 1 a). Panels b) and c) show the system structure as density maps. Colloidal layer next to the wall extends from the liquid phase towards the vapor promoting the formation of menisci, which structures, at the mesoscopic level, are not smooth but show layering. Note also that in the liquid phase the few polymers coils are surrounded by colloidal particles and their behavior turn colloid-like. Conversely, in the polymer rich phase colloids are mostly attached to the walls and polymers are depleted from them. From the maps, both, colloid and polymer densities at bulk can be obtained. Capillarity effects such as condensation and evaporation can be studied from this implementations when implementing an insertion method for determining polymer and colloid chemical potential.

3. Conclusion

The coexistence properties and the fluid structure of a mixture of colloids and polymer coils under slit confinement has been studied by means of molecular dynamic simulations by making use of the Asakura-Oosawa model. Results are related with capillarity phenomena such as condensation and evaporation, depending on the wall-species forces.

References

Interaction studies of methyl acetate in aqueous solutions of quinoxaline derivatives: effect of temperature and concentration

Gnanapragasam Raphael, Indra Bahadur, Eno E. Ebenso

Department of Chemistry, School of Mathematical and Physical Sciences, Materials Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

Corresponding Authors e-mail: bahadur.indra@gmail.com (I. Bahadur)

Keywords: Quinoxaline, Methyl acetate, Apparent molar volume, Apparent molar adiabatic compressibility, Redlich-Mayer type equation.

The aim of the present work, to examine the effect of temperature and concentration on interactions of methyl acetate with aqueous solutions of quinoxaline derivatives using volumetric and acoustic properties. In addition to this, the density, \( d \), and sound velocity, \( u \), of methyl acetate in aqueous solutions of quinoxaline derivatives namely: (N-{-3-[1-methanesulfonyl-5-(quinoxalin-6-y1)-4,5-dihydropyrazol-3-yl] phenyl} methane sulfonamide [MQDPMS], N-{-2-[1-acetyl-5-(quinoxalin-5-y1)-4, 5-dihydropyrazol-3-yl] phenyl} methane sulfonamide [AQDPMS], N-{-2-[1-propanoyl-5-(quinoxalin-6-y1)-4,5-dihydro-1H-pyrazol-3-yl] phenyl} methane sulfonamide [2PQDPMS] and N-{-3-[1-propanoyl-5-(quinoxalin-6-y1)-4,5-dihydro-1H-pyrazol-3-yl] phenyl} methane sulfonamide [3PQDPMS] have been measured at (293.15, 298.15, 303.15 and 308.15) K and at pressure \( p = 0.1 \) MPa. These data have been used to calculate the derived properties such as apparent molar volume, \( \phi V \), and apparent molar adiabatic compressibility, \( \phi k \), for the mixtures. The standard partial molar volume, \( \nu^0 \), standard partial molar volume of transfer, \( \Delta \nu^0 \), standard partial molar adiabatic compressibility, \( k^0 \), and standard partial molar adiabatic compressibility of transfer, \( k^0 \), have been evaluated using Redlich-Mayer type equation. These results have been interpreted in terms of effect of temperature and concentration on interactions such as solute-solute, solute-solvent and solvent-solvent which exist in the mixtures. Furthermore, apparent molar expansivity, \( E^0 \), and Hepler’s constant values, \( \partial^2 \nu^0 / \partial T^2 \), have been evaluated to support the conclusions obtained from the volumetric and acoustic studies.
Screening of environmental friendly ionic liquid as a solvent for the different types of separations problem: insight from activity coefficients at infinite dilution measurement using gas-liquid chromatography technique

Indra Bahadur*, b, Muven Naidooa, Pratheka Naidooa, Samir Ramdatha, Deresh Ramjugernatha,*,
Eno E. Ebenson

aThermodynamics Research Unit, School of Chemical Engineering, University of KwaZulu-Natal,
Howard College Campus, King George V Avenue, Durban, 4041, South Africa
bDepartment of Chemistry, School of Mathematical and Physical Sciences, Materials Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

Corresponding author e-mail: bahadur.indra@gmail.com; (I. Bahadur);

Keywords: Activity coefficient at infinite dilution; 1–Ethyl–3–methylimidazolium n-octylsulphate;
Gas–liquid chromatography; Separation, Selectivity.

This work was focussed on screening the environmental friendly imidazolium-based ionic liquid for the (alkane/aromatic), (alkane/alk-1-ene), (cycloalkane/aromatic) and (water/alkan-1-ol) separations using gas-liquid chromatography (GLC) technique. In this regard the activity coefficients at infinite dilution, \( \gamma_{13}^\infty \), for 29 organic solutes (alkanes, cycloalkanes, alkenes, alkynes, aromatics, alkanols and ketones) and water were measured at temperatures of \((318.15, 333.15, 348.15 \text{ and } 358.15) \text{ K}\) in the ionic liquid 1–ethyl–3–methylimidazolium n-octylsulphate \([\text{EMIM}]^{+}[\text{OS}]^{-}\). Stationary phase loadings of \((23.77 \text{ and } 40.76) \% \text{ by mass}\) were used to ensure repeatability of measurements. Uncertainties were determined using the law of propagation of uncertainty with an average absolute deviation of 2.53 %. Density, viscosity and refractive index values have also been measured for the pure IL to confirm the purity. Partial molar excess enthalpies at infinite dilution, \(\Delta H_{13}^{\infty}\), were also determined. Selectivities, \(S_{ij}^{\infty}\), and capacities, \(k_{ij}^{\infty}\), were determined for the (alkane/aromatic), (alkane/alk-1-ene), (cycloalkane/aromatic) and (water/alkan-1-ol) separations. The separating ability of the investigated ionic liquid was compared against previously investigated and industrial solvents such as sulfolane, n-methyl-2-pyrroldidine (NMP) and n-formylmorpholine (NFM).
Thermodynamic study of aqueous mixtures of 3-Butoxypropan-1-amine

Ángela F. S. Santos¹, Maria Luisa C. J. Moita², Luis C. S. Nobre¹ and Isabel M. S. Lampreia¹

¹Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, ²Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa

Corresponding author e-mail: afsantos@fc.ul.pt

1. Introduction

Alkoxyamines are versatile compounds with great affinity for water since they have in their structure the alkoxy and amine functional groups. They have been used in industry for the immobilization of various compounds such as biomolecules by means of condensation reactions with aldehydes or ketones forming oxime bonds, which increase their stability [1]. Additionally, the strong electron-donor functional groups of alkoxyamines have been largely used in polymer chemistry to produce sequence-controlled polymerization and cyclization reactions [2]. As far as we know only three volumetric studies, two of them carried out in our laboratory, are reported in the literature concerning aqueous mixtures of these compounds [3-5]. Pursuing our volumetric studies dedicated to improve our comprehension embracing molecular interactions in binary systems water + amphiphilic molecules in this work we measured density, \( \rho \), and sound speed, \( u \), in aqueous mixtures of 3-butoxypropan-1-amine (BPA), spanning the temperature range (283.15 to 303.15) K and over the entire composition range. These studies are undertaken in order to study the influence of structure, chain length and type of hydrophilic groups on the aggregation and hydration schemes. A comparison of the present results with those obtained for the system water + 3-ethoxypropan-1-amine (EPA) is made addressing the changes produced by the hydrophobic characteristics of the molecules.

2. Results and derived quantities

Based on the measured \( \rho \) and \( u \) values derived properties such as excess molar, volumes and isentropic compressions and excess apparent and partial, molar volumes and isentropic compressions were derived. Negative values were obtained for the two first excess molar properties as well as for the excess partial molar properties of the two components and interpreted in terms of hydration and changes in aggregation patterns, across the whole composition and temperature ranges. Comparison of the temperature dependence of limiting excess partial molar volumes and isentropic compressions with that obtained for the system water(1) + EPA(2) is shown in the following figure as an example.

\[ V_2^{E_{\infty}} : \cdot, \text{water}(1) + \text{BPA}(2); \circ, \text{water}(1) + \text{EPA}(2). \quad K_{S,2}^{E_{\infty}} : \square, \text{water}(1) + \text{BPA}(2); \Box, \text{water}(1) + \text{EPA}(2) \]
3. Conclusion
The profile of the curves of partial molar properties, which entails first order derivatives of the molar volumes and molar isentropic compressions, shows at least three different regimes of molecular aggregation.

Comparing the behaviour of the two aqueous systems: BPA + water and EPA + water we conclude that while BPA seems to behave as a structure making compound when infinitely diluted in water, EPA seems to act as a structure breaking.

References
Thermodynamic study on CO₂ separation with a novel ionic liquid

Yujiao Xie¹, Dilip Raut², Jyri-Pekka Mikkola²,3, Xiaoyan Ji¹

¹Division of Energy Science, Luleå University of Technology, 97187 Luleå, Sweden, ²Chemical-Biological Centre, Technical Chemical, Department of Chemistry, Umeå University, Umeå, Sweden, ³Process Chemistry Centre, Laboratory of Industrial, Chemistry and Reaction Engineering, Åbo Akademi University, 20500, Turku/Åbo, Finland

Corresponding author e-mail: yujiao.xie@ltu.se

1. Introduction

CO₂ separation plays an important role in the development of renewable energy and mitigating of environmental effects [1]. Ionic Liquid (ILs) has shown great potential to be used as liquid absorbents for CO₂ separation due to its advantages of non-volatility, environment-benign and functionality. The research work on conventional ILs is intensive, but most of the cases for CO₂ are physical absorption with a relative low CO₂ absorption capacity at low pressure. Recently, chemical absorption based on the utilization of ILs have been developed to enhance the CO₂ absorption capacity [2], albeit the research is still in its infancy.

2. Research work

Fukaya et al. [3] reported that 1-allyl-3-methylimidazolium formate ([Amim][HCO₂]) exhibited higher solubility for various polysaccharides because of the strong hydrogen bond ability. In this work, the CO₂ solubility in [Amim][HCO₂] was determined at temperatures from 298.15 to 333.15 K and at pressures up to 2 MPa. The measured experimental data was represented by thermodynamic model. The energy consumption for CO₂ separation was calculated and compared with the conventional ILs.

3. Conclusion

It is expected that this novel IL could potentially be of interest for industrial applications in CO₂ separation processes.

References

Tetrahedra volume distributions in Lennard-Jones fluids

M. Valdez-Gonzalez and M. Robles


Corresponding author e-mail: mrp@ier.unam.mx

In this work we present results on a geometrical study of a Lennard-Jones fluid. Using three dimensional molecular dynamics simulations, we obtained stable thermodynamic states in different known phases and applied Delaunay tetrahedralizations to their molecular positions. The statistical properties for the tetrahedral volumes were obtained with the aim of compare, specially, the statistical and the thermodynamic entropy. In addition, we also examined the time evolution for the obtained distributions when the system evolves from one thermodynamic state to another. The final aim is to find new out of equilibrium relations and new analysis methods in the study of phase transitions.
Equation of state and phase diagram of double Yukawa fluids

J. Montes, M. Robles and M. López de Haro

Instituto de Energías Renovables. Universidad Nacional Autónoma de México. Priv. Xochicalco S/N
Col. Centro, 62580 Morelos, México.

Corresponding author e-mail: mjp@ier.unam.mx

In this work we present a theoretical study on the equation of state for double Yukawa fluids. We use a perturbation framework with the hard-sphere fluid as the reference system. The introduction of a rational function approximation for the Laplace transform of the radial distribution function for the hard-sphere fluid, allows us, to first order, to derive an analytical equation of state, from which the phase diagram are obtained. The results are compared with simulation and with other approaches. The analytical expressions obtained may be relevant in the development of theories for more realistic potentials.
Surface Tension and Dielectric Permittivity of Water at the Graphitic Interfaces

Aziz Ghoufi1, Anthony Szymczyk2, R. Renou1,2, Patrice Malfreyt3

1Institut de Physique de Rennes, CNRS, UMR 6251, Université de Rennes 1, Rennes, France 2Institut des Sciences Chimiques de Rennes, CNRS, UMR 6226, Université de Rennes 1, Rennes, France 3Institut de Chimie de Clermont-Ferrand, ICCF, UMR CNRS 6296, Clermont-Ferrand, France

Corresponding author e-mail: aziz.ghoufi@univ-rennes1.fr

This work focuses on the exploration structure-dynamics relationship for water and ions transport through the graphitic membranes such as graphene and graphyne nanopores. The objective is to gain a fundamental understanding of the nanoscopic mechanisms of ions and water transport through the graphene and graphyne nanosheets (Figure 1) for the desalination water application. Indeed, the graphitic materials can be considered as a model platform to rationalize the solid-fluid interactions. Among the physical properties impacting the water transport across a membrane, the surface tension ($\gamma$) and the dielectric permittivity ($\varepsilon$) are probably the most important. In this work we predicted the surface tension and the dielectric properties of water close to the graphitic surfaces (graphene, nanoporous graphene, graphyne and boron nitride) and we provided a microscopic standpoint to understand the differences in $\varepsilon$ and $\gamma$ between different materials.
Experimental and quantum chemical studies of the inhibition of copper with Sodium Dodecyl Sulphate (SDS) in acid medium

Nkiko, Mojisola O. 1,2, Oluwabi, Abayomi 2, Ahmed, Sikiru Akinseye 3

1Department of Physical and Chemical Sciences, Elizade University, P. M. B. 002, Ilara – Mokin, Ondo State. Nigeria, 2Department of Chemistry, Federal University of Agriculture, Abeokuta, P.M.B 2240, Abeokuta. Nigeria, 3Ondo State University of Science and Technology, Okitipupa, Ondo State, Nigeria

* Corresponding author email: chrismoj3@yahoo.co.uk

Keywords: corrosion inhibition, copper, gasometric methods, adsorption, inhibition efficiency, sodium dodecyl sulphate

The inhibitive effect of sodium dodecyl sulphate (SDS) on the corrosion of copper (Cu) in nitric acid solution has been studied using gasometric methods. Inhibition efficiency increases with time and concentration of SDS. Corrosion rate of copper decreases as concentration of SDS increases. Adsorption of the SDS on the surface obeyed the Freudlich adsorption isotherm. The high negative values of the kinetic parameter B suggest that the inhibitor’s effectiveness will increase with temperature. The equilibrium constant of and the free energy of adsorption of SDS to copper is and large. This observation implies that the adsorption mechanism may be chemisorption. The quantum chemical calculation of copper dodecyl sulphate shows that the energy change in the HOMO – LUMO energy of the moiety is positive and small. This observation implies that the SDS is an efficient inhibitor. The high dipole moment obtained implies that corrosion inhibition of Cu is enhanced by adsorption of SDS and this is observed to correlate with the observed experimental inhibition efficiency.

The Brinell hardness test which is a measure of the tensile strength shows that SDS provides protection for Cu in acid solutions.
Liquid – Liquid Phase Behavior of Solutions of 1,3-diethylimidazolium bis(trifluoromethylsulfonyl)imide in n-Alkyl Alcohols

Marisa A. A. Rocha¹, Wolffram Schröer², Bernd Rathke¹

¹Technische Thermodynamik, Universität Bremen, Badgasteiner Str. 1, D-28359 Bremen, Germany, ²Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Str. NW II, D-28359 Bremen, Germany

Corresponding author: Marisa A. A. Rocha, mrocha@uni-bremen.de

In this work, the liquid-liquid phase diagrams of binary mixtures of the 1,3-diethylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid ([C₂C₂im][NTf₂]) with n-alkyl alcohols (propan-1-ol, butan-1-ol, hexan-1-ol, and octan-1-ol), are presented. The phase diagrams were determined at atmospheric pressure and over a temperature range of (258 – 386) K. Partial miscibility with an upper critical solution temperature (UCST) between (284 – 386) K, was observed for the studied systems. It was found a decrease in the alkyl chain of the alcohols leads to a decrease in the UCST.

The symmetry effect is explored, based on the comparison with the asymmetric 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid ([C₃C₁im][NTf₂]) [1]. Additionally, the influence of the chain length of the alcohol on the shape and location of the phase diagram is assessed.

References
Thermodynamic properties of mixed solvent electrolyte solutions from the SAFT-VR+DE equation of state

Gaurav Das¹, Stepan Hlushak¹, M. Carolina dos Ramos¹ and Clare McCabe¹,²

¹Department of Chemical and Biomolecular Engineering and ²Department of Chemistry, Vanderbilt University, Nashville, TN 37235

A number of SAFT based approaches have been developed for the study of electrolyte solutions. Typically, these are based on the so-called primitive model, which describes ions in a dielectric continuum. Recently, the statistical associating fluid theory for potentials of variable range (SAFT-VR) approach was combined with the mean spherical approximation for the non-primitive model of electrolytes.² Here the ions are described in an explicit dipolar solvent, enabling long-range ion-ion, ion-dipole, and dipole-dipole interactions to be explicitly considered. The resulting theoretical framework, termed SAFT-VR+DE was validated against computer simulations results of model electrolyte solutions at different ion concentrations and different ratios of the cation, anion, and solvent segment diameters.² Through comparisons with other commonly used approaches to incorporate electrostatic interactions (i.e., Debye-Huckel theory and the primitive model), the importance of properly accounting for the difference in size between the ions and solvent and an accurate description of the dielectric constant was demonstrated. By using the non-primitive model in the SAFT-VR+DE approach we avoid the need to provide input values for the dielectric constant, either by finding experimental data or developing correlations for mixed solvent electrolyte systems.

Once the SAFT-VR+DE approach was validated against simulation data, it was been applied to describe experimental 1:1 aqueous electrolyte solutions. Both fully dissociated and partially dissociated models, depending upon the concentration range, were considered in order to capture ion association at high salt concentrations. Salt specific binary interaction parameters between the cations and water solvent were obtained by fitting to experimental mean ionic activity coefficient data. Using a single fitted parameter for most salt systems studied, SAFT-VR+DE was found to predict thermodynamic properties such as osmotic coefficient, water activity coefficient, solution density, Gibbs free energy of hydration and dielectric constant across different salt concentrations and temperatures in good agreement with experiment. The approach has also be applied to study mixed solvent electrolyte solutions, in the first such application of the non primitive model. The thermodynamic properties of model mixed solvent electrolytes as well as water-alcohol-salt systems were studied. An accurate description of the effect of ion concentration on the dielectric constant was found to be important for obtaining accurate predictions, further supporting the importance of a theory in which an accurate dielectric constant can be calculated in contrast to widely used primitive model approaches that rely on empirical models for the calculation of the dielectric constant.

References
**ppT behaviour of three branched ethers: experimental results and SAFT modeling**

*Victor Antón, Carlos Lafuente, Héctor Artigas, Félix M. Royo*

Depto. Química Física, Fac. Ciencias, Universidad de Zaragoza, 50009 Zaragoza (Spain)

Corresponding author e-mail: celadi@unizar.es

**Keywords:** Branched ethers; prT behavior, pc-SAFT.

Densities, $\rho$, over a temperature range from 283.15 to 333.15 K (steps of 5 K) and a pressure range from 0.1 to 65.0 MPa (steps of 50 MPa) of three branched ethers (diisopropyl ether, methyl tert-butyl ether and ethyl tert-butyl ether) have been measured using a high-pressure, high-temperature vibrating tube Anton Paar DMA HP cell connected to an evaluation unit Anton Paar DMA5000.

These densities have been correlated with temperature and pressure using the TRIDEN equation [1] that combines the Tait equation [2] for isothermal compressed densities with a modified Rackett equation [3,4] for the liquid saturation densities:

$$\rho_0 = \frac{A_R}{B_D^{1 + \alpha_2 C_R \rho_R}}$$

(1)

$$\rho = \frac{\rho_0}{1 - C_T \ln \left( \frac{B_T \rho}{B_T \rho_R} \right)}$$

(2)

$$B_T = b_0 + b_1 \left( \frac{T}{E_T} \right) + b_2 \left( \frac{T}{E_T} \right)^2 + b_3 \left( \frac{T}{E_T} \right)^3$$

(3)

Using this equation some derived properties have been also obtained: isobaric thermal expansion, $\alpha_p$, and isothermal compressibility, $\kappa_T$.

![Figure 1. Experimental and correlated densities, $\rho$, for diisopropyl ether, calculated isobaric thermal expansions, $\alpha_p$, for methyl tert-butyl ether and isothermal compressibility, $\kappa_T$, for ethyl tert-butyl ether.](image)

In addition the experimental densities together with vapour pressures obtained from the literature have been employed to estimate the pc-SAFT model parameters [5,6] for the studied ethers.

**Acknowledgement**

The authors are grateful for financial assistance from Diputación General de Aragón and Ministerio de Economía y Competitividad (CTQ2013-44867-P).
Molecular Simulation Study of the CO$_2$-N$_2$O Analogy

Maximilian Kohns, Erik von Harbou, Martin Horsch, Hans Hasse

Laboratory of Engineering Thermodynamics (LTD), University of Kaiserslautern, Germany

Corresponding author e-mail: maximilian.kohns@mv.uni-kl.de

Reactive absorption of CO$_2$ is an important technological process. In modeling that process, the physical solubility of CO$_2$ is a key property. However, in many cases that solubility is difficult or impossible to determine experimentally as physical and chemical effects, which occur simultaneously, cannot be separated. The resulting lack of data on the physical solubility of CO$_2$ is a serious drawback for developing sound models for reactive absorption processes. A common strategy to circumvent that problem is using the so-called CO$_2$-N$_2$O analogy. N$_2$O and CO$_2$ have similar thermodynamic pure component properties, but N$_2$O does not react with the industrially relevant solvents with which CO$_2$ reacts. Hence, the physical solubility of N$_2$O in these solvents can be determined. The CO$_2$-N$_2$O analogy in its most common form says that the ratio of the physical solubilities of N$_2$O and CO$_2$ in some solvent of interest is the same as that in pure water. The analogy is just a work-around that has proved to be useful in many cases but has no strong theoretical background.

In the present work, we have therefore studied the physical basis of the CO$_2$-N$_2$O analogy by molecular simulation. Henry's law constants of CO$_2$ and N$_2$O are determined for the solvents water, methanol, and ethanol in a wide temperature range. Additionally, mixed solvents are considered. Molecular models for the solvents [1-4] and CO$_2$ [5,6] are taken from the literature. Both for CO$_2$ and N$_2$O, models of two different classes are used: a two-site and a three-site Lennard-Jones model with a superimposed point quadrupole. The N$_2$O models were developed in the present study to enable a direct comparison with the corresponding CO$_2$ models. The model parameters are determined by fitting to the saturated liquid density, the vapor pressure, and the enthalpy of vaporization. The employed optimization strategies include a Pareto approach [7]. For the investigated solvents, the CO$_2$-N$_2$O analogy is only partly confirmed.

References

Liquid-liquid equilibrium of mixtures containing microalgae oil, its ethylic biodiesel, ethanol and glycerol at 298.15 K, 313.15 K and 328.15 K

Fabio R. M. Batista¹, K.W. Lucchesi¹, Antonio J. A. Meirelles¹

¹University of Campinas, School of Food Engineering, Campinas, São Paulo - Brazil

Corresponding author e-mail: f.fabio.batista@gmail.com

Keywords: microalgae, nrtl, biodiesel, uniquac, modeling

1. Introduction

Aiming to minimize the effects of a possible conflict “biofuel vs food”, particular emphasis has been accorded to biodiesel production from microalgae since these microorganisms can develop quickly in fresh or salt water, without using arable land, have a high potential to oil production and are able to produce a high amount of bioproducts with high economic value as polyunsaturated fatty acid, proteins, pigments, carbohydrates among other¹.

Biodiesel is produced through transesterification reaction, that is composed of a set of three reversible reactions in which the triglyceride (vegetable oil) is converted into biodiesel in the presence of a reagent alcohol (methanol or ethanol) and a catalyst, forming glycerol as byproduct. The partial miscibility of the reaction components makes this process is conducted in a biphasic environment where coexist an alcoholic phase and an oil phase. Thus, the study of the reaction components distribution in both phases is important for the optimization of biodiesel production process with consequent increase in productivity.

2. Methodology and results

This work studied the liquid-liquid equilibrium of the systems microalgae ethylic biodiesel + ethanol + glycerol (system 1) and microalgae ethylic biodiesel + ethanol + microalgae oil (system 2) at different temperatures (298.15 K, 313.15K and 328.15 K). The study of these equilibrium are important to improve the biodiesel purification and reaction. A donation of microalgae oil of specie chlorella protothecoides was obtained from SOLEY INSTITUTE. Ethylic biodiesel was produced by homogeneous catalysis. Liquid-liquid equilibrium data were determined² and modelled taking into account the thermodynamic models NRTL and UNIQUAC. Fig. 1 and Fig 2 show the equilibrium for system 1 at 313.15 K and system 2 at 298.15 K.

Fig.1 - Liquid-liquid equilibrium of system 1 at 313.15 K
3. Conclusion

High amounts of ethanol in the system hamper the biodiesel purification steps due to the solubility increase of biodiesel on glycerol in the presence of ethanol (System 1). On the other hand, the decrease of ethanol concentration during the reaction can reduce the biphasic region impairing the reaction efficiency (system 2). This justifies the need for an excess of alcohol during the reaction. However, this excess should be balanced to avoid difficulties in the purification process. Regarding modelling, NRTL model showed to be more appropriate in the equilibrium description since their average deviations were lower than the UNIQUAC model.

References

Evaluation of the solubility of Paraffins in Circular Pipes by Simulation

Oliveira, E.C.L.; Neto, E.L.B.; Pereira, C.G.

Department of Chemical Engineering, Federal University of Rio Grande do Norte Av. Senador Salgado Filho, CEP 59072-970, Natal - RN, Brazil

Corresponding author e-mail: camila@eq.ufrn.br

1. Introduction

Oil is one of the most important sources of energy in maintaining global energy matrix. The new oil fields are producing increasingly heavier petroleum and, consequently, with high viscosity values. However, the paraffin deposition on the inner walls of the production lines and transportation is one of the most critical issues for the industry, especially in deep water. During the flow of crude oil, paraffin is deposited as crystals on the inner wall of the pipe; and over time, tends to drastically reduce the cross-sectional area of the flow, reaching the total blockade of the pipeline. In this context, the objective of this work was to develop a simulator with a graphic interface to evaluate the solubilization of paraffin process in pipelines and to evaluate the effect of diameter of pipe, time of pumping, and the pipe wall external temperature on solubilization. The profiles of mass of adhered paraffin and external temperature of pipe wall were also evaluated. Mathematical models [1-3] based on the phenomena involved in the solubilization of paraffin process (mass transfer phenomenon and solid-liquid equilibrium) were implemented using VBA for Excel®. Experimental data from literature [4] were used to compare and validate the procedure used. The graphical environment was developed using Matlab®.

2. Results and Discussion

Figure 1 shows the effect of diameter of pipe in the solubilization of paraffin. It can be verified that the smaller diameter pipe (2 in) promoted higher solubilization. It was expected the opposite, because of the higher superficial area presented by larger diameter pipe (4 in). However, this phenomenon can be explained, when analyzing the input flow. As the solvent flow rate in both cases was the same, the velocity in the pipe of smaller diameter (2 in) is much greater than in the process occurring in the larger diameter pipe (4 in), thereby providing a more efficient solubilization. As a result, the thickness wax decreased for the process that used the smaller diameter pipe (Figure 1a).

Figure 2 presents the temperature profile of the solvent in the solubilization of paraffin flowing in a pipe of 2 and 4 in of diameter. Figure 3 shows the effect of the external temperature of the pipe wall on the solubilization of paraffin.
It can be observed in Figure 2 that the temperature of the solvent decreased with increasing length of pipe in both conditions. However, the time of the process was less significant when a pipe with larger diameter was used. It happened because of lower solubilization of paraffin in the pipe of larger diameter. The paraffin not solubilized was adhered in the pipe wall and this promoted an increase in thermal insulation, preventing heat loss to the environment, even when higher processing time was applied.

Figure 2: Profile of the temperature in the paraffin solubilization in a pipe with 10 m of length and diameter of (a) 2 in SCH 40 and (b) 4 in SCH 40, considering different operation time (min).

According to Figure 3, the process occurring at higher external temperature (310.15 K) had higher solubilization of the paraffin (observed in Figure 3b by lower amount of adhered paraffin, i.e, lower thickness wax in the wall of pipe). This occurred due to the lower thermal exchange between the solvent (318 K) and the external ambient. At higher temperature of solvent, higher was the equilibrium concentration, and then higher was the solubilization of paraffin.

3. Conclusion
The mathematical models and calculation routines used in the present study were validated, allowing predictive assessment of the paraffin solubilization process. The simulator allowed to observe the profile of temperature and concentration of adhered paraffin through the pipe at different positions (axial and radial) along time. The results of simulation demonstrated that as higher the diameter of pipe, higher time is required in the solubilization process. In relation to the pipe wall external temperature, higher temperature, the greater is the amount of solubilized paraffin.
The paraffin not solubilized was adhered in the pipe wall and this promoted an increase in thermal insulation, preventing heat loss to the environment, even when higher processing time was applied.

According to Figure 3, the process occurring at higher external temperature (310.15 K) had higher solubilization of the paraffin (observed in Figure 3b by lower amount of adhered paraffin, i.e., lower thickness wax in the wall of pipe). This occurred due to the lower thermal exchange between the solvent (318 K) and the external ambient. At higher temperature of solvent, higher was the equilibrium concentration, and then higher was the solubilization of paraffin.

3. Conclusion

The mathematical models and calculation routines used in the present study were validated, allowing predictive assessment of the paraffin solubilization process. The simulator allowed to observe the profile of temperature and concentration of adhered paraffin through the pipe at different positions (axial and radial) along time. The results of simulation demonstrated that as higher the diameter of pipe, higher time is required in the solubilization process. In relation to the pipe wall external temperature, higher temperature, the greater is the amount of solubilized paraffin.

References

Vapor-liquid equilibria for pseudo-binary systems containing refined vegetable oil (cottonseed and soybean oils) and solvent (n-hexane and ethanol) at low pressures

Patrícia C. Belting¹, Iêda L. M. Silva², Adolfo L. Figueredo², Osvaldo Chiavone-Filho², Camila G. Pereira², Roberta Ceriani³, Antonio J. A. Meirelles¹

¹Food Engineering Department, Faculty of Food Engineering, University of Campinas, Av. Monteiro Lobato 80, Cidade Universitária Zeferino Vaz, 13083-862, Campinas-SP, Brazil, ²Chemical Engineering Department, Federal University of Rio Grande do Norte, Av. Senador Salgado Filho 3000, 59066-800, Natal-RN, Brazil, ³Faculty of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, Cidade Universitária Zeferino Vaz, 13083-852, Campinas-SP, Brazil

Corresponding author e-mail: camila@eq.ufrn.br

1. Introduction

The search for an alternative fuel to petroleum and can supply the market, makes biodiesel a product of interest to be considered clean and renewable fuel. The transesterification of vegetable oils is the most used method to produce biodiesel. In this context, the knowledge of the phase equilibrium of the involved systems is fundamental in the separation step. The objective of this work was to determine vapor-liquid equilibrium (VLE) data for systems of interest in vegetable oil industry and biofuel production. The following systems were investigated: refined cottonseed oil + n-hexane at 41.3 kPa and refined soybean oil + ethanol at 101.3 kPa. The binary system oleic acid + ethanol at 101.3 kPa was also studied experimentally. VLE measurements were performed using a modified Othmer-type ebuliometer. The apparatus promotes only the recirculation of the condensed vapor phase, allowing its use for more viscous species. An oscillating tube densimeter was applied to determine the concentrations of the liquid and vapor phases. The excess volume behavior was also determined on the basis of density-composition calibration curve. Complete VLE data (TPxy) were properly correlated using UNIQUAC model. Average global deviations to respect to temperature and pressure were less than 1% and thermodynamic consistency tests of these data were checked using a maximum likelihood data reduction. The experimental data were compared with the predicted results using UNIFAC group contribution method, with the pseudo-binary mixture assumption.

2. Results and Discussion

Figure 1 presents the experimental data for the systems cottonseed oil + n-hexane at 41.3 kPa and refined soybean oil + ethanol at 101.3 kPa with the correlation using UNIQUAC equation [1]. The results obtained for the system cottonseed oil + n-hexane showed good agreement with available data [2]. It is noteworthy that the calculations were performed considering these systems as pseudo-binary. Thus, the vegetable oils were treated as a single triacylglycerol with the same unsaturation degree, number of carbon and average molar mass of the original vegetable oil composition. For this reason, the average molar masses of the vegetable oils were calculated using the respective fatty acid compositions, considering that all fatty acids present in the vegetable oil are esterified to glycerol molecules to form triacylglycerols. Due to the molecular mass difference, mass fraction scale has been used for the data representation and correlation.

Table 1 presents mean deviations of UNIQUAC model for the studied systems. Figure 2 shows the experimental data of VLE for the system oleic acid + ethanol at 101.3 kPa. It is noteworthy that the excess volume of the studied mixtures was also described with density-composition curves. Cottonseed oil + n-hexane presented negative excess volumes and oleic acid + ethanol showed positive values.
Figure 1: Experimental and correlated VLE data for the systems: (a) cottonseed oil + n-hexane at 41.3 kPa, (b) refined soybean oil + ethanol at 101.3 kPa; concentrations are in mass fraction.

Table 1: Mean deviations of the VLE correlation results of the studied systems using UNIQUAC

<table>
<thead>
<tr>
<th>System</th>
<th>$T$ (K)</th>
<th>$P$ (kPa)</th>
<th>$\text{AAD}^a$ ($x$)</th>
<th>$\Delta T^b$ (%)</th>
<th>$\text{AAD}^c$ ($y$)</th>
<th>$\Delta P^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cottonseed oil + n-hexane</td>
<td>315 - 436</td>
<td>41.3</td>
<td>0.0115</td>
<td>0.83</td>
<td>0.0004</td>
<td>0.40</td>
</tr>
<tr>
<td>soybean oil + ethanol</td>
<td>351 - 391</td>
<td>101.3</td>
<td>0.0018</td>
<td>0.31</td>
<td>0.0011</td>
<td>0.03</td>
</tr>
<tr>
<td>oleic acid + ethanol</td>
<td>351 - 388</td>
<td>101.3</td>
<td>0.0018</td>
<td>0.22</td>
<td>0.0601</td>
<td>0.03</td>
</tr>
</tbody>
</table>

$^a \text{AAD} = \frac{1}{N} \sum_{i=1}^{N} |\text{calc} - \text{exp}|$; $^b \Delta = \frac{100}{N} \sum_{i=1}^{N} |\text{calc} - \exp| / \exp$; $^c$converting to mole fraction: 0.0103.

Figure 2: VLE and excess volume data for the system oleic acid + ethanol at 101.3 kPa; concentrations are in mass fraction; excess volume data at 298.15 K.

3. Conclusion

The results demonstrated the consistency of the experimental with the aid of the deviation test, using the maximum likelihood method ($\Delta y < 0.01$). The approach of pseudo-binary mixture was adequate to describe VLE and density data of the studied systems.

References

The density of hexafluoropropylene (HFP) at temperatures between
(283 and 473) K and pressures up to 70 MPa

C.-W. Lin, J. P. M. Trusler

Department of Chemical Engineering, Imperial College London, South Kensington Campus,
London, SW7 2AZ, United Kingdom

Corresponding author e-mail: c.lin09@alumni.imperial.ac.uk

1. Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have been largely phased out for use in air conditioning and refrigeration systems due to the presence of chlorine atoms which are known to cause damage to the ozone layer. Hydrofluorocarbons (HFCs), which were introduced as alternative working fluids, will also be phased out of use over the next decade because, while their ozone depletion potential is low, they are potent greenhouse gases. As a result, a new generation of working fluids based on the family of hydrofloroalkenes, which have both zero ozone depletion potential and very low global warming potential, are being considered. An important and promising member of this family is hexafluoropropylene (HFP).

In order to exploit fully the potential of HFP in a wide range of air conditioning and refrigeration system applications, especially for the design and implementation of commercial and industrial processes, it is essential to acquire its thermophysical properties. However, experimental measurements of these properties of HFP are scarce. Nevertheless, some properties including density ($p < 10$ MPa), vapour pressure ($T < 370$ K) [1] and speed of sound ($p < 400$ MPa) [2] have been investigated. Therefore, the aim of this study is to enhance our understanding of the thermodynamic properties of HFP by measuring density at pressure up to 70 MPa and temperature between (283 and 473) K.

2. Experimental methods

A high pressure vibrating-tube densimeter (DMA HP) was used in this study. The temperature of the densimeter was controlled by an integrated Peltier thermostat with uncertainty of 0.01 K and the relative uncertainty of the pressure measurements was 0.05%. A hand pump was used to inject liquid HFP and raise the pressure up to 70 MPa. The calibration of the densimeter was based on two reference fluids, water and argon, rather than a signal reference fluid and vacuum as commonly practised. The resulting uncertainty of density can be reduced approximately (1 to 2) kg·m$^{-3}$ while measuring densities between (200 and 800) kg·m$^{-3}$.

3. Conclusion

Density of HFP has been measured from temperature between (283 and 473) K and pressure up to 70 MPa. The experimental results from this study combined with direct measurements of speed of sound and heat capacity over wide ranges of temperature and pressure can be used to develop advanced analytical equations of state and derive all of the thermodynamic properties for HFP by numerical-integration algorithms [3]. This will extend the understanding of HFP and improve the development of thermodynamic models for air conditioning and refrigeration system applications.

References
Prediction of thermodynamics properties of ionic liquids using perturbed hard–trimer chain equation of state

M. A. Faghihi, M.M. Alavianmehr, F.Akbari, S.M.Hosseini,

Department of Chemistry, Shiraz University of Technology, Shiraz, 71555-313, IRAN

Corresponding author e-mail: Alavianmehr@sutech.ac.ir

1. Introduction

This work is the continuation of our previous studied [1,2] on the modeling (correlation & prediction) of thermodynamic properties of ILs using equation of state (EOS) based on the perturbed hard-chain theory (PHCT) [3] and statistical associating fluid theory (SAFT)[4,5]. In this paper, we aimed to develop an alternative PHC equation of state to predict thermodynamic properties of ILs, whose the reference physical model has been taken from the trimer chain expression of the SAFT and van der Waals dispersion forces as the perturbation. The significance of the present EOS was its superiority against the our previous work in predicting further first derivative thermodynamic properties like thermal expansion coefficients, but also the second derivatives ones like heat capacities of ILs with reasonably good accuracies.

2. Theory

The most promising method for the calculation of thermophysical properties of highly non-simple liquids today is the use of EOSs that are based on perturbation theory of liquids. This theory considers an appropriate reference system (e.g., hard-sphere) to describe the repulsive interactions of the molecules, whereas long range attractions or the formation of hydrogen bonds are considered as perturbations of that reference system. Moreover, the chain-like structure of polymer molecules is explicitly taken into account.

The general frame of the proposed EOS can be summarized as follows:

\[ Z = \frac{P}{\rho k_B T} = Z_{HS} + Z_{MVHS} = 3Z_{MV}^{HS} - 2 \left\{ 1 + \eta \frac{\partial \ln g_{MV}^{HS}(\sigma^+)}{\partial \eta} \right\} - \frac{a(T) \rho}{k_B T} \]

where, \( g_{MV}^{HS}(\sigma^+) \) represents the radial distribution function of hard spheres at contact proposed by Malijevsky and Veverka (MV) equation [6]:

\[ g_{MV}^{HS}(\sigma^+) = \frac{(1 - 0.444\eta + 0.66108\eta^2 - 0.20373\eta^3 - 0.081225\eta^4 + 0.0769\eta^5)}{(1 + 0.0560\eta + 0.5979\eta^2 + 0.3076\eta^3)(1 - \eta)^3} \]

Two temperature-dependent parameters appeared in the EOS, were determined using corresponding states correlations based on the molecular scaling parameters reflecting the dispersive energy parameters of trimers and the segment diameter.

3. Conclusion

The performance new PHC EOS has been checked by predicting the densities, isothermal compressibilities, thermal expansions and heat capacities with uncertainties equal to ±0.54%, ±8.67%, ±6.33% and ±20%.
References

Vapor liquid equilibrium measurements and modeling of 1-propanethiol + 1-butanethiol + CH₄ ternary system at 303, 335 and 368 K with a pressure variation from 1 to 9 MPa.

Javeed A. Awana, Ioannis Tsivintzelis, Christophe Coquelet, Georgios M. Kontogeorgis

a Center for Energy Resources Engineering, Department of Chemical and Biochemical Engineering, Technical university of Denmark, Building 229, DK-2800 Kgs. Lyngby, Denmark. b CTP–Center for the Thermodynamics of Processes, MINES ParisTech, PSL Research University, Rue Saint Honore, 77305 Fontainebleau, France, c Institute of Chemical Engineering and Technology, Faculty of Engineering and Technology University of the Punjab, Lahore, Pakistan.

Corresponding author email: javeedawan@yahoo.com. (Dr. Javeed A. Awan)

We report new vapor-liquid equilibrium (VLE) measurements of 1-propanethiol + 1-butanethiol + CH₄ ternary system performed at three different temperatures (303, 335 and 368 K) with a pressure variation from 1 to 8 MPa. The total system pressure was maintained by CH₄. The inlet mole fraction of 1-propanethiol ($x = 5.43 \times 10^{-1}$) and 1-butanethiol ($x = 4.56 \times 10^{-1}$) in the liquid phase were same in all experiments. A static analytic method was used for performing all the measurements. The objective is to provide experimental VLE data for the 1-propanethiol + 1-butanethiol + CH₄ ternary system for which data are not available in the literature. These data will help to understand the mutual interactions between liquid thiols in the presence of CH₄. The new VLE data have been modeled successfully with Cubic-Plus-Association (CPA) equation of state.
Development of SAFT for Nuclear Waste Management

Alex Brown¹, Dr. Mark Bankhead¹, Dr. Martin Whittle², Dr. Karl P Travis²

¹National Nuclear Laboratory, ²Sheffield University

Corresponding author e-mail: alex.t.brown@nnl.co.uk

The nuclear industry has a need for robust and accurate thermodynamic modelling tools for predicting physical properties of effluent wastes arising from the clean-up of legacy plants. Due to the complex chemistry and materials changes that can occur in waste processing, the industry has a long-standing requirement for integrated physical property models. To meet these requirements NNL is creating a computer model based on Statistical Associating Fluid Theory (SAFT). SAFT is a thermodynamic tool based on the perturbation theory developed by Wertheim in the 1980s, and works by dividing the Helmholtz energy into several distinct terms. SAFT was chosen over other methods such as Pitzer and the Non Random Two Liquid (NRTL) models because: it is promising in the modelling of chemically complex solutions including heterogeneous wastes, has a strong foundation in statistical mechanics, and requires less data to make predictions.

We present results obtained using the SAFT-HS approach which uses the original theory developed by Chapman et al [1] but with extensions similar to those developed by Schreckenberg et al [2] to include electrolytes. The application of the Nelder-Mead algorithm to fitting saturated liquid density versus temperature data will be presented along with the SAFT parameters derived using this algorithm for various chemical species (e.g. toluene, naphthalene and methanol). The results of using these parameters to predict vapour liquid equilibrium will be shown with their good fits to experimental data. To model electrolytes, two extra terms were incorporated into the SAFT equation of state to represent the Born and mean spherical approximation contributions. This electrolyte model has predicted mean activity coefficients that are similar to those measured experimentally for systems such as lithium bromide and potassium chloride. This is important as many effluent wastes that occur in the nuclear industry contain electrolytes. Finally, we discuss current work in developing a model of nitrate salts and the use of SAFT to make solubility calculations. Following the completion of the SAFT code development, NNL intends to use this as a tool to help accelerate the adoption of SAFT in the nuclear industry and to support commercial SAFT software as part of the industry’s chemical engineering toolbox.

References


Fused coarse-grained model of aromatic ionic liquids and their behavior in pore electrodes

Bin Li1, Ke Ma2, Cliff Woodward2 and Jan Forsman1

1 Department of Theoretical Chemistry, Chemical Centre, Lund University, P.O. Box 124, S-22100 Lund, Sweden, 2School of Physical, Environmental and Mathematical Sciences, University of New South Wales, Canberra, Canberra ACT 2600, Australia.

Corresponding author e-mail: jan.forsman@teokem.lu.se

Keywords: ionic liquids, coarse-grained model, electrodes

1. Introduction

Room temperature ionic liquids are salts which are in a liquid state at temperatures less than 100 °C. They display many interesting features, such as high viscosity, low volatility, and find many applications, for instance as electrolytes in supercapacitors.

We have constructed a fused-sphere coarse-grained model of aromatic ionic liquids [Cxmim][BF4]. This is a further development of our previous coarse-grained model [1]. We have used molecular dynamics simulations to analyze the structural properties, for example, bulk densities, radial distribution function etc, but also dynamical properties, like diffusion coefficient and shear viscosities. We compare the results from simulations of the coarse-grained model with corresponding data from simulations on atomistic models, and experimental data. The transferability in different temperature and different alkyl chain length is also studied to get the same tendencies as the atomistic simulation and experiment results.

We use the fused coarse-grained model to study the behavior of ionic liquids in cylindrical electrodes under different pore diameters. The system includes a 3-layer carbon nanotube in the middle and enough pairs of ionic liquids to make sure that the density region out of the cylinder matches the bulk density, Partial charges are distributed on all the particles of the inner layer of the cylinder. We observe the occupancy number of ionic liquids inside the cylindrical electrode. Number density profiles versus the distance from the center axis of the cylinder are also calculated, at different surface charge densities and for different cylinder diameters. For narrow cylinders, it is difficult for ionic liquids enter the cylinders. For cylinders with large diameters, ionic liquids can enter the cylinder, especially for anions because of smaller molecule size than cations, and the electrical double layer structure can be generated in the cylinders with charged surfaces. The capacitance is also being calculated for different cylinder diameters, with relevance to the behaviour of porous electrodes. We are currently making attempts to construct a classical density functional treatment, based on our coarse-grained ionic liquid model.

3. Conclusion

We build a transferable fused coarse-grained model of ionic liquids to study the structural and electrical properties in cylindrical electrodes.

References

Participants
# List of participants

<table>
<thead>
<tr>
<th>Lastname</th>
<th>Name</th>
<th>Company</th>
<th>Mail</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Austria</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kahl</td>
<td>Gerhard</td>
<td>Institut für Theoretische Physik, TU Wien</td>
<td><a href="mailto:gerhard.kahl@tuwien.ac.at">gerhard.kahl@tuwien.ac.at</a></td>
</tr>
<tr>
<td><strong>Brazil</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Batista</td>
<td>Fabio R M</td>
<td>University of Campinas – UNICAMP</td>
<td><a href="mailto:f.fabio.batista@gmail.com">f.fabio.batista@gmail.com</a></td>
</tr>
<tr>
<td>Pereira</td>
<td>Camila</td>
<td>UFRN</td>
<td><a href="mailto:camila@eq.ufrn.br">camila@eq.ufrn.br</a></td>
</tr>
<tr>
<td><strong>Chile</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Garrido</td>
<td>José Matías</td>
<td>Universidad de Concepción</td>
<td><a href="mailto:josemagarrido@udec.cl">josemagarrido@udec.cl</a></td>
</tr>
<tr>
<td>Mejia</td>
<td>Andres</td>
<td>Universidad de Concepcion</td>
<td><a href="mailto:amejia@udec.cl">amejia@udec.cl</a></td>
</tr>
<tr>
<td><strong>Czech Republic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cervinka</td>
<td>Ctirad</td>
<td>University of Chemistry and Technology Prague</td>
<td><a href="mailto:cervinkc@vscht.cz">cervinkc@vscht.cz</a></td>
</tr>
<tr>
<td>Nezbeda</td>
<td>Ivo</td>
<td>J E Purkinje University</td>
<td><a href="mailto:ivonez@icpf.cas.cz">ivonez@icpf.cas.cz</a></td>
</tr>
<tr>
<td><strong>Danmark</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Almeida</td>
<td>Susana</td>
<td>DTU-CERE</td>
<td><a href="mailto:susal@kt.dtu.dk">susal@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Andersson</td>
<td>Martin</td>
<td>Department of Chemistry, University of Copenhagen</td>
<td><a href="mailto:ma@nano.ku.dk">ma@nano.ku.dk</a></td>
</tr>
<tr>
<td>Biede</td>
<td>Anne Louise</td>
<td>DTU-CERE</td>
<td><a href="mailto:alb@kt.dtu.dk">alb@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Bjørner</td>
<td>Martin</td>
<td>DTU-CERE</td>
<td><a href="mailto:mgabj@kt.dtu.dk">mgabj@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Carlsson</td>
<td>Christian Ove</td>
<td>DTU-CERE</td>
<td><a href="mailto:cc@kt.dtu.dk">cc@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Feilberg</td>
<td>Karen</td>
<td>Danish Hydrocarbon Research and Technology Center</td>
<td><a href="mailto:klfe@dtu.dk">klfe@dtu.dk</a></td>
</tr>
<tr>
<td>Fosbol</td>
<td>Philip</td>
<td>DTU-CERE</td>
<td><a href="mailto:pfl@kt.dtu.dk">pfl@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Karakatsani</td>
<td>Eirini</td>
<td>Haldor Topsoe A/S</td>
<td><a href="mailto:eika@topsoe.dk">eika@topsoe.dk</a></td>
</tr>
<tr>
<td>Knudsen</td>
<td>Kim</td>
<td>Haldor Topsoe A/S</td>
<td><a href="mailto:kik@topsoe.dk">kik@topsoe.dk</a></td>
</tr>
<tr>
<td>Kontogeorgis</td>
<td>Georgios</td>
<td>DTU-CERE</td>
<td><a href="mailto:gk@kt.dtu.dk">gk@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Liang</td>
<td>Xiaodong</td>
<td>DTU-CERE</td>
<td><a href="mailto:xlia@kt.dtu.dk">xlia@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Paterson</td>
<td>Duncan</td>
<td>DTU-CERE</td>
<td><a href="mailto:dunpat@kemi.dtu.dk">dunpat@kemi.dtu.dk</a></td>
</tr>
<tr>
<td>Regueira</td>
<td>Teresa</td>
<td>DTU-CERE</td>
<td><a href="mailto:tere@kemi.dtu.dk">tere@kemi.dtu.dk</a></td>
</tr>
<tr>
<td>Schlaikjer</td>
<td>Anders</td>
<td>DTU-CERE</td>
<td><a href="mailto:andsh@kt.dtu.dk">andsh@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Stenby</td>
<td>Erling H.</td>
<td>DTU-CERE</td>
<td><a href="mailto:ehst@kemi.dtu.dk">ehst@kemi.dtu.dk</a></td>
</tr>
<tr>
<td>Lastname</td>
<td>Name</td>
<td>Company</td>
<td>Mail</td>
</tr>
<tr>
<td>-------------</td>
<td>----------------</td>
<td>---------------------------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Danmark</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Varzandeh</td>
<td>Farhad</td>
<td>DTU-CERE</td>
<td><a href="mailto:farvar@kemi.dtu.dk">farvar@kemi.dtu.dk</a></td>
</tr>
<tr>
<td>von Solms</td>
<td>Nicolas</td>
<td>DTU-CERE</td>
<td><a href="mailto:nvs@kt.dtu.dk">nvs@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Wagner</td>
<td>Patricia</td>
<td>DTU-CERE</td>
<td><a href="mailto:pw@kt.dtu.dk">pw@kt.dtu.dk</a></td>
</tr>
<tr>
<td>Yan</td>
<td>Wei</td>
<td>DTU-CERE</td>
<td><a href="mailto:weya@kemi.dtu.dk">weya@kemi.dtu.dk</a></td>
</tr>
<tr>
<td>France</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Durand</td>
<td>Olivier</td>
<td>CEA</td>
<td><a href="mailto:olivier.durand@cea.fr">olivier.durand@cea.fr</a></td>
</tr>
<tr>
<td>Galliero</td>
<td>Guillaume</td>
<td>Pau University</td>
<td><a href="mailto:guillaume.galliero@univ-pau.fr">guillaume.galliero@univ-pau.fr</a></td>
</tr>
<tr>
<td>Ghoufi</td>
<td>Aziz</td>
<td>Université de Rennes</td>
<td><a href="mailto:aziz.ghoufi@univ-rennes.fr">aziz.ghoufi@univ-rennes.fr</a></td>
</tr>
<tr>
<td>Lach</td>
<td>Adeline</td>
<td>BRGM/LaTEP</td>
<td><a href="mailto:A.Lach@brgm.fr">A.Lach@brgm.fr</a></td>
</tr>
<tr>
<td>Legoix</td>
<td>Ludovic</td>
<td>IFREMER</td>
<td><a href="mailto:ludovic.legoix@gmail.com">ludovic.legoix@gmail.com</a></td>
</tr>
<tr>
<td>Nieto Draghi</td>
<td>Carlos</td>
<td>IPP Energies nouvelles</td>
<td><a href="mailto:carlos.nieto@ifpen.fr">carlos.nieto@ifpen.fr</a></td>
</tr>
<tr>
<td>Ungerer</td>
<td>Philippe</td>
<td>Materials Design S.A.R.L.</td>
<td><a href="mailto:pungerer@materialsdesign.com">pungerer@materialsdesign.com</a></td>
</tr>
<tr>
<td>Germany</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Althans</td>
<td>Daniel</td>
<td>TU Berlin</td>
<td><a href="mailto:daniel.altans@tu-berlin.de">daniel.altans@tu-berlin.de</a></td>
</tr>
<tr>
<td>Enders</td>
<td>Sabine</td>
<td>TU Berlin</td>
<td><a href="mailto:sabine.enders@tu-berlin.de">sabine.enders@tu-berlin.de</a></td>
</tr>
<tr>
<td>Fonseca</td>
<td>José</td>
<td>Covestro Deutschland AG</td>
<td><a href="mailto:jose.fonseca@bayer.com">jose.fonseca@bayer.com</a></td>
</tr>
<tr>
<td>Horsch</td>
<td>Martin</td>
<td>University of Kaiserslautern</td>
<td><a href="mailto:martin.horsch@mv.uni-kl.de">martin.horsch@mv.uni-kl.de</a></td>
</tr>
<tr>
<td>Kohns</td>
<td>Maximilian</td>
<td>Thermodynamics, University of Kaiserslautern</td>
<td><a href="mailto:maximilian.kohns@mv.uni-kl.de">maximilian.kohns@mv.uni-kl.de</a></td>
</tr>
<tr>
<td>Langenbach</td>
<td>Kai</td>
<td>University of Kaiserslautern</td>
<td><a href="mailto:Kai.Langenbach@mv.uni-kl.de">Kai.Langenbach@mv.uni-kl.de</a></td>
</tr>
<tr>
<td>Miethe</td>
<td>Iljana</td>
<td>Linde AG, Engineering Division</td>
<td><a href="mailto:iljana.miethe@linde-le.com">iljana.miethe@linde-le.com</a></td>
</tr>
<tr>
<td>Rocha</td>
<td>Marisa</td>
<td>Universität Bremen</td>
<td><a href="mailto:mrocha@uni-bremen.de">mrocha@uni-bremen.de</a></td>
</tr>
<tr>
<td>Rudolph</td>
<td>Hendryk</td>
<td>TU Berlin</td>
<td><a href="mailto:hendryk.rudolph@tu-berlin.de">hendryk.rudolph@tu-berlin.de</a></td>
</tr>
<tr>
<td>Vrabec</td>
<td>Jadran</td>
<td>University of Paderborn</td>
<td><a href="mailto:jadran.vrabec@ubp.de">jadran.vrabec@ubp.de</a></td>
</tr>
<tr>
<td>Walowski</td>
<td>Christoph</td>
<td>TU Berlin</td>
<td><a href="mailto:christoph.walowski@tu-berlin.de">christoph.walowski@tu-berlin.de</a></td>
</tr>
<tr>
<td>Werth</td>
<td>Stephan</td>
<td>Technical University Kaiserslautern</td>
<td><a href="mailto:stephan.werth@mv.uni-kl.de">stephan.werth@mv.uni-kl.de</a></td>
</tr>
<tr>
<td>Zeiner</td>
<td>Tim</td>
<td>TU Dortmund</td>
<td><a href="mailto:tim.zaier@bci.tu-dortmund.de">tim.zaier@bci.tu-dortmund.de</a></td>
</tr>
<tr>
<td>Greece</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aslanidou</td>
<td>Dimitra</td>
<td>Department of Chemical Engineering, Aristotle</td>
<td><a href="mailto:aslanidou.dimitra@gmail.com">aslanidou.dimitra@gmail.com</a></td>
</tr>
<tr>
<td>Vergadou</td>
<td>Niki</td>
<td>NCSRD &quot;Demokritos&quot;</td>
<td><a href="mailto:n.vergadou@inn.demokritos.gr">n.vergadou@inn.demokritos.gr</a></td>
</tr>
<tr>
<td>Guinea</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bah</td>
<td>Mamadou Pathe</td>
<td>AMIN ELECTRONICS AND ELECTRICALS</td>
<td><a href="mailto:officework8@gmail.com">officework8@gmail.com</a></td>
</tr>
<tr>
<td>Lastname</td>
<td>Name</td>
<td>Company</td>
<td>Mail</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------------</td>
<td>-----------------------------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td><strong>India</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bhandary</td>
<td>Debdip</td>
<td>Indian Institute of Technology Kanpur</td>
<td><a href="mailto:debdip@iitk.ac.in">debdip@iitk.ac.in</a></td>
</tr>
<tr>
<td><strong>Iran</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alalvianmehr</td>
<td>Mohammad Mehdi</td>
<td>Shiraz University of Technology</td>
<td><a href="mailto:alavianmehr@sutech.ac.ir">alavianmehr@sutech.ac.ir</a></td>
</tr>
<tr>
<td>Bagherinia</td>
<td>Mohammad Ali</td>
<td>Islamic Azad University, Lahijan Branch</td>
<td><a href="mailto:mabagherinia@yahoo.com">mabagherinia@yahoo.com</a></td>
</tr>
<tr>
<td>Giahi</td>
<td>Masoud</td>
<td>Lahijan Branch, Islamic Azad University</td>
<td><a href="mailto:giahi_m@yahoo.com">giahi_m@yahoo.com</a></td>
</tr>
<tr>
<td><strong>Israel</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Marcus</td>
<td>Yizhak</td>
<td>Hebrew University of Jerusalem</td>
<td><a href="mailto:ymarcus@vms.huji.ac.il">ymarcus@vms.huji.ac.il</a></td>
</tr>
<tr>
<td><strong>Japan</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tsuji</td>
<td>Tomoya</td>
<td>Nihon University</td>
<td><a href="mailto:tsuji.tomoya@nihon-u.ac.jp">tsuji.tomoya@nihon-u.ac.jp</a></td>
</tr>
<tr>
<td><strong>Mexico</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Del Rio Haza</td>
<td>Fernando</td>
<td>Universidad Autonoma Metropolitana</td>
<td><a href="mailto:fdr@xanum.uam.mx">fdr@xanum.uam.mx</a></td>
</tr>
<tr>
<td>Diaz-Leyva</td>
<td>Pedro</td>
<td>Universidad Autonoma Metropolitana</td>
<td><a href="mailto:pdleyva@xanum.uam.mx">pdleyva@xanum.uam.mx</a></td>
</tr>
<tr>
<td>Estrada-Alexanders</td>
<td>Andres</td>
<td>Universidad Autonoma Metropolitana</td>
<td><a href="mailto:afea@xanum.uam.mx">afea@xanum.uam.mx</a></td>
</tr>
<tr>
<td>Figueroa-Gerstenmaier</td>
<td>Susana</td>
<td>Universidad de Guanajuato</td>
<td><a href="mailto:sufigueroa0802@gmail.com">sufigueroa0802@gmail.com</a></td>
</tr>
<tr>
<td>Robles</td>
<td>Miguel</td>
<td>Instituto de Energias Renovables, Universidad Nacional Autónoma de México</td>
<td><a href="mailto:mzp@ier.unam.mx">mzp@ier.unam.mx</a></td>
</tr>
<tr>
<td><strong>Netherlands</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zubeir</td>
<td>Lawien</td>
<td>Eindhoven University of Technology</td>
<td><a href="mailto:lf.zubeir@tue.nl">lf.zubeir@tue.nl</a></td>
</tr>
<tr>
<td><strong>Nigeria</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nkiko</td>
<td>Mojisola</td>
<td>ELIZADE UNIVERSITY, NIGERIA</td>
<td><a href="mailto:chrismoj3@yahoo.co.uk">chrismoj3@yahoo.co.uk</a></td>
</tr>
<tr>
<td><strong>Pakistan</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Awan</td>
<td>Javeed</td>
<td>Institute of Chemical Engineering and Technology, University of the Punjab, Lahore</td>
<td><a href="mailto:javeedawan@yahoo.com">javeedawan@yahoo.com</a></td>
</tr>
<tr>
<td><strong>Poland</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sliwinska-Bartkowiak</td>
<td>Malgorzata</td>
<td>Adam Mickiewicz University</td>
<td><a href="mailto:msb@amu.edu.pl">msb@amu.edu.pl</a></td>
</tr>
<tr>
<td>Lastname</td>
<td>Name</td>
<td>Company</td>
<td>Mail</td>
</tr>
<tr>
<td>----------</td>
<td>------------</td>
<td>-------------------------------------------------------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>Portugal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filipe</td>
<td>Eduardo</td>
<td>Instituto Superior Técnico</td>
<td><a href="mailto:efilipe@ist.utl.pt">efilipe@ist.utl.pt</a></td>
</tr>
<tr>
<td>Lampreia</td>
<td>Isabel</td>
<td>Faculdade de Ciencias da Universidade de Lisboa</td>
<td><a href="mailto:millampreia@fc.ul.pt">millampreia@fc.ul.pt</a></td>
</tr>
<tr>
<td>Moita</td>
<td>Maria-Luisa</td>
<td>Faculdade de Ciencias da Universidade de Lisboa</td>
<td><a href="mailto:mlmoita@fc.ul.pt">mlmoita@fc.ul.pt</a></td>
</tr>
<tr>
<td>Palma</td>
<td>André</td>
<td>University of Aveiro</td>
<td><a href="mailto:andre.palma@ua.pt">andre.palma@ua.pt</a></td>
</tr>
<tr>
<td>Santos</td>
<td>Angela</td>
<td>Faculdade de Ciencias da Universidade de Lisboa</td>
<td><a href="mailto:afsantos@fc.ul.pt">afsantos@fc.ul.pt</a></td>
</tr>
<tr>
<td>Qatar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Economou</td>
<td>Ioannis</td>
<td>Texas A&amp;M University at Qatar</td>
<td><a href="mailto:ioannis.economou@qatar.tamu.edu">ioannis.economou@qatar.tamu.edu</a></td>
</tr>
<tr>
<td>Michalis</td>
<td>Vasileios</td>
<td>Texas A&amp;M University at Qatar</td>
<td><a href="mailto:vasileios.michalis@qatar.tamu.edu">vasileios.michalis@qatar.tamu.edu</a></td>
</tr>
<tr>
<td>Russia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manyakina</td>
<td>Marina</td>
<td>Lobachevsky State University of Nizhni Novgorod</td>
<td><a href="mailto:manyakina@yandex.ru">manyakina@yandex.ru</a></td>
</tr>
<tr>
<td>Shipilova</td>
<td>Anastasia</td>
<td>Lobachevsky State University of Nizhni Novgorod</td>
<td><a href="mailto:28_stasy@bk.ru">28_stasy@bk.ru</a></td>
</tr>
<tr>
<td>Slovakia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cifra</td>
<td>Peter</td>
<td>Polymer Institute SAS</td>
<td><a href="mailto:peter.cifra@savba.sk">peter.cifra@savba.sk</a></td>
</tr>
<tr>
<td>South Africa</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bahadur</td>
<td>Indra</td>
<td>North-West University, Mafikeng, South Africa</td>
<td><a href="mailto:bahadur.indra@gmail.com">bahadur.indra@gmail.com</a></td>
</tr>
<tr>
<td>Raphael</td>
<td>Gnanapragasam</td>
<td>Department of Chemistry, North-West University, Mafikeng Campus, South Africa</td>
<td><a href="mailto:raphaelrufus22@gmail.com">raphaelrufus22@gmail.com</a></td>
</tr>
<tr>
<td>Spain</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lafuente</td>
<td>Carlos</td>
<td>Universidad de Zaragoza</td>
<td><a href="mailto:celadi@unizar.es">celadi@unizar.es</a></td>
</tr>
<tr>
<td>Royo</td>
<td>Félix</td>
<td>Universidad de Zaragoa</td>
<td><a href="mailto:femer@unizar.es">femer@unizar.es</a></td>
</tr>
<tr>
<td>Sweden</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ahlström</td>
<td>Peter</td>
<td>University of Borås</td>
<td><a href="mailto:peter.ahlstrom@hb.se">peter.ahlstrom@hb.se</a></td>
</tr>
<tr>
<td>Ji</td>
<td>Xiaoyan</td>
<td>Lulea University of Technology</td>
<td><a href="mailto:xiaoyan.ji@ltu.se">xiaoyan.ji@ltu.se</a></td>
</tr>
<tr>
<td>Li</td>
<td>Bin</td>
<td>Lund University</td>
<td><a href="mailto:bin.li@teokem.lu.se">bin.li@teokem.lu.se</a></td>
</tr>
<tr>
<td>Xie</td>
<td>Yujiao</td>
<td>Lulea Univeristy of Technology</td>
<td><a href="mailto:yujiao.xie@ltu.se">yujiao.xie@ltu.se</a></td>
</tr>
<tr>
<td>Lastname</td>
<td>Name</td>
<td>Company</td>
<td>Mail</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------------------</td>
<td>--------------------------------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>Al Ghafri</td>
<td>Saif</td>
<td>Imperial College London</td>
<td><a href="mailto:sa1806@ic.ac.uk">sa1806@ic.ac.uk</a></td>
</tr>
<tr>
<td>Allen</td>
<td>Michael P.</td>
<td>Warwick University</td>
<td><a href="mailto:M.P.Allen@warwick.ac.uk">M.P.Allen@warwick.ac.uk</a></td>
</tr>
<tr>
<td>Avendaño</td>
<td>Carlos</td>
<td>University of Manchester</td>
<td><a href="mailto:carlos.avendano@manchester.ac.uk">carlos.avendano@manchester.ac.uk</a></td>
</tr>
<tr>
<td>Bankhead</td>
<td>Mark</td>
<td>National Nuclear Laboratory</td>
<td><a href="mailto:mark.bankhead@nnl.co.uk">mark.bankhead@nnl.co.uk</a></td>
</tr>
<tr>
<td>Bock</td>
<td>Henry</td>
<td>Heriot Watt University</td>
<td><a href="mailto:h.bock@hw.ac.uk">h.bock@hw.ac.uk</a></td>
</tr>
<tr>
<td>Bourne</td>
<td>Tom</td>
<td>University of Manchester</td>
<td><a href="mailto:tombourne86@gmail.com">tombourne86@gmail.com</a></td>
</tr>
<tr>
<td>Brandani</td>
<td>Stefano</td>
<td>University of Edinburgh</td>
<td><a href="mailto:s.brandani@ed.ac.uk">s.brandani@ed.ac.uk</a></td>
</tr>
<tr>
<td>Brown</td>
<td>Alex</td>
<td>National Nuclear Laboratory</td>
<td><a href="mailto:alex.t.brown@nnl.co.uk">alex.t.brown@nnl.co.uk</a></td>
</tr>
<tr>
<td>Di Lecce</td>
<td>Silvia</td>
<td>Imperial College London</td>
<td><a href="mailto:silvia.di-lecce12@imperial.ac.uk">silvia.di-lecce12@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Dufal</td>
<td>Simon</td>
<td>Imperial College London</td>
<td><a href="mailto:simon.dufal07@imperial.ac.uk">simon.dufal07@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Eriksen</td>
<td>Daniel</td>
<td>Imperial College London</td>
<td><a href="mailto:daniel.kunisch-eriksen10@imperial.ac.uk">daniel.kunisch-eriksen10@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Fayaz-Torshizi</td>
<td>Maziar</td>
<td>Imperial College London</td>
<td><a href="mailto:maziar.fayaz-torshizi10@imperial.ac.uk">maziar.fayaz-torshizi10@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Febra</td>
<td>Sara</td>
<td>Imperial College London</td>
<td><a href="mailto:s.febra14@imperial.ac.uk">s.febra14@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Galindo</td>
<td>Amparo</td>
<td>Imperial College London</td>
<td><a href="mailto:a.galindo@imperial.ac.uk">a.galindo@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Jackson</td>
<td>George</td>
<td>Imperial College London</td>
<td><a href="mailto:g.jackson@imperial.ac.uk">g.jackson@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Gibbons</td>
<td>Richard</td>
<td>University of Manchester</td>
<td><a href="mailto:richandhelen@gibbons.entadsl.com">richandhelen@gibbons.entadsl.com</a></td>
</tr>
<tr>
<td>Gowers</td>
<td>Richard</td>
<td>Imperial College London</td>
<td><a href="mailto:richard.gowers@manchester.ac.uk">richard.gowers@manchester.ac.uk</a></td>
</tr>
<tr>
<td>Graham</td>
<td>Edward</td>
<td>Imperial College London</td>
<td><a href="mailto:eg910@imperial.ac.uk">eg910@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Gray</td>
<td>Sarah</td>
<td>Durham University</td>
<td><a href="mailto:s.j.gray@durham.ac.uk">s.j.gray@durham.ac.uk</a></td>
</tr>
<tr>
<td>Haslam</td>
<td>Andrew</td>
<td>Imperial College London</td>
<td><a href="mailto:a.haslam@imperial.ac.uk">a.haslam@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Hutacharoen</td>
<td>Panatpong</td>
<td>Imperial College London</td>
<td><a href="mailto:p.hutacharoen13@imperial.ac.uk">p.hutacharoen13@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Iriarte Carretero</td>
<td>Irene</td>
<td>Imperial College London</td>
<td><a href="mailto:ii108@ic.ac.uk">ii108@ic.ac.uk</a></td>
</tr>
<tr>
<td>Jackson</td>
<td>Niall</td>
<td>Imperial College London</td>
<td><a href="mailto:niall.jackson@gmail.com">niall.jackson@gmail.com</a></td>
</tr>
<tr>
<td>Jaeger</td>
<td>Frederike</td>
<td>Imperial College London</td>
<td><a href="mailto:frederike.jaeger13@imperial.ac.uk">frederike.jaeger13@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Jimenez Serratos</td>
<td>Maria Guadalupe</td>
<td>Imperial College London</td>
<td><a href="mailto:m.jimenez-serratos@imperial.ac.uk">m.jimenez-serratos@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Lau</td>
<td>Gabriel</td>
<td>Imperial College London</td>
<td><a href="mailto:gabriel.lau07@imperial.ac.uk">gabriel.lau07@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Lazarou</td>
<td>Georgia</td>
<td>Imperial College London</td>
<td><a href="mailto:georgia.lazarou12@imperial.ac.uk">georgia.lazarou12@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Lin</td>
<td>Chih-Wei</td>
<td>University of Edinburgh</td>
<td><a href="mailto:c.lin09@alumni.imperial.ac.uk">c.lin09@alumni.imperial.ac.uk</a></td>
</tr>
<tr>
<td>Madge</td>
<td>Jim</td>
<td>Durham University</td>
<td><a href="mailto:jim.madge@durham.ac.uk">jim.madge@durham.ac.uk</a></td>
</tr>
<tr>
<td>Masters</td>
<td>Andrew</td>
<td>University of Manchester</td>
<td><a href="mailto:andrew.masters@manchester.ac.uk">andrew.masters@manchester.ac.uk</a></td>
</tr>
<tr>
<td>Miller</td>
<td>Mark</td>
<td>Durham University</td>
<td><a href="mailto:m.a.miller@durham.ac.uk">m.a.miller@durham.ac.uk</a></td>
</tr>
<tr>
<td>Mu</td>
<td>Junju</td>
<td>University of Manchester</td>
<td><a href="mailto:junju.mu@postgrad.manchester.ac.uk">junju.mu@postgrad.manchester.ac.uk</a></td>
</tr>
<tr>
<td>Muller</td>
<td>Erich</td>
<td>Imperial College London</td>
<td><a href="mailto:e.muller@imperial.ac.uk">e.muller@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Muscatello</td>
<td>Jordan</td>
<td>Imperial College London</td>
<td><a href="mailto:jordan.muscatello05@imperial.ac.uk">jordan.muscatello05@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Lastname</td>
<td>Name</td>
<td>Company</td>
<td>Mail</td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
<td>-----------------------------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>Noro</td>
<td>Massimo</td>
<td>Unilever</td>
<td><a href="mailto:massimo.noro@unilever.com">massimo.noro@unilever.com</a></td>
</tr>
<tr>
<td>Shahruddin</td>
<td>Sara</td>
<td>Imperial College London</td>
<td><a href="mailto:s.shahruddin14@imperial.ac.uk">s.shahruddin14@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Striolo</td>
<td>Alberto</td>
<td>University College London</td>
<td><a href="mailto:a.striolo@ucl.ac.uk">a.striolo@ucl.ac.uk</a></td>
</tr>
<tr>
<td>Sweatman</td>
<td>Martin</td>
<td>University of Edinburgh</td>
<td><a href="mailto:martin.sweatman@ed.ac.uk">martin.sweatman@ed.ac.uk</a></td>
</tr>
<tr>
<td>Tasche</td>
<td>Jos</td>
<td>Durham University</td>
<td><a href="mailto:jos.tasche@durham.ac.uk">jos.tasche@durham.ac.uk</a></td>
</tr>
<tr>
<td>Thind</td>
<td>Romnik</td>
<td>Durham University</td>
<td><a href="mailto:romnik.thind@durham.ac.uk">romnik.thind@durham.ac.uk</a></td>
</tr>
<tr>
<td>Trusler</td>
<td>Martin</td>
<td>Imperial College London</td>
<td><a href="mailto:m.trusler@imperial.ac.uk">m.trusler@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Underwood</td>
<td>Thomas</td>
<td>Durham University</td>
<td><a href="mailto:thomas.underwood@durham.ac.uk">thomas.underwood@durham.ac.uk</a></td>
</tr>
<tr>
<td>van Duijneveld</td>
<td>Jeroen</td>
<td>University of Bristol</td>
<td><a href="mailto:J.S.van-Duijneveldt@bristol.ac.uk">J.S.van-Duijneveldt@bristol.ac.uk</a></td>
</tr>
<tr>
<td>Walker</td>
<td>Martin</td>
<td>Durham University</td>
<td><a href="mailto:martin.walker2@durham.ac.uk">martin.walker2@durham.ac.uk</a></td>
</tr>
<tr>
<td>Williams</td>
<td>Chris</td>
<td>University of Manchester</td>
<td><a href="mailto:christopher.williams-2@manchester.ac.uk">christopher.williams-2@manchester.ac.uk</a></td>
</tr>
<tr>
<td>Wilson</td>
<td>Mark</td>
<td>Durham University</td>
<td><a href="mailto:mark.wilson@durham.ac.uk">mark.wilson@durham.ac.uk</a></td>
</tr>
<tr>
<td>Yatsyshin</td>
<td>Petr</td>
<td>Imperial College London</td>
<td><a href="mailto:p.yatsyshin@imperial.ac.uk">p.yatsyshin@imperial.ac.uk</a></td>
</tr>
<tr>
<td>Zhang</td>
<td>Jiafei</td>
<td>Imperial College London</td>
<td><a href="mailto:jiafei.zhang@ic.ac.uk">jiafei.zhang@ic.ac.uk</a></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lastname</th>
<th>Name</th>
<th>Company</th>
<th>Mail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debenedetti</td>
<td>Pablo</td>
<td>Princeton University</td>
<td><a href="mailto:pdebene@princeton.EDU">pdebene@princeton.EDU</a></td>
</tr>
<tr>
<td>Mahynski</td>
<td>Nathan</td>
<td>Princeton University</td>
<td><a href="mailto:nathan.mahynski@gmail.com">nathan.mahynski@gmail.com</a></td>
</tr>
<tr>
<td>McCabe</td>
<td>Clare</td>
<td>Vanderbilt University</td>
<td><a href="mailto:c.mccabe@vanderbilt.edu">c.mccabe@vanderbilt.edu</a></td>
</tr>
<tr>
<td>Panagiotopoulos</td>
<td>Athanassios</td>
<td>Princeton University</td>
<td><a href="mailto:azp@princeton.edu">azp@princeton.edu</a></td>
</tr>
<tr>
<td>Ritz</td>
<td>Mariah</td>
<td>North Carolina State University</td>
<td><a href="mailto:mjrritz@ncsu.edu">mjrritz@ncsu.edu</a></td>
</tr>
<tr>
<td>Santiso</td>
<td>Erik</td>
<td>North Carolina State University</td>
<td><a href="mailto:eesantis@ncsu.edu">eesantis@ncsu.edu</a></td>
</tr>
<tr>
<td>Srivastava</td>
<td>Deepti</td>
<td>North Carolina State University</td>
<td><a href="mailto:dsrivas@ncsu.edu">dsrivas@ncsu.edu</a></td>
</tr>
<tr>
<td>Weiser</td>
<td>Laura</td>
<td>North Carolina State University</td>
<td><a href="mailto:ljweiser@ncsu.edu">ljweiser@ncsu.edu</a></td>
</tr>
<tr>
<td>Author</td>
<td>Page</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aasberg-Petersen, K.</td>
<td>56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adjiman, C. S.</td>
<td>101, 120, 143, 148</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ahlström, P.</td>
<td>112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ahmadi, R.</td>
<td>157</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ahmed, S. A.</td>
<td>190</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Akbari, F.</td>
<td>204</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al Ghafri, S. Z.</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alahmad, A.</td>
<td>175</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alavianmehr, M. M.</td>
<td>157, 204</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Albrecht, T.</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allen, M. P.</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Almeida, S.</td>
<td>125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Althans, D.</td>
<td>113</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Álvarez-Ramírez, F.</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anastácio, M.</td>
<td>48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andersson, M. P.</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andersson, T.</td>
<td>112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>André, L.</td>
<td>165</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Androulaki, E.</td>
<td>57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antón, V.</td>
<td>193</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Artigas, H.</td>
<td>193</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aslanidou, D.</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avendano, C.</td>
<td>78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Awan, J. A.</td>
<td>206</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Azaroual, M.</td>
<td>165</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bagherinia, M. A.</td>
<td>138</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bahadur, I.</td>
<td>182, 183</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bankhead, M.</td>
<td>79, 207</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barré, L.</td>
<td>155</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Batista, F. R. M.</td>
<td>196</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Becker, S.</td>
<td>107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Belting, P. C.</td>
<td>201</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benková, Z.</td>
<td>61, 159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bennetzen, M. V.</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Berlin, M.</td>
<td>112</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Author</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bhandary, D.</td>
<td>61</td>
</tr>
<tr>
<td>Bianchi, E.</td>
<td>115</td>
</tr>
<tr>
<td>Björner, M. G.</td>
<td>80</td>
</tr>
<tr>
<td>Blas, F. J.</td>
<td>153</td>
</tr>
<tr>
<td>Bock, H.</td>
<td>47</td>
</tr>
<tr>
<td>Bohlén, M.</td>
<td>112</td>
</tr>
<tr>
<td>Bolton, K.</td>
<td>112</td>
</tr>
<tr>
<td>Bourasseau, E.</td>
<td>45</td>
</tr>
<tr>
<td>Bourne, T.</td>
<td>151</td>
</tr>
<tr>
<td>Braga, C.</td>
<td>68</td>
</tr>
<tr>
<td>Brandani, E.</td>
<td>81</td>
</tr>
<tr>
<td>Brandani, P.</td>
<td>81</td>
</tr>
<tr>
<td>Brandani, S.</td>
<td>81</td>
</tr>
<tr>
<td>Bresme, E.</td>
<td>74, 75, 90</td>
</tr>
<tr>
<td>Brown, A.</td>
<td>207</td>
</tr>
<tr>
<td>Carbone, P.</td>
<td>58, 77</td>
</tr>
<tr>
<td>Cárdenas, H.</td>
<td>105</td>
</tr>
<tr>
<td>Castro, L. V.</td>
<td>117</td>
</tr>
<tr>
<td>Ceriani, R.</td>
<td>201</td>
</tr>
<tr>
<td>Červinka, C.</td>
<td>121</td>
</tr>
<tr>
<td>Cézac, P.</td>
<td>165</td>
</tr>
<tr>
<td>Chiavone-Filho, O.</td>
<td>201</td>
</tr>
<tr>
<td>Christiansen, L. J.</td>
<td>56</td>
</tr>
<tr>
<td>Ciantar, M.</td>
<td>72</td>
</tr>
<tr>
<td>Cifra, P.</td>
<td>159</td>
</tr>
<tr>
<td>Collell, J.</td>
<td>69</td>
</tr>
<tr>
<td>Coquelet, C.</td>
<td>206</td>
</tr>
<tr>
<td>Cordeiro, M. N. D. S.</td>
<td>61</td>
</tr>
<tr>
<td>Costa, J. B.</td>
<td>125</td>
</tr>
<tr>
<td>Costandy, J.</td>
<td>70</td>
</tr>
<tr>
<td>Coutinho, J. A. P.</td>
<td>150, 177, 178</td>
</tr>
<tr>
<td>Crespo, E.</td>
<td>178</td>
</tr>
<tr>
<td>Creton, B.</td>
<td>117</td>
</tr>
<tr>
<td>Cubillas, P.</td>
<td>52</td>
</tr>
<tr>
<td>Das, G.</td>
<td>192</td>
</tr>
<tr>
<td>Author</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Debenedetti, P. G.</td>
<td>32</td>
</tr>
<tr>
<td>del Río, E.</td>
<td>85, 162, 169</td>
</tr>
<tr>
<td>Di Lecce, S.</td>
<td>75</td>
</tr>
<tr>
<td>Díaz-Leyva, P.</td>
<td>162, 169</td>
</tr>
<tr>
<td>Ding, M.</td>
<td>84</td>
</tr>
<tr>
<td>Domin, K.</td>
<td>122</td>
</tr>
<tr>
<td>Donval, J.-P.</td>
<td>149</td>
</tr>
<tr>
<td>dos Ramos, M. C.</td>
<td>192</td>
</tr>
<tr>
<td>Dowlatabadi, S. D.</td>
<td>157</td>
</tr>
<tr>
<td>Dronskowski, R.</td>
<td>121</td>
</tr>
<tr>
<td>Dufal, S.</td>
<td>62, 83, 101, 120, 143, 148</td>
</tr>
<tr>
<td>Duff, N.</td>
<td>97</td>
</tr>
<tr>
<td>Durand, O.</td>
<td>45</td>
</tr>
<tr>
<td>Ebenso, E. E.</td>
<td>182, 183</td>
</tr>
<tr>
<td>Economou, I. G.</td>
<td>57, 70, 87</td>
</tr>
<tr>
<td>Enders, S.</td>
<td>113, 119, 136</td>
</tr>
<tr>
<td>Erastova, V.</td>
<td>52</td>
</tr>
<tr>
<td>Erdtmann, E.</td>
<td>112</td>
</tr>
<tr>
<td>Erikse, D. K.</td>
<td>83, 145</td>
</tr>
<tr>
<td>Escobedo, F. A.</td>
<td>78</td>
</tr>
<tr>
<td>Estrada-Alexanders, A.</td>
<td>162, 169</td>
</tr>
<tr>
<td>Eyssautier, I.</td>
<td>155</td>
</tr>
<tr>
<td>Fadaei, E.</td>
<td>157</td>
</tr>
<tr>
<td>Faghihi, M. A.</td>
<td>204</td>
</tr>
<tr>
<td>Fayaz-Torshizi, M.</td>
<td>124</td>
</tr>
<tr>
<td>Febra, S.</td>
<td>143</td>
</tr>
<tr>
<td>Fennell, P. S.</td>
<td>50</td>
</tr>
<tr>
<td>Ferrari, S.</td>
<td>115</td>
</tr>
<tr>
<td>Figueredo, A. L.</td>
<td>201</td>
</tr>
<tr>
<td>Figueroa-Gerstenmaier, S.</td>
<td>179, 180</td>
</tr>
<tr>
<td>Filipe, E. J. M.</td>
<td>48</td>
</tr>
<tr>
<td>Filippini, G.</td>
<td>45</td>
</tr>
<tr>
<td>Fischlchweiger, M.</td>
<td>119</td>
</tr>
<tr>
<td>Ford, I.</td>
<td>46, 168</td>
</tr>
<tr>
<td>Forsman, J.</td>
<td>208</td>
</tr>
<tr>
<td>Forte, E.</td>
<td>79, 148</td>
</tr>
<tr>
<td>Freire, L. A. C.</td>
<td>54</td>
</tr>
<tr>
<td>Fulem, M.</td>
<td>121</td>
</tr>
<tr>
<td>Galliero, G.</td>
<td>33</td>
</tr>
<tr>
<td>Gang, O.</td>
<td>158</td>
</tr>
<tr>
<td>Ganley, W. I.</td>
<td>127</td>
</tr>
<tr>
<td>Garcia, A. R.</td>
<td>48</td>
</tr>
<tr>
<td>Garrido, J. M.</td>
<td>153</td>
</tr>
<tr>
<td>Ghoufi, A.</td>
<td>84, 142, 189</td>
</tr>
<tr>
<td>Giahi, M.</td>
<td>163</td>
</tr>
<tr>
<td>Gibbons, R. M.</td>
<td>137, 161</td>
</tr>
<tr>
<td>Gil-Villegas, A.</td>
<td>85, 179</td>
</tr>
<tr>
<td>Gkournmpis, T.</td>
<td>112</td>
</tr>
<tr>
<td>Gowers, R. J.</td>
<td>77</td>
</tr>
<tr>
<td>Gray, S.</td>
<td>172</td>
</tr>
<tr>
<td>Greenwell, H. C.</td>
<td>52</td>
</tr>
<tr>
<td>Gubbins, K E.</td>
<td>122, 123</td>
</tr>
<tr>
<td>Gusarova, E. V.</td>
<td>173</td>
</tr>
<tr>
<td>Guzmán, O.</td>
<td>85</td>
</tr>
<tr>
<td>Haeckel, M.</td>
<td>149</td>
</tr>
<tr>
<td>Hardy, A.</td>
<td>47</td>
</tr>
<tr>
<td>Haslam, A. J.</td>
<td>83, 145</td>
</tr>
<tr>
<td>Hasse, H.</td>
<td>102, 107, 110, 195</td>
</tr>
<tr>
<td>Held, C.</td>
<td>67</td>
</tr>
<tr>
<td>Herdecs, C.</td>
<td>124</td>
</tr>
<tr>
<td>Hlushak, S.</td>
<td>192</td>
</tr>
<tr>
<td>Horsch, M.</td>
<td>102, 107, 110, 195</td>
</tr>
<tr>
<td>Hoshina, T.-a.</td>
<td>160</td>
</tr>
<tr>
<td>Hosseini, S. M.</td>
<td>204</td>
</tr>
<tr>
<td>Hunt, P.</td>
<td>46, 168</td>
</tr>
<tr>
<td>Hutacharoen, P.</td>
<td>101</td>
</tr>
<tr>
<td>Ilharco, L.</td>
<td>48</td>
</tr>
<tr>
<td>Iriarte-Carretero, L.</td>
<td>90</td>
</tr>
<tr>
<td>Jackson, G.</td>
<td>46, 62, 68, 78, 83, 101, 120, 143, 145, 148, 155, 168</td>
</tr>
<tr>
<td>Jackson, N.</td>
<td>74</td>
</tr>
<tr>
<td>Jaeger, E.</td>
<td>59</td>
</tr>
<tr>
<td>Jazzdewska, M.</td>
<td>122</td>
</tr>
<tr>
<td>Ji, X.</td>
<td>68, 186</td>
</tr>
<tr>
<td>Jiang, H.</td>
<td>87</td>
</tr>
<tr>
<td>Jover, J.</td>
<td>155</td>
</tr>
<tr>
<td>Kahl, G.</td>
<td>115</td>
</tr>
<tr>
<td>Kalliadasis, S.</td>
<td>109</td>
</tr>
<tr>
<td>Karakatsani, E.</td>
<td>56</td>
</tr>
<tr>
<td>Klamt, A.</td>
<td>103</td>
</tr>
<tr>
<td>Klein, P.</td>
<td>102</td>
</tr>
<tr>
<td>Knyazev, A. V.</td>
<td>173, 175</td>
</tr>
<tr>
<td>Kohns, M.</td>
<td>107, 195</td>
</tr>
<tr>
<td>Kontogeorgis, G. M.</td>
<td>49, 80, 125, 140, 206</td>
</tr>
<tr>
<td>Kritikos, G.</td>
<td>57</td>
</tr>
<tr>
<td>Kroon, M. C.</td>
<td>64</td>
</tr>
<tr>
<td>Author</td>
<td>Page</td>
</tr>
<tr>
<td>-------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Kumar, S. K.</td>
<td>37, 158</td>
</tr>
<tr>
<td>Lach, A.</td>
<td>165</td>
</tr>
<tr>
<td>Lafuente, C.</td>
<td>193</td>
</tr>
<tr>
<td>Lampreia, I. M. S.</td>
<td>184</td>
</tr>
<tr>
<td>Langenbach, K.</td>
<td>110, 119</td>
</tr>
<tr>
<td>Lassin, A.</td>
<td>165</td>
</tr>
<tr>
<td>Lau, G.</td>
<td>46, 168</td>
</tr>
<tr>
<td>Lazarou, G.</td>
<td>83, 120, 148</td>
</tr>
<tr>
<td>Legoi, L.</td>
<td>149</td>
</tr>
<tr>
<td>Levitz, P.</td>
<td>155</td>
</tr>
<tr>
<td>Li, B.</td>
<td>208</td>
</tr>
<tr>
<td>Lin, C.-W.</td>
<td>203</td>
</tr>
<tr>
<td>Liu, W.</td>
<td>158</td>
</tr>
<tr>
<td>Llovel, F.</td>
<td>177, 178</td>
</tr>
<tr>
<td>Lobanov, O.</td>
<td>68</td>
</tr>
<tr>
<td>Long, Y.</td>
<td>122</td>
</tr>
<tr>
<td>López de Haro, M.</td>
<td>188</td>
</tr>
<tr>
<td>Lu, X.</td>
<td>67</td>
</tr>
<tr>
<td>Lucchesi, K. W.</td>
<td>196</td>
</tr>
<tr>
<td>Lundsgaard, R.</td>
<td>125</td>
</tr>
<tr>
<td>Ma, K.</td>
<td>208</td>
</tr>
<tr>
<td>Madge, I.</td>
<td>128</td>
</tr>
<tr>
<td>Mahynski, N. A.</td>
<td>37, 158</td>
</tr>
<tr>
<td>Mainland, G. C.</td>
<td>62</td>
</tr>
<tr>
<td>Malfreyt, P.</td>
<td>189</td>
</tr>
<tr>
<td>Manyakina, M. E.</td>
<td>175</td>
</tr>
<tr>
<td>Marcos, J.</td>
<td>48</td>
</tr>
<tr>
<td>Marcus, Y.</td>
<td>135</td>
</tr>
<tr>
<td>Martins, L. F. G.</td>
<td>48</td>
</tr>
<tr>
<td>Martos, L. G.</td>
<td>125</td>
</tr>
<tr>
<td>Masters, A. J.</td>
<td>92, 151</td>
</tr>
<tr>
<td>Matar, O.</td>
<td>59, 146</td>
</tr>
<tr>
<td>McCabe, C.</td>
<td>35, 192</td>
</tr>
<tr>
<td>Meirelles, A. J. A.</td>
<td>196, 201</td>
</tr>
<tr>
<td>Mejía, A.</td>
<td>105, 153</td>
</tr>
<tr>
<td>Mellot-Draznieks, C.</td>
<td>72</td>
</tr>
<tr>
<td>Meskinfam, M.</td>
<td>163</td>
</tr>
<tr>
<td>Mester, Z.</td>
<td>86</td>
</tr>
<tr>
<td>Michalis, V. K.</td>
<td>70</td>
</tr>
<tr>
<td>Michelsen, M.</td>
<td>99</td>
</tr>
<tr>
<td>Mikkola, J.-P.</td>
<td>186</td>
</tr>
<tr>
<td>Miller, M.</td>
<td>128</td>
</tr>
<tr>
<td>Moita, M. L. C. J.</td>
<td>184</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Author</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moncho-Jordá, A.</td>
<td>180</td>
</tr>
<tr>
<td>Montes, J.</td>
<td>188</td>
</tr>
<tr>
<td>Morgado, P.</td>
<td>48</td>
</tr>
<tr>
<td>Mostofi, A.</td>
<td>66</td>
</tr>
<tr>
<td>Moucka, F.</td>
<td>89</td>
</tr>
<tr>
<td>Moultos, O. A.</td>
<td>87</td>
</tr>
<tr>
<td>Mu, J.</td>
<td>92</td>
</tr>
<tr>
<td>Muscatello, J.</td>
<td>59, 66</td>
</tr>
<tr>
<td>Müller, E. A.</td>
<td>46, 59, 66, 68, 78, 105, 124, 146, 153, 155, 168</td>
</tr>
<tr>
<td>Naidoo, M.</td>
<td>183</td>
</tr>
<tr>
<td>Naidoo, P.</td>
<td>183</td>
</tr>
<tr>
<td>Námer, P.</td>
<td>159</td>
</tr>
<tr>
<td>Neto, E. L. B.</td>
<td>198</td>
</tr>
<tr>
<td>Nezbeda, I.</td>
<td>89</td>
</tr>
<tr>
<td>Nieto-Draghi, C.</td>
<td>72, 117, 155</td>
</tr>
<tr>
<td>Nikiko, M. O.</td>
<td>190</td>
</tr>
<tr>
<td>Nobre, L. C. S.</td>
<td>184</td>
</tr>
<tr>
<td>Noro, M.</td>
<td>36</td>
</tr>
<tr>
<td>Noya, E. G.</td>
<td>115</td>
</tr>
<tr>
<td>Odriozola, G.</td>
<td>180</td>
</tr>
<tr>
<td>Ohya, K.-h.</td>
<td>160</td>
</tr>
<tr>
<td>Oliveira, E. C. L.</td>
<td>198</td>
</tr>
<tr>
<td>Oliveira, M. B.</td>
<td>150, 177, 178</td>
</tr>
<tr>
<td>Oluwabi, A.</td>
<td>190</td>
</tr>
<tr>
<td>Palma, A.</td>
<td>150, 177, 178</td>
</tr>
<tr>
<td>Panagiotopoulos, A.Z.</td>
<td>37, 86, 87, 158</td>
</tr>
<tr>
<td>Panatpong, H.</td>
<td>120</td>
</tr>
<tr>
<td>Panayiotou, C.</td>
<td>49</td>
</tr>
<tr>
<td>Pannacci, N.</td>
<td>117</td>
</tr>
<tr>
<td>Papaioannou, V.</td>
<td>101, 120, 143</td>
</tr>
<tr>
<td>Paterson, D.</td>
<td>99</td>
</tr>
<tr>
<td>Pereira, C. G.</td>
<td>54, 198, 201</td>
</tr>
<tr>
<td>Pérez-Mendoza, J. R.</td>
<td>179</td>
</tr>
<tr>
<td>Piñeiro, M. M.</td>
<td>153</td>
</tr>
<tr>
<td>Plácido-Flores, E.</td>
<td>169</td>
</tr>
<tr>
<td>Pogiatzis, T.</td>
<td>120</td>
</tr>
<tr>
<td>Queimada, A. J.</td>
<td>150</td>
</tr>
<tr>
<td>Rahman, S.</td>
<td>68, 146</td>
</tr>
<tr>
<td>Ramdath, S.</td>
<td>183</td>
</tr>
<tr>
<td>Ramírez-Gutiérrez, D.</td>
<td>117</td>
</tr>
<tr>
<td>Ramjugernath, D.</td>
<td>183</td>
</tr>
<tr>
<td>Ramos, J. E.</td>
<td>85</td>
</tr>
<tr>
<td>Raphael, G.</td>
<td>182</td>
</tr>
<tr>
<td>Author</td>
<td>Page</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Raptis, V.</td>
<td>68</td>
</tr>
<tr>
<td>Rathke, B.</td>
<td>191</td>
</tr>
<tr>
<td>Raut, D.</td>
<td>186</td>
</tr>
<tr>
<td>Regueira, T.</td>
<td>133</td>
</tr>
<tr>
<td>Renou, R.</td>
<td>142, 189</td>
</tr>
<tr>
<td>Ritz, M.</td>
<td>97</td>
</tr>
<tr>
<td>Robles, M.</td>
<td>187, 188</td>
</tr>
<tr>
<td>Rocha, M. A. A.</td>
<td>191</td>
</tr>
<tr>
<td>Royo, F. M.</td>
<td>193</td>
</tr>
<tr>
<td>Rubin, A.</td>
<td>125</td>
</tr>
<tr>
<td>Rudolph, H.</td>
<td>136</td>
</tr>
<tr>
<td>Ruffine, L.</td>
<td>149</td>
</tr>
<tr>
<td>Sadeqzadeh, M.</td>
<td>120</td>
</tr>
<tr>
<td>Santiso, E. E.</td>
<td>93, 97</td>
</tr>
<tr>
<td>Santos, A. F. S.</td>
<td>184</td>
</tr>
<tr>
<td>Sautet, P.</td>
<td>72</td>
</tr>
<tr>
<td>Savushkin, I. A.</td>
<td>175</td>
</tr>
<tr>
<td>Savva, N.</td>
<td>109</td>
</tr>
<tr>
<td>Saxe, P.</td>
<td>69</td>
</tr>
<tr>
<td>Schlaikjer, A.</td>
<td>140</td>
</tr>
<tr>
<td>Schröer, W.</td>
<td>191</td>
</tr>
<tr>
<td>Segura, H.</td>
<td>105, 153</td>
</tr>
<tr>
<td>Serin, J.-P.</td>
<td>165</td>
</tr>
<tr>
<td>Serratos, M. G. J.</td>
<td>146</td>
</tr>
<tr>
<td>Shahruddin, S.</td>
<td>146</td>
</tr>
<tr>
<td>Shanker, R. M.</td>
<td>101, 120, 148</td>
</tr>
<tr>
<td>Shen, G.</td>
<td>67</td>
</tr>
<tr>
<td>Shipilova, A. S.</td>
<td>173</td>
</tr>
<tr>
<td>Silva, I. L. M.</td>
<td>201</td>
</tr>
<tr>
<td>Singh J. K.</td>
<td>61</td>
</tr>
<tr>
<td>Siperstein, F. R.</td>
<td>58</td>
</tr>
<tr>
<td>Sliwinska-Bartkowiak, M.</td>
<td>122</td>
</tr>
<tr>
<td>Smith, W. R.</td>
<td>89</td>
</tr>
<tr>
<td>Sonne, J.</td>
<td>125</td>
</tr>
<tr>
<td>Spyriouni, T.</td>
<td>64</td>
</tr>
<tr>
<td>Srivastava, D.</td>
<td>123</td>
</tr>
<tr>
<td>Stenby, E. H.</td>
<td>99, 132, 133</td>
</tr>
<tr>
<td>Stipp, S. L. S.</td>
<td>103</td>
</tr>
<tr>
<td>Stipsitz, M.</td>
<td>115</td>
</tr>
<tr>
<td>Stoffel, R. P.</td>
<td>121</td>
</tr>
<tr>
<td>Striolo, A.</td>
<td>40</td>
</tr>
<tr>
<td>Stubos, A. K.</td>
<td>70</td>
</tr>
<tr>
<td>Stöbener, K.</td>
<td>102</td>
</tr>
<tr>
<td>Sutton, A.</td>
<td>66</td>
</tr>
<tr>
<td>Sweatman, M. B.</td>
<td>44</td>
</tr>
<tr>
<td>Szymczyk, A.</td>
<td>84, 142, 189</td>
</tr>
<tr>
<td>Tasche, J.</td>
<td>95</td>
</tr>
<tr>
<td>Teixeira, M.</td>
<td>48</td>
</tr>
<tr>
<td>Thind, R.</td>
<td>170</td>
</tr>
<tr>
<td>Thomsen, K.</td>
<td>140</td>
</tr>
<tr>
<td>Topette-Reyes, C.</td>
<td>162</td>
</tr>
<tr>
<td>Travis, K.</td>
<td>79, 207</td>
</tr>
<tr>
<td>Trinh, T. T.</td>
<td>72</td>
</tr>
<tr>
<td>Trusler, J. P. M.</td>
<td>50, 62, 203</td>
</tr>
<tr>
<td>Tsali, A.</td>
<td>49</td>
</tr>
<tr>
<td>Tsimpanogiannis, I. N.</td>
<td>70, 87</td>
</tr>
<tr>
<td>Tsivintzelis, I.</td>
<td>49, 206</td>
</tr>
<tr>
<td>Tsuji, T.</td>
<td>160</td>
</tr>
<tr>
<td>Turner, C. H.</td>
<td>123</td>
</tr>
<tr>
<td>Underwood, T.</td>
<td>52</td>
</tr>
<tr>
<td>Ungerer, P.</td>
<td>69</td>
</tr>
<tr>
<td>Valdez-Gonzalez, M.</td>
<td>187</td>
</tr>
<tr>
<td>van Duijneveldt, J. S.</td>
<td>127</td>
</tr>
<tr>
<td>Varzandeh, F.</td>
<td>132</td>
</tr>
<tr>
<td>Vega, L. E.</td>
<td>177, 178</td>
</tr>
<tr>
<td>Vergadou, N.</td>
<td>57</td>
</tr>
<tr>
<td>von Harbou, E.</td>
<td>195</td>
</tr>
<tr>
<td>von Solms, N.</td>
<td>125</td>
</tr>
<tr>
<td>Walker, M.</td>
<td>94, 171</td>
</tr>
<tr>
<td>Walowski, C.</td>
<td>136</td>
</tr>
<tr>
<td>Wang, C.</td>
<td>125</td>
</tr>
<tr>
<td>Weiser, L. J.</td>
<td>93</td>
</tr>
<tr>
<td>Werth, S.</td>
<td>102, 110</td>
</tr>
<tr>
<td>Whittle, M.</td>
<td>79, 207</td>
</tr>
<tr>
<td>Williams, C. D.</td>
<td>58</td>
</tr>
<tr>
<td>Wilson, M. R.</td>
<td>94, 95, 170, 171, 172</td>
</tr>
<tr>
<td>Woodward, C.</td>
<td>208</td>
</tr>
<tr>
<td>Woolston, P.</td>
<td>127</td>
</tr>
<tr>
<td>Xie, Y.</td>
<td>186</td>
</tr>
<tr>
<td>Yan, W.</td>
<td>99, 132, 133</td>
</tr>
<tr>
<td>Yatsyshin, P.</td>
<td>109</td>
</tr>
<tr>
<td>Yiannourakou, M.</td>
<td>69</td>
</tr>
<tr>
<td>Yosefnia, S.</td>
<td>138</td>
</tr>
<tr>
<td>Zeiner, T.</td>
<td>167</td>
</tr>
<tr>
<td>Zhang, J.</td>
<td>50</td>
</tr>
<tr>
<td>Zubeir, L. F.</td>
<td>64</td>
</tr>
</tbody>
</table>