Development of CPA for Electrolyte Mixtures

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Introduction

• Electrolytes play a key role in many industrial processes. In many industries, the petroleum industry in particularly, scaling of salts can be a problem, and also salt can have big effects on the equilibrium between two compounds, by salting out, salting in, or even by inducing an otherwise nonexistent liquid-liquid equilibrium phase slit, thus being helpful in many separation processes.

• Our electrolyte CPA Equation of State have been developed through the past years, and was first presented by Maribo-Mogensen et al [1] illustrating the possible applications of the model, and later extended to solid-liquid equilibria by Schlaikjer et al. [2].

• In the initial first work with this model the parameterizations have been done on a salt specific basis, thus each salt is parameterized individually yielding an issue with dealing with salt mixtures. In this work a Ion specific parameterization is presented along with its performance for some key systems.

Parameter Estimation

We have parameterized the model for 10 cations and 7 anions to osmotic coefficient and mean ionic activity coefficient data up to an ionic strength of 6, in the temperature range: 273.15 K – 591 K [3].

The parameterization is conducted simultaneously for all the ions to the data of 55 salts that can be combined by the 17 ions. In table 1 below the deviations from the activity coefficient and osmotic coefficient data used in the estimation is shown. On average the relative deviation in activity coefficient is 5.9% and in osmotic coefficient 4.2%. Density is accurately accounted for by the 17 ions.

Table 1: Relative absolute deviation for activity coefficient and Osmotic coefficient data for all the salts in the estimation.

<table>
<thead>
<tr>
<th>RAD (%)</th>
<th>H+</th>
<th>Na+</th>
<th>K+</th>
<th>Li+</th>
<th>Cs+</th>
<th>Rb+</th>
<th>Mg2+</th>
<th>Ca2+</th>
<th>Sr2+</th>
<th>Ba2+</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>- 7.2/3.7</td>
<td>5.6/2.6</td>
<td>6.3/6.1</td>
<td>8.3/29</td>
<td>- - - -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>6.5/2.8</td>
<td>10.5/1.3</td>
<td>6.7/5.4</td>
<td>10.4/4.2</td>
<td>7.6/42</td>
<td>17/12</td>
<td>7.1/3.4</td>
<td>9.7/5.0</td>
<td>5.5/5.2</td>
<td>94/64</td>
</tr>
<tr>
<td>Br</td>
<td>4.2/12.5</td>
<td>5.5/2.4</td>
<td>4.3/0.8</td>
<td>8.2/5.6</td>
<td>5.4/17</td>
<td>11.1/2</td>
<td>6.8/1.8</td>
<td>14.1/3.0</td>
<td>8.7/2.6</td>
<td>5.2/5.7</td>
</tr>
<tr>
<td>I</td>
<td>8.2/9.9</td>
<td>5.3/4.6</td>
<td>6.8/0.5</td>
<td>- 4.0/14</td>
<td>6.6/18</td>
<td>13.7/19</td>
<td>6.8/4.8</td>
<td>46/26</td>
<td>5.5/3.6</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>- 5.0/4.4</td>
<td>4.0/7.1</td>
<td>- 6.4/26</td>
<td>33/26</td>
<td>- - - -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO3</td>
<td>4.7/3.5</td>
<td>6.5/6.1</td>
<td>2.1/5.5</td>
<td>4.8/40</td>
<td>5.0/10.2</td>
<td>6.1/19</td>
<td>5.9/4.1</td>
<td>12.4/5.5</td>
<td>5.0/6.0</td>
<td>2.9/9.4</td>
</tr>
<tr>
<td>SO4</td>
<td>- 7.0/9.4</td>
<td>5.6/4.3</td>
<td>10.7/5.1</td>
<td>6.7/66</td>
<td>1.5/16</td>
<td>36/49</td>
<td>10.7/16</td>
<td>- - - -</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Electrolyte CPA Equation of State

The Electrolyte CPA Equation of State as proposed by Maribo-Mogensen et al. [1] is a direct extension to the CPA Equation of State. The model takes the long range electrostatic interactions in to account the Born term and accounts for ion solvation through the Debye-Hückel Theory. The model is build as a ion specific framework, where instead of using the traditional van der Waals one fluid mixing rule, the Huron-Vidal/NRTL mixing rule is applied for the interaction between solvent and ions. The mixing rule is simplified by setting the non-randomness parameter to zero by default, yielding:

\[
\frac{\Delta U_{ij}}{RT} = \frac{\Delta U_{ij}^{\text{Born}}}{RT} + a_i \left(1 - \frac{T}{T^*}\right)^2 - a_{ij} \left(1 - \frac{T}{T^*}\right)^3
\]

For the binary energy parameter in the Huron-Vidal/NRTL mixing rule, a temperature dependence is found to be needed:

\[
\frac{\Delta U_{ij}^{\text{Born}}}{RT} = \frac{\Delta U_{ij}^{\text{Born}}}{RT} + a_i \left(1 - \frac{T}{T^*}\right)^2 - a_{ij} \left(1 - \frac{T}{T^*}\right)^3
\]

Here there are 3 adjustable parameters: \(a_i\), \(T^*_i\), \(T^*_R\), where the reference energy parameter is the energy parameter at the reference temperature (298.15 K). In total the model utilizes 2 pure compound adjustable parameters along with the three interaction parameters from the above temperature dependence for each ion, while the dielectric constant is adopted from a model by Maribo-Mogensen et al. [4], and the Born radius is adjusted to match the hydration enthalpy.

Mixed Salt Osmotic coefficients

Application Examples

- A parameter set with ion-specific parameters have been developed and show acceptable deviations from osmotic and activity coefficient data on average.
- For a few problematic salts ion-ion interaction parameters is needed to yield acceptable deviations.
- The parameters have successfully been applied to mixed salt systems for predicting the osmotic coefficient, as well as mixed solvent systems, also with very promising results.

References