The (Water + Alcohol + Alkali Halide) Mixed-Solvent Electrolyte Systems: Data Status and Consistency Analysis Using Electrolyte-NRTL Model

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The (water + alcohol + alkali halide) mixed-solvent electrolyte systems: Data status and consistency analysis using electrolyte-NRTL model

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Highlights:
- Proposed a consistent e-NRTL model for mixed-solvent electrolyte solutions
- Identified inconsistent datasets and proposed a reference database
- Predicted VLE based on MIAC using the consistent e-NRTL

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Consistency analysis framework

Gibbs-Duhem equation at constant $T$ and $p$:

$$\sum n_{i,\text{solv}} d \ln x_{i,\text{solv}} y_{i,\text{solv}} + n_s \sum v d \ln m_\pm y_\pm^m = 0$$

Experimental MIAC (mean ionic activity coefficient) data are usually available from EMF measurements.
Solvent activity coefficient can be obtained from VLE data.

$$y_{i,\text{solv}} = \frac{y_{i,\text{solv}} p}{x_{i,\text{solv}} P_{i,\text{solv}}^{\text{sat}}}$$

In principle, a model should be equally good for MIAC and VLE.

However, e-NRTL, as in the original papers, in ASPEN, and in Carnot, violates the Gibbs-Duhem equation, without accounting for all the derivatives over solvent composition.
Consistent e-NRTL

E-NRTL is selected for data analysis because it is industrially relevant, has been constructed on some theoretical considerations, and potentially requires very few parameters.

$$\ln \gamma_i^* = \frac{1}{RT} \left( \frac{\partial G_{ex,LC}^{\text{ex,LC}}}{\partial n_i} \right)_{T,p,j(j\neq i)} + \frac{1}{RT} \left( \frac{\partial G_{ex,PDH}^{\text{ex,PDH}}}{\partial n_i} \right)_{T,p,j(j\neq i)} + \frac{1}{RT} \left( \frac{\partial \Delta G_{ex,Born}^{\text{ex,Born}}}{\partial n_i} \right)_{T,p,j(j\neq i)}$$

In ASPEN e-NRTL, derivatives over solvent composition are not complete for PDH and Born terms.

VLE $\Rightarrow \frac{\partial G^E}{\partial n_{\text{solv}}}$

MIAC $\Rightarrow \frac{\partial G^E}{\partial n_{\text{ion}}} - \frac{\partial G^E}{\partial n_{\text{ion}}}^{\text{Mixed Solvent}}$

$\Delta G^{\text{transfer}} \Rightarrow \frac{\partial G^E}{\partial n_{\text{ion}}}^{\text{Mixed Solvent}} - \frac{\partial G^E}{\partial n_{\text{ion}}}^{\text{Pure Water}}$

LLE $\Rightarrow \frac{\partial G^E}{\partial n_{\text{solv}}} \text{ and } \frac{\partial G^E}{\partial n_{\text{ion}}}$

SLE $\Rightarrow \frac{\partial G^E}{\partial n_{\text{ion}}} \text{ and } K^{\text{dissoc}}$

* Arrow direction denotes derivatives

Data selection: water + NaCl

Scatter in available data can be strongly reduced by removing sets with high deviations

40 datasets for MIAC at 25 °C

18 selected datasets (1937-2011)
Water + ethanol + KCl

- The consistent e-NRTL mode is compared with the original.
- Objective functions for the alcohol-salt parameters are compared.

<table>
<thead>
<tr>
<th></th>
<th>Fitted to MIAC, original</th>
<th>Fitted to MIAC, consistent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water + ethanol + KCl</td>
<td>AveDev (%)</td>
<td>MaxDev (%)</td>
</tr>
<tr>
<td>VLE: Yang et al. 1979, $p$</td>
<td>1.9</td>
<td>4.4</td>
</tr>
<tr>
<td>VLE: Yang et al. 1979, $y$</td>
<td>3.8</td>
<td>6</td>
</tr>
<tr>
<td>MIAC: Mussini et al. 1995</td>
<td>4.4</td>
<td>12</td>
</tr>
</tbody>
</table>

For MIAC: No difference between original and consistent model

For VLE: The consistent model shows less deviations
Water + ethanol + LiCl/NaCl/KCl – consistent model

- Results are similar for other mixtures.
- Inconsistent datasets are identified.

<table>
<thead>
<tr>
<th></th>
<th>Fitted to MIAC</th>
<th></th>
<th>Fitted to VLE and MIAC</th>
<th>Fitted to VLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AveDev (%)</td>
<td>MaxDev (%)</td>
<td>AveDev (%)</td>
<td>MaxDev (%)</td>
</tr>
<tr>
<td>Water + ethanol + LiCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VLE: Shaw &amp; Butler 1930, $p$</td>
<td>14</td>
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<td>7.9</td>
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<tr>
<td>VLE: Shaw &amp; Butler 1930, $y$</td>
<td>3.9</td>
<td>12</td>
<td>1.9</td>
<td>14</td>
</tr>
<tr>
<td>MIAC Hernández-Luis et al. 2008</td>
<td>3.5</td>
<td>13</td>
<td>3.7</td>
<td>19</td>
</tr>
</tbody>
</table>

|                          |                |                       |                        |               |
| Water + ethanol + NaCl   |                |                       |                        |               |
| VLE: Yang et al. 1979, $p$ | 1.1             | 2.6                   | 2                      | 5.4           |
| VLE: Yang et al. 1979, $y$ | 2.6             | 3.9                   | 1.8                    | 3.5           |
| MIAC: Esteso et al. 1989 | 6               | 19                    | 6.1                    | 19            |
| MIAC: Abedi et al. 2016  | 4.5             | 26                    | 4.5                    | 26            |
| MIAC: Manontov et al. 2016 | 3.3             | 12                    | 3                      | 9.1           |

|                          |                |                       |                        |               |
| Water + ethanol + KCl    |                |                       |                        |               |
| VLE: Yang et al. 1979, $p$ | 1.1             | 2.5                   | 1.1                    | 2.9           |
| VLE: Yang et al. 1979, $y$ | 3               | 4.3                   | 2.4                    | 3.3           |
| MIAC: Mussini et al. 1995 | 4.4             | 12                    | 4.5                    | 13            |

LiCl : Probable inconsistent data

When data are consistent, we recommend using MIAC as objective function.

Given sufficient data, alcohol-salt parameters should be obtained from ternary MIAC.
Conclusions

• A consistent e-NRTL model is proposed, including the correct derivatives over solvent composition and the Born term. The modification is only relevant to mixed-solvent electrolytes.
• For water + ethanol + LiCl/NaCl/KCl and the involved binaries, inconsistent datasets are identified; a reference database is proposed. Ongoing work will include other water + alcohol + alkali halide mixtures.
• For ternary mixtures:
  – VLE can be predicted accurately from MIAC using the consistent e-NRTL.
  – VLE predictions are less accurate using the original e-NRTL.

Perspective

External consistency can be investigated by analyzing the trend of model parameters.

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