Thermodynamic consistency in modeling of SLE and VLE in aqueous alkanolamine solutions

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Outline

- Introduction
- Theory
  - VLE (Vapor-Liquid Equilibrium)
  - SLE (Solid-Liquid Equilibrium)
- Modeling: NRTL Framework as an example
- Results
  - MEA + H₂O
  - DEEA + H₂O
  - AMP + H₂O
- Conclusions
Introduction

- Rigorous thermodynamic models based on excess Gibbs energy (eNRTL and eUNIQUAC) are capable of representing both Solid-Liquid-Equilibria (SLE) and Vapor-Liquid-Equilibria (VLE) in aqueous alkanolamine solutions.

- A robust and accurate modeling relies on the quality and type of data used to regress the parameters to get the best representation of the data.

- Different apparatuses provide different equilibrium data:
  - Ebulliometer experiments usually generate PTxy data which can be used to determine the activity coefficient for both amine and water.
  - A calorimetric measurement can provide excess enthalpy of mixing and reaction as well heat capacity.
  - Freezing point depression measurements provide SLE and water activity data.

- When comparing activity coefficients of water from VLE and SLE data often inconsistencies are seen: e.g.
  - the excess enthalpies calculated were slightly skewed toward higher amine concentrations when a best fit to freezing point depressions was achieved.
  - the minimum value of the excess enthalpy was fitted optimally but the freezing point depression was found to be under-predicted, in particular at higher concentrations.
Examples: MEA + H₂O

Posey, 1996

VLE (P-T-x and P-T-x-y), Excess Enthalpy and Freezing Point.

Schmidt, et al., 2007

VLE (P-T-x and P-T-x-y) and Excess Enthalpy.
To find the origin of the discrepancy between measured data used for the thermodynamic modeling of the activity coefficient of water.
Theory

**VLE**

\[
m_l(T, p) = m_l(T, p)
\]

\[
m_v(T, p) = m_v(T, p) + RT \ln f^\ell_i
\]

\[
m_s(T, p) = m_s(T, p) + RT \ln f^v_i
\]

\[
f^\ell_i = f^v_i
\]

\[
\chi_i \gamma_i \gamma^* = P \chi_i \gamma^*_i
\]

\[
F^i = \frac{f^i}{f^i_0} \exp \left[ - \frac{V^i(P - P^i_0)}{RT} \right] - 1
\]

\[
\ln g_i = \frac{\hat{G}^E/RT}{g_i} \ln \gamma_i \gamma^*_i
\]

\[
- \frac{H^E}{RT^2} = \frac{\hat{G}^E/RT}{g_i} \gamma_i \gamma^*_i
\]

\[
C_P^E = \frac{\hat{H}^E}{g_i} \gamma_i \gamma^*_i
\]

**SL E**

\[
m_l(T, p) = m_l(T, p)
\]

\[
m_v(T, p) = m_v(T, p) + RT \ln f^\ell_i
\]

\[
m_s(T, p) = m_s(T, p) + RT \ln f^s_i
\]

\[
DG = R \ln \frac{f^\ell_i}{f^s_i} = - RT \ln a_i
\]

\[
DG = DH - TDS
\]

\[
DH = DH^f_i + \hat{O}_T DC_p dT
\]

\[
DS = DS^f_i + \hat{O}_T DC_p dT
\]

\[
DC_p = C_p^\ell - C_p^s
\]

Prasnis, et al., 1999, Molecular Thermodynamics of Fluid-Phase Equilibria
Hojjati and Rohani, 2006, Measurement and prediction solubility of Paracetamol in Water-Isopopanol solution
Case 1

\[- \ln x_i g_i = \frac{DH_f^\circ}{RT_f} (T_R - 1) + \frac{1}{RT_f} \int_{T_f}^{T} \dot{O} D_{C_p} dT - \frac{1}{RT_f} \int_{T_f}^{T} \dot{O} \frac{D_{C_p}}{T} dT\]

\[\ln x_i g_i = \frac{DH_f^\circ}{RT_f} (1 - T_R)\]

\[T_R = \frac{T_f}{T}\]


Case 2

\[- \ln x_i g_i = \frac{DH_f^\circ}{RT_f} \ln T_R\]

\[D_{C_p} @ D S_f^\circ\]

Case 3

\[- \ln x_i g_i = \frac{DH_f^\circ}{RT_f} (T_R - 1) + \frac{D_{C_p}}{RT} (1 + \ln T_R - T_R)\]

\[D_{C_p} @ k_{T_f}\]
Case 4

\[ DC_p = a + bT \]

\[ - \ln x_i g_i = \frac{DH_f^o}{RT_f} (T_R - 1) + \frac{1}{RT_f} \dot{O} DC_p dT - \frac{1}{RT_f} \ddot{O} DC_P dT \]


Case 5

\[ DC_p = a + bT + \frac{c}{(T - T_Q)} \]

\[ - \ln x_i g_i = \frac{DH_f^o}{RT_f} (T_R - 1) + \frac{a}{R} (1 + \ln T_R - T_R) + \frac{bT_f}{2RT} (T - T_f)^2 + c \frac{(T - 1) \ln \frac{T - T_Q}{T_f - T_Q} - \ln T_R}{T} \]

- Fosbøl, et al. (2009 and 2011)
Thermo physical property of water as solvent

\[ \Delta C_p = C_p(I) - C_p(s) \]

\[ \Delta C_p = a + b \cdot T \]

\[ T_f = 273.15 K \]

\[ D \text{H}_f^i = 6009.4 \frac{J}{mol} \]

\[ D C_p = 37.97 \frac{J}{K \cdot mol} \]

\[ D C_p = 75.929 - 0.1405 x \frac{J}{K \cdot mol} \]

\[ D C_p = 75.929 - 0.1405 x - 2.4563 \times 10^{-4} \frac{J}{(T - 200) K \cdot mol} \]

Modeling

\[
\text{OF} = \sum_{i=1}^{n} \left( \frac{\hat{g}_i^\text{Exp} - g_i^\text{calc}}{g_i^\text{Exp}} \right)^2 + \sum_{i=1}^{n} \left( \frac{\hat{p}_i^\text{Exp} - p_i^\text{calc}}{p_i^\text{Exp}} \right)^2 + \sum_{i=1}^{n} \left( \frac{\left( H_i^\text{Exp} \right)^E - \left( \frac{H_i^\text{Exp} \cdot E}{E_i^\text{Exp}} \right)^\text{calc}}{\left( H_i^\text{Exp} \right)^E} \right)^2 + \sum_{i=1}^{n} \left( \frac{\left( Q_i^\text{Exp} \right)^F - (Q_i^\text{Exp})^F}{Q_i^\text{Exp}} \right)^2
\]

\[
\text{AARD} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{\hat{\hat{A}}_{\text{model}} - \hat{\hat{A}}_{\text{exp}}}{\hat{A}_{\text{exp}}} \right|
\]

<table>
<thead>
<tr>
<th>Species</th>
<th>Melting/ Freezing Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0</td>
</tr>
<tr>
<td>MEA</td>
<td>10.3</td>
</tr>
<tr>
<td>AMP</td>
<td>67</td>
</tr>
<tr>
<td>DEEA</td>
<td>-70</td>
</tr>
</tbody>
</table>

Results

Case 1

Case 2

Case 3
\[ \text{MEA} + \text{H}_2\text{O} \]

\[ \Phi_1 (\ degree) \]

\[ x_1 (-) \]

- Fosbøl, et al., 2011
- Cheng, et al., 1992

\[ \theta \]

\[ \text{MEA} + \text{H}_2\text{O} \]
AMP + H₂O

Case 4

Case 5

Fosbøl, et al., 2011
DEEA + H$_2$O

Arshad, et al., 2013
Conclusions

- 5 different cases to estimate the freezing point depression were tested for aqueous MEA, DEEA and AMP solutions.
- Physical/thermo physical properties of Water/Ice were only used.
- When the freezing point differences between solute (alkanolamine) and solvent (water) is larger, none of the suggested cases were able to predict the data.
- A systematic error in the measurements??
- Challenge to the selected thermodynamic model??
- The required thermal and physical properties should be from the alkanolamines solution??
FutureWork

- AMP + H₂O
- DEEA + H₂O

Fosbøl, et al., 2011
Arshad, et al., 2013
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