Development of an Association-Based Model for Bio-Derived Chemicals

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Background
As global demand for renewable chemicals and fuels increases, new pathways for their manufacture are being proposed. As global demand for renewable chemicals and fuels increases, new pathways for their manufacture are being proposed. In processes such as recovery of isobutanol from fermentations or upgrading of bio-oil, polar solutions are ubiquitous and hydrogen bonding causes large deviations from ideal behavior. Existing thermodynamic models are inadequate in modeling such systems and, as a result, design of separation equipment is heavily hampered. Therefore, there is a growing demand for phase equilibria models with greater accuracy.

A hydrogen bond is a dipole-dipole contact between a hydrogen atom on a ‘proton donor’ and a neighboring strongly electronegative ‘proton acceptor’.

\[
\begin{align*}
H & \quad O \\
\alpha & \quad \beta \\
R & \quad R
\end{align*}
\]

Figure 1: ‘Monomers’ associate to form chains or oligomers

The interaction creates chain-like structures, oligomers.

Effect of Association
The importance of accounting for association is illustrated in Figure 2 for ethanol + n-hexane.

Determing Monomer Fraction
There are two approaches for calculating the monomer fraction:

1. Macroscopic: Vapor pressure data is fitted using ethers as homomorphs for alcohols. Molecular behavior is not evaluated. The relationship between \( K \) and the number of carbons in primary alcohols is illustrated in Figure 3.

\[
K \text{ vs. Number of carbons}
\]

Figure 3: Relationship between equilibrium constant \( K \) and the number of carbon atoms in primary alcohols

2. Microscopic: Using experimental IR and NMR data, force fields can be developed to accurately model molecular behavior. Simulation based on the force fields can then be run to effectively capture ‘screenshots’ of the mixture and quantify the monomer fraction.

Comparison of Modeling Methods
For a system of 1-pentanol in n-heptane, deviation from ideality (\( \gamma \)) for varying compositions of alcohol is given in Figure 4, where, for chemical theory, \( K \) is found by fitting pure vapor pressure, and the prediction of mixture behavior is excellent. The curvature of experimental data is well-represented by both methods.

\[
\begin{align*}
\text{Mole Fraction of 1-Pentanol} & \quad \gamma
\end{align*}
\]

Figure 4: Deviation from ideality for 1-pentanol–n-heptane at 91.3 kPa; experimental: (○) 1-pentanol, (Δ) n-heptane; (—) chemical theory prediction, (—) Wertheim’s theory model.

Association Modeling Methods
Two modeling methods are chemical theory and Wertheim’s perturbation theory.

<table>
<thead>
<tr>
<th>Chemical theory</th>
<th>Wertheim’s theory</th>
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<tbody>
<tr>
<td>• H-bonding represented as a chemical reaction ( nA_1 \leftrightarrow A_n ) with equilibrium constant ( K )</td>
<td>• Statistical mechanics approach</td>
</tr>
<tr>
<td>• Key parameter: ( K )</td>
<td>• Calculates probability of bond formation</td>
</tr>
<tr>
<td>• Hydrogen bonding is represented differently, the two approaches have similar forms and both require accurate calculation of the monomer fraction, ( X_{11} ).</td>
<td>• Key parameter: ( \Delta )</td>
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<td>• Can the association be determined without fitting to mixture data?</td>
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Future Work
• The physical contribution to non-idealities will be calculated using NRTL.
• Molecular force fields will be tuned to fit IR and NMR spectroscopic data for a microscopic model of monomer fraction via molecular simulation.
• Current \( K \) results from macroscopic fitting will be compared to microscopic approach results.
• Scope will be expanded for mixtures with multiple associating components.
• Improved models will be implemented into Aspen Plus commercial process design software to create a robust process simulation tool for wide use in industry.