Solubility of Phenylacetic Acid in Binary Solvent Mixtures

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Introduction

This work continues a systematic search (1-8) for mixing models and equations which will provide reasonable predictions for the thermochernical properties of a solute in binary solvent mixtures. In an earlier paper, Acree and Bertrand (3) reported benzonic acid and \( m \)-tolilic acid solubilities in solvent mixtures containing carbon tetrachloride. The experimental data were interpreted with solution models based on a monomeric treatment

\[
RT \ln \left( \frac{x_{\text{form}}^{\text{act}} / x_{\text{mon}}^{\text{act}}}{x_{\text{form}}^{\text{act}} / x_{\text{mon}}^{\text{act}}} \right) = (1 - \phi_{\text{act}}^{\text{act}}) \left[ \phi_1 \phi_2 (\Delta G_{\text{form}}^{\text{act}}) x_{\text{1}} x_{\text{2}} + \phi_2 \phi_3 (\Delta G_{\text{act}}^{\text{act}}) x_{\text{1}} x_{\text{3}} \right] \]

and a dimeric treatment

\[
RT \ln \left( \frac{x_{\text{form}}^{\text{act}} / x_{\text{mon}}^{\text{act}}}{x_{\text{form}}^{\text{act}} / x_{\text{mon}}^{\text{act}}} \right) = (1 - \phi_{\text{act}}^{\text{act}}) \left[ \phi_1 \phi_2 (\Delta G_{\text{form}}^{\text{act}}) x_{\text{1}} x_{\text{2}} + \phi_2 \phi_3 (\Delta G_{\text{act}}^{\text{act}}) x_{\text{1}} x_{\text{3}} \right] \]

in an adsorption cell

\[
\text{Registry No. O_2, 7782-44-7; N}_2, 7727-37-9; \text{ Ar}, 7440-37-1.\]

Literature Cited

(8) Harwell Subroutine Library, Routine VA05A, AERE, Harwell, U.K.

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Solubility of Phenylacetic Acid in Binary Solvent Mixtures

Phenylacetic acid (98.5%) was recrystallized several times from cyclohexane, mp 76.5 ± 0.5 °C [lit. (9) mp 77 °C]. The recrystallized acid was titrated to a thymol blue end point with freshly standardized sodium methoxide by the method of Fritz and Lisicki (10), except toluene was substituted for benzene. The purity of the phenylacetic acid was calculated to be 99.7 ± 0.5%. Cyclohexane (99%), \( n \)-heptane (99%), \( n \)-octane (99±%), and iso-octane (99±%) were stored over molecular sieves (type 4A) and distilled shortly before use. Carbon tetrachloride (99%) was purified by the method of Scatchard et al. (11), stored in contact with mercury under an argon atmosphere, and distilled shortly before use.

Solvent mixtures were prepared with weight with sufficient accuracy to allow calculation of compositions to 0.0001 mole fraction. Solvents and excess carboxylic acid were placed in amber glass containers and allowed to equilibrate in a constant-temperature shaker bath at 25.0 ± 0.1 °C for several days. Attainment of equilibrium was verified by repetitive measurements after several additional days. Acid solubilities were determined by transferring weight aliquots through a coarse filter into flasks containing blank nonaqueous titration solvent. The solutions were titrated with freshly standardized...
Table I. Comparison between Experimental and Predicted Solubilities for Phenylacetic Acid in Binary Solvent Mixtures at 25.0 °C

<table>
<thead>
<tr>
<th>solvent compositions</th>
<th>deviation (%)</th>
<th>( \Delta G_{mix} ) ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_1 )</td>
<td>( X_2 )</td>
<td>( \Delta G_{mix} )</td>
</tr>
<tr>
<td>( C_6H_{12} ) (1) + ( C_6H_{12} ) (2)</td>
<td>0.0000</td>
<td>0.0134</td>
</tr>
<tr>
<td>( C_6H_{12} ) (1) + ( C_6H_{12} ) (2)</td>
<td>0.0491</td>
<td>0.0176</td>
</tr>
<tr>
<td>( C_6H_{12} ) (1) + ( C_6H_{12} ) (2)</td>
<td>0.0892</td>
<td>0.0200</td>
</tr>
<tr>
<td>( C_6H_{12} ) (1) + ( C_6H_{12} ) (2)</td>
<td>0.0409</td>
<td>0.0225</td>
</tr>
<tr>
<td>( C_6H_{12} ) (1) + ( C_6H_{12} ) (2)</td>
<td>1.0000</td>
<td>0.0247</td>
</tr>
</tbody>
</table>

* Deviation (%) = \( 100 \left( \frac{X_{calc} - X_{exp}}{X_{exp}} \right) \)

Discussion

Comparisons between experimental and predicted values are shown in the last four columns of Table I for the six binary solvent systems studied. Properties used in the calculations include the activity of the solid monomeric solute, \( a^{soln}_{3,mon} = 0.4197 \), calculated from

\[
\ln a^{soln}_{3,mon} = \int_{T_m}^{T} \left( \frac{\Delta F_{3}^{soln}}{RT^2} \right) dT
\]

and

\[
a^{soln}_{3,mon} = (a^{soln}_{3,mon})^2
\]

the enthalpy of fusion data, \( \Delta F_{3}^{fus} = 3464 \text{ cal/mol} \) at the normal melting point temperature \( T_{mp} = 77 \text{ °C} \). The enthalpy of fusion is actually for the transition of the solid to a mixture of monomers and dimers; but for consistency in these calculations, the melt is considered to be completely monomeric for the monomer model and completely dimeric for the dimer model. The molar volume of phenylacetic acid, \( \tilde{V}_{3,mon} = 121.8 \text{ cm}^3/\text{mol} \), was obtained by adding an incremental \( \text{C}_7\text{H}_{15} \text{ volume of 17.4 cm}^3/\text{mol to the molar volume of benzoic acid} \( \tilde{V}_{3,mon} = 104.4 \text{ cm}^3/\text{mol} \). For systems studied in this investigation, a 10% error in estimating \( \tilde{V}_{3,mon} \) affects the predicted solubilities by less than 1%. Solvent properties used in the calculations are listed in Table II.

Inspection of Table I reveals that eq 3 and 4 are comparable with overall average (rms) deviations of 6.7% and 6.6%, respectively, and are superior to equations based on the monomeric model. This is in agreement with observations from an earlier study involving benzoic and m-toluic acids. Although the magnitudes of the deviations between predicted and experimental phenylacetic acid solubilities appear large in comparison to the 2-4% deviations noted for benzoic acid solubilities, it must be noted that the phenylacetic acid solubilities cover up to a 15-fold range whereas the benzoic acid solubilities cover a much smaller 5-fold range. Furthermore, phenylactic acid is more soluble than benzoic acid in these solvent systems, and there is a greater possibility for specific interactions between the carboxylate group and the \( \pi \)-electron cloud on an adjacent solute molecule, which would violate the basic assumptions used in deriving eq 1-4. Despite these shortcomings, eq 3 and 4 do provide very reasonable predictions for the solubility of phenylacetic acid in the six binary solvent systems considered.

Glossary

- \( a^{soln} \) activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure supercooled liquid
- \( \Delta G_{fus} \) partial molar Gibbs free energy of the solute (Raoult's law), extrapolated back to infinite dilution
- \( \Delta G_{fus} \) partial molar Gibbs free energy of the solute (Flory-Huggins model), extrapolated back to infinite dilution
- \( \Delta G_{ex} \) excess Gibbs free energy of the binary solvent mixture based on Raoult's law
- \( \Delta G_{ex} \) excess Gibbs free energy of the binary solvent mixture based on the Flory-Huggins solution model
- \( \Delta F_{fus}^{soln} \) enthalpy of fusion of the solute
- \( \tilde{V}_{3,comp} \) molar volume of component / mole fraction compositions of the solvent mixture, \( X_{3,comp} \) calculated as if the solute were not present.
Isobaric Vapor–Liquid Equilibria of the Binary Systems Consisting of Anisaldehyde, Methyl Anisate, and Anisyl Alcohol at 2 kPa

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BASF Aktiengesellschaft, D-6700 Ludwigshafen/Rhein, Federal Republic of Germany

The vapor pressures of the three pure components anisaldehyde, methyl anisate, and anisyl alcohol have been determined experimentally, together with the three binary vapor–liquid equilibria. The vapor pressures have been measured ebulliometrically, and the vapor–liquid equilibria by using a recirculation-type equilibrium still. The methyl anisate/anisyl alcohol system forms an azeotrope. Data reduction based on the Wilson, NRTL, and UNIQUAC models provides a correlation for the activity coefficients $y_i$.

**Introduction**

In connection with the problem of separating anisaldehyde (4-methoxybenzaldehyde), methyl anisate (methyl 4-methoxybenzoate), and anisyl alcohol (4-methoxybenzyl alcohol) by distillation, the vapor pressures of the pure components, and the three corresponding binary vapor–liquid phase equilibria, have been measured. Because anisyl alcohol is thermally unstable, the separation by distillation has to be carried out under reduced pressure. Hence, the binary vapor–liquid phase equilibria have been measured at 2 kPa.

**Purity of Components.** The reagents were manufactured by BASF Aktiengesellschaft, Federal Republic of Germany. Their purity was confirmed by gas chromatography. The aldehyde and alcohol had a mole fraction purity better than 99.5%, while the mole fraction purity of the ester was 99.9%.

**Apparatus and Procedure.** The vapor pressures of the pure components have been determined ebulliometrically with an apparatus similar to apparatus I, described by Ambrose and Sprake (1). The apparatus used to obtain vapor–liquid equilibria data was a modified Hunsmann vapor–liquid recirculation still (2) with several modifications suggested by Brunner and Scholz (3, 4).

Pressures were measured by means of a high-accuracy electronic manometer from MKS Instruments Inc., Burlington, MA, with an accuracy of $\Delta p/p = 5 \times 10^{-5}$. The pressure transducer was calibrated against a dead-weight gage. The pressure constancy $\Delta p/p$ was better than $5 \times 10^{-4}$. The temperatures (IPTS-68) were measured by using a calibrated temperature meter (from Systemtechnik, Sweden, 1220 series) which had a digital resolution of 0.01 K and whose accuracy was estimated to be 0.02 K. The temperatures measured were reproducible within 0.05 K.

**Experimental Section**

**Table I.** Experimental Vapor Pressure of Anisaldehyde

<table>
<thead>
<tr>
<th>$t/°C$</th>
<th>$p^°/kPa$</th>
<th>$t/°C$</th>
<th>$p^°/kPa$</th>
<th>$t/°C$</th>
<th>$p^°/kPa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>74.7</td>
<td>0.15</td>
<td>110.9</td>
<td>1.00</td>
<td>189.0</td>
<td>20.0</td>
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<tr>
<td>83.6</td>
<td>0.25</td>
<td>126.3</td>
<td>2.00</td>
<td>212.6</td>
<td>40.0</td>
</tr>
<tr>
<td>92.5</td>
<td>0.40</td>
<td>146.0</td>
<td>4.50</td>
<td>235.8</td>
<td>70.0</td>
</tr>
<tr>
<td>100.4</td>
<td>0.60</td>
<td>167.9</td>
<td>10.0</td>
<td>248.7</td>
<td>100.0</td>
</tr>
</tbody>
</table>

**Table II.** Experimental Vapor Pressure of Methyl Anisate

<table>
<thead>
<tr>
<th>$t/°C$</th>
<th>$p^°/kPa$</th>
<th>$t/°C$</th>
<th>$p^°/kPa$</th>
<th>$t/°C$</th>
<th>$p^°/kPa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>108.6</td>
<td>0.54</td>
<td>151.4</td>
<td>3.70</td>
<td>181.5</td>
<td>11.20</td>
</tr>
<tr>
<td>121.3</td>
<td>1.00</td>
<td>160.2</td>
<td>5.20</td>
<td>191.8</td>
<td>15.70</td>
</tr>
<tr>
<td>132.7</td>
<td>1.71</td>
<td>168.2</td>
<td>7.00</td>
<td>198.7</td>
<td>19.50</td>
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<tr>
<td>137.9</td>
<td>2.15</td>
<td></td>
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</table>

**Table III.** Experimental Vapor Pressure of Anisyl Alcohol

<table>
<thead>
<tr>
<th>$t/°C$</th>
<th>$p^°/kPa$</th>
<th>$t/°C$</th>
<th>$p^°/kPa$</th>
<th>$t/°C$</th>
<th>$p^°/kPa$</th>
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<tr>
<td>80.6</td>
<td>0.060</td>
<td>114.3</td>
<td>0.00</td>
<td>162.2</td>
<td>5.00</td>
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<tr>
<td>87.9</td>
<td>0.10</td>
<td>127.3</td>
<td>1.00</td>
<td>178.8</td>
<td>9.99</td>
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<tr>
<td>98.6</td>
<td>0.20</td>
<td>141.4</td>
<td>2.00</td>
<td></td>
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**Literature Cited**


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