Solubility of Anthracene in Ternary Propanol + Butanol + 2,2,4-Trimethylpentane Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in ternary 1-propanol + 1-butanol + 2,2,4-trimethylpentane, 1-propanol + 2-butanol + 2,2,4-trimethylpentane, 2-propanol + 1-butanol + 2,2,4-trimethylpentane, and 2-propanol + 2-butanol + 2,2,4-trimethylpentane solvent mixtures at 25 °C. Nineteen compositions were studied for each of the four solvent systems. Results of these measurements are used to test the predictive ability of the ternary solvent form of the combined NIMS/Redlich–Kister equation. Computations showed that the model predicted the observed solubility behavior to within an overall average absolute deviation of about 0.9%.

Introduction
Solid–liquid equilibrium data of organic nonelectrolyte systems are becoming increasingly important in the petroleum industry, particularly in light of present trends toward heavier feedstocks and the known carcinogenicity/mutagenicity of many of the larger polycyclic aromatic compounds. Solubility data for a number of polycyclic aromatic hydrocarbons (i.e., anthracene and pyrene) and heteroatom polynuclear aromatics (i.e., carbazole, dibenzothiophene, and xanthene) have been published in the recent chemical literature. For a listing of references, see Acree (1994, 1995a,b). Despite efforts by experimentalists and scientific organizations, in terms of both new experimental measurements and critically evaluated data compilations, there still exist numerous systems for which solubility data are not readily available.

To address this problem, researchers have turned to group contribution methods and semiempirical equations to predict desired quantities from either pure component properties or measured binary data. In earlier studies we have used the binary solvent reduction of a predictive expression derived from a combined two- and three-body interactional mixing model as a mathematical representation for describing how the measured isothermal solubility of a crystalline solute varies with binary solvent composition. The binary reduction, referred to as the combined NIBS/Redlich–Kister equation, was found to accurately describe the observed solubility behavior in a large number of different binary solvent systems. We now extend our solubility studies to ternary solvent mixtures. Anthracene solubilities have been measured in the four ternary propanol + butanol + 2,2,4-trimethylpentane, 2-propanol + 1-butanol + 2,2,4-trimethylpentane, and 2-propanol + 2-butanol + 2,2,4-trimethylpentane solvent mixtures at 25 °C. Nineteen compositions were studied for each of the four solvent systems. Results of these measurements are used to test the predictive ability of expressions based upon the general mixing model used in deriving the combined NIBS/Redlich–Kister equation.

Experimental Methods

Anthracene (Acros, 99.9+%) was recrystallized three times from 2-propanone. 1-Propanol (Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), and 2,2,4-trimethylpentane (Aldrich, HPLC, 99.7+%) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mol % or better. Ternary solvent mixtures were prepared by mass so that compositions could be calculated to 0.0001 mole fraction. Excess solute and solvent were placed in sealed amber glass bottles and allowed to equilibrate with periodic agitation in a constant-temperature bath for at least 3 days. Attainment of equilibrium was verified both by repetitive measurements at a minimum of three additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at higher temperature.

Karl Fischer titrations performed on select samples both prior to and after equilibration gave, to within experimental uncertainty, identical water contents (mass/mass %) of <0.01%. The method of spectrophotometric analysis is discussed in an earlier paper (Powell et al., 1997). Experimental anthracene solubilities in the four propanol + butanol + 2,2,4-trimethylpentane solvent mixtures are listed in Table 1. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ±1.5%.

Results and Discussion

Expressions for predicting the thermodynamic properties of ternary nonelectrolyte systems have served as the point of departure for mathematical representation of experimental excess molar Gibbs energy, excess molar heat capacity, excess molar enthalpy, and excess molar volume data. Differences between predicted and observed values are expressed as

$$\left(\frac{Z_{E}}{Z_{E}^{E}}\right)^{exp} - \left(\frac{Z_{E}}{Z_{E}^{E}}\right)^{calc} = x_{A}x_{B}x_{C}Q_{ABC}$$

(1)

with Q-functions of varying complexity. For most systems encountered, the experimental data can be adequately
The parameters are denoted by the symbols sufficient precision to justify more than a few parameters, though rarely are experimental data determined with sufficient precision to warrant computerized storage in equation form. With computerized data storage and retrieval becoming increasingly popular, it seems appropriate to discuss the various mathematical expressions that have been proposed in the chemical literature for describing the variation of solute solubility with binary solvent composition. Mathematical representations not only provide a means to screen experimental data sets for possible outliers in need of redetermination but also facilitate interpolation at solvent compositions falling between measured data points.

Acree and co-workers (Acree, 1992; Acree and Zvaigzne, 1994; Acree et al., 1991) suggested a possible mathematical representation for isothermal solubility data based upon the combined NIBS/Redlich–Kister model

\[
\ln x_{A}^{(sat)} = x_{B}^{(sat)} \ln(x_{A}^{(sat)})_{B} + x_{C}^{(sat)} \ln(x_{A}^{(sat)})_{C} +
\]

where \(x_{A}^{(sat)}\) and \(x_{B}^{(sat)}\) refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present and \((x_{A}^{(sat)})_{B}\) denotes the measured solute solubility in pure solvent \(i\). The various \(S_{i}\) “curve-fit” parameters can be evaluated via least-squares analysis. Published papers (Zvaigzne et al., 1993; Zvaigzne and Acree, 1994; Acree et al., 1994; Acree and Zvaigzne, 1994) have reported the calculated \(S_{i}\) parameters for anthracene dissolved in the eight subbinary solvent systems, as well as the measured mole fraction solubilities in 1-propanol \((x_{A}^{(sat)} = 0.000\text{591})\), 2-propanol \((x_{A}^{(sat)} = 0.000\text{411})\), 1-butanol \((x_{A}^{(sat)} = 0.000\text{801})\), 2-butanol \((x_{A}^{(sat)} = 0.000\text{585})\) and 2,2,4-trimethylpentane \((x_{A}^{(sat)} = 0.000\text{747})\). Numerical values of the \(S_{i}\) parameters have been tabulated in Table 2 for convenience.

Equation 3 expresses the “excess” logarithmic molar fraction solubility, relative to the simple \(x_{A}^{(sat)} \ln(x_{A}^{(sat)})_{B} + x_{C}^{(sat)} \ln(x_{A}^{(sat)})_{C}\) arithmetic average, in terms of the Redlich–Kister equation. For a ternary solvent system, the mathematical representation takes the form of

\[
\ln x_{A}^{(sat)} = x_{B}^{(sat)} \ln(x_{A}^{(sat)})_{B} + x_{C}^{(sat)} \ln(x_{A}^{(sat)})_{C} + x_{D}^{(sat)} \ln(x_{A}^{(sat)})_{D} + x_{B}^{(sat)} \sum_{i=0}^{r} S_{i,BC}(x_{B}^{(sat)} - x_{C}^{(sat)})^{i} + x_{C}^{(sat)} \sum_{j=0}^{s} S_{j,BC}(x_{C}^{(sat)} - x_{D}^{(sat)})^{j} + x_{B}^{(sat)} x_{C}^{(sat)} \sum_{k=0}^{t} S_{k,CD}(x_{C}^{(sat)} - x_{D}^{(sat)})^{k}
\]
Table 3. Summarized Comparison Between Observed Anthracene Solubilities in Ternary Propanol + Butanol + 2,2,4-Trimethylpentane Solvent Mixtures and Predicted Values Based upon the Combined NIMS/Redlich–Kister Equation 4

<table>
<thead>
<tr>
<th>Ternary solvent mixture</th>
<th>% dev. a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-propanol (B) + 1-butanol (C) + 2,2,4-trimethylpentane (D)</td>
<td>0.77</td>
</tr>
<tr>
<td>1-propanol (B) + 2-butanol (C) + 2,2,4-trimethylpentane (D)</td>
<td>0.52</td>
</tr>
<tr>
<td>2-propanol (B) + 1-butanol (C) + 2,2,4-trimethylpentane (D)</td>
<td>1.11</td>
</tr>
<tr>
<td>2-propanol (B) + 2-butanol (C) + 2,2,4-trimethylpentane (D)</td>
<td>1.27</td>
</tr>
</tbody>
</table>

a Deviation (%) = (100/19)\[\sum((x_A^{(\text{sat})})_{\text{calc}} - (x_A^{(\text{sat})})_{\text{exp}})/(x_A^{(\text{sat})})_{\text{exp}}]\]

In keeping with our established terminology, the generalized mathematical representation given below

\[\ln x_A^{(\text{sat})} = \sum x_i^{(\text{sat})} \ln(x_A^{(\text{sat})})_i + \sum \sum x_i x_j \sum S_k ij (x_i^2 - x_i^3)\]

will be referred to hereafter as the combined nearly ideal multiple solvent (NIMS)/Redlich–Kister expression. The double summation extends over all binary combinations of solvents. Equation 4 can be used to predict the solubility as a function of ternary solvent composition, provided that all of the various curve-fit parameters are known. The predictive ability of eq 4 is summarized in Table 3 for anthracene dissolved in the four propanol + butanol + 2,2,4-trimethylpentane systems. Examination of the numerical entries in Table 3 reveals that eq 4 predicts the solubility of anthracene to within an overall average absolute deviation of 0.92%, which is comparable to the experimental uncertainty of ±1.5%. For the four systems studied, eq 4 was found to provide very accurate predictions of the observed solubility behavior.

Literature Cited


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