Experimental solubilities are reported for anthracene dissolved in 12 binary mixtures containing 1-propanol or 1-butanol with hexane, heptane, octane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane at 25 °C. Results of these measurements are used to test two mathematical representations based upon the combined nearly ideal binary solvent (NIBS)/Redlich–Kister equation and modified Wilson model. For the systems studied, the combined NIBS/Redlich–Kister equation was found to provide the better mathematical representation, with deviations between experimental and back-calculated values being on the order of ±1.5% or less.

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 known carcinogenicity/mutagenicity of many of the larger polycyclic aromatic compounds. Solubility data for a number of polycyclic aromatic hydrocarbons (1–5) (i.e., anthracene and pyrene) and heteroatom polynuclear aromatics (6–9) (i.e., carbazole, dibenzothiophene, and xanthene) have been published in the recent chemical literature. 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 actual solubility data are not readily available.

To address this problem, researchers have turned to group contribution methods and semiempirical expressions to predict desired quantities. Group contribution methods have proved fairly successful in estimating solid solubility in pure and binary solvent mixtures from structural information (10–17). Practical application though is limited to systems for which all group interaction parameters are known. Generally, interaction parameters are evaluated from solid–liquid and liquid–vapor equilibrium data. It is important that the data base contain as many different functional groups as possible, preferably with adequate representation from both mono- and multifunctional solute/solvent molecules to permit evaluation of potential synergistic effects. The data base should contain sufficient experimental values near infinite dilution in the event that one wishes to determine separate interaction parameters for finite concentration and infinite dilution activity coefficient predictions. The UNIFAC model (18) now has two sets of group interaction parameters, with the publication of the infinite dilution values by Bastos et al. (19).

Predictive expressions for solid–liquid equilibria have also been derived from simple thermodynamic mixing models. The nearly ideal binary solvent (NIBS) model (20–22) developed previously provides a relatively simple method for estimating the excess partial molar properties of a solute, Z_A^E, at infinite dilution in a binary solvent (components B and C)

\[ Z_A^E = f_B^o Z_A^B + f_C^o Z_A^C - \Gamma_A (x_B^o \Gamma_B + x_C^o \Gamma_C)^{-1} Z_{BC} \]  

(1)

in terms of a weighted mole fraction average of solute properties in the two pure solvents, \( Z_A^B \) and \( Z_A^C \), and a contribution due to the unmixing of the solvent pair by the presence of the solute. Equation 1 with \( Z_A^B = Z_A^C \) gives accurate predictions for naphthalene, iodine, p-dibromobenzene, benzil, p-benzoquinone, biphenyl, toluate, thiophene, carbazole, benzoic acid, and phenylacetic acid solubilities in systems of nonspecific physical interactions when molar volumes are used as weighting factors (\( \Gamma_A = V_{li} \)) (9, 22–26). Approximation of weighting factors with molecular surface areas enables eq 1 to provide accurate predictions for anthracene (1) and pyrene (3) solubilities in binary solvent mixtures containing benzene. More recently (27, 28), both the NIBS and modified Wilson (29) models have served as the point of departure for the mathematical representation of solute solubility as a function of solvent composition

\[ \ln x_A^{\text{set}} = x_B^o \ln (x_A^{\text{set}})_B + x_C^o \ln (x_A^{\text{set}})_C + x_B^o x_C^o \sum_{i=0}^{N} S_i (x_B^o - x_C^o)^i \]  

\[ \ln (x_A^{\text{solid}}/x_A^{\text{set}}) = 1 - x_B^o [1 - \ln (x_A^{\text{solid}})_A/(x_A^{\text{set}})_A] / (x_B^o + x_C^o \Lambda_{BC}^o) - x_C^o [1 - \ln (x_A^{\text{solid}})_C/(x_A^{\text{set}})_C] / (x_B^o \Lambda_{BC}^o + x_C^o) \]  

(3)

(4)

with the various \( S_i \) and \( \Lambda_{ij}^o \) coefficients computed from measured solubility data via least-squares analysis. The various symbols are defined in the Glossary.

Continued development of solution models for describing the thermodynamic properties of a solute in binary solvent systems requires that a large data base be available for assessing the applications and limitations of derived expressions. Currently, only a limited data base exists for crystalline nonelectrolyte solubility in binary solvent mixtures. For this reason, anthracene solubilities were determined in six alkane + 1-propanol and six alkane + 1-butanol mixtures. Results of these measurements are used to further test the descriptive abilities of eqs 3 and 4.

Experimental Methods

Anthracene (Aldrich, 99.9+%) was used as received. Cyclohexane (Aldrich, HPLC), hexane (Aldrich, 99%), heptane (Aldrich, HPLC), octane (Aldrich, 99+%, anhydrous), methylcyclohexane (Aldrich, 99+%, anhydrous), and 2,2,4-trimethylpentane (Aldrich, HPLC) were stored over molecular sieves to remove trace water shortly before use. 1-Propanol
Table I. Experimental Mole Fraction Solubilities of Anthracene (A) in Binary Alkane + 1-Propanol Solvent Mixtures at 25.0 °C

<table>
<thead>
<tr>
<th>x_A</th>
<th>x_B</th>
<th>x_A^expt</th>
<th>x_A^cal</th>
<th>x_B^expt</th>
<th>x_B^cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.001274</td>
<td>0.5447</td>
<td>0.001371</td>
<td>0.8712</td>
<td>0.000740</td>
</tr>
<tr>
<td>0.1751</td>
<td>0.001288</td>
<td>0.6331</td>
<td>0.001990</td>
<td>0.9411</td>
<td>0.000661</td>
</tr>
<tr>
<td>0.3162</td>
<td>0.001237</td>
<td>0.7297</td>
<td>0.001988</td>
<td>1.0000</td>
<td>0.000591</td>
</tr>
</tbody>
</table>

Table II. Experimental Mole Fraction Solubilities of Anthracene (A) in Binary Alkane + 1-Butanol Solvent Mixtures at 25.0 °C

<table>
<thead>
<tr>
<th>x_A</th>
<th>x_B</th>
<th>x_A^expt</th>
<th>x_A^cal</th>
<th>x_B^expt</th>
<th>x_B^cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.001274</td>
<td>0.4876</td>
<td>0.001218</td>
<td>0.8479</td>
<td>0.000981</td>
</tr>
<tr>
<td>0.1460</td>
<td>0.001316</td>
<td>0.5800</td>
<td>0.001162</td>
<td>0.9247</td>
<td>0.000887</td>
</tr>
<tr>
<td>0.2668</td>
<td>0.001310</td>
<td>0.6804</td>
<td>0.001068</td>
<td>1.0000</td>
<td>0.000801</td>
</tr>
</tbody>
</table>

(Alrich, 99%, anhydrous) and 1-butanol (Alrich, HPLC, 99.8%+) were stored over both anhydrous sodium sulfate and molecular sieves before being fractionally distilled. Gas chromatographic analysis showed solvent purities to be 99.7% or better. Karl Fisher titration gave water contents (w/w) of <0.003% and <0.01% for 1-propanol and 1-butanol, respectively. Binary solvent mixtures were prepared by weight so that compositions could be calculated to 0.0001 mole fraction.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant-temperature water bath at 25.0 ± 0.1 °C for several days. Attainment of equilibrium was verified by repetitive measurements after several additional days and by approaching equilibrium from supersaturation by prequillibrating the solutions at a higher temperature. Aliquots of saturated anthracene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol. Concentrations were determined spectrophotometrically at 356 nm on a Bausch and Lomb Spectronic 2000. Experimental anthracene solubilities in the 12 binary alkane + 1-propanol and alkane + 1-butanol mixtures studied are listed in Tables I and II, respectively. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ±1%. Experimental anthracene solubilities in the pure alkane solvents are in excellent agreement with published values in the chemical literature (1).

Results and Discussion

The ability of eqs 3 and 4 to mathematically represent the experimental solubility of anthracene in 12 binary alkane + 1-propanol and alkane + 1-butanol solvent systems is summarized in Table III in the form of "curve-fit" parameters and percent deviations in back-calculated solubilities for the two-parameter expressions. In the case of eq 3 the three-parameter form was also considered. During the course of evaluating parameters for the modified Wilson equation, it was noted on a = \Delta V_E versus \Delta V_L versus percent deviation three-dimensional map there existed several parameter pairs which described the anthracene solubility to within the same level of error. For example, in the case of anthracene solubilities in hexane + 1-butanol mixtures, the percent deviation was approximately 0.4% for \Delta V_E = 1.690 and \Delta V_L = 1.085, 1.2% for \Delta V_E = 1.810 and \Delta V_L = 1.000, and 1.2% for \Delta V_E = 1.1400 and \Delta V_L = 1.200. No special attempt was made to optimize calculated values as we wished only to learn if eq 4 could be used to mathematically represent experimental data in systems covering modest ranges in mole fraction solubilities. Any parameter set having ±1.5% deviation was sufficient for this purpose.

The numerical value of \alpha_A^solid = 0.0104 49 (1) in the modified Wilson computations was calculated from the molar enthalpy of fusion, \Delta H_f^m(A), at the normal melting point temperature of the solute, T_m:

$$\ln \alpha_A^\text{solid} = -\Delta H_f^m(T_m - T)/(RTT_m)$$

(5)

Attempts to eliminate \alpha_A^solid from the mathematical representation in favor of a simplified version (\alpha_A^solid = 1) proved unsuccessful.

Careful examination of Table III reveals that eq 4 provides fairly reasonable (though by no means perfect) mathematical representations of all 12 systems studied. Back-calculated and experimental values generally differ by less than ±2%, except those for 1-butanol mixtures containing 2,2,4-trimethylpentane and for 1-propanol mixtures containing cyclohexane and methylcyclohexane. These three systems exhibit modest maximum anthracene solubilities near pure alkane, and the "optimum" set of \Delta V_E values fails to predict the observed solubility maxima. In comparison, the three-parameter mathematical representation based upon the combined NIBS/Redlich–Kister models, eq 3, correctly predicts the solubility maxima and describes the data to within an average absolute deviation of ±0.5%, which is comparable to the experimental uncertainty. There may be one or two individual data points within each system, however, for which the deviations exceed ±2%.

From a computational standpoint, eq 3 will likely be preferred because most research groups involved in reporting
### Glossary

- \( \sigma^\text{solid} \): activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid.
- \( f_{B^o}^o \): weighted molar fraction composition of the binary solvent mixture, calculated as if the solute were not present.
- \( \Delta H_A^\text{fus} \): molar enthalpy of fusion of the solute.
- \( S_A^{\text{eq}} \): adjustable curve-fit parameter in the combined NIBS/Redlich–Kister mathematical representation.
- \( x_{B^o}^o \): mole fraction composition of the binary solvent mixture, calculated as if the solute were not present.

### Table III. Mathematical Representation of Anthracene Solubilities in Several Binary Alkane (B) + 1-Propanol (C) and Alkane (B) + 1-Butanol (C) Solvent Mixtures

<table>
<thead>
<tr>
<th>Binary solvent system</th>
<th>2-param eq 3 ( S_A^{\text{eq}} )</th>
<th>( % \text{ dev}^b )</th>
<th>3-param eq 3 ( S_A^{\text{eq}} )</th>
<th>( % \text{ dev}^b )</th>
<th>eq 4 ( \Delta V_j^{\text{adj}} )</th>
<th>( % \text{ dev}^{\text{adj}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane + 1-propanol</td>
<td>1.033</td>
<td>0.5</td>
<td>0.982</td>
<td>0.2</td>
<td>1.360</td>
<td>0.5</td>
</tr>
<tr>
<td>Heptane + 1-propanol</td>
<td>1.184</td>
<td>1.0</td>
<td>1.068</td>
<td>0.4</td>
<td>1.410</td>
<td>0.7</td>
</tr>
<tr>
<td>Octane + 1-propanol</td>
<td>1.340</td>
<td>0.9</td>
<td>1.275</td>
<td>0.3</td>
<td>1.240</td>
<td>0.6</td>
</tr>
<tr>
<td>Cyclohexane + 1-propanol</td>
<td>1.207</td>
<td>1.0</td>
<td>1.121</td>
<td>0.5</td>
<td>1.300</td>
<td>1.6</td>
</tr>
<tr>
<td>Methylcyclohexane + 1-propanol</td>
<td>1.291</td>
<td>0.8</td>
<td>1.235</td>
<td>0.5</td>
<td>1.344</td>
<td>1.4</td>
</tr>
<tr>
<td>2,2,4-trimethylpentane + 1-propanol</td>
<td>0.892</td>
<td>0.9</td>
<td>0.935</td>
<td>0.4</td>
<td>1.100</td>
<td>0.6</td>
</tr>
<tr>
<td>Hexane + 1-butanol</td>
<td>0.703</td>
<td>0.5</td>
<td>0.737</td>
<td>0.4</td>
<td>1.690</td>
<td>0.4</td>
</tr>
<tr>
<td>Heptane + 1-butanol</td>
<td>0.779</td>
<td>0.8</td>
<td>0.723</td>
<td>0.2</td>
<td>1.476</td>
<td>0.5</td>
</tr>
<tr>
<td>Octane + 1-butanol</td>
<td>0.933</td>
<td>0.6</td>
<td>0.909</td>
<td>0.4</td>
<td>1.460</td>
<td>0.5</td>
</tr>
<tr>
<td>Cyclohexane + 1-butanol</td>
<td>0.810</td>
<td>0.9</td>
<td>0.741</td>
<td>0.5</td>
<td>2.377</td>
<td>0.5</td>
</tr>
<tr>
<td>Methylcyclohexane + 1-butanol</td>
<td>0.948</td>
<td>1.1</td>
<td>0.850</td>
<td>1.0</td>
<td>2.387</td>
<td>0.9</td>
</tr>
<tr>
<td>2,2,4-trimethylpentane + 1-butanol</td>
<td>0.576</td>
<td>0.5</td>
<td>0.636</td>
<td>0.3</td>
<td>2.600</td>
<td>1.8</td>
</tr>
</tbody>
</table>

\( ^a \) Combined NIBS/Redlich–Kister curve-fit parameters are ordered as \( S_{A^0}^o, S_A^c, \) and \( S_A^{\text{eq}} \). \( ^b \) Deviation (%) = \((100/N)\sum\ln(x_{A^0}^o/x_{A^c}^o)\). \( ^c \) Adjustable parameters for the modified Wilson equation are ordered as \( \Delta V_j^{\text{adj}} \) and \( \Delta V_j^{\text{adj}} \).

### Literature Cited

(14) Basu, R. S.; Pham, H.; Wilson, D. P. Int. J. Thermophys. 1986, 7, 519.

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