Solubility of Anthracene in Binary Alcohol + 2-Propoxyethanol Solvent Mixtures


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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 polyyclic aromatic compounds. Solubility data for a number of polyyclic aromatic hydrocarbons (i.e., anthracene and pyrene) and heteroatom polyaromatics (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 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. Practical application, though, is limited to systems for which all group interaction parameters are known. Interaction parameters can be evaluated from experimental measurements and critically-evaluated data compilations, there still exist numerous systems for which solubility data are not readily available.

Continued development of solution models for describing the thermodynamic properties of a solute in binary solvent systems requires that a large database be available for assessing the applications and limitations of derived expressions. Currently, only a limited database exists for crystalline nonelectrolyte solubility in binary solvent mixtures. For this reason, anthracene solubilities were determined in seven binary alcohol + 2-propanoic acid solvent mixtures. Results of these measurements are used to further test the descriptive abilities of several previously derived expressions.

Experimental Methods

Anthracene (Aldrich, 99.9+%), 2-propanoic acid (Aldrich, 99+%), 1-propanoic acid (Aldrich, 99+% anhydrous), 2-propanoic acid (Aldrich, 99+% anhydrous), 1-butanoic acid (Aldrich, HPLC, 99.8+%), 2-butanoic acid (Aldrich, 99+% anhydrous), 1-pentanoic acid (Aldrich, 99%), 3-methyl-1-butanoic acid (Aldrich, 99+% anhydrous) and 1-octanoic acid (Aldrich, 99+%, anhydrous) were stored over both anhydrous sodium sulfate and molecular sieves before being fractionally distilled. Gas chromatographic analysis showed solvent purities to be 99.7 mol % or better. Karl Fischer titration gave water contents (mass/mass %) of <0.01% for all seven acids used. Binary solvent mixtures were prepared by mass 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 bath at (25.0 ± 0.1) °C for at last three days (often longer). Attainment of equilibrium was verified by repetitive measurements after a minimum of three additional days and by approaching equilibrium from supersaturation by preequilibrating 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 for spectrophotometric analysis at 356 nm on a Bausch and Lomb Spectronic 2000. Concentrations of the dilute solutions were determined from a Beer–Lambert law absorbance versus concentration working curve derived from measured absorbances of standard solutions of known molar concentration. Molar absorptivities of the nine standard solutions varied systematically with molar concentration, and ranged from ca. ε/L mol⁻¹ cm⁻¹ = 7450 to ε/L mol⁻¹ cm⁻¹ = 7150 for anthracene concentrations ranging from C/M = 6.75 × 10⁻⁵ to C/M = 2.25 × 10⁻⁴. Experimental anthracene solubilities in the seven binary alcohol + 2-propanoic acid mixtures studied 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 ±1.3%.

Results and Discussion

Acree and co-workers (Acree and Zvaigzne, 1991; Acree et al., 1991; Acree, 1992) suggested possible mathematical representations for isothermal solubility data based upon either a combined NIBS/Redlich–Kister model.
Present, the binary solvent calculated as if the solute were not be evaluated via least squares analysis. In eqs 1 and 2
\[
\ln x_A^{\text{sat}} = \ln x_A^{\text{SAT}} + x_C \ln x_C^{\text{SAT}} + \sum_{i=0}^{N} S_i (x_B^{\text{SAT}} - x_B)
\]
(1)

or modified Wilson equation (Comer and Kopecni, 1990)

\[
\ln[a_A(s)/x_A^{\text{sat}}] = 1 - x_B^{\text{SAT}}(1 - \ln[a_A(s)/(x_A^{\text{SAT}})_B])/(x_B^{\text{SAT}} + x_B^{\text{adj}}) - x_C(1 - \ln[a_A(s)/(x_A^{\text{SAT}})_C])/(x_B^{\text{adj}} + x_C)
\]
(2)

where the various $S_i$ and $\Lambda_{ij}^{\text{adj}}$ "curve-fit" parameters can be evaluated via least squares analysis. In eqs 1 and 2 $x_B^{\text{SAT}}$ and $x_C^{\text{SAT}}$ refer to the initial molar fraction composition of the binary solvent calculated as if the solute were not present, $a_A(s)$ is the activity of the solid solute, and $x_A^{\text{SAT}}$ is the saturated molar fraction solubility of the solute in pure solvent $i$. The numerical value of $a_A(s)$ was 0.01049 (Acree and Ryttig, 1983) used in the modified Wilson calculations was calculated from

\[
\ln a_A(s) = -\Delta_{\text{fus}} H_A(T_{\text{mp}} - T)/(RT_{\text{mp}})
\]
(3)

the molar enthalpy of fusion $\Delta_{\text{fus}} H_A$ (J mol$^{-1}$) = 28 860

\begin{table}
\centering
\caption{Experimental Mole Fraction Solubilities of Anthracene ($x_A^{\text{SAT}}$) in Binary Alcohol (B) + 2-Propoxyethanol (C) Solvent Mixtures at 25.0 °C}
\begin{tabular}{cccc}
\hline
\hline
Binary Solvent System & $x_A^{\text{sat}}$ & $x_B^{\text{sat}}$ & $x_C^{\text{sat}}$ \\
\hline
1-Propanol + 2-Propanol & 0.479 & 0.34 & 0.181 & 0.61 \\
1-Butanol + 2-Propanol & 0.457 & 0.33 & 0.213 & 0.58 \\
2-Butanone + 2-Propanol & 0.425 & 0.36 & 0.210 & 0.52 \\
1-Pentanol + 2-Propanol & 0.410 & 0.37 & 0.220 & 0.51 \\
3-Methyl-1-butanol + 2-Propanol & 0.395 & 0.38 & 0.225 & 0.53 \\
1-Octanol + 2-Propanol & 0.382 & 0.40 & 0.238 & 0.42 \\
\hline
\end{tabular}
\end{table}

\begin{table}
\centering
\caption{Mathematical Representation of Anthracene Solubilities in Several Binary Alcohol (B) + 2-Propoxyethanol (C) Solvent Mixtures}
\begin{tabular}{cccc}
\hline
\hline
Binary Solvent System & $S^n$ & $\% \text{dev}^b$ & $\Lambda_{BC}^{\text{adj}}$ & $\% \text{dev}^b$ \\
\hline
1-propanol + 2-propanol & 0.952 & 0.1 & 1.03 & 0.6 \\
1-butanol + 2-propanol & 0.715 & 0.3 & 1.02 & 0.4 \\
2-butanol + 2-propanol & 0.700 & 0.2 & 1.01 & 0.2 \\
1-pentanol + 2-propanol & 0.700 & 0.2 & 1.01 & 0.2 \\
3-methyl-1-butanol + 2-propanol & 0.889 & 0.3 & 1.03 & 0.7 \\
1-octanol + 2-propanol & 0.296 & 0.6 & 1.17 & 1.7 \\
\hline
\end{tabular}
\end{table}

\* Combined NIBS/Redlich–Kister curve-fit parameters are ordered as $S_0$, $S_1$, and $S_2$. b Dev (%) = (100 |$x_A^{\text{exp}} - x_A^{\text{calc}}$| / $x_A^{\text{exp}}$) 

(Weast, 1983) at the normal melting point temperature of the solute, $T_{\text{mp}} K = 490.0$

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the seven binary alcohol + 2-propanoyethanol solvent systems is summarized in Table 2 in the form of curve-fit parameters and percent deviations in back-calculated solubilities. Careful examination of Table 2 reveals that both equations provide an accurate mathematical representation for how the solubility of anthracene varies with solvent composition.

From the seven anthracene systems studied, the overall average absolute deviation between the experimental and calculated values is 0.3% and 0.6% for eqs 1 and 2, respectively, which is less than the experimental uncertainty.

From a computational standpoint, eq 1 will likely be preferred because most research groups involved in reporting thermodynamic properties have computer programs for evaluating the Redlich–Kister coefficients. With this idea in mind, we recommend not only that the future presentation of experimental isothermal solubility data for slightly soluble solid solutes dissolved in binary solvent mixtures include a tabulation of the actual observed values but if possible that the solubility data be mathematically represented by eq 1. Realizing that a single equation will not be applicable to all systems encountered, we further suggest eq 2 as an alternative mathematical representation for systems having extremely large solubility ranges and/or highly asymmetrical $x_C^{\text{SAT}}$ versus $x_B^{\text{SAT}}$ curves, such as the carbazole + alkane + tetrahydropyran systems reported previously (Acree et al., 1991).

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\textbf{Literature Cited}
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