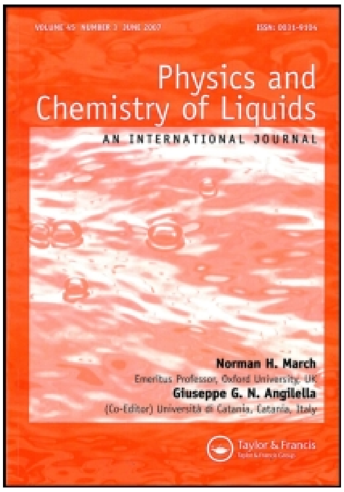

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SOLUBILITY OF ANTHRACENE IN BINARY ALCOHOL + 1-CHLOROBUTANE SOLVENT MIXTURES AT 298.2 K

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Experimental solubilities are reported for anthracene dissolved in six binary alcohol + 1-chlorobutane solvent mixtures at 25°C. The alcohol cosolvents studied were 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol and 3-methyl-1-butanol. Results of these measurements are used to test a mathematical representation based upon the combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister equation. For the six systems studied, the Combined NIBS/Redlich-Kister equation was found to mathematically describe the experimental data, with overall average absolute deviations between measured and calculated values being approximately ± 0.4%.

Keywords and Phrases: Anthracene solubilities; Binary solvent mixtures; Alcohol cosolvents

INTRODUCTION

Solid–liquid equilibrium data of organic nonelectrolyte systems are becoming increasingly important in the petroleum industry, particularly in light of present trends towards heavier feedstocks and known carcinogenicity/mutagenicity of many of the larger polycyclic aromatic compounds. Solubility data for a number of polycyclic aromatic

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*Corresponding author. e-mail: acree@unt.edu hydrocarbons (*i.e.*, anthracene and pyrene) and hetero-atom polynuclear aromatics (*i.e.*, carbazole, dibenzothiophene and xanthene) have been published in the recent chemical literature (for listing of references see Acree [1 – 3]). Despite efforts by experimentalists and scientific organizations, both in terms of 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 predictive methods as a means to generate desired quantities. Numerous equations have been suggested for predicting solute solubilities in binary solvent mixtures. For the most part, the predictive methods do provide fairly reasonable estimates for noncomplexing systems. There still remains, however, the need to develop better predictive expressions and mixing models to describe the more nonideal complexing systems believed to contain hydrogen bonding solvent components. 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 binary alcohol + 1-chlorobutane solvent mixtures. Results of these measurements are used to further test the descriptive ability of a previously derived expression.

EXPERIMENTAL METHODS

Anthracene (Aldrich, 99.9+%) was used as received. 1-Propanol (Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), 2-methyl-1-propanol (Aldrich, 99.5%, anhydrous), 3-methyl-1-butanol (Aldrich, 99+%, anhydrous) and 1-chlorobutane (Aldrich, HPLC, 99.5+%) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mole percent or better. Binary solvent mixtures were prepared by mass so that compositions could be calculated to 0.0001 mole fraction.

TABLE I Experimental mole fraction solubilities of anthracene (x_A^{sat}) in binary alcohol (B) + 1-chlorobutane (C) solvent mixtures at 25.0°C

x_c^o	x_A^{sat}
1-Propanol (B) + 1-Chlorobutane (C)	
0.0000	0.000591
0.0731	0.000813
0.1551	0.001126
0.3173	0.001902
0.4139	0.002451
0.5158	0.003093
0.7338	0.004631
0.8610	0.005514
1.0000	0.005863
2-Propanol (B) + 1-Chlorobutane (C)	
0.0000	0.000411
0.0805	0.000635
0.1540	0.000890
0.3197	0.001667
0.4269	0.002262
0.5299	0.002909
0.7374	0.004291
0.8571	0.005011
1.0000	0.005863
1-Butanol (B) + 1-Chlorobutane (C)	
0.0000	0.000801
0.0942	0.001085
0.1903	0.001429
0.3633	0.002234
0.4660	0.002830
0.5578	0.003428
0.7581	0.004781
0.8696	0.005421
1.0000	0.005863
2-Butanol (B) + 1-Chlorobutane (C)	
0.0000	0.000585
0.1013	0.000908
0.1830	0.001243
0.3546	0.002090
0.4685	0.002709
0.5766	0.003347
0.7704	0.004525
0.8708	0.005103
1.0000	0.005863
2-Methyl-1-propanol (B) + 1-Chlorobutane (C)	
0.0000	0.000470
0.0938	0.000720
0.1779	0.001008
0.3648	0.001855

TABLE I (Continued)

x_C^0	x_A^{sat}
0.4822	0.002570
0.5632	0.003066
0.7648	0.004474
0.8815	0.005308
1.0000	0.005863
3-Methyl-1-butanol (B) + 1-Chlorobutane (C)	
0.0000	0.000727
0.1061	0.001013
0.2037	0.001345
0.4165	0.002317
0.5132	0.002901
0.6148	0.003583
0.8018	0.004847
0.8844	0.005417
1.0000	0.005863

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 with periodic agitation for at least three days (often longer). Attainment of equilibrium was verified both by repetitive measurements after a minimum of three additional days and by approaching equilibrium from supersaturation by pre-equilibrating 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 concentrations. The calculated molar absorptivities of the nine standard solutions varied systematically with molar concentration and ranged from approximately $\varepsilon \approx 7450$ Liter mol^{-1} cm^{-1} to $\varepsilon \approx 7150$ Liter mol^{-1} cm^{-1} for anthracene concentrations ranging from $C = 6.75 \times 10^{-5}$ Molar to $C = 2.25 \times 10^{-4}$ Molar. Experimental anthracene solubilities in the six binary alcohol + 1-chlorobutane solvent mixtures are listed in Table I. 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

Acree and Zvaigzne [4] suggested that isothermal solubility data in binary solvent mixtures be reported in the chemical literature in terms of a mathematical representation based upon the Combined NIBS/Redlich-Kister model

$$\ln x_A^{\text{sat}} = x_B^o \ln(x_A^{\text{sat}})_B + x_C^o \ln(x_A^{\text{sat}})_C + x_B^o x_C^o \sum_{i=0}^{N} S_i (x_B^o - x_C^o)^i \quad (1)$$

with the various S_i "curve-fit" parameters evaluated *via* least squares analysis. In Eq. (1) x_B^o and x_C^o refer to the initial mole fraction composition of the binary solvent calculated as if solute (A) were not present, N is the number of curve-fit parameters used, and $(x_A^{\text{sat}})_i$ is the saturated mole fraction solubility of the solute in pure solvent i.

The Combined NIBS/Redlich-Kister model has been shown to provide very accurate mathematical representations of anthracene, pyrene and carbazole solubilities in a large number of both complexing and noncomplexing solvent mixtures [1–3]. Jouyban-Gharamaleki and coworkers [5–8] successfully used the volume fraction, Φ_i, modification of Eq. (1)

$$\ln x_A^{\text{sat}} = \Phi_B^o \ln(x_A^{\text{sat}})_B + \Phi_C^o \ln(x_A^{\text{sat}})_C + \Phi_B^o \Phi_C^o \sum_{i=0}^{N} S_i (\Phi_B^o - \Phi_C^o)^i \quad (2)$$

to describe the solubility behavior of various drug molecules in binary aqueous-organic solvent mixtures. In the case of structurally similar drug molecules the numerical values of the S_i coefficients were found to be nearly constant in a given binary solvent mixture [8]. More recently, Deng *et al.* [9–12] and Pribyla *et al.* [13–18] have shown that the S_i coefficients determined by regressing experimental anthracene solubility data in binary alkane + alkane, alkane + alcohol, alcohol + alcohol, alcohol + ether and alkane + ether solvent mixtures allows one to predict anthracene solubilities in ternary alkane + alkane + alcohol, alkane + alcohol + alcohol and alkane + alcohol + ether solvent mixtures. The predictive expression for the ternary solvent mixture is

$$\ln x_A^{\mathrm{sat}} = x_B^o \ln(x_A^{\mathrm{sat}})_B + x_C^o \ln(x_A^{\mathrm{sat}})_C + x_D^o \ln(x_A^{\mathrm{sat}})_D + x_B^o x_C^o \sum_{i=0}^{r} S_{i,BC}(x_B^o - x_C^o)^i + x_B^o x_D^o \sum_{j=0}^{s} S_{j,BD}(x_B^o - x_D^o)^j + x_C^o x_D^o \sum_{k=0}^{t} S_{k,CD}(x_C^o - x_D^o)^k \quad (3)$$

a mole fraction average of the logarithmic solute solubilities in the three pure solvents plus a Redlich-Kister summation term for each solvent pair.

The ability of Eq. (1) to mathematically represent the experimental solubility of anthracene in the six alcohol + 1-chlorobutane solvent mixtures is summarized in Table II in the form of "curve-fit" parameters and percent deviations in back-calculated solubilities. Each percent deviation is based upon the measured anthracene solubility data at the seven different binary solvent compositions. Careful examination of Table II reveals that Eq. (1) provided a fairly

TABLE II Mathematical representation of anthracene solubilities in several binary alcohol (B) + 1-chlorobutane (C) solvent mixtures

Binary solvent system	*Equation* (1)	
component (*B*) + *component* (*C*)	S_i[a]	% *Dev.*[b]
1-Propanol + 1-Chlorobutane	1.915 0.055 0.438	0.7
2-Propanol + 1-Chlorobutane	2.244 0.698 0.189	0.3
1-Butanol + 1-Chlorobutane	1.354 −0.186 0.210	0.2
2-Butanol + 1-Chlorobutane	1.819 0.570	0.4
2-Methyl-1-propanol + 1-Chlorobutane	1.881 0.218 0.281	0.4
3-Methyl-1-butanol + 1-Chlorobutane	1.229 −0.228 0.199	0.4

[a] Combined NIBS/Redlich-Kister curve-fit parameters are ordered as S_0, S_1 and S_2.
[b] Deviation(%) $= (100/N) \sum |[(x_A^{\mathrm{sat}})^{\mathrm{calc}} - (x_A^{\mathrm{sat}})^{\mathrm{exp}}]/(x_A^{\mathrm{sat}})^{\mathrm{exp}}|$.

accurate mathematical representation for how the solubility of anthracene varies with solvent composition. For the six anthracene systems studied, Eq. (1) was found to mathematically describe the observed mole fraction solubility data to within an overall average absolute deviation of about ± 0.4%, which is considerably less than the experimental uncertainty.

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