Solubility of Anthracene in Binary Alcohol + 2-Methyl-1-propanol and Alcohol + 3-Methyl-1-butanol Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in binary 2-propanol + 3-methyl-1-butanol, 2-propanol + 2-methyl-1-propanol, 1-propanol + 2-methyl-1-propanol, 1-octanol + 2-methyl-1-propanol, 1-butanol + 3-methyl-1-butanol, 2-butanol + 3-methyl-1-butanol, 2-butanol + 2-methyl-1-propanol, 1-octanol + 3-methyl-1-butanol, and 2-methyl-1-propanol + 3-methyl-1-butanol solvent mixtures 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 and modified Wilson equations were found to provide very reasonable mathematical representations, with most deviations between experimental and back-calculated values being on the order of ±1.0% 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 (*i.e.*, anthracene and pyrene) and heteroatom polynuclear aromatics (*i.e.*, carbazole, dibenzothiophene, and xanthene) have been published in the recent chemical literature (for listing of references, see: Acree, 1994, 1995, and in press). 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 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. 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 equilibria 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.

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 de-

termined in nine binary alcohol + alcohol solvent mixtures containing either 2-methyl-1-propanol or 3-methyl-1-butanol. Results of these measurements are used to further test the descriptive abilities of several previously derived expressions.

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+%, anhydrous), 3-methyl-1-butanol (Aldrich 99+%, anhydrous) and 1-octanol (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 alcohols 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 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 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. Concentrations were determined spectrophotometrically at 356 nm on a Bausch and Lomb Spectronic 2000. Experimental anthracene solubilities in the nine binary alcohol + alcohol 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 ±1.0%.

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

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Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Binary Alcohol (B) + Alcohol (C) Solvent Mixtures at 25.0 °C

$x_C^{0\,a}$	$x_A^{sat} \times 10^4$	$x_C^{0\,a}$	$x_A^{sat} \times 10^4$
3-Methyl-1-butanol (B) + 2-Butanol (C)			
0.0000	7.27	0.6485	6.35
0.1335	7.25	0.8191	6.20
0.2423	7.03	0.9090	5.97
0.4392	6.72	1.0000	5.85
0.5401	6.55		
2-Butanol (B) + 2-Methyl-1-propanol (C)			
0.0000	5.85	0.6002	5.13
0.1118	5.73	0.7892	4.94
0.2077	5.58	0.8840	4.84
0.3966	5.34	1.0000	4.70
0.4964	5.24		
1-Octanol (B) + 2-Methyl-1-propanol (C)			
0.0000	21.60	0.7215	9.01
0.1766	18.72	0.8697	6.70
0.3099	16.17	0.9351	5.68
0.5312	12.19	1.0000	4.70
0.6295	10.55		
3-Methyl-1-butanol (B) + 1-Butanol (C)			
0.0000	7.27	0.6471	7.81
0.1294	7.45	0.8112	7.93
0.2385	7.51	0.9031	8.01
0.4402	7.68	1.0000	8.01
0.5442	7.75		
3-Methyl-1-butanol (B) + 2-Methyl-1-propanol (C)			
0.0000	7.27	0.6456	5.67
0.1375	6.92	0.8175	5.23
0.2373	6.68	0.8981	4.97
0.4385	6.18	1.0000	4.70
0.5407	5.92		
3-Methyl-1-butanol (B) + 1-Octanol (C)			
0.0000	7.27	0.5109	14.25
0.0810	8.30	0.7229	17.18
0.1578	9.33	0.8415	19.10
0.3162	11.55	1.0000	21.60
0.4024	12.69		
1-Propanol (B) + 2-Methyl-1-propanol (C)			
0.0000	5.91	0.5554	5.29
0.0933	5.84	0.7554	5.04
0.1757	5.72	0.8733	4.91
0.3481	5.52	1.0000	4.70
0.4479	5.40		
2-Methyl-1-propanol (B) + 2-Propanol (C)			
0.0000	4.70	0.6500	4.39
0.1341	4.68	0.8204	4.25
0.2400	4.63	0.8973	4.21
0.4458	4.54	1.0000	4.11
0.5484	4.48		
3-Methyl-1-butanol (B) + 2-Propanol (C)			
0.0000	7.27	0.6833	5.19
0.1561	6.89	0.8398	4.63
0.2741	6.51	0.9209	4.36
0.4809	5.86	1.0000	4.11
0.5887	5.51		

^{a} x_C^0 is the initial mole fraction of component C calculated as if the solute were not present.

either a combined NIBS/Redlich–Kister model

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

or Modified Wilson equation (Comer and Kopecni, 1990)

$$\ln [a_A(s)/x_A^{sat}] = 1 - x_B^0 \{1 - \ln [a_A(s)/(x_A^{sat})_B]\}/(x_B^0 + x_C^0 \Lambda_{BC}^{adj}) - x_C^0 \{1 - \ln [a_A(s)/(x_A^{sat})_C]\}/(x_B^0 \Lambda_{CB}^{adj} + x_C^0) \quad (2)$$

where the various S_i and Λ_{ij}^{adj} "curve-fit" parameters can be evaluated via least squares analysis. In eqs 1 and 2

Table 2. Mathematical Representation of Anthracene Solubilities in Several Binary Alcohol (B) + Alcohol (C) Solvent Mixtures

binary solvent system component (B) + component (C)	eq 1		eq 2	
	$S_i{}^a$	% dev^b	$\Lambda_{ij}^{adj\,c}$	% dev^b
3-methyl-1-butanol + 2-butanol	0.093	0.8	2.229	0.4
	0.087		0.513	
2-butanol + 2-methyl-1-propanol^a		0.3	1.005	0.3
			0.993	
1-octanol + 2-methyl-1-propanol	0.940	0.5	0.601	1.3
	-0.340		1.933	
	0.341			
3-methyl-1-butanol + 1-butanol	0.065	0.4	0.929	0.3
			1.117	
3-methyl-1-butanol + 2-methyl-1-propanol	0.124	0.2	0.769	0.2
	-0.041		1.305	
3-methyl-1-butanol + 1-octanol	0.467	0.2	1.557	0.5
	0.166		0.641	
1-propanol + 2-methyl-1-propanol	0.078	0.4	0.569	0.4
	-0.019		1.705	
2-methyl-1-propanol + 2-propanol	0.098	0.2	0.193	0.3
	0.014		4.861	
3-methyl-1-butanol + 2-propanol	0.236	0.2	1.097	0.2
	0.036		1.037	

^{a} Combined NIBS/Redlich–Kister curve-fit parameters are ordered as S_0, S_1, and S_2. No curve-fit parameters were required in the case of the 2-butanol + 2-methyl-1-propanol system. ^{b} Deviation (%) = $(100/N) \sum |[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$. ^{c} Adjustable parameters for the modified Wilson equation are ordered as Λ_{BC}^{adj} and Λ_{CB}^{adj}.

x_B^0 and x_C^0 refer to the initial mole 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 $(x_A^{sat})_i$ is the saturated mole fraction solubility of the solute in pure solvent i. The numerical value of $a_A(s) = 0.010\,49$ (Acree and Rytting, 1983) used in the Modified Wilson computations was calculated from

$$\ln a_A(s) = -\Delta_{fus}H_A (T_{mp} - T)/(RTT_{mp}) \quad (3)$$

the molar enthalpy of fusion, $\Delta_{fus}H_A$, at the normal melting point temperature of the solute, T_{mp}.

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the nine binary alcohol + alcohol 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 representations provide very reasonable mathematical descriptions for how the solubility of anthracene varies with solvent composition. For the most part, back-calculated and experimental values differ by less than ±1.0%, which is comparable to 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 that the future presentation of experimental isothermal solubility data for slightly soluble solid solutes dissolved in binary solvent mixtures include not only 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 $\ln x_A^{sat}$ versus x_B^0 curves, such as the carbazole + alkane + tetrahydropyran systems reported previously (Acree et al., 1991).

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