Solubility of Anthracene and Pyrene in Binary Alcohol + Alcohol Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in binary 1-octanol + 2-propanol, 2-butanol + 1-butanol, 1-octanol + 1-butanol, 3-methyl-1-butanol + 1-propanol, and 2-methyl-1-propanol + 1–butanol mixtures at 25 °C, and for pyrene dissolved in binary solvent mixtures containing 2-ethyl-1-hexanol with 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-octanol, 2-methyl-1-propanol, and 3-methyl-1-butanol at 26 °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 12 systems studied, the combined NIBS/Redlich–Kister equation was found to provide an accurate mathematical representation of the experimental data, with an overall average absolute deviation between measured and calculated values being on the order of 0.4%. Slightly larger deviations were noted in the case of the modified Wilson equation.

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 a listing of references see Acree (1994, 1995a,b). 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 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 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.

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 and pyrene solubilities were determined in several binary alcohol + alcohol solvent mixtures. Results of these measurements are used to further test the descriptive abilities of several previously derived expressions.

Experimental Methods

Pyrene (Aldrich, 99+%) was recrystallized several times from anhydrous methanol, and anthracene (Aldrich, 99.9+%) was used as received. 2-Ethyl-1-hexanol (Aldrich, 99+%), 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 for at least three days (often longer) in a constant temperature water bath at (25.0 ± 0.1) and (26.0 ± 0.1) °C for anthracene and pyrene, respectively. Attainment of equilibrium was verified by repetitive measurements after a mimimum 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. Concentrations were determined spectrophotometrically at 356 nm (anthracene) and 372 nm (pyrene) on a Bausch and Lomb Spectronic 2000. Experimental anthracene and pyrene solubilities in the binary alcohol + alcohol mixtures studied are listed in Tables 1 and 2. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ±1.3%.

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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^o	x_A^{sat}	x_C^o	x_A^{sat}
3-Methyl-1-butanol (B) + 1-Propanol (C)			
0.0000	0.000 727	0.6906	0.000 652
0.1603	0.000 718	0.8525	0.000 622
0.2772	0.000 704	0.9232	0.000 611
0.4912	0.000 678	1.0000	0.000 591
0.5974	0.000 664		
1-Octanol (B) + 2-Propanol (C)			
0.0000	0.002 160	0.7587	0.000 851
0.2027	0.001 890	0.8887	0.000 614
0.3521	0.001 604	0.9359	0.000 528
0.5756	0.001 191	1.0000	0.000 411
0.6738	0.001 011		
1-Octanol (B) + 1-Butanol (C)			
0.0000	0.002 160	0.7283	0.001 196
0.1778	0.001 973	0.8662	0.000 997
0.3148	0.001 772	0.9559	0.000 876
0.5327	0.001 470	1.0000	0.000 801
0.6223	0.001 345		
2-Butanol (B) + 1-Butanol (C)			
0.0000	0.000 585	0.6062	0.000 692
0.1124	0.000 601	0.7936	0.000 740
0.2029	0.000 618	0.8888	0.000 771
0.3966	0.000 647	1.0000	0.000 801
0.5029	0.000 677		
2-Methyl-1-propanol (B) + 1-Butanol (C)			
0.0000	0.000 470	0.6086	0.000 671
0.1155	0.000 510	0.7919	0.000 733
0.2080	0.000 536	0.8909	0.000 769
0.4044	0.000 597	1.0000	0.000 801
0.5053	0.000 630		

Table 2. Experimental Mole Fraction Solubilities of Pyrene (x_A^{sat}) in Binary Alcohol (B) + 2-Ethyl-1-hexanol (C) Solvent Mixtures at 26.0 °C

x_C^o	x_A^{sat}	x_C^o	x_A^{sat}
1-Propanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.004 26	0.4405	0.007 74
0.0573	0.004 73	0.6606	0.009 46
0.1103	0.005 17	0.8155	0.010 81
0.2400	0.006 18	1.0000	0.012 50
0.3210	0.006 84		
2-Propanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.002 90	0.4282	0.006 54
0.0573	0.003 40	0.6540	0.008 50
0.1094	0.003 87	0.8071	0.010 13
0.2468	0.005 10	1.0000	0.012 50
0.3177	0.005 65		
1-Butanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.006 22	0.4703	0.008 81
0.0656	0.006 68	0.6889	0.010 21
0.1314	0.007 07	0.8218	0.011 11
0.2770	0.007 76	1.0000	0.012 50
0.3609	0.008 18		
2-Butanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.004 39	0.4632	0.008 04
0.0651	0.004 85	0.6592	0.009 68
0.1296	0.005 31	0.8325	0.011 18
0.2768	0.006 51	1.0000	0.012 50
0.3679	0.007 23		
2-Methyl-1-propanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.003 26	0.4824	0.007 22
0.0639	0.003 76	0.7042	0.009 20
0.1292	0.004 33	0.8052	0.010 22
0.2622	0.005 37	1.0000	0.012 50
0.3592	0.006 15		
3-Methyl-1-butanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.005 46	0.5090	0.008 41
0.0765	0.005 97	0.7344	0.010 09
0.1506	0.006 34	0.8285	0.010 88
0.3152	0.007 22	1.0000	0.012 50
0.4104	0.007 80		
1-Octanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.020 77	0.6056	0.014 83
0.0991	0.019 65	0.7955	0.013 65
0.2050	0.018 50	0.8911	0.013 06
0.4039	0.016 49	1.0000	0.012 50
0.5023	0.015 77		

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

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

or modified Wilson equation (Comer and Kopecni, 1990)

$$\begin{aligned} \ln[a_A(s)/x_A^{sat}] = \\ & 1 - x_B^o\{1 - \ln[a_A(s)/(x_A^{sat})_B]\}/(x_B^o + x_C^o \Lambda_{BC}^{adj}) - \\ & x_C^o\{1 - \ln[a_A(s)/(x_A^{sat})_C]\}/(x_B^o \Lambda_{CB}^{adj} + x_C^o) \end{aligned} \tag{2}$$

where the various S_i and Λ_{ij}^{adj} "curve-fit" parameters can be evaluated via least squares analysis. In eqs 1 and 2 x_B^o and x_C^o 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 values of $a_A(s) = 0.010\,49$ for anthracene (Acree and Rytting, 1983) and $a_A(s) = 0.1312$ for pyrene (Judy *et al.*, 1987) used in the modified Wilson computations were calculated from

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

$\Delta_{fus}H_A$ is the molar enthalpy of fusion 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 and pyrene in the binary alcohol + alcohol solvent systems is summarized in Tables 3 and 4 in the form of "curve-fit" parameters and percent deviations in back-calculated solubilities. Careful

Table 3. Mathematical Representation of Anthracene Solubilities in Several Binary Alcohol (B) + Alcohol (C) Solvent Mixtures

	eq 1		eq 2	
binary solvent system (component B + component C)	S_i[a]	% dev[b]	Λ_{ij}^{adj} [c]	% dev[b]
3-methyl-1-butanol + 1-propanol	0.125 −0.030 0.103	0.2	0.673 1.529	0.3
1-octanol + 2-propanol	1.352 −0.561 0.697	0.3	0.397 2.473	0.7
1-octanol + 1-butanol	0.528 −0.150 0.408	0.5	0.561 1.805	0.5
2-butanol + 1-butanol	−0.072	0.4	0.533 2.009	0.4
2-methyl-1-propanol + 1-butanol	0.100 0.001 0.133	0.2	1.593 0.581	0.5

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2. [b] Dev/% = $(100/N)\sum|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$. [c] Adjustable parameters for the modified Wilson equation are ordered as Λ_{BC}^{adj} and Λ_{CB}^{adj}.

Table 4. Mathematical Representation of Pyrene Solubilities in Several Binary Alcohol (B) + 2-Ethyl-1-hexanol (C) Solvent Mixtures

binary solvent system (component B + component C)	eq 1		eq 2	
	S_i[a]	% dev[b]	Λ_{ij}^{adj}[c]	% dev[b]
1-propanol + 2-ethyl-1-hexanol	0.500 0.300	0.5	1.669 0.597	1.0
2-propanol + 2-ethyl-1-hexanol	0.696 0.573 0.274	0.3	1.825 0.541	2.6
1-butanol + 2-ethyl-1-hexanol	0.048 0.152 0.291	0.4	1.145 0.873	1.0
2-butanol + 2-ethyl-1-hexanol	0.486	0.3	1.973 0.425	0.2
2-methyl-1-propanol + 2-ethyl-1-hexanol	0.594 0.405	0.6	1.609 0.617	1.6
3-methyl-1-butanol + 2-ethyl-1-hexanol	0.024 0.139 0.252	0.4	1.089 0.917	1.0
1-octanol + 2-ethyl-1-hexanol	−0.094	0.3	2.105 0.585	0.2

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2. [b] Dev/% = $(100/N)\sum|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$. [c] Adjustable parameters for the modified Wilson equation are ordered as Λ_{BC}^{adj} and Λ_{CB}^{adj}.

examination of Tables 3 and 4 reveals that the combined NIBS/Redlich−Kister equation provided the better mathematical representation for how the solubility varied with solvent composition. For the five anthracene and seven pyrene systems studied, the overall average absolute deviation between the experimental and calculated values is 0.4%, which is less than the experimental uncertainty. Slightly larger deviations were noted in the case of the modified Wilson equation.

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 $\ln x_A^{sat}$ versus x_B^{o} curves, such as the carbazole + alkane + tetrahydropyran systems reported previously (Acree *et al.*, 1991).

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