Solubility of Anthracene in Binary Alcohol + 2-Pentanol and Alcohol + 4-Methyl-2-pentanol Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in 16 binary mixtures containing either 2-pentanol or 4-methyl-2-pentanol with 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 1-octanol, 2-methyl-1-propanol and 3-methyl-1-butanol 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 16 systems studied, both equations were found to provide an accurate mathematical representation of the experimental data, with an overall average absolute deviation between measured and calculated values being 0.3% and 0.5% for the combined NIBS/Redlich−Kister and modified Wilson equations, respectively.

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, 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 semi-empirical 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 liquid−vapor, liquid−liquid, and solid−liquid 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 determined in 16 binary alcohol + 2-pentanol and alcohol + 4-methyl-2-pentanol 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+%) 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), 1-pentanol (Aldrich 99%), 2-methyl-1-propanol (Aldrich 99+%, anhydrous), 3-methyl-1-butanol (Aldrich 99+%, anhydrous), 1-octanol (Aldrich 99+%, anhydrous), 2-pentanol (Acros 99+%), and 4-methyl-2-pentanol (Acros 99+%) 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 10 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 at last 3 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 concentration. Molar absorptivities of the nine standard solutions varied systematically with molar concentration and ranged from approximately $\epsilon/(\mathrm{L\ mol^{-1}\ cm^{-1}}) = 7450$ to $\epsilon/(\mathrm{L\ mol^{-1}\ cm^{-1}}) = 7150$ for anthracene concentrations ranging from $C/(\mathrm{mol\ L^{-1}}) = 6.75 \times 10^{-5}$ to $C/(\mathrm{mol\ L^{-1}}) = 2.25 \times 10^{-4}$. Experimental anthracene solubilities in the eight binary alcohol + 2-pentanol and eight binary alcohol + 4-methyl-2-pentanol mixtures studied are listed in Tables 1 and 2,

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Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Binary Alcohol (B) + 2-Pentanol (C) Solvent Mixtures at 25.0 °C

x_C^o	x_A^{sat}	x_C^o	x_A^{sat}
1-Propanol (B) + 2-Pentanol (C)			
0.0000	0.000 591	0.5184	0.000 693
0.0754	0.000 605	0.7333	0.000 737
0.1340	0.000 617	0.8555	0.000 763
0.3093	0.000 650	1.0000	0.000 800
0.4323	0.000 679		
2-Propanol (B) + 2-Pentanol (C)			
0.0000	0.000 411	0.5097	0.000 610
0.0812	0.000 445	0.7304	0.000 692
0.1532	0.000 476	0.8564	0.000 739
0.3184	0.000 538	1.0000	0.000 800
0.4117	0.000 586		
1-Butanol (B) + 2-Pentanol (C)			
0.0000	0.000 801	0.5644	0.000 798
0.0983	0.000 797	0.7670	0.000 802
0.1779	0.000 803	0.8801	0.000 796
0.3629	0.000 804	1.0000	0.000 800
0.4531	0.000 800		
2-Butanol (B) + 2-Pentanol (C)			
0.0000	0.000 585	0.5592	0.000 699
0.0923	0.000 601	0.7635	0.000 741
0.1738	0.000 618	0.8817	0.000 769
0.3568	0.000 650	1.0000	0.000 800
0.4481	0.000 677		
2-Methyl-1-propanol (B) + 2-Pentanol (C)			
0.0000	0.000 470	0.5678	0.000 645
0.0929	0.000 497	0.7592	0.000 706
0.1744	0.000 525	0.8556	0.000 745
0.3584	0.000 575	1.0000	0.000 800
0.4603	0.000 607		
1-Pentanol (B) + 2-Pentanol (C)			
0.0000	0.001 097	0.6137	0.000 912
0.1438	0.001 048	0.7819	0.000 857
0.2514	0.001 003	0.8761	0.000 828
0.4638	0.000 950	1.0000	0.000 800
0.5418	0.000 932		
3-Methyl-1-butanol (B) + 2-Pentanol (C)			
0.0000	0.000 727	0.6382	0.000 779
0.1465	0.000 746	0.7709	0.000 787
0.2478	0.000 751	0.9005	0.000 796
0.4688	0.000 764	1.0000	0.000 800
0.5703	0.000 772		
1-Octanol (B) + 2-Pentanol (C)			
0.0000	0.002 160	0.7177	0.001 191
0.1481	0.001 989	0.8523	0.001 007
0.2618	0.001 841	0.9345	0.000 891
0.4964	0.001 485	1.0000	0.000 800
0.6001	0.001 348		

Table 2. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Binary Alcohol (B) + 4-Methyl-2-pentanol (C) Solvent Mixtures at 25.0 °C

x_C^o	x_A^{sat}	x_C^o	x_A^{sat}
1-Propanol (B) + 4-Methyl-2-pentanol (C)			
0.0000	0.000 591	0.4714	0.000 660
0.0621	0.000 606	0.6903	0.000 699
0.1344	0.000 617	0.8427	0.000 740
0.2855	0.000 635	1.0000	0.000 779
0.3712	0.000 645		
2-Propanol (B) + 4-Methyl-2-pentanol (C)			
0.0000	0.000 411	0.4856	0.000 578
0.0727	0.000 440	0.7048	0.000 659
0.1381	0.000 460	0.8458	0.000 710
0.2927	0.000 512	1.0000	0.000 779
0.3827	0.000 542		
1-Butanol (B) + 4-Methyl-2-pentanol (C)			
0.0000	0.000 801	0.5283	0.000 771
0.0894	0.000 787	0.7448	0.000 773
0.1639	0.000 781	0.8511	0.000 778
0.3256	0.000 777	1.0000	0.000 779
0.4213	0.000 775		
2-Butanol (B) + 4-Methyl-2-pentanol (C)			
0.0000	0.000 585	0.5267	0.000 689
0.0776	0.000 601	0.7373	0.000 733
0.1529	0.000 616	0.8539	0.000 755
0.3215	0.000 649	1.0000	0.000 779
0.4234	0.000 669		
2-Methyl-1-propanol (B) + 4-Methyl-2-pentanol (C)			
0.0000	0.000 470	0.5312	0.000 624
0.0782	0.000 492	0.7464	0.000 694
0.1532	0.000 513	0.8586	0.000 728
0.3293	0.000 563	1.0000	0.000 779
0.4411	0.000 596		
1-Pentanol (B) + 4-Methyl-2-pentanol (C)			
0.0000	0.001 097	0.5579	0.000 876
0.0988	0.001 059	0.7586	0.000 833
0.1781	0.001 024	0.8682	0.000 809
0.3605	0.000 955	1.0000	0.000 779
0.4934	0.000 901		
3-Methyl-1-butanol (B) + 4-Methyl-2-pentanol (C)			
0.0000	0.000 727	0.6268	0.000 765
0.0918	0.000 737	0.7599	0.000 770
0.1797	0.000 742	0.8811	0.000 775
0.3346	0.000 749	1.0000	0.000 779
0.5108	0.000 758		
1-Octanol (B) + 4-Methyl-2-pentanol (C)			
0.0000	0.002 160	0.6361	0.001 246
0.1228	0.002 057	0.8159	0.001 021
0.2448	0.001 865	0.9045	0.000 916
0.4543	0.001 490	1.0000	0.000 779
0.5803	0.001 317		

respectively. 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

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

or modified Wilson equation (Comer and Kopecni, 1990)

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

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 value of $a_A(s) = 0.010\,49$ (Acree and Rytting, 1983) used in the modified Wilson computations was calculated from

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

the molar enthalpy of fusion, $\Delta_{fus}H_A$/J mol^{-1} = 28 860 (Weast, 1983), at the normal melting point temperature of the solute, T_{mp}/K = 490.0.

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the 16 binary alcohol + 2-pentanol and alcohol + 4-methyl-2-pentanol solvent systems is summarized in Table 3 in the form of "curve-fit" parameters and percent deviations in back-

Table 3. Mathematical Representation of Anthracene Solubilities in Several Binary Alcohol (B) + 2-Pentanol (C) and Alcohol (B) + 4-Methyl-2-pentanol (C) Solvent Mixtures

	eq 1		eq 2	
binary solvent system component (B) + component (C)	S_i[a]	% dev[b]	$\Lambda_{ij}^{\text{adj}}$ [c]	% dev[b]
1-propanol + 2-pentanol[a]		0.3	1.057 0.941	0.2
2-propanol + 2-pentanol	0.216 0.134	0.4	1.472 0.675	0.8
1-butanol + 2-pentanol[a]		0.3	1.000 1.000	0.3
2-butanol + 2-pentanol[a]		0.3	1.000 1.002	0.3
2-methyl-1-propanol + 2-pentanol	0.059	0.4	1.028 1.000	0.4
1-pentanol + 2-pentanol[a]		0.5	0.941 1.057	0.5
3-methyl-1-butanol + 2-pentanol	0.034	0.3	1.561 0.637	0.3
1-octanol + 2-pentanol	0.497 −0.089 0.179	0.3	1.120 1.360	0.6
1-propanol + 4-methyl-2-pentanol	−0.045 0.119	0.7	0.815 1.220	0.6
2-propanol + 4-methyl-2-pentanol	0.106 0.123 0.095	0.4	1.258 0.788	0.6
1-butanol + 4-methyl-2-pentanol	−0.097 −0.077	0.2	2.652 0.361	0.2
2-butanol + 4-methyl-2-pentanol	0.060	0.2	0.883 1.202	0.1
2-methyl-1-propanol + 4-methyl-2-pentanol	0.064	0.2	1.260 0.767	0.2
1-pentanol + 4-methyl-2-pentanol	−0.103 0.056 0.141	0.4	2.680 0.436	0.4
3-methyl-1-butanol + 4-methyl-2-pentanol	0.042	0.3	1.608 0.622	0.2
1-octanol + 4-methyl-2-pentanol	0.379 0.028 0.566	0.3	2.140 1.025	1.5

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 1-propanol + 2-pentanol, 1-butanol + 2-pentanol, 2-butanol + 2-pentanol, and 1-pentanol + 2-pentanol systems. Deviation (%) = $(100/7)\sum_{i=1}^{7}|[(x_A^{\text{sat}})_i^{\text{calc}} - (x_A^{\text{sat}})_i^{\text{exp}}]/(x_A^{\text{sat}})_i^{\text{exp}}|$. [c] Adjustable parameters for the modified Wilson equation are ordered $^{\text{adj}}_{\text{BC}}$ and $\Lambda^{\text{adj}}_{\text{CB}}$.

calculated solubilities. Careful examination of Table 3 reveals that both equations provide an accurate mathematical representation for how the solubility of anthracene varies with solvent composition. For the 16 anthracene systems studied, the overall average absolute deviation between the experimental and calculated values is 0.3% and 0.5% 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 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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