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Solubility of Anthracene in Binary Alkane + 2-Ethyl-1-hexanol and Alkane + 1-Pentanol Solvent Mixtures at 298.2 K

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Experimental solubilities are reported for anthracene dissolved in six binary alkane + 2-ethyl-1-hexanol and four binary alkane + 1-pentanol solvent mixtures at 25 °C. The alkane cosolvents studied were hexane, heptane, octane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane. Results of these measurements are used to test two mathematical representations based upon the combined nearly ideal binary solvent (NIBS)/Redlich−Kister and modified Wilson equations. For the 10 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 0.6% and 1.0% for the combined NIBS/Redlich−Kister and modified Wilson equations, respectively.

Introduction

This work continues our establishment of a solubility database for crystalline nonelectrolyte solutes dissolved in binary solvent mixtures containing either alcohol or alkoxyalcohol cosolvents. Such systems exhibit hydrogen-bond formation, and the measured solubility data is being used to test the limitations and applications of various thermodynamic mixing models. To date, we have shown that predictive expressions derived from mobile order theory and the Kretschmer−Wiebe model provide very reasonable estimates for the solubility behavior of anthracene in 57 different binary alcohol + alcohol solvent mixtures (Powell et al., 1997b), and for pyrene in 42 different binary alcohol + alcohol mixtures (McHale et al., 1997). Deviations between predicted and observed values were on the order of ±2%, with the various alcohol self-association stability constants determined from a regressional analysis of vapor−liquid equilibria for binary alkane + alcohol systems. Both thermodynamic treatments included formation of homogeneous self-associated and heterogeneous cross-associated hydrogen-bonded chains.

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

x_C°	x_A^{sat}	x_C°	x_A^{sat}
Hexane (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.001 274	0.5590	0.001 529
0.0983	0.001 422	0.7647	0.001 504
0.1794	0.001 469	0.8718	0.001 451
0.3597	0.001 516	1.0000	0.001 397
0.4565	0.001 525		
Heptane (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.001 571	0.5718	0.001 615
0.1116	0.001 647	0.7850	0.001 517
0.1972	0.001 669	0.8865	0.001 464
0.3931	0.001 656	1.0000	0.001 397
0.4806	0.001 639		
Octane (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.001 838	0.6148	0.001 712
0.1190	0.00 1907	0.8102	0.001 606
0.2139	0.001 898	0.8932	0.001 527
0.4149	0.001 835	1.0000	0.001 397
0.5098	0.001 785		
Cyclohexane (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.001 553	0.5098	0.001 596
0.0590	0.001 658	0.7412	0.001 535
0.1441	0.001 689	0.8616	0.001 492
0.3159	0.001 659	1.0000	0.001 397
0.4036	0.001 632		
Methylcyclohexane (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.001 649	0.5499	0.001 633
0.0890	0.001 830	0.7667	0.001 563
0.1771	0.001 819	0.8751	0.001 498
0.3610	0.001 726	1.0000	0.001 397
0.4509	0.001 685		
2,2,4-Trimethylpentane (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.001 074	0.6103	0.001 387
0.1144	0.001 184	0.7935	0.001 415
0.2135	0.001 232	0.8027	0.001 419
0.4193	0.001 325	0.8974	0.001 414
0.5143	0.001 357	1.0000	0.001 397

Powell et al. (1997c) recently utilized mobile order theory and the Kretschmer−Wiebe model to describe the solubility behavior of anthracene in binary alkane + alcohol solvent mixtures. The study examined whether the two mixing models could predict anthracene solubilities using association constants and binary interaction parameters deduced from vapor−liquid equilibria (VLE) data for the same alkane + alcohol system. The authors found that both models performed satisfactorily. The Kretschmer−Wiebe model did provide, however, slightly better fits of the VLE data and slightly better predictions of anthracene solubilities. In fairness it should be noted that for many of the systems the VLE data was at a higher temperature than the solubility data, and the calculated stability constants were extrapolated back to $T/(\mathrm{K}) = 298.15$ using an assumed value of $\Delta H^\circ/(\mathrm{kJ\ mol^{-1}}) = -25.1$ for the standard enthalpy of hydrogen-bond formation. Subsequent computations (Acree and Campbell, 1997) indicate that this value is much too large. More reasonable values are $\Delta H^\circ/(\mathrm{kJ\ mol^{-1}}) = -19.6$ and $\Delta H^\circ/(\mathrm{kJ\ mol^{-1}}) = -10.6$ for the Kretschmer−Wiebe and mobile order models, respectively. The lower

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

x_C°	x_A^{sat}	x_C°	x_A^{sat}
Octane (B) + 1-Pentanol (C)			
0.0000	0.001 838	0.6974	0.001 476
0.1484	0.001 859	0.8585	0.001 256
0.2791	0.001 816	0.9270	0.001 166
0.5026	0.001 668	1.0000	0.001 097
0.6018	0.001572		
Cyclohexane (B) + 1-Pentanol (C)			
0.0000	0.001 553	0.6088	0.001 427
0.0946	0.001 643	0.7975	0.001 248
0.2023	0.001 646	0.8991	0.001 154
0.4103	0.001 578	1.0000	0.001 097
0.5108	0.001501		
Methylcyclohexane (B) + 1-Pentanol (C)			
0.0000	0.001 649	0.6304	0.001 451
0.1269	0.001 778	0.8161	0.001 245
0.2316	0.001 734	0.9074	0.001 157
0.4458	0.001 615	1.0000	0.001 097
0.5347	0.001 542		
2,2,4-Trimethylpentane (B) + 1-Pentanol (C)			
0.0000	0.001 074	0.7171	0.001 196
0.1428	0.001 182	0.8640	0.001 143
0.2960	0.001 224	0.9318	0.001 115
0.5244	0.001 235	1.0000	0.001 097
0.6141	0.001 214		

enthalpy values do improve each model's predictive ability, and it may be necessary at some later date to reexamine several of the conclusions reached by Powell et al.

To increase the solubility database available for such comparisons, we are in the process of measuring additional solubility data for pyrene (Hernández et al., 1998) and anthracene in binary alkane + alcohol solvent mixtures. In the present communication we report anthracene solubilities in six binary solvent mixtures containing 2-ethyl-1-hexanol with hexane, heptane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane and in four binary solvent mixtures containing 1-pentanol with octane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane at 298.15 K. Anthracene solubilities in binary hexane + 1-pentanol and heptane + 1-pentanol mixtures are reported in an earlier publication (Powell et al., 1997c).

Experimental Methods

Anthracene (Acros, 99.9+%) was recrystallized three times from 2-propanone. 2-Ethyl-1-hexanol (Acros, 99+%), 1-pentanol (Aldrich, 99%), hexane (Aldrich, 99+%), heptane (Aldrich, HPLC), octane (Aldrich, 99+%, anhydrous), cyclohexane (Aldrich, HPLC), methylcyclohexane (Aldrich, 99+%, anhydrous), and 2,2,4-trimethylpentane (Aldrich, HPLC) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mol% or better. Binary solvent mixtures were prepared by mass so that compositions could be calculated to 0.0001 mole fraction. Karl Fischer titrations performed on select samples both prior to and after equilibration gave, to within experimental uncertainty, identical water contents (mass/mass %) of <0.01%. The methods of sample equilibration and spectrophotometric analysis are discussed in an earlier paper (Powell et al., 1997a). Experimental anthracene solubilities in the six binary alkane + 2-ethyl-1-hexanol and four binary alkane + 1-pentanol solvent mixtures are listed in Tables 1 and

Table 3. Mathematical Representation of Anthracene Solubilities in Several Binary Alkane (B) + Alcohol (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]
hexane + 2-ethyl-1-hexanol	0.527	0.8	2.478	0.9
	0.344		0.709	
	0.417			
heptane + 2-ethyl-1-hexanol	0.389	0.2	1.927	0.3
	0.166		0.883	
	0.131			
octane + 2-ethyl-1-hexanol	0.430	0.3	1.898	1.0
	0.023		1.028	
	0.356			
cyclohexane + 2-ethyl-1-hexanol	0.278	0.8	2.884	1.5
	0.323		0.593	
	0.810			
methylcyclohexane + 2-ethyl-1-hexanol	0.327	1.1	2.913	2.5
	0.458		0.651	
	0.944			
2,2,4-trimethylpentane + 2-ethyl-1-hexanol	0.394	0.3	1.492	0.7
	0.118		0.941	
	0.233			
octane + 1-pentanol	0.688	0.7	1.695	0.6
	0.130		1.289	
	−0.241			
cyclohexane + 1-pentanol	0.591	0.7	2.681	0.7
	0.472		0.854	
	0.010			
methylcyclohexane + 1-pentanol	0.622	0.9	2.884	1.0
	0.524		0.883	
	0.058			
2,2,4-trimethylpentane + 1-pentanol	0.530	0.5	2.043	0.3
	0.242		0.767	
	−0.011			

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2. [b] Deviation (%) = $(100/N)\sum|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$; where N represents the number of binary solvent compositions in each solvent set. For 9 of the 10 solvent mixtures studied $N = 7$. In the case of the 2,2,4-trimethylpentane + 2-ethyl-1-hexanol solvent system, anthracene solubilities were determined at eight binary solvent compositions, and $N = 8$. [c] Adjustable parameters for the modified Wilson equation are ordered as Λ_{BC}^{adj} and Λ_{CB}^{adj}.

2, respectively. 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 (1991) suggested possible mathematical representations for isothermal solubility data based upon either a combined NIBS/Redlich−Kister model

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

or a modified Wilson equation

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

where the various S_i and Λ_{ij}^{adj} "curve-fit" parameters can be evaluated via least-squares analysis. In eqs 1 and 2 x_B° and x_C° refer to the initial mole fraction composition of the binary solvent calculated as if solute A were not present, $a_A(s)$ is the activity of the solid solute, N is the number of curve-fit parameters used, and $(x_A^{sat})_i$ is the saturated mole fraction solubility of the solute in pure solvent i. The numerical value of the activity of the solid solute used in the modified Wilson computations was $a_A(s) = 0.009\,84$. The computation of $a_A(s)$ from enthalpy of fusion data is discussed in greater detail in a previously published paper (Powell et al., 1997a).

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the 10 binary alkane + alcohol mixtures is summarized in Table 3 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, except for the binary 2,2,4-trimethylpentane + 2-ethyl-1-hexanol solvent mixture. Solubilities were determined at eight binary solvent compositions for this latter solvent system. 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 10 anthracene systems studied, the overall average absolute deviation between the experimental and calculated values is 0.6% and 1.0% for eqs 1 and 2, respectively, which is less than the experimental uncertainty.

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