Solubility of Anthracene in Binary Alkane + 1-Propanol and Alkane + 1-Butanol Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in 12 binary mixtures containing 1-propanol or 1-butanol with hexane, heptane, octane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane 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 equation was found to provide the better mathematical representation, with deviations between experimental and back-calculated values being on the order of ±1.5% 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 (*1–5*) (i.e., anthracene and pyrene) and heteroatom polynuclear aromatics (*6–9*) (i.e., carbazole, dibenzothiophene, and xanthene) have been published in the recent chemical literature. 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 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 (*10–17*). 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. The UNIFAC model (*18*) now has two sets of group interaction parameters, with the publication of the infinite dilution values by Bastos et al. (*19*).

Predictive expressions for solid–liquid equilibria have also been derived from simple thermodynamic mixing models. The nearly ideal binary solvent (NIBS) model (*20–22*) developed previously provides a relatively simple method for estimating the excess partial molar properties of a solute, Z_A^E, at infinite dilution in a binary solvent (components B and C)

$$Z_A^E = f_B{}^\circ (Z_A^E)_B + f_C{}^\circ (Z_B^E)_C - \Gamma_A (x_B{}^\circ \Gamma_B + x_C{}^\circ \Gamma_C)^{-1} Z_{BC}^E \quad (1)$$

$$f_B{}^\circ = 1 - f_C{}^\circ = x_B{}^\circ \Gamma_B / (x_B{}^\circ \Gamma_B + x_C{}^\circ \Gamma_C) \quad (2)$$

in terms of a weighted mole fraction average of solute properties in the two pure solvents, $(Z_A^E)_B$ and $(Z_A^E)_C$, and a contribution due to the unmixing of the solvent pair by the presence of the solute. Equation 1 with $Z^E = G^E$ gives accurate predictions for naphthalene, iodine, *p*-dibromobenzene, benzil, *p*-benzoquinone, biphenyl, tolylacetic acid, thianthrene, carbazole, benzoic acid, and phenylacetic acid solubilities in systems of nonspecific physical interactions when molar volumes are used as weighting factors ($\Gamma_i = V_i$) (*9, 22–26*). Approximation of weighting factors with molecular surface areas enables eq 1 to provide accurate predictions for anthracene (*1*) and pyrene (*3*) solubilities in binary solvent mixtures containing benzene. More recently (*27, 28*), both the NIBS and modified Wilson (*29*) models have served as the point of departure for the mathematical representation of solute solubility as a function of solvent composition

$$\ln x_A^{sat} = x_B{}^\circ \ln(x_A^{sat})_B + x_c{}^\circ \ln(x_A^{sat})_C + x_B{}^\circ x_C{}^\circ \sum_{i=0}^{N} S_i (x_B{}^\circ - x_C{}^\circ)^i \quad (3)$$

$$\ln(a_A^{solid}/x_A^{sat}) = 1 - x_B{}^\circ \{1 - \ln[a_A^{solid}/(x_A^{sat})_B]\}/(x_B{}^\circ + x_C{}^\circ \Lambda_{BC}^{adj}) - x_C{}^\circ \{1 - \ln[a_A^{solid}/(x_A^{sat})_C]\}/(x_B{}^\circ \Lambda_{CB}^{adj} + x_C{}^\circ) \quad (4)$$

with the various S_i and Λ_{ij}^{adj} coefficients computed from measured solubility data via least-squares analysis. The various symbols are defined in the Glossary.

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 alkane + 1-propanol and six alkane + 1-butanol mixtures. Results of these measurements are used to further test the descriptive abilities of eqs 3 and 4.

Experimental Methods

Anthracene (Aldrich, 99.9+%) was used as received. Cyclohexane (Aldrich, HPLC), hexane (Aldrich, 99%), heptane (Aldrich, HPLC), octane (Aldrich, 99+%, anhydrous), methylcyclohexane (Aldrich, 99+%, anhydrous), and 2,2,4-trimethylpentane (Aldrich, HPLC) were stored over molecular sieves to remove trace water shortly before use. 1-Propanol

Table I. Experimental Mole Fraction Solubilities of Antracene (A) in Binary Alkane + 1-Propanol Solvent Mixtures at 25.0 °C

$x_c{}^\circ$	x_A^{sat}	$x_c{}^\circ$	x_A^{sat}	$x_c{}^\circ$	x_A^{sat}
Hexane (B) + 1-Propanol (C)					
0.0000	0.001 274	0.5447	0.001 071	0.8712	0.000 740
0.1751	0.001 288	0.6331	0.000 990	0.9411	0.000 661
0.3162	0.001 237	0.7297	0.000 898	1.0000	0.000 591
Heptane (B) + 1-Propanol (C)					
0.0000	0.001 571	0.5674	0.001 182	0.8824	0.000 762
0.1719	0.001 566	0.6622	0.001 077	0.9398	0.000 681
0.3272	0.001 456	0.7444	0.000 953	1.0000	0.000 591
Octane (B) + 1-Propanol (C)					
0.0000	0.001 838	0.5892	0.001 300	0.8939	0.000 784
0.1908	0.001 779	0.6806	0.001 145	0.9477	0.000 682
0.3483	0.001 632	0.7661	0.001 013	1.0000	0.000 591
Cyclohexane (B) + 1-Propanol (C)					
0.0000	0.001 553	0.4886	0.001 288	0.8511	0.000 795
0.1335	0.001 576	0.5890	0.001 150	0.9226	0.000 699
0.2567	0.001 543	0.6893	0.001 010	1.0000	0.000 591
Methylcyclohexane (B) + 1-Propanol (C)					
0.0000	0.001 649	0.5326	0.001 294	0.8687	0.000 781
0.1539	0.001 697	0.6305	0.001 154	0.9328	0.000 687
0.2943	0.001 578	0.7206	0.001 018	1.0000	0.000 591
2,2,4-Trimethylpentane (B) + 1-Propanol (C)					
0.0000	0.001 074	0.5891	0.000 929	0.8968	0.000 693
0.2141	0.001 089	0.6884	0.000 862	0.9454	0.000 649
0.3510	0.001 057	0.7911	0.000 783	1.0000	0.000 591

Table II. Experimental Mole Fraction Solubilities of Anthracene (A) in Binary Alkane + 1-Butanol Solvent Mixtures at 25.0 °C

$x_c{}^\circ$	x_A^{sat}	$x_c{}^\circ$	x_A^{sat}	$x_c{}^\circ$	x_A^{sat}
Hexane (B) + 1-Butanol (C)					
0.0000	0.001 274	0.4876	0.001 218	0.8479	0.000 931
0.1460	0.001 316	0.5800	0.001 162	0.9247	0.000 857
0.2668	0.001 310	0.6804	0.001 068	1.0000	0.000 801
Heptane (B) + 1-Butanol (C)					
0.0000	0.001 571	0.5171	0.001 333	0.8622	0.000 972
0.1562	0.001 576	0.6174	0.001 230	0.9315	0.000 886
0.2876	0.001 511	0.7033	0.001 142	1.0000	0.000 801
Octane (B) + 1-Butanol (C)					
0.0000	0.001 838	0.5368	0.001 467	0.8738	0.000 998
0.1645	0.001 828	0.6389	0.001 336	0.9365	0.000 892
0.3070	0.001 725	0.7313	0.001 207	1.0000	0.000 801
Cyclohexane (B) + 1-Butanol (C)					
0.0000	0.001 553	0.4380	0.001 414	0.8255	0.000 978
0.1151	0.001 622	0.5390	0.001 291	0.9086	0.000 895
0.2108	0.001 586	0.6811	0.001 152	1.0000	0.000 801
Methylcyclohexane (B) + 1-Butanol (C)					
0.0000	0.001 649	0.4783	0.001 453	0.8449	0.000 995
0.1358	0.001 710	0.5740	0.001 329	0.9221	0.000 892
0.2675	0.001 671	0.6764	0.001 193	1.0000	0.000 801
2,2,4-Trimethylpentane (B) + 1-Butanol (C)					
0.0000	0.001 074	0.5376	0.001 051	0.8819	0.000 870
0.1567	0.001 125	0.6387	0.000 996	0.9443	0.000 838
0.3031	0.001 121	0.7330	0.000 956	1.0000	0.000 801

(Aldrich, 99+%, anhydrous) and 1-butanol (Aldrich, HPLC, 99.8+%) were stored over both anhydrous sodium sulfate and molecular sieves before being fractionally distilled. Gas chromatographic analysis showed solvent purities to be 99.7% or better. Karl Fisher titration gave water contents (w/w) of <0.003% and <0.01% for 1-propanol and 1-butanol, respectively. Binary solvent mixtures were prepared by weight 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 12 binary alkane + 1-propanol and alkane + 1-butanol mixtures studied are listed in Tables I and II, respectively. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ±1%. Experimental anthracene solubilities in the pure alkane solvents are in excellent agreement with published values in the chemical literature (1).

Results and Discussion

The ability of eqs 3 and 4 to mathematically represent the experimental solubility of anthracene in 12 binary alkane + 1-propanol and alkane + 1-butanol solvent systems is summarized in Table III in the form of "curve-fit" parameters and percent deviations in back-calculated solubilities for the two-parameter expressions. In the case of eq 3 the three-parameter form was also considered. During the course of evaluating parameters for the modified Wilson equation, it was noted on a Λ_{BC}^{adj} versus Λ_{CB}^{adj} versus percent deviation three-dimensional map there existed several parameter pairs

which described the anthracene solubility to within the same level of error. For example, in the case of anthracene solubilities in hexane + 1-butanol mixtures, the percent deviation was approximately 0.4% for Λ_{BC}^{adj} = 1.690 and Λ_{CB}^{adj} = 1.088, 1.2% for Λ_{BC}^{adj} = 1.810 and Λ_{CB}^{adj} = 1.000, and 1.2% for Λ_{BC}^{adj} = 1.400 and Λ_{CB}^{adj} = 1.200. No special attempt was made to optimize calculated Λ_{ij}^{adj} values as we wished only to learn if eq 4 could be used to mathematically represent experimental data in systems covering modest ranges in mole fraction solubilities. Any parameter set having ±1.5% deviation was sufficient for this purpose.

The numerical value of a_A^{solid} = 0.010 49 (1) used in the modified Wilson computations was calculated from the molar enthalpy of fusion, ΔH_A^{fus}, at the normal melting point temperature of the solute, T_{mp}:

$$\ln a_A^{solid} = -\Delta H_A^{fus}(T_{mp} - T)/(RTT_{mp}) \qquad (5)$$

Attempts to eliminate a_A^{solid} from the mathematical representation in favor of a simplified version (a_A^{solid} = 1) proved unsuccessful.

Careful examination of Table III reveals that eq 4 provides fairly reasonable (though by no means perfect) mathematical representations of all 12 systems studied. Back-calculated and experimental values generally differ by less than ±2%, except those for 1-butanol mixtures containing 2,2,4-trimethylpentane and for 1-propanol mixtures containing cyclohexane and methylcyclohexane. These three systems exhibit modest maximum anthracene solubilities near pure alkane, and the "optimum" set of Λ_{ij}^{adj} values fails to predict the observed solubility maxima. In comparison, the three-parameter mathematical representation based upon the combined NIBS/Redlich–Kister models, eq 3, correctly predicts the solubility maxima and describes the data to within an average absolute deviation of ±0.5%, which is comparable to the experimental uncertainty. There may be one or two individual data points within each system, however, for which the deviations exceed ±2%.

From a computational standpoint, eq 3 will likely be preferred because most research groups involved in reporting

Table III. Mathematical Representation of Anthracene Solubilities in Several Binary Alkane (B) + 1-Propanol (C) and Alkane (B) + 1-Butanol (C) Solvent Mixtures

binary solvent system	2-param eq 3		3-param eq 3		eq 4	
	$S_i{}^a$	% dev[b]	$S_i{}^a$	% dev[b]	Λ_{ij}^{adj} [c]	% dev[b]
hexane + 1-propanol	1.033	0.5	0.982	0.2	1.360	0.5
	−0.121		−0.075		1.440	
			0.186			
heptane + 1-propanol	1.184	1.0	1.098	0.4	1.410	0.7
	−0.182		−0.106		1.580	
			0.324			
octane + 1-propanol	1.340	0.9	1.275	0.3	1.240	0.6
	−0.361		−0.290		1.880	
			0.250			
cyclohexane + 1-propanol	1.207	1.0	1.121	0.5	1.300	1.6
	0.015		0.040		1.600	
			0.256			
methylcyclohexane + 1-propanol	1.291	0.8	1.235	0.5	1.344	1.4
	0.047		0.088		1.667	
			0.204			
2,2,4-trimethylpentane + 1-propanol	0.892	0.9	0.825	0.4	1.100	0.6
	−0.192		−0.103		1.500	
			0.291			
hexane + 1-butanol	0.703	0.5	0.737	0.4	1.690	0.4
	0.183		0.165		1.088	
			−0.124			
heptane + 1-butanol	0.779	0.8	0.723	0.2	1.476	0.5
	−0.032		0.004		1.291	
			0.201			
octane + 1-butanol	0.933	0.6	0.909	0.4	1.460	0.5
	−0.033		−0.014		1.500	
			0.088			
cyclohexane + 1-butanol	0.810	0.9	0.741	0.5	2.377	0.5
	0.336		0.345		1.010	
			0.223			
methylcyclohexane + 1-butanol	0.948	1.1	0.850	1.0	2.387	0.9
	0.282		0.146		1.080	
			0.295			
2,2,4-trimethylpentane + 1-butanol	0.576	0.5	0.536	0.3	2.600	1.8
	0.121		0.151		0.680	
			0.142			

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

thermodynamic properties have computer programs for evaluating the Redlich–Kister coefficients. In the case of the two-parameter Redlich–Kister fit, the computations require only a simple linear least-squares analysis of [ln x_A^{sat} − $x_B{}^o$ ln(x_A^{sat})$_B$ − $x_C{}^o$ ln(x_A^{sat})$_C$]/$x_B{}^o x_C{}^o$ versus $x_B{}^o$ − $x_C{}^o$. With this idea in mind, we recommend that not only the future presentations 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 3. Realizing that a single equation will not be applicable to all systems encountered, we further suggest eq 4 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 (*28*).

Glossary

a_A^{solid} — activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid

$f_B{}^o$,$f_C{}^o$ — weighted mole fraction composition of the binary solvent mixture, calculated as if the solute were not present

ΔH_A^{fus} — molar enthalpy of fusion of the solute

S_i — adjustable curve-fit parameter in the combined NIBS/Redlich–Kister mathematical representation

$x_B{}^o$,$x_C{}^o$ — mole fraction composition of the binary solvent mixture, calculated as if the solute were not present

x_A^{sat} — saturated mole fraction solubility of the solute

$(x_A^{sat})_i$ — saturated mole fraction solubility of the solute in pure solvent component i

Z_{BC}^E — excess molar thermodynamic property of the binary solvent mixture at mole fraction composition $x_B{}^o$

$(Z_A^E)_i$ — excess partial molar property of the solute in pure solvent component i

Λ_{ij}^{adj} — adjustable curve-fit parameter in the modified Wilson mathematical representation

Γ_i — weighting factor for component i

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