Solubility of Pyrene in Binary Alkane + 1-Propanol and Alkane + 2-Propanol Solvent Mixtures

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Experimental solubilities are reported for pyrene in 12 binary mixtures containing 1-propanol or 2-propanol with hexane, heptane, octane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane 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 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 ±1.3% 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. 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 (10, 11) now has two sets of group interaction parameters, with the publication of the infinite dilution values by Bastos et al. (12).

Predictive expressions for solid–liquid equilibria have also been derived from simple thermodynamic mixing models. The nearly ideal binary solvent (NIBS) model (13–15) 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)

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

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

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, 14–19). 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 (20, 21), both the NIBS and modified Wilson (22) models have served as the point of departure for the mathematical representation of solute solubility as a function of solvent composition

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

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

with the various S_i and Λ_{ij}^{adj} coefficients computed from measured solubility data *via* least-squares analysis. In eqs 3 and 4 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 component *i*.

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, pyrene solubilities were determined in six alkane + 1-propanol and six alkane + 2-propanol mixtures. Results of these measurements are used to further test the descriptive abilities of eqs 3 and 4.

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Table I. Experimental Mole Fraction Solubilities of Pyrene in Binary Alkane + 1-Propanol Solvent Mixtures at 26.0 °C

x_C^o	x_A^{sat}	x_C^o	x_A^{sat}	x_C^o	x_A^{sat}
		Hexane (B) + 1-Propanol (C)			
0.0000	0.008 57	0.5431	0.007 87	0.8734	0.005 45
0.1727	0.009 44	0.6400	0.007 28	0.9338	0.004 90
0.3063	0.008 95	0.7258	0.006 69	1.0000	0.004 26
		Heptane (B) + 1-Propanol (C)			
0.0000	0.011 02	0.5599	0.009 16	0.8810	0.005 68
0.1927	0.011 54	0.6656	0.008 14	0.9416	0.004 95
0.3280	0.010 89	0.7383	0.007 34	1.0000	0.004 26
		Octane (B) + 1-Propanol (C)			
0.0000	0.013 72	0.5930	0.010 22	0.8873	0.006 12
0.1959	0.013 89	0.6798	0.009 10	0.9504	0.005 07
0.3597	0.012 61	0.7584	0.008 00	1.0000	0.004 26
		Cyclohexane (B) + 1-Propanol (C)			
0.0000	0.011 00	0.4938	0.009 69	0.8750	0.005 73
0.1513	0.011 92	0.5957	0.008 76	0.9251	0.005 01
0.2741	0.011 41	0.6894	0.007 65	1.0000	0.004 26
		Methylcyclohexane (B) + 1-Propanol (C)			
0.0000	0.012 92	0.5273	0.010 45	0.8672	0.005 99
0.1734	0.013 36	0.6238	0.009 21	0.9384	0.004 99
0.2997	0.012 71	0.7164	0.007 98	1.0000	0.004 26
		2,2,4-Trimethylpentane (B) + 1-Propanol (C)			
0.0000	0.007 20	0.5925	0.006 59	0.8887	0.005 11
0.2131	0.007 38	0.6783	0.006 24	0.9421	0.004 72
0.3581	0.007 21	0.7710	0.005 84	1.0000	0.004 26

Table II. Experimental Mole Fraction Solubilities of Pyrene in Binary Alkane + 2-Propanol Solvent Mixtures at 26.0 °C

x_C^o	x_A^{sat}	x_C^o	x_A^{sat}	x_C^o	x_A^{sat}
		Hexane (B) + 2-Propanol (C)			
0.0000	0.008 57	0.5251	0.007 00	0.8651	0.004 12
0.1676	0.008 67	0.6303	0.006 19	0.9301	0.003 52
0.2966	0.008 25	0.7199	0.005 47	1.0000	0.002 90
		Heptane (B) + 2-Propanol (C)			
0.0000	0.011 02	0.5561	0.008 30	0.8890	0.004 30
0.1872	0.011 17	0.6558	0.007 24	0.9390	0.003 67
0.3336	0.010 29	0.7436	0.006 18	1.0000	0.002 90
		Octane (B) + 2-Propanol (C)			
0.0000	0.013 72	0.5829	0.009 40	0.9006	0.004 51
0.1971	0.013 50	0.6836	0.007 96	0.9459	0.003 77
0.3555	0.012 10	0.7639	0.006 73	1.0000	0.002 90
		Cyclohexane (B) + 2-Propanol (C)			
0.0000	0.011 00	0.4936	0.008 75	0.8559	0.004 51
0.1496	0.011 33	0.5936	0.007 64	0.9212	0.003 76
0.2625	0.010 82	0.6755	0.006 70	1.0000	0.002 90
		Methylcyclohexane (B) + 2-Propanol (C)			
0.0000	0.012 92	0.5220	0.009 60	0.8660	0.004 69
0.1691	0.013 25	0.6240	0.008 19	0.9336	0.003 74
0.2953	0.012 21	0.7238	0.006 73	1.0000	0.002 90
		2,2,4-Trimethylpentane (B) + 2-Propanol (C)			
0.0000	0.007 20	0.5803	0.005 92	0.8908	0.003 80
0.1987	0.007 46	0.6848	0.005 32	0.9434	0.003 36
0.3622	0.006 90	0.7661	0.004 78	1.0000	0.002 90

Experimental Methods

Pyrene (Aldrich, 99+%) was recrystallized several times from methanol. 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 (Aldrich, 99+%, anhydrous) and 2-propanol (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-Fisher titration gave water contents (mass/mass %) of <0.003% and <0.01% for 1-propanol and 2-propanol, respectively. 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 26.0 ± 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 pre-equilibrating the solutions at a higher temperature. Aliquots of saturated pyrene 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 372 nm on a Bausch and Lomb Spectronic 2000. Experimental pyrene solubilities in the 12 binary alkane + 1-propanol and alkane + 2-propanol 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 ±1.5%.

Results and Discussion

The ability of eqs 3 and 4 to mathematically represent the experimental solubility of pyrene in 12 binary alkane + 1-propanol and alkane + 2-propanol 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 and 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 that there existed several parameter pairs which described the pyrene solubility to within the same level of error. For example, in the case of pyrene solubilities in methylcyclohexane + 1-propanol mixtures, the percent deviation was approximately 0.4% for Λ_{BC}^{adj} = 1.605 and Λ_{CB}^{adj} = 1.450, 1.3% for Λ_{BC}^{adj} = 1.500 and Λ_{CB}^{adj} = 1.550, and 0.8% for Λ_{BC}^{adj} = 1.550 and Λ_{CB}^{adj} = 1.500. 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 $a_A(s)$ = 0.1312 (2) used in the modified Wilson computations was calculated from

$$\ln a_A(s) = -\Delta_{fus}H(T_m - T)/(RTT_m) \tag{5}$$

where $\Delta_{fus}H$ is the molar enthalpy of fusion at the normal melting point temperature of the solute, T_m. Attempts to eliminate $a_A(s)$ from the mathematical representation in favor of a simplified version ($a_A(s)$ = 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 ±1.5%, except for a few of the systems which exhibit a maximum in the mole fraction solubility versus solvent composition curve near the pure alkane cosolvent. Equation 4 underpredicted the solubility maxima by ca. 2–3%. In comparison, the three-parameter mathematical representation based upon the combined NIBS/Redlich–Kister model, eq 3, correctly predicts the solubility maxima and describes the data to within an overall average absolute deviation of ±0.4%, 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 ±1.3%.

From a computational standpoint, eq 3 will likely be preferred because most research groups involved in reporting thermodynamic properties have computer programs for

Table III. Mathematical Representation of Pyrene Solubilities in Several Binary Alkane (B) + 1-Propanol (C) and Alkane (B) + 2-Propanol (C) Solvent Mixtures

binary solvent system	eq 3				eq 4	
	$S_i{}^a$	% dev[b]	$S_i{}^a$	% dev[b]	$A_{ij}^{\text{adj } c}$	% dev[b]
hexane + 1-propanol	1.334	2.3	1.188	0.6	1.340	1.4
	−0.045		0.073		1.348	
			0.544			
heptane + 1-propanol	1.476	1.1	1.383	0.4	1.249	0.7
	−0.190		−0.202		1.577	
			0.280			
octane + 1-propanol	1.703	2.4	1.528	0.3	1.032	1.1
	−0.627		−0.419		1.936	
			0.701			
cyclohexane + 1-propanol	1.459	0.9	1.396	0.7	1.749	0.6
	0.232		0.268		1.281	
			0.226			
methylcyclohexane + 1-propanol	1.544	0.8	1.507	0.4	1.605	0.4
	−0.042		−0.011		1.450	
			0.138			
2,2,4-trimethylpentane + 1-propanol	0.936	0.9	0.864	0.1	0.804	0.6
	−0.352		−0.255		1.744	
			0.304			
hexane + 2-propanol	1.511	0.7	1.460	0.3	1.080	0.4
	−0.302		−0.265		1.628	
			0.190			
heptane + 2-propanol	1.948	2.0	1.799	0.2	1.072	0.9
	−0.636		−0.478		1.908	
			0.581			
octane + 2-propanol	2.225	3.0	1.988	0.4	0.936	1.1
	−1.082		−0.795		2.248	
			0.942			
cyclohexane + 2-propanol	1.830	1.4	1.726	0.1	1.464	0.8
	−0.219		−0.165		1.556	
			0.372			
methylcyclohexane + 2-propanol	2.054	1.8	1.921	0.3	1.404	1.0
	−0.380		−0.279		1.744	
			0.491			
2,2,4-trimethylpentane + 2-propanol	1.423	1.4	1.329	0.5	0.904	0.8
	−0.345		−0.232		1.752	
			0.378			

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

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 $[\ln x_A^{\text{sat}} - x_B^o \ln(x_A^{\text{sat}})_B - x_C^o \ln(x_A^{\text{sat}})_C]/x_B^o x_C^o$ versus $x_B^o - x_C^o$. 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 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 (21).

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