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Solubility of Anthracene in Binary Alkane + Methyl *tert*-Butyl Ether Solvent Mixtures at 298.15 K

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Experimental solubilities are reported for anthracene dissolved in seven binary mixtures containing methyl *tert*-butyl ether (also called 2-methoxy-2-methylpropane) with hexane, heptane, octane, cyclohexane, methylcyclohexane, 2,2,4-trimethylpentane, and *tert*-butylcyclohexane (also called (1,1-dimethylethyl)-cyclohexane) 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 seven 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 on the order of 0.5%.

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 (*e.g.*, anthracene and pyrene) and heteroatom polynuclear aromatics (*e.g.*, 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, 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. 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 seven binary alkane + methyl *tert*-butyl ether solvent mixtures. Results of these measurements are used to further test the descriptive abilities of several previously derived expressions.

Experimental Methods

Anthracene (Gold Label, Aldrich 99.9+%) was used as received. Cyclohexane (Aldrich, HPLC), hexane (Aldrich, 99%), heptane (Aldrich, HPLC), octane (Aldrich, 99+%, anhydrous), methylcyclohexane (Aldrich, 99+%, anhydrous), 2,2,4-trimethylpentane (Aldrich, HPLC), *tert*-butylcyclohexane (Aldrich, 99%, also called (1,1-dimethylethyl)cyclohexane), and methyl *tert*-butyl ether (Arco, 99.9+%, also called 2-methoxy-2-methylpropane) were stored over molecular sieves before being fractionally distilled. 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.

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 least 3 days (often longer). Attainment of equilibrium was verified both by repetitive measurements after a minimum of 3 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. Molar absorptivities of the nine standard solutions varied systematically with molar concentration and ranged from circa $\epsilon/(\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}) = 7450$ to $\epsilon/(\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}) = 7150$ for anthracene concentrations ranging from $C/\mathrm{M} = 6.75 \times 10^{-5}$ to $C/\mathrm{M} = 2.25 \times 10^{-4}$. Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of anthracene, volume(s) of volumetric flask(s) used, and any dilutions required to place the measured absorbances on the Beer−Lambert law absorbance versus concentration working curve and then dividing by the mass of the saturated solution analyzed. Mole fraction solubilities were computed from (mass/mass) solubility fractions using the binary solvent initial mole fraction compositions and molar masses of the solute and both cosolvents. Experimental

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

x_C^o	x_A^{sat}	x_C^o	x_A^{sat}
Hexane (B) + Methyl *tert*-Butyl Ether (C)			
0.0000	0.001 27	0.6328	0.002 42
0.1216	0.001 44	0.7979	0.002 74
0.2175	0.001 59	0.9058	0.002 94
0.4207	0.001 97	1.0000	0.003 05
0.5240	0.002 18		
Heptane (B) + Methyl *tert*-Butyl Ether (C)			
0.0000	0.001 57	0.6492	0.002 55
0.1425	0.001 71	0.8292	0.002 84
0.2263	0.001 84	0.9098	0.002 97
0.4551	0.002 19	1.0000	0.003 05
0.5581	0.002 37		
Octane (B) + Methyl *tert*-Butyl Ether (C)			
0.0000	0.001 84	0.6774	0.002 72
0.1376	0.001 98	0.8451	0.002 92
0.2592	0.002 11	0.9173	0.003 01
0.4711	0.002 39	1.0000	0.003 05
0.5759	0.002 55		
Cyclohexane (B) + Methyl *tert*-Butyl Ether (C)			
0.0000	0.001 55	0.5822	0.002 68
0.0935	0.001 74	0.7800	0.002 89
0.1765	0.001 95	0.9079	0.002 95
0.3737	0.002 42	1.0000	0.003 05
0.4779	0.002 58		
Methylcyclohexane (B) + Methyl *tert*-Butyl Ether (C)			
0.0000	0.001 65	0.5953	0.002 77
0.1120	0.001 89	0.7875	0.002 98
0.2070	0.002 08	0.9008	0.003 03
0.4072	0.002 45	1.0000	0.003 05
0.5135	0.002 65		
2,2,4-Trimethylpentane (B) + Methyl *tert*-Butyl Ether (C)			
0.0000	0.001 07	0.6793	0.002 17
0.1411	0.001 20	0.8453	0.002 64
0.2681	0.001 38	0.9404	0.002 91
0.4838	0.001 75	1.0000	0.003 05
0.5787	0.001 94		
tert-Butylcyclohexane (B) + Methyl *tert*-Butyl Ether (C)			
0.0000	0.001 98	0.6928	0.002 97
0.1560	0.002 19	0.8487	0.003 01
0.2707	0.002 37	0.9207	0.003 04
0.4880	0.002 72	1.0000	0.003 05
0.5887	0.002 85		

anthracene solubilities in the seven binary alkane + methyl *tert*-butyl ether solvent mixtures studied are listed in Table 1. 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

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

or modified Wilson equation (Comer and Kopecni, 1990)

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

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 solvent mole fraction composition (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 solute activity is defined as the ratio of the fugacity of the solid to the fugacity of the hypothetical pure supercooled liquid solute. The numerical value of $a_A(s) = 0.010\,49$ (Acree and Rytting, 1983) used in the modified Wilson computations was calculated from

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

the molar enthalpy of fusion, $\Delta_{fus}H_A/\text{J mol}^{-1} = 28\,860$ (Weast, 1983), at the normal melting point temperature of the solute, $T_{mp}/\text{K} = 490.0$. The above expression assumes that the molar enthalpy of fusion is independent of temperature over the range of $T/\text{K} = 490.0{-}298.2$.

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the seven binary alkane + methyl *tert*-butyl ether solvent systems is summarized in Table 2 in the form of "curve-fit" parameters and percent deviations in back-calculated solubilities. Careful examination of Table 2 reveals that both equations provide an accurate mathematical representation for how the solubility of anthracene varies with solvent composition. For the seven anthracene systems studied, the overall average absolute deviation between experimental and calculated values is 0.4% and 0.6% for eqs 1 and 2, respectively, which is less than the experimental uncertainty.

Table 2. Mathematical Representation of Anthracene Solubilities in Several Binary Alkane (B) + Methyl *tert*-Butyl Ether (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]
hexane + methyl *tert*-butyl ether	0.318	0.2	1.020	0.4
	−0.244		3.860	
heptane + methyl *tert*-butyl ether	0.149	0.5	0.862	0.5
	−0.268		3.857	
octane + methyl *tert*-butyl ether	0.116	0.2	0.783	0.3
	−0.203		4.081	
	0.098			
cyclohexane + methyl *tert*-butyl ether	0.741	0.7	3.763	1.2
	0.174		0.100	
	−0.365			
methylcyclohexane + methyl *tert*-butyl ether	0.638	0.2	1.664	0.4
			2.516	
2,2,4-trimethylpentane + methyl *tert*-butyl ether	−0.072	0.5	1.202	0.5
	−0.294		0.216	
tert-butylcyclohexane + methyl *tert*-butyl ether	0.438	0.4	1.320	1.0
	−0.126		3.130	
	−0.197			

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2. [b] Deviation (%) = $(100/7)\sum|[(x_A^{sat})_i^{calc} - (x_A^{sat})_i^{exp}]/(x_A^{sat})_i^{exp}|$. [c] Adjustable parameters for the modified Wilson equation are ordered as Λ_{BC}^{adj} and Λ_{CB}^{adj}.

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 also, 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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