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Solubility of Anthracene in Binary Alkane + 2-Butoxyethanol Solvent Mixtures at 298.2 K

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Experimental solubilities are reported for anthracene dissolved in seven binary alkane + 2-butoxyethanol solvent mixtures at 25 °C. The alkane cosolvents studied were hexane, heptane, octane, cyclohexane, methylcyclohexane, 2,2,4-trimethylpentane, and *tert*-butylcyclohexane (also called (1,1-dimethylethyl)-cyclohexane). 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 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 0.5% and 0.8% 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, 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 predictive methods as a means to generate desired quantities. Numerous equations have been suggested for predicting solute solubilities in binary solvent mixtures. For example, we (Acree et al., 1994a,b; Powell et al., 1997a) recently derived equations for predicting anthracene solubilities in associated solutions based upon the mobile order theory and Kretschmer−Wiebe model. Both solution models provided reasonable accurate estimations of the observed anthracene solubility behavior in 36 different binary alkane + alcohol solvent mixtures. Only monofunctional alcohol cosolvents were considered at the time because of the lack of solubility data for systems containing polyfunctional alcohols. In present study anthracene solubilities are reported in seven binary alkane + 2-butoxyethanol solvent mixtures. The lone electron pairs on the ether linkage provide an additional sight for hydrogen-bond formation. Results of these measurements will later be used to test the limitations and applications of existing association models once a sufficient solubility database is established for polycyclic aromatic hydrocarbon solutes dissolved in alkane + alkoxyalcohol solvent mixtures.

Experimental Methods

Anthracene (Acros, 99.9+ %) was recrystallized three times from 2-propanone. 2-Butoxyethanol (Acros, 99+ %), hexane (Aldrich, 99+ %), heptane (Aldrich, HPLC), octane (Aldrich, 99+ %, anhydrous), cyclohexane (Aldrich, HPLC), methylcyclohexane (Aldrich, 99+ %, anhydrous), 2,2,4-trimethylpentane (Aldrich, HPLC), and *tert*-butylcyclohexane (Aldrich, 99%, also called (1,1-dimethylethyl)cyclohexane) 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., 1997b).

Experimental anthracene solubilities in the seven binary alkane + 2-butoxyethanol solvent mixtures 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 ±1.5%.

Results and Discussion

Acree and Zvaigzne (1991) suggested possible mathematical representations for isothermal solubility data based upon either a combined NIBS/Redlich−Kister model

$$\ln x_{\mathrm{A}}^{\mathrm{sat}} = x_{\mathrm{B}}^{\circ} \ln(x_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{B}} + x_{\mathrm{C}}^{\circ} \ln(x_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{C}} + x_{\mathrm{B}}^{\circ} x_{\mathrm{C}}^{\circ} \sum_{i=0}^{N} S_i (x_{\mathrm{B}}^{\circ} - x_{\mathrm{C}}^{\circ})^i \tag{1}$$

or modified Wilson equation

$$\ln[a_{\mathrm{A}}(s)/x_{\mathrm{A}}^{\mathrm{sat}}] = 1 - x_{\mathrm{B}}^{\circ}\{1 - \ln[a_{\mathrm{A}}(s)/(x_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{B}}]\}/(x_{\mathrm{B}}^{\circ} + x_{\mathrm{C}}^{\circ}\Lambda_{\mathrm{BC}}^{\mathrm{adj}}) - x_{\mathrm{C}}^{\circ}\{1 - \ln[a_{\mathrm{A}}(s)/(x_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{C}}]\}/(x_{\mathrm{B}}^{\circ}\,\Lambda_{\mathrm{CB}}^{\mathrm{adj}} + x_{\mathrm{C}}^{\circ}) \tag{2}$$

where the various S_i and $\Lambda_{ij}^{\mathrm{adj}}$ “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, $a_{\mathrm{A}}(s)$ is the activity of the solid solute, N is the number of

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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., 1997b).

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the seven binary alkane + 2-butoxyethanol mixtures is summarized in Table 2 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 compostions. 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 the experimental and calculated values is 0.5% and 0.8% for eqs 1 and 2, respectively, which is less than the experimental uncertainty.

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

x_C^o	x_A^{sat}	x_C^o	x_A^{sat}
Hexane (B) + 2-Butoxyethanol (C)			
0.0000	0.001 274	0.6013	0.003 188
0.1152	0.001 748	0.7970	0.003 526
0.2026	0.002 092	0.8974	0.003 642
0.3970	0.002 726	1.0000	0.003 785
0.4984	0.002 952		
Heptane (B) + 2-Butoxyethanol (C)			
0.0000	0.001 571	0.6334	0.003 302
0.1162	0.002 013	0.8369	0.003 608
0.2221	0.002 340	0.9286	0.003 690
0.4265	0.002 916	1.0000	0.003 785
0.5177	0.003 127		
Octane (B) + 2-Butoxyethanol (C)			
0.0000	0.001 838	0.6293	0.003 435
0.1061	0.002 225	0.8453	0.003 683
0.2312	0.002 604	0.9243	0.003 733
0.4565	0.003 187	1.0000	0.003 785
0.5513	0.003 333		
Cyclohexane (B) + 2-Butoxyethanol (C)			
0.0000	0.001 553	0.5532	0.003 282
0.0917	0.002 026	0.7600	0.003 532
0.1736	0.002 356	0.8636	0.003 655
0.3516	0.002 897	1.0000	0.003 785
0.4437	0.003 092		
Methylcyclohexane (B) + 2-Butoxyethanol (C)			
0.0000	0.001 649	0.6058	0.003 342
0.1210	0.002 254	0.8149	0.003 576
0.2126	0.002 560	0.9037	0.003 679
0.4039	0.003 035	1.0000	0.003 785
0.5074	0.003 248		
2,2,4-Trimethylpentane (B) + 2-Butoxyethanol (C)			
0.0000	0.001 074	0.6370	0.002 864
0.0977	0.001 389	0.8417	0.003 376
0.2275	0.001 747	0.9188	0.003 551
0.4395	0.002 348	1.0000	0.003 785
0.5470	0.002 659		
tert-Butylcyclohexane (B) + 2-Butoxyethanol (C)			
0.0000	0.001 978	0.6725	0.003 662
0.1313	0.002 522	0.8348	0.003 770
0.2591	0.002 896	0.9273	0.003 780
0.4588	0.003 317	1.0000	0.003 785
0.5696	0.003 512		

Table 2. Mathematical Representation of Anthracene Solubilities in Several Binary Alkane (B) + 2-Butoxyethanol (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 + 2-butoxyethanol	1.217	0.3	3.400	0.7
	0.679		0.303	
	0.224			
heptane + 2-butoxyethanol	0.928	0.5	3.160	0.7
	0.488		0.332	
	0.123			
octane + 2-butoxyethanol	0.832	0.3	3.790	1.1
	0.366		0.274	
	0.105			
cyclohexane + 2-butoxyethanol	1.081	0.4	3.970	0.5
	0.863		0.100	
	0.565			
methylcyclohexane + 2-butoxyethanol	0.992	0.7	4.730	0.3
	0.868		2.971	
	0.489			
2,2,4-trimethylpentane + 2-butoxyethanol	0.883	0.8	2.260	0.6
	0.548		3.970	
	0.198			
tert-butylcyclohexane + 2-butoxyethanol	0.883	0.6	4.080	1.7
	0.427		0.245	
	0.275			

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

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