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Solubility of Anthracene in Ternary Dibutyl Ether + Alcohol + Heptane Solvent Mixtures at 298.15 K

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Experimental solubilities are reported for anthracene dissolved in ternary dibutyl ether + 1-propanol + heptane, dibutyl ether + 2-propanol + heptane, dibutyl ether + 1-butanol + heptane, dibutyl ether + 2-butanol + heptane, and dibutyl ether + 2-methyl-1-propanol + heptane solvent mixtures at 25 °C and atmospheric pressure. Nineteen compositions were studied for each of the five solvent systems. Results of these measurements are used to test the predictive ability of the ternary solvent form of the combined NIMS/Redlich−Kister equation. Computations showed that the model predicted the observed solubility behavior to within an overall average absolute deviation of about 1.5%, which is comparable to the experimental uncertainty of ±1.5%.

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 the 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 a 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.

In the present study anthracene solubilities have been measured in five ternary dibutyl ether + alcohol + heptane systems at 25 °C. Nineteen ternary compositions were studied for each of the five systems. Results of these measurements are used to test the predictive ability of expressions based upon the general mixing model used in deriving the combined NIBS/Redlich−Kister equation.

Experimental Methods

Anthracene (Acros, 99.9+%) was recrystallized three times from 2-propanone. 1-Propanol (Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), 2-methyl-1-propanol (Aldrich, 99.5%, anhydrous), heptane (Aldrich, HPLC, 99+%), and dibutyl ether (Aldrich, 99.3%, anhydrous) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mol % or better. Ternary solvent mixtures were prepared by mass so that compositions could be calculated to 0.0001 mole fraction. The methods of sample equilibration and spectrophotometric analysis are discussed in an earlier paper (Powell et al., 1997). Experimental anthracene solubilities in the five dibutyl ether + alcohol + heptane 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 co-workers (Acree, 1992; Acree and Zvaigzne, 1991; Acree et al., 1991) suggested the combined NIBS/Redlich−Kister equation for the mathematical representation of isothermal solubility data in binary solvent systems

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

where x_B° and x_C° refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present and $(x_A^{\mathrm{sat}})_i$ denotes the measured solute solubility in pure solvent i. The various S_i curve-fit parameters can be evaluated with a least-squares analysis. For a ternary solvent system, the mathematical representation takes the form

$$\ln x_A^{\mathrm{sat}} = x_B^\circ \ln(x_A^{\mathrm{sat}})_B + x_C^\circ \ln(x_A^{\mathrm{sat}})_C + x_D^\circ \ln(x_A^{\mathrm{sat}})_D + x_B^\circ x_C^\circ \sum_{i=0}^{r} S_{i,\mathrm{BC}} (x_B^\circ - x_C^\circ)^i + x_B^\circ x_D^\circ \sum_{j=0}^{s} S_{j,\mathrm{BD}} (x_B^\circ - x_D^\circ)^j + x_C^\circ x_D^\circ \sum_{k=0}^{t} S_{k,\mathrm{CD}} (x_C^\circ - x_D^\circ)^k$$

Recent studies have shown that eq 2 provides reasonably accurate predictions for anthracene solubilities in ternary two alkane + alcohol (Deng and Acree, 1998a; Deng et al., 1999a) and alkane + two alcohol (Deng and Acree, 1998b; Deng et al., 1998 and 1999b) solvent mixtures. Such systems exhibit fairly large deviations from solution ideality arising from the self-association of each alcohol cosol-

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Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Ternary Dibutyl Ether (B) + Alcohol (C) + Heptane (D) Solvent Mixtures at 298.15 K

x_B°	x_C°	x_A^{sat}	x_B°	x_C°	x_A^{sat}	x_B°	x_C°	x_A^{sat}
			Dibutyl Ether (B) + 1-Propanol (C) + Heptane (D)					
0.2156	0.4883	0.001 771	0.0582	0.6332	0.001 247	0.0728	0.3039	0.001 604
0.0833	0.8087	0.001 042	0.2409	0.6702	0.001 635	0.0598	0.7858	0.001 030
0.1736	0.3808	0.001 777	0.3160	0.5829	0.001 957	0.1475	0.1787	0.001 796
0.1508	0.6460	0.001 441	0.1106	0.2440	0.001 706	0.0682	0.5334	0.001 382
0.5668	0.2090	0.002 802	0.5496	0.2765	0.002 789	0.2989	0.1932	0.002 128
0.5307	0.3533	0.002 694	0.3491	0.4060	0.002 158	0.3801	0.1870	0.002 310
0.1062	0.8154	0.001 073						
			Dibutyl Ether (B) + 2-Propanol (C) + Heptane (D)					
0.2275	0.5065	0.001 686	0.0664	0.6514	0.001 119	0.0802	0.3299	0.001 554
0.0843	0.8172	0.000 873	0.2460	0.6726	0.001 467	0.0585	0.8147	0.000 829
0.1837	0.4095	0.001 705	0.3283	0.5865	0.001 801	0.1689	0.1899	0.001 821
0.1528	0.6687	0.001 280	0.1244	0.2662	0.001 679	0.0735	0.5603	0.001 256
0.5867	0.2124	0.002 844	0.5708	0.2795	0.002 763	0.3320	0.1972	0.002 228
0.5445	0.3604	0.002 651	0.3601	0.4187	0.002 126	0.4149	0.2018	0.002 380
0.1119	0.8176	0.000 927						
			Dibutyl Ether (B) + 1-Butanol (C) + Heptane (D)					
0.2513	0.4580	0.001 993	0.0757	0.6158	0.001 447	0.0808	0.2986	0.001 703
0.0964	0.7913	0.001 248	0.2762	0.6356	0.001 916	0.0656	0.7851	0.001 209
0.1983	0.3638	0.001 895	0.3584	0.5467	0.002 223	0.1690	0.1717	0.001 931
0.1682	0.6280	0.001 664	0.1297	0.2351	0.001 796	0.0802	0.5185	0.001 556
0.6137	0.1748	0.003 024	0.5962	0.2489	0.002 910	0.3376	0.1781	0.002 338
0.5788	0.3198	0.002 861	0.3900	0.3754	0.002 425	0.4234	0.1801	0.002 544
0.1250	0.7955	0.001 330						
			Dibutyl Ether (B) + 2-Butanol (C) + Heptane (D)					
0.2524	0.4595	0.001 880	0.0746	0.6175	0.001 308	0.0826	0.2921	0.001 659
0.1268	0.7278	0.001 278	0.2759	0.6369	0.001 726	0.0652	0.7881	0.001 060
0.1964	0.3626	0.001 866	0.3640	0.5399	0.002 047	0.1714	0.1637	0.001 892
0.1781	0.6210	0.001 542	0.1280	0.2295	0.001 772	0.0784	0.5205	0.001 460
0.6113	0.1772	0.002 909	0.5913	0.2523	0.002 858	0.3387	0.1759	0.002 233
0.5762	0.3165	0.002 762	0.3941	0.3715	0.002 319	0.4265	0.1711	0.002 420
0.1269	0.7901	0.001 171						
			Dibutyl Ether (B) + 2-Methyl-1-Propanol (C) + Heptane (D)					
0.2541	0.4532	0.001 815	0.0753	0.6137	0.001 175	0.0833	0.2919	0.001 562
0.0958	0.7912	0.000 968	0.2807	0.6333	0.001 616	0.0679	0.7838	0.000 917
0.1957	0.3630	0.001 784	0.3619	0.5407	0.002 003	0.1731	0.1666	0.001 888
0.1773	0.6224	0.001 382	0.1286	0.2319	0.001 752	0.0798	0.5198	0.001 310
0.6149	0.1748	0.002 910	0.5963	0.2453	0.002 832	0.3384	0.1793	0.002 223
0.5803	0.3132	0.002 725	0.3924	0.3733	0.002 213	0.4235	0.1839	0.002 461
0.1278	0.7938	0.001 026						

vent and, in mixtures containing two alcohol cosolvents, from the formation of heterogeneous hydrogen-bonded chains between dissimilar alcohol molecules.

The predictive ability of eq 2 is summarized in Table 3 for anthracene dissolved in the five dibutyl ether + alcohol + heptane systems. Unlike the case of the ternary two alkane + alcohol and alkane + two alcohol solvent mixtures studied previously, hydrogen-bond formation is terminated each time that an alcohol molecule hydrogen bonds with dibutyl ether. Published papers (Zvaigzne et al., 1993 and 1994; Zvaigzne and Acree, 1994; Powell and Acree, 1995; Acree et al., 1994) have reported the calculated S_i parameters for anthracene dissolved in ten of the eleven sub-binary solvent systems, as well as the measured mole fraction solubilities in 1-propanol ($x_A^{sat} = 0.000\,591$), 2-propanol ($x_A^{sat} = 0.000\,411$), 1-butanol ($x_A^{sat} = 0.000\,801$), 2-butanol ($x_A^{sat} = 0.000\,585$), 2-methyl-1-propanol ($x_A^{sat} = 0.000\,470$), heptane ($x_A^{sat} = 0.001\,571$) and dibutyl ether ($x_A^{sat} = 0.003\,615$). Solubility data for the eleventh binary solvent system were reported several years prior to the development of the combined NIBS/Redlich−Kister equation. We have determined the numerical values of the S_i parameters for the binary dibutyl ether + heptane solvent system by curve fitting the experimental anthracene mole fraction solubility data of Marthandan and Acree (1987) in accordance with eq 1. Numerical values of the S_i parameters have been tabulated in Table 2 for convenience. Examination of the numerical entries in Table 3 reveals that eq 2 predicts the solubility of anthracene to within an overall average absolute deviation of 1.5%, which is

Table 2. Combined NIBS/Redlich−Kister Parameters Calculated from Anthracene Solubilities in the Sub-binary Solvent Systems

solvent (B) + solvent (C)	S_i[a]
2-methyl-1-propanol (B) + heptane (C)	1.284 0.301 0.266
2-propanol (B) + heptane (C)	1.491 0.587 0.566
2-butanol (B) + heptane (C)	1.225 0.292
1-propanol (B) + heptane (C)	1.098 0.106 0.324
1-butanol (B) + heptane (C)	0.723 −0.004 0.201
dibutyl ether (B) + 1-propanol (C)	2.167 −0.931 0.891
dibutyl ether (B) + 2-propanol (C)	2.588 −1.235 0.866
dibutyl ether (B) + 1-butanol (C)	1.736 −0.488 0.574
dibutyl ether (B) + 2-butanol (C)	2.109 −0.849 0.726
dibutyl ether (B) + 2-methyl-1-propanol (C)	2.231 −0.932 0.927
dibutyl ether (B) + heptane (C)	0.220

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2.

Table 3. Summarized Comparison between Observed Anthracene Solubilities in Ternary Dibutyl Ether + Alcohol + Heptane Solvent Mixtures and Predicted Values Based upon the Combined NIMS/Redlich–Kister Equation 2

ternary solvent mixture	% dev[a]	% max. dev[b]
dibutyl ether (B) + 1-propanol (C) + heptane (D)	1.78	4.55
dibutyl ether (B) + 2-propanol (C) + heptane (D)	1.37	2.90
dibutyl ether (B) + 1-butanol (C) + heptane (D)	1.70	3.49
dibutyl ether (B) + 2-butanol (C) + heptane (D)	1.22	3.21
dibutyl ether (B) + 2-methyl-1-propanol (C) + heptane (D)	1.65	3.32

[a] Deviation (%) = $(100/N)\sum|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$, where N corresponds to the number of data points for each ternary system. In the present study, solubilities were determined at 19 different ternary solvent compositions. [b] Maximum deviation (%) = $100|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$.

comparable to the experimental uncertainty of ±1.5%. For the five systems studied, eq 2 was found to provide very accurate predictions of the observed solubility behavior.

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