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Solubility of Pyrene in Ternary Propanol + Butanol + Heptane Solvent Mixtures at 299.15 K

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Experimental solubilities are reported for pyrene dissolved in ternary 1-propanol + 1-butanol + heptane, 2-propanol + 1-butanol + heptane, 1-propanol + 2-butanol + heptane, and 2-propanol + 2-butanol + heptane solvent mixtures at 26 °C and atmospheric pressure. Nineteen compositions were studied for each of the four 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 1.6%, 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 refs 1−3. 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 pyrene solubilities have been measured in the four ternary propanol + butanol + heptane systems at (26.0 ± 0.1) °C. Nineteen ternary compositions were studied for each of the four 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. Subsequent studies will interpret the measured pyrene solubilities using both mobile order theory and the Kretschmer−Wiebe association model. Powell *et al.*[4] and McHale *et al.*[5] showed that these latter two solution models provided reasonably accurate descriptions for the solubility behavior of pyrene and anthracene in binary alkane + alcohol and alcohol + alcohol solvent mixtures. Neither model has been used to describe solubility in ternary solvent systems.

Experimental Methods

Pyrene (Aldrich, 98%) was recrystallized three times from anhydrous methanol. 1-Propanol (Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), and heptane (Aldrich, HPLC, 99+%) 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.[6] Experimental pyrene solubilities in the four propanol + butanol + 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[7−9] suggested the combined NIBS/Redlich−Kister equation for the mathematical representation of isothermal solubility data in binary solvent systems

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

where $x_{\rm B}^{\circ}$ and $x_{\rm C}^{\circ}$ refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present and $(x_{\rm A}^{\rm sat})_i$ denotes the measured solute solubility in pure solvent i. The various S_i curve-fit parameters can be evaluated with a least-squares analysis. Equation 1 has been shown to provide very accurate mathematical representations of anthracene, pyrene, and carbazole solubilities in a large number of both complexing and noncomplexing solvent mixtures.[1−3]

For a ternary solvent system, the mathematical representation takes the form

$$\ln x_{\rm A}^{\rm sat} = x_{\rm B}^{\circ} \ln(x_{\rm A}^{\rm sat})_{\rm B} + x_{\rm C}^{\circ} \ln(x_{\rm A}^{\rm sat})_{\rm C} + x_{\rm D}^{\circ} \ln(x_{\rm A}^{\rm sat})_{\rm D} + x_{\rm B}^{\circ} x_{\rm C}^{\circ} \sum_{i=0}^{r} S_{i,\rm BC} (x_{\rm B}^{\circ} - x_{\rm C}^{\circ})^i + x_{\rm B}^{\circ} x_{\rm D}^{\circ} \sum_{j=0}^{s} S_{j,\rm BD} (x_{\rm B}^{\circ} - x_{\rm D}^{\circ})^j + x_{\rm C}^{\circ} x_{\rm D}^{\circ} \sum_{k=0}^{t} S_{k,\rm CD} (x_{\rm C}^{\circ} - x_{\rm D}^{\circ})^k \qquad (2)$$

Recent studies have shown that eq 2 provides reasonably accurate predictions for anthracene solubilities in ternary two alkane + alcohol[10,11] and alkane + two alcohol[12−14]

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Table 1. Experimental Mole Fraction Solubilities of Pyrene (x_A^{sat}) in Ternary Propanol (B) + Butanol (C) + Heptane (D) Solvent Mixtures at 299.15 K

x_B°	x_C°	x_A^{sat}	x_B°	x_C°	x_A^{sat}
		1-Propanol (B) + 1-Butanol (C) + Heptane (D)			
0.4268	0.3473	0.007 84	0.2405	0.2000	0.010 99
0.1904	0.7216	0.006 89	0.7624	0.1528	0.005 75
0.3478	0.2863	0.009 16	0.5900	0.2515	0.006 77
0.3137	0.5261	0.007 34	0.1687	0.2741	0.011 09
0.7862	0.0923	0.006 05	0.1371	0.7247	0.007 49
0.7548	0.1880	0.005 60	0.3088	0.1357	0.010 73
0.2449	0.6912	0.006 51	0.1610	0.4716	0.009 58
0.1503	0.5605	0.008 91	0.5346	0.1263	0.008 60
0.4578	0.4763	0.006 08	0.6266	0.1086	0.007 98
0.5646	0.3767	0.005 82			
		2-Propanol (B) + 1-Butanol (C) + Heptane (D)			
0.4260	0.3485	0.007 08	0.2383	0.1934	0.010 53
0.1891	0.7151	0.006 63	0.7364	0.1824	0.004 53
0.3457	0.2954	0.008 47	0.5874	0.2533	0.005 73
0.3120	0.5326	0.006 76	0.1624	0.2618	0.010 88
0.7617	0.0855	0.005 07	0.1236	0.7389	0.007 31
0.7621	0.1806	0.004 20	0.3130	0.1334	0.009 91
0.2429	0.6918	0.006 23	0.1500	0.4773	0.009 42
0.1416	0.5685	0.008 66	0.5294	0.1233	0.007 82
0.4558	0.4820	0.005 36	0.6180	0.1175	0.006 72
0.5569	0.3776	0.004 98			
		1-Propanol (B) + 2-Butanol (C) + Heptane (D)			
0.4121	0.3645	0.007 01	0.2324	0.1840	0.010 71
0.1800	0.7236	0.005 64	0.7798	0.1359	0.005 35
0.3364	0.2948	0.008 71	0.6009	0.2438	0.006 22
0.3126	0.5283	0.006 38	0.1114	0.3023	0.010 86
0.7874	0.0952	0.005 81	0.1173	0.7440	0.006 29
0.7481	0.1966	0.005 04	0.3165	0.1362	0.010 33
0.2276	0.7153	0.005 20	0.1632	0.4591	0.008 85
0.1313	0.5819	0.008 13	0.5306	0.1133	0.008 53
0.4578	0.4799	0.005 17	0.6259	0.1045	0.007 52
0.5656	0.3757	0.005 07			
		2-Propanol (B) + 2-Butanol (C) + Heptane (D)			
0.4256	0.3557	0.006 43	0.2437	0.1969	0.010 12
0.1939	0.7079	0.005 52	0.7699	0.1406	0.004 35
0.3249	0.2931	0.008 40	0.5856	0.2544	0.005 52
0.3231	0.5142	0.006 04	0.1731	0.2669	0.010 30
0.7823	0.0998	0.004 55	0.1311	0.7358	0.006 05
0.7542	0.1869	0.004 12	0.3008	0.1362	0.010 08
0.2420	0.6862	0.005 15	0.1517	0.4706	0.008 95
0.1477	0.5632	0.007 89	0.5248	0.1234	0.007 64
0.4706	0.4670	0.004 55	0.6183	0.1150	0.006 57
0.5602	0.3759	0.004 46			

Table 2. Summarized Comparison between Observed Pyrene Solubilities in Ternary Propanol + Butanol + Heptane Solvent Mixtures and Predicted Values Based upon the Combined NIMS/Redlich−Kister Equation (Eq 2)

ternary solvent mixture	% dev[a]
1-propanol (B) + 1-butanol (C) + heptane (D)	1.74
2-propanol (B) + 1-butanol (C) + heptane (D)	1.45
1-propanol (B) + 2-butanol (C) + heptane (D)	1.70
2-propanol (B) + 2-butanol (C) + heptane (D)	1.36

[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.

solvent mixtures. Such systems exhibit fairly large deviations from solution ideality arising from the self-association of each alcohol cosolvent and, in mixtures containing two alcohol cosolvents, from the formation of heterogeneous hydrogen-bonded chains between dissimilar alcohol molecules.

Table 3. Combined NIBS/Redlich−Kister Parameters Calculated from Pyrene Solubilities in the Sub-Binary Solvent Systems

solvent (B) + solvent (C)	S_i[a]
2-propanol (B) + heptane (C)	1.799
	0.478
	0.581
2-butanol (B) + heptane (C)	1.583
	0.232
	0.392
1-propanol (B) + heptane (C)	1.383
	0.202
	0.280
1-butanol (B) + heptane (C)	1.075
	−0.189
	0.388
1-propanol (B) + 1-butanol (C)	0.127
	−0.065
2-propanol (B) + 1-butanol (C)	0.215
1-propanol (B) + 2-butanol (C)	none[b]
2-propanol (B) + 2-butanol (C)	0.270

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2. [b] Experimental solubility data accurately described without the use of the S_i curve-fit parameters.

The predictive ability of eq 2 is summarized in Table 2 for pyrene dissolved in the four propanol + butanol + heptane systems. Published papers[15−17] have reported the calculated S_i parameters for pyrene dissolved in seven of the eight sub-binary solvent systems. Solubility data for the remaining binary solvent system is available in the chemical literature; however, the authors did not use the combined NIBS/Redlich−Kister equation at the time the data were originally published. We have determined the numerical values of the S_i parameters for the binary 1-butanol + heptane solvent system by curve fitting the experimental pyrene mole fraction solubility data of Borders *et al.*[18] in accordance with eq 1. Numerical values of the S_i parameters have been tabulated in Table 3 for convenience. Experimental mole fraction solubilities in 1-propanol (x_A^{sat} = 0.004 26), 2-propanol (x_A^{sat} = 0.002 90), 1-butanol (x_A^{sat} = 0.006 22), 2-butanol (x_A^{sat} = 0.004 39), and heptane (x_A^{sat} = 0.011 02) were also taken from the chemical literature.[19−22] Examination of the numerical entries in Table 2 reveals that eq 2 predicts the solubility of pyrene to within an overall average absolute deviation of 1.6%, which is comparable to the experimental uncertainty of ±1.5%. For the four systems studied, eq 2 was found to provide very accurate predictions of the observed solubility behavior.

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