Solubility of Anthracene in Ternary Methyl *tert*-Butyl Ether + Alcohol + 2,2,4-Trimethylpentane Solvent Mixtures at 298.15 K

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Experimental solubilities are reported for anthracene dissolved in ternary methyl *tert*-butyl ether + 1-propanol + 2,2,4-trimethylpentane, methyl *tert*-butyl ether + 2-propanol + 2,2,4-trimethylpentane, methyl *tert*-butyl ether + 1-butanol + 2,2,4-trimethylpentane, methyl *tert*-butyl ether + 2-butanol + 2,2,4-trimethylpentane, and methyl *tert*-butyl ether + 2-methyl-1-propanol + 2,2,4-trimethylpentane 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 1.7%, 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 carcino-genicity/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.[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 anthracene solubilities have been measured in the five ternary methyl *tert*-butyl ether + alcohol + 2,2,4-trimethylpentane systems at (25.0 ± 0.1) °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. Subsequent studies will interpret the measured anthracene 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

Anthracene (Aldrich, 99.9+%) was used as received. 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), 2,2,4-trimethylpentane (Aldrich, HPLC, 99.7+%), and methyl *tert*-butyl ether (Arco, 99.9%) 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 anthracene solubilities in the five methyl *tert*-butyl ether + alcohol + 2,2,4-trimethylpentane 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%.

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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,

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

where x_B^0 and x_C^0 refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present and $(x_A^{sat})_i$ 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 of

$$\ln x_A^{sat} = x_B^0 \ln(x_A^{sat})_B + x_C^0 \ln(x_A^{sat})_C + x_D^0 \ln(x_A^{sat})_D + x_B^0 x_C^0 \sum_{i=0}^{r} S_{i,BC}(x_B^0 - x_C^0)^i + x_B^0 x_D^0 \sum_{j=0}^{s} S_{j,BD}(x_B^0 - x_D^0)^j + x_C^0 x_D^0 \sum_{k=0}^{t} S_{k,CD}(x_C^0 - x_D^0)^k \quad (2)$$

Recent studies have shown that eq 2 provides reasonably accurate predictions for anthracene solubilities in ternary

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Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Ternary Methyl *tert*-Butyl Ether (B) + Alcohol (C) + 2,2,4-Trimethylpentane (D) Solvent Mixtures at 298.15 K

x_B^0	x_C^0	x_A^{sat}	x_B^0	x_C^0	x_A^{sat}
Methyl *tert*-Butyl Ether (B) + 1-Propanol (C) + 2,2,4-Trimethylpentane (D)					
0.3022	0.4800	0.001 600	0.1683	0.2757	0.001 360
0.1115	0.8065	0.000 979	0.6553	0.2404	0.002 409
0.2499	0.4044	0.001 488	0.4532	0.3780	0.001 930
0.2072	0.6457	0.001 276	0.1153	0.3511	0.001 242
0.6787	0.1790	0.002 437	0.0777	0.8149	0.000 890
0.6282	0.2999	0.002 348	0.2289	0.2005	0.001 464
0.1462	0.7985	0.001 023	0.0987	0.5773	0.001 102
0.0925	0.6599	0.001 038	0.4327	0.1895	0.001 839
0.3160	0.6206	0.001 537	0.5133	0.1858	0.002 064
0.4845	0.4368	0.001 987			
Methyl *tert*-Butyl Ether (B) + 2-Propanol (C) + 2,2,4-Trimethylpentane (D)					
0.3025	0.4726	0.001 460	0.1770	0.2681	0.001 322
0.1206	0.7908	0.000 804	0.6584	0.2294	0.002 338
0.2525	0.3923	0.001 376	0.4583	0.3673	0.001 810
0.2070	0.6393	0.001 109	0.1127	0.3450	0.001 165
0.6818	0.1686	0.002 368	0.0794	0.8074	0.000 724
0.6307	0.2938	0.002 241	0.2333	0.1945	0.001 405
0.1496	0.7893	0.000 834	0.1051	0.5692	0.001 011
0.0976	0.6857	0.000 913	0.4251	0.1994	0.001 806
0.3152	0.6239	0.001 342	0.5172	0.1817	0.001 986
0.4167	0.5169	0.001 631			
Methyl *tert*-Butyl Ether (B) + 1-Butanol (C) + 2,2,4-Trimethylpentane (D)					
0.3297	0.4312	0.001 732	0.1847	0.2425	0.001 402
0.1350	0.7684	0.001 194	0.6817	0.2069	0.002 490
0.2702	0.3551	0.001 591	0.4894	0.3289	0.001 993
0.2799	0.5637	0.001 543	0.1286	0.3028	0.001 332
0.7041	0.1461	0.002 518	0.0935	0.7783	0.001 105
0.6701	0.2538	0.002 571	0.2380	0.1708	0.001 473
0.1717	0.7595	0.001 302	0.1111	0.5273	0.001 279
0.1023	0.6194	0.001 223	0.4425	0.1612	0.001 862
0.3537	0.5745	0.001 791	0.5261	0.1594	0.002 062
0.4492	0.4738	0.002 040			
Methyl *tert*-Butyl Ether (B) + 2-Butanol (C) + 2,2,4-Trimethylpentane (D)					
0.3282	0.4312	0.001 618	0.1751	0.2358	0.001 377
0.1349	0.7721	0.001 025	0.6829	0.2037	0.002 384
0.2709	0.3482	0.001 528	0.4879	0.3308	0.001 945
0.2341	0.5960	0.001 357	0.1069	0.3059	0.001 267
0.7080	0.1379	0.002 437	0.0923	0.7822	0.000 947
0.6683	0.2531	0.002 394	0.4887	0.1040	0.001 881
0.1919	0.7358	0.001 168	0.1066	0.5314	0.001 150
0.1111	0.6038	0.001 114	0.4415	0.1627	0.001 854
0.3550	0.5714	0.001 662	0.5336	0.1569	0.002 052
0.4500	0.4744	0.001 924			
Methyl *tert*-Butyl Ether (B) + 2-Methyl-1-Propanol (C) + 2,2,4-Trimethylpentane (D)					
0.3310	0.4287	0.001 505	0.1858	0.2349	0.001 328
0.1367	0.7633	0.000 877	0.6859	0.1989	0.002 328
0.2781	0.3455	0.001 451	0.4993	0.3194	0.001 877
0.2387	0.5900	0.001 200	0.1303	0.3031	0.001 207
0.7001	0.1460	0.002 284	0.0957	0.7748	0.000 819
0.6674	0.2535	0.002 302	0.2420	0.1668	0.001 422
0.1780	0.7542	0.000 946	0.1158	0.5180	0.001 068
0.1080	0.6133	0.001 005	0.4469	0.1594	0.001 794
0.3615	0.5652	0.001 457	0.5327	0.1546	0.001 963
0.4562	0.4708	0.001 699			

two alkane + alcohol[10,11] and alkane + two alcohol[12−14] 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.

The predictive ability of eq 2 is summarized in Table 3 for anthracene dissolved in the five methyl *tert*-butyl ether + alcohol + 2,2,4-trimethyl-pentane systems. Unlike 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 methyl *tert*-butyl ether. Published papers[15−20] have reported the calculated S_i parameters for anthracene dissolved in 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), 2,2,4-

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) + 2,2,4-trimethylpentane (C)	0.972
	0.100
	0.462
2-propanol (B) + 2,2,4-trimethylpentane (C)	1.193
	0.369
	0.333
2-butanol (B) + 2,2,4-trimethylpentane (C)	1.070
	0.213
1-propanol (B) + 2,2,4-trimethylpentane (C)	0.825
	0.103
	0.291
1-butanol (B) + 2,2,4-trimethylpentane (C)	0.536
	−0.151
	0.142
methyl *tert*-butyl ether (B) + 1-propanol (C)	1.688
	−0.283
	0.272
methyl *tert*-butyl ether (B) + 2-propanol (C)	1.976
	−0.514
	0.651
methyl *tert*-butyl ether (B) + 1-butanol (C)	1.305
	−0.190
	0.282
methyl *tert*-butyl ether (B) + 2-butanol (C)	1.580
	−0.272
	0.294
methyl *tert*-butyl ether (B) + 2-methyl-1-propanol (C)	1.652
	−0.428
	0.352
methyl *tert*-butyl ether (B) + 2,2,4-trimethylpentane (C)	−0.072
	0.294

[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 Methyl *tert*-Butyl Ether + Alcohol + 2,2,4-Trimethylpentane Solvent Mixtures and Predicted Values Based upon the Combined NIMS/Redlich−Kister Equation (2)

ternary solvent mixture	% dev.[a]
methyl *tert*-butyl ether (B) + 1-propanol (C) + 2,2,4-trimethylpentane (D)	1.60
methyl *tert*-butyl ether (B) + 2-propanol (C) + 2,2,4-trimethylpentane (D)	1.61
methyl *tert*-butyl ether (B) + 1-butanol (C) + 2,2,4-trimethylpentane (D)	1.93
methyl *tert*-butyl ether (B) + 2-butanol (C) + 2,2,4-trimethylpentane (D)	1.63
methyl *tert*-butyl ether (B) + 2-methyl-1-propanol (C) + 2,2,4-trimethylpentane (D)	1.68

[a] Deviation (%) = $(100/N)\Sigma \mid [(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp} \mid$, 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.

trimethylpentane ($x_A^{sat} = 0.001\,074$), and methyl *tert*-butyl ether ($x_A^{sat} = 0.003\,050$). 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 1.7%, which is 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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