Solubility of Anthracene in Ternary Methyl *tert*-Butyl Ether + Alcohol + Cyclohexane 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 + cyclohexane, methyl *tert*-butyl ether + 2-propanol + cyclohexane, methyl *tert*-butyl ether + 1-butanol + cyclohexane, methyl *tert*-butyl ether + 2-butanol + cyclohexane, and methyl *tert*-butyl ether + 2-methyl-1-propanol + cyclohexane 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 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.[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 five ternary methyl *tert*-butyl ether + alcohol + cyclohexane 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), cyclohexane (Aldrich, HPLC, 99.9+%), 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 + cyclohexane 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

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

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 $(x_A^{sat})_i$ 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

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

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 Anthracene (x_A^{sat}) in Ternary Methyl *tert*-Butyl Ether (B) + Alcohol (C) + Cyclohexane (D) Solvent Mixtures at 298.15 K

$x°_B$	$x°_C$	x_A^{sat}	$x°_B$	$x°_C$	x_A^{sat}
Methyl *tert*-Butyl Ether (B) + 1-Propanol (C) + Cyclohexane (D)					
0.3609	0.3797	0.002 108	0.1254	0.2070	0.001 847
0.1106	0.7642	0.001 097	0.4682	0.2435	0.002 454
0.2156	0.3313	0.001 919	0.4188	0.3410	0.002 234
0.1861	0.5961	0.001 505	0.0928	0.2731	0.001 711
0.6372	0.1605	0.002 763	0.0766	0.7673	0.001 040
0.6054	0.2827	0.002 527	0.1829	0.1550	0.002 009
0.1427	0.7713	0.001 139	0.0858	0.4915	0.001 458
0.0837	0.5888	0.001 309	0.3584	0.1570	0.002 355
0.3018	0.5987	0.001 640	0.4554	0.1701	0.002 509
0.3884	0.5038	0.001 926			
Methyl *tert*-Butyl Ether (B) + 2-Propanol (C) + Cyclohexane (D)					
0.2684	0.4257	0.001 814	0.1359	0.2086	0.001 894
0.1104	0.7651	0.000 908	0.6158	0.2294	0.002 543
0.2071	0.3401	0.001 828	0.4239	0.3334	0.002 145
0.1942	0.5880	0.001 358	0.0917	0.2700	0.001 695
0.6292	0.1609	0.002 702	0.0785	0.7589	0.000 878
0.6041	0.2785	0.002 452	0.1798	0.1527	0.002 003
0.1476	0.7665	0.000 933	0.0907	0.4852	0.001 384
0.0837	0.5791	0.001 213	0.3556	0.1580	0.002 374
0.3053	0.5976	0.001 485	0.4460	0.1585	0.002 497
0.3940	0.5050	0.001 732			
Methyl *tert*-Butyl Ether (B) + 1-Butanol (C) + Cyclohexane (D)					
0.2924	0.3834	0.002 029	0.1302	0.1867	0.001 887
0.1261	0.7353	0.001 317	0.6408	0.1929	0.002 721
0.2219	0.2995	0.002 012	0.4470	0.3027	0.002 385
0.2108	0.5456	0.001 703	0.0951	0.2279	0.001 804
0.6489	0.1337	0.002 751	0.0838	0.7343	0.001 240
0.6380	0.2493	0.002 632	0.1815	0.1329	0.002 011
0.1627	0.7392	0.001 372	0.0941	0.4406	0.001 613
0.0926	0.5374	0.001 513	0.3650	0.1327	0.002 401
0.3406	0.5590	0.001 892	0.4531	0.1367	0.002 578
0.4386	0.4583	0.002 157			
Methyl *tert*-Butyl Ether (B) + 2-Butanol (C) + Cyclohexane (D)					
0.2945	0.3777	0.002 005	0.1417	0.1748	0.001 923
0.1268	0.7317	0.001 145	0.6446	0.1956	0.002 631
0.2292	0.2879	0.002 021	0.4488	0.2987	0.002 332
0.2184	0.5452	0.001 632	0.0917	0.2284	0.001 802
0.6551	0.1352	0.002 762	0.0853	0.7320	0.001 076
0.6462	0.2438	0.002 619	0.1655	0.1368	0.002 016
0.1666	0.7336	0.001 192	0.0957	0.4342	0.001 567
0.0909	0.5448	0.001 403	0.3628	0.1365	0.002 403
0.3364	0.5587	0.001 730	0.4469	0.1467	0.002 520
0.4409	0.4484	0.002 060			
Methyl *tert*-Butyl Ether (B) + 2-Methyl-1-Propanol (C) + Cyclohexane (D)					
0.2866	0.3853	0.001 806	0.1388	0.1798	0.001 824
0.1285	0.7310	0.000 984	0.6134	0.1835	0.002 560
0.2268	0.2948	0.001 863	0.4470	0.3010	0.002 166
0.2201	0.5440	0.001 429	0.1026	0.2305	0.001 714
0.6512	0.1402	0.002 672	0.0936	0.7256	0.000 944
0.4803	0.4359	0.001 960	0.1453	0.1375	0.001 868
0.1668	0.7338	0.001 030	0.0978	0.4371	0.001 426
0.0977	0.5295	0.001 265	0.3661	0.1325	0.002 275
0.3440	0.5467	0.001 575	0.3237	0.4255	0.001 786
0.4361	0.4523	0.001 871			

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) + cyclohexane (C)	1.116
	−0.172
	0.341
2-propanol (B) + cyclohexane (C)	1.589
	0.143
	0.248
2-butanol (B) + cyclohexane (C)	1.260
	−0.206
1-propanol (B) + cyclohexane (C)	1.121
	−0.040
	0.256
1-butanol (B) + cyclohexane (C)	0.741
	−0.345
	0.223
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) + cyclohexane (C)	0.741
	−0.174
	−0.365

[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 + Cyclohexane Solvent Mixtures and Predicted Values Based upon the Combined NIMS/Redlich−Kister Equation (Eq 2)

ternary solvent mixture	% dev[a]
methyl *tert*-butyl ether (B) + 1-propanol (C) + cyclohexane (D)	1.70
methyl *tert*-butyl ether (B) + 2-propanol (C) + cyclohexane (D)	1.66
methyl *tert*-butyl ether (B) + 1-butanol (C) + cyclohexane (D)	1.73
methyl *tert*-butyl ether (B) + 2-butanol (C) + cyclohexane (D)	1.78
methyl *tert*-butyl ether (B) + 2-methyl-1-propanol (C) + cyclohexane (D)	1.63

[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.

The predictive ability of eq 2 is summarized in Table 3 for anthracene dissolved in the five methyl *tert*-butyl ether + alcohol + cyclohexane 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), cyclohexane (x_A^{sat} = 0.001 553), 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 devia-

tion 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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