

Solubility of Anthracene in Ternary Methyl *tert*-Butyl Ether + Alcohol + Heptane 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 + heptane, methyl *tert*-butyl ether + 2-propanol + heptane, methyl *tert*-butyl ether + 1-butanol + heptane, methyl *tert*-butyl ether + 2-butanol + heptane, and methyl *tert*-butyl 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 1.6%, which is comparable to the experimental uncertainty of $\pm 1.5\%$.

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, dibenzothiofene, 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 + heptane 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.

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), heptane (Aldrich, HPLC, 99+%), 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.⁴ Experimental anthracene solubilities in the

five methyl *tert*-butyl ether + alcohol + heptane solvent mixtures are listed in Table 1. The numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within $\pm 1.5\%$.

Results and Discussion

Acree and co-workers^{5–7} suggested the combined NIBS/Redlich–Kister equation for the mathematical representation of isothermal solubility data in binary solvent systems

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

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 $(x_A^{\text{sat}})_i$ 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

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

The number of curve-fit coefficients needed to describe the solute solubility in the sub-binary solvent systems is indicated by r , s , and t in eq 2. Each summation starts at zero, and the number of coefficients is always one greater than the numerical value r , s , and t . For example, if three coefficients were used in describing the solubility of anthracene in the BC sub-binary solvent system, then the summation would go to $r = 2$. Recent studies have shown that eq 2 provides reasonably accurate predictions for anthracene solubilities in ternary two alkane + alcohol^{8,9} and alkane + two alcohol^{10–12} solvent mixtures. Such

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Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Ternary Methyl *tert*-Butyl Ether (B) + Alcohol (C) + Heptane (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 <i>tert</i> -Butyl Ether (B) + 1-Propanol (C) + Heptane (D)					
0.2947	0.4682	0.001 808	0.1617	0.2541	0.001 747
0.1100	0.7996	0.001 041	0.6442	0.2377	0.002 504
0.2370	0.3877	0.001 772	0.4380	0.3753	0.002 112
0.2008	0.6364	0.001 430	0.1122	0.3485	0.001 620
0.6685	0.1665	0.002 606	0.0817	0.8003	0.001 007
0.6234	0.2953	0.002 455	0.2252	0.1761	0.001 906
0.1479	0.7864	0.001 099	0.1045	0.5491	0.001 400
0.0972	0.6397	0.001 274	0.4171	0.1774	0.002 241
0.3048	0.6218	0.001 584	0.5027	0.1723	0.002 364
0.4049	0.5218	0.001 860			
Methyl <i>tert</i> -Butyl Ether (B) + 2-Propanol (C) + Heptane (D)					
0.2981	0.4593	0.001 647	0.1605	0.2579	0.001 648
0.1152	0.7896	0.000 851	0.6447	0.2380	0.002 438
0.2456	0.3720	0.001 677	0.4527	0.3594	0.001 997
0.2049	0.6272	0.001 235	0.1123	0.3186	0.001 529
0.6691	0.1703	0.002 549	0.0848	0.7918	0.000 828
0.6300	0.2941	0.002 436	0.2166	0.1846	0.001 818
0.1504	0.7829	0.000 893	0.0969	0.5478	0.001 254
0.0924	0.6382	0.001 106	0.4052	0.1804	0.002 107
0.3091	0.6181	0.001 385	0.4890	0.1818	0.002 256
0.4051	0.5175	0.001 670			
Methyl <i>tert</i> -Butyl Ether (B) + 1-Butanol (C) + Heptane (D)					
0.3186	0.4215	0.001 951	0.1650	0.2237	0.001 808
0.1244	0.7650	0.001 290	0.6740	0.1968	0.002 660
0.2514	0.3428	0.001 888	0.4775	0.3220	0.002 315
0.2343	0.6079	0.001 646	0.1085	0.2898	0.001 703
0.6864	0.1531	0.002 672	0.0924	0.7674	0.001 247
0.6494	0.2620	0.002 589	0.2210	0.1638	0.001 908
0.1646	0.7591	0.001 334	0.1105	0.5035	0.001 555
0.1017	0.6011	0.001 444	0.4260	0.1563	0.002 281
0.3504	0.5685	0.001 888	0.5097	0.1507	0.002 406
0.4497	0.4698	0.002 124			
Methyl <i>tert</i> -Butyl Ether (B) + 2-Butanol (C) + Heptane (D)					
0.3189	0.4228	0.001 853	0.1649	0.2250	0.001 796
0.1326	0.7613	0.001 104	0.6730	0.1997	0.002 615
0.2637	0.3344	0.001 880	0.4787	0.3215	0.002 221
0.2319	0.5806	0.001 501	0.1207	0.2804	0.001 659
0.6940	0.1418	0.002 665	0.0938	0.7647	0.001 041
0.6557	0.2575	0.002 529	0.2274	0.1576	0.001 922
0.1704	0.7523	0.001 165	0.1113	0.5096	0.001 425
0.1045	0.5936	0.001 297	0.4222	0.1570	0.002 224
0.3546	0.5662	0.001 691	0.5136	0.1474	0.002 376
0.4394	0.4763	0.001 935			
Methyl <i>tert</i> -Butyl Ether (B) + 2-Methyl-1-Propanol (C) + Heptane (D)					
0.3156	0.4155	0.001 739	0.1707	0.2189	0.001 758
0.1463	0.7468	0.000 997	0.6803	0.2013	0.002 431
0.2614	0.3293	0.001 782	0.4752	0.3194	0.002 069
0.2333	0.5789	0.001 371	0.1239	0.2790	0.001 604
0.6904	0.1447	0.002 521	0.0943	0.7631	0.000 910
0.6657	0.2504	0.002 359	0.2230	0.1799	0.001 854
0.1724	0.7503	0.000 994	0.1141	0.4995	0.001 348
0.1072	0.5909	0.001 205	0.4188	0.1582	0.002 172
0.3531	0.5647	0.001 549	0.5096	0.1539	0.002 273
0.4487	0.4690	0.001 813			

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 2 for anthracene dissolved in the five methyl *tert*-butyl ether + alcohol + heptane 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^{13–18} have reported the calculated S_i parameters for anthracene dis-

Table 2. Summarized Comparison between Observed Anthracene Solubilities in Ternary Methyl *tert*-butyl Ether + Alcohol + Heptane Solvent Mixtures and Predicted Values Based upon the Combined NIMS/Redlich–Kister Equation (Eq 2)

ternary solvent mixture	% dev ^a
methyl <i>tert</i> -butyl ether (B) + 1-propanol (C) + heptane (D)	1.85
methyl <i>tert</i> -butyl ether (B) + 2-propanol (C) + heptane (D)	1.60
methyl <i>tert</i> -butyl ether (B) + 1-butanol (C) + heptane (D)	1.92
methyl <i>tert</i> -butyl ether (B) + 2-butanol (C) + heptane (D)	1.16
methyl <i>tert</i> -butyl ether (B) + 2-methyl-1-propanol (C) + heptane (D)	1.60

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

Table 3. 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 1.098
1-propanol (B) + heptane (C)	1.098 0.106 0.324
1-butanol (B) + heptane (C)	0.723 −0.004 0.201
methyl <i>tert</i> -butyl ether (B) + 1-propanol (C)	1.688 −0.283 0.272
methyl <i>tert</i> -butyl ether (B) + 2-propanol (C)	1.976 −0.514 0.651
methyl <i>tert</i> -butyl ether (B) + 1-butanol (C)	1.305 −0.190 0.282
methyl <i>tert</i> -butyl ether (B) + 2-butanol (C)	1.580 −0.272 0.294
methyl <i>tert</i> -butyl ether (B) + 2-methyl-1-propanol (C)	1.652 −0.428 0.352
methyl <i>tert</i> -butyl ether (B) + heptane (C)	0.149 0.268

^a Combined NIBS/Redlich–Kister curve-fit parameters are ordered as S_0 , S_1 , and S_2 .

solved in the 11 sub-binary solvent systems, as well as the measured mole fraction solubilities in 1-propanol ($x_A^{\text{sat}} = 0.000 591$), 2-propanol ($x_A^{\text{sat}} = 0.000 411$), 1-butanol ($x_A^{\text{sat}} = 0.000 801$), 2-butanol ($x_A^{\text{sat}} = 0.000 585$), 2-methyl-1-propanol ($x_A^{\text{sat}} = 0.000 470$), heptane ($x_A^{\text{sat}} = 0.001 571$), and methyl *tert*-butyl ether ($x_A^{\text{sat}} = 0.003 050$). Numerical values of the S_i parameters have been tabulated in Table 3 for convenience. Examination of the numerical entries in Table 2 reveals that eq 2 predicts the solubility of anthracene to within an overall average absolute deviation of 1.6%, which is comparable to the experimental uncertainty of $\pm 1.5\%$. For the five systems studied, eq 2 was found to provide very accurate predictions of the observed solubility behavior.

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