*J. Chem. Eng. Data* **2000,** *45,* 965−967

# Solubility of Anthracene in Ternary 1,4-Dioxane + Alcohol + Heptane Solvent Mixtures at 298.15 K

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Experimental solubilities are reported for anthracene dissolved in ternary 1,4-dioxane + 1-propanol + heptane, 1,4-dioxane + 2-propanol + heptane, 1,4-dioxane + 1-butanol + heptane, 1,4-dioxane + 2-butanol + heptane, and 1,4-dioxane + 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 3.7%.

## 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 anthracene solubilities have been measured in the five ternary 1,4-dioxane + 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, 99.9+%), and 1,4-dioxane (Aldrich, 99.8%, 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.[4] Experimental anthracene solubilities in the five 1,4-dioxane + 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[5−7] suggested the combined NIBS/Redlich−Kister equation for the mathematical representation of isothermal solubility data in binary solvent systems

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

where $x_{\mathrm{B}}^{\circ}$ and $x_{\mathrm{C}}^{\circ}$ refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present and $(x_{\mathrm{A}}^{\mathrm{sat}})_i$ 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

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

The generallized predictive expression, which is hereafter referred to as the combined nearly ideal multicomponent solvent (NIMS)/Redlich−Kister equation

$$\ln x_{\mathrm{A}}^{\mathrm{sat}} = \sum_{I}^{\mathrm{solv}} x_I^{\circ} \ln(x_{\mathrm{A}}^{\mathrm{sat}})_I + \sum_{I}^{\mathrm{solv}} \sum_{J}^{\mathrm{solv}} x_I^{\circ} x_J^{\circ} \Big[\sum_{k=0}^{N} S_{k,IJ} (x_I^{\circ} - x_J^{\circ})^k\Big] \tag{3}$$

contains a mole fraction average of the logarithm mole fraction solute solubilities in the pure solvents plus a double summation term that extends over all binary combinations of solvents. Recent studies have shown that eq 2 provides reasonably accurate predictions for anthracene solubilities in ternary two alkane + alcohol[8,9] and

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10.1021/je0001173 CCC: $19.00

**Table 1. Experimental Mole Fraction Solubilities of Anthracene ($x_A^{sat}$) in Ternary 1,4-Dioxane (B) + Alcohol (C) + Heptane (D) Solvent Mixtures at 298.15 K**

| $x_B^\circ$ | $x_C^\circ$ | $x_A^{sat}$ | $x_B^\circ$ | $x_C^\circ$ | $x_A^{sat}$ |
|---|---|---|---|---|---|
| 1,4-Dioxane (B) + 1-Propanol (C) + Heptane (D) | | | | | |
| 0.3712 | 0.4165 | 0.003 703 | 0.2154 | 0.2433 | 0.002 909 |
| 0.1536 | 0.7590 | 0.001 606 | 0.7117 | 0.1964 | 0.006 375 |
| 0.3074 | 0.3502 | 0.003 491 | 0.5300 | 0.3409 | 0.004 906 |
| 0.2641 | 0.5860 | 0.002 585 | 0.1528 | 0.3148 | 0.002 429 |
| 0.7397 | 0.1349 | 0.007 021 | 0.1116 | 0.7763 | 0.001 409 |
| 0.6998 | 0.2406 | 0.006 017 | 0.2817 | 0.1617 | 0.003 554 |
| 0.1930 | 0.7471 | 0.001 822 | 0.1363 | 0.5273 | 0.002 020 |
| 0.1225 | 0.6222 | 0.001 786 | 0.4946 | 0.1541 | 0.005 229 |
| 0.3907 | 0.5470 | 0.003 299 | 0.5777 | 0.1538 | 0.005 803 |
| 0.4856 | 0.4491 | 0.004 110 | | | |
| 1,4-Dioxane (B) + 2-Propanol (C) + Heptane (D) | | | | | |
| 0.3675 | 0.4154 | 0.003 551 | 0.2134 | 0.2442 | 0.002 804 |
| 0.1522 | 0.7588 | 0.001 408 | 0.7214 | 0.1835 | 0.006 332 |
| 0.3065 | 0.3374 | 0.003 358 | 0.5299 | 0.3067 | 0.004 814 |
| 0.2740 | 0.5728 | 0.002 476 | 0.1573 | 0.3073 | 0.002 344 |
| 0.7351 | 0.1327 | 0.006 720 | 0.1135 | 0.7663 | 0.001 225 |
| 0.7021 | 0.2307 | 0.005 916 | 0.2785 | 0.1774 | 0.003 318 |
| 0.2017 | 0.7363 | 0.001 642 | 0.1279 | 0.5364 | 0.001 798 |
| 0.1216 | 0.6242 | 0.001 593 | 0.4940 | 0.1587 | 0.004 969 |
| 0.3939 | 0.5433 | 0.003 137 | 0.5810 | 0.1525 | 0.005 899 |
| 0.4911 | 0.4421 | 0.004 024 | | | |
| 1,4-Dioxane (B) + 1-Butanol (C) + Heptane (D) | | | | | |
| 0.3978 | 0.3721 | 0.004 077 | 0.2677 | 0.2487 | 0.003 252 |
| 0.1791 | 0.7173 | 0.001 927 | 0.7456 | 0.1586 | 0.006 637 |
| 0.3311 | 0.3028 | 0.003 643 | 0.5647 | 0.2682 | 0.005 332 |
| 0.2954 | 0.5348 | 0.003 049 | 0.1538 | 0.2737 | 0.002 415 |
| 0.7559 | 0.1144 | 0.007 020 | 0.1269 | 0.7392 | 0.001 638 |
| 0.7332 | 0.2023 | 0.006 308 | 0.2913 | 0.1419 | 0.003 510 |
| 0.2174 | 0.7125 | 0.002 165 | 0.1500 | 0.4790 | 0.002 254 |
| 0.1372 | 0.5726 | 0.002 046 | 0.5006 | 0.1305 | 0.005 255 |
| 0.4316 | 0.4963 | 0.003 815 | 0.5964 | 0.1223 | 0.006 243 |
| 0.5311 | 0.4000 | 0.004 590 | | | |
| 1,4-Dioxane (B) + 2-Butanol (C) + Heptane (D) | | | | | |
| 0.3958 | 0.3749 | 0.003 924 | 0.2280 | 0.2060 | 0.002 913 |
| 0.1755 | 0.7208 | 0.001 766 | 0.7494 | 0.1508 | 0.006 777 |
| 0.3299 | 0.3063 | 0.003 605 | 0.5642 | 0.2633 | 0.005 162 |
| 0.2952 | 0.5319 | 0.002 922 | 0.1549 | 0.2741 | 0.002 456 |
| 0.7658 | 0.1021 | 0.007 224 | 0.1214 | 0.7442 | 0.001 536 |
| 0.7317 | 0.1986 | 0.006 391 | 0.2935 | 0.1365 | 0.003 614 |
| 0.2285 | 0.7000 | 0.002 135 | 0.1460 | 0.4828 | 0.002 226 |
| 0.1424 | 0.5685 | 0.002 015 | 0.5046 | 0.1277 | 0.005 263 |
| 0.4323 | 0.4953 | 0.003 699 | 0.5973 | 0.1211 | 0.006 181 |
| 0.5372 | 0.3914 | 0.004 569 | | | |
| 1,4-Dioxane (B) + 2-Methyl-1-Propanol (C) + Heptane (D) | | | | | |
| 0.4012 | 0.3672 | 0.003 745 | 0.2283 | 0.2030 | 0.002 919 |
| 0.1782 | 0.7163 | 0.001 567 | 0.7456 | 0.1544 | 0.006 841 |
| 0.3714 | 0.2850 | 0.003 805 | 0.5612 | 0.2702 | 0.005 041 |
| 0.3100 | 0.5193 | 0.002 760 | 0.1623 | 0.2702 | 0.002 415 |
| 0.7631 | 0.1072 | 0.006 943 | 0.1308 | 0.7330 | 0.001 310 |
| 0.7344 | 0.1962 | 0.006 208 | 0.2986 | 0.1420 | 0.003 492 |
| 0.2270 | 0.7036 | 0.001 791 | 0.1437 | 0.4852 | 0.001 971 |
| 0.1515 | 0.5619 | 0.001 860 | 0.5166 | 0.1284 | 0.005 369 |
| 0.4411 | 0.4901 | 0.003 459 | 0.6000 | 0.1242 | 0.005 988 |
| 0.5318 | 0.3966 | 0.004 341 | | | |

**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<br>0.301<br>0.266 |
| 2-propanol (B) + heptane (C) | 1.491<br>0.587<br>0.566 |
| 2-butanol (B) + heptane (C) | 1.225<br>0.292 |
| 1-propanol (B) + heptane (C) | 1.098<br>0.106<br>0.324 |
| 1-butanol (B) + heptane (C) | 0.723<br>−0.004<br>0.201 |
| 1,4-dioxane (B) + 1-propanol (C) | 2.308<br>−1.305<br>0.112 |
| 1,4-dioxane (B) + 2-propanol (C) | 2.559<br>−1.745<br>0.748 |
| 1,4-dioxane (B) + 1-butanol (C) | 1.792<br>−1.140<br>−0.330 |
| 1,4-dioxane (B) + 2-butanol (C) | 2.178<br>−1.504<br>0.709 |
| 1,4-dioxane (B) + 2-methyl-1-propanol (C) | 2.326<br>−1.232<br>0.210 |
| 1,4-dioxane (B) + heptane (C) | 1.619<br>0.368<br>0.242 |

[a] The 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 1,4-Dioxane + Alcohol + Heptane Solvent Mixtures and Predicted Values Based upon the Combined NIMS/Redlich−Kister Equation (Eq 2)**

| ternary solvent mixture | % dev[a] |
|---|---|
| 1,4-dioxane (B) + 1-propanol (C) + heptane (D) | 4.0 |
| 1,4-dioxane (B) + 2-propanol (C) + heptane (D) | 4.4 |
| 1,4-dioxane (B) + 1-butanol (C) + heptane (D) | 3.5 |
| 1,4-dioxane (B) + 2-butanol (C) + heptane (D) | 3.4 |
| 1,4-dioxane (B) + 2-methyl-1-propanol (C) + heptane (D) | 3.2 |

[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.

alkane + two alcohol[10−12] 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 1,4-dioxane + 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 1,4-dioxane. Published papers[13−17] 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 at 25 °C 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 ($x_A^{sat}$ = 0.001 553), and 1,4-dioxane ($x_A^{sat}$ = 0.008 329). 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 1,4-dioxane + heptane solvent system by curve fitting the experimental anthracene mole fraction solubility data of Procyk et al.[18] 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 3.7%, which is about 2.5 times larger than the experimental uncertainty of ±1.5% in the measured anthracene solubilities.

We note that the difference between predicted and observed values is also larger than the ±2% error that was observed in our earlier studies involving anthracene dissolved in ternary alkane + alkane + alcohol,[8,9] alkane + alcohol + alcohol,[10−12] and dibutyl ether + alkane + alcohol mixtures.[19−21] In all fairness, we should mention that the earlier studies covered much smaller 4- to 8-fold ranges in anthracene mole fraction solubilities. One should not expect the same level of predictive accuracy in systems that cover significantly larger solubility ranges. The five ternary 1,4-dioxane + alcohol + heptane systems studied here cover up to a 20-fold range in mole fraction solubility. Anthracene is 20 times more soluble in 1,4-dioxane ($x_A^{sat} = 0.008\,329$) than in 2-propanol ($x_A^{sat} = 0.000\,411$). The predictive accuracy of most solution models does decrease both with increasing solution nonideality and with greater dissimilarities between the solute solubility in the pure solvents. The combined NIMS/Redlich−Kister solution model is no different than other solution models in this regard.

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Received for review April 19, 2000. Accepted June 30, 2000. I.C. thanks the University of North Texas and the U.S. Department of Education for support provided under the Ronald E. McNair Postbaccalaureate Achievement Program. M.S. thanks the UNT Texas Academy of Math and Science (TAMS) for an undergraduate summer research fellowship.

JE0001173