# Solubility of Anthracene in Ternary 1,4-Dioxane + Alcohol + 2,2,4-Trimethylpentane Solvent Mixtures at 298.15 K

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Experimental solubilities are reported for anthracene dissolved in ternary 1,4-dioxane + 1-propanol + 2,2,4-trimethylpentane, 1,4-dioxane + 2-propanol + 2,2,4-trimethylpentane, 1,4-dioxane + 1-butanol + 2,2,4-trimethylpentane, 1,4-dioxane + 2-butanol + 2,2,4-trimethylpentane, and 1,4-dioxane + 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 4.0%.

## 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, in terms of both 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 + 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.

## Experimental Methods

Anthracene (Aldrich, 99.9+%) was used as received. The manufacturer's stated purity was checked by gas chromatography using a sample of anthracene dissolved in benzene. The chromatogram contained only three peaks, which corresponded to the benzene solvent peak, the anthracene solute peak, and a trace impurity peak that was also present in the neat benzene solvent. 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 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 within 0.0001 mole fraction.

Excess solute and solvent were equilibrated in sealed amber glass bottles at a constant temperature of (25.0 ± 0.1) °C for at least 3 days. Aliquots of the saturated anthracene solutions were transferred into a tared volumetric flask to determine the amount of sample, and diluted quantitatively with methanol for spectroscopic analysis at 356 nm. Absorbances of the standard solutions of known anthracene concentration were always recorded immediately prior to analysis of the ternary solvent mixtures to minimize uncertainties/errors associated with setting the analysis wavelength and with fluctuations in radiation source intensity. A single cuvette was used for all absorbance measurements, thus eliminating path length errors/uncertainties from the experimental determinations. A more detailed description of methods of sample equilibration and spectrophotometric analysis appears in an earlier paper.[4] Experimental anthracene solubilities in the five 1,4-dioxane + 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%. For all solvent compositions studied, each replicate measurement differed by no more than ±1.5% of the value given in Table 1. The stated reproducibility should correctly reflect all errors/uncertainties in the sample weighings, volumetric glassware calibration, dilutions, and absorbance measurements since each independent determination began with the removal of an aliquot of the saturated anthracene solution from the amber glass bottle.

## Results and Discussion

Acree and co-workers[5−7] suggested the combined NIBS/Redlich−Kister equation for the mathematical representa-

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

| $x_B^o$ | $x_C^o$ | $x_A^{sat}$ | $x_B^o$ | $x_C^o$ | $x_A^{sat}$ |
|---|---|---|---|---|---|
| 1,4-Dioxane (B) + 1-Propanol (C) + 2,2,4-Trimethylpentane (D) | | | | | |
| 0.3824 | 0.4276 | 0.003 572 | 0.2277 | 0.2584 | 0.002 334 |
| 0.1520 | 0.7702 | 0.001 487 | 0.7244 | 0.1926 | 0.006 102 |
| 0.3239 | 0.3608 | 0.002 991 | 0.5445 | 0.3125 | 0.004 755 |
| 0.2666 | 0.5766 | 0.002 373 | 0.1604 | 0.3299 | 0.001 899 |
| 0.7407 | 0.1434 | 0.006 409 | 0.1079 | 0.7861 | 0.001 257 |
| 0.7078 | 0.2375 | 0.005 865 | 0.2997 | 0.1747 | 0.002 859 |
| 0.1971 | 0.7474 | 0.001 725 | 0.1319 | 0.5565 | 0.001 628 |
| 0.1287 | 0.6383 | 0.001 523 | 0.5152 | 0.1585 | 0.004 563 |
| 0.3874 | 0.5574 | 0.003 102 | 0.6016 | 0.1545 | 0.005 330 |
| 0.4932 | 0.4514 | 0.003 966 | | | |
| 1,4-Dioxane (B) + 2-Propanol (C) + 2,2,4-Trimethylpentane (D) | | | | | |
| 0.3807 | 0.4253 | 0.003 153 | 0.2314 | 0.2491 | 0.002 256 |
| 0.1570 | 0.7615 | 0.001 304 | 0.7291 | 0.1844 | 0.006 114 |
| 0.3275 | 0.3555 | 0.002 821 | 0.5434 | 0.3132 | 0.004 520 |
| 0.2711 | 0.5875 | 0.002 297 | 0.1595 | 0.3271 | 0.001 824 |
| 0.7533 | 0.1324 | 0.006 562 | 0.1141 | 0.7783 | 0.001 111 |
| 0.7084 | 0.2322 | 0.005 881 | 0.2960 | 0.1822 | 0.002 706 |
| 0.1971 | 0.7463 | 0.001 560 | 0.1323 | 0.5525 | 0.001 515 |
| 0.1357 | 0.6304 | 0.001 403 | 0.5120 | 0.1600 | 0.004 478 |
| 0.3942 | 0.5466 | 0.003 006 | 0.5969 | 0.1526 | 0.005 466 |
| 0.4988 | 0.4431 | 0.003 806 | | | |
| 1,4-Dioxane (B) + 1-Butanol (C) + 2,2,4-Trimethylpentane (D) | | | | | |
| 0.4126 | 0.3784 | 0.003 645 | 0.2378 | 0.2256 | 0.002 389 |
| 0.1800 | 0.7311 | 0.001 842 | 0.7535 | 0.1575 | 0.006 357 |
| 0.3476 | 0.3129 | 0.003 398 | 0.5751 | 0.2735 | 0.005 086 |
| 0.3025 | 0.5422 | 0.002818 | 0.1659 | 0.2925 | 0.002 014 |
| 0.7721 | 0.1123 | 0.006 796 | 0.1281 | 0.7505 | 0.001 547 |
| 0.7336 | 0.2039 | 0.006 256 | 0.3010 | 0.1574 | 0.002 888 |
| 0.2219 | 0.7118 | 0.002 104 | 0.1510 | 0.5004 | 0.001 891 |
| 0.1431 | 0.5956 | 0.001 775 | 0.5303 | 0.1386 | 0.004 769 |
| 0.4396 | 0.4986 | 0.003 752 | 0.6200 | 0.1263 | 0.005 643 |
| 0.5378 | 0.3996 | 0.004 567 | | | |
| 1,4-Dioxane (B) + 2-Butanol (C) + 2,2,4-Trimethylpentane (D) | | | | | |
| 0.4110 | 0.3781 | 0.003 696 | 0.2397 | 0.2177 | 0.002 407 |
| 0.1809 | 0.7261 | 0.001 721 | 0.7523 | 0.1578 | 0.006 739 |
| 0.3419 | 0.3168 | 0.003 151 | 0.5753 | 0.2752 | 0.005 168 |
| 0.3009 | 0.5439 | 0.002 690 | 0.1697 | 0.2876 | 0.001 971 |
| 0.7612 | 0.1210 | 0.006 849 | 0.1310 | 0.7489 | 0.001 438 |
| 0.7369 | 0.2019 | 0.006 540 | 0.3092 | 0.1515 | 0.002 872 |
| 0.2264 | 0.7101 | 0.001 991 | 0.1539 | 0.5008 | 0.001 788 |
| 0.1425 | 0.5908 | 0.001 664 | 0.5263 | 0.1385 | 0.004 659 |
| 0.4354 | 0.4994 | 0.003 591 | 0.6128 | 0.1296 | 0.005 635 |
| 0.5362 | 0.4014 | 0.004 637 | | | |
| 1,4-Dioxane (B) + 2-Methyl-1-Propanol (C) + 2,2,4-Trimethylpentane (D) | | | | | |
| 0.4093 | 0.3787 | 0.003 409 | 0.2394 | 0.2206 | 0.002 337 |
| 0.1800 | 0.7254 | 0.001 444 | 0.7509 | 0.1623 | 0.006 201 |
| 0.3446 | 0.3136 | 0.002 977 | 0.5763 | 0.2733 | 0.004 698 |
| 0.3053 | 0.5398 | 0.002 401 | 0.1731 | 0.2856 | 0.001 893 |
| 0.7692 | 0.1149 | 0.006 714 | 0.1281 | 0.7457 | 0.001 182 |
| 0.7352 | 0.2016 | 0.006 135 | 0.3013 | 0.1651 | 0.002 702 |
| 0.2201 | 0.6960 | 0.001 663 | 0.1618 | 0.4950 | 0.001 561 |
| 0.1583 | 0.5389 | 0.001 514 | 0.5260 | 0.1375 | 0.004 388 |
| 0.4370 | 0.5014 | 0.003 199 | 0.6187 | 0.1247 | 0.005 230 |
| 0.5390 | 0.3968 | 0.003 952 | | | |

tion of isothermal solubility data in binary solvent systems

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

where $x_B^o$ and $x_C^o$ 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

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

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 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 + 2,2,4-trimethylpentane 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 1,4-dioxane. Published papers[13−17] have reported the calculated $S_i$ parameters for anthracene dissolved in 10 of the 11 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-

**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 |
| 1,4-dioxane (B) + 1-propanol (C) | 2.308 |
| | −1.305 |
| | 0.112 |
| 1,4-dioxane (B) + 2-propanol (C) | 2.559 |
| | −1.745 |
| | 0.748 |
| 1,4-dioxane (B) + 1-butanol (C) | 1.792 |
| | −1.140 |
| | −0.330 |
| 1,4-dioxane (B) + 2-butanol (C) | 2.178 |
| | −1.504 |
| | 0.709 |
| 1,4-dioxane (B) + 2-methyl-1-propanol (C) | 2.326 |
| | −1.232 |
| | 0.210 |
| 1,4-dioxane (B) + 2,2,4-trimethylpentane (C) | 1.476 |
| | 0.422 |
| | 0.338 |

[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 1,4-Dioxane + Alcohol + 2,2,4-Trimethylpentane Solvent Mixtures and Predicted Values Based upon the Combined NIMS/Redlich−Kister Eq 2**

| ternary solvent mixture | % dev[a] |
|---|---|
| 1,4-dioxane (B) + 1-propanol (C) + 2,2,4-trimethylpentane (D) | 3.5 |
| 1,4-dioxane (B) + 2-propanol (C) + 2,2,4-trimethylpentane (D) | 4.9 |
| 1,4-dioxane (B) + 1-butanol (C) + 2,2,4-trimethylpentane (D) | 4.8 |
| 1,4-dioxane (B) + 2-butanol (C) + 2,2,4-trimethylpentane (D) | 4.3 |
| 1,4-dioxane (B) + 2-methyl-1-propanol (C) + 2,2,4-trimethylpentane (D) | 2.5 |

[a] Dev (%) = $(100/N)\sum|[(x_A^{sat})^{calcd} - (x_A^{sat})^{exptl}]/(x_A^{sat})^{exptl}|$, 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.

1-propanol ($x_A^{sat}$ = 0.000 470), 2,2,4-trimethylpentane ($x_A^{sat}$ = 0.001 074), and 1,4-dioxane ($x_A^{sat}$ = 0.008 329). Solubility data for the 11th 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 + 2,2,4-trimethylpentane 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 4.0%, 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 4−8-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 + 2,2,4-trimethylpentane systems studied here cover up to a 20-fold range in mole fraction solubility. 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 from other solution models in this regard.

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