# Solubility of Anthracene in Ternary Propanol + Butanol + Cyclohexane Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in ternary 1-propanol + 1-butanol + cyclohexane, 1-propanol + 2-butanol + cyclohexane, 2-propanol + 1-butanol + cyclohexane, and 2-propanol + 2-butanol + cyclohexane solvent mixtures at 298.15 K. Nineteen compositions were studied for each of the four solvent systems. Results of these measurements are used to test the predictive ability of the ternary solvent form of the combined NIBS/Redlich–Kister equation. Computations showed that the model predicted the observed solubility behavior to within an overall average absolute deviation of about 1.6%.

## 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 (1994, 1995a,b). 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.

To address this problem, researchers have turned to group contribution methods and semiempirical equations to predict desired quantities from either pure component properties or measured binary data. In earlier studies we have used the binary solvent reduction of a predictive expression derived from a combined two- and three-body interactional mixing model as a mathematical representation for describing how the measured isothermal solubility of a crystalline solute varies with binary solvent composition. The binary reduction, referred to as the combined NIBS/Redlich–Kister equation, was found to accurately describe the observed solubility behavior in a large number of different binary solvent systems. We now extend our solubility studies to ternary solvent mixtures. Anthracene solubilities have been measured in the four ternary propanol + butanol + cyclohexane systems at 25 °C. Nineteen ternary compositions were studied for each of the four 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 (Acros, 99.9+ %) was recrystallized three times from 2-propanone. 1-Propanol (Aldrich, 99+ %,

anhydrous), 2-propanol (Aldrich, 99+ %, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+ %), 2-butanol (Aldrich, 99+ %, anhydrous), and cyclohexane (Aldrich, HPLC, 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. Karl Fischer titrations performed on select samples both prior to and after equilibration gave, to within experimental uncertainty, identical water contents (mass/mass %) of <0.01%. The methods of sample equilibration and spectrophotometric analysis are discussed in an earlier paper (Powell et al., 1997). Experimental anthracene solubilities in the four propanol + butanol + 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%.

## Results and Discussion

Expressions for predicting the thermodynamic properties of ternary nonelectrolyte systems have served as the point of departure for mathematical representation of experimental excess molar Gibbs energy, excess molar heat capacity, excess molar enthalpy, and excess molar volume data. Differences between predicted and observed values are expressed as

$$(Z_{ABC}^E)^{exp} - (Z_{ABC}^E)^{calc} = x_A x_B x_C Q_{ABC} \quad (1)$$

with $Q$-functions of varying complexity. For most systems encountered, the experimental data can be adequately represented by a power series expansion

$$Q_{ABC} = A_{ABC} + \sum_{i=1}^{r} B_{AB}^{(i)} (x_A - x_B)^i + \sum_{j=1}^{s} B_{AC}^{(j)} (x_A - x_C)^j + \sum_{k=1}^{t} B_{BC}^{(k)} (x_B - x_C)^k \quad (2)$$

though rarely are experimental data determined with sufficient precision to justify more than a few parameters.

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**Table 1. Experimental Mole Fraction Solubilities of Anthracene ($x_A^{sat}$) in Ternary Propanol (B) + Butanol (C) + Cyclohexane (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-Propanol (B) + 1-Butanol (C) + Cyclohexane (D) |
| 0.4028 | 0.3242 | 0.001 03 | 0.2050 | 0.1611 | 0.001 47 |
| 0.1855 | 0.6881 | 0.000 908 | 0.7561 | 0.1317 | 0.000 762 |
| 0.3161 | 0.2543 | 0.001 24 | 0.5720 | 0.2322 | 0.000 898 |
| 0.3021 | 0.4885 | 0.000 962 | 0.1425 | 0.2171 | 0.001 46 |
| 0.7549 | 0.0932 | 0.000 801 | 0.1260 | 0.7052 | 0.000 961 |
| 0.7477 | 0.1763 | 0.000 722 | 0.2620 | 0.1061 | 0.001 45 |
| 0.2323 | 0.6835 | 0.000 845 | 0.1323 | 0.4225 | 0.001 28 |
| 0.1248 | 0.5214 | 0.001 17 | 0.4857 | 0.1009 | 0.001 16 |
| 0.4545 | 0.4645 | 0.000 792 | 0.5820 | 0.0966 | 0.001 04 |
| 0.5566 | 0.3649 | 0.000 758 | | | |
| 1-Propanol (B) + 2-Butanol (C) + Cyclohexane (D) |
| 0.3954 | 0.3274 | 0.000 968 | 0.1987 | 0.1628 | 0.001 44 |
| 0.1829 | 0.6898 | 0.000 744 | 0.7537 | 0.1327 | 0.000 722 |
| 0.3100 | 0.2560 | 0.001 18 | 0.5693 | 0.2327 | 0.000 842 |
| 0.2990 | 0.4892 | 0.000 865 | 0.1343 | 0.2183 | 0.001 47 |
| 0.7618 | 0.0907 | 0.000 783 | 0.1273 | 0.7061 | 0.000 807 |
| 0.7512 | 0.1751 | 0.000 676 | 0.2663 | 0.1078 | 0.001 43 |
| 0.2376 | 0.6800 | 0.000 687 | 0.1323 | 0.4217 | 0.001 22 |
| 0.1330 | 0.5172 | 0.001 06 | 0.4864 | 0.0989 | 0.001 15 |
| 0.4588 | 0.4628 | 0.000 672 | 0.5819 | 0.0959 | 0.001 01 |
| 0.5606 | 0.3622 | 0.000 676 | | | |
| 2-Propanol (B) + 1-Butanol (C) + Cyclohexane (D) |
| 0.3954 | 0.3278 | 0.000 947 | 0.2010 | 0.1705 | 0.001 43 |
| 0.1837 | 0.6868 | 0.000 865 | 0.7444 | 0.1414 | 0.000 629 |
| 0.2950 | 0.2483 | 0.001 22 | 0.5644 | 0.2340 | 0.000 799 |
| 0.3002 | 0.4961 | 0.000 894 | 0.1469 | 0.2222 | 0.001 44 |
| 0.7621 | 0.0887 | 0.000 657 | 0.1256 | 0.7022 | 0.000 929 |
| 0.7514 | 0.1725 | 0.000 583 | 0.2530 | 0.1066 | 0.001 41 |
| 0.2348 | 0.6791 | 0.000 798 | 0.1564 | 0.4067 | 0.001 23 |
| 0.1296 | 0.5185 | 0.001 13 | 0.4811 | 0.1002 | 0.001 08 |
| 0.4555 | 0.4697 | 0.000 700 | 0.5771 | 0.1016 | 0.000 936 |
| 0.5520 | 0.3711 | 0.000 662 | | | |
| 2-Propanol (B) + 2-Butanol (C) + Cyclohexane (D) |
| 0.3961 | 0.3220 | 0.000 901 | 0.1891 | 0.1695 | 0.001 41 |
| 0.1687 | 0.7065 | 0.000 718 | 0.7587 | 0.1331 | 0.000 591 |
| 0.2997 | 0.2619 | 0.001 15 | 0.5631 | 0.2387 | 0.000 738 |
| 0.2991 | 0.4964 | 0.000 797 | 0.1236 | 0.2196 | 0.001 44 |
| 0.7598 | 0.0919 | 0.000 641 | 0.1233 | 0.7068 | 0.000 789 |
| 0.7422 | 0.1829 | 0.000 550 | 0.2564 | 0.1142 | 0.001 38 |
| 0.2324 | 0.6804 | 0.000 651 | 0.1228 | 0.4273 | 0.001 20 |
| 0.1274 | 0.5218 | 0.001 04 | 0.4746 | 0.1033 | 0.001 06 |
| 0.4458 | 0.4727 | 0.000 599 | 0.5815 | 0.0972 | 0.000 911 |
| 0.5459 | 0.3711 | 0.000 600 | | | |

**Table 2. Combined NIBS/Redlich–Kister Parameters Calculated from Anthracene Solubilities in the Sub-binary Solvent Systems**

| solvent (B) + solvent (C) | $S_i^a$ |
|---|---|
| 1-propanol (B) + 1-butanol (C) | 0.117 |
| | −0.015 |
| 1-propanol (B) + cyclohexane (C) | 1.121 |
| | −0.040 |
| | 0.256 |
| 1-butanol (B) + cyclohexane (C) | 0.741 |
| | −0.345 |
| | 0.223 |
| 2-propanol (B) + 1-butanol (C) | 0.243 |
| | 0.011 |
| 2-propanol (B) + cyclohexane (C) | 1.589 |
| | 0.143 |
| | 0.248 |
| 1-propanol (B) + 2-butanol (C) | 0.000 |
| | 0.000 |
| 2-propanol (B) + 2-butanol (C) | 0.097 |
| | 0.013 |
| 2-butanol (B) + cyclohexane (C) | 1.260 |
| | −0.206 |

$^a$ 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 Propanol + Butanol + Cyclohexane Solvent Mixtures and Predicted Values Based upon the Combined NIBS/Redlich–Kister Equation 4**

| ternary solvent mixture | % Dev.$^a$ |
|---|---|
| 1-propanol (B) + 1-butanol (C) + cyclohexane (D) | 1.45 |
| 1-propanol (B) + 2-butanol (C) + cyclohexane (D) | 1.76 |
| 2-propanol (B) + 1-butanol (C) + cyclohexane (D) | 1.70 |
| 2-propanol (B) + 2-butanol (C) + cyclohexane (D) | 1.57 |

$^a$ Deviation (%) = $(100/19)\sum |[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}/(x_A^{sat})^{exp}|$.

Conceptually, these ideas can be extended to solute solubilities in binary solvent mixtures; however, there has never been up until recently a sufficiently large solid solute solubility database to warrant computerized storage in equational form. With computerized data storage and retrieval becoming increasingly popular, it seems appropriate to discuss the various mathematical expressions that have been proposed in the chemical literature for describing the variation of solute solubility with binary solvent composition. Mathematical representations not only provide a means to screen experimental data sets for possible outliers in need of redetermination but also facilitate interpolation at solvent compositions falling between measured data points.

Acree and co-workers (Acree, 1992; Acree and Zvaigzne, 1991; Acree et al., 1991) suggested a possible mathematical representation for isothermal solubility data based upon the combined NIBS/Redlich–Kister model

$$\ln x_A^{sat} = x_B^o \ln(x_A^{sat})_B + x_C^o \ln(x_A^{sat})_C +$$
$$x_B^o x_C^o \sum_{i=0}^{n} S_i (x_B^o - x_C^o)^i \quad (3)$$

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 via least-squares analysis. Published papers (Zvaigzne et al. 1993; Zvaigzne and Acree, 1994; Acree et al., 1994; Acree and Zvaigzne, 1994) have reported the calculated $S_i$ parameters for anthracene dissolved in the eight 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 ($x_A^{sat} = 0.000\ 585$), and cyclohexane ($x_A^{sat} = 0.001\ 553$). Numerical values of the $S_i$ parameters have been tabulated in Table 2 for convenience.

Equation 3 expresses the "excess" logarithmic mole fraction solubility, relative to the simple $x_B^o \ln(x_A^{sat})_B + x_C^o \ln(x_A^{sat})_C$ arithmetic average, in terms of the Redlich–Kister equation. For a ternary solvent system, the mathematical representation takes the form of

$$\ln x_A^{sat} = x_B^o \ln(x_A^{sat})_B + x_C^o \ln(x_A^{sat})_C + x_D^o \ln(x_A^{sat})_D +$$
$$x_B^o x_C^o \sum_{i=0}^{r} S_{i,BC}(x_B^o - x_C^o)^i + x_B^o x_D^o \sum_{j=0}^{s} S_{j,BD} (x_B^o - x_D^o)^j +$$
$$x_C^o x_D^o \sum_{k=0}^{t} S_{k,CD} (x_C^o - x_D^o)^k \quad (4)$$

Equation 4 can be used to predict the solubility as a function of ternary solvent composition, provided that all of the various curve-fit parameters are known. The predic-

tive ability of eq 4 is summarized in Table 3 for anthracene dissolved in the four propanol + butanol + cyclohexane systems. Examination of the numerical entries in Table 3 reveals that eq 4 predicts the solubility of anthracene to within an overall average absolute deviation of 1.62%, which is comparable to the experimental uncertainty of ±1.5%. For the four systems studied, eq 4 was found to provide very accurate predictions of the observed solubility behavior.

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