# Solubility of Pyrene in Binary Alcohol + 1-Propanol and Alcohol + 2-Propanol Solvent Mixtures

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Experimental solubilities are reported for pyrene dissolved in 11 binary mixtures containing 1-propanol and 2-propanol with 1-butanol, 2-butanol, 2-methyl-1-propanol, 3-methyl-1-butanol, and 1-octanol at 26 °C. Results of these measurements are used to test two mathematical representations based upon the combined nearly ideal binary solvent (NIBS)/Redlich−Kister equation and modified Wilson model. For the systems studied, both equations were found to provide a fairly accurate mathematical representation of the experimental pyrene solubilities, with an average absolute deviation between experimental and back-calculated values of *ca.* ±0.5%.

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## 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 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, in terms of both new experimental measurements and critically-evaluated data compilations, there still exist numerous systems for which actual solubility data are not readily available.

To address this problem, researchers have turned to group contribution methods and semiempirical expressions to predict desired quantities. Group contribution methods have proved fairly successful in estimating solid solubility in pure and binary solvent mixtures from structural information. Practical application though is limited to systems for which all group interaction parameters are known. Generally, interaction parameters are evaluated from solid−liquid and liquid−vapor equilibrium data. It is important that the data base contain as many different functional groups as possible, preferably with adequate representation from both mono- and multifunctional solute/solvent molecules to permit evaluation of potential synergistic effects. The data base should contain sufficient experimental values near infinite dilution in the event that one wishes to determine separate interaction parameters for finite concentration and infinite dilution activity coefficient predictions.

Continued development of solution models for describing the thermodynamic properties of a solute in binary solvent systems requires that a large data base be available for assessing the applications and limitations of derived expressions. Currently, only a limited data base exists for crystalline nonelectrolyte solubility in binary solvent mixtures. For this reason, pyrene solubilities were determined in 11 binary alcohol + 1-propanol and alcohol + 2-propanol solvent mixtures. Results of these measurements are used to further test the descriptive abilities of several previously derived expressions.

**Table 1. Experimental Mole Fraction Solubilities of Pyrene ($x_A^{sat}$) in Binary Alcohol (B) + 1-Propanol (C) Solvent Mixtures at 26.0 °C**

| $x_C^o$ | $x_A^{sat}$ | $x_C^o$ | $x_A^{sat}$ |
|---|---|---|---|
| 2-Propanol (B) + 1-Propanol (C) | | | |
| 0.0000 | 0.002 90 | 0.6029 | 0.003 67 |
| 0.1113 | 0.003 06 | 0.7979 | 0.003 95 |
| 0.2138 | 0.003 17 | 0.8974 | 0.004 16 |
| 0.4118 | 0.003 40 | 1.0000 | 0.004 26 |
| 0.5035 | 0.003 55 | | |
| 1-Butanol (B) + 1-Propanol (C) | | | |
| 0.0000 | 0.006 22 | 0.6450 | 0.004 96 |
| 0.1265 | 0.006 06 | 0.8337 | 0.004 60 |
| 0.2295 | 0.005 87 | 0.9162 | 0.004 43 |
| 0.4508 | 0.005 43 | 1.0000 | 0.004 26 |
| 0.5503 | 0.005 15 | | |
| 2-Butanol (B) + 1-Propanol (C) | | | |
| 0.0000 | 0.004 39 | 0.6530 | 0.004 27 |
| 0.1202 | 0.004 38 | 0.8275 | 0.004 28 |
| 0.2429 | 0.004 33 | 0.9105 | 0.004 26 |
| 0.4566 | 0.004 30 | 1.0000 | 0.004 26 |
| 0.5510 | 0.004 27 | | |
| 2-Methyl-1-propanol (B) + 1-Propanol (C) | | | |
| 0.0000 | 0.003 26 | 0.6510 | 0.003 85 |
| 0.1281 | 0.003 41 | 0.8251 | 0.004 01 |
| 0.2296 | 0.003 48 | 0.9171 | 0.004 14 |
| 0.4522 | 0.003 66 | 1.0000 | 0.004 26 |
| 0.5446 | 0.003 75 | | |
| 3-Methyl-1-butanol (B) + 1-Propanol (C) | | | |
| 0.0000 | 0.005 46 | 0.6886 | 0.004 69 |
| 0.1508 | 0.005 35 | 0.8444 | 0.004 48 |
| 0.2637 | 0.005 22 | 0.9269 | 0.004 37 |
| 0.5110 | 0.004 93 | 1.0000 | 0.004 26 |
| 0.6012 | 0.004 81 | | |
| 1-Octanol (B) + 1-Propanol (C) | | | |
| 0.0000 | 0.020 77 | 0.7663 | 0.008 24 |
| 0.2155 | 0.017 62 | 0.8895 | 0.006 16 |
| 0.3558 | 0.015 04 | 0.9439 | 0.005 24 |
| 0.5782 | 0.011 38 | 1.0000 | 0.004 26 |
| 0.6799 | 0.009 68 | | |

## Experimental Methods

Pyrene (Aldrich, 99+%) was recrystallized several times from methanol. 1-Propanol (Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous),

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**Table 2. Experimental Mole Fraction Solubilities of Pyrene ($x_A^{sat}$) in Binary Alcohol (B) + 2-Propanol (C) Solvent Mixtures at 26.0 °C**

| $x_C^o$ | $x_A^{sat}$ | $x_C^o$ | $x_A^{sat}$ |
|---|---|---|---|
| | 1-Butanol (B) + 2-Propanol (C) | | |
| 0.0000 | 0.006 22 | 0.6423 | 0.003 98 |
| 0.1320 | 0.005 81 | 0.8276 | 0.003 39 |
| 0.2301 | 0.005 45 | 0.9133 | 0.003 15 |
| 0.4486 | 0.004 67 | 1.0000 | 0.002 90 |
| 0.5611 | 0.004 24 | | |
| | 2-Butanol (B) + 2-Propanol (C) | | |
| 0.0000 | 0.004 39 | 0.6412 | 0.003 57 |
| 0.1198 | 0.004 30 | 0.8312 | 0.003 22 |
| 0.2436 | 0.004 15 | 0.9411 | 0.003 03 |
| 0.4375 | 0.003 90 | 1.0000 | 0.002 90 |
| 0.5411 | 0.003 74 | | |
| | 2-Methyl-1-propanol (B) + 2-Propanol (C) | | |
| 0.0000 | 0.003 26 | 0.6428 | 0.003 12 |
| 0.1397 | 0.003 30 | 0.8276 | 0.003 03 |
| 0.2361 | 0.003 28 | 0.9084 | 0.002 99 |
| 0.4363 | 0.003 23 | 1.0000 | 0.002 90 |
| 0.5441 | 0.003 18 | | |
| | 3-Methyl-1-butanol (B) + 2-Propanol (C) | | |
| 0.0000 | 0.005 46 | 0.6818 | 0.003 68 |
| 0.1376 | 0.005 16 | 0.8539 | 0.003 23 |
| 0.2738 | 0.004 79 | 0.9218 | 0.003 07 |
| 0.4860 | 0.004 22 | 1.0000 | 0.002 90 |
| 0.5862 | 0.003 94 | | |
| | 1-Octanol (B) + 2-Propanol (C) | | |
| 0.0000 | 0.020 77 | 0.7599 | 0.006 81 |
| 0.2046 | 0.016 96 | 0.8875 | 0.004 74 |
| 0.3515 | 0.014 27 | 0.9437 | 0.003 84 |
| 0.5724 | 0.010 11 | 1.0000 | 0.002 90 |
| 0.6743 | 0.008 28 | | |

**Table 3. Mathematical Representation of Pyrene Solubilities in Several Binary Alcohol (B) + 1-Propanol (C) and Alcohol (B) + 2-Propanol (C) Solvent Mixtures**

| binary solvent system | eq 1 | | eq 2 | |
|---|---|---|---|---|
| component B + component C | $S_i$[a] | % dev[b] | $\Lambda_{ij}^{adj}$ [c] | % dev[b] |
| 2-propanol + 1-propanol | 0.036 | 0.5 | 1.041<br>0.961 | 0.6 |
| 1-butanol + 1-propanol | 0.127<br>0.065 | 0.4 | 1.729<br>0.661 | 0.3 |
| 2-butanol + 1-propanol[d] | | 0.5 | 0.817<br>1.205 | 0.3 |
| 2-methyl-1-propanol + 1-propanol[d] | | 0.8 | 0.937<br>1.065 | 0.6 |
| 3-methyl-1-butanol + 1-propanol | 0.081<br>0.061 | 0.2 | 0.325<br>2.825 | 0.2 |
| 1-octanol + 1-propanol | 1.153<br>−0.562<br>0.685 | 0.3 | 0.433<br>2.293 | 1.1 |
| 1-butanol + 2-propanol | 0.215 | 0.5 | 1.353<br>0.865 | 0.2 |
| 2-butanol + 2-propanol | 0.270 | 0.3 | 1.057<br>1.045 | 0.3 |
| 2-methyl-1-propanol + 2-propanol | 0.185 | 0.4 | 1.601<br>0.677 | 0.4 |
| 3-methyl-1-butanol + 2-propanol | 0.190<br>0.089 | 0.2 | 1.293<br>0.877 | 0.2 |
| 1-octanol + 2-propanol | 1.450<br>−0.882<br>1.076 | 1.3 | 0.405<br>2.437 | 1.7 |

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as $S_0$, $S_1$, and $S_2$. [b] Deviation (%) = $(100/N)\sum|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$. [c] Adjustable parameters for the modified Wilson equation are ordered as $\Lambda_{BC}^{adj}$ and $\Lambda_{CB}^{adj}$. [d] Experimental solubility data accurately described without the use of $S_i$ curve-fit parameters.

2-methyl-1-propanol (Aldrich, 99+%, anhydrous), 3-methyl-1-butanol (Aldrich, 99+%, anhydrous), and 1-octanol (Aldrich, 99+%, anhydrous) were stored over both anhydrous sodium sulfate and molecular sieves before being fractionally distilled. Gas chromatographic analysis showed solvent purities to be 99.7 mol % or better. Karl Fischer titration gave water contents (mass/mass %) of <0.01% for all seven alcohols used. Binary solvent mixtures were prepared by mass so that compositions could be calculated to 0.0001 mole fraction.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature water bath at (26.0 ± 0.1) °C for several days. Attainment of equilibrium was verified by repetitive measurements after several additional days and by approaching equilibrium from supersaturation by preequilibrating the solutions at a higher temperature. Aliquots of saturated pyrene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol. Concentrations were determined spectrophotometrically at 372 nm on a Bausch and Lomb Spectronic 2000. Experimental pyrene solubilities in the 11 binary alcohol + 1-propanol and alcohol + 2-propanol mixtures studied are listed in Tables 1 and 2, respectively. 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 (Acree and Zvaigzne, 1991; Acree *et al.*, 1991; Acree, 1992) suggested possible mathematical representations for isothermal solubility data based upon either a combined NIBS/Redlich−Kister model

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

or modified Wilson equation (Comer and Kopecni, 1990)

$$\ln[a_A(s)/x_A^{sat}] = 1 - x_B^o\{1 - \ln[a_A(s)/(x_A^{sat})_B]\}/(x_B^o + x_C^o\Lambda_{BC}^{adj}) - x_C^o\{1 - \ln[a_A(s)/(x_A^{sat})_C]\}/(x_B^o\Lambda_{CB}^{adj} + x_C^o) \quad (2)$$

where the various $S_i$ and $\Lambda_{ij}^{adj}$ "curve-fit" parameters can be evaluated via least squares analysis. In eqs 1 and 2 $x_B^o$ and $x_C^o$ refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present, $a_A(s)$ is the activity of the solid solute, and $(x_A^{sat})_i$ is the saturated mole fraction solubility of the solute in pure solvent $i$. The numerical value of $a_A(s) = 0.1312$ (Judy *et al.*, 1987) used in the modified Wilson computations was calculated from

$$\ln a_A(s) = -\Delta_{fus}H_A(T_{mp} - T)/(RTT_{mp}) \quad (3)$$

$\Delta_{fus}H_A$ is the molar enthalpy of fusion, at the normal melting point temperature of the solute, $T_{mp}$.

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of pyrene in the 11 binary alcohol + 1-propanol and alcohol + 2-propanol solvent systems is summarized in Table 3 in the form of curve-fit parameters and percent deviations in back-calculated solubilities. Careful examination of Table 3 reveals that both equations provide a fairly accurate mathematical representation for how the solubility of pyrene varies with solvent composition. For the most part, back-calculated and experimental values differ by less than ±1%, which is slightly less than the experimental uncertainty associated with the observed values.

From a computational standpoint, eq 1 will likely be preferred because most research groups involved in reporting thermodynamic properties have computer programs for evaluating the Redlich–Kister coefficients. With this idea in mind, we recommend not only that the future presentation of experimental isothermal solubility data for slightly soluble solid solutes dissolved in binary solvent mixtures include a tabulation of the actual observed values but if possible that the solubility data be mathematically represented by eq 1. Realizing that a single equation will not be applicable to all systems encountered, we further suggest eq 2 as an alternative mathematical representation for systems having extremely large solubility ranges and/or highly asymmetrical ln $x_A^{sat}$ versus $x_B^{\circ}$ curves, such as the carbazole + alkane + tetrahydropyran systems reported previously (Acree *et al.*, 1991).

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