

# Solubility of Anthracene in Binary Alkane + 3-Methyl-1-butanol Solvent Mixtures

Anita I. Zvaigzne and William E. Acree, Jr.\*

Department of Chemistry, University of North Texas, Denton, Texas 76203-5068

---

Experimental solubilities are reported for anthracene dissolved in seven binary mixtures containing 3-methyl-1-butanol with hexane, heptane, octane, cyclohexane, methylcyclohexane, 2,2,4-trimethylpentane, and *tert*-butylcyclohexane at 25 °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, the combined NIBS/Redlich–Kister and modified Wilson equations were found to provide very reasonable mathematical representations, with deviations between experimental and back-calculated values being on the order of  $\pm 1.5\%$  or less.

---

## 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 xanthenes) have been published in the recent chemical literature. 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. The UNIFAC model (1) now has two sets of group interaction parameters, with the publication of the infinite dilution values by Bastos *et al.* (2).

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, anthracene solubilities were de-

termined in seven binary alkane + 3-methyl-1-butanol solvent mixtures. Results of these measurements are used to further test the descriptive abilities of several previously derived expressions.

## Experimental Methods

Anthracene (Aldrich, 99.9+%) was used as received. Cyclohexane (Aldrich, HPLC), hexane (Aldrich, 99%), heptane (Aldrich, HPLC), octane (Aldrich, 99+%, anhydrous), methylcyclohexane (Aldrich, 99+%, anhydrous), 2,2,4-trimethylpentane (Aldrich, HPLC), and *tert*-butylcyclohexane (Aldrich, 99%) were stored over molecular sieves to remove trace water shortly before use. 3-Methyl-1-butanol (Aldrich, 99+%, anhydrous) was 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-Fisher titration gave a water content (mass/mass %) of <0.01% for 3-methyl-1-butanol. 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  $25.0 \pm 0.1$  °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 anthracene 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 356 nm on a Bausch and Lomb Spectronic 2000. Experimental anthracene solubilities in seven binary alkane + 3-methyl-1-butanol mixtures studied 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  $\pm 1.3\%$ .

## Results and Discussion

Acree and co-workers (3, 4) suggested possible mathematical representations for isothermal solubility data

\* To whom correspondence should be addressed.

**Table 1. Experimental Mole Fraction Solubilities of Anthracene (A) in Binary Alkane (B) + 3-Methyl-1-butanol (C) Solvent Mixtures at 25.0 °C**

$x_C^\circ$	$x_A^{\text{sat}}$	$x_C^\circ$	$x_A^{\text{sat}}$
Hexane (B) + 3-Methyl-1-butanol (C)			
0.0000	0.001 274	0.6401	0.001 064
0.1275	0.001 341	0.8269	0.000 890
0.2355	0.001 312	0.9115	0.000 813
0.4384	0.001 221	1.0000	0.000 727
0.5447	0.001 146		
Heptane (B) + 3-Methyl-1-butanol (C)			
0.0000	0.001 571	0.6681	0.001 128
0.1431	0.001 554	0.8383	0.000 916
0.2545	0.001 500	0.9151	0.000 823
0.4751	0.001 337	1.0000	0.000 727
0.5713	0.001 234		
Octane (B) + 3-Methyl-1-butanol (C)			
0.0000	0.001 838	0.6958	0.001 199
0.1537	0.001 814	0.8537	0.000 952
0.2672	0.001 728	0.9265	0.000 844
0.4914	0.001 488	1.0000	0.000 727
0.5939	0.001 345		
Cyclohexane (B) + 3-Methyl-1-butanol (C)			
0.0000	0.001 553	0.5993	0.001 153
0.1048	0.001 607	0.7958	0.000 934
0.2011	0.001 561	0.8896	0.000 836
0.3923	0.001 389	1.0000	0.000 727
0.4977	0.001 277		
Methylcyclohexane (B) + 3-Methyl-1-butanol (C)			
0.0000	0.001 649	0.6437	0.001 153
0.1290	0.001 709	0.8247	0.000 923
0.2350	0.001 633	0.9137	0.000 821
0.4367	0.001 422	1.0000	0.000 727
0.5422	0.001 299		
2,2,4-Trimethylpentane (B) + 3-Methyl-1-butanol (C)			
0.0000	0.001 074	0.6973	0.000 937
0.1476	0.001 114	0.8537	0.000 831
0.2838	0.001 103	0.9196	0.000 782
0.4998	0.001 042	1.0000	0.000 727
0.6038	0.000 990		
<i>tert</i> -Butylcyclohexane (B) + 3-Methyl-1-butanol (C)			
0.0000	0.001 978	0.7072	0.001 217
0.1685	0.001 938	0.8650	0.000 944
0.2866	0.001 843	0.9274	0.000 852
0.5168	0.001 545	1.0000	0.000 727
0.6089	0.001 400		

based upon either a combined NIBS/Redlich–Kister model

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

or Modified Wilson equation (5)

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

where the various  $S_i$  and  $\Lambda_{ij}^{\text{adj}}$  “curve-fit” parameters can be evaluated via least-squares analysis. In eqs 1 and 2  $x_B^\circ$  and  $x_C^\circ$  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  $(x_A^{\text{sat}})_i$  is the saturated mole fraction solubility of the solute in pure solvent  $i$ . The numerical value of  $a_A(s) = 0.010 49$  (6) used in the modified Wilson computations was calculated from

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

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

**Table 2. Mathematical Representation of Anthracene Solubilities in Several Binary Alkane (B) + 3-Methyl-1-butanol (C) Solvent Mixtures**

binary solvent system	two-param eq 1		eq 2	
	$S_1^a$	% dev <sup>b</sup>	$\Lambda_{ij}^{\text{adj}}$ <sup>c</sup>	% dev <sup>b</sup>
hexane +	0.857	0.8	1.709	0.3
3-methyl-1-butanol	0.186		1.149	
heptane +	0.802	0.3	1.437	0.3
3-methyl-1-butanol	0.021		1.341	
octane +	1.014	0.6	1.477	0.2
3-methyl-1-butanol	-0.112		1.529	
cyclohexane +	0.786	1.1	2.449	0.3
3-methyl-1-butanol	0.378		0.977	
methylcyclohexane +	0.880	0.9	2.453	0.4
3-methyl-1-butanol	0.358		1.061	
2,2,4-trimethylpentane +	0.663	0.3	1.449	0.2
3-methyl-1-butanol	0.095		1.121	
<i>tert</i> -butylcyclohexane +	1.092	0.5	1.701	0.4
3-methyl-1-butanol	-0.087		1.561	

<sup>a</sup> Combined NIBS/Redlich–Kister curve-fit parameters are ordered as  $S_0$  and  $S_1$ . <sup>b</sup> Deviation (%) =  $(100/N)\sum|\ln[(x_A^{\text{sat}})^{\text{calc}}/(x_A^{\text{sat}})^{\text{exp}}]|$ . <sup>c</sup> Adjustable parameters for the modified Wilson equation are ordered as  $\Lambda_{BC}^{\text{adj}}$  and  $\Lambda_{CB}^{\text{adj}}$ .

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the seven binary alkane + 3-methyl-1-butanol solvent systems is summarized in Table 2 in the form of curve-fit parameters and percent deviations in back-calculated solubilities. Careful examination of Table 2 reveals that both representations provide very reasonable mathematical descriptions for how the solubility of anthracene varies with solvent composition. For the most part, back-calculated and experimental values differ by less than  $\pm 1.5\%$ , which is comparable to the experimental uncertainty. Both expressions describe the synergistic solubility behavior evidenced by the maxima in the anthracene mole fraction solubility versus solvent composition curves for mixtures containing 3-methyl-1-butanol with hexane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane. Synergistic behavior is in line with published studies involving nonpolar and stable intramolecularly hydrogen-bonded solutes dissolved in binary hydrocarbon + alcohol, halo-hydrocarbon + alcohol, and cyclohexane + methylene iodide mixtures (7–13).

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  $\ln x_A^{\text{sat}}$  versus  $x_B^\circ$  curves, such as the carbazole + alkane + tetrahydropyran systems reported previously (4).

## Literature Cited

- (1) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
- (2) Bastos, J. C.; Soares, M. E.; Medina, A. G. *Ind. Eng. Chem. Res.* **1988**, *27*, 1269.

- (3) Acree, W. E., Jr.; Zvaigzne, A. I. *Thermochim. Acta* **1991**, 178, 151.
- (4) Acree, W. E., Jr.; McCargar, J. W.; Zvaigzne, A. I.; Teng, I.-L. *Phys. Chem. Liq.* **1991**, 23, 27.
- (5) Comer, J. F.; Kopečni, M. M. *Anal. Chem.* **1990**, 62, 991.
- (6) Acree, W. E., Jr.; Rytting, J. H. *J. Pharm. Sci.* **1983**, 72, 292.
- (7) Domanska, U. *Fluid Phase Equilib.* **1990**, 55, 125.
- (8) Domanska, U. *Ind. Eng. Chem. Res.* **1990**, 29, 470.
- (9) Domanska, U. *Pol. J. Chem.* **1981**, 55, 1715.
- (10) Buchowski, H. *Pol. J. Chem.* **1979**, 53, 1127.
- (11) Domanska, U. *Ind. Eng. Chem. Res.* **1987**, 26, 1153.
- (12) Domanska, U.; Hofman, T. *J. Solution Chem.* **1985**, 14, 531.
- (13) Coon, J. E.; Sediawan, W. B.; Auwaerter, J. E.; McLaughlin, E. *J. Solution Chem.* **1988**, 17, 519.

Received for review October 25, 1993. Revised April 14, 1994.  
Accepted May 11, 1994.\* This research was supported in part by a  
grant from the National Science Foundation (CTS-8922485).

\* Abstract published in *Advance ACS Abstracts*, August 15, 1994.