

Solubility of Anthracene in Binary Alkane + Chlorocyclohexane and Alkane + 1-Chlorooctane Solvent Mixtures at 298.2 K

Carmen E. Hernández, Karen S. Coym, Lindsay E. Roy, Joyce R. Powell, Mary E. R. McHale, and William E. Acree, Jr.*

Department of Chemistry, University of North Texas, Denton, Texas 76203-5070

Experimental solubilities are reported for anthracene dissolved in seven binary alkane + chlorocyclohexane and seven binary alkane + 1-chlorooctane solvent mixtures at 25 °C. The alkane cosolvents studied were hexane, heptane, octane, cyclohexane, methylcyclohexane, 2,2,4-trimethylpentane, and *tert*-butylcyclohexane (also called (1,1-dimethylethyl)cyclohexane). Results of these measurements are used to test two mathematical representations based upon the combined nearly ideal binary solvent (NIBS)/Redlich–Kister and modified Wilson equations. For the 14 systems studied, both equations were found to provide an accurate mathematical representation of the experimental data, with an overall average absolute deviation between measured and calculated values being 0.5% and 0.8% for the combined NIBS/Redlich–Kister and modified Wilson equations, respectively.

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, 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 predictive methods as a means to generate desired quantities. Numerous equations have been suggested for predicting solute solubilities in binary solvent mixtures. For the most part, the predictive methods do provide fairly reasonable estimates for noncomplexing systems. There still remains, however, the need to develop better predictive expressions and mixing models to describe the more nonideal complexing systems believed to contain hydrogen-bonding solvent components. 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 determined in seven binary alkane + chlorocyclohexane and seven binary alkane + 1-chlorooctane solvent mixtures. Results of these measurements are used to further test the descriptive abilities of two previously derived expressions.

Experimental Methods

Anthracene (Acros, 99.9+%) was recrystallized three times from 2-propanone. Chlorocyclohexane (Aldrich, 99%), 1-chlorooctane (Aldrich, 99%), hexane (Aldrich, 99+%),

Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Binary Alkane (B) + Chlorocyclohexane (C) Solvent Mixtures at 25.0 °C

x_C^c	x_A^{sat}	x_C^c	x_A^{sat}
Hexane (B) + Chlorocyclohexane (C)			
0.0000	0.001 274	0.6173	0.004 402
0.1112	0.001 735	0.8145	0.005 450
0.2203	0.002 236	0.8978	0.005 919
0.4256	0.003 355	1.0000	0.006 353
0.5154	0.003 809		
Heptane (B) + Chlorocyclohexane (C)			
0.0000	0.001 571	0.6565	0.004 688
0.1331	0.002 072	0.8369	0.005 656
0.2419	0.002 543	0.9205	0.005 995
0.4466	0.003 550	1.0000	0.006 353
0.5560	0.004 197		
Octane (B) + Chlorocyclohexane (C)			
0.0000	0.001 838	0.6759	0.004 881
0.1498	0.002 373	0.8457	0.005 697
0.2540	0.002 825	0.9223	0.005 993
0.5037	0.003 889	1.0000	0.006 353
0.5822	0.004 330		
Cyclohexane (B) + Chlorocyclohexane (C)			
0.0000	0.001 553	0.5864	0.004 413
0.1044	0.002 029	0.7843	0.005 355
0.1966	0.002 475	0.8797	0.005 800
0.3658	0.003 320	1.0000	0.006 353
0.4713	0.003 803		
Methylcyclohexane (B) + Chlorocyclohexane (C)			
0.0000	0.001 649	0.6302	0.004 673
0.1083	0.002 175	0.8082	0.005 465
0.2219	0.002 675	0.8832	0.005 915
0.4146	0.003 582	1.0000	0.006 353
0.5062	0.004 060		
2,2,4-Trimethylpentane (B) + Chlorocyclohexane (C)			
0.0000	0.001 074	0.6562	0.003 920
0.1416	0.001 499	0.8554	0.005 185
0.2708	0.001 974	0.9287	0.005 753
0.4788	0.002 951	1.0000	0.006 353
0.5672	0.003 422		
<i>tert</i> -Butylcyclohexane (B) + Chlorocyclohexane (C)			
0.0000	0.001 978	0.6916	0.004 738
0.1530	0.002 471	0.8522	0.005 506
0.2741	0.002 930	0.9252	0.005 878
0.5020	0.003 899	1.0000	0.006 353
0.5898	0.004 373		

heptane (Aldrich, HPLC), octane (Aldrich, 99+%, anhydrous), cyclohexane (Aldrich, HPLC), methylcyclohexane (Aldrich, 99+%, anhydrous), 2,2,4-trimethylpentane (Aldrich, HPLC), and *tert*-butylcyclohexane (Aldrich, 99%, also

* To whom correspondence should be addressed. E-mail: acree@unt.edu.

Table 2. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Binary Alkane (B) + 1-Chlorooctane (C) Solvent Mixtures at 25.0 °C

x_C^c	x_A^{sat}	x_C^c	x_A^{sat}
Hexane (B) + 1-Chlorooctane (C)			
0.0000	0.001 274	0.5365	0.004 579
0.0909	0.001 718	0.7350	0.005 924
0.1663	0.002 130	0.8715	0.006 918
0.3360	0.003 217	1.0000	0.007 780
0.4170	0.003 773		
Heptane (B) + 1-Chlorooctane (C)			
0.0000	0.001 571	0.5606	0.004 767
0.0921	0.001 972	0.7790	0.006 315
0.1797	0.002 419	0.8782	0.007 036
0.3626	0.003 518	1.0000	0.007 780
0.4635	0.004 152		
Octane (B) + 1-Chlorooctane (C)			
0.0000	0.001 838	0.5938	0.004 974
0.0999	0.002 238	0.7855	0.006 289
0.1944	0.002 673	0.8862	0.007 061
0.3811	0.003 728	1.0000	0.007 780
0.4837	0.004 354		
Cyclohexane (B) + 1-Chlorooctane (C)			
0.0000	0.001 553	0.4924	0.004 676
0.0712	0.002 000	0.7109	0.006 161
0.1381	0.002 427	0.8321	0.006 751
0.3005	0.003 516	1.0000	0.007 780
0.3771	0.004 001		
Methylcyclohexane (B) + 1-Chlorooctane (C)			
0.0000	0.001 649	0.5373	0.004 936
0.0814	0.002 152	0.7485	0.006 219
0.1521	0.002 556	0.8662	0.006 973
0.3321	0.003 642	1.0000	0.007 780
0.4287	0.004 192		
2,2,4-Trimethylpentane (B) + 1-Chlorooctane (C)			
0.0000	0.001 074	0.5981	0.004 474
0.1078	0.001 498	0.7796	0.006 085
0.1980	0.001 929	0.8966	0.007 045
0.3939	0.003 073	1.0000	0.007 780
0.4958	0.003 728		
<i>tert</i> -Butylcyclohexane (B) + 1-Chlorooctane (C)			
0.0000	0.001 978	0.6093	0.005 389
0.1053	0.002 479	0.7960	0.006 524
0.2018	0.002 967	0.8900	0.007 081
0.4072	0.004 138	1.0000	0.007 780
0.4934	0.004 662		

called (1,1-dimethylethyl)cyclohexane) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mol % or better. 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 ± 0.1) °C with periodic agitation for at least 3 days (often longer). Attainment of equilibrium was verified both by repetitive measurements after a minimum of 3 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 for spectrophotometric analysis at 356 nm on a Bausch and Lomb Spectronic 2000. Concentrations of the dilute solutions were determined from a Beer–Lambert law absorbance versus concentration working curve derived from measured absorbances of standard solutions of known molar concentration. Apparent molar absorptivities of the nine standard solutions varied systematically with molar concentration and ranged from approximately $\epsilon/(\text{L mol}^{-1} \text{cm}^{-1}) = 7450$ to $\epsilon/(\text{L mol}^{-1} \text{cm}^{-1}) = 7150$ for anthracene concentrations ranging from $C/(\text{mol L}^{-1}) = 6.75 \times 10^{-5}$ to $C/(\text{mol L}^{-1}) = 2.25 \times 10^{-4}$. Identical molar absorptivities

Table 3. Mathematical Representation of Anthracene Solubilities in Several Binary Alkane (B) + Chloroalkane (C) Solvent Mixtures

binary solvent system component (B) + component (C)	eq 1		eq 2	
	S_i^a	% dev. ^b	$\Lambda_{ij}^{\text{adj } c}$	% dev. ^b
hexane + chlorocyclohexane	1.098	0.6	2.043	1.1
	0.209		0.506	
	0.085			
heptane + chlorocyclohexane	0.796	0.4	1.724	1.6
			0.564	
octane + chlorocyclohexane	0.571	0.8	1.579	1.3
			0.651	
cyclohexane + chlorocyclohexane	0.940	0.3	2.188	0.2
	0.346		0.564	
	0.119			
methylcyclohexane + chlorocyclohexane	0.841	0.8	1.869	1.0
	0.327		0.477	
	0.353			
2,2,4-trimethylpentane + chlorocyclohexane	0.626	0.2	1.376	0.8
	0.146		0.680	
	-0.133			
<i>tert</i> -butylcyclohexane + chlorocyclohexane	0.402	0.5	1.521	0.9
	0.075		0.854	
	-0.263			
hexane + 1-chlorooctane	1.287	0.3	2.159	0.6
	0.397		0.506	
heptane + 1-chlorooctane	0.918	0.8	1.782	0.9
			0.564	
octane + 1-chlorooctane	0.618	0.7	1.579	0.9
			0.651	
cyclohexane + 1-chlorooctane	1.265	0.6	1.898	0.6
	0.657		0.332	
	0.320			
methylcyclohexane + 1-chlorooctane	1.034	0.7	1.376	0.5
	0.553		0.303	
	0.446			
2,2,4-trimethylpentane + 1-chlorooctane	1.065	0.5	1.753	1.1
	0.083		0.593	
	0.220			
<i>tert</i> -butylcyclohexane + 1-chlorooctane	0.721	0.2	1.724	0.3
	0.165		0.593	

^a Combined NIBS/Redlich–Kister curve-fit parameters are ordered as S_0 , S_1 , and S_2 . ^b Deviation (%) = $(100/7) \sum |[(x_A^{\text{sat}})^{\text{calc}} - (x_A^{\text{sat}})^{\text{exp}}]/(x_A^{\text{sat}})^{\text{exp}}|$. ^c Adjustable parameters for the modified Wilson equation are ordered as $\Lambda_{BC}^{\text{adj}}$ and $\Lambda_{CB}^{\text{adj}}$.

were obtained for select anthracene standard solutions that contained up to 5 vol % of the neat alkane and chloroalkane cosolvents. Experimental anthracene solubilities in the seven binary alkane + chlorocyclohexane and seven binary alkane + 1-chlorooctane solvent mixtures 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 ±1.8%.

Results and Discussion

Acree and co-workers (Acree and Zvaigzne, 1991) suggested possible mathematical representations for isothermal solubility data based upon either a combined NIBS/Redlich–Kister model

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

or modified Wilson equation

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

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^0 and x_C^0 refer to the initial mole fraction composition of the binary solvent calculated as if solute A were not present, $a_A(s)$ is the activity of the solid solute, N is the number of curve-fit parameters used, and $(x_A^{\text{sat}})_i$ is the saturated mole fraction solubility of the solute in pure solvent i . The numerical value of $a_A(s)$ used in the modified Wilson computations was $a_A(s) = 0.00984$ (Powell *et al.*, 1997).

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the 14 binary alkane + chloroalkane solvent systems is summarized in Table 3 in the form of "curve-fit" parameters and percent deviations in back-calculated solubilities. Each percent deviation is based upon the measured anthracene solubility data at the seven different binary solvent compositions. Careful examination of Table 3 reveals that both equations provide an accurate mathematical representation for how the solubility of anthracene varies with solvent composition. For the 14 anthracene systems studied, the overall average absolute deviation between the experimental and calculated values is 0.5% and 0.8% for eqs 1 and 2, respectively, which is less than the experimental uncertainty.

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