Solubility of Benzophenone in Binary Alkane + Carbon Tetrachloride Solvent Mixtures

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Experimental solubilities are reported for benzophenone dissolved in six binary mixtures containing carbon tetrachloride and hexane, heptane, octane, nonane, decane or dodecane at 25 °C. Results of these measurements are used to test some mathematical representations based upon the general single model (GSM), the mixture response model, and the NIBS/Redlich−Kister model. For the six systems studied, the general single model (GSM) was found to provide the more accurate mathematical representation of these experimental data, with an overall average standard deviation between measured and calculated mole fraction values of 4%.

Introduction

Solubility is no doubt one of the most important physicochemical properties and is particularly useful in a wide variety of phenomena relevant to biological, pharmaceutical, environmental, and petroleum industries. It is also important to know the solubility of the reagents and products in order to design the separation process properly. Solubility data for a number of polycylic aromatic hydrocarbons have been published in the chemical litterature.[1−3] Despite efforts by experimentalists, there still exist numerous systems for which solubility data are not readily available.

The use of binary solvent mixtures is a highly versatile and very powerful means of altering (increasing or decreasing) the solubility of a solute. Binary solvent mixtures can alter the solubility of an extremely wide variety of solutes. In some cases solubility can be improved by several orders of magnitude in solvent mixtures.

Continued development of solution models for describing the thermodynamic properties of a solute in binary solvent systems requires that a large database be available for assessing the applications and limitations of derived expressions. Recently, several sets of data have been reported for polycyclic aromatic hydrocarbons in binary solvent mixtures.[4] Few aromatic solutes were studied with an aldehyde or ketone functional group.[5] For this reason, benzophenone solubilities were determined in six binary alkane + carbon tetrachloride solvent mixtures. The results of these measurements are used to further test the descriptive abilities of several previously derived expressions.

Experimental Section

Benzophenone (Merck, >99%), carbon tetrachloride (BDH, 99.8%), hexane (Merck, 99%), heptane (Merck, 99%), octane (Merck, >99%), nonane (Fluka, >99%), decane (Merck, >99%), dodecane (BDH, 99%), and ethanol (Merck, >99%) were used as received without further purification. Binary solvent mixtures were prepared by mass so that compositions could be calculated to ±0.0001 mole fraction (x_C° or x_A°).

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The volume fractions of solvents (f_C) before addition of solute were calculated from $f_C = x_C^\circ V_C^m/(x_C^\circ V_C^m + x_A^\circ V_A^m)$, where x_C° and x_A° are the mole fractions of the solvents and V_C^m and V_A^m are their molar volumes.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature water bath (Multi Temp III thermostat) at 25.0 ± 0.1 °C for longer than 3 days. Attainment of equilibrium was verified by measurements at various times. Aliquots of saturated benzophenone solutions were transferred into a tared volumetric flask to determine the mass of sample and were diluted quantitatively with ethanol for spectrophotometric analysis at 270 nm on a UV−visible spectrophotometer Shimadzu model UV-265-FW. The concentrations of the dilute solutions were determined from a Beer−Lambert law. The calculated molar absorptivity of ϵ/L·mol^{-1}·cm^{-1} = 28 was obtained from the measured absorbances of several standard solutions of known molar concentrations (very dilute). The experimental benzophenone solubilities (solute mole fraction, x_m) in the six binary carbon tetrachloride (C) + alkane (A) solvent mixtures studied are listed in Table 1. The numerical values represent the average of three independent determinations, with measured values being reproducible to within ±2%.

Results and Discussion

In all systems studied, the benzophenone solubility increased with an increase in CCl_4 concentration in the mixture. Modeling of experimental solubility data enables researchers to represent mathematical aspects of solubility. According to these models, an unexperienced solute solubility could be predicted in different solvent systems. Recently Barzegar-Jalali and co-workers suggested a general single model (GSM) for expressing the solubility of a solute in a binary solvent mixture and applied the model in various systems.[6−8]

$$\log x_m = \sum_{j=0}^{P} S_j (f_C)^j \qquad (1)$$

where the various S_j are curve fit parameters, f_C is the volume fraction of one of the solvents in a binary solvent system (in this study, f_C is the volume fraction of CCl_4),

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Table 1. Experimental Mole Fraction Solubilities of Benzophenone (x_m) in Binary Alkane (A) + Carbon Tetrachloride (C) Solvent Mixtures at 25.0 °C

x_C° [a]	f_C [b]	x_m	x_C°	f_C	x_m
Hexane (A) + Carbon Tetrachloride (C)			Nonane (A) + Carbon Tetrachloride (C)		
0.0000	0.0000	0.0235	0.0000	0.0000	0.0601
0.0786	0.0592	0.0309	0.0768	0.0430	0.0643
0.1698	0.1311	0.0472	0.1373	0.0792	0.0776
0.3610	0.2942	0.1063	0.2321	0.1405	0.1086
0.6000	0.5254	0.1582	0.4267	0.2868	0.1555
0.7173	0.6518	0.1582	0.5567	0.4043	0.2310
0.7776	0.7207	0.1636	0.6263	0.4752	0.2806
0.8872	0.8530	0.1714	0.6637	0.5160	0.2890
1.0000	1.0000	0.5503	0.7181	0.5794	0.2964
			0.9114	0.8475	0.3597
			1.0000	1.0000	0.5503
Heptane (A) + Carbon Tetrachloride (C)			Decane (A) + Carbon Tetrachloride (C)		
0.0000	0.0000	0.0426	0.0000	0.0000	0.0483
0.1064	0.0727	0.0585	0.0540	0.0279	0.0605
0.1829	0.1285	0.0724	0.1444	0.0772	0.0679
0.3244	0.2402	0.1379	0.2268	0.1270	0.0778
0.4041	0.3087	0.2141	0.3941	0.2438	0.1238
0.5075	0.4042	0.2571	0.5323	0.3606	0.1962
0.6220	0.5200	0.3012	0.5989	0.4253	0.2322
0.7094	0.6164	0.3242	0.6424	0.4710	0.2410
0.8099	0.7372	0.3542	0.7351	0.5790	0.2761
0.9158	0.8774	0.3653	0.8364	0.7171	0.3418
1.0000	1.0000	0.5503	1.0000	1.0000	0.5503
Octane (A) + Carbon Tetrachloride (C)			Dodecane (A) + Carbon Tetrachloride (C)		
0.0000	0.0000	0.0698	0.0000	0.0000	0.0291
0.1584	0.1005	0.1040	0.1246	0.0570	0.0342
0.2880	0.1938	0.1502	0.2086	0.1007	0.0406
0.3126	0.2149	0.1520	0.2868	0.1459	0.0415
0.4439	0.3216	0.2612	0.3888	0.2128	0.0584
0.5686	0.4391	0.4056	0.4975	0.2960	0.0788
0.6451	0.5192	0.4509	0.6001	0.3892	0.1036
0.7448	0.6342	0.5155	0.7122	0.5124	0.1447
0.7930	0.6946	0.5337	0.8225	0.6631	0.1767
0.8928	0.8319	0.5406	0.9083	0.8080	0.1853
1.0000	1.0000	0.5503	1.0000	1.0000	0.5503

[a] x_C° is the mole fraction of carbon tetrachloride before addition of solute. [b] f_C is the volume fraction of carbon tetrachloride before addition of solute.

Table 2. Curve Fitting Parameters of Benzophenone Solubilities in Six Binary Carbon Tetrachloride (C) + Alkane (A) Solvent Mixtures

binary solvent system	eq 2		eq 3		eq 4		binary solvent system	eq 2		eq 3		eq 4	
	S_j [a]	SD [d]	W_i [b]	SD [d]	K_i [c]	SD [d]		S_j [a]	SD [d]	W_i [b]	SD [d]	K_i [c]	SD [d]
hexane + CCl_4	−1.650	3.35	−4.041	7.55	1.385	3.78	nonane + CCl_4	−1.234	3.36	−2.983	6.13	0.743	5.26
	2.65		−2.416		−2.772			1.655		−1.252		0	
	0		0.0351		−8.317			0		0.012		−3.590	
	−4.602		0		−4.534			0		0		−1.840	
	0		4.878					−4.038		3.213			
	3.334							3.359					
heptane + CCl_4	−1.410	5.12	−3.373	6.43	1.981	3.78	decane + CCl_4	−1.308	4.02	−3.088	7.74	0	4.29
	2.620		−1.508		0			1.878		−0.646		1.866	
	0		0.0174		−4.375			0		0		−0.780	
	−5.256		0		−2.163			−2.738		0		−5.505	
	3.780		4.831					1.909		1.995			
octane + CCl_4	−1.189	5.76	−2.505	12.77	1.844	1.74	dodecane + CCl_4	−1.570	2.37	−3.744	1.59	−1.500	8.46
	2.301		−0.588		2.428			1.684		−1.780		0	
	−1.385		0		−0.942			0		0.023		−5.506	
			0		−2.305			0		0		−6.912	
			2.522					−4.352		2.712			
								3.972					

[a] Curve fit parameters are ordered as S_0, S_1, S_2, S_3, S_4, and S_5. [b] Curve fit parameters are ordered as W_1, W_2, W_3, W_4, and W_5. [c] Curve fit parameters are ordered as K_0, K_1, K_2, and K_3. [d] $SD = 100 \times (\sum_{i=1}^{N} |x_m^{calc} - x_m^{exp}|)/N$.

and x_m is the saturated mole fraction solubility of the solute in the solvent mixture. The best fitting is obtained with $P = 5$ or

$$\log x_m = S_0 + S_1 f_C^1 + S_2 f_C^2 + S_3 f_C^3 + S_4 f_C^4 + S_5 f_C^5 \quad (2)$$

The statistically based mixture response model was introduced by Ochsner et al.[9]

$$\ln x_m = W_1 f'_A + W_2 f'_C + \frac{W_3}{f'_A} + \frac{W_4}{f'_C} + W_5 f'_C f'_A \quad (3)$$

where f'_A and f'_C are the modified volume fractions of

carbon tetrachloride and alkane before addition of solute, which were calculated by $f_i' = 0.96f_i + 0.02$ (where f_i is the volume fraction of solvent i before addition of solute), and W_1-W_5 denote the curve fitting parameters.

Another theoretical model, that is, the NIBS/Redlich−Kister model in the general form, is[10]

$$\ln x_n = x_A^\circ \ln(x_m^{sat})_A + x_C^\circ \ln(x_m^{sat})_C + x_A^\circ x_C^\circ \sum_{i=0}^{N} K_i (x_A^\circ - x_C^\circ)^i \quad (4)$$

where x_C° and x_A° are the initial mole fractions of solvents before addition of solute, $(x_m^{sat})_i$ is the saturated mole fraction solubility of solute in pure solvent i, and K_i are curve fit parameters.

The ability of eqs 2−4 to mathematically represent the experimental solubility of benzophenone in six binary carbon tetrachloride + alkane solvent systems is summarized in Table 2 in the from of curve fit parameters and standard deviations in calculated solubilities (mole fractions). Some of the curve fit parameters which do not significantly improve the fit were deleted by statistical analysis for all models. The fitness ability of the equations is evaluted by comparing standard deviation (SD) values. Table 2 reveals that all equations provide nearly good mathematical representations for how the solubility of benzophenone varies with solvent composition. For all of the benzophenone systems studied here, the general single model (GSM) was found to provide the more accurate mathematical representation of the experimental data, with an overall average standard deviation of 4%.

From a computational standpoint, eqs 2 and 4 will likely be preferred because the expressions contain provisions for the inclusion of additional coefficients as might be needed to mathematically describe the experimental data.

This study shows that, for benzophenone solubility in solvent mixtures, the accuracy of the general single model (GSM) is better than that of the NIBS/Redlich−Kister model (eq 4) and better than that of the mixture response model (eq 3). So, we recommend that, for presentation of experimental solubility data of solid solutes in binary mixture solvents in addition to the tabulation of experimental solubility data, these data be mathematically represented by eq 1 as an alternative because it is accurate and simple.

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