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SHORT ARTICLE

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Solubility of 2-Chloro-4,6-dinitroresorcinol in Ethanol, Methanol, Acetic Acid, Ethyl Acetate, and Water

Li Zhang, Zhen Hu, Bo Jiang, and Y. D. Huang*

School of Chemical Engineering and Technology, State Key Laboratory of Urban Water Resource and Environment Department of Applied Chemistry, Harbin Institute of Technology, 150001 Harbin, China

ABSTRACT: The solubility of 2-chloro-4,6-dinitroresorcinol in ethanol at (299.35 to 343.75) K, methanol at (299.75 to 333.35) K, acetic acid at (299.35 to 343.15) K, ethyl acetate at (298.75 to 344.95) K, and water at (298.85 to 341.95) K was measured using the ultraviolet absorption method. The 2-chloro-4,6-dinitroresorcinol solubility in each solvent increases with increasing temperature. Results of these measurements were correlated with a semiempirical equation. For the systems studied, the semiempirical equation was found to provide reasonable mathematical representation, and the three parameters of the semiempirical equation were obtained.

INTRODUCTION

2-Chloro-4,6-dinitroresorcinol is a yellow crystal (Figure 1). It is an intermediate compound used to synthesize 4,6-diamino-resorcinol which is useful in the preparation of poly-*p*-phenylene-benzobisoxazole (PBO) fiber.[1,2] PBO fiber is an organic fiber demonstrating remarkably high modulus and strength values, far in excess of almost all other so-called high-performance polymeric fibers.[3−5] In previous studies, 2-chloro-4,6-dinitroresorcinol was synthesized from 4,6-dinitro-1,2,3-trichlorobenzene by hydrolysis with an alkanol and a base.[2] Then 2-chloro-4,6-dinitroresorcinol was contacted with a hydrogen-reducing agent in the presence of acetic acid solvent and a catalyst under reaction conditions to form 4,6-diamino-resorcinol. The products of 2-chloro-4,6-dinitroresorcinol were purified by extraction and recrystallization.[6] During the synthesis and purification process, the common solvents, including ethanol, methanol, acetic acid, ethyl acetate, and water, were often used. Therefore, it is necessary to know the solubility data of 2-chloro-4,6-dinitroresorcinol in these solvents. What's more, solubility data for a solute−solvent system are also important physicochemical parameters to determine or estimate some crystallization parameters and reaction kinetics or thermodynamics study. There, however, has been no report as to 2-chloro-4,6-dinitroresorcinol solubility data in some solvents.

In the present study, the solubility of 2-chloro-4,6-dinitroresorcinol in ethanol, methanol, acetic acid, ethyl acetate, and water was determined by the ultraviolet absorption method. This method is faster, less expensive, and more available than other methods including the high-performance liquid chromatography method[7−9] and the laser technique.[10,11] Results of these measurements were correlated by the three-parameter semiempirical equation. The parameters of the semiempirical equation were obtained.

EXPERIMENTAL SECTION

Materials. 2-Chloro-4,6-dinitroresorcinol prepared in the laboratory was recrystallized prior to use. Its mass fraction purity, determined by high-performance liquid chromatography measurement, was greater than 99.97 %. Its melting point temperature is 458.15 K by thermal gravimetric and thermal decomposition analysis. Deionized water was distilled before use. Ethanol, methanol, acetic acid, and ethyl acetate were analytical research grade reagents from Tianjin Chemical Reagent Co.

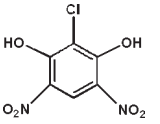

Figure 1. Molecular structure of 2-chloro-4,6-dinitroresorcinol.

Apparatus and Procedures. The apparatus and the procedure were similar to that described in the literature[12,13] and described only briefly here. The temperature was controlled to be constant (fluctuates within 0.05 K) through a thermostatted bath.[14] The masses of the mixtures were weighed using an analytical balance with an uncertainty of ± 0.0001. The estimated error in the mole fraction is less than 0.0001.

An excess amount solute was added to the solvents in a 100 mL glass vessel with a thermometer and a stir bar. The contents of the vessel were heated very slowly with continuous stirring. To make the solution attain equilibrium, it was constantly stirred for 2.5 h at the designed temperature, and then the stirring was stopped to let the solution settle for 1.5 h. Clear liquid (about 5 mL) was dropped into the sampling vial by a heated pipet. The mass of the clear liquid was determined by an analytical balance with an uncertainty of ± 0.0001 g. To make the solute dissolve completely at room temperature, more solvent was added into the sampling vial. By repeating the above procedure three times at very different designed temperatures, a series of diluted clear liquid samples were obtained. The concentrations of diluted clear liquid and calibration curves were analyzed by the UV−visible

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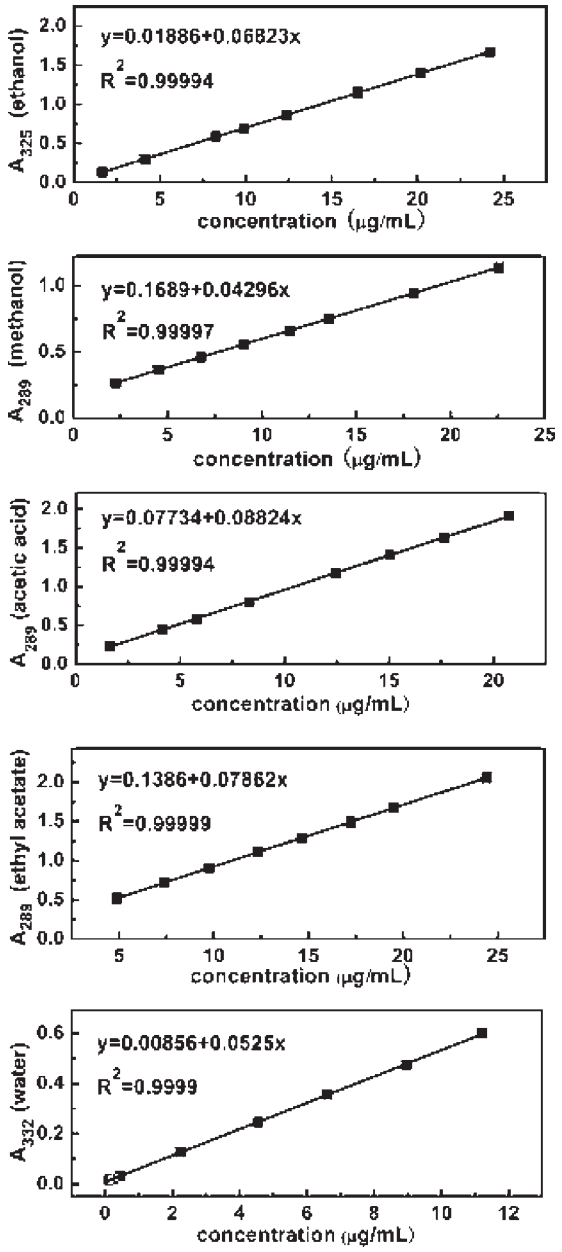

Figure 2. Calibration curves of 2-chloro-4,6-dinitroresorcinol in ethanol, methanol, acetic acid, ethyl acetate, and water.

spectrophotometer at room temperature. On the basis of the calibration curves, the concentrations of diluted clear liquid samples at room temperature were obtained. The diluted volume was known, so the mass of solute in the diluted clear liquid was obtained. In the course of dilution cooling, the mass of solute is constant. So the mass of solute in the undiluted clear liquid at designed temperature was obtained. Then the mass of solvent in the undiluted clear liquid at designed temperature was also obtained. The mean values were used to calculate the mole fraction solubility x_1 based on the following equation

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \quad (1)$$

where m_1 and m_2 represent the mass of the solute and solvent, and M_1 and M_2 are the molecular weights of the solute and the solvent, respectively.

RESULTS AND DISCUSSION

Typical calibration curves obtained from a dilution row with eight concentrations were shown in Figure 2. A linear correlation between the absorbance and 2-chloro-4,6-dinitroresorcinol concentration was observed in ethanol at λ = 289 nm, methanol at λ = 325 nm, acetic acid at λ = 289 nm, ethyl acetate at λ = 289 nm, and water at λ = 332 nm. Linear regression analysis was performed to determine the linearity of correlation between the two parameters. As shown by a greater coefficient of determination (R^2) using linear regression analysis, ultraviolet absorption measurement was able to accurately measure the solubility of 2-chloro-4,6-dinitroresorcinol in ethanol, methanol, acetic acid, ethyl acetate, and water.

The solubilities of 2-chloro-4,6-dinitroresorcinol in ethanol, methanol, acetic acid, ethyl acetate, and water at different temperatures were presented in Table 1 and more visually given in Figure 3.

The solubility of a solid in a liquid may be expressed in a very general manner by eq 2

$$\ln x_1 = -\frac{\Delta H_{f,1}}{RT_{f,1}}\left(\frac{T_{f,1}}{T} - 1\right) - \frac{\Delta C_{pf,1}}{R}\left(\frac{T_{f,1}}{T} - 1\right) + \frac{\Delta C_{pf,1}}{R}\ln\frac{T_{f,1}}{T} - \ln\gamma_1 \quad (2)$$

where x_1, γ_1, $\Delta H_{f,1}$, $\Delta C_{pf,1}$, $T_{f,1}$, R, and T stand for the mole fraction of the solute, activity coefficient, enthalpy of fusion, difference in the solute heat capacity between the solid and liquid at the melting temperature, melting temperature of the solute, gas constant, and equilibrium temperature in the saturated solution, respectively. For regular solutions,[14−16] the activity coefficient is given by

$$\ln\gamma_1 = A + \frac{B}{T} \quad (3)$$

where A and B stand for empirical constants. Introducing γ_1 from eq 3 into eq 2 and subsequent rearrangements result in eq 4

$$\ln x_1 = \left[\frac{\Delta H_{f,1}}{RT_{f,1}} + \frac{\Delta C_{pf,1}}{R}(1 + \ln T_{f,1}) - A\right] - \left[B + \left(\frac{\Delta H_{f,1}}{RT_{f,1}} + \frac{\Delta C_{pf,1}}{R}\right)T_{f,1}\right]\frac{1}{T} - \frac{\Delta C_{pf,1}}{R}\ln T \quad (4)$$

Further, eq 4 can be written as

$$\ln x_1 = a + \frac{b}{T} + c\ln T \quad (5)$$

where T is the absolute temperature, the unit of which is K, and a, b, and c are empirical constants.

The solubility data were correlated with eq 5, and the comparisons between experimental and calculated results were presented in Table 1. The values of the parameters (a, b, and c) in eq 5 and the root-mean-square deviations (rmsd) were listed in Table 2. It can be seen that the

Table 1. Mole Fraction Solubility of 2-Chloro-4,6-dinitroresorcinol in Ethanol, Methanol, Acetic Acid, Ethyl Acetate, and Water

T/K	x_1	$10^6(x_1^{calc} - x_1)$	T/K	x_1	$10^6(x_1^{calc} - x_1)$
	Ethanol			Ethanol	
299.35	0.00297	−0.14724	326.35	0.00882	0.00000
303.15	0.00355	0.00000	329.85	0.00989	0.00000
307.35	0.00428	−1.00000	332.65	0.01080	−2.34912
310.75	0.00493	0.00000	335.45	0.01175	0.00000
314.25	0.00568	1.73694	339.15	0.01307	0.00000
317.65	0.00648	0.00000	343.75	0.01480	2.60774
320.15	0.00711	1.00000			
	Methanol			Methanol	
299.75	0.00172	0.61735	318.15	0.00456	1.00000
305.95	0.00239	−1.00000	320.75	0.00524	0.00000
308.75	0.00277	−2.67000	323.35	0.00600	2.91358
311.25	0.00316	0.00000	327.05	0.00731	0.00000
313.65	0.00359	1.60436	330.15	0.00860	0.00000
315.95	0.00406	0.00000	333.35	0.01019	−8.62162
	Acetic Acid			Acetic Acid	
299.35	0.00649	−2.04808	323.95	0.01791	0.00000
305.55	0.00872	1.75702	327.65	0.02019	1.59814
311.45	0.01125	2.00000	334.65	0.02480	−0.51120
315.05	0.01300	−8.60629	336.45	0.02604	−1.06621
318.75	0.01494	0.00000	340.45	0.02886	0.00000
321.85	0.01668	0.40000	343.15	0.03079	−1.63061
	Ethyl Acetate			Ethyl Acetate	
298.75	0.04491	−0.94118	327.25	0.06705	0.00000
302.65	0.04741	0.00000	331.85	0.07159	0.00000
306.25	0.04985	−0.56413	333.35	0.07314	−3.57347
309.95	0.05250	0.00000	337.15	0.07720	0.15000
313.85	0.05547	0.78422	342.55	0.08339	0.00000
318.15	0.05894	0.00000	344.95	0.08630	−4.12424
323.15	0.06327	−7.48978			
T/K	10^5x_1	$10^6(x_1^{calc} - x_1)$	T/K	10^5x_1	$10^6(x_1^{calc} - x_1)$
	Water			Water	
298.85	3.49024	−1.55605	320.65	7.61815	0.00000
301.15	3.65000	0.09956	323.15	8.17402	1.38888
303.65	4.22863	−1.85743	325.85	9.12015	0.00000
306.35	4.59298	−1.00000	327.45	9.79090	−1.63168
309.05	4.85744	1.26101	330.15	10.63590	−1.00000
311.35	5.43537	0.00000	332.25	11.28910	0.00000
313.35	5.67074	1.84325	336.35	13.03400	−1.49429
315.75	6.29335	1.00000	339.55	14.22940	0.00000
318.15	6.80000	1.71400	341.95	15.19681	1.54346

semiempirical equation can be used to describe the variation with temperature of the solubility of 2-chloro-4,6-dinitroresorcinol. The rmsd is defined as

$$\sigma_x = \left[\frac{1}{n}\sum_{i=1}^{n}(x_{1,\mathrm{calc}i} - x_{1,i})^2\right]^{1/2} \quad (6)$$

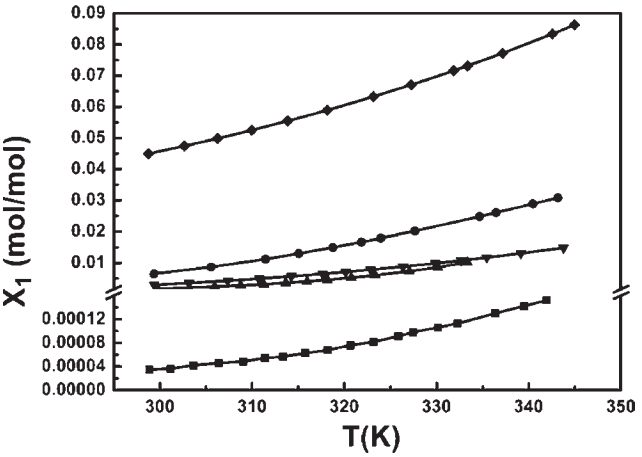

Figure 3. Solubility of 2-chloro-4,6-dinitroresorcinol in different solvents: ▼, ethanol; ▲, methanol; ●, acetic acid; ♦, ethyl acetate; ■, water; −, calculated x_1 from eq 2.

Table 2. Parameters for Correlation Equations of Different Solvents

solvent	a	b	c	$10^6\sigma_x$
ethanol	188.312	−12321.9	−26.8290	1.28430
methanol	−200.328	4600.26	31.3194	2.81225
acetic acid	272.522	−16201.0	−39.1887	2.77070
ethyl acetate	−66.0698	1755.90	10.0163	2.59759
water	9.59052	−3987.56	−1.15019	1.20216

where n is the number of experimental points; $x_{1,\mathrm{cal}i}$ represents the solubility calculated from eq 5; and $x_{1,i}$ is the experimental solubility value.

From Figure 3, it can be seen that the 2-chloro-4,6-dinitroresorcinol solubility in each solvent increases with increasing temperature. In addition, the solubility of 2-chloro-4,6-dinitroresorcinol in ethyl acetate is obviously greater than in ethanol, methanol, acetic acid, and water, and the least solubility of 2-chloro-4,6-dinitroresorcinol is shown in water among the solvents studied. Referring to the fact that the polarities of the five solvents used in the experiments decrease in the following order, water (100) > methanol (76.2) > ethanol (65.4) > acetic acid (64.8) > ethyl acetate (23),[17] in the reverse order of the solubilities, it can be concluded that the weaker the polarity of the solvent used, the higher the solubility of the 2-chloro-4,6-dinitroresorcinol. As seen from Figure 3, the influence of the temperature on the solubility of 2-chloro-4,6-dinitroresorcinol is great in water, when the temperature changes from (298.85 to 341.95) K. The solubility of 2-chloro-4,6-dinitroresorcinol in water is greater at higher temperature than at lower temperature. As stated previously, 2-chloro-4,6-dinitroresorcinol should be refined by extraction with ethyl acetate as the solvent and recrystallization with one of acetic acid, ethanol, and methanol as the solvent. Moreover, 2-chloro-4,6-dinitroresorcinol has to be washed in cold water.

From Table 2, we can find that the values of parameter c in all five solvents are relatively small, which represents the relatively small $\Delta C_{pf,1}$ ($c = \Delta C_{pf,1}/R$). This is true for 2-chloro-4,6-dinitroresorcinol in ethanol, methanol, acetic acid, ethyl acetate, and water, so the last terms of eq 5 were neglected.

For a given compound, the values of a and b reflect the variations in the solution activity coefficient and provide an indication of the effect of solution nonidealities on the solubility of the solute.[14]

CONCLUSION

The ultraviolet absorption method can be used to accurately measure the solubility of 2-chloro-4,6-dinitroresorcinol in ethanol, methanol, acetic acid, ethyl acetate, and water. The solubility of 2-chloro-4,6-dinitroresorcinol in ethanol at (299.35 to 343.75) K, methanol at (299.75 to 333.35) K, acetic acid at (299.35 to 343.15) K, ethyl acetate at (298.75 to 344.95) K, and water at (298.85 to 341.95) K was determined. The 2-chloro-4,6-dinitroresorcinol solubility in pure solvents increases with increasing temperature and in the following order: water < methanol < ethanol < acetic acid < ethyl acetate. The semiempirical equation was a reasonable mathematical representation to fit the experimental data, and the parameters (a, b, and c) were obtained.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ydhuang.hit1@yahoo.com.cn. Tel./fax: +86 451 86413711.

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