Short Articles

Solubility of Bis(benzoxazolyl-2-methyl) Sulfide in Different Pure Solvents and Ethanol + Water Binary Mixtures between (273.25 and 325.25) K

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The solubilities of bis(benzoxazolyl-2-methyl) sulfide in ethanol, 1-butanol, 2-propanol, chlorobenzene, toluene, *o*-xylene, and ethanol + water were measured by a synthetic method. The laser monitoring observation technique was used to determine the disappearance of the solid phase in the solid + liquid mixture. All data were measured in the temperature range from (273.25 to 325.25) K at atmosphere pressure. The effect of solvent composition and temperature on the solubility was discussed. For all solvents studied, the data are well fitted with a semiempirical Apelblat equation.

Introduction

Bis(benzoxazolyl-2-methyl) sulfide (CAS Registry No. 66000-36-0) is used as an intermediate to manufacture the fluorescent whiting agent EBF, which is very useful in the dyestuff industry.[1−3] This dibenzazolyl compound is straw yellow powdered crystal with a molecular formula of $C_{16}H_{12}N_2O_2S$ and a molecular weight of 296.34. Its chemical structure is shown in Figure 1.

Bis(benzoxazolyl-2-methyl) sulfide is crystallized from solution in the manufacture and purification process. The crystallization process is the critical step that determines the quality of the final product. To determine the proper solvent and to design an optimized crystallizer, it is necessary to know its solubility in different solvent systems. A systematic study of the solubility of this dibenzazolyl compound in different solvent systems has not been reported in the literature.

In this study, the solubilities of bis(benzoxazolyl-2-methyl) sulfide in ethanol, 1-butanol, 2-propanol, chlorobenzene, toluene, *o*-xylene, and ethanol + water were measured in the temperature range from (273.25 to 325.25) K at atmosphere pressure by a laser monitoring observation technique, and the modified Apelblat equation was used for the correlation of the experimental data.

Experimental Section

Materials. Bis(benzoxazolyl-2-methyl) sulfide was prepared by the phase transfer catalysis reaction between 2-chloromethylbenzoxazole and sodium sulfide.[1,2] The obtained product was recrystallized twice from alcohol. It was dried in a vacuum oven for 12 h at room temperature and stored in a desiccator. The melting point of the product measured by differential scanning calorimetry is (349 to 350) K, and the literature value is (348 to 349) K.[1] Its purity was determined by HPLC to be 98.7 % by mass. The sample was analyzed with elementary analysis, mass spectrometric detection, and infrared spectrometer detection. The results show that it is the target product. Other reagents including ethanol, 1-butanol, 2-propanol, chlorobenzene, toluene, and *o*-xylene are analytical research grade reagents from Shanghai Chemical Reagent Co. Double distilled water was used in the experiments.

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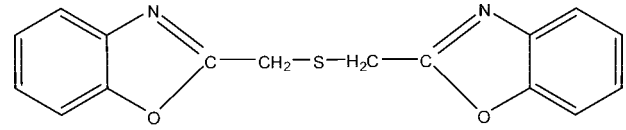

Figure 1. Chemical structure of bis(benzoxazolyl-2-methyl) sulfide.

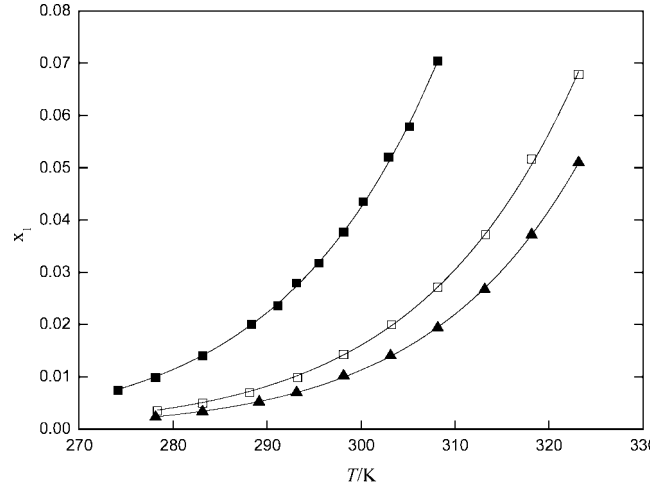

Figure 2. Mole fraction solubility of bis(benzoxazolyl-2-methyl) sulfide x_1 in different solvents: ■, ethanol; □, 1-butanol; ▲, 2-propanol; —, calculated values.

Apparatus and Procedure. The method employed in this work was classed as a synthetic method, which was much faster and more reliable than the analytical method.[4,5] The apparatus for the solubility measurement is the same as described in the literature[6−8] and described briefly here.

The laser monitoring system consists of a laser generator, a photoelectric transformer, and a recorder. The experiments were carried out in a magnetically stirred, jacketed glass vessel (250 cm^3). A constant temperature was maintained by circulating water through the outer jacket from a thermoelectric controller (type 501, Shanghai Laboratory Instrument Works Co., Ltd.) at the required temperature. The jacket temperature could be maintained within ± 0.05 K of the required temperature. A condenser was fitted to reduce the solvent's evaporation. A

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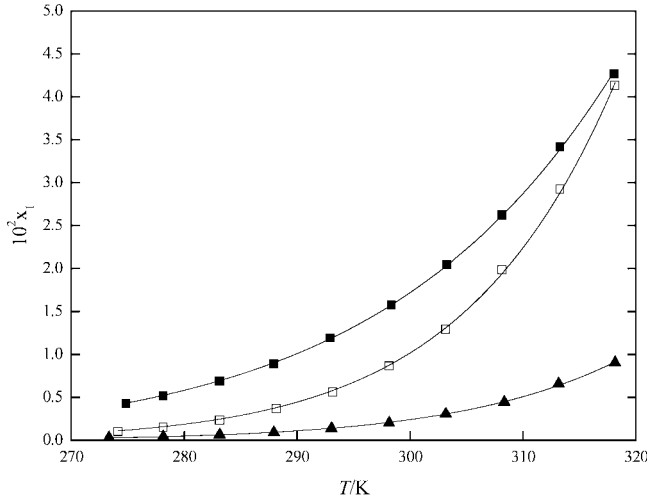

Figure 3. Mole fraction solubility of bis(benzoxazolyl-2-methyl) sulfide x_1 in different solvents: ■, chlorobenzene; □, toluene; ▲, *o*-xylene; —, calculated values.

mercury-in-glass thermometer was inserted into the inner chamber of the vessel for the measurement of the temperature. The uncertainty of the temperature was ± 0.05 K. The masses of the solute and the solvents were weighed using a Mettler H542 balance with an uncertainty of ± 0.00001 g.

The solubilities of bis(benzoxazolyl-2-methyl) sulfide in various organic solvents were measured as follows. Predetermined amounts of bis(benzoxazolyl-2-methyl) sulfide (m_1) and solvent (m_2, about 80 g ± 0.001 g) were placed in the inner chamber of the vessel. The contents of the vessel were stirred continuously at the required temperature. In the early stages of the experiment, the laser beam was decreased by the undissolved particles of solute in the solution. As the particles of the solute dissolved, the intensity of the laser beam increased gradually. When the solute dissolved completely, the solution was clear, and the laser intensity reached maximum. Then, an additional solute of known mass (about (1 to 3) mg), which was determined by a preliminary experiment, was introduced into the vessel. This procedure was repeated until the penetrated laser intensity could not return to the maximum, which means the last addition could not dissolve completely. The amount of solute leading to the laser intensity decrease was less than 1.0 mg. The uncertainty in the solubility values was estimated to be 1.0 %. The interval of addition depended on the speed of dissolving at that temperature, and it should last more than 30 min. The total amount of the solute consumed was recorded. The same solubility experiment was conducted three times, and each time had good agreement.

The mean values were used to calculate the mole fraction solubility x_1 based on

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \quad (1)$$

where m_1, m_2, and m_3 represent the masses of solute, solvents, and water. M_1, M_2, and M_3 are the molecular weights of solute, solvents, and water, respectively. With regard to pure solvents system, m_1 and m_2 represent the masses of solute and solvents, M_1 and M_2 are the molecular weights of solute and solvents, and $m_3 = 0$.

Reliability Analysis. To verify the reliability of this method, a testifying experiment was carried out with sodium bicarbonate. The solubility of the substance in water was measured by the present method, and the experimental data were compared with that published in ref 9 as shown in Table 1. It is seen that the experimental data agree with that in the literature. The biggest relative deviation is < 0.3 % for the sodium bicarbonate−water system. So the present method is very suitable for solubility measurement for the solid−liquid system.

Table 1. Comparison of the Experimental Solubility of Sodium Bicarbonate in Water with the Literature Data

T/°C	20	25	30	35	45
experimental data/wt %	8.72	9.29	9.91	10.58	11.98
literature data/wt %	8.70	9.30	9.90	10.60	12.00
relative deviation/%	0.23	−0.11	0.10	−0.19	−0.17

Table 2. Mole Fraction Solubility x_1 of Bis(benzoxazolyl-2-methyl) Sulfide in Pure Solvents

T/K	10^2x_{1exptl}	$(x_{1exptl} - x_{1calcd})/x_{1exptl}$	*T*/K	10^2x_{1exptl}	$(x_{1exptl} - x_{1calcd})/x_{1exptl}$
		Ethanol			
274.15	0.741	−0.025	295.55	3.175	−0.008
278.15	0.978	−0.026	298.15	3.768	−0.003
283.15	1.401	−0.009	300.25	4.345	0.007
288.35	2.001	−0.001	302.95	5.201	0.017
291.15	2.355	−0.021	305.15	5.785	−0.013
293.15	2.790	0.018	308.15	7.044	8.24E-6
		1-Butanol			
278.35	0.349	−0.039	303.25	1.994	0.006
283.15	0.494	−0.032	308.15	2.711	−0.001
288.15	0.698	−0.035	313.25	3.722	−0.005
293.25	0.986	−0.038	318.15	5.163	0.020
298.15	1.422	0.002	323.15	6.786	−0.009
		2-Propanol			
278.15	0.231	−0.019	303.15	1.403	0.007
283.15	0.333	−0.025	308.15	1.939	−0.003
289.15	0.523	−0.008	313.15	2.676	−0.009
293.15	0.703	0.004	318.15	3.723	0.001
298.15	1.047	0.026	323.15	5.102	0.001
		Chlorobenzene			
274.85	0.424	−0.022	298.35	1.573	−0.002
278.15	0.514	−0.018	303.25	2.046	0.005
283.15	0.684	−0.013	308.15	2.621	0.002
287.95	0.889	−0.015	313.25	3.415	0.009
292.95	1.190	0.006	318.05	4.268	−0.006
		Toluene			
274.15	0.0608	−0.089	298.15	0.861	−0.016
278.15	0.0971	−0.061	303.15	1.392	−0.014
283.15	0.176	−0.061	308.15	2.402	0.020
288.15	0.306	−0.043	313.25	2.923	0.015
293.15	0.522	−0.040	318.15	4.132	−0.008
		o-Xylene			
273.35	0.0297	0.075	298.15	0.203	−0.025
278.15	0.0431	0.039	303.15	0.305	0.001
283.15	0.0640	0.017	308.35	0.443	−0.014
287.95	0.0899	−0.035	313.15	0.656	0.028
293.05	0.138	−0.013	318.15	0.904	−0.009

Results and Discussion

The measured solubilities of bis(benzoxazolyl-2-methyl) sulfide in ethanol, 1-butanol, 2-propanol, chlorobenzene, toluene, and *o*-xylene between (273.25 and 325.25) K are listed in Table 2 and plotted in Figure 2 and Figure 3. The temperature dependence of the bis(benzoxazolyl-2-methyl) sulfide solubility in different solvents was correlated by the modified Apelblat equation[10−13]

$$\ln x = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \quad (2)$$

where x is the mole fraction solubility of bis(benzoxazolyl-2-methyl) sulfide; T is the measured absolute temperature; and A, B, and C are the model parameters. The values of the model parameters which were obtained by the least-squares method are presented in Table 4. The comparison between calculated values of x and experimental ones is also shown in Table 2. The calculated results show satisfactory agreement with the experimental data. The values of the root-mean-square devia-

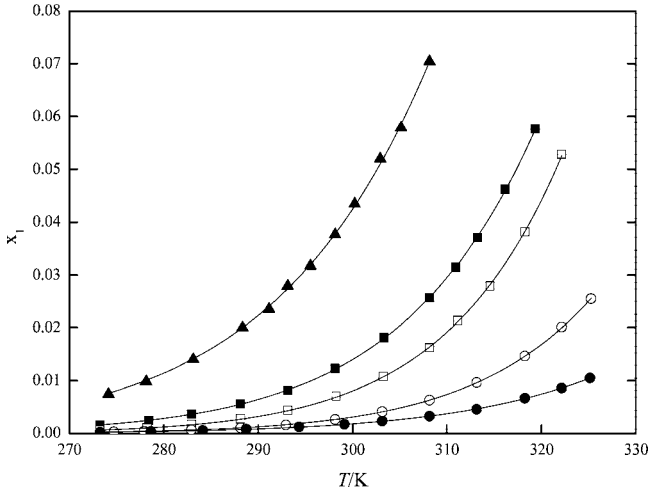

Figure 4. Mole fraction solubility of bis(benzoxazolyl-2-methyl) sulfide in ethanol + water mixed solvent with w = mass fraction of water: ▲, w = 0 %; ■, w = 1.96 %; □, w = 4.97 %; ○, w = 11.32 %; ●, w = 19.76 %; —, calculated values.

Table 3. Mole Fraction Solubilities x_1 of Bis(benzoxazolyl-2-methyl) Sulfide in Ethanol (1 − w) + Water (w) with w = Mass Fraction

T/K	$10^2 x_{1\text{exptl}}$	$(x_{1\text{exptl}} - x_{1\text{calcd}})/x_{1\text{exptl}}$	T/K	$10^2 x_{1\text{exptl}}$	$(x_{1\text{exptl}} - x_{1\text{calcd}})/x_{1\text{exptl}}$
		w = 0.0 %			
274.15	0.741	−0.025	295.55	3.175	−0.008
278.15	0.978	−0.026	298.15	3.768	−0.003
283.15	1.401	−0.009	300.25	4.345	0.007
288.35	2.001	−0.001	302.95	5.201	0.017
291.15	2.355	−0.021	305.15	5.785	−0.013
293.15	2.790	0.018	308.15	7.044	0.001
		w = 1.96 %			
273.25	0.152	−0.048	303.35	1.806	0.003
278.45	0.241	−0.030	308.15	2.573	−0.001
282.95	0.366	0.013	310.95	3.149	−0.004
288.15	0.558	0.011	313.25	3.706	−0.007
293.15	0.807	−0.019	316.15	4.621	0.005
298.15	1.227	0.012	319.35	5.767	0.001
		w = 4.97 %			
273.25	0.0615	−0.011	303.25	1.074	0.006
278.25	0.112	0.011	308.15	1.616	−0.012
282.95	0.171	0.035	311.15	2.137	0.010
288.15	0.275	0.022	314.55	2.793	−0.009
293.15	0.454	0.013	318.25	3.814	−0.004
298.25	0.706	0.032	322.15	5.284	0.003
		w = 11.32 %			
274.75	0.0268	−0.076	303.15	0.407	−0.005
277.95	0.0381	−0.041	308.15	0.627	−0.004
282.95	0.0627	−0.028	313.15	0.961	0.002
288.15	0.104	−0.014	318.25	1.459	−0.001
292.95	0.159	−0.035	322.15	2.013	0.007
298.15	0.262	−0.004	325.25	2.549	−0.004
		w = 19.76 %			
273.25	0.0215	−0.037	303.15	0.234	0.027
278.65	0.0355	0.021	308.15	0.325	−0.004
284.15	0.0530	−0.018	313.15	0.452	−0.026
288.75	0.0758	−0.020	318.25	0.667	0.012
294.35	0.121	0.019	322.15	0.859	0.001
299.15	0.170	0.001	325.15	1.047	−0.001

tions (rmsd) are also listed in Table 4. The rmsd (σ) of the mole fraction is defined as

$$\text{rmsd} = \left\{ \frac{1}{N} \sum_{i-1}^{N} (x_i^{\text{calcd}} - x_i^{\text{exptl}})^2 \right\}^{1/2} \qquad (3)$$

where N is the number of experimental points; x_i^{calcd} represents the solubility calculated from eq 2; and x_i^{exptl} represents the experimental solubility values.

From Table 2 and Figure 2 to Figure 3, we could draw the following conclusions: (i) The solubility of bis(benzoxazolyl-2-methyl) sulfide in the six pure solvents increases with temperature. (ii) The solubility of bis(benzoxazolyl-2-methyl) sulfide in these solvents decreases in the order ethanol > chlorobenzene > 1-butanol > 2-propanol > toluene > *o*-xylene at T = 298.15 K. Because the yield is a very important target for industrial profit, relatively high solubility of the solute is needed. By further comparison of the solubility of bis(benzoxazolyl-2-methyl) sulfide in alcohols, it is shown that ethanol can be a more appropriate solvent because of its more obvious dependence on temperature and its high solvency.

Table 4. Parameters of Equation 2 for Bis(benzoxazolyl-2-methyl) Sulfide in Pure Solvents

solvent	A	B	C	$10^4\sigma$
ethanol	−85.148	−1161.62	15.053	4.22
1-butanol	−87.344	−1301.67	15.349	4.18
2-propanol	−89.155	−1442.67	15.687	1.22
chlorobenzene	−87.459	−274.410	14.781	1.49
toluene	−82.557	−2705.30	15.251	2.51
o-xylene	−88.674	−2159.20	15.751	0.70

Table 5. Parameters of Equation 2 for Bis(benzoxazolyl-2-methyl) Sulfide + Ethanol + Water System at Various Compositions of Water (w) in the Mixed Solvent

100 w	A	B	C	$10^4\sigma$
0.00	−85.148	−1161.62	15.053	4.22
1.96	−85.167	−2223.70	15.483	1.34
4.97	−85.461	−3240.91	16.031	1.50
11.32	−84.882	−3233.28	15.759	0.53
19.76	−87.309	2014.82	15.377	0.46

Because bis(benzoxazolyl-2-methyl) sulfide is insoluble in pure water, the ethanol and water binary solvent can be an ideal system for the drowning-out crystallization of this compound. We consider that the solubility of bis(benzoxazolyl-2-methyl) sulfide in ethanol decreases with an increase in water concentration at a fixed temperature. The solubility of this compound in ethanol + water was also experimentally measured in the temperature range from (273.25 to 325.25) K. The mass fraction (w) of water in ethanol which is on a solute-free basis is (1.96, 4.97, 11.32, and 19.76) %, respectively. The solubilities are listed in Table 3 and plotted in Figure 4 to confirm the above conclusions. From Figure 4, it can be seen that the existence of water has an apparent influence on the solubility especially at the higher temperature. According to the experimental data, the solubility of bis(benzoxazolyl-2-methyl) sulfide in ethanol containing some water is much smaller than that in pure ethanol at the lower temperature. This means that a higher yield of recrystallization of bis(benzoxazolyl-2-methyl) sulfide can be gained when ethanol containing water is used as the recrystallization solvent. Meanwhile, the throughput of this compound in the ethanol + water mixture is limited to the lower solubility, but it can be overcome by dissolving bis(benzoxazolyl-2-methyl) sulfide at a higher temperature. Furthermore, the solvent (ethanol containing 4.97 % water) can be recycled to reduce costs. So, it is confirmed that the ethanol + water mixture containing 4.97 % can be used as a good solvent in the recrystallization procedure of bis(benzoxazolyl-2-methyl) sulfide.

The temperature dependence of bis(benzoxazolyl-2-methyl) sulfide solubility in ethanol + water is also described by the modified Apelblat equation. The comparison between calculated values and experimental ones is listed in Table 3. Values of parameters A, B, and C and rmsd are listed in Table 5. The calculated solubilities of bis(benzoxazolyl-2-methyl) sulfide show good agreement with the experimental values. The rmsd of the mole fraction is less than $4.3 \cdot 10^{-4}$.

Conclusions

The solubilities of bis(benzoxazolyl-2-methyl) sulfide in six pure solvents and an ethanol + water mixture were experimen-

tally determined by the synthetic method. The solubility of bis(benzoxazolyl-2-methyl) sulfide increases with the increase of temperature and decreases sharply as water concentration increases. The modified Apelblat equation can be used to correlate the solubility data of bis(benzoxazolyl-2-methyl) sulfide in these organic solvents. The changing regularity of the solubility of bis(benzoxazolyl-2-methyl) sulfide in other pure and mixed solvents needs to be further studied.

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