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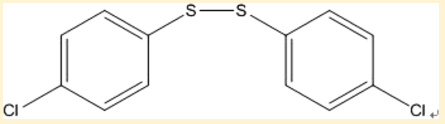
Solubilities of 4,4′-Dichlorodiphenyl Disulfide in Six Organic Solvents between (303.15 and 333.15) K

Yana Wang,[†] Yinxia Jia,[†] Chao Qian,*[,†] Ming Tao,[‡] Xuehao Lv,[‡] and Xinzhi Chen[†]

[†]Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Zhejiang University, Hangzhou 310027, China

[‡]Jiangxi Renming Pharmaceutical Chemicals Ltd., Jiujiang 332700, China

ABSTRACT: The solubility data of 4,4′-dichlorodiphenyl disulfide in solvents (ethanol, methanol, ethyl acetate, methylbenzene, chloroform, acetone) were measured between (303.15 and 333.15) K under atmospheric pressure using synthetic method and laser monitoring technique. The experimental data was correlated with the Apelblat equation and measured up to experimental data. For six solvents studied, the average relative errors σ are all less than 2.6 %, and the root-mean-square deviations are all less than 0.45 %.



INTRODUCTION

4,4′-Dichlorodiphenyl disulfide is an important pesticide for agriculture. The molecular structure 4,4′-dichlorodiphenyl disulfide (CAS Registry No. 1142-19-4) is illustrated in Figure 1. There are some separation and purification ways to decrease

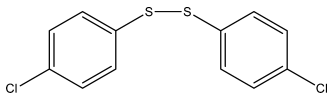


Figure 1. Chemical structure of 4,4′-dichlorodiphenyl disulfide.

byproducts in the pharmaceutical industry, which is determined by the knowledge of the thermodynamic properties, such as solubility, density, and so on. Crystallization and recrystallization are important in purification, for which the solubilities in suitable solvents are crucial role.[1,2] Therefore, it is essential to obtain the solubility data of 4,4′-dichlorodiphenyl disulfide in different solvents.

Solutes with high quality make the solubility data more reliable.[3] Besides, the foundation of thermodynamic models and the measurements of the solid−liquid equilibrium (SLE) are important research. Equations like the Apelblat equation, Wilson equation, Hansen equation, and nonrandom two-liquid (NRTL) equation are usually used to study the solubilities of solids.[4] Considering the practical crystallization process in this paper, ethanol, methanol, ethyl acetate, methylbenzene, chloroform, and acetone are chosen as solvents.

EXPERIMENTAL SECTION

Materials. 4,4′-Dichlorodiphenyl disulfide was obtained from Jiangxi Renming Pharmaceutical Chemicals Ltd. and was recrystallized several times from ethanol to yield purified samples. The mass fraction purities were higher than 0.995, which were determined by high-performance liquid chromatography (HPLC).

Analytical grade ethanol (> 0.997w), methanol (> 0.995w), ethyl acetate (> 0.995w), methylbenzene (> 0.995w), chloroform (> 0.996w), and acetone (> 0.995w) were purchased from Sinopharm Chemical Reagent Co., Ltd. They were all used without any purification.

Apparatus and Procedure. The 4,4′-dichlorodiphenyl disulfide solubilities were measured using the synthetic method.[5] Referring to the real experiment conditions, we used a set of experimental facility to measure the solubilities. The apparatus is shown as Figure 2. First, we use a jacked vessel (200 mL) as a container in the experiment and an electronic analytical balance (type AR2140, China, ± 0.1 mg) to weigh the solutes and solvents. The temperature of solution was determined by a microthermometer (uncertainty of 0.01 K) in the vessel. An electromagnetic agitator was used to stir the solution constantly.

In the first step, a certain amount of 4,4′-dichlorodiphenyl disulfide was put into the container with the solvent and blended for 1 h. At first, a part of 4,4′-dichlorodiphenyl disulfide in the solution which was not dissolved yet diminished the laser light. Then, the penetrated light rose steadily to maximum when the solute was dissolved in the solvent totally. In the next step, a small quantity of 4,4′-dichlorodiphenyl disulfide was added to the container, until the solution did not dissolve it anymore. The interval of each steps adding solute should last about 30 min, to ensure the particles dissolved completely and record the data. The solubility of 4,4′-dichlorodiphenyl disulfide was calculated as follows:

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

where m_1 and m_2 are the masses of 4,4′-dichlorodiphenyl disulfide and solvent (ethanol, methanol, ethyl acetate, methylbenzene, chloroform, acetone), respectively. M_1 and M_2 are the respective molecular masses.

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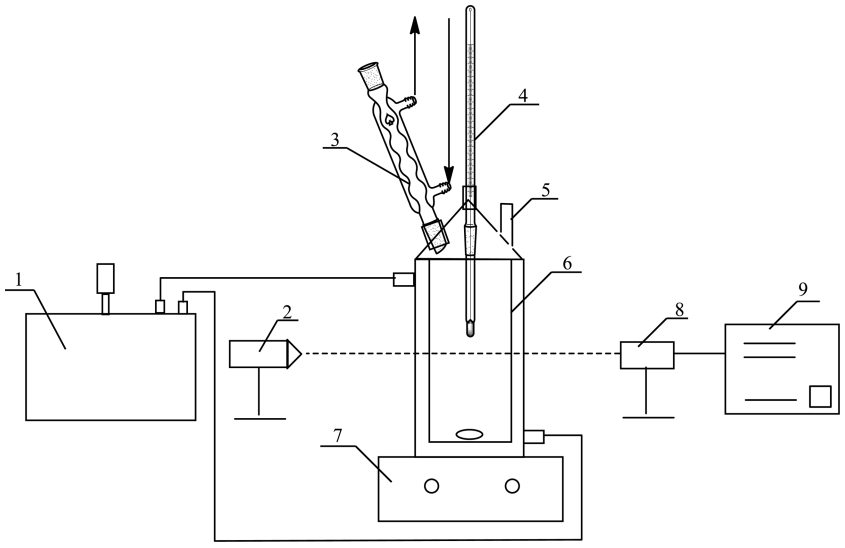

Figure 2. Solubility apparatus. 1, thermostat; 2, laser generator; 3, condenser; 4, precise mercurial thermometer; 5, feed inlet; 6, jacked dissolution vessel; 7, magnetic stirring apparatus; 8, laser acceptor; 9, signal display.

The experiment in each solvent was repeated for three times with reasonable reproducibility. The uncertainty of the measurement was about 2.0 %.

RESULTS AND DISCUSSION

The solubility data of 4,4′-dichlorodiphenyl disulfide in six solvents between (303.15 and 333.15) K is shown in Table 1. The temperature and solubility data of the experiment are related by the Apelblat equation.[6,7]

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

where x is mole fraction solubility of 4,4′-dichlorodiphenyl disulfide; T is temperature. A, B, and C are dimensionless parameters, which are shown in Table 2.

The root-mean-square deviation is defined as[8]

$$\mathrm{rmsd} = \left[\frac{\sum_{i=1}^{n}(x_{ci} - x_i)^2}{n}\right]^{1/2} \tag{3}$$

where x_{ci} represents the solubility calculated from Apelblat equation; x_i represents the experimental solubility; n represents the number of data.

The relative deviations ε is defined as

$$\varepsilon = \frac{|x_{ci} - x_i|}{x_i} \cdot 100\,\% \tag{4}$$

The average relative error σ is defined as

$$\sigma = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{x_{ci} - x_i}{x_i}\right| \cdot 100\,\% \tag{5}$$

The solubility data of 4,4′-dichlorodiphenyl disulfide in each solvent are shown in Figure 3. It is harder for the solute to dissolve in methanol than other five solvents, while it is easier in chloroform. The solubility data goes up with the increasing temperature, with high solubilities in ethyl acetate, methylbenzene, chloroform, and acetone, and lower solubilities in ethanol and methanol. Furthermore, it is shown in Table 1 that the solubilities in ethanol and methanol are most sensitive to temperature, while the sensitivity in ethyl acetate and methylbenzene is lower, and lowest in chloroform and acetone. Equation 2 provides an accurate representation of the

Table 1. Experimental Mole Fraction Solubilities of 4,4′-Dichlorodiphenyl Disulfide in Selected Solvents with the Temperature Range from (303.15 to 333.15) K and Pressure p = 0.1 MPa[a]

T/K	x·100	ε/%	T/K	x·100	ε/%
		Ethanol			
304.35	0.0264	2.01	322.55	1.52	0.744
307.45	0.0783	1.92	328.35	1.95	0.324
312.35	0.305	3.64	333.15	2.05	1.32
317.35	0.786	0.905			
		Methanol			
303.15	0.0140	3.29	322.45	0.795	0.310
307.65	0.0610	4.77	328.15	0.996	5.18
314.15	0.259	0.721	332.65	1.05	3.35
318.95	0.552	0.134			
		Ethyl Acetate			
303.95	2.01	2.84	322.45	15.2	0.0853
307.90	3.80	2.13	329.75	20.2	2.39
312.35	6.67	3.07	332.85	22.3	2.09
319.05	11.7	3.49			
		Methylbenzene			
303.20	2.19	3.29	322.75	16.0	2.26
307.85	4.46	4.01	327.65	20.0	3.13
314.05	8.64	1.82	332.75	24.4	2.74
317.55	11.4	0.594			
		Chloroform			
303.15	12.2	1.07	317.85	34.4	0.705
307.95	17.4	1.91	322.15	43.9	1.39
312.55	24.3	0.966	328.15	56.7	1.17
		Acetone			
302.95	10.2	0.797	317.25	27.1	0.580
308.05	14.5	1.22	322.55	37.0	1.36
313.25	20.8	0.764	328.15	48.3	0.902

[a]Standard uncertainties u are $u(T)$ = 0.01 K, $u_r(p)$ = 0.05, $u_r(x)$ = 0.01, and $u_r(\varepsilon)$ = 0.01.

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Table 2. Parameters of the Modified Apelblat Equation and Deviations for 4,4′-Dichlorodiphenyl Disulfide in Selected Solvents (0.1 MPa)

solvent	A	B	C	R^2	σ/%	rmsd·100
ethanol	9045.85	−438821	−1331.23	0.99690	1.55119	0.0124159
methanol	8084.22	−392239	−1189.87	0.99933	2.53622	0.0236326
ethyl acetate	3219.20	−158517	−472.560	0.99866	2.30098	0.309308
methylbenzene	2727.33	−135027	−400.003	0.99823	2.54846	0.384528
chloroform	863.863	−45659.0	−125.189	0.99906	1.20186	0.419215
acetone	516.781	−29486.0	−73.8149	0.99944	0.937683	0.297568

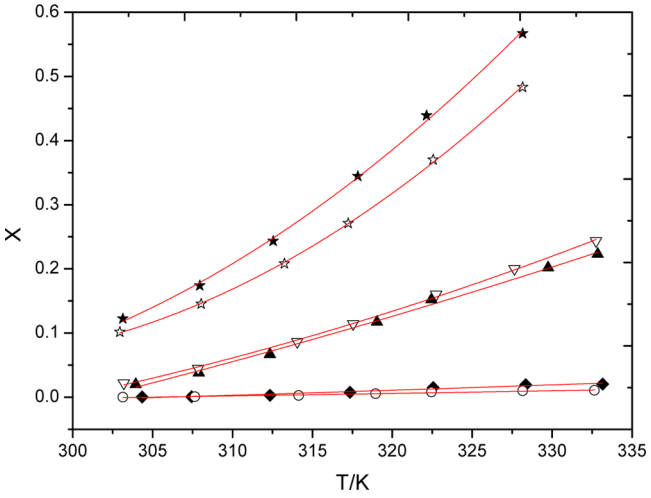

Figure 3. Experimental solubilities of 4,4′-dichlorodiphenyl disulfide in six solvents: ○, methanol; ◆, ethanol; ▲, ethyl acetate; ▽, methylbenzene; ☆, acetone; ★, chloroform and fitted lines.

experimental values in Table 1, with the average relative error less than 3 %.

CONCLUSIONS

The solubilities of 4,4′-dichlorodiphenyl disulfide have been measured between (303.15 and 333.15) K by the synthetic method with a laser monitoring technique. Obviously, the solubilities of the study increases with the rising temperature in six solvents, while it is highest in chloroform and lowest in methanol. It is much more sensitive with temperature of the solubility in ethanol and methanol than others. The experimental data could be fitted well to the Apelblat equation. So the correlation equation and experimental solubility in the study contribute to finding the optimization of synthesis and purification process of 4,4′-dichlorodiphenyl disulfide.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-571-87951615; fax: +86-571-87951742; e-mail: supmoney@163.com.

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Notes

The authors declare no competing financial interest.

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