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Dissolution Kinetics and Thermodynamics of Thiourea in Triethylene Glycol + Water Mixtures

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Isopropyl mercaptan is an important pharmaceutical intermediate and chemical material. The dissolution of thiourea in solvents is very important for the production of isopropyl mercaptan. The aims of this study are to examine the dissolution kinetics and thermodynamics of thiourea in solvents at 297.15, 307.65, 317.05 and 332.85 K in the mass fraction of triethylene glycol being 0.63 and to present an alternative process for producing isopropyl mercaptan. In order to investigate the dissolution kinetics and thermodynamics of thiourea in triethylene glycol solution, the concentrations of solution, reaction temperature were selected as experimental parameters. It was determined that the dissolution rate of thiourea increased with increasing solution concentration and temperature. An empirical equation was used in fitting the data. The activation energy and entropy change ΔS^o of the process was found to be 38.4709 and 0.1070 kJ/mol, respectively.

Key Words: Dissolution kinetics, Thermodynamics, Thiourea, Triethylene glycol, Isopropyl mercaptan, Activation energy.

INTRODUCTION

Isopropyl mercaptan is an important pharmaceutical intermediate and chemical material. In recent years, the market demand is increasing steadily and has aroused attention globally. The thiourea and triethylene glycol are the main materials for the production of isopropyl mercaptan[1,2], the solubilities of thiourea in triethylene glycol increase with increasing temperature. But so far, no study is found in the literature concerning with the dissolution kinetics and thermodynamics of thiourea in triethylene glycol solution. However in the study on the preparation methods of isopropyl mercaptan, it is necessary to investigate the dissolution rate at different temperature and thermodynamics properties of solution of thiourea in solvents. Hence the dissolution kinetics and thermodynamics of thiourea in triethylene glycol solution was investigated in this paper.

EXPERIMENTAL

Thiourea and triethylene glycol were of AR grade and were obtained from Shanghai Chemical Reagent Co. and have purities of 0.995 in mass fraction. Deionized water was used.

The dissolution experiments were carried out in a 50 mL cylindrical glass reactor equipped with a mechanical stirrer, a reaction temperature control unit (a constant-temperature bath) and a condenser for avoiding loss of solution by evaporation. The apparatus is shown in Fig. 1. The experimental procedure is as follows: the triethylene glycol solution of the mass fraction of triethylene glycol being 0.63 was loaded in the glass reactor. The reactor jacket was heated to the desired temperature and the stirring speed was set at a rate of 600-700 rpm. A given amount of solid sample was added into the solution. The dissolution process was carried out for various reaction times. During the experimental process, a sample was taken out from the reactor at intervals and the concentration of thiouea in triethylene glycol solution was determined through solid-liquid separation using the cooling method.

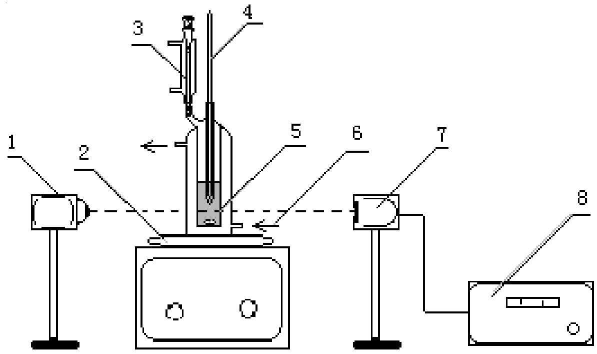

Fig. 1. Solubility experimental apparatus (1) laser generator; (2) magnetic stirrer; (3) condenser; (4) microthermometer; (5) dissolution vessel; (6) port of circulating water for temperature controlling; (7) photoelectric converter; (8) digital display

Each experiment was replicated twice and the arithmetic average of sample was used. These experiments could be repeated with a maximum deviation of approximately 1.5 %.

Test of apparatus: In order to ensure proper operation of the apparatus, the solubility of NaCl in water was measured and compared with the values reported in the literature[3]. The experimental measurements agreed with the reported values with a mean relative deviation of 0.20 %. The measured values are listed in Table-1.

TABLE-1
SOLUBILITY OF NaCl IN WATER

Temperature (K)	293.15	313.15	333.15	353.15
Solubility (g)	36.1	36.7	37.3	38.5
Literature[4] (g)	36.0	36.6	37.3	38.4
100 (RD)	0.277	0.272	0	0.260

RESULTS AND DISCUSSION

Effect of temperatures on the dissolution of thiourea: The solubility curves of thiourea in triethylene glycol solution at intervals and at different temperatures are presented in Tables-2. Table-2 shows that the solubility of thiourea increases as the temperature increases.

TABLE-2
DATA FOR THE DISSOLUTION OF THIOUREA IN TRIETHYLENE GLYCOL + WATER MIXTURES

t (min)	c (mol/L)	c_c (mol/L)	100 (RD)
297.15 K			
2.07	1.0068	1.0062	0.06
5.00	1.7387	1.7527	-0.81
8.93	2.2471	2.2703	-1.03
14.58	2.7156	2.6493	2.44
21.15	2.8878	2.8801	0.27
27.63	3.0055	3.0135	-0.27
35.03	3.0658	3.1109	-1.47
40.08	3.1903	3.1581	1.01
50.75	3.1966	3.2282	-0.99
307.65 K			
2.08	0.9587	0.9729	-1.49
3.63	1.4914	1.5269	-2.38
5.63	2.0775	2.0819	-0.21
7.67	2.5478	2.509	1.52
10.57	3.0020	2.9453	1.89
14.20	3.2835	3.3036	-0.61
19.30	3.5459	3.5990	-1.50
27.35	3.7864	3.8211	-0.91
42.97	3.9151	3.9551	-1.02
68.05	3.9769	3.9929	-0.40
317.05 K			
2.15	2.8570	2.9187	-2.16
4.18	3.6681	3.6996	-0.86
12.67	4.4340	4.4993	-1.47
20.68	4.6398	4.6701	-0.65
32.37	4.7401	4.7649	-0.52
48.82	4.8087	4.8181	-0.19
332.85 K			
0.95	3.5353	3.5653	-0.85
2.35	4.8186	4.7658	1.10
4.85	5.3764	5.3532	0.43
9.62	5.5885	5.6472	-1.05
15.42	5.7180	5.7557	-0.66
20.57	5.8051	5.7983	0.12

Kinetic analysis: The kinetic equation which describes the dissolution rate of solid can be expressed by the Stumm equation[4-6].

$$\frac{dc}{dt} = K(c_w - c)^n \quad (1)$$

where c_s = saturation concentration of thiouea; c = concentration at t time; K represents the rate constant and n represents reaction order.

The calculated concentrations of thiourea in triethylene glycol solution at intervals in eqn. 1 are given in Table-2. The c-t curves in eqn. 1 are shown in Fig. 2. The values of parameters K, n, the correlation coefficient (R^2) and the root-mean-square deviation (σ) are listed in Table-3.

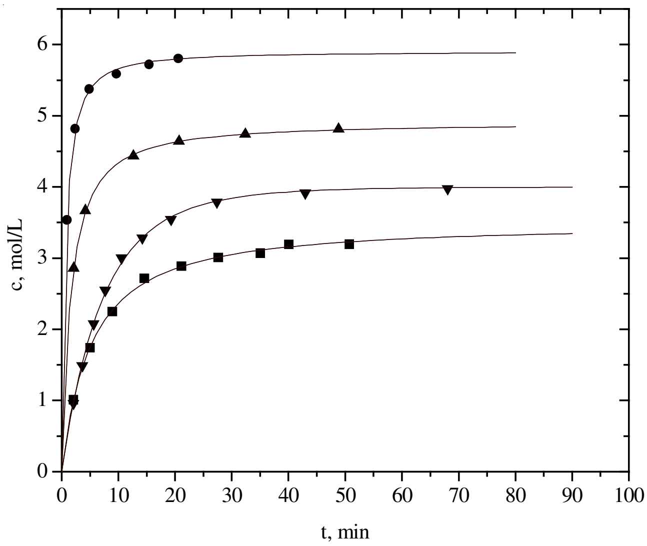

Fig. 2. c-t curve for the dissolution of thiourea in triethylene glycol-water mixtures symbols: ■: 297.15 K, ▼: 307.65 K, ▲: 317.05 K, ●: 332.85 K

TABLE-3
CALCULATION RESULTS OF K, n DURING THE DISSOLUTION PROCESS OF THIOUREA IN TRIETHYLENE GLYCOL SOLUTION

T (K)	Stumm equation	R^2	σ (%)
297.15	$dc/dt = 0.06665(3.48 - c)^{1.84458}$	0.99911	3.22
307.65	$dc/dt = 0.11636(4.0 - c)^{1.11318}$	0.99938	3.53
317.05	$dc/dt = 0.17721(4.9 - c)^{1.77988}$	0.99993	4.22
332.85	$dc/dt = 0.35677(5.9 - c)^{1.78398}$	0.99965	3.90

$$\sigma = \left[\frac{1}{N}\sum_{i=1}^{N}(c_{ci} - c_i)^2\right]^{1/2} \quad (2)$$

where N = number of experimental points; c_{ci} represents the concentration calculated from eqn. 1; c_i represents the experimental concentration values.

The relative deviations between the experimental value and calculated value are also listed in Table-2. The relative deviations (RD) are calculated by using the following formula.

$$\text{Relative deviation (RD)} = \frac{(c - c_c)}{c} \quad (3)$$

From Table-2, it can be seen that the relative deviations in eqn. 1 among all of these values do not exceed 2.44 %; From Table-3, it can also be seen that the correlation coefficient (R^2) is greater than 0.99 and the root-mean-square deviation does not exceed 4.22 %, which indicates that the Stumm equation is fit to correlate the dissolution kinetics data of thiourea in triethylene glycol solution and the dissolution process of thiourea in solution is a diffusion process. From Fig. 2, it is shown that the higher the temperature, the greater the solubility of thiourea, the faster the rate of proliferation and the less the dissolution time.

Estimation of thermodynamic function: The temperature dependence of the chemical reactions can be given in the Arrhenius equation:

$$K = K_0 \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where K is rate constant; K_0 is a pre-exponential factor; E_a represents activation energy; R is gas constant and T represents temperature.

ΔG^o was calculated by using the following equation in the sealed process of constant temperature and constant pressure:

$$\Delta G^o = -RT \ln K \tag{5}$$

When the equilibrium was reached in a certain temperature range, ΔH^o and ΔS^o was calculated by using the van't Hoff equation:

$$\ln K = -\left(\frac{\Delta H^o}{RT}\right) + \left(\frac{\Delta S^o}{R}\right) \tag{6}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{7}$$

According to eqn. 6, the slope of the curve between ln K *versus* 1/T should give a straight line whose slope equals to $-\Delta H^o/R$ and the intercept equals to $\Delta S^o/R$. ΔH^o, ΔS^o and ΔG^o of dissolution process could be calculated by using eqns. 5-7. Fig. 3 showed the Arrhenius plots for dissolution of thiourea in solvents. The activation energies derived from the curves was found as 38.4709 kJ/mol. The ΔS^o derived from the curves was found as 0.1070 kJ/mol.

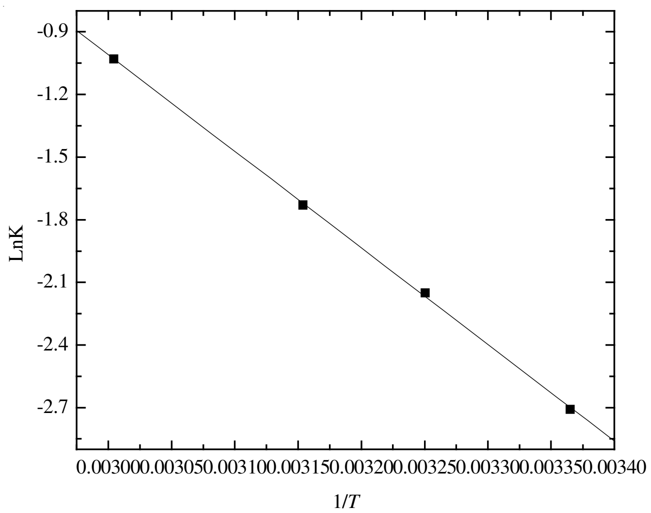

Fig. 3. Arrhenius plot of the dissolution process

The result of ΔG^o are listed in Table-4 which shows the value of ΔG^o descended with increasing solution temperature.

TABLE-4
CALCULATED RESULTS OF GIBBS ENERGY CHANGE ΔG^o (KJ mol^{-1})

T (K)	297.15	307.65	317.05	332.85
ΔG^o (KJ mol^{-1})	6.6706	5.5469	4.5410	2.8501

As can be seen from the result, the value of ΔH^o, ΔS^o and ΔG^o are all positive. It suggests that the dissolution process of thiourea in solvents is the process of endothermic and entropy increase.

Conclusion

The solubilities and dissolution rate of thiourea in triethylene glycol solution were measured at intervals and at different temperatures. The higher the temperature, the better the dissolution of the thiourea and the dissolution rate increases with an increase of temperature. The Stumm equation is used to correlate the dissolution kinetics data and the calculated value by the models show good agreement with the experimental data. The result of fitting indicates the dissolution process of thiourea in triethylene glycol solution belong to the diffusion process. The value of ΔH^o, ΔS^o and ΔG^o are all positive, which suggest that the dissolution process of thiourea in triethylene glycol solution is the process of endothermic and entropy increase. The experimental dissolution kinetics and correlation equation in this work can be used as essential data and model for the synthesis of isopropyl mercaptan.

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