Journal of the Korean Chemical Society
2010, *Vol. 54, No. 1*
Printed in the Republic of Korea
DOI 10.5012/jkcs.2010.54.01.088

트리글리콜용액에서 싸이오우레아 용해 반응속도론

Hua Li*, Feng Guo†, Guoqin Hu, Lei Zhao, and Yadong Zhang
School of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou, Henan, China, 450001
†*Daqing Petrochemical Research Center of Petrochemical Research Institute of PetroChina, Daqing, Heilongjiang, China, 163714*
(접수 2009. 8. 12; 수정 2009. 12. 13; 게재확정 2009. 12. 22)

Dissolution Kinetics of Thiourea in Triglycol Solution

Hua Li*, Feng Guo†, Guoqin Hu, Lei Zhao, and Yadong Zhang
School of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou, Henan, China, 450001
†*Daqing Petrochemical Research Center of Petrochemical Research Institute of PetroChina, Daqing, Heilongjiang, China, 163714*
(Received August 12, 2009; Revised December 13, 2009; Accepted December 22, 2009)

요약. 이소프로필 멀케푸탄은 중요한 약품 중간체이며 싸이오우레아와 트리글리콜은 이소프로필 멀케푸탄을 합성을 하는데 중요한 화합물이다. 그러므로 트리글리콜 용액에서의 싸이오우레아의 용해는 이소프로필 멀케푸탄의 생산에 중요하다. 트리글리콜용액에서 싸이오우레아의 용해 반응속도론을 조사하고 이소프로필 멀케푸탄을 생산하는 대체 공정을 제시하는 것이 본 연구의 목적이다. 트리글리콜용액에서 싸이오우레아의 용해 반응속도론을 조사하기 위하여 용액 농도와 반응 온도를 중점적으로 관찰하였다. 싸이오우레아의 용해속도는 용액농도와 온도가 증가할수록 증가하였다.

주제어: 용해, 반응속도론, 싸이오우레아, 트리글리콜, 용액, 확산

ABSTRACT. Isopropyl mercaptan is an important pharmaceutical intermediate and chemical material. And thiourea and triglycol are the main materials for the synthesis of isopropyl mercaptan. Therefore the dissolution of thiourea in triglycol solution is very important for the production of isopropyl mercaptan. The aims of this study are to examine the dissolution kinetics of thiourea in triglycol solution, and to present an alternative process for producing isopropyl mercaptan. In order to investigate the dissolution kinetics of thiourea in triglycol solution, the concentrations of solution and reaction temperature were selected as experimental parameters. It was determined that the dissolution rate of thiourea increased with the increase in solution concentration and temperature. An empirical equation was used in fitting the data. Statistical analysis indicated small errors and the results should be reliable.

Keywords: Dissolution, Kinetics, Thiourea, Triglycol, Solution, Diffusion

INTRODUCTION

Isopropyl mercaptan is an important pharmaceutical intermediate and chemical material. In recent years, the market demand is increasing steadily, and has aroused attention from both home and abroad. Thiourea and triglycol are the main materials for the production of isopropyl mercaptan;[1,2] the solubilities of thiourea in triglycol increase with rising temperature. But so far, no study has been found in the literature concerning the dissolution kinetics of thiourea in triglycol solution. However in the study of the preparation methods of isopropyl mercaptan, it is necessary to investigate the dissolution rate at different temperatures. Hence the dissolution kinetics of thiourea in triglycol solution is investigated in this paper.

EXPERIMENTAL

Materials

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

Apparatus and Procedure

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 was shown in *Fig*. 1. The experimental procedure was as follows: the triglycol solution at a definite concentration (the mass fractions of triglycol were 0.72, 0.82, 0.91 and 1.00 respectively) was placed 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 r/min. A given amount of solid sample was added into the solution. The dissolution process was carried out for various reaction time. During the experimental process, a sample was taken out from the reactor at intervals and the concentration of thiouea in triglycol solu-

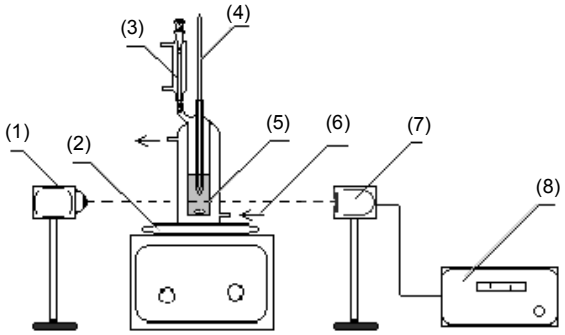

Fig. 1. Solubility experimental apparatus. (1) laser generator; (2) magnetic stirrer; (3) condenser; (4) microthermometer; (5) dissolution vessel; (6) port of circulating water for temperature controlling; (7) photoelectric converter; (8) digital display.

Table 1. Solubility of NaCl in water

T/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

Table 2. Data for the dissolution of thiourea in triglycol + water mixtures (w = 0.72)

t/min	c/(mol/L)	C_c/(mol/L)	100 RD
	298.15 K		
4.07	2.6435	2.6059	1.42
11.17	3.1407	3.2267	-2.74
22.35	3.4572	3.4827	-0.74
37.65	3.6278	3.6071	0.57
55.02	3.7673	3.6711	2.55
	308.25 K		
2.75	2.7830	2.7518	1.12
6.80	3.4860	3.5554	-1.99
13.60	3.9542	3.9460	0.21
19.75	4.0906	4.0855	0.12
27.40	4.2129	4.1766	0.86
43.53	4.2822	4.2674	0.35
	317.25 K		
2.42	3.0707	3.0933	-0.74
6.23	4.0250	3.9596	1.63
12.70	4.3148	4.3513	-0.85
20.78	4.5031	4.5174	-0.32
30.13	4.5967	4.6026	-0.13
46.18	4.6540	4.6703	-0.35
64.22	4.7076	4.7065	0.02
84.43	4.7472	4.7289	0.39
	332.35 K		
1.63	3.2365	3.2244	0.37
3.97	4.4327	4.4493	-0.37
7.70	5.0507	5.0532	-0.05
14.80	5.3720	5.3919	-0.37
23.75	5.5473	5.5265	0.38
37.23	5.6397	5.6014	0.68

tion was determined throngh solid-liquid separation using the cooling method.

Each experiment was replicated twice and an arithmetic average of the 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 were listed in *Table* 1.

RESULTS AND DISCUSSION

Effect of temperatures on the dissolution of thiourea

The solubility curves of thiourea in triglycol solution at intervals and at different temperatures, and different triglycol mass fractions were presented in *Table* 2-5, respectively. *Table* 2-5 showed that the solubility of thiourea increased as the temperature rised.

Table 3. Data for the dissolution of thiourea in triglycol + water mixtures (w = 0.82)

t/min	c/(mol/L)	C_c/(mol/L)	100 RD
	297.65 K		
4.10	2.4529	2.4181	1.42
12.32	3.2219	3.3001	-2.43
25.38	3.6333	3.6345	-0.03
40.33	3.7643	3.7657	-0.04
57.83	3.8661	3.8359	0.78
93.77	3.8817	3.8992	-0.45
	307.55 K		
2.75	2.5531	2.5450	0.32
7.80	3.5915	3.6107	-0.54
17.02	4.0978	4.0848	0.32
30.60	4.2730	4.2799	-0.16
50.27	4.3767	4.3747	0.05
86.32	4.4521	4.4333	0.42
	318.25 K		
2.15	2.7341	2.7472	-0.48
5.28	3.7937	3.7673	0.70
10.42	4.2746	4.2793	-0.11
17.13	4.4974	4.5113	-0.31
28.78	4.6655	4.6598	0.12
45.27	4.7309	4.7372	-0.13
65.02	4.7733	4.7763	-0.06
89.20	4.7924	4.7994	-0.15
	332.75 K		
1.60	3.0638	3.0733	-0.31
3.82	4.2344	4.2104	0.57
7.27	4.7599	4.7737	-0.29
12.80	5.0619	5.0697	-0.15
20.41	5.2080	5.2121	-0.08
29.47	5.2831	5.2815	0.03
45.48	5.3426	5.3321	0.20

Table 4. Data for the dissolution of thiourea in triglycol + water mixtures (w = 0.91)

t/min	c/(mol/L)	C_c/(mol/L)	Rel dev, %
	298.45 K		
9.08	1.6156	1.6346	-1.17
20.12	2.2212	2.1694	2.33
30.27	2.3715	2.4015	-1.26
42.62	2.5636	2.5685	-0.19
57.33	2.6917	2.6930	-0.05
	308.65 K		
13.90	2.5167	2.5448	-1.11
21.95	3.1828	3.1218	1.92
31.92	3.5125	3.5313	-0.54
43.92	3.7885	3.8139	-0.67
60.48	4.0157	4.0291	-0.33
87.23	4.2234	4.2003	0.55
127.11	4.3154	4.3106	0.11
	318.75 K		
3.88	2.7851	2.8082	-0.83
9.08	3.6410	3.5712	1.92
18.87	3.9878	4.0341	-1.16
30.78	4.1951	4.2514	-1.34
48.93	4.4596	4.4033	1.26
	333.65 K		
2.82	3.1062	3.0358	2.27
5.97	3.8278	3.9240	-2.51
11.65	4.4405	4.4838	-0.98
18.71	4.7486	4.7445	0.09
29.02	4.9618	4.9074	1.10
43.83	5.0289	5.0094	0.39

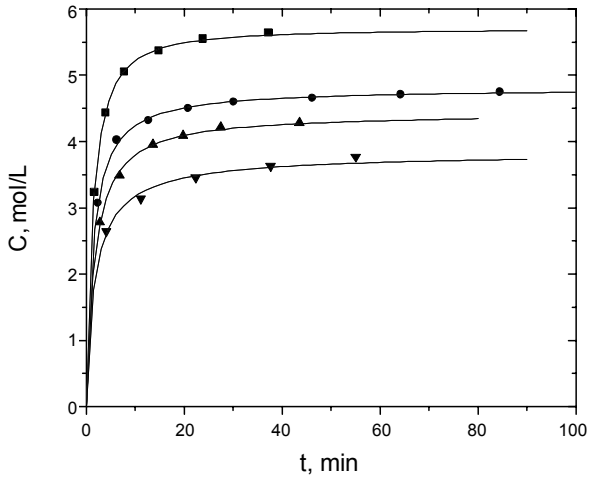

Fig. 2. *C-t* curve for the dissolution of thiourea in triglycol-water mixtures (w = 0.72). Symbols: ▼: 298.15 K, ▲: 308.25 K, ●: 317.25 K, ■: 332.35 K.

Effect of triglycol mass fractions on the dissolution of thiourea

To investigate the effect of the triglycol mass fractions on dissolution rate, the experiments were carried out in the mass fractions of 0.72, 0.82, 0.91 and 1.00 respectively. The results plotted in *Fig*. 2-5 showed that the dissolution rate decreased with the increase in triglycol mass fraction.

Table 5. Data for the dissolution of thiourea in triglycol + water mixtures (w = 1.00)

t/min	c/(mol/L)	C_c/(mol/L)	100 RD
	298.65 K		
10.68	0.2009	0.2052	-2.14
20.82	0.3822	0.3886	-1.68
33.68	0.5966	0.6061	-1.59
44.55	0.7866	0.7776	1.15
56.27	0.9575	0.9505	0.73
71.47	1.1455	1.1576	-1.06
92.53	1.4277	1.4152	0.88
120.82	1.6983	1.7134	-0.89
	308.75 K		
4.55	0.2852	0.2811	1.42
9.30	0.5525	0.5504	0.38
16.35	0.9276	0.9092	1.99
23.72	1.2580	1.2382	1.58
32.20	1.5420	1.5666	-1.60
42.58	1.8682	1.9071	-2.08
56.92	2.3156	2.2870	1.23
82.48	2.7418	2.7726	-1.12
118.05	3.2440	3.1859	1.79
167.50	3.4538	3.4868	-0.96
	317.65 K		
7.07	0.5834	0.5869	-0.60
15.33	1.2109	1.1882	1.87
27.80	1.9422	1.9461	-0.20
44.98	2.7302	2.7464	-0.59
57.07	3.1647	3.1738	-0.29
78.15	3.7526	3.7155	0.99
98.25	4.0258	4.0540	-0.70
128.70	4.3661	4.3517	0.33
170.05	4.5198	4.5256	-0.13
	332.95 K		
2.13	2.7560	2.7722	-0.59
6.20	3.9613	3.9202	1.04
14.73	4.4905	4.5197	-0.65
28.72	4.7978	4.7978	0.00
45.28	4.9218	4.9219	-0.01
63.37	4.9815	4.9890	-0.15
85.80	5.0394	5.0358	0.07

Kinetic analysis

The kinetic equation which describes the dissolution rate of solid could be expressed in the Stumm equation.[4,5,6]

$$\frac{dC}{dt} = K(C_s - C)^n \quad (1)$$

Where C_s is the saturation concentration of thiouea; C represents the concentration at t time; K is the rate constant; n is reaction order.

The calculated concentrations of thiourea in triglycol solution at intervals in eq 1 were given in *Table* 2-5. The *C-t* curves in eq 1 were shown in *Fig*. 2-5. The values of parameters K, n,

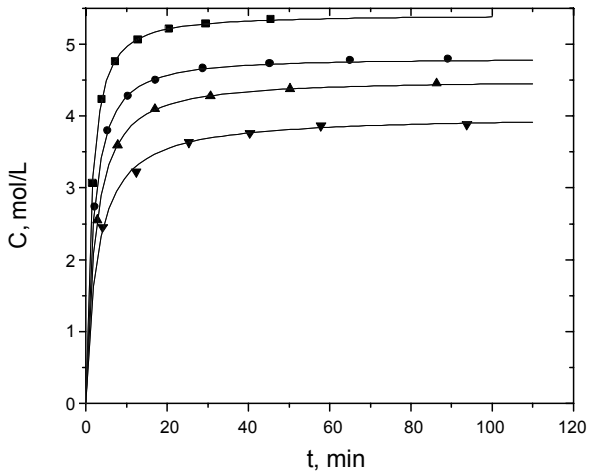

Fig. 3. *C-t* curve for the dissolution of thiourea in triglycol-water mixtures (w = 0.82). Symbols: ▼: 297.65 K, ▲: 307.55 K, ●: 318.25 K, ■: 332.75 K.

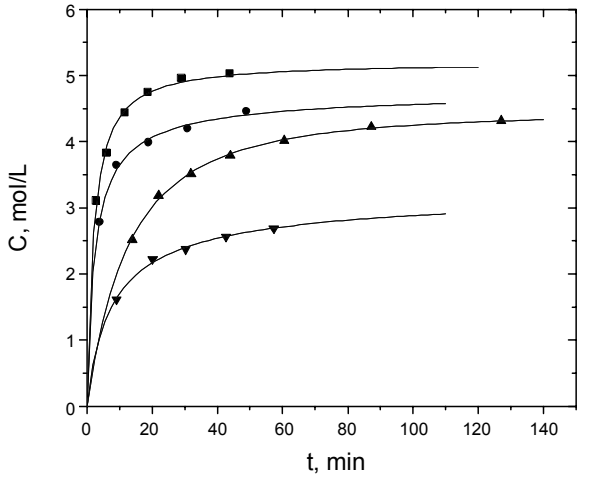

Fig. 4. *C-t* curve for the dissolution of thiourea in triglycol-water mixtures (w = 0.91). Symbols: ▼: 298.45 K, ▲: 308.65 K, ●: 318.75 K, ■: 333.65 K.

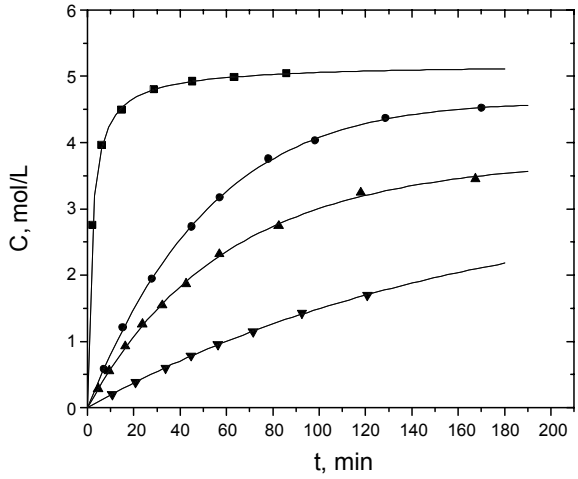

Fig. 5. *C-t* curve for the dissolution of thiourea in triglycol-water mixtures (w = 1.00). Symbols: ▼: 298.65 K, ▲: 308.75 K, ●: 317.65 K, ■: 332.95 K.

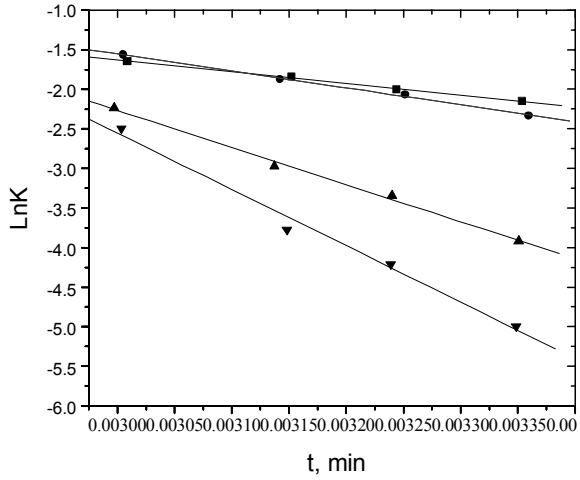

Fig. 6. Arrhenius plot of the dissolution process. Symbols: ■: w = 0.72, ●: w = 0.82, ▲: w = 0.91, ▼: w = 1.00.

the correlation coefficient (R^2) and the root-mean-square deviation (σ) were listed in *Table* 6.

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

Where N is the number of experimental points; c_{ci} represents the concentration calculated from eq 1; c_i represents the experimental concentration value.

The relative deviations between the experimental value and calculated value were also listed in *Table* 2-5. The relative deviations (RD) were calculated by using the following formula.

$$\mathrm{RD} = \frac{c - c_c}{c} \quad (3)$$

From *Table* 2-5, it could be seen that the relative deviations in eq 1 among all of these values did not exceed 2.74%; from *Table* 6, it could also be learned that the correlation coefficient (R^2) was greater than 0.99 and the root-mean-square deviation did not exceed 6.19%, which indicated that the Stumm equation was fit to correlate the dissolution kinetics data of thiourea in triglycol + water mixtures and the dissolution process of thiourea in triglycol + water mixtures was a diffusion process. From *Fig*. 2-5, it was shown that for the mixed solvent of the same mass fraction of triglycol, the higher the temperature, the greater the solubility of thiourea, the faster the rate of proliferation, and the less the dissolution time.

Activation energies

The temperature dependence of the chemical reactions can

Table 6. Calculation results of K, n during the dissolution process of thiourea in triglycol + water mixtures

w	T/K	Stumm equation	R^2	σ, %
0.72	298.15	$dC/dt = 0.11673(3.85 - C)^{2.20255}$	0.99809	6.19
0.72	308.25	$dC/dt = 0.13533(4.43 - C)^{1.9941}$	0.99932	3.52
0.72	317.25	$dC/dt = 0.15894(4.8 - C)^{1.98088}$	0.99963	2.95
0.72	332.35	$dC/dt = 0.19331(5.7 - C)^{1.74765}$	0.99989	2.13
0.82	297.65	$dC/dt = 0.09689(4 - C)^{1.95461}$	0.99875	3.77
0.82	307.55	$dC/dt = 0.12645(4.5 - C)^{1.82217}$	0.99994	1.30
0.82	318.25	$dC/dt = 0.15339(4.85 - C)^{1.81748}$	0.99994	1.23
0.82	332.75	$dC/dt = 0.20936(5.4 - C)^{1.7411}$	0.99996	1.22
0.91	298.45	$dC/dt = 0.01985(3.35 - C)^{2.55149}$	0.99922	2.82
0.91	308.65	$dC/dt = 0.03523(4.45 - C)^{1.52172}$	0.99956	2.99
0.91	318.75	$dC/dt = 0.05122(4.8 - C)^{2.37074}$	0.99899	5.27
0.91	333.65	$dC/dt = 0.1071(5.2 - C)^{1.90175}$	0.99868	5.69
1.00	298.65	$dC/dt = 0.00677(3.18 - C)^{0.9283}$	0.9992	1.01
1.00	308.75	$dC/dt = 0.01481(3.8 - C)^{1.10152}$	0.99932	3.02
1.00	317.65	$dC/dt = 0.02298(4.6 - C)^{0.88408}$	0.99986	1.91
1.00	332.95	$dC/dt = 0.0823(5.2 - C)^{2.18528}$	0.99986	2.02

Table 7. Calculation results of activation energy according to the Arrhenius equation

w	Ea/(kJ/mol)
0.72	12.309
0.82	17.769
0.91	38.946
1.00	59.199

be given in the Arrhenius equation:

$$K = K_0 \exp(-E_a / RT) \quad (4)$$

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

According to this equation, the slope of the curve between ln K versus 1/T should give a straight line whose slope equals to $-E_a/R$. *Fig*. 6 showed the Arrhenius plots for dissolution of thiourea in different triglycol solutions. The activation energies derived from these curves were found as 12.31 kJ/mol, 17.77 kJ/mol, 38.95 kJ/mol, 59.20 kJ/mol for the triglycol mass fractions of 0.72, 0.82, 0.91 and 1.00 respectively. This indicated that the triglycol mass fractions significantly affected the dissolution of thiourea. The activation energy of thiourea in triglycol solution increased with the increasing triglycol mass fraction. The results of activation energy were listed in *Table* 7.

CONCLUSION

The solubilities and dissolution rate of thiourea in triglycol solution were measured at intervals, at different temperatures and in different triglycol mass fractions. The higher the temperature, the better the dissolution of thiourea; the dissolution rate increased with that of the temperature.

The Stumm equation was used to correlate the dissolution kinetics data and the calculated value in the models was in good agreement with the experimental data. The result of fitting indicated the dissolution process of thiourea in triglycol + water mixtures was a diffusion process.

The experimental dissolution kinetics and correlation equation in this work can be used as essential data and model for the synthesis of isopropyl mercaptan.

REFERENCES

1. Liu, Y. P.; Sun, B. G.; Xie, J. C.; Zheng, F. P.; Xiao, Y. *Chem. Reagents*. **2004**, *26*, 291.
2. Zhang, K. Q.; Sun, B. G. *Fine Chemicals*. **1998**, *15*, 30.
3. Liu, G. Q.; Ma, L. X.; Liu**,** J. Data Handbook of Physical and Chemical Properties for Chemistry and Chemical Engineering (Inorganic Vol.); Chemical Industry Press: Peking, China, **2002**; p 477.
4. John, W. M.; Rolf, S. A. *Earth Sci. Reviews*. **2002**, *58*, 51.
5. John, W. M. *Reviews in Mineralogy*. **1998**, *11*, 227.
6. Sjoberg, E. L.; David, T. R. *Chem. Geology*. **1984**, *42*, 119.