Measurement and Correlation for Solubility of Thiourea in Triglycol + Water at Temperatures from (292.05 to 357.75) K

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The solubility of thiourea in triglycol + water had been determined from (292.05 to 357.75) K by the synthetic method. The experimental data were correlated with the modified Apelblat equation.

Introduction

Isopropyl mercaptan is an important pharmaceutical intermediate and chemical material with wide use and optimum application prospect. We have developed a new technique for the synthesis of isopropyl mercaptan using thiourea as the raw material and triglycol as solvent.[1,2] This new technique is characterized by a high-boiling solvent, high product purity, and mild reaction conditions. In the synthesis and purification process of isopropyl mercaptan, it is very important to know the solubilities of thiourea in triglycol + water mixtures because the solubilities of thiourea in triglycol directly influence the product yield, but no solubility of thiourea in triglycol + water has been reported so far. Therefore, in this study, the solubilities of thiourea in triglycol + water mixtures with the mass fraction of triglycol being 0.63, 0.72, 0.82, 0.91, and 1.00, respectively, were determined from (292.05 to 357.75) K. The experimental data were correlated with the modified Apelblat equation, and the solubilities correlated by models agree with the experimental data to within ± 2.6 %.

Experimental Section

Materials. Thiourea and triglycol were of AR grade, and they were obtained from Shanghai Chemical Reagent Co. and have mass fraction purities of 0.995. Deionized water was used.

Solubility Measurement. The solubility of thiourea in triglycol + water was measured by a synthetic method at atmospheric pressure using the apparatus.[3] The laser monitoring observation technique was used to determine the dissolution temperature of the solid−liquid mixture of known composition. The laser monitoring system consists of a laser generator, a photoelectric transformer, and a light intensity display. The experiments were carried out in a 50 mL jacketed glass vessel with a magnetic stirrer, and a constant temperature (± 0.02 K) was maintained at the required temperature by circulating water through the outer jacket from a thermoelectric controller. A glass sleeving with a mercury glass thermometer was inserted into the inner chamber of the vessels for the measurement of the temperature. The uncertainty of temperature was ± 0.02 K (calibrated by using a standard thermometer).

Predetermined amounts of thiourea and the solvent were weighed using an electronic balance with an uncertainty of ± 0.0001 g and transferred into the vessel. The contents of the vessel were heated very slowly at a rate of 1 $K \cdot h^{-1}$ when the system was in equilibrium. In the early stage of the experiment, the laser beam was blocked by the particles of thiourea in the solution, so the intensity of the laser beam penetrating the vessel was lower. The intensity increased gradually along with the increase of the amount of thiourea dissolved. When the last portion of thiourea just disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the temperature was recorded. The solubility expressed by mole fraction was calculated as follows[4]

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{1}$$

where m_1 represents the mass of solute and m_2 and m_3 represent the mass of solvents, respectively. M_1 is the molecular mass of solute, and M_2 and M_3 are the molecular mass of solvents, respectively.

Each experiment was repeated three times, and the relative deviation of the uncertainty in the mole fraction solubility is less than 2 %.

Test of Apparatus. To prove the feasibility and the uncertainty of the measurement, the solubility of NaCl and thiourea in water was measured and compared with the values reported in the literature.[5,6] The experimental measurements agreed with the reported values with a mean relative deviation of 0.18 % and 2.5 %, respectively. The measured values are listed in Table 1.

Table 1. Solubility of NaCl and Thiourea in Water

NaCl				
T/K	293.15	313.15	333.15	353.15
x	0.1001	0.1016	0.1031	0.1061
x(lit.)[5]	0.0999	0.1014	0.1031	0.1059
100 RD	0.25	0.25	0.00	0.23

Thiourea			
T/K	293.15	298.15	348.15
x	0.03105	0.03733	0.2218
x(lit.)[6]	0.03142	0.03897	0.2174
100 RD	−1.19	−4.39	1.98

Result and Discussion

The measured solubilities of thiourea in triglycol solution at different temperatures are presented in Table 2. The temperature dependence of thiourea in triglycol + water mixtures is described by the modified Apelblat equation[7]

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

where x is the mole fraction solubility of thiourea; T is the absolute temperature; and A, B, and C are the model parameters. The adjustable parameters A, B, and C can be obtained from simplex optimization.

$$\text{the objective function } F = \min \sum_{i=1}^{N} (x_{ci} - x_i)^2 \qquad (3)$$

The solubility curves by eq 2 are shown in Figure 1. The values of parameters A, B, and C and the root-mean-square deviation:

$$\mathrm{rmsd} = \left[\frac{1}{N-1}\sum_{i=1}^{N}(x_{ci} - x_i)^2\right]^{1/2} \qquad (4)$$

where N is the number of experimental points; x_{ci} represents the solubilities calculated from eq 2; and x_i represents the experimental solubility values. The relative deviations between the experimental value and calculated value are also listed in Table 2. Relative deviations (RD) are calculated according to

$$\mathrm{RD} = \frac{x - x_c}{x} \qquad (5)$$

The relative average deviations (RAD) by eq 2 are listed in Table 3. The RAD is defined as

$$\mathrm{RAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{x_i - x_{ci}}{x_i}\right| \qquad (6)$$

From Table 3, it can be found that the calculated solubilities show good agreement with the experimental data, the overall rmsd of 78 data points for the thiourea in triglycol + water being $1.18 \cdot 10^{-2}$. The relative deviations by eq 2 among all of these values do not exceed 2.6 %, and the relative average deviations is 1.3 %, 1.2 %, 0.67 %, 0.3 %, and 0.3 %, respectively, which indicates that the modified Apelblat equation is suitable to correlate the solubility data of thiourea in triglycol + water mixtures.

The graphical presentation of solubility of thiourea in triglycol + water mixtures is shown in Figure 1. It can be observed from Figure 1 that all of the solubilities follow the order $w = 1.00 > w = 0.91 > w = 0.82 > w = 0.72 > w = 0.63$ (where w is the mass fraction). This is because the polarity of triglycol is higher

Table 2. Solubilities of Thiourea in Triglycol + Water Mixtures

T/K	x	100 RD	T/K	x	100 RD
		$w = 0.63$			
303.45	0.1449	−0.11	322.75	0.1883	0.00
307.65	0.1515	−1.52	326.05	0.2002	1.87
312.15	0.1605	−1.89	329.55	0.2086	1.52
315.85	0.1675	−2.65	334.25	0.2229	2.21
318.75	0.1780	−0.34	338.45	0.2322	1.12
		$w = 0.72$			
293.15	0.1686	−2.34	318.85	0.2316	0.79
296.15	0.1792	0.08	321.15	0.2387	1.53
300.25	0.1885	0.32	323.75	0.2435	0.97
304.65	0.1989	0.62	327.25	0.2547	2.13
309.25	0.2057	−1.06	330.15	0.2621	2.27
313.65	0.2170	−0.40	332.85	0.2682	2.12
316.45	0.2244	0.05	335.95	0.2744	1.66
		$w = 0.82$			
292.05	0.2222	−1.12	320.35	0.2824	−0.02
292.25	0.2226	−1.12	321.65	0.2851	−0.08
292.85	0.2232	−1.34	324.35	0.2924	0.39
297.25	0.2344	−0.10	327.55	0.2987	0.08
301.35	0.2399	−1.18	331.15	0.3044	−0.74
301.55	0.2459	1.12	332.85	0.3085	−0.66
305.75	0.2527	0.41	336.65	0.3173	−0.69
305.95	0.2552	1.23	339.95	0.3254	−0.57
311.65	0.2642	0.14	342.55	0.3330	−0.15
310.55	0.2651	1.34	345.65	0.3414	0.10
314.85	0.2726	0.74	348.65	0.3525	1.14
319.15	0.2774	−0.88			
		$w = 0.91$			
309.75	0.3248	−0.67	336.05	0.3714	−0.05
311.25	0.3313	0.62	339.05	0.3778	0.14
313.15	0.3345	0.68	342.25	0.3843	0.22
315.95	0.3372	0.16	345.65	0.3910	0.21
319.35	0.3418	−0.11	348.15	0.3947	−0.14
321.55	0.3472	0.39	351.75	0.4045	0.45
324.85	0.3497	−0.50	354.35	0.4098	0.40
327.85	0.3547	−0.56	357.75	0.4166	0.26
332.05	0.3637	−0.14			
		$w = 1.00$			
318.35	0.4561	−0.28	339.35	0.4922	0.01
321.65	0.4653	0.45	342.65	0.4957	−0.29
324.55	0.4691	0.18	345.55	0.5000	−0.27
327.15	0.4749	0.47	348.95	0.5058	−0.08
331.05	0.4778	−0.27	352.15	0.5109	0.05
333.55	0.4839	0.16	354.85	0.5155	0.24
335.95	0.4845	−0.50	357.75	0.5195	0.27

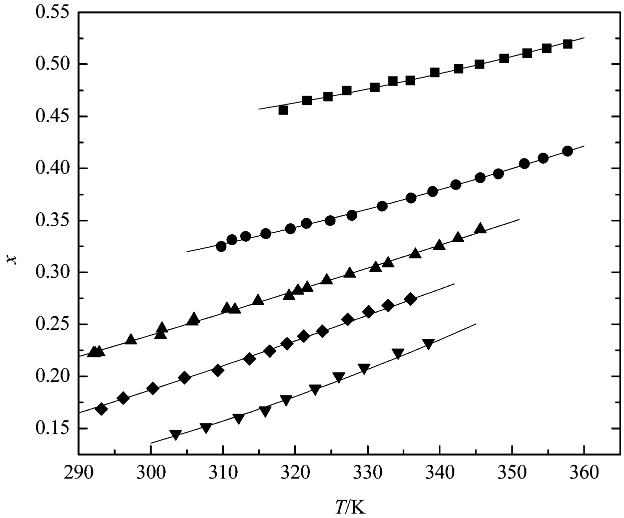

Figure 1. Solubility curves of thiourea in triglycol + water mixtures: ▼, $w = 0.63$; ◆, $w = 0.72$; ▲, $w = 0.82$; ●, $w = 0.91$; ■, $w = 1.00$.

Table 3. Parameters of Thiourea in Triglycol + Water Mixtures by Equation 2

w	A	B	C	10^3 rmsd	10^2 RAD
0.63	−20.04	−280.27	3.33	3.16	1.32
0.72	12.61	−1532.54	−1.61	3.54	1.17
0.82	−16.05	23.25	2.55	2.20	0.67
0.91	−31.12	999.51	4.67	1.43	0.34
1.00	13.76	−1023.49	−1.97	1.46	0.25

than water, and the greater the proportion of triglycol in the triglycol + water mixtures, the greater the solubility of thiourea, which agrees with the principle that like dissolves like.

Conclusion

The solubility of thiourea in triglycol + water has been determined from (292.05 to 357.75) K by a suitable experimental method and solubility apparatus.

The modified Apelblat equation based on solid−liquid phase equilibrium principles is used to correlate the solubility data of thiourea in triglycol + water mixtures. It appears that the relative deviation among all these values does not exceed 2.65 %, and the average relative deviation is 0.75 %. The solubilities calculated by the model show good agreement with the experimental data.

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

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