

# Solubilities and Enthalpies of Solution for Thiourea in Ethanol or Methanol + Water

Hua Li,\* Feng Guo, Guoqin Hu, Lei Zhao, and Yadong Zhang

School of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou Science Road #100, Zhengzhou, Henan, China, 450001

The solubilities of thiourea in ethanol or methanol + water from (289.75 to 330.85) K and the enthalpies of solution of thiourea in methanol, ethanol, or water had been determined with the suitable experimental methods and apparatus. The experimental data of solubilities were correlated with the modified Apelblat equation. The solubilities correlated by the model show good agreement with experimental data. The enthalpies of solution for thiourea in methanol, ethanol, or water were also determined. It was concluded that the solvent proton-donor ability and existing steric hindrances for hydrogen bonding and other intermolecular interactions play a decisive role in the solvation of thiourea.

## Introduction

Isopropyl mercaptan is an important pharmaceutical intermediate and chemical material. In recent years, the market demand has been increasing steadily and has aroused attention from both home and abroad. Thiourea is one of the main materials for the production of isopropyl mercaptan.<sup>1,2</sup> In industrial manufacturing, the selection of solvents for the preparation process of isopropyl mercaptan is a very important step. To choose the proper solvent for the synthesis of isopropyl mercaptan, it is necessary to know the solubility data and thermodynamic properties of the solution of thiourea in different solvents; in addition, the knowledge of the enthalpy of solution is essential data for the analysis of energy consumption in the chemical process. Ethanol or methanol is one of the selected solvents; the solubilities of thiourea in ethanol or methanol have direct effects on the product yield, but the solubilities of thiourea in ethanol or methanol which have been published<sup>3,4</sup> were only limited to (293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K. Until now, as far as we know, virtually no data have been published on the thermodynamic characteristics of solution (solvation) of thiourea in solvents such as methanol or ethanol. Therefore, in the present study, the solubilities of thiourea in ethanol or methanol + water mixtures with the mass fraction of ethanol or methanol, being 0.54, 0.65, 0.76, 0.88, and 1.00, respectively, were determined from (289.75 to 330.85) K. The experimental data were correlated with the modified Apelblat equation, and the solubilities correlated by models agree with the experimental data to within  $\pm 5\%$ ; the enthalpies of solution of thiourea in methanol, ethanol, or water were also determined at 293.15 K and molalities of solute in ethanol, methanol, or water in the range of  $m = (0.174 \text{ to } 0.749) \text{ mol} \cdot \text{kg}^{-1}$  by using a precise isoperibol ampule-type calorimeter. The enthalpic effects of the solute (thiourea) in the different solvents under consideration are discussed.

## Experimental Section

**Materials.** Thiourea, methanol, ethanol, and potassium chloride were of analytical reagent grade, and they were obtained

from Shanghai Chemical Reagent Co. and have mass fraction purities of 0.995. Potassium chloride was dried in a vacuum drier for 3 days before use. Deionized water was used.

**Solubility Measurement.** The solubility of thiourea in ethanol or methanol + water was measured in a synthetic method at atmospheric pressure by using the apparatus described previously in ref 5. The laser monitoring observation technique was used to determine the dissolution temperature of the solid–liquid mixture of the known composition. The thermometer (WNG-01 model, Beijing) was used to measure the temperature of the jacketed glass vessel. The uncertainty of the temperature was  $\pm 0.02$  K.

Predetermined amounts of thiourea and the solvents were weighed using an electronic balance (HZK-110 type, Shanghai) with an uncertainty of  $\pm 0.0001$  g and transferred into the vessel. The contents of the vessel were heated very slowly at a rate of  $1 \text{ K} \cdot \text{h}^{-1}$ . When the system was in equilibrium, the equilibrium temperature was recorded according to the experimental procedure described previously.<sup>5</sup> The solubility expressed by mole fraction was calculated as follows,<sup>6</sup>

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

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.

**Test of the 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.<sup>7,4</sup> 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.

**Enthalpy Measurement.** The calorimeter apparatus was shown schematically in Figure 1. A fixed amount of thiourea was dissolved in 50 g of the solvent in the calorimeter (adiabatic) under isobaric conditions; then, the temperature change during the dissolution process was measured with the digital Beckman thermometer. As there is no heat exchange between the adiabatic

\* To whom correspondence should be addressed. E-mail: lihua@zzu.edu.cn. Fax: 0086-371-63886154.

**Table 1. Solubility of NaCl and Thiourea in Water**

NaCl				
<i>T</i> /K	293.15	313.15	333.15	353.15
<i>x</i>	0.1001	0.1016	0.1031	0.1061
<i>x</i> (lit.) <sup>7</sup>	0.0999	0.1014	0.1031	0.1059
100 RD	0.25	0.25	0.00	0.23
Thiourea				
<i>T</i> /K	293.15	298.15	348.15	
<i>x</i>	0.03105	0.03733	0.2218	
<i>x</i> (lit.) <sup>4</sup>	0.03142	0.03897	0.2174	
100 RD	-1.19	-4.39	1.98	

system and the environment, the dissolution enthalpies can be obtained from eq 2.

$$\Delta_{\text{sol}}H_m = -\frac{M}{m_1}[(m_1C_1 + m_2C_2) + C_3]\Delta T \quad (2)$$

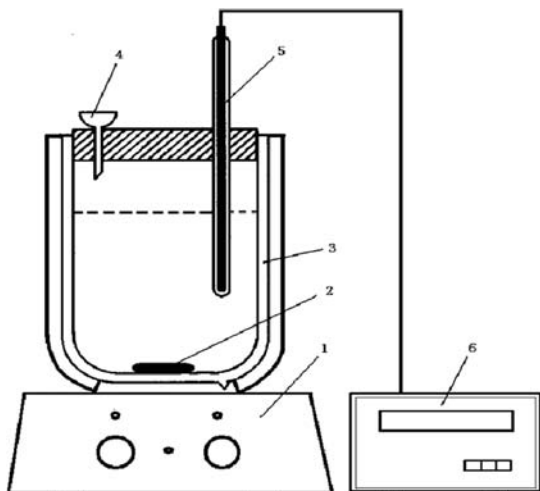
where  $\Delta_{\text{sol}}H_m$  is the enthalpy of solution;  $C_1$  and  $C_2$  are the heat capacity of solute and solvent, respectively;  $m_1$  represents the mass of the solute;  $m_2$  is the mass of the solvent;  $M$  represents the mole mass of the solute;  $\Delta T$  is the temperature change; and  $C_3$  represents the heat capacity of the calorimeter.

The measurement of the enthalpy of solution was carried out in a heat-insulated system at the conditions of constant pressure and nonvolume work, so that the total value of enthalpy of the system remains unchanged. Thermometric and thermal sensitivities of the apparatus were up to  $10^{-5}$  K and  $2 \cdot 10^{-3}$  J·mm<sup>-1</sup> on a scale of the recording device, correspondingly.

**Enthalpy Absorbed by Calorimeter.** The dissolution experiment was first performed with KCl as the standard sample according to its known dissolution enthalpies, and the heat capacity  $C_3$  of calorimeter could be obtained at first; then, the temperature change during the dissolution process of sample was measured. The integrated dissolution enthalpies of the sample can be calculated with eq 2.

Because of the heat provided by the stirring during the dissolution and also to the fact that the system is not strictly adiabatic, there was a little heat exchange between the system and the environment. The measured temperatures must be corrected in an appropriate method (Reynolds' graphing method)<sup>8</sup> to eliminate the heat exchange and get the real value of  $\Delta T$ .

The experimental process was performed as follows: 1.0305 g of crushed KCl was weighed. A portion of 50 mL distilled



**Figure 1.** Apparatus for determining the dissolution enthalpy. 1, magnetic stirrer; 2, stir magneton; 3, adiabatic apparatus; 4, funnel; 5, sensor; 6, SWC-IIC Beckman thermometer.

**Table 2. Literature Data<sup>7</sup> of Potassium Chloride + Water Solutions**

<i>T</i>	$\Delta_{\text{sol}}H_m$	$\rho$	$C_2$	$C_1$
K	kJ·mol <sup>-1</sup>	g·cm <sup>-3</sup>	kJ·kg <sup>-1</sup> ·K <sup>-1</sup>	kJ·kg <sup>-1</sup> ·K <sup>-1</sup>
300.15	17.205	0.9964	4.176	0.669

water at room temperature was put into the calorimeter, and the digital sensor of the Beckman thermometer was plugged on. The stirrer was turned on at (60 to 90) rpm. Observe the temperature change, and read the temperature difference. Add the known mass of KCl into the calorimeter immediately, and read the temperature. Measure the solution temperature in the calorimeter. The real temperature difference  $\Delta T$  during the solution process of KCl can be obtained in the Reynolds' graphing method, and  $C_3$  can be calculated. Repeat the determination three times, and take the average. The temperature difference was found to be  $-0.921$  K after calibrating with Reynolds' graphic method. The literature data<sup>7</sup> of potassium chloride + water solution is listed in Table 2. The enthalpy measured ( $C_3$ , calculated according to eq 2) is therefore  $0.0495$  kJ·K<sup>-1</sup>.

According to the calculated value of  $C_3$ , the enthalpies of solution of potassium chloride in water at 298.15 K were determined. The value observed here is  $\Delta_{\text{sol}}H_m$  ( $m = 0.111$  mol·kg<sup>-1</sup> (H<sub>2</sub>O)) =  $(17.60 \pm 0.04)$  kJ·mol<sup>-1</sup>. It is in very good agreement with the literature data:  $(17.58 \pm 0.02)$ <sup>9</sup> kJ·mol<sup>-1</sup> and  $(17.22 \pm 0.04)$ <sup>10</sup> kJ·mol<sup>-1</sup>. The relative deviations of measurements did not exceed 0.5 %.

**Enthalpy of Solution.** The measurements of the enthalpy of solution were carried out over the molality range of (0.174 to 0.749) mol·kg<sup>-1</sup>. A known mass of thiourea was first placed in the calorimeter, and then the solvent was put into the calorimeter quickly. The operation was repeated three times according to the above-described experimental procedure. The enthalpy of solution was calculated according to eq 2. The uncertainty of enthalpy was  $\pm 0.04$  kJ·mol<sup>-1</sup>.

## Results and Discussion

**Solubilities of Thiourea in Ethanol or Methanol + Water.** The measured solubilities of thiourea in ethanol or methanol solution at different temperatures are presented in Table 3. The dependence of thiourea on temperature in ethanol or methanol + water mixtures is described in the modified Apelblat equation:<sup>11</sup>

$$\ln x = A + \frac{B}{T/K} + C \ln(T/K) \quad (3)$$

where  $x$  is the mole fraction solubility of thiourea;  $T$  represents 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.

The root-mean-square deviation (rmsd) is defined as:<sup>5</sup>

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

where  $N$  is the number of experimental points,  $x_{ci}$  represents the solubilities calculated from equations, and  $x_i$  represents the experimental solubility values.

Relative deviations (RD) are calculated according to:<sup>5</sup>

$$\text{RD} = \frac{x - x_c}{x} \quad (5)$$

The relative average deviations (RAD) is defined as,<sup>5</sup>

Table 3. Mole Fraction Solubility of Thiourea  $x$  in Ethanol or Methanol + Water Mixtures

$T/K$	$x$	100 RD	$T/K$	$x$	100 RD	$T/K$	$x$	100 RD
Ethanol + Water								
	$w = 0.54$		304.85	0.04761	-1.56	305.65	0.08095	1.56
			307.35	0.05028	-2.45	307.95	0.08687	2.33
292.35	0.05368	0.41	309.15	0.05282	-2.04	311.35	0.09388	0.87
294.85	0.05855	1.47	312.25	0.05569	-4.58	313.25	0.09930	1.30
297.80	0.06383	1.15	312.85	0.06000	1.46	316.85	0.1086	0.52
301.55	0.07179	1.57	317.35	0.06578	-0.46	318.95	0.1152	0.71
304.90	0.07919	1.31	323.75	0.07700	-0.29	321.85	0.1233	-0.32
307.60	0.08621	1.70	324.55	0.07967	1.17	323.85	0.1301	-0.39
310.15	0.09282	1.48	326.45	0.08322	0.97	326.65	0.1380	-2.10
312.40	0.09809	0.31		$w = 1.00$			$w = 0.76$	
314.75	0.1046	-0.31	292.65	0.02239	0.99	289.75	0.05367	-0.85
316.65	0.1108	-0.10	293.85	0.02274	-0.33	295.25	0.06136	-0.86
318.35	0.1145	-1.87	299.45	0.02563	-1.68	298.15	0.06563	-1.23
	$w = 0.65$		302.75	0.02806	-0.39	300.05	0.06914	-0.65
294.00	0.05268	-3.70	305.85	0.02945	-2.87	302.35	0.07381	0.27
296.80	0.06129	3.91	308.95	0.03236	-0.65	304.85	0.07860	0.42
302.05	0.06916	2.16	309.40	0.03306	0.42	306.85	0.08293	0.89
303.25	0.07082	1.40	311.65	0.03451	-0.52	308.75	0.08720	1.25
304.75	0.07268	0.09	312.55	0.03502	-1.11	310.65	0.09115	1.03
307.05	0.07598	-1.44	312.75	0.03528	-0.84	314.25	0.09900	0.46
308.15	0.07877	-0.66	313.90	0.03642	-0.32	315.55	0.1020	0.31
308.95	0.08026	-0.84	314.35	0.03749	1.51	317.15	0.1053	-0.44
309.35	0.08215	0.46	315.55	0.03839	1.14	320.15	0.1120	-1.66
311.25	0.08583	-0.01	316.40	0.03864	-0.17	321.65	0.1182	0.04
312.85	0.08837	-1.17	318.20	0.03993	-1.03	323.25	0.1234	0.46
314.35	0.09152	-1.47	320.00	0.04216	0.28	326.15	0.1319	0.01
315.75	0.09505	-1.20	Methanol + Water $w = 0.54$			329.35	0.1422	-0.33
316.85	0.09868	-0.21		$w = 0.54$		330.85	0.1483	0.19
318.10	0.1029	0.83	293.85	0.05630	0.99		$w = 0.88$	
319.30	0.1065	1.34	296.20	0.06124	2.77	295.65	0.05818	0.29
322.25	0.1135	0.37	299.35	0.06717	3.17	297.65	0.06116	0.77
322.95	0.1153	0.19	303.05	0.07359	1.98	300.45	0.06481	0.24
323.75	0.1172	-0.14	306.35	0.08078	2.07	302.75	0.06783	-0.43
	$w = 0.76$		309.15	0.08768	2.44	304.25	0.07041	-0.10
293.05	0.05414	0.35	312.25	0.09468	1.51	306.35	0.07350	-0.57
293.25	0.05539	2.12	315.05	0.1022	1.38	308.15	0.07652	-0.66
298.35	0.06128	-0.10	318.45	0.1110	0.21	310.25	0.08064	-0.19
302.25	0.06512	-3.43	321.95	0.1217	-0.29	312.75	0.08589	0.41
304.65	0.06905	-3.27	323.15	0.1258	-0.31	316.05	0.09256	0.34
305.95	0.07377	0.32	324.55	0.1322	0.75		$w = 1.00$	
309.25	0.07817	-1.67	327.25	0.1409	-0.32	298.65	0.05336	0.40
314.05	0.08761	-1.45	330.35	0.1512	-1.78	301.45	0.05652	-0.12
314.95	0.09208	1.44		$w = 0.65$		304.35	0.06059	0.42
317.35	0.09825	2.38	290.65	0.05286	-0.01	307.85	0.06429	-1.30
319.45	0.09856	-2.12	294.45	0.05963	1.63	309.05	0.06671	-0.20
	$w = 0.88$		296.25	0.06348	2.91	311.25	0.07024	0.23
293.85	0.03732	2.43	300.65	0.07040	1.26	314.55	0.07608	1.18
296.55	0.04042	3.35	301.75	0.07246	1.14	319.45	0.08210	-1.46
300.35	0.04456	3.28	302.85	0.07525	1.90	321.25	0.08716	0.81

<sup>a</sup>  $w$  is the mass fraction of ethanol or methanol in the ethanol or methanol + water mixture.

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

The solubility curves by eq 3 are shown in Figures 2 and 3. The values of parameters  $A$ ,  $B$ , and  $C$ , the relative average deviations (RAD), and the root-mean-square deviation (rmsd) in eq 3 are listed in Table 4. The relative deviations between the experimental value and the calculated value are also listed in Table 3.

From Table 4, it can be found that the calculated solubilities show good agreement with the experimental data, in which the overall rmsd of 69 data points for the thiourea in ethanol solution and 66 data points for the thiourea in methanol solution being  $5.47 \cdot 10^{-3}$  and  $4.59 \cdot 10^{-3}$ , respectively. The relative deviations by eq 3 among all of these values do not exceed 4.6 %; the relative average deviations are 1.1 %, which indicates that the modified Apelblat equation is suited to correlate the solubility data of thiourea in ethanol or methanol solution.

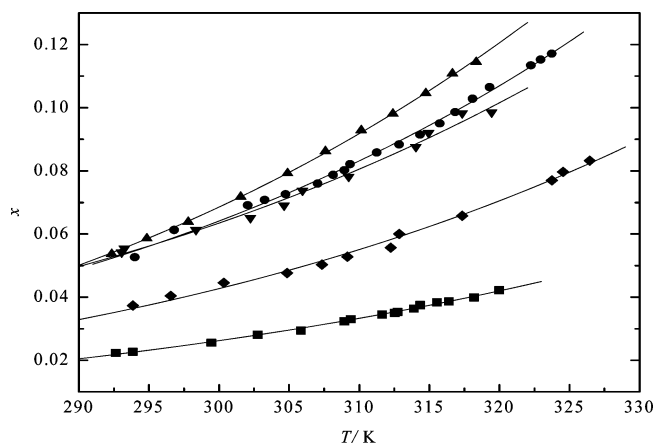
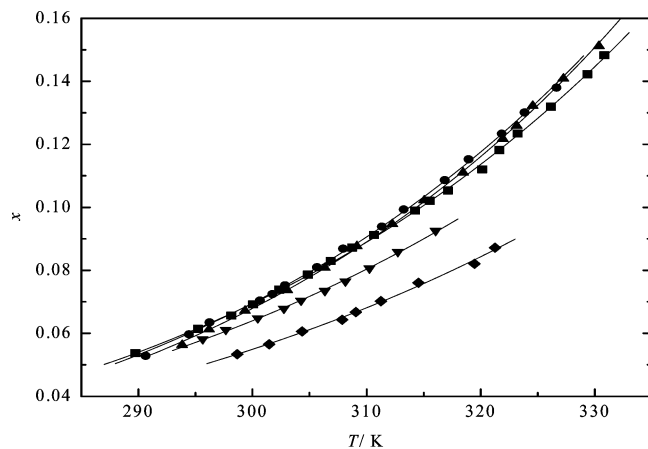


Figure 2. Mole fraction solubility  $x$  of thiourea in ( $w$ ) ethanol + ( $1 - w$ ) water:  $\blacktriangle$ ,  $w = 0.54$ ;  $\bullet$ ,  $w = 0.65$ ;  $\blacktriangledown$ ,  $w = 0.76$ ;  $\square$ ,  $w = 0.88$ ;  $\blacksquare$ ,  $w = 1.00$ ; solid lines, calculated values where  $w$  is the mass fraction of ethanol.



**Figure 3.** Mole fraction solubility  $x$  of thiourea in  $(w)$  methanol +  $(1-w)$  water: ▲,  $w = 0.54$ ; ●,  $w = 0.65$ ; ■,  $w = 0.76$ ; ▼,  $w = 0.88$ ; □,  $w = 1.00$ ; solid lines, calculated values where  $w$  is the mass fraction of methanol.

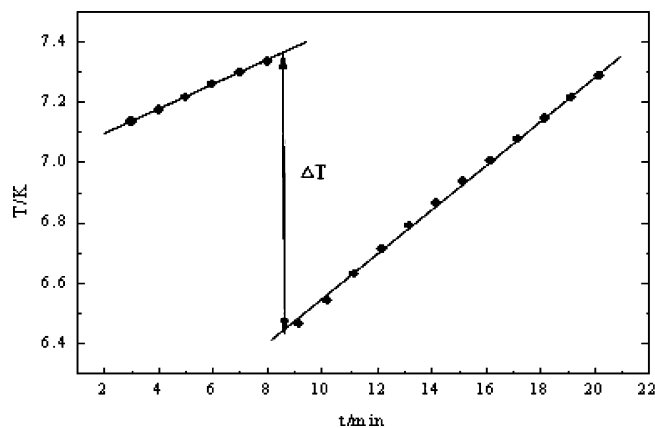
**Table 4. Parameters of Thiourea in Ethanol or Methanol + Water by Equation 3**

$w$	$A$	$B$	$C$	$10^3$ rmsd	$10^2$ RAD
Ethanol + Water					
0.54	-92.45	1703.37	14.74	1.07	1.06
0.65	-49.29	60.62	8.13	1.08	1.14
0.76	-56.58	573.42	9.10	1.55	1.70
0.88	-56.41	412.59	9.10	1.19	2.00
1.00	-68.84	1107.37	10.78	0.346	0.886
Methanol + Water					
0.54	-100.95	2251.79	15.91	1.52	1.42
0.65	-98.71	2203.34	15.55	1.35	1.26
0.76	-99.07	2441.47	15.48	0.711	0.632
0.88	-99.51	2596.47	15.45	0.338	0.402
1.00	-31.07	-454.13	5.20	0.673	0.679

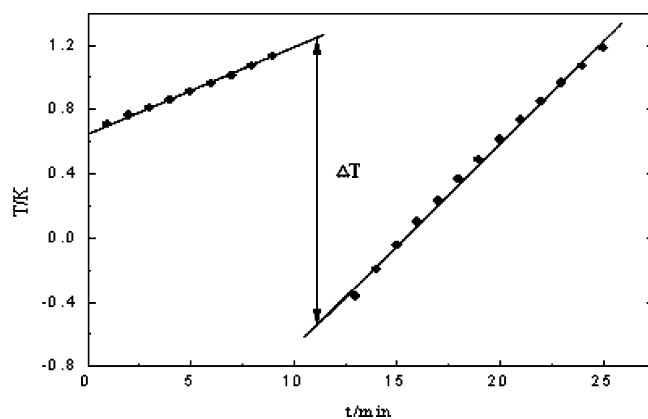
**Table 5. Comparison of Experiment Data and Literature Data for Mole Fraction Solubility of Thiourea  $x$  in Pure Ethanol and Methanol**

$T/K$	$x$	$x(\text{lit.})$	$100(x - x(\text{lit.}))/x$
Ethanol			
293.15	0.0224	0.0225 <sup>3</sup>	-0.30
298.15	0.0253	0.0253 <sup>3</sup>	-0.12
303.15	0.0284	0.0284 <sup>3</sup>	0.13
308.15	0.0320	0.0319 <sup>3</sup>	0.22
313.15	0.0359	0.0359 <sup>3</sup>	0.03
318.15	0.0403	0.0402 <sup>3</sup>	0.24
293.15	0.0224	0.0220 <sup>4</sup>	2.15
298.15	0.0253	0.0252 <sup>4</sup>	0.31
Methanol			
293.15	0.0469	0.0457 <sup>3</sup>	2.56
298.15	0.0526	0.0517 <sup>3</sup>	1.71
298.66	0.0534	0.0534 <sup>3</sup>	0.00
303.15	0.0588	0.0585 <sup>3</sup>	0.45
308.15	0.0656	0.0661 <sup>3</sup>	-0.82
313.15	0.0730	0.0746 <sup>3</sup>	-2.17
318.15	0.0811	0.0841 <sup>3</sup>	-3.59
293.15	0.0469	0.0480 <sup>4</sup>	-2.24
298.15	0.0526	0.0537 <sup>4</sup>	-2.12

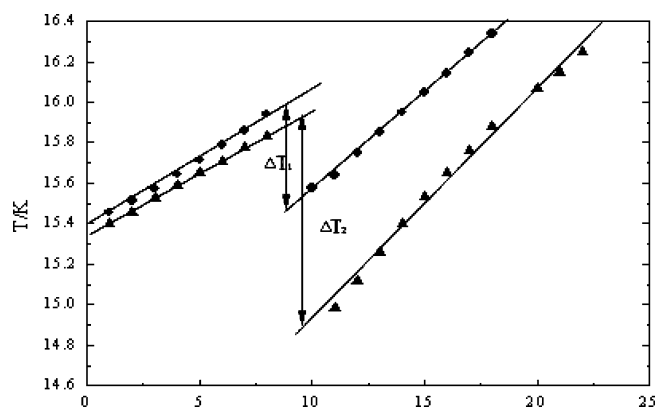
The graphical presentation of the solubility of thiourea in ethanol or methanol + water mixtures is shown in Figures 2 and 3. It can be observed from Figures 2 and 3 that all of the solubilities follow the order  $w = 0.54 > w = 0.65 > w = 0.76 > w = 0.88 > w = 1.00$  (where  $w$  is the mass fraction). This is because the polarity of water is higher than that of ethanol or methanol. The greater the proportion of ethanol or methanol in the ethanol or methanol + water mixtures, the smaller the solubility of thiourea, which agrees with the principle that like dissolves like.



**Figure 4.** Renault scheme of potassium chloride + water solutions.



**Figure 5.** Renault scheme of thiourea + water solutions: ●,  $m = 0.455$  mol·kg<sup>-1</sup>.



**Figure 6.** Renault scheme of thiourea + ethanol solutions: ●,  $m = 0.174$  mol·kg<sup>-1</sup>; ▲,  $m = 0.347$  mol·kg<sup>-1</sup>.

The uncertainties of measured variables are listed in Table 5. The experimental solubility values of thiourea in pure ethanol or methanol are compared with the literature value;<sup>3,4</sup> the relative deviations do not exceed 3.59 %, and the experimental data relatively agree with the literature values.

**Enthalpies of Solution of Thiourea in Methanol, Ethanol, or Water.** The temperature change during the dissolution process of potassium chloride in water is shown in Figure 4; the temperature changes during the dissolution process of thiourea in water, ethanol, or methanol in the calorimeter are shown in Figures 5, 6, and 7, respectively. The calculated results are listed in Table 6. The final concentration of the thiourea solutions ranged from (0.174 to 0.749) mol·kg<sup>-1</sup>. The comparison of the experimental value for dissolution enthalpy of thiourea in water at 293.15 K and the literature value are given



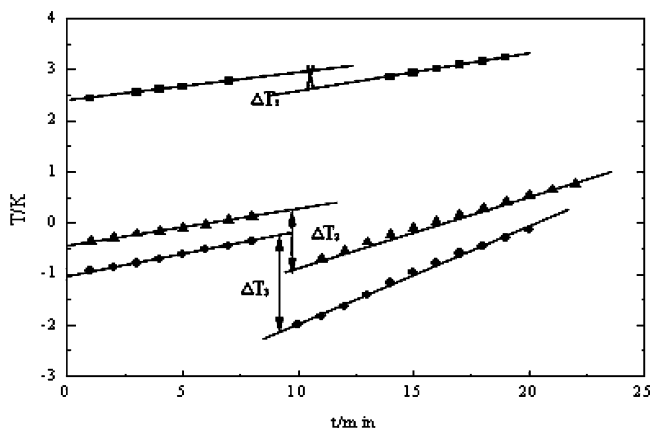


Figure 7. Renault scheme of thiourea + methanol solutions: ■,  $m = 0.250 \text{ mol} \cdot \text{kg}^{-1}$ ; ▲,  $m = 0.499 \text{ mol} \cdot \text{kg}^{-1}$ ; ●,  $m = 0.749 \text{ mol} \cdot \text{kg}^{-1}$ .

Table 6. Dissolution Enthalpy of Thiourea in Different Solvents and Related Parameters

solvent	$m$ $\text{mol} \cdot \text{kg}^{-1}$	$m_1$ g	$C_2$ $\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	$\rho$ $\text{g} \cdot \text{cm}^{-3}$	$\Delta T$ K	$\Delta_{\text{sol}}H_m$ $\text{kJ} \cdot \text{mol}^{-1}$
water	0.445	1.6898	4.181	0.9977	-1.786	20.94
ethanol	0.174	0.5218	2.375	0.7893	-0.543	11.39
ethanol	0.347	1.0436	2.375	0.7893	-1.142	12.04
methanol	0.250	0.7527	2.512	0.7915	-0.387	5.87
methanol	0.499	1.5041	2.512	0.7915	-0.898	6.85
methanol	0.749	2.2575	2.512	0.7915	-1.941	9.93

Table 7. Comparison of the Experimental Value for the Dissolution Enthalpy of Thiourea in Water and the Literature Value<sup>11</sup>

$T$ K	$\Delta_{\text{sol}}H_m$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{sol}}H_m(\text{lit.})$ $\text{kJ} \cdot \text{mol}^{-1}$	$100(\Delta_{\text{sol}}H_m - \Delta_{\text{sol}}H_m(\text{lit.}))/$ $(\Delta_{\text{sol}}H_m)$
293.15	20.94	21.85	-4.35

in Table 7. The observed value of the dissolution enthalpy of thiourea in water ( $20.94 \text{ kJ} \cdot \text{mol}^{-1}$ ) is in very good agreement with literature data<sup>12</sup> ( $21.85 \text{ kJ} \cdot \text{mol}^{-1}$ ).

As can be seen from Table 6, the values of the dissolution enthalpies of thiourea in methanol, ethanol, or water are all positive, and they increase with the increase of the molality of thiourea, which indicates that the dissolution process of thiourea in methanol, ethanol, or water needs the absorption of heat to destroy the crystal lattice and is an endothermic reaction.

Among the systems investigated, the structure-related ones are the factors that have effects on the formation of strong H-bonds in the solvation of thiourea. Considering all of the solutions studied, the solvent proton-donor ability and existing steric hindrances for hydrogen bonding and other intermolecular interactions play a decisive role in the solvation of thiourea.

At the same temperature, when the ratio of solute and solvent is the same, the enthalpy of solution of thiourea in different solvents can be arranged following the sequence water > ethanol > methanol.

## Conclusion

The solubilities of thiourea in ethanol or methanol + water from (289.75 to 330.85) K and the enthalpies of solution of thiourea in methanol, ethanol, or water have been determined with suitable experimental methods and apparatus.

The modified Apelblat equation based on solid-liquid phase equilibrium principles is used to correlate the solubility data of thiourea in ethanol or methanol + water. It appears that the relative deviation among all of these values does not exceed 4.6 %; the average relative deviation is 1.1 %, and the solubilities calculated in the model show good agreement with the experimental data.

The values of the dissolution enthalpies of thiourea in methanol, ethanol, or water are all positive, and they increase with the increase of the molalities of thiourea, which indicates that the dissolution process of thiourea in methanol, ethanol, or water needs the absorption of heat to destroy the crystal lattice and is an endothermic reaction. The solvent proton-donor ability and existing steric hindrances for hydrogen bonding and other intermolecular interactions play a decisive role in the solvation of thiourea.

The experimental solubilities and the enthalpies of solution that have been determined in this work can be used as essential data for the synthesis of isopropyl mercaptan.

## Literature Cited

- (1) Liu, Y. P.; Sun, B. G.; Xie, J. C.; Zheng, F. P.; Xiao, Y. Study on Synthesis of 2-Propene-1-Thiol. *Chem. Reagents (Beijing, China)* **2004**, *26*, 291–292.
- (2) Zhang, K. Q.; Sun, B. G. The Synthesis of Furfural Diisopropyl Mercaptan. *Fine Chem.* **1998**, *15*, 30–31.
- (3) Kim, K. J.; Lee, C. H.; Ryu, S. K. Solubility of Thiourea in  $C_1$  to  $C_6$  1-Alcohols. *J. Chem. Eng. Data* **1994**, *39*, 228–230.
- (4) Reid, E. E. *Organic Chemistry of Bivalent Sulfur*; Chemistry Publishing Co., Inc.: New York, 1963; Vol. V, p 19.
- (5) Li, H.; Guo, F.; Hu, G. Q. Measurement and Correlation for Solubility of Thiourea in Triglycol + Water at Temperatures from (292.05 to 357.75) K. *J. Chem. Eng. Data* **2007**, *54*, 2100–2102.
- (6) Shi, X. H.; Zhou, C. R.; Gao, Y. G.; Chen, X. Z. Measurement and Correlation for Solubility of (S)-(+)-2,2-Dimethylcyclopropane Carbox Amide in Different Solvents. *Chin. J. Chem. Eng.* **2006**, *14*, 547–550.
- (7) 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, 2002.
- (8) He, D. H.; Ma, Y.; Zhang, L. Q. *Basic Physics Chemistry Experiment*; Higher Education Press: Peking, 2008.
- (9) Wads, I.; Goldberg, R. N. Standards in isothermal microcalorimetry. *Pure Appl. Chem.* **2001**, *73*, 1625–1639.
- (10) Archer, G. Thermodynamic Properties of the KCl +  $H_2O$  System. *J. Phys. Chem. Ref. Data* **1999**, *28*, 1–17.
- (11) Apelblat, A.; Manzurola, E. Solubilities of o-acetylsalicylic, 4-aminosalicylic, 3,5-dinitrosalicylic, and p-toluic Acid, and Magnesium-DL-aspartate in Water from  $T = (278 \text{ to } 348) \text{ K}$ . *J. Chem. Thermodyn.* **1999**, *31*, 85–91.
- (12) Taniewska-Osińska, S.; Pałecz, B. Enthalpies of solution of thiourea in water from 293.15 to 333.15 K. *J. Chem. Thermodyn.* **1980**, *12*, 775–778.

Received for review December 05, 2008. Accepted September 19, 2009.

JE900543Q