Measurement and Correlation for Solubility of 2-Bromopropane and Thiourea in Water†

Hua Li,* Feng Guo, and Lei Zhao

College of Chemical Engineering, Zhengzhou University, Zhengzhou, Henan, China, 450001

The solubility of 2-bromopropane and thiourea in water had been determined from (295.25 to 354.75) K by analytical and synthetic methods, respectively. The experimental data were correlated with the modified Apelblat equation and quadratic equation separately. The solubilities correlated by the model show good agreement with experimental data.

Introduction

Isopropyl mercaptan is an important medicine intermediate and chemical material. Its synthesis reaction is as follows

$$CH_3CHBrCH_3 + NH_2CSNH_2 \rightarrow CH_3CHSHCH_3 + Na_2SO_4 \quad (1)$$

The main materials for synthesis isopropyl mercaptan were 2-bromopropane and thiourea. In industrial manufacture, the selection of solvents for the preparation process of isopropyl mercaptan is a very important step. To choose the proper solvent for synthesis of isopropyl mercaptan, it is necessary to know the solubility data of 2-bromopropane and thiourea in different solvents, in which water is one of the cheapest solvents; the solubilities of 2-bromopropane and thiourea in water directly influence the product yield, but the solubilities of thiourea in water which have been published[1] were only limited at 293.15 K, 298.15 K, and 348.15 K; and the solubilities of 2-bromopropane in water are only limited in the literature[2] at 291.15 K. There are few reports of the solubilities of 2-bromopropane and thiourea in water over a wide temperature range. In the present study, the solubility of 2-bromopropane and thiourea in water has been determined from (295.25 to 354.75) K. The experimental data were correlated with the modified Apelblat equation and the quadratic equation separately. The solubilities correlated by two models agree with the experimental data to within ± 4.38 % and ± 3.85 %, respectively.

Experimental Section

Materials. 2-Bromopropane and thiourea were AR grade, and they were obtained from Shanghai Chemical Reagent Co. and have purities of 0.995 in mass fraction. The water used in the experiments was double-distilled.

Apparatus and Procedure. The solubility of 2-bromopropane in water was measured by an analytical method at atmospheric pressure.[3,4] The experiments were carried out in a magnetically stirred, jacketed glass vessel (50 cm^3). A constant temperature (± 0.02 K) was maintained by circulating water through the outer jacket from a thermoelectric controller at the required temperature.

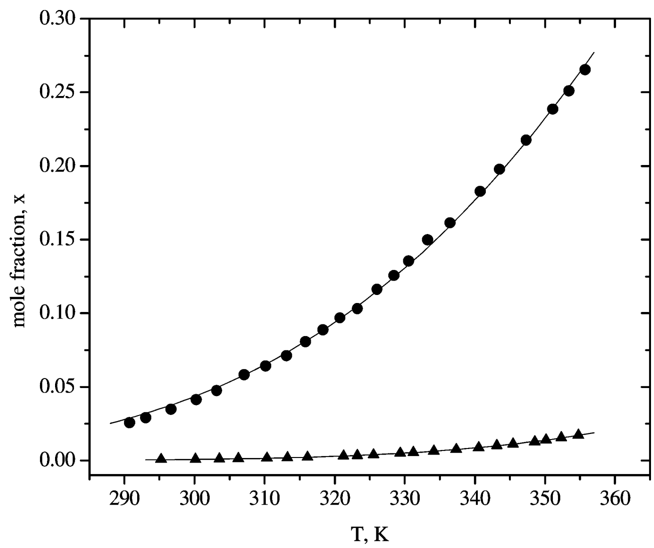

Figure 1. Solubility of 2-bromopropane and thiourea in water by eq 3. ▲, 2-bromopropane; ●, thiourea; −, calculated value from eq 3.

Solvents for the solubility measurement were prepared by mass using an electronic balance (type AW 120, Shimadzu Co.) with an accuracy of ± 0.0001 g. 2-Bromopropane saturated solutions were prepared with 2-bromopropane + water. The solution was allowed to reach equilibrium with excess 2-bromopropane at corresponding temperature. After the 24 h equilibration, samples were analyzed by UV spectrophotometry. For each equilibration cell, after the first 24 h, samples were taken at 4 h intervals to confirm that the equilibrium had been reached.

The solubility of thiourea in water was measured by a synthetic method at atmospheric pressure. 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 bushing with a mercury glass thermometer was inserted into the inner chamber of the vessels for the measurement of the

* To whom correspondence should be addressed. E-mail: lihua@zzu.edu.cn. Fax: 0086-371-67781722. Present address: College of Chemical Engineering, Zhengzhou University, Zhengzhou Science Road 100#, Zhengzhou, Henan, China, 450001.

† Part of the “William A. Wakeham Festschrift”.

10.1021/je800796h CCC: $40.75
Published on Web 01/06/2009

Table 1. Solubility of Propionic Acid and NaCl in Water

	propionic acid			
temperature, K	293.15	303.15	313.15	323.15
solubility, g/100 g H_2O	73.6	79.9	86.4	92.8
literature,[6] g/100 g H_2O	73.5	79.8	86.2	92.6
relative deviation, %	0.14	0.13	0.23	0.22
	NaCl			
temperature, K	293.15	313.15	333.15	353.15
solubility, g/100 g H_2O	36.1	36.7	37.3	38.5
literature,[6] g/100 g H_2O	36.0	36.6	37.3	38.4
relative deviation, %	0.277	0.272	0	0.260

temperature. The uncertainty of temperature was ± 0.02 K (corrected by Liming Research Institute of Chemical Industry).

Predetermined amounts of thiourea and water were weighed using an electronic balance with an accuracy 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 would arrive at a balance. In the early stage of the experiment, the laser beam was blocked by the unsolved 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[5]

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{2}$$

where m_1 and m_2 represent the mass of solute and solvent. M_1 and M_2 are the molecular mass of solute and solvent.

Each experiment was repeated three times, and the deviation of determined solubility data is less than 2 %.

Test of Apparatus. To ensure proper operation of the apparatus, the solubility of propionic acid and NaCl in water was measured and compared with the values reported in the literature.[6] The experimental measurements agreed with the reported values with a mean relative deviation of 0.18 % and 0.202 %, respectively. The measured values are listed in Table 1.

Results and Discussion

The measured solubilities of 2-bromopropane and thiourea in water at different temperatures are presented in Table 2.

Apelblat Equation. The temperature dependence of 2-bromopropane and thiourea in water is described by the modified Apelblat equation.[7]

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

where x is the mole fraction solubility of 2-bromopropane and thiourea; T is the absolute temperature; and A, B, and C are the model parameters. The calculated solubilities x_c of 2-bromopropane and thiourea by eq 3 are given in Table 2. The solubility curves by eq 3 are shown Figure 1. The values of parameters A, B, and C and the root-mean-square deviation are

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

where N is the number of experimental points; x_{ci} represents the solubilities calculated from eq 3; and x_i represents the experimental solubility values. The relative deviations between the experimental value and calculated value are also listed in

Table 2. Solubilities of 2-Bromopropane and Thiourea in Water

		x_c		rel dev, %	
T/K	x	eq 3	eq 7	eq 3	eq 7
		2-bromopropane			
295.25	0.0005867	0.0006124	0.0005861	−4.38	−2.68
300.15	0.0008204	0.0008506	0.0008182	−3.68	0.10
303.55	0.001038	0.001061	0.001025	−2.24	0.27
306.25	0.001214	0.001260	0.001222	−3.82	1.24
310.35	0.001569	0.001627	0.001586	−3.67	−0.65
313.25	0.001888	0.001940	0.001899	−2.74	−1.09
316.15	0.002272	0.002305	0.002266	−1.46	−0.6
321.25	0.003072	0.003098	0.003066	−0.83	0.25
323.25	0.003429	0.003469	0.003441	−1.15	0.20
325.55	0.003935	0.003943	0.003922	−0.21	−0.35
329.35	0.004835	0.004853	0.004844	−0.38	0.33
331.25	0.005364	0.005374	0.005371	−0.18	−0.19
334.15	0.006295	0.006263	0.006270	0.51	−0.13
337.35	0.007434	0.007392	0.007407	0.57	0.39
340.55	0.008705	0.008694	0.008713	0.12	0.36
343.15	0.01013	0.009896	0.009911	2.31	−0.09
345.45	0.01116	0.01108	0.01108	0.74	2.17
348.55	0.01269	0.01286	0.01283	−1.37	0.72
350.15	0.01387	0.01388	0.01382	−0.07	−1.12
352.35	0.01543	0.01539	0.01528	0.26	0.36
354.75	0.01713	0.01720	0.01700	−0.40	0.98
		thiourea			
290.75	0.02558	0.02561	0.02596	−0.1	−1.47
293.05	0.02893	0.02891	0.02914	0.08	−0.73
296.65	0.03467	0.03469	0.03476	−0.07	−0.25
300.25	0.04132	0.0413	0.04121	0.04	0.28
303.15	0.04742	0.04726	0.04705	0.35	0.78
307.1	0.05825	0.05644	0.05601	3.12	3.85
310.15	0.06415	0.06412	0.06376	0.04	0.61
313.15	0.07103	0.07254	0.07212	−2.13	−1.54
315.85	0.08064	0.08061	0.08029	0.04	0.43
318.35	0.08864	0.08865	0.08841	−0.01	0.26
320.75	0.09688	0.09684	0.09670	0.04	0.18
323.25	0.1031	0.1058	0.1059	−2.62	−2.69
326.05	0.1162	0.1166	0.1168	−0.31	−0.49
328.45	0.1256	0.1262	0.1266	−0.48	−0.81
330.55	0.1354	0.1351	0.1356	0.24	−0.17
333.25	0.1498	0.1469	0.1477	1.98	1.41
336.45	0.1614	0.1617	0.1627	−0.19	−0.79
340.75	0.1827	0.1827	0.1838	−0.01	−0.63
343.55	0.1977	0.1970	0.1982	0.35	−0.23
347.35	0.2176	0.2174	0.2181	0.10	−0.23
351.15	0.2386	0.2385	0.2384	0.03	0.07
353.45	0.2509	0.2518	0.2508	−0.34	0.04
355.75	0.2653	0.2651	0.2632	0.08	0.80

Table 2. Relative deviations are calculated according to

$$\text{relative deviations (\%)} = \left(\frac{x - x_c}{x}\right) \cdot 100 \tag{5}$$

The absolute average deviations (AAD) by eq 3 are listed in Table 3. The AAD is defined as

$$\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{x_i - x_{ci}}{x_i}\right| \tag{6}$$

Quadratic Equation. The temperature dependence of 2-bromopropane and thiourea in water is also described by the quadratic equation

$$\ln x = A + B(T/\mathrm{K}) + C(T/\mathrm{K})^2 \tag{7}$$

where x is the mole fraction solubility of 2-bromopropane and thiourea; T is the absolute temperature; and A, B, and C are the model parameters. The objective function that was used to determine the parameters A, B, and C in eq 5 by optimization is $\sum_{i=1}^{N} (x_{ci} - x_i)^2$.

The calculated solubilities x_c of 2-bromopropane and thiourea by eq 7 are also given in Table 2. The solubility curves by eq

Table 3. Parameters of 2-Bromopropane and Thiourea in Water by Equation 3

component	A	B	C	10^4 rmsd	10^2 AAD
2-bromopropane	31.224	−6763.9	−2.763	0.74	1.48
thiourea	187.385	−12164.7	−26.304	1.02	0.55

Table 4. Parameters of 2-Bromopropane and Thiourea in Water by Equation 7

component	A	B	C	10^3 rmsd	10^2 AAD
2-bromopropane	−46.149	0.193	$-2.1 \cdot 10^{-4}$	0.075	0.59
thiourea	−38.257	0.187	$-2.344 \cdot 10^{-4}$	1.11	0.78

7 are shown in Figure 2. The defined relative deviation and AAD were the same eqs 5 and 6. The absolute average deviations (AAD) by eq 7 are listed in Table 4.

From Table 3, it can be found that the calculated solubilities by eq 3 and eq 7 show good agreement with the experimental data, the rmsd of 44 data points for 2-bromopropane and thiourea in water by eq 3 and eq 7 being $1.76 \cdot 10^{-4}$ and $1.185 \cdot 10^{-3}$, respectively. The relative deviations by eq 3 among all of these values do not exceed 4.38 %, and the absolute average deviation by eq 3 is 1.01 %. The relative deviations by eq 7 among all of these value do not exceed 3.85 %, and the absolute average deviation by eq 3 is 0.685 %, which indicates that the modified Apelblat equation and the quadratic equation are fit to correlate the solubility data of 2-bromopropane and thiourea in water.

The uncertainties of measured variables were listed in Table 5. The experimental solubility values of thiourea and 2-bromopropane in water are compared with Reid[1] and Takeuchi,[2] and the experimental data relatively agree with the literature values.

The two models predict the estimated values with less than 9 % relative deviation. The excellent agreement between the measured and calculated value shows that the two models are able to describe 2-bromopropane and thiourea in water with sufficient accuracy.

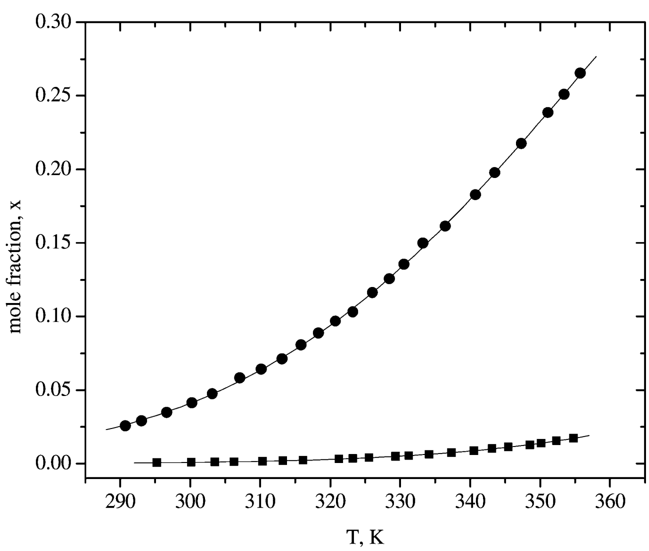

Figure 2. Solubility of 2-bromopropane and thiourea in water by eq 7. ■, 2-bromopropane; ●, thiourea; −, calculated value from eq 7.

Table 5. Comparison of Experimental Data and Literature Data for Solubility of Thiourea and 2-Bromopropane in Water

	x			$[100(x - x(\text{lit.}))]/(x)$	
T/K	eq 3	eq 7	x(lit.)	eq 3	eq 7
		thiourea			
293.15	0.02905	0.02929	0.03142[1]	−8.16	−7.27
298.15	0.03733	0.03734	0.03897[1]	−4.39	−4.37
348.15	0.2218	0.2224	0.2174[1]	1.98	2.25
		2-bromopropane			
291.15	0.0004610	0.0004400	0.0004195[2]	9.00	4.66

Conclusion

The solubility of 2-bromopropane and thiourea in water has been determined from (295.25 to 354.75) K by a suitable experimental method and solubility apparatus. The modified Apelblat equation based on liquid−liquid and solid−liquid phase equilibrium principles and the quadratic equation is used to correlate the solubility data of 2-bromopropane and thiourea in water, respectively. It appears from the RMSD of 44 data points for the 2-bromopropane and thiourea in water by eq 3 and eq 7 being $1.76 \cdot 10^{-4}$ and $1.185 \cdot 10^{-3}$, respectively, that the solubilities calculated by the models show good agreement with the experimental data. The quadratic equation is better than the modified Apelblat equation compared with the three-parameter equation.

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.

Literature Cited

(1) Reid, E. E.; M. A.; Ph.D.; L L. D. *Organic Chemistry of Bivalent Sulfur*; Chemistry Publishing Co., INC.: New York, 1963; Vol. V, p 19.
(2) Takeuchi, Y.; Ichihara, G.; Kamijima, M. A Review on Toxicity of 2-Bromopropane: Mainly on its Reproductive Toxicity. *J. Occup. Health* **1997**, *39*, 179–191.
(3) Song, C. Y.; Shen, H. Z.; Zhao, J. H. Solubilities of 2-Methyl-1,4-naphthoquinone in Water + (Methanol, Ethanol, 1-Propanol, 2-Propanol, 1,2-Propanediol, and Glycerin, Respectively) from 293.15 to 337.92 K. *J. Chem. Eng. Data* **2007**, *52*, 2018–2019.
(4) Hao, H. X.; Hou, B. H.; Wang, J. K.; Zhang, M. J. Solubility of Erythritol in Different Solvents. *J. Chem. Eng. Data* **2005**, *50*, 1454–1456.
(5) 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.
(6) 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; pp 51−477.
(7) Apelblat, A.; Manzurola, E. Solubilities of o-acetylsalicylic, 4-aminosalicylic, 3,5-dinitrosalicylic, and p-toluic acid, and magnesium-DLaspartatein water from T = (278 to 348) K. *J. Chem. Thermodyn.* **1999**, *31*, 85–91.

Received for review October 26, 2008. Accepted December 3, 2008.

JE800796H