Solubility of Ammonium Thiocyanate in Different Solvents

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The solubility of ammonium thiocyanate in different solvents (acetone, water, methanol, ethanol, ethanol + water mixtures) was measured by a synthetic method at different temperatures and at atmospheric pressure. The laser monitoring observation technique was used to determine the disappearance of the solid phase in a solid + liquid mixture. The results of these measurements were correlated with the modified Apelblat equation.

Introduction

In the coking process, the sulfur and nitrogen in the raw coal are partially converted to sulfurated hydrogen and hydrogen cyanide, which are mixed into coke oven gas. Sulfurated hydrogen and hydrogen cyanide are poisonous and corrosive; therefore, sulfurated hydrogen and hydrogen cyanide must be removed from coke oven gas. A desulphurization process is needed, on which the discharged waste liquor contains relatively high concentrations of ammonium thiocyanate. Solvent extraction can be regarded as a means of recovering ammonium thiocyanate. To choose the proper extraction solvent, it is necessary to know solubility data of ammonium thiocyanate in different solvents.

In this Article, solubility measurements of ammonium thiocyanate in acetone, water, methanol, ethanol, and 95 % and 50 % ethanol (mass fraction) at different temperature were performed. Experimental data were correlated by the modified Apelblat equation.[1,2]

Experimental Section

A white powdered crystal of ammonium thiocyanate was used, and its mass fraction purity is higher than 99.0 % (purchased from the Tianjin Kewei of China). The solvents used were of analytical reagent grade (purchased from the Tianjin Kewei of China). Distilled deionized water of HPLC grade was used.

The solubility of ammonium thiocyanate in different solvents was measured by a synthetic method that is described in the literature.[3−5] During the measurement, predetermined excess amounts of solute and solvent of known masses were transferred to the equilibrium vessel. The contents of the vessel were continuously stirred at an invariant and required temperature for 30 min. Then, additional solvent of known mass was introduced to the cell. When the last portion of solute had just disappeared, the intensity of the laser beam penetrating the vessel reached a maximum, and the solvent mass consumed in the measurement was recorded. Together with the mass of solute, the solubility would be obtained. The saturated mole fraction solubility of ammonium thiocyanate can be obtained as follows

$$x_A = \frac{m_A/M_A}{m_A/M_A + m_B/M_B + m_C/M_C} \quad (1)$$

With regard to a pure solvent system, m_A and m_B represent the masses of solute and solvent, M_A and M_B represent the molecular weights of solute and solvent, and $m_C = 0$. For the binary ethanol + water system, m_A, m_B, and m_C represent the masses of solute, ethanol, and water. M_A, M_B, and M_C are the molecular weights of solute, ethanol, and water, respectively.

Table 1. Mole Fraction Solubility of Ammonium Thiocyanate in Different Solvents at Different Temperature

T/K	$x_1^{exptl}10^2$	$100(x_1^{exptl} - x_1^{calcd})/x_1^{exptl}$	T/K	$x_1^{exptl}10^2$	$100(x_1^{exptl} - x_1^{calcd})/x_1^{exptl}$
Ethanol			95 % Ethanol (Mass Fraction)		
279.70	11.75	−0.71	282.00	13.91	0.33
286.10	12.50	−0.27	289.30	14.83	0.07
290.70	13.18	0.86	295.50	15.72	−0.08
299.50	14.31	1.11	301.80	16.68	−0.50
305.40	14.80	−0.88	309.40	18.02	−0.73
311.20	15.78	0.26	315.20	19.36	0.17
319.20	16.89	−0.22	322.80	20.78	−1.24
327.50	18.20	−0.31	327.30	22.17	0.11
333.00	19.10	−0.48	333.00	23.68	0.09
338.00	20.20	0.59	338.00	25.11	0.06
50 % Ethanol (Mass Fraction)			Water		
279	18.43	2.31	276.80	23.70	−0.67
284	20.50	3.66	285.50	26.76	0.43
289	21.91	1.62	295.00	29.82	−0.27
294	23.13	−1.23	302.30	32.62	0.19
298	24.71	−0.92	308.80	35.26	0.63
305	27.19	−1.77	314.80	37.73	0.81
313	30.36	−1.7	324.60	41.18	−0.83
318	32.61	−0.92	331.20	43.80	−1.43
323	34.56	−1.15	336.00	46.87	0.56
328	36.85	−0.45	341.00	49.19	0.49
333	39.34	0.66	345.00	52.25	−1.01
338	41.88	1.77			
343	44.11	2.09			
Methanol			Acetone		
279.60	16.93	0.02	279.00	23.58	−4.38
283.90	17.94	1.73	284.10	27.05	−4.51
291.10	18.95	−0.02	288.00	30.08	−4.36
296.00	19.88	−0.46	293.00	36.16	0.87
304.90	21.99	0.01	298.00	41.69	1.97
309.40	23.34	0.81	303.00	48.95	4.97
317.50	24.91	−1.99	308.00	55.67	5.05
326.20	27.69	−1.79	313.00	61.41	2.33
333.00	30.89	1.19	318.00	70.06	3.01
			323.00	74.11	−3.72
			328.00	81.11	−1.65

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10.1021/je800621p CCC: $40.75
Published on Web 02/10/2009

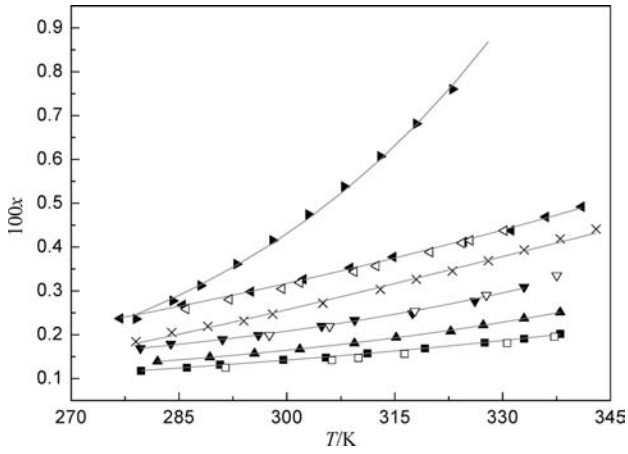

Figure 1. Mole fraction solubility of ammonium thiocyanate in different solvents: solid left triangle, acetone; solid right triangle, water; ▼, methanol; ▲, 95 % ethanol; ×, 50 % ethanol; ■, ethanol; open left triangle, ▽, and □, solubility of ammonium thiocyanate in water, methanol, and ethanol in the literature,[6] respectively.

Table 2. Curve-Fitting Parameters of Solubility Curve of Ammonium Thiocyanate in Different Solvent

solvent	*A*	*B*	*C*	10^2rmsd
acetone	−58.534	596.62	9.7658	3.765
ethanol	−37.592	899.46	5.7231	0.641
95 % ethanol	−76.877	2582.6	11.653	0.498
50 % ethanol	41.551	3076.1	5.7252	1.756
methanol	−77.293	2554.9	11.783	1.542
water	−11.673	−416.13	2.0883	0.745

All experiments were conducted three times, and the mean values were used to calculate the mole fraction solubility. The relative uncertainty of the experimental solubility values is within 0.05.

Results and Discussion

The measured solubility of ammonium thiocyanate at different temperature is listed in Table 1 and graphically plotted in Figure 1. In Table 1, x_1^{exptl} expresses the experimental solubility value. x_1^{calcd} expresses the calculated solubility value. Solubility data of ammonium thiocyanate in water, methanol and ethanol were compared with those in the literature[6] that are also reported in Figure 1. The result indicates that there is good agreement between experimental data in this Article and the reported literature data. The solubility data in Table 1 are described by the modified Apelblat equation

$$\ln x = A + B/T + C \ln T \tag{2}$$

where x is the mole fraction solubility of ammonium thiocyanate, T is the absolute temperature, and A, B, and C are the model parameters. The values of parameters A, B, and C and the root-mean-square relative deviations (rmsd) are listed in Table 2. The rmsd is defined as

$$\text{rmsd} = \left\{ \frac{1}{N} \sum_{i=1}^{N} \left(\frac{x_i^{\text{calcd}} - x_i^{\text{exptl}}}{x_i^{\text{exptl}}} \right)^2 \right\}^{1/2} \tag{3}$$

where N is the number of experimental points.

Conclusions

From Tables 1 and 2 and Figure 1, we can draw the following conclusions: (1) The solubility of ammonium thiocyanate in acetone, ethanol, water, methanol, and 95 % and 50 % ethanol is a function of temperature, and it increases with temperature. (2) The solubility of ammonium thiocyanate in the six solvents basically ranks in the order acetone > water > 50 % ethanol > methanol > 95 % ethanol > ethanol. (3) The calculated solubility of ammonium thiocyanate sets a good coherence with the experimental values, and the experimental solubility and correlation equation in this work can be used as essential data and models in the recovery of ammonium thiocyanate.

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Received for review August 6, 2008. Accepted January 7, 2009.

JE800621P