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Enthalpy of Solution and Viscosity of Mixtures of Urea and Sulfuric Acid

Cui-hong Hou,* Guang-long Wang, Bao-lin Zhang, and Deng-gao Jiang

College of Chemical Engineering, Zhengzhou University, Zhengzhou, Henan, China 450002

As the basically theoretical research and first step to the industrialization of a new process for urea−sulfuric acid compound fertilizer, some physical properties such as the enthalpy and viscosity of the mixture of urea and sulfuric acid are determined.

1. Introduction

In recent years, the compound fertilizer proportion in developed countries has been over 60% of the total production, while in China, the figure is only 20% and urea and single superphosphate are the main raw materials of compound fertilizer. Traditional urea superphosphate compound fertilizer is produced by mixing urea and superphosphate together, where they react with each other, producing free water and a complex of urea phosphates. The high solubility leads to a difficulty in granulation.

The new process of urea−superphosphate compound fertilizer, developed by France in 1992,[1] is a process where phosphoric ores react with urea−sulfuric acid solution directly and thus produce compound fertilizer in one step. It eliminates some defects of the traditional process, shortens the long curing period, and decreases fluorine pollution. The new process has been paid much attention,[2,3] but there has not been an industrial set achieved in China.

The key technology of the new process is the utilization of urea−sulfuric acid solution. Urea−sulfuric acid refers to the complex that is formed by 1 mol of sulfuric acid with a few moles of urea; its major constitution depends on the mole ratio of urea to sulfuric acid, which can be adjusted to meet the needs of production. Viscosity and enthalpy of the urea−sulfuric acid solution are very important to the process design and industrial practice, although studies in this aspect are seldom developed.[2,3,5] Hence, our experiments were performed to provide some basic data for further study on this process.

2. Experimental Section

2.1. Materials and Method. Urea (AR grade, 99% in purity), fuming sulfuric acid (SO_3 content was (20 to 23)%), and distilled water were used. The viscosity of urea−sulfuric acid solutions was determined by a rotary viscometer (model ADT-79, manufactured by Tongji, China). The uncertainty of the viscometer was ±0.1 mPa·s. The temperature was controlled by a precise temperature control water bath; the temperature uncertainty was ±0.5 K. The viscometer was calibrated by water before the determination. When the mole ratios of urea to sulfuric acid are 1.3:1 and 3.6:1, two eutectics are formed.[1] Both eutectics have a melting point of about 10 °C. According to the process demand, the ratio of urea to sulfuric acid might be as high as up to 4:1. So the ratios varied from 1.3:1 to 4.0:1 in the experiment, that is, 1.3:1, 1.8:1, 2.5:1, 3.0:1, 3.6:1, and 4.0:1. The corresponding urea mole fractions are 0.565, 0.643, 0.714, 0.750, 0.783, and 0.800, respectively. The urea−sulfuric acid solutions were prepared by weighing the urea; the uncertainty of mass was ±0.0001 g. The sulfuric acid and water were measured by volume, with an accuracy of ±0.05 mL. There are different crystallization temperatures for different urea−sulfuric acid solutions. The available temperature ranged from above their crystallization temperature to 85 °C. The crystallization points of the selected solutions were measured by decreasing the temperature and observing the crystallizing process. The results were shown in Table 1 at the accuracy of 0.5 °C. The addition of water makes the urea−sulfuric acid solution more steady and the crystallization points lower. To keep the water content less than 5% in the product to meet the national standard of compound fertilizers, the mole ratio of water to sulfuric acid should be about 1:1.

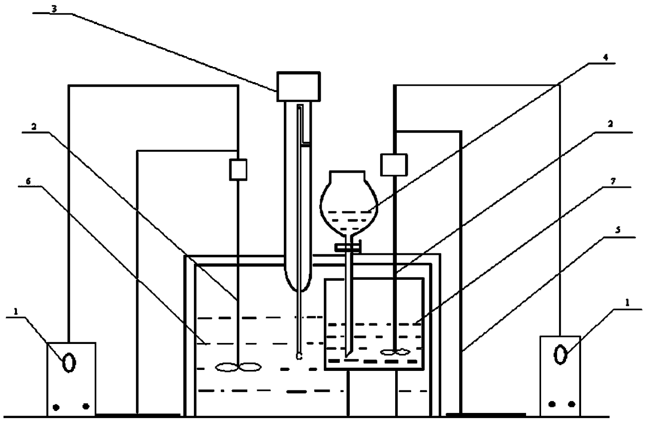

Figure 1. Apparatus for determining the enthalpy of urea + sulfuric acid solutions: 1, speed regulator; 2, agitator; 3, Beckmann thermometer; 4, separatory funnel; 5, adiabatic apparatus; 6, 1500 mL of water; 7, urea + sulfuric acid solution.

Table 1. Crystallization Temperature *t*/°C of the Urea + Sulfuric Acid Solutions at Different Urea Mole Fractions, x_1

	x_1					
	0.565	0.643	0.714	0.750	0.783	0.800
t/°C	<0	50	28	14	13.9	<0

2.2. Enthalpy Measurement. Enthalpy of solution was measured by the modified oxygen bomb calorimeter ap-

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* To whom correspondence should be addressed. E-mail: hch92@sina.com. Fax: 0086-371-3886796.

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Table 2. Viscosity, η/(mPa·s), of Urea + Sulfuric Acid Solutions at Different Mole Fractions of Urea, x_1, at Different Temperatures t/°C

	η/mPa·s at the following x_1					
t/°C	0.565	0.643	0.714	0.750	0.783	0.800
18					7500	
19					7050	840
20					6550	870
21					6100	810
22	2600				5600	750
23	2400				4950	685
24	2250				4300	620
25	2150				4000	560
26	2000				3580	475
27	1800				3150	458
28	1650				2850	412
29	1500		635		2480	350
30	1350		530		2150	320
32	1200		500		1900	290
33	1050		470		1700	260
34	1000		435		1500	240
35	900		410		1300	212
36	850		380		1200	195
37	535		360		1050	172
38	490		340	7000	950	168
39	460		310	6000	850	152
40	425		290	4900	780	142
41	390		265	4450	680	130
42	350		245	3700	620	122
43	330		225	3150	580	115
44	305		200	2600	500	105
45	282		190	2000	450	95
46	260		170	1700	410	85
47	245		155	1500	400	70
48	225		135	1250	350	65.5
49	215		130	1100	310	62.5
50	205		130	800	238	59.5
51	195		122		218	56.5
52	180		120	325	205	54
54	160		110	290	190	52
55	152		102	248	180	49.5
56	145		92	205	150	47
57	135		90	195	138	45
58	132		85	175	130	42.5
59	128		60.5	170	120	40.5
60	122		57.5	148	110	39
61	115	4100	55.5	135	110	37.5
62	110	3350	53	128	100	36
63	105	2800	50.5	122	73.5	34.8
64	100	2280	47.5	115	57	33
65	95	1920	44	95	52	31.8
66	90	1400	42.2	90	50	31
67	69	1100	40.5	85.5	48	29.8
68	67.8	1080	39.5	81	46	28
69	64.5	900	37.5	78.5	44.5	26.8
70	61.2	720	36	76	44.2	25.2
71	60	550	35	75	45.2	24
72	58	122	34	74.8	50	23
73	56	130	32.5	77	61	23
74	54	84.8	31	81.5	65.5	23.5
75	52.2	81.2	29	93	78	23.5
76	50.2	78	29		70	26
77	49	74.8	30		65	27
78	47.5	69.8	34		62	23.5
79	46	69	40	85	58	21
80	44.5	67.2	36	79.5	7500	20
81	42.8	66.2	33	72.5	7050	19.8
82	41.2	67	635	70	6550	19
83	40	67.5	530	63.5	6100	18.5
84	38.2	4100	500	62	5600	840
85	37	3350	470	55.5	4950	870

Table 3. Viscosity, η/(mPa·s), of Urea + Sulfuric Acid + Water Solutions (Mole Fraction of Urea, x_1; of Sulfuric Acid, x_2) at Different Temperatures t/°C

	η/mPa·s at the following x_1 and x_2					
t/°C	x_1=0.394/ x_2=0.303	x_1=0.474/ x_2=0.263	x_1=0.556/ x_2=0.222	x_1=0.600/ x_2=0.200	x_1=0.643/ x_2=0.179	x_1=0.667/ x_2=0.167
16					850	
17				695	780	
18			775	630	710	
19	240		770	555	642	
20	220		720	530	595	
21	215		665	490	535	300
22	200		615	440	480	290
23	190		555	400	445	270
24	178		520	370	410	260
25	168		480	332	370	240
26	155		440	310	340	220
27	142	300	405	270	310	215
28	138	295	370	260	268	205
29	130	280	320	240	242	195
30	125	255	305	220	220	180
32	120	250	285	205	202	170
33	110	230	265	190	198	165
34	105	215	245	180	182	158
35	100	200	225	168	168	150
36	95	188	202	152	155	145
37	86.2	178	195	142	145	138
38	81.2	165	180	132	132	130
39	76.2	152	170	125	125	125
40	72	145	160	118	120	120
41	69	135	148	110	110	118
42	65.5	130	138	102	105	115
43	62.2	120	128	100	100	110
44	59.5	110	120	92	92	110
45	57	105	115	91	71	105
46	54.5	100	110	90	68.9	100
47	52	98	105	79.5	66	98
48	50	84	98	73.8	63	95
49	48	78.8	90	70.5	59.5	
50	46	73.8	75	66	56	38
51	44	70	73	61	54	38.2
52	42	67.5	69.5	56	51.5	38
54	40.5	64.5	66	54	49.5	37.5
55	39	62.2	63	52	45.5	36.5
56	37.5	59	59.5	49	43	35.5
57	36.2	57	57	47	41.8	31.2
58	35	54	55	44	40	31
59	33.5	52	52	42	38.2	28
60	32.5	50	49.5	41	36.5	27
61	31.5	47.5	47.2	39.5	35	24.2
62	30.5	45.2	45	38	33.8	24
63	29.5	42.2	43	36	32.5	25
64	28	41.8	41	34.8	31.2	23
65	27	40	39	33	30	23
66	26.2	38	37.8	32	29	22
67	25.5	36.8	36	31	27.5	21.5
68	25	35	34.8	29.8	26.5	20
69	24	33.8	33.5	28.2	25.5	18.5
70	23.2	32.5	32.2	27.5	24.5	17
71	22.5	31	30.5	26	24	16.5
72	21.8	30	29.8	25.5	22.8	16.8
73	21	29	27.5	25	22	16
74	20.5	28	27.2	24.5	21.2	
75	20	27	26	24	20.8	
76	19.5	26	25.2	24	20.2	
77	19	25	24.5	24.5	20	
78	17.8	24.2	23.5	25	20	
79	17	23.5	22.5	22	20.5	
80	16.8	22.8	22	21	20	
81	16.2	22	22	20.5	20	
82	16	21.2	21.5	20	18.5	
83	15	20.5	22.2	18	18	
84	15	20	25	19	17.8	
85	14.5	19.5	21.2			

paratus, as shown in Figure 1. Distilled water (1500 mL) was contained in an adiabatic system, where an agitator was set to keep the water temperature uniform and the accurate temperature can be read by a Beckmann thermometer. A stainless steel calorimeter was fixed in the water in which the preparation of urea−sulfuric acid solutions was performed under agitating; sulfuric acid was added through a separating funnel. The apparatus was close to adiabatic; enthalpy loss was measured by water at 323 K, and the temperature decrement rate was 0.01 K/min.

The measurement of enthalpy of solution was based on the following considerations.

$$Q_{\mathrm{solute}}/\mathrm{kJ} = Q_{\mathrm{water}}/\mathrm{kJ} + Q_{\mathrm{calorimeter}}/\mathrm{kJ} \tag{1}$$

$$Q_{\mathrm{water}}/\mathrm{kJ} = C_{\mathrm{water}}/(\mathrm{kJ{\cdot}g^{-1}{\cdot}K^{-1}}) \times M_{\mathrm{water}}/\mathrm{g} \times \Delta t/\mathrm{K} \tag{2}$$

$$Q_{\mathrm{calorimeter}}/\mathrm{kJ} = \lambda/(\mathrm{kJ{\cdot}min^{-1}}) \times \Delta\Theta/\mathrm{min} \tag{3}$$

where Q_{solute} is the enthalpy of solution; Q_{water} is the

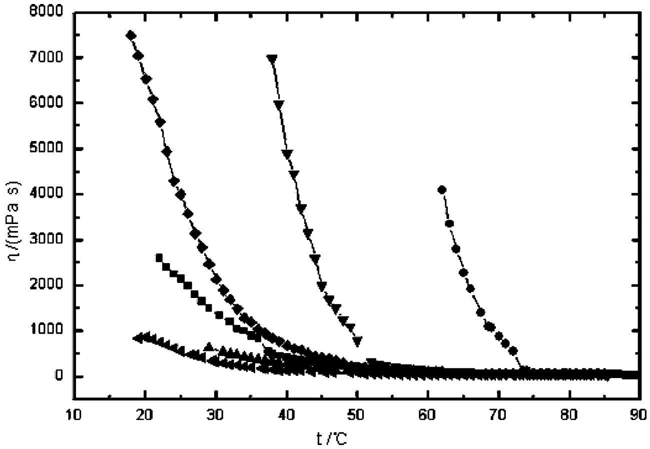

Figure 2. Viscosity, η, of urea + sulfuric acid solutions at different mole fractions of urea, x_1, at different temperatures t: ■, $x_1 = 0.565$; ●, $x_1 = 0.643$; ▲, $x_1 = 0.714$; ▼, $x_1 = 0.750$; ◆, $x_1 = 0.783$: triangle solid left, $x_1 = 0.800$.

enthalpy absorbed by mass water, C_{water} is the specific heat of water, M_{water} is the mass of the water, Δt is the water temperature increment; $Q_{calorimeter}$ is the enthalpy absorbed by the calorimeter, λ is the enthalpy absorption rate of the calorimeter, $\Delta\Theta$ is the time elapsed.

When urea and sulfuric acid solutions were mixed in the calorimeter, most of the released enthalpy was conducted to the outer mass water (Q_{water}), resulting in the increment of water temperature through the excellent heat conductive calorimeter except that a small part of it was absorbed by calorimeter itself. Therefore, the enthalpy absorbed by the calorimeter ($Q_{calorimeter}$) should be first calculated by measuring the known integral enthalpy of the solution of sulfuric acid; the other part absorbed by the mass water outside the calorimeter could also be calculated when the water temperature increment was measured. So the enthalpy of solution (Q_{solute}) could be achieved.

2.2.1. Enthalpy Absorbed by Calorimeter. In this experiment, 70 mL of distilled water was placed in the calorimeter first, and then 10 mL of 92% sulfuric acid was fed into the calorimeter, when the time was recorded as 0. Then the temperature of the water outside the calorimeter increased quickly. When the temperature reached the maximum, the time was recorded. Such operation was repeated three times, and the average was adopted for calculation. After calibrating, the maximum temperature increment was 1.470 K within 7.0 min. Ten milliliters of 92% sulfuric acid (density, $\rho = 1.8188$ g/mL; integral enthalpy of 148.81 J/g H_2SO_4)[4] mixed with 70 mL of distilled water formed a 20.6% dilute sulfuric acid (integral enthalpy of 729.66 J/g H_2SO_4) solution.[4] Therefore, the dilution heat of sulfuric acid from 92% to 20.6% was 9.719 kJ. The enthalpy absorbed by the water outside the calorimeter was 9.217 kJ (calculated according to formula 2). Then, the enthalpy absorbed by the calorimeter was 0.502 kJ. The enthalpy absorption rate of the calorimeter was determined as $\lambda = 0.0717$ kJ/min.

2.2.2. Enthalpy of Solution. The temperature range of the Beckmann thermometer was adjusted to (44 to 49) °C, and the temperature of mass water outside the calorimeter was kept at 46 °C. A known mass of urea was first placed in the calorimeter; then sulfuric acid was added into the calorimeter quickly, and the time was recorded. The maximum temperature increment (Δt/°C) was read on the Beckmann thermometer, and the time elapsed ($\Delta\ \Theta$/min) was recorded. The operation was repeated three times. The enthalpy of solution was calculated according to formulas 1, 2, and 3.

2.3. Test of the Apparatus. To ensure proper operation of the apparatus, the enthalpy of a urea + sulfuric acid solution was measured and compared with one of the reported values in the literature.[5] The experimental measurements agreed with the reported values with a mean relative deviation of 4.1%. The measured values are listed in Table 7.

3. Results and Discussion

The experiment was done with the chosen ratio of urea + sulfuric acid, determining the viscosity with the rotary viscometer. Results are given in Table 2 and Table 3. Accordingly, the viscosity−temperature relationship is shown in Figure 2 and Figure 3, respectively.

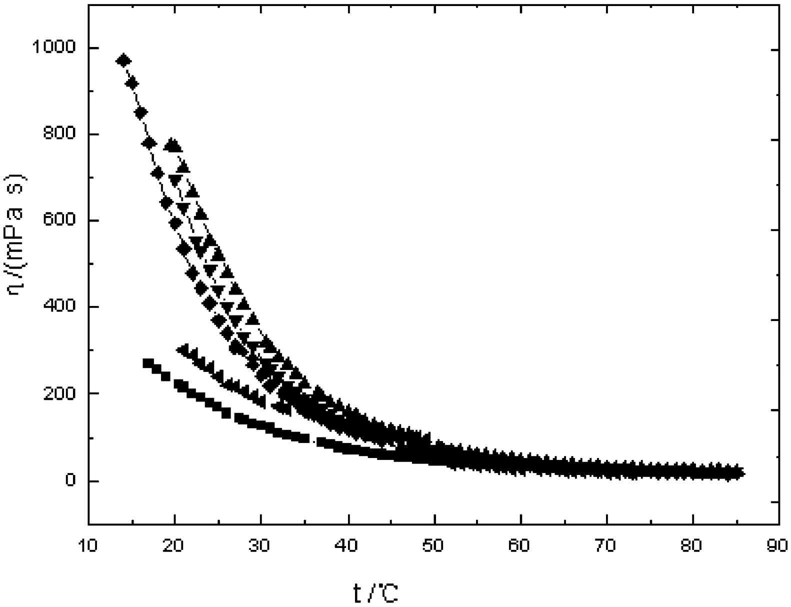

Figure 3. Viscosity, η, of urea + sulfuric acid + water solutions (mole fraction of urea, x_1; of sulfuric acid, x_2) at different temperatures t: ■, $x_1 = 0.394$, $x_2 = 0.303$; ●, $x_1 = 0.474$, $x_2 = 0.263$; ▲, $x_1 = 0.566$, $x_2 = 0.222$; ▼, $x_1 = 0.600$, $x_2 = 0.200$; ◆, $x_1 = 0.643$, $x_2 = 0.179$; triangle solid left, $x_1 = 0.667$, $x_2 = 0.167$.

Table 4. Viscosity, η/(mPa·s), of Sulfuric Acids Normally Used in Superphosphate Production at Different Temperatures t/°C

	η/mPa·s at the following t/°C								
	0	10	20	25	32	45	60	80	100
65% H_2SO_4	14	10	7.6	6.5	5.6	4.4	3.2	2.4	1.9
93% H_2SO_4	49.0	36.0	23.2	20.5	16.0	11.8	8.0	5.3	3.6
98% H_2SO_4	51.0	37.0	24.4	21.8	16.7	12.5	8.7	5.5	3.8
120% H_2SO_4			34.0	29.8	21.5	15.4	10.4	6.6	4.6

Table 5. Indices of Viscosity−Temperature Correlation of $CO(NH_2)_2 + H_2SO_4$ Solution at Different Mole Fractions of Urea, x_1

	x_1					
	0.565	0.643	0.714	0.750	0.783	0.800
η_0	0	0	0	0	0	0
A_1	21721.36	1.67×10^9	6651.16	3.58058×10^6	245109.89	5922.28
B_1	10.61	4.81	10.74	6.40	5.26	10.23
A_2	23.74	0	72.81	0	3122.64	20.29
B_2	21455.52	0	22.11	8.80	20.66	2207.53
R^2	0.99283	0.99201	0.9969	0.99691	0.99823	0.99387

Table 6. Indices of Viscosity−Temperature Correlation of $CO(NH_2)_2 + H_2SO_4 + H_2O$ Solution

	x_1=0.394/ x_2=0.303	x_1=0.474/ x_2=0.263	x_1=0.556/ x_2=0.222	x_1=0.660/ x_2=0.200	x_1=0.643/ x_2=0.179	x_1=0.667/ x_2=0.167
η_0	−64.71	−156.09	0	0	0	0
A_1	799.55	1980.22	4035.89	5072.16	3569.32	1361.42
B_1	14.07	14.31	11.88	9.12	10.58	11.84
A_2	105.50	171.88	19.47	247.52	60.40	1470.81
B_2	271.12	7979.21	0	31.74	67.07	18.77
R^2	0.99982	0.99856	0.99925	0.99976	0.9994	0.99655

In superphosphate production, the sulfuric acid concentration is normally 65% (mass) (dilute acid process) or 93% and 98% (concentrated acid process). The viscosity is listed in Table 4,[4] together with that of the fuming sulfuric acid. As we can see, the viscosity of $CO(NH_2)_2 + H_2SO_4$ and $CO(NH_2)_2 + H_2SO_4 + H_2O$ solutions is much more than that of Table 4.

On the basis of the experimental data, a correlation of viscosity to temperature at different mole ratios of urea sulfuric acid solution is fitted as a second-order exponential decay equation:

$$\eta = \eta_0 + A_1 \exp(-(t - t_0)/B_1) + A_2 \exp(-(t - t_0)/B_2) \quad (4)$$

where η is viscosity and t_0 is the initial temperature measured. η_0, B_1, B_2, A_1, and A_2 are correlation parameters, which varied with the solution ratio (see Table 5 and Table 6). The correlation conformed to the experimental data well; the linear correlation coefficient R^2 is more than 0.99 (see Table 5 and Table 6).

In the correlation (eq 4), A_1 is the prominent index affecting the viscosity, which indicates the slope of the curve. When A_1 is greater, the viscosity changes greatly with the temperature. From Table 2 and Figure 2, we can see that when x_1 (mole fraction of urea) is 0.643, 0.750, or 0.783, the slope of the curve is much greater than that of $x_1 = 0.800$ or $x_1 = 0.714$. Comparing Figure 2 and Figure 3, we also find that when water is added in the mixture, the viscosity of the solution becomes lower than that of the urea−sulfuric acid solution.

In general, at the same temperature, the viscosity of the solution is increased with the increment of its concentration, and sulfuric acid−water solution showed the same. But the $CO(NH_2)_2 + H_2SO_4$ and $CO(NH_2)_2 + H_2SO_4 + H_2O$ solutions do not conform to this rule.

The viscosity of urea−sulfuric acid solutions does not increase with the increment of urea fraction monotonically. This is because the urea−sulfuric acid complexes that formed in different ratios of urea−sulfuric acid solution do not exist as a definite constitution. The following complexes may occur in the urea sulfuric acid solution: $H_2SO_4 \cdot CO(NH_2)_2$, $H_2SO_4 \cdot 2CO(NH_2)_2$, and $H_2SO_4 \cdot 4CO(NH_2)_2$.

With the increment of temperature, the viscosity of $CO(NH_2)_2 + H_2SO_4$ and $CO(NH_2)_2 + H_2SO_4 + H_2O$ solutions decreases greatly.

The enthalpy of solution in the preparation of urea−sulfuric acid solution is shown in Table 7. As to the same volume of sulfuric acid, the enthalpy of solution changed with the mole fraction of urea in the mixture of urea and sulfuric acid, but the enthalpy did not increased uniformly with the increment of urea mole fractions. For example, from Table 7 we can see that when the mole fraction of urea $x_1 = 0.50$, that is, $CO(NH_2)_2/H_2SO_4$ = 1:1 (mol), the enthalpy of solution is 51.92 kJ/mol urea; when $x_1 = 0.667$, that is, $CO(NH_2)_2/H_2SO_4$ = 2:1 (mol), the enthalpy of solution is 70.03 kJ/mol H_2SO_4, which is equal to 34.38 kJ/mol urea. Therefore, when the mixture of urea + sulfuric acid solution is prepared, the first 1 mol urea creates the maximum enthalpy; when the second 1 mol urea is fed, the enthalpy increases slowly; when more urea is fed, no more enthalpy occurs.

4. Conclusions

(1) The viscosity of $CO(NH_2)_2 + H_2SO_4$ and $CO(NH_2)_2 + H_2SO_4 + H_2O$ solution systems is much greater than that of the acid normally used in superphosphate production.

(2) With the increment of temperature, the viscosity of $CO(NH_2)_2 + H_2SO_4$ and $CO(NH_2)_2 + H_2SO_4 + H_2O$ solutions decreases greatly. The equation correlation of viscosity to temperature at different mole ratios of urea−sulfuric acid solution can be fitted as the following equation.

$$\eta = \eta_0 + A_1 \exp(-(t - t_0)/B_1) + A_2 \exp(-(t - t_0)/B_2)$$

(3) In general, at the same temperature, the viscosity of the solution should increase with the increment of solution

Table 7. Enthalpy of Solution in the Preparation of $CO(NH_2)_2 + H_2SO_4$ Solutions

urea mole fraction x_1	time elapsed $\Delta\Theta$/min	calibration temperature increment Δt/°C	Q_{water}/kJ	$Q_{calorimeter}$/kJ	Q_{solute}/kJ	Q_{solute}/(kJ/mol H_2SO_4)	Q_{solute}/(kJ/mol urea)	Q_{solute}/(kJ/kg urea−H_2SO_4 solution)
0.500	6.0	1.340	8.402	0.430	8.832	51.92	51.92	296.79
0.600	10.5	1.640	10.283	0.752	11.035	64.65	31.76	310.43
0.667	11.5	1.775	11.129	0.824	11.953	70.03	34.38	289.15
0.714	11.0	1.583	9.925	0.788	10.714	62.76	24.52	227.39, 218.26[a]
0.750	10.5	1.500	9.186	0.752	9.938	58.22	18.91	187.91
0.778	11.0	1.415	8.872	0.788	9.660	56.59	15.66	164.60
0.800	13.5	1.265	7.932	0.967	8.899	52.13	12.25	137.99

[a] Luo-ting Yu (ref 5).

concentration, and the sulfuric acid−water solution did the same. But the $CO(NH_2)_2 + H_2SO_4$ and $CO(NH_2)_2 + H_2SO_4 + H_2O$ solutions do not conform to the above rule.

(4) When water is added in the $CO(NH_2)_2 + H_2SO_4$ mixture, the viscosity of $CO(NH_2)_2 + H_2SO_4 + H_2O$ can be greatly lowered.

(5) The enthalpy of solution changed with the mole fraction of urea in the mixture of urea and sulfuric acid solutions, but the enthalpy of solution is not increased uniformly with the urea feeding. The enthalpy of solution was maximum when the first 1 mol urea was added in sulfuric acid, where the urea mole fraction $x_1 = 0.5$; then, with the feeding of urea, the increment of enthalpy of solution was slower.

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