

Interaction of Sulfur Dioxide with Aqueous Solutions of Amides

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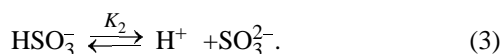
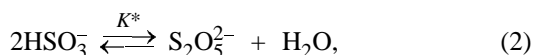
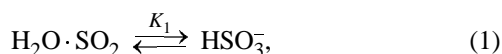
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Abstract—The interactions in the systems H_2O –Am– SO_2 (Am is formamide, dimethylformamide, acetamide, urea, tetramethylurea, *tert*-butylurea) at 278 and 293 K were studied pH-metrically. The results suggest formation of intermolecular and ion–molecule associates. The composition and stability of the compounds formed strongly depend on the structure and concentration of the solution components and on temperature.

The possible reactions of SO_2 with compounds of various classes are very diverse, and studies of the behavior of SO_2 in aqueous solutions are of not only theoretical but also practical importance [1].

It is known that sulfur dioxide forms a hydrate (“sulfurous acid”) in aqueous solutions. However, actually, according to the experimental data, this is an associate $\text{H}_2\text{O} \cdot \text{SO}_2$ rather than a covalent compound H_2SO_3 . According to [2], sulfur dioxide hydrate undergoes further transformations:



Sulfur dioxide reacts with amines in water to form ionic and covalent adducts [3]. Sulfite compounds react with carbonyl derivatives. The reactions of sulfurous compounds with ketones and aldehydes in aqueous solutions were studied in [4, 5].

Amides as Lewis bases occupy a particular place in coordination chemistry. Their molecules have two electron-donor centers: carbonyl oxygen and amine nitrogen atoms. The available experimental and theoretical data indicate that both protonation of amides and their coordination with metal ions mainly occur via O atom [6–8]. However, according to the NMR and UV data, the proton in dilute aqueous solutions of acids can also add to the nitrogen atom of amides [9, 10]. The coordination mode depends on various factors [11].

It should be noted that the interaction of amides

with SO_2 was studied only in a few papers. Our previous potentiometric study of the interaction of SO_2 with aqueous (0.1, 0.25, and 0.5 M) solutions of urea in the temperature range 273–313 K [12–15] revealed formation of the compounds $h\text{H}_2\text{O} \cdot m\text{CO}(\text{NH}_2)_2 \cdot n\text{SO}_2$ with the molar ratios $m : n = 4 : 1, 2 : 1, 3 : 2, 1 : 1, 4 : 5$, and $1 : 2$. According to [12], the temperature affects not only the stability of SO_2 –urea associates in water but also the nature of bonding in the associates. Okhotnikova *et al.* [16] studied the system H_2O – $\text{CO}(\text{NH}_2)_2$ – SO_2 conductometrically in the range 298–353 K. Data on interactions of SO_2 with other amides are lacking.

The goal of this study was to analyze potentiometrically the interaction of SO_2 with aqueous solutions of amides and to determine the component composition of these systems.

To this end, we studied absorption of SO_2 with aqueous solutions of formamide, dimethylformamide, acetamide, tetramethylurea, and *tert*-butylurea and compared the results with the available data on the interaction of SO_2 with aqueous urea solutions at 278 and 293 K.

From the results of potentiometric studies of the interaction of aqueous amide solutions with SO_2 , we plotted the integral (Fig. 1) and differential (Fig. 2) titration curves. The integral pH-metric curves contained several plateaus (Fig. 1), and the differential curves, more than two extrema (Fig. 2), suggesting formation of different compounds by amides and SO_2 in water (Table 1). In most cases, the extrema in the differential curves are observed at $Q_{\text{Am}} : Q_{\text{SO}_2} = 2 : 1$ and $1 : 1$ (Q_{Am} is the total content of the amide in solution, equal to 0.1 M). This fact suggests formation of the compounds $2\text{Am} \cdot \text{SO}_2 \cdot n\text{H}_2\text{O}$ (I) and $\text{Am} \cdot \text{SO}_2 \cdot m\text{H}_2\text{O}$ (II) (where Am is formamide, dimethylformamide, acetamide, urea, tetramethylurea, *tert*-butyl-

[†] Deceased.

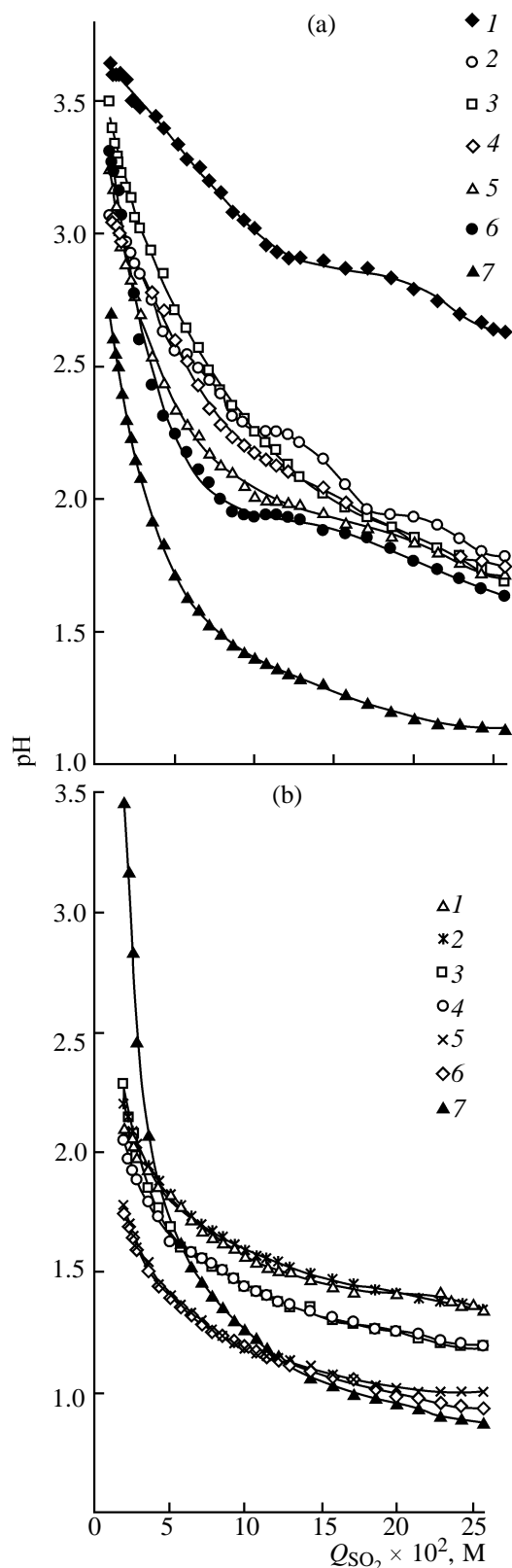


Fig. 1. pH of (1–6) 0.10 M solutions of amides and (7) water as a function of the amount of SO_2 taken up (Q_{SO_2} , M) at (a) 278 and (b) 293 K. Amide: (1) urea [12], (2) tetramethylurea, (3) formamide, (4) acetamide, (5) *tert*-butylurea, and (6) dimethylformamide.

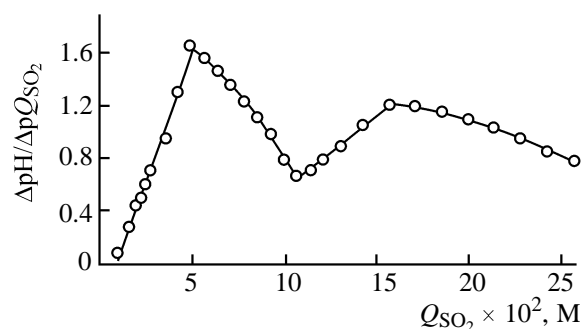
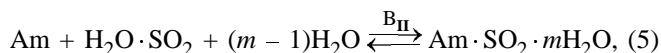
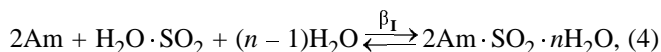


Fig. 2. Differential curve of titration of a 0.10 M acetamide solution with gaseous SO_2 at 278 K.

urea) at 278 K (other ratios were not taken into account further).

Since the pH values at 278 K of aqueous solutions containing SO_2 and amides are higher than those of the amide-free solutions with the same SO_2 content (Fig. 1a), the following reactions can be assumed in these systems:



Also, dissociation of **I** and **II** into counterions (uronium cations and hydrosulfite and pyrosulfite anions) is possible.

As for the interaction of SO_2 with aqueous solutions of amides at 293 K, here we could expect a similar course of the pH-metric titration curves. Indeed, in the differential curves we observed extrema at $Q_{\text{Am}} : Q_{\text{SO}_2} = 2 : 1$ and $1 : 1$ (Table 1). However, at 293 K the pH values of aqueous solutions containing amides and SO_2 are lower compared to the amide-free solutions with the same SO_2 content (Fig. 1b). Such a relationship is characteristic of all the systems studied at $Q_{\text{SO}_2} \leq 0.05 \text{ M}$ and of solutions of acetamide and *tert*-butylurea at $Q_{\text{SO}_2} \leq 0.1 \text{ M}$.

We believe that such a change in the pH is caused by the shift of the equilibrium of reaction (1) to the right on adding amides to aqueous solutions of SO_2 . This shift, in turn, is due to easier association of the amide molecules with hydrosulfite or pyrosulfite ions than with the neutral SO_2 molecules. This results in predominant formation of anionic ion–molecule associates $2\text{Am} \cdot \text{HSO}_3^-$ (**III**) or $4\text{Am} \cdot \text{S}_2\text{O}_5^{2-}$ (**IV**) (Am = formamide, dimethylformamide, acetamide, urea, tetramethylurea, *tert*-butylurea), and $\text{Am} \cdot \text{HSO}_3^-$ (**V**) or

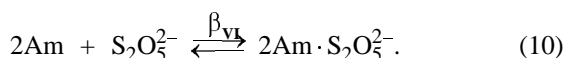
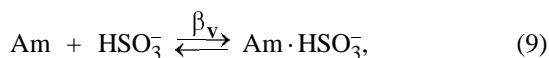
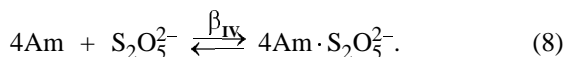
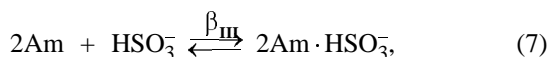
Table 1. Composition of compounds in the systems $\text{H}_2\text{O}-\text{Am}-\text{SO}_2$

Amide	Composition of complex, $Q_{\text{Am}} : Q_{\text{SO}_2}$	
	278 K	293 K
Formamide	2:1, 1:1, 4:5, 2:3, 1:2	2:1, 8:5, 8:7, 1:1, 2:3, 1:2
Dimethylformamide	4:1, 2:1, 4:3, 1:1, 2:3, 4:7, 1:2	2:1, 1:1, 2:3, 1:2, 4:9
Acetamide	2:1, 1:1, 2:3	4:1, 2:1, 4:3, 1:1, 4:5, 4:7, 1:2
Urea	2:1, 4:3, 1:1, 4:5, 2:3, 1:2	2:1, 4:3, 8:7, 1:1, 4:5, 2:3, 1:2
Tetramethylurea	4:1, 2:1, 1:1, 4:5, 2:3, 1:2	2:1, 4:3, 1:1, 4:5, 2:3, 1:2
<i>tert</i> -Butylurea	2:1, 1:1, 2:3, 1:2	2:1, 3:2, 1:1, 7:8, 1:2

Table 2. Values of parameters in Eq. (16)

$T, \text{ K}$	$Q_{\text{SO}_2}, \text{ M}$	Constant	A_0	$-A_1$	A_2	$-A_3$	R	n
278	0.01–0.20	K_1	3.86	35.46	311.24	829.28	0.990	28
		K^*	–2.25	25.74	191.87	440.69	0.985	28
293	0.02–0.20	K_1	4.86	62.71	465.57	1104.3	0.975	20
		K^*	–2.40	7.49	13.06	0	0.975	20

$2\text{Am} \cdot \text{S}_2\text{O}_5^{2-}$ (**VI**) (Am = acetamide, *tert*-butylurea). In the systems with formamide, dimethylformamide, urea, and tetramethylurea ($0.05 < Q_{\text{SO}_2} \leq 0.1 \text{ M}$, 293 K), the major species are compounds of type **II**:



It should be noted that, at 293 K, the pH values of aqueous formamide solutions virtually coincide with those of dimethylformamide solutions at $Q_{\text{SO}_2} > 0.05 \text{ M}$; the same is true for the urea and tetramethylurea solutions. This fact indicates that the replacement of the hydrogen atoms of the amino groups in urea and formamide by the methyl groups does not affect the nature of interactions in formation of associates of type **II** at 293 K.

It is known [17] that amides, especially formamide, can undergo acid-catalyzed hydrolysis with the formation of ammonium compounds. However, in all the cases the qualitative reactions for ammonium ions gave negative results.

After the supply of SO_2 was stopped, the pH values of the reaction systems did not change during the

period of 2 h and more. This fact indicates the establishment of an equilibrium in the systems. Thus, reactions (1)–(10) can be considered as equilibrium.

To determine the relative concentrations of sulfur compounds in an aqueous SO_2 solution, it is first necessary to determine K_1 and K^* , since equilibrium (3) at $\text{pH} < 4.5$ can be neglected.

We constructed a system of equations reflecting the law of mass action [Eqs. (11), (12)] and the conditions of material balance [Eq. (13)] and electroneutrality [Eq. (14)].

$$K_1 = [\text{H}^+][\text{HSO}_3^-]/[\text{H}_2\text{O} \cdot \text{SO}_2], \quad (11)$$

$$K^* = [\text{S}_2\text{O}_5^{2-}]/[\text{HSO}_3^-]^2, \quad (12)$$

$$Q_{\text{SO}_2} = [\text{H}_2\text{O} \cdot \text{SO}_2] + 2[\text{S}_2\text{O}_5^{2-}] + [\text{HSO}_3^-], \quad (13)$$

$$[\text{H}^+] = 2[\text{S}_2\text{O}_5^{2-}] + [\text{HSO}_3^-]. \quad (14)$$

The concentration constants K_1 and K^* were calculated by solving the system of Eqs. (11)–(14) using the pseudo-gradient method (for details, see [18, 19]). According to our results, the concentration dependence of $\text{p}K_1$ and $\text{p}K^*$ can be described by Eq. (15) with the parameters given in Table 2.

$$\text{p}K_i = A_0 + A_1 Q_{\text{SO}_2} + A_2 Q_{\text{SO}_2}^2 + A_3 Q_{\text{SO}_2}^3. \quad (15)$$

From these data, we constructed the diagrams of the component composition of aqueous solutions of SO_2 at 278 and 293 K (Fig. 3).

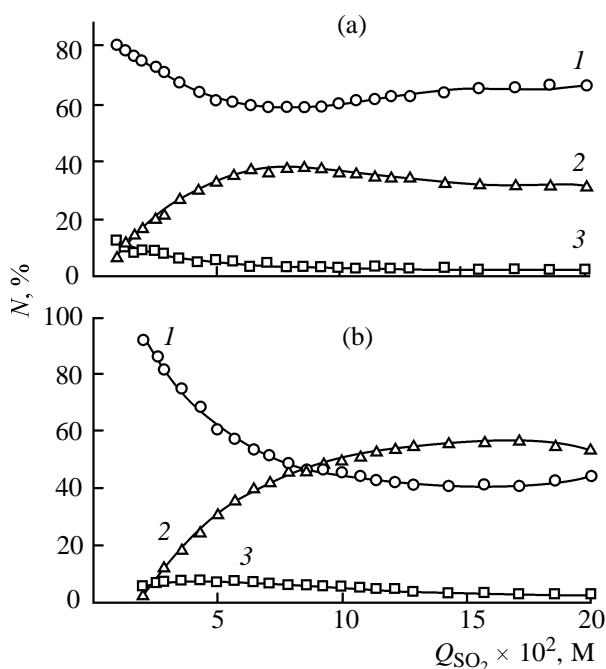


Fig. 3. Composition of aqueous SO_2 solutions as a function of Q_{SO_2} at (a) 278 and (b) 293 K. (N) Mole fraction of (1) $\text{H}_2\text{O} \cdot \text{SO}_2$, (2) HSO_3^- , and (3) $\text{S}_2\text{O}_5^{2-}$ (relative to the total SO_2 content in the system).

$$N_{\text{H}_2\text{O} \cdot \text{SO}_2} = [\text{H}_2\text{O} \cdot \text{SO}_2] / Q_{\text{SO}_2}, \quad (16)$$

$$N_{\text{HSO}_3^-} = [\text{HSO}_3^-] / Q_{\text{SO}_2}, \quad (17)$$

$$N_{\text{S}_2\text{O}_5^{2-}} = 2[\text{S}_2\text{O}_5^{2-}] / Q_{\text{SO}_2}. \quad (18)$$

Figure 3a shows that the mole fraction of sulfur dioxide hydrate (curve 1) in the system $\text{SO}_2\text{--H}_2\text{O}$ at 278 K first decreases from ~80 to ~58%, reaches a minimum at Q_{SO_2} 0.078 M, and then increases to ~66% (at Q_{SO_2} 0.2 M). The mole fraction of pyrosulfite ions (curve 2) as a function of the total content of SO_2 in the system, on the contrary, first increases from ~7 to ~38%, reaches a maximum at Q_{SO_2} 0.078 M, and then decreases to ~32% (at Q_{SO_2} 0.2 M). The mole fraction of hydrosulfite ions (curve 3) decreases from ~12 to ~2% with an increase in Q_{SO_2} in the examined range.

As seen from Fig. 3b, in the $\text{SO}_2\text{--H}_2\text{O}$ system at 293 K, $N_{\text{HSO}_3^-} < N_{\text{S}_2\text{O}_5^{2-}} < N_{\text{H}_2\text{O} \cdot \text{SO}_2}$ at $0.025 \leq Q_{\text{SO}_2} \leq 0.085$ M and $N_{\text{HSO}_3^-} < N_{\text{H}_2\text{O} \cdot \text{SO}_2} < N_{\text{S}_2\text{O}_5^{2-}}$ at $0.085 \leq Q_{\text{SO}_2} \leq 0.2$ M. The content of hydrosulfite ions is 2–7% in the entire concentration range studied. However, at 293 K, the above method allows determination of the component composition of the equilibrium $\text{SO}_2\text{--H}_2\text{O}$ mixture and of the concentration constants K_1 and K^* only at $Q_{\text{SO}_2} \geq 0.02$ M. This is apparently

due to the fact that, at $Q_{\text{SO}_2} < 0.02$ M, the relative content of pyrosulfite ions is negligible.

Taking into account Eqs. (11), (12), (19), and (20) reflecting the law of mass action and Eqs. (21)–(23) reflecting the conditions of material balance and electroneutrality, we calculated the apparent association constants β_{I} at 278 K ($0.01 \leq Q_{\text{SO}_2} \leq 0.05$ M):

$$\beta_{\text{I}} = [\text{I}] / ([\text{Am}]_2 [\text{H}_2\text{O} \cdot \text{SO}_2]), \quad (19)$$

$$K_a = [\text{Am}][\text{H}^+] / [\{\text{AmH}\}^+], \quad (20)$$

$$Q_{\text{SO}_2} = [\text{H}_2\text{O} \cdot \text{SO}_2] + 2[\text{S}_2\text{O}_5^{2-}] + [\text{HSO}_3^-] + [\text{I}], \quad (21)$$

$$Q_{\text{Am}} = [\text{Am}] + [\{\text{AmH}\}^+] + 2[\text{I}], \quad (22)$$

$$[\{\text{AmH}\}^+] + [\text{H}^+] = [\text{HSO}_3^-] + 2[\text{S}_2\text{O}_5^{2-}] + [\text{OH}^-], \quad (23)$$

where Q_{Am} is the total Am content in the system.

For the range $0.05 < Q_{\text{SO}_2} \leq 0.10$ M at 278 K (Fig. 1b), we took into account the simultaneous presence of **I** and **II**. To do this, we used a system of equations based on the law of mass action [Eqs. (11), (12), (19), (20), (24)] and the conditions of material balance [Eqs. (25), (26)] and electroneutrality [Eq. (23)]:

$$\beta_{\text{II}} = [\text{II}] / ([\text{Am}][\text{H}_2\text{O} \cdot \text{SO}_2]), \quad (24)$$

$$Q_{\text{SO}_2} = [\text{H}_2\text{O} \cdot \text{SO}_2] + 2[\text{S}_2\text{O}_5^{2-}] + [\text{HSO}_3^-] + [\text{I}] + [\text{II}], \quad (25)$$

$$Q_{\text{Am}} = [\text{Am}] + [\{\text{AmH}\}^+] + 2[\text{I}] + [\text{II}]. \quad (26)$$

As experimental determination of the concentrations of **III** and **IV** at 293 K $0.05 < Q_{\text{SO}_2} \leq 0.10$ M was impossible, it was difficult to determine β_{III} and β_{IV} . Therefore, we considered the apparent equilibrium constants:

$$\beta_{\text{III}} = \frac{[\text{III}] + 2[\text{IV}]}{[\text{Am}]^2 [\text{HSO}_3^-]}, \quad (27)$$

$$\beta_{\text{IV}} = \frac{[\text{III}] + 2[\text{IV}]}{[\text{Am}]^4 [\text{S}_2\text{O}_5^{2-}]}. \quad (28)$$

In this case, to calculate the equilibria, it is necessary to use a system of equations based on the law of mass action [Eqs. (11), (12), (20), (27), (28)] and the conditions of material balance and electroneutrality [Eqs. (29)–(31)].

$$Q_{\text{SO}_2} = [\text{H}_2\text{O} \cdot \text{SO}_2] + 2[\text{S}_2\text{O}_5^{2-}] + [\text{HSO}_3^-] + [\text{III}] + 1[\text{IV}], \quad (29)$$

$$Q_{\text{Am}} = [\text{Am}] + [\{\text{AmH}\}^+] + 2[\text{III}] + 4[\text{IV}], \quad (30)$$

$$[\{\text{AmH}\}^+] + [\text{H}^+] = [\text{HSO}_3^-] + 2[\text{S}_2\text{O}_5^{2-}] + [\text{OH}^-] + [\text{III}] + 2[\text{IV}]. \quad (31)$$

Using similar reasonings, we calculated the equilibria for the range $0.05 < Q_{\text{SO}_2} \leq 0.10$ M at 293 K.

In the calculations, we took pK_a for formamide, dimethylformamide, acetamide, urea, and tetramethylurea equal to -0.25 , -0.70 , 0.10 , 0.50 , and 0.40 , respectively [20, 21]. The influence of temperature on the protonation of the amides was taken into account according to [22].

From these data, we constructed the diagrams of the component composition of the systems. The diagram for acetamide is shown as example in Fig. 4. In all the systems studied, the mole fraction of $\{\text{AmH}\}^+$ does not exceed 0.1% of Q_{Am} , i.e., the protonation of amides [Eq. (7)] in these cases can be neglected. We found no published data on the protonation of *tert*-butylurea; in view of the above facts, the $\{\text{AmH}\}^+$ concentration in aqueous solutions of *tert*-butylurea was assumed to be zero.

Comparison of Figs. 3 and 4 shows that the component composition of aqueous SO_2 solutions largely depends on Q_{SO_2} and temperature, and also on the presence and structure of amides.

It should be noted that, in the vicinity of points in which the curves of pH-metric titration of aqueous solutions with sulfur dioxide in the presence of an amide intercept with the curves taken in the absence of amides, it is impossible to determine the component composition of the systems (discontinuities of the second kind arise) and association constants (at 293 K), because in this case (Fig. 4b) the differences between the pH values of the solutions in the presence and in the absence of amides, at the same SO_2 content, are comparable with the experimental error [18].

From the experimental data, following the above-described schemes, we calculated the apparent association constants $\beta_{\text{I}}-\beta_{\text{IV}}$. The concentration dependences of $p\beta_i$ ($-\log\beta_i$) can be described by Eq. (32) with the parameters given in Tables 3 and 4.

$$p\beta_i = A_i + B_i Q_{\text{SO}_2}. \quad (32)$$

Tables 3 and 4 show that the $p\beta_i$ values characterizing complexation processes (4), (5), and (7)–(10) are negative, suggesting spontaneous occurrence of these reactions.

According to the calculations, the dissociation of **I** and **II** into the counterions (as assumed above) is improbable, because the constants of these processes are less than unity (therefore, the equations of these reactions and their equilibrium constants are not given in this paper).

Table 3. Parameters of Eq. (32) for 278 K

Am	$-A_i$	$-B_i$	R	n
Q_{SO_2} 0.01–0.05 M, $i = \text{I}$				
Formamide	3.00	47.10	0.981	11
Dimethylformamide	3.22	12.16	0.957	11
Acetamide	2.05	64.90	0.998	11
Urea	2.91	84.43	0.982	11
Tetramethylurea	2.13	59.68	0.994	11
<i>tert</i> -Butylurea	2.64	31.31	0.983	11
Q_{SO_2} 0.01–0.05 M, $i = \text{II}$				
Formamide	2.07	19.73	0.980	8
Dimethylformamide	1.19	16.92	0.987	8
Acetamide	1.85	18.93	0.989	8
Urea	2.84	33.52	0.971	12
Tetramethylurea	1.69	21.70	0.977	8
<i>tert</i> -Butylurea	1.28	19.57	0.980	8

It should be noted that our model for calculating equilibria in the systems $\text{H}_2\text{O}-\text{Am}-\text{SO}_2$ (in contrast to the model suggested in [11]), in parallel with the possible association, takes into account the first step of dissociation of sulfurous acid and the dimerization

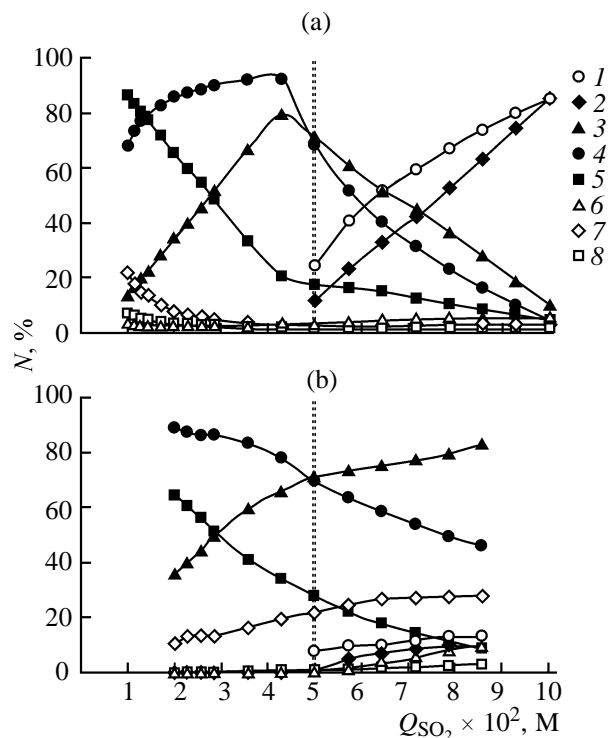


Fig. 4. Distribution of chemical species in the system $\text{CH}_3\text{CONH}_2-\text{SO}_2-\text{H}_2\text{O}$ as influenced by Q_{SO_2} at (I) 278 and (b) 293 K. (N) Mole fraction of species relative to the total content of (1–4, 6–8) S and (2, 3, 5) N. Species: (1, 2) **II**, (3, 4) (a) **I** and (b) **III**, (5) CH_3CONH_2 , (6) $\text{S}_2\text{O}_5^{2-}$, (7) $\text{H}_2\text{O} \cdot \text{SO}_2$, and (8) HSO_3^- .

Table 4. Parameters of Eq. (32) for 293 K

Complex <i>i</i>	Am	$-A_i$	$-B_i$	R	n
Q_{SO_2} 0.02–0.05 M					
III	Formamide	4.33	33.54	0.974	7
III	Dimethylformamide	4.26	21.46	0.974	7
III	Acetamide	5.57	12.63	0.964	7
III	Urea	4.40	44.68	0.985	9
III	Tetramethylurea	4.20	34.61	0.972	7
III	<i>tert</i> -Butylurea	5.59	12.59	0.984	7
IV	Formamide	8.71	94.68	0.992	7
IV	Dimethylformamide	8.02	58.47	0.990	7
IV	Acetamide	10.39	43.85	0.982	7
IV	Urea	8.42	102.44	0.997	9
IV	Tetramethylurea	7.85	91.21	0.997	7
IV	<i>tert</i> -Butylurea	10.36	43.71	0.994	7
Q_{SO_2} 0.05–0.10 M					
II	Formamide	1.15	–15.70	0.982	8
II	Dimethylformamide	1.89	–10.26	0.991	8
II	Urea	1.29	–15.21	0.996	8
II	Tetramethylurea	1.27	–15.69	0.984	8
Q_{SO_2} 0.05–0.08 M					
V	Acetamide	3.58	14.83	0.983	6
V	<i>tert</i> -Butylurea	3.56	14.85	0.994	6
VI	Acetamide	6.45	34.68	0.985	6
VI	<i>tert</i> -Butylurea	6.48	34.70	0.999	6

of hydrosulfite ions into pyrosulfite ions [Eqs. (1) and (2)].

The lack of correlation between the stability of these compounds and the basicity of the amides suggests that interaction of SO_2 with aqueous solutions of amides results in formation of different types of associates at the same composition [18], i.e., the coordination modes are different. The above-described effects are most probably due to selective solvation in aqueous-amide solutions of SO_2 [23].

Thus, the interactions in water–amide– SO_2 systems and the component composition of these systems largely depend on the structure and concentration of the components and on temperature. When calculating equilibria in these systems, it is necessary to take into account both the first step of sulfurous acid dissociation and the dimerization of hydrosulfite ions into pyrosulfite ions. The protonation of amides in these systems can be neglected.

EXPERIMENTAL

As starting reagents we used analytically pure grade formamide, dimethylformamide, acetamide, and

tetramethylurea; *tert*-butylurea was prepared according to [24]. The experimental procedure is described in detail in [12–14]. The experiments were performed at 278 and 293 K.

Ammonium ions were determined qualitatively with Nessler's reagent.

In the course of experiments, the SO_2 concentration was monitored iodometrically at the outlet from the reaction mixture at 15–20-s intervals [25]. The amount of converted SO_2 was determined experimentally by Schoeniger's method [26] and calculated as follows:

$$Q_{SO_2} = \frac{q([SO_2]_{in} - [SO_2]_f)}{V_1}, \text{ M}, \quad (33)$$

where V_1 is the solution volume, l; $[SO_2]_{in}$ and $[SO_2]_f$, SO_2 concentration in the gas mixture before and after the reaction, respectively, M; q , gas mixture volume, l, passed through the reactor in time τ .

Three replicate experiments were performed in each case. The random error of the experiment at $Q_{SO_2} \geq 0.01$ M did not exceed 2.5% in all the cases.

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