

INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

A Study of Complexation in the System Constituted by Water, Carbamide, and Sulfur Dioxide at 293 K

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Abstract—Electronic absorption spectroscopy and potentiometry were applied to study complexation at 293 K in a system constituted by water, carbamide, and sulfur dioxide. The composition and stability of the molecular and ionic complexes formed was determined in relation to the concentration of components in solution.

A study of the complexation of sulfur dioxide with carbamide in water is of theoretical and practical importance [1]. Carbamide, which exhibits properties of a weak base, reacts with mineral acids to give products of salt nature [2–5]; however, only a limited number of publications have been concerned with the chemistry of compounds formed by this ligand and SO₂. Potentiometry has been used to study the reaction of sulfur dioxide with aqueous solutions of carbamide at temperatures in the range from 273 to 313 K [1, 6, 7]. In [8], the interaction in the system constituted by water, carbamide, and sulfur dioxide was studied by means of conductometry at 298–353 K. However, the presently existing interpretations of the mechanism of interaction between SO₂ and aqueous solutions of carbamide are contradictory.

The aim of this study was to examine equilibrium processes in the systems H₂O–SO₂ and H₂O–CO(NH₂)₂–SO₂ at 293 K by spectrophotometry and potentiometry.

EXPERIMENTAL

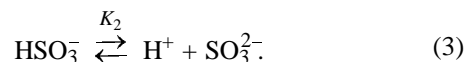
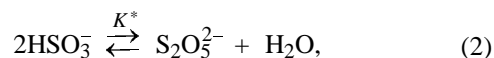
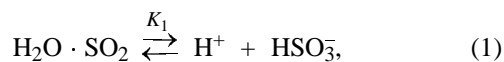
As starting substances were used gaseous sulfur dioxide and analytically pure carbamide (Ur). The water used to prepare all solutions was distilled and deoxygenated by bubbling with nitrogen for 4–6 h. The concentration of Ur in the systems studied was monitored photometrically [9].

Aqueous solutions of SO₂ were prepared by saturating deoxygenated water with gaseous sulfur dioxide purified by the method described in [10] and by diluting the resulting solution to required concentrations.

The concentration of sulfur(IV) was determined by iodometry [11] and by Scheniger's procedure [12]. The values yielded by these methods coincided. No sulfate ions were found in the system under study, which contradicts the model suggested in [8].

Electronic absorption spectra were recorded on Specord M400 (230 to 310 nm) and SF-18 (256 and 276 nm) spectrophotometers in 1-cm-thick quartz cuvettes. The potentiometric measurements were performed with a pH-150M pH-meter with an ESK-10601 combined glass electrode.

Published data on physicochemical properties of sulfur(IV) anions [13–15] suggest that sulfur dioxide dissolved in water exists as equilibrium forms H₂O·SO₂, HSO₃[–], S₂O₅^{2–}, and SO₃^{2–}:



It is known that the electronic spectra of aqueous solutions of SO₂ show three absorption peaks at λ 276 (A₂₇₆), 256 (A₂₅₆), and 210 nm. The peak at 276 nm corresponds to sulfur dioxide hydrate; light absorption at about 256 nm, to the pyrosulfite ion; and the peak at about 210 nm, to the disulfite ion [13, 16, 17].

Published data on ion-molecular equilibria in the H₂O–SO₂ system at 293 K are obtained with account of only reactions (1) and (3), with reaction (2) disregarded [18].

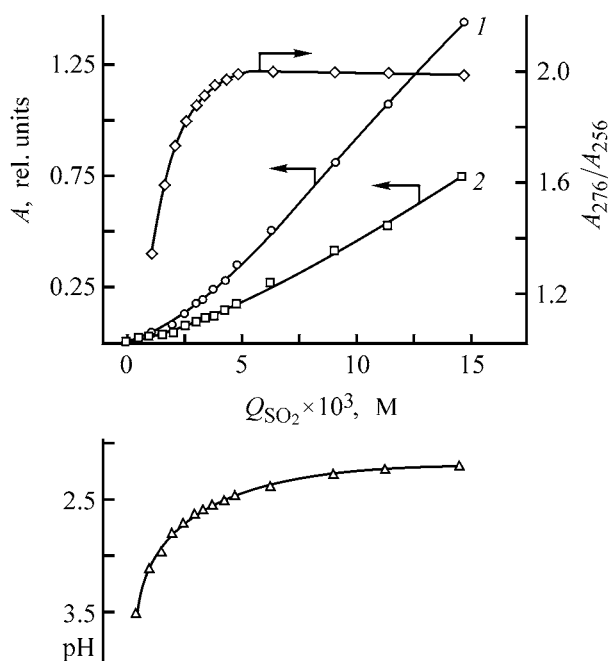


Fig. 1. Spectrophotometric and potentiometric characteristics of aqueous solutions of sulfur dioxide at 293 K. (A) Optical density and (Q_{SO_2}) concentration of SO_2 in solution. λ (nm): (1) 276 and (2) 256.

Spectrophotometric studies of the equilibrium system $\text{H}_2\text{O}-\text{SO}_2$ at 293 K (Fig. 1) demonstrated that the optical densities A_{276} and A_{256} increase virtually in direct proportion to the total content of SO_2 in the solutions under study (at $Q_{\text{SO}_2} \geq 2.5 \times 10^{-3}$ M, where Q_{SO_2} is the total content of SO_2 in solution, M). Consequently, the solutions analyzed are described by the Bouguer–Lambert–Beer law in the concentration range $Q_{\text{SO}_2} = (2.5-15.0) \times 10^{-3}$ M. However, $A_{276}/A_{256} \neq \varepsilon_{276}/\varepsilon_{256}$ in this range. This indicates that A_{256} is an additive quantity. Analysis of the data in Fig. 1 shows that, as the total content of sulfur dioxide in water increases, the $A_{276} : A_{256}$ ratio grows and reaches a constant value at $Q_{\text{SO}_2} = 4.0 \times 10^{-3}$ M.

Table 1. Comparison of published and experimental data obtained by analysis of electronic absorption spectra of aqueous solutions of sulfur dioxide

Equilibrium form	λ , nm	ε , $\text{M}^{-1} \text{cm}^{-1}$
$\text{SO}_2 \cdot \text{H}_2\text{O}$	276	~ 500 [16, 19], 500*
$\text{S}_2\text{O}_5^{2-}$	256	2217 [13], 5790 [20], 1940*
HOSO_2^-	256	3.8 [13], 2.5*

* Data obtained in the present study.

To find the quantitative relationships between the concentrations of oxo compounds of sulfur in an aqueous solution of SO_2 , it is necessary to determine the constants K_1 and K^* , since equilibrium (3) can be disregarded at $\text{pH} < 4$. To calculate the dimerization constant of hydrosulfite ions, K^* , the molar absorption coefficients ε of hydrosulfite and disulfite ions were preliminarily determined. The molar absorption coefficients of HSO_3^- and $\text{S}_2\text{O}_5^{2-}$ at 256 nm were found by extrapolation of the dependences $A_{256}/Q_{\text{SO}_2} = f(Q_{\text{SO}_2})$ and $A_{256}/Q_{\text{SO}_2} = f(1/\sqrt{Q_{\text{SO}_2}})$ to intersection with the ordinate axis [13].

The molar absorption coefficient of sulfur dioxide hydrate was determined at $\lambda = 276$ nm in a similar way. Comparison of the resulting values of $\varepsilon_{\text{H}_2\text{O} \cdot \text{SO}_2}$, $\varepsilon_{\text{HSO}_3^-}$, and $\varepsilon_{\text{S}_2\text{O}_5^{2-}}$ with those previously known (Table 1) shows a good coincidence of these values with the calculated data.

The concentration constants K_1 and K^* were calculated with account of Eqs. (4) and (5) (which reflect the mass action law), the additivity rule (6) and (7), and material balance and electroneutrality conditions (8) and (9):

$$K_1 = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{O} \cdot \text{SO}_2]}, \quad (4)$$

$$K^* = \frac{[\text{S}_2\text{O}_5^{2-}]}{[\text{HSO}_3^-]^2}, \quad (5)$$

$$A_{276} = \varepsilon_{\text{H}_2\text{O} \cdot \text{SO}_2}^{276} [\text{H}_2\text{O} \cdot \text{SO}_2], \quad (6)$$

$$A_{256} = \varepsilon_{\text{S}_2\text{O}_5^{2-}}^{256} [\text{S}_2\text{O}_5^{2-}] + \varepsilon_{\text{HSO}_3^-}^{256} [\text{HSO}_3^-], \quad (7)$$

$$Q_{\text{SO}_2} = [\text{H}_2\text{O} \cdot \text{SO}_2] + 2[\text{S}_2\text{O}_5^{2-}] + [\text{HSO}_3^-], \quad (8)$$

$$[\text{H}^+] = 2[\text{S}_2\text{O}_5^{2-}] + [\text{HSO}_3^-]. \quad (9)$$

In processing of the experimental data, a linear dependence of the ionic strength I of the aqueous solutions on the amount of sulfur dioxide dissolved in these solutions was established ($2.5 \times 10^{-3} \leq Q_{\text{SO}_2} \leq 15.0 \times 10^{-3}$ M):

$$I = 0.8113Q_{\text{SO}_2} + 0.0002, \quad R^2 = 0.99, \quad (10)$$

where R^2 is the statistical significance of approximation.

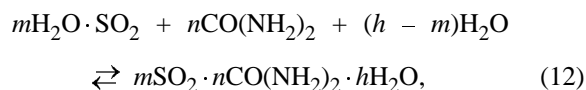
The dependences of the concentration constants K_1 and K^* on the total concentration of SO_2 ($2.5 \times 10^{-3} \leq$

$Q_{\text{SO}_2} \leq 15.0 \times 10^{-3}$ M) are shown in Fig. 2. These dependences can also be described by the equation whose parameters are listed in Table 2:

$$\text{p}K = A_0 + A_1 \sqrt{Q_{\text{SO}_2}} + A_2 Q_{\text{SO}_2}, \quad (11)$$

where $\text{p}K = -\log K$.

Ur can react with sulfur dioxide in water in several ways: (i) via direct addition [Eq. (12)] and (ii) via protonation of Ur [Eq. (13)] [7]:



The equilibrium processes in the system H_2O –Ur– SO_2 were studied spectrophotometrically in the spectral range 230–310 nm. For this purpose, light absorption of 30 solutions was recorded at 16 wavelengths. The number of light-absorbing species was determined by analyzing a matrix with orthogonal rows by the Mark method [21].

Analysis of how the matrix rank depends on the prescribed experimental error (Fig. 3) shows that the number of types of light-absorbing species in the system under study is, in all probability, four. In this case, the error in determining the optical density must fall within the range $0.0018 \leq S_A \leq 0.004$ units of light absorption. If, however, the error is lowered to 0.00016, and further to 0.00006, the results of calculations point to five forms; if, by contrast, the error is increased to 0.0042–0.0046 light-absorption units, the number obtained is three. A similar tendency was observed in [22] when analyzing the matrix rank for a system constituted by hafnium(IV), perchloric acid, and chloranilic acid.

It should also be noted that the number of different types of light-absorbing species in the system H_2O – SO_2 is three. Then, it is highly probable that the number of types of light-absorbing species in the system H_2O –Ur– SO_2 is greater than three.

It was established that the absorption peaks are not shifted upon complexation, whereas the optical densities of the peaks change significantly. Therefore, all further studies were carried out by analyzing the light absorption at 276 and 256 nm.

The composition of the complexes in solution was determined using the method of molar ratios [22].

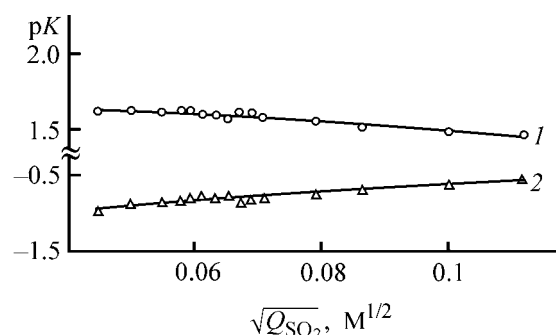


Fig. 2. (1) $\text{p}K_1$ and (2) $\text{p}K^*$ vs. the total content of SO_2 , Q_{SO_2} .

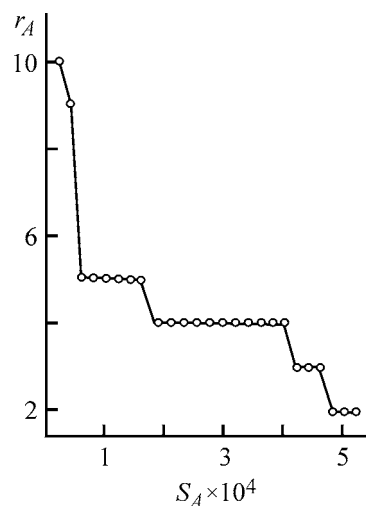


Fig. 3. Matrix rank r_A vs. the prescribed experimental error S_A for the system H_2O –Ur– SO_2 .

The calculations were based on deviations of the optical densities from additivity, ΔA ($\Delta A = A_\Sigma - A_{\text{SO}_2} - A_{\text{Ur}}$, where A_Σ is the total optical density of all the components of a solution; and A_{SO_2} and A_{Ur} are the optical densities of solutions of the components SO_2 and Ur at concentrations equal to those in the series under study). The resulting values of ΔA were used to construct ΔA –composition diagrams for the solution series under study (Fig. 4).

When analyzing the data in Fig. 4 (curves 1, 2), it should be noted that compounds of composition

Table 2. Values of parameters in Eq. (11) ($R^2 = 0.91$)

$\text{p}K$	A_0	A_1	A_2
$\text{p}K_1$	1.7917	0.7902	–37.652
$\text{p}K^*$	–1.2925	8.7247	–19.152

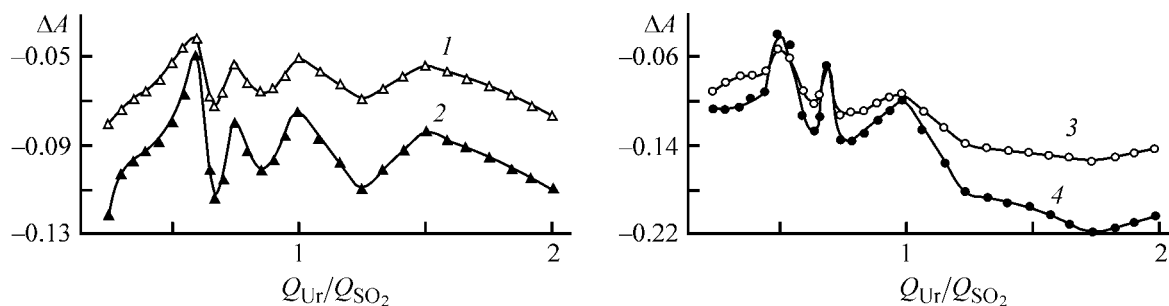


Fig. 4. ΔA vs. the composition of the system constituted by water, carbamide, and sulfur dioxide at 293 K. Q_{SO_2} (M): (1, 2) 5.0×10^{-3} and (3, 4) 7.5×10^{-3} . pH: (1, 2) 2.66 ± 0.02 and (3, 4) 2.42 ± 0.02 . λ (nm): (1, 3) 256 and (2, 4) 276.

$[mSO_2 \cdot nCO(NH_2)_2 \cdot hH_2O]$, in which $m:n = 5:3$, $3:2$, $4:3$, $6:5$, $1:1$, $4:5$, and $2:3$, exist in the 5.0×10^{-3} M solution of sulfur dioxide. A 7.5×10^{-3} M solution of SO_2 is characterized by the ratios $m:n = 2:1$, $3:2$, $4:3$, $1:1$, and $4:7$ (Fig. 4, curves 3 and 4). Similarly, it was also established that complexes of composition $[SO_2 \cdot CO(NH_2)_2 \cdot hH_2O]$ (I) and $[2SO_2 \cdot CO(NH_2)_2 \cdot hH_2O]$ (II) exist in a 2.5×10^{-3} M solution of sulfur dioxide.

With account of Eqs. (4), (5), (14), and (15) (which reflect the mass action law), the material balance and electroneutrality conditions (16)–(18), the numerical values of the arbitrary complexation constants β_1 and β_2 were calculated for compounds (I) and (II), respectively (Table 3):

$$\beta = \frac{[mSO_2 \cdot nCO(NH_2)_2 \cdot hH_2O]}{[H_2O \cdot SO_2]^m [CO(NH_2)_2]^n}, \quad (14)$$

$$K_a = \frac{[CO(NH_2)_2][H^+]}{[CO(NH_2)_2H^+]}, \quad (15)$$

$$Q_{SO_2} = [H_2O \cdot SO_2] + 2[S_2O_5^{2-}] + [HSO_3^-] + mc_K, \quad (16)$$

$$Q_{Ur} = [CO(NH_2)_2] + [CO(NH_2)_2H^+] + nc_K, \quad (17)$$

$$[CO(NH_2)_2H^+] + [H^+] = [HSO_3^-] + 2[S_2O_5^{2-}] + [OH^-], \quad (18)$$

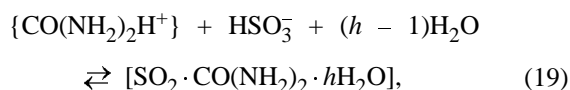
where $c_K = [[mSO_2 \cdot nCO(NH_2)_2 \cdot hH_2O]]$; Q_{SO_2} and Q_{Ur} , the total content of sulfur dioxide and Ur, respectively, in the system under study; $p\beta = -\log \beta$.

In the calculations, the value of pK_a was taken to be 0.18 [23].

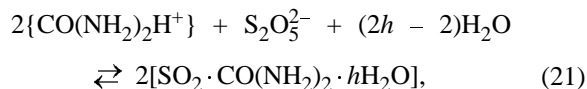
The arbitrary constants β_3 and β_4 characterize the acid–base interaction of uronium cations with hydrosulfite and disulfite ions, respectively:

Table 3. Results obtained in spectrophotometric studies of the system H_2O – $CO(NH_2)_2$ – SO_2 at 293 K

Parameter	Concentration $Q_{SO_2} \times 10^3$, M		
	2.5	5.0	7.5
$Q_{Ur} \times 10^3$, M	1.85–2.50	4.50–5.00	6.00–7.50
pH	2.90	2.66	2.42
$p\beta_1 \pm \Delta p\beta_1$	-4.03 ± 0.051	-3.74 ± 0.057	-3.28 ± 0.065
$p\beta_3 \pm \Delta p\beta_3$	-5.98 ± 0.051	-5.62 ± 0.057	-5.02 ± 0.065
$p\beta_4 \pm \Delta p\beta_4$	-11.8 ± 0.10	-10.4 ± 0.12	-9.37 ± 0.13
$\log \varepsilon_{K(I)}^{276}$	2.04	1.91	1.95
$\log \varepsilon_{K(I)}^{256}$	1.80	1.56	1.51
$Q_{Ur} \times 10^3$, M	1.25	1.50–2.50	2.25–3.75
pH	2.91	2.66	2.42
$p\beta_2 \pm \Delta p\beta_2$	-8.06 ± 0.042	-7.67 ± 0.268	-6.74 ± 0.182
$\log \varepsilon_{K(II)}^{276}$	2.40	2.20	2.33
$\log \varepsilon_{K(II)}^{256}$	1.98	1.86	1.95



$$\beta_3 = \frac{[\text{SO}_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot h\text{H}_2\text{O}]}{[\text{HSO}_3^-][\{\text{CO}(\text{NH}_2)_2\text{H}^+\}]} \quad (20)$$



$$\beta_4 = \frac{[\text{SO}_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot h\text{H}_2\text{O}]}{[\text{S}_2\text{O}_5^{2-}][\{\text{CO}(\text{NH}_2)_2\text{H}^+\}]^2} \quad (22)$$

It was established in the study that compounds (I) and (II) absorb in the UV spectral range:

$$A_{276} = \varepsilon_{\text{H}_2\text{O} \cdot \text{SO}_2}^{276} [\text{H}_2\text{O} \cdot \text{SO}_2] + \varepsilon_{\text{K}}^{276} c_{\text{K}}, \quad (23)$$

$$A_{256} = \varepsilon_{\text{S}_2\text{O}_5^{2-}}^{256} [\text{S}_2\text{O}_5^{2-}] + \varepsilon_{\text{HSO}_3^-}^{256} [\text{HSO}_3^-] + \varepsilon_{\text{K}}^{256} c_{\text{K}}, \quad (24)$$

where $\varepsilon_{\text{K}}^{276}$ and $\varepsilon_{\text{K}}^{256}$ are the molar absorption coefficients of the forming complexes at 276 and 256 nm, respectively.

The fact that the values of $\varepsilon_{\text{K(I)}}^{276}$, $\varepsilon_{\text{K(I)}}^{256}$ and $\varepsilon_{\text{K(II)}}^{276}$, $\varepsilon_{\text{K(II)}}^{256}$ for compounds (I) and (II), respectively (Table 3) depend on the total content of sulfur dioxide and Ur in solution presumably indicates that the composition of complexes (I) and (II) also depends on the concentrations of these components in solution.

Analysis of the data in Table 3 shows that, as the solutions are diluted, the stability of the compounds increases, which would be impossible if hydrolysis dominated over complexation. Hence follows that the complexes are hydrated from the very beginning and a further increase in the concentration of water does not lead to displacement of other species from the compounds.

In all probability, the effects described above are due to selective solvation in aqueous-carbamide solutions of sulfur dioxide.

CONCLUSION

Joint application of spectrophotometric and potentiometric methods enables a conclusion that both molecular and ion complexes can be formed in the system $\text{H}_2\text{O}-\text{CO}(\text{NH}_2)_2-\text{SO}_2$. The composition and stability of the forming compounds strongly depend on

the concentration of components in solution. It is established that the hydration of the complexes dominates over their hydrolysis in the system under study.

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