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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

On Reaction of Sulfur Dioxide with Aqueous Solutions of Carbamide

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Abstract—A mechanism of SO_2 chemisorption by aqueous solutions of carbamide was suggested. The effective rate constants of accumulation of hydrogen ions in the reaction of sulfur dioxide with aqueous solutions of carbamide in the range 278–313 K were determined.

One of the main tendencies in the use of methods for desulfurization of waste gases consists in that simple absorption purification methods of nonregenerating type with limestone, lime, or other sorbents give way to technological processes of regenerating type, which enable removal of absorbed sulfur dioxide from the system, with its subsequent utilization [1]. The possibility of generation of sulfur dioxide in the form of a virtually 100% gas can be ensured with the use of aqueous solutions of nitrogen-containing bases as sorbents [2].

The problems of SO_2 dissolution in water and aqueous solutions are widely discussed. The mechanism of sulfur dioxide dissolution in water and aqueous solutions in the ionic form was rather well described in [3–5]. This mechanism can be, in general terms, represented as follows:

gas–liquid equilibrium

$$SO_2^g \rightleftarrows SO_2^l, \tag{1}$$

specific equilibrium

$$SO_2^l + H_2O \rightleftarrows SO_2 \cdot H_2O, \tag{2}$$

$$SO_2 \cdot H_2O \rightleftarrows H^+ + HSO_3^-, \tag{3}$$

$$2HSO_3^- \rightleftarrows S_2O_5^{2-} + H_2O, \tag{4}$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-}, \tag{5}$$

where SO_2^g and SO_2^l stand for sulfur dioxide in the gas phase and that dissolved in water, respectively.

Also, Labutin *et al.* [6] suggested the molecular mechanism of sulfur dioxide dissolution in water

$$SO_2^g \rightleftarrows SO_2^l, \tag{6}$$

$$SO_2^l + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} SO_2^g \cdot H_2O, \tag{7}$$

$$SO_2^l + SO_2 \cdot H_2O \underset{k_4}{\overset{k_3}{\rightleftarrows}} H_2S_2O_5, \tag{8}$$

$$H_2S_2O_5 + H_2O \underset{k_6}{\overset{k_5}{\rightleftarrows}} SO_2 \cdot H_2O. \tag{9}$$

Based on the assumptions that the first stage of physical dissolution [Eq. (6)] is fast and obeys the Henry law and the third stage [Eq. (8)] has equilibrium nature with account of the limiting action of the second and fourth stages [Eqs. (7) and (9)], the authors of [6] note that

$$\frac{dc_{SO_2 \cdot H_2O}}{d\tau} = K_I - K_{II}c_{SO_2 \cdot H_2O} - K_{III}c^2_{SO_2 \cdot H_2O}, \tag{10}$$

where $K_I = k_1p/m$, $K_{II} = k_2 - (2k_5k_3p/k_4m)$, $K_{III} = 2k_6$, p is the partial pressure of SO_2, and m is the Henry constant. The total content of sulfurous acid, $c_{SO_2 \cdot H_2O}$, is directly proportional to the total content of the disulfurous acid, $c_{H_2S_2O_5}$:

$$c_{H_2S_2O_5} = K_{IV}c_{SO_2 \cdot H_2O}, \tag{11}$$

$$K_{IV} = k_3p/k_4m.$$

At the same time, a particular place among the existing widely diverse absorption methods for desulfurization of discharged gases [1, 7–9] is occupied by the carbamide technique [2, 10, 11]. This can be accounted for by the fact that carbamide is a virtually nontoxic product manufactured on large scale and its aqueous solutions have high absorption capacity and are easily regenerated [2], which allows their further utilization. However, the mechanism of reaction between sulfur dioxide and aqueous solutions of carbamide remains poorly understood.

In the opinion of the authors of [10, 11], the reaction of SO_2 with aqueous solutions of carbamide proceeds via its acid hydrolysis to give CO_2, H_2O, and $(NH_4)_2SO_4$. However, according to [12, 13], the rate of hydrolysis of carbamide is so slow that, in actual practice, its solutions in water can be considered stable up to 80°C. Only heating to 90–100°C or presence of the urease enzyme accelerates the hydrolysis of carbamide.

In [14, 15], a mechanism of SO_2 chemisorption by aqueous solutions of carbamide was suggested. This mechanism consists in that the acid–base reaction of the generated forms of sulfurous acid with carbamide occurs via complexation. The inorganic acid neutralizes the weak organic base via protonation [Eqs. (12)–(14)] or direct addition to its molecule to give associates [Eq. (15)]:

$$[CO(NH_2)_2H]^+ + HSO_3^- \rightleftarrows [CO(NH_2)_2H]HSO_3, \quad (12)$$

$$2[CO(NH_2)_2H]^+ + S_2O_5^{2-} \rightleftarrows [CO(NH_2)_2H]_2S_2O_5, \quad (13)$$

$$2[CO(NH_2)_2H]^+ + SO_3^- \rightleftarrows [CO(NH_2)_2H]_2SO_3, \quad (14)$$

$$CO(NH_2)_2 + SO_2 + nH_2O \rightleftarrows CO(NH_2)_2 \cdot SO_2 \cdot nH_2O. \quad (15)$$

According to published data, carbamide exhibits weak basic properties ($pk_a \sim 0.5$ [16], 0.18, 0.31 [17]). This indicates that the uronium cation is a stronger acid than $SO_2 \cdot H_2O$ (pk_a ~2.0 [4]). Consequently, formation of salts [Eqs. (12)–(14)] in aqueous solutions is unlikely.

It is not improbable that donor–acceptor reaction of SO_2 with carbamide, which acts as a ligand with respect to sulfur dioxide, results in that associates are formed in water [Eq. (15)].

A model proposed by the authors of [6] can be well applied to description of the reaction of sulfur dioxide with aqueous solutions of carbamide.

The total content of sulfur dioxide in solution, Q, at temperatures higher than 278 K is given by

$$Q = c_{SO_2 \cdot H_2O} + c_{H_2S_2O_5} + [SO_2^l]. \quad (16)$$

With account of (11) and (15), Eq. (10) takes the form

$$\frac{dc_{SO_2 \cdot H_2O}}{d\tau} = K_I - K_{II}\left(\frac{Q - p/m}{1 + K_{IV}}\right) - K_{III}\left(\frac{Q - p/m}{1 + K_{IV}}\right)^2. \quad (17)$$

The total content of sulfurous acid in solution

$$c_{SO_2 \cdot H_2O} = [SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^{2-}]. \quad (18)$$

Since it is known [5] that disulfurous acid does not exist in free form, the accumulation of hydrogen ions apparently occurs mainly via dissociation of sulfurous acid by the first stage. Since sulfurous acid is a weak acid, it can be written at its low concentrations that

$$\frac{d[H^+]}{d\tau} = k\frac{dc_{SO_2 \cdot H_2O}}{d\tau}. \quad (19)$$

After rearrangements Eq. (19) can be written as

$$\frac{d[H^+]}{d\tau} = K_I' + K_{II}'Q + K_{III}'Q^2, \quad (20)$$

where K_I', K_{II}', and K_{III}' are empirical constants:

$$K_I' = kK_I + k\frac{K_{II}}{1 + K_{IV}}\frac{p}{m} - k\frac{K_{III}}{(1 + K_{IV})^2}\frac{p^2}{m^2}, \quad (21)$$

$$K_{II}' = k\frac{2K_{III}}{(1 + K_{IV})^2}\frac{p}{m} - k\frac{K_{II}}{1 + K_{IV}}, \quad (22)$$

$$K_{III}' = -k\frac{K_{III}}{(1 + K_{IV})^2}. \quad (23)$$

To verify the adequacy of the model developed, published data on the reaction of sulfur dioxide with 0.1 and 0.25 M aqueous solutions of carbamide [15, 14] were processed in terms of this model and the reaction of SO_2 with 0.5 M carbamide solutions was studied in the interval 278–313 K.

EXPERIMENTAL

The experimental procedure employed was described in detail in [15, 16].

Model solutions were prepared with distilled water and carbamide of analytically pure or pure grades, additionally purified by recrystallization. The concentration of carbamide in the systems studied was monitored by photometry [18].

Purified sulfur dioxide [19] was continuously bubbled at constant volumetric flow rate of 8 ml min^{-1} through a model solution placed in a thermostated cell (solution volume 250 ml). Together with pneumatic agitation, mechanical stirring was also used, which ensured ideal mixing of the components. The concentration of hydrogen ions was measured in the course of experiments with an ESL-43-07 glass electrode. An EVL-1M3 silver chloride reference electrode was filled with a saturated aqueous solution of potassium chloride at 298 K.

The measurements were done at 278–313 K.

In the course of an experiment, c_{SO_2} was monitored after the reaction mixture at 15–30-s intervals by iodometry [20]. The amount of reacted SO_2 was determined by the Scheniger method [21] and calculated using the formula

$$Q = \frac{q(c^{\text{in}}_{SO_2} - c^{\text{fin}}_{SO_2})}{V_l \cdot 64}, \qquad (24)$$

where V_l is the solution volume (ml); $c^{\text{in}}_{SO_2}$ and $c^{\text{fin}}_{SO_2}$, the SO_2 concentrations before and after the reaction (M); q, the volume of the reaction mixture (ml) passed through the reactor during a time τ.

The experiments were performed to constant determined parameters of the system. During an entire experiment, there was no sulfur dioxide at the outlet, which points to its nearly 100% absorption. It was established experimentally that raising the intensity of stirring to more than 50 rpm has no effect on the run of the pH curves, i.e., the reaction of SO_2 with aqueous solutions of carbamide proceeds under these conditions in the kinetic region. In addition, the authors of [6] maintain that, at SO_2 content in the gas phase exceeding 4 vol %, the overall rate of sulfur dioxide dissolution in aqueous solutions is limited by the rate of the SO_2 hydration stage.

As shown by the experiments, the concentration of carbamide sorbing SO_2 remains virtually constant in each set of runs over the entire range of the temperatures studied. No sulfate ions were found in the systems under study, which contradicts the model proposed in [10, 11].

The curves describing how the pH value varies with the amount of absorbed SO_2, Q (M), in solutions are shown in Figs. 1a [15], 1b [14], and 1c. Processing of these data by the least-squares method yielded dependences $[H^+] = f_{T,c_{KA}}(Q)$ in the form of third-order polynomials

$$[H^+] = A_{T,c_{KA}} + B_{T,c_{KA}}Q + C_{T,c_{KA}}Q^2 + D_{T,c_{KA}}Q^3, \qquad (25)$$

where $A_{T,c_{KA}}$, $B_{T,c_{KA}}$, $C_{T,c_{KA}}$, and $D_{T,c_{KA}}$ are constants for each of the runs, which depend both on tempera-

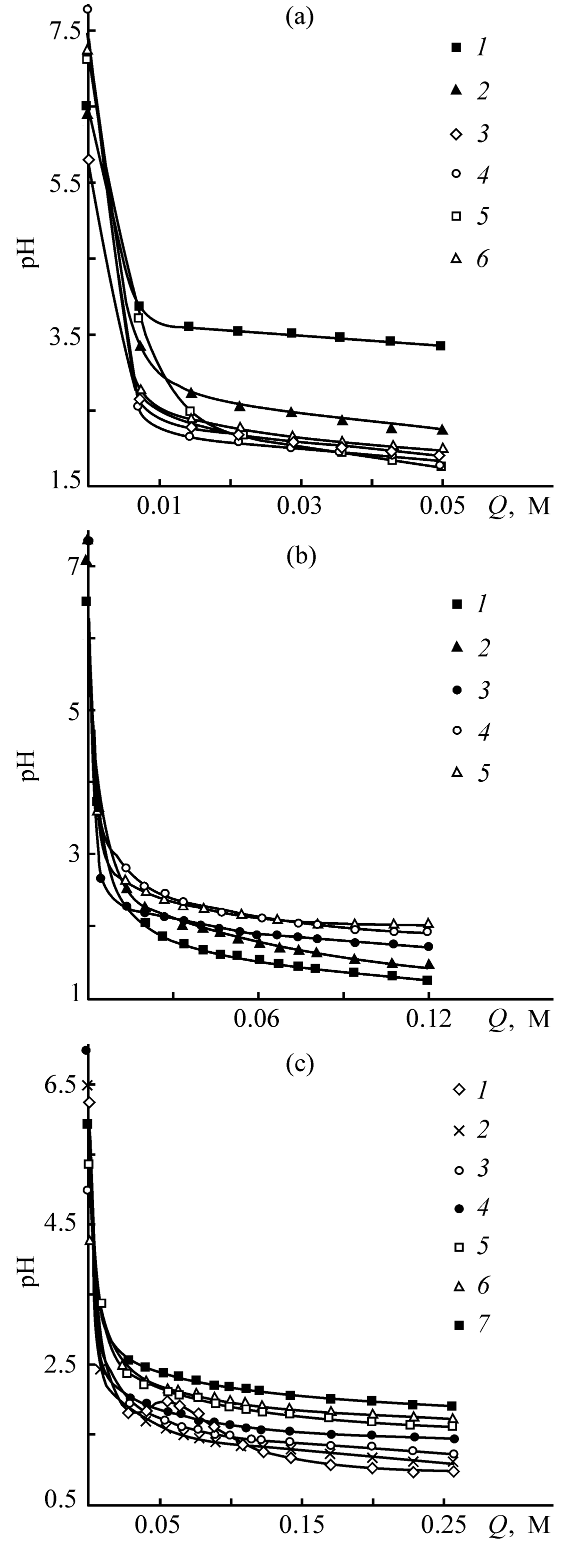

Fig. 1. Variation of the pH value with the amount Q of sulfur dioxide absorbed by (a) 0.1, (b) 0.25, and (c) 0.5 M solution of carbamide. Temperature (K): (a) (*1*) 278, (*2*) 283, (*3*) 288, (*4*) 293, (*5*) 303, and (*6*) 313; (b) (*1*) 288, (*2*) 293, (*3*) 303, (*4*) 308, and (*5*) 313; (c) (*1*) 278, (*2*) 283, (*3*) 288, (*4*) 293, (*5*) 303, (*6*) 308, and (*7*) 313.

Parameters of Eq. (20) for 0.1, 0.25, and 0.5 M carbamide solutions

T, K	c_{KA} = 0.10 M, $0 \le Q \le 0.05$ M				c_{KA} = 0.25 M, $0 \le Q \le 0.12$ M				c_{KA} = 0.50 M, $0 \le Q \le 0.25$ M			
	$K'_{\mathrm{I}} \times 10^4$	$K'_{\mathrm{II}} \times 10^3$	$K'_{\mathrm{III}} \times 10^2$	R^2	$K'_{\mathrm{I}} \times 10^4$	$K'_{\mathrm{II}} \times 10^3$	$K'_{\mathrm{III}} \times 10^2$	R^2	$K'_{\mathrm{I}} \times 10^4$	$K'_{\mathrm{II}} \times 10^3$	$K'_{\mathrm{III}} \times 10^2$	R^2
278	0.39	–2.25	–3.76	0.98	–	–	–	–	–4.42	2.19	8.5	0.98
283	2.17	–1.91	0.63	0.99	–	–	–	–	8.33	–4.99	1.20	0.99
288	8.79	–43.78	76.32	0.98	8.60	–4.25	1.03	0.99	8.06	–7.53	2.30	0.99
293	7.43	–16.68	14.57	0.99	3.06	4.53	–2.95	0.99	4.91	–3.68	0.84	0.99
303	2.17	27.22	–44.97	0.99	3.95	–4.11	1.36	0.99	2.80	–1.97	0.51	0.99
313	4.99	–9.11	5.25	0.99	2.15	–2.12	0.65	0.99	1.36	–0.88	0.23	0.99

ture T and on the total content of carbamide, c_{KA}, in the reaction mixture.

With account of the fact that SO_2 was delivered during an entire run at a constant volumetric flow rate and virtually its whole amount reacted with the absorbers, it can be written that

$$Q = a\tau, \tag{26}$$

where a is a constant dependent on the gas supply rate, and τ is the time during which the gas is supplied. Substitution of (26) into Eq. (25) and subsequent differentiation with respect to time yields

$$\left(\frac{\partial[\mathrm{H}^+]}{\partial\tau}\right)_{T,\,c_{\mathrm{KA}}} = aB_{T,\,c_{\mathrm{KA}}} + 2a^2C_{T,\,c_{\mathrm{KA}}}\tau + 3a^3D_{T,\,c_{\mathrm{KA}}}\tau^2 \tag{27}$$

or

$$\left(\frac{\partial[\mathrm{H}^+]}{\partial\tau}\right)_{T,\,c_{\mathrm{KA}}} = aB_{T,\,c_{\mathrm{KA}}} + 2aC_{T,\,c_{\mathrm{KA}}}Q + 3aD_{T,\,c_{\mathrm{KA}}}Q^2. \tag{28}$$

If Eqs. (19) and (23) are compared, it can be written

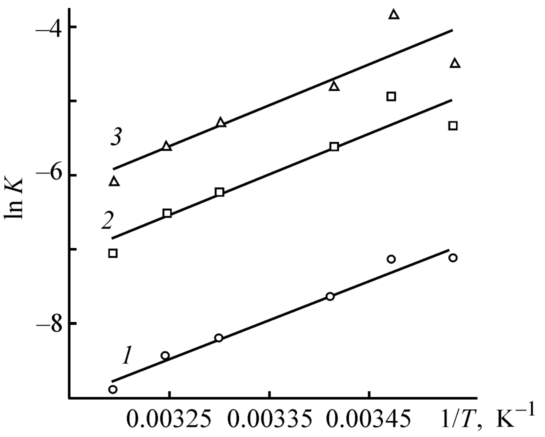

Fig. 2. Parameters of Eq. (20) for 0.5 M carbamide solution vs. temperature *T*. (*1*) K'_{I}, (*2*) K'_{II}, and (*3*) K'_{III}.

$$K'_{\mathrm{I}} = aB_{T,c_{\mathrm{KA}}},\quad K'_{\mathrm{II}} = 2aC_{T,c_{\mathrm{KA}}},\quad K'_{\mathrm{III}} = 3aD_{T,c_{\mathrm{KA}}}.$$

The processing of the data in Figs. 1a–1c made it possible to determine the average values of the empirical constants K'_{I}, K'_{II}, and K'_{III} (see table). The temperature dependences of these constants for a 0.5 M solution of carbamide can be represented in the interval 283–313 K as

$$K'_{\mathrm{I}} = 8.722 \times 10^{-10}\exp(\Delta\theta_1/RT),$$

$$K'_{\mathrm{II}} = -1.322 \times 10^{-10}\exp(\Delta\theta_2/RT),$$

$$K'_{\mathrm{III}} = 1.106 \times 10^{-10}\exp(\Delta\theta_3/RT),$$

where $\Delta\theta_1 = 38.94$, $\Delta\theta_2 = 41.38$, and $\Delta\theta_3 = 42.80$ kJ mol^{-1}.

Analysis of the temperature dependence of the empirical constants (Fig. 2) shows that their absolute values decrease with increasing temperature, i.e., the exponents in the temperature dependences of K'_{I}, K'_{II}, and K'_{III} are positive by virtue of the relationship between the activation energies (k_1–k_6) and the exponent in the temperature dependence of the Henry constant.

However, the temperature dependences of K'_{I}, K'_{II}, and K'_{III} for 0.1 and 0.25 M solutions (see table) are more complicated and can be represented as $K'_{\mathrm{I}} = f(T)$. For example, for a 0.25 M carbamide solution with sulfur dioxide concentration $0 \le Q_{\mathrm{SO_2}} \le 0.12$ M at 288–313 K

$$K'_{\mathrm{I}} = 3 \times 10^{-8}T^4 - 3 \times 10^{-5}T^3 + 0.015T^2 - 3.0189T + 228.25,$$

$$K'_{\mathrm{II}} = -7 \times 10^{-7}T^4 + 0.0009T^3 - 0.4105T^2 + 82.672T - 6241.8,$$

$$K'_{\mathrm{III}} = 4 \times 10^{-6}T^4 - 0.0044T^3 + 1.9847T^2 - 399.6T + 30162.$$

For a 0.1 M carbamide solution with sulfur dioxide concentration $0 \le Q_{SO_2} \le 0.05$ M in the range 278–313 K

$$K'_{\mathrm{I}} = -2 \times 10^{-10}T^6 + 4 \times 10^{-7}T^5 - 0.0003T^4 + 0.1018T^3 - 22.129T^2 - 2565T - 123\,819,$$

$$K'_{\mathrm{II}} = -3 \times 10^{-8}T^6 + 5 \times 10^{-5}T^5 - 0.0373T^4 + 14.634T^3 - 3232.7T^2 + 380\,754T - 2 \times 10^7,$$

$$K'_{\mathrm{III}} = 8 \times 10^{-7}T^6 - 0.0014T^5 + 1.0154T^4 - 398.32T^3 + 87\,863T^2 - 10^7T + 5 \times 10^8.$$

It should be noted that in all cases the approximation is characterized by a correlation factor $R^2 > 0.97$.

Apparently, the acidity of the medium is a measure of sulfur dioxide hydration by water, since this gives $SO_2 \cdot H_2O$ [Eq. (2)] and one of products of its dissociation are hydrogen ions [Eqs. (3) and (5)].

Thus, aqueous solutions of carbamide strongly affect solvation of SO_2 by water, probably forming various associates with sulfur dioxide. The effect of carbamide on the hydration of sulfur dioxide has complex nature. For example, the acidity of the medium decreases in a 0.5 M carbamide solution with the temperature increasing from 278 to 313 K. This can be accounted for by the fact that, under the specific action of carbamide, the affinity of water for sulfur dioxide decreases in solutions with increasing temperature.

CONCLUSIONS

(1) The possibility of effective absorption of sulfur dioxide by carbamide solutions in the temperature range 278–313 K was established.

(2) It was found that the temperature of the reaction medium and its composition strongly affect the acid-base reaction in SO_2–water–carbamide systems.

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