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Anionic Complexes as Products of Reactions in SO_2–Carbamide(Acetamide)–H_2O Systems

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Abstract—Evaluation of the contribution of hydrosulfite and pyrosulfite ions in the formation of anionic complexes in the sulfur(IV) oxide–amide–water systems was carried out considering the data of the pH-metric and redox-metric studies. Microconstants of the formation of anionic complexes of carbamide and acetamide with the above-mentioned anions were calculated.

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During the recent development of the absorption methods of purification of the exhaust gases from sulfur(IV) oxide it was shown that SO_2 reacts with water solutions of nitrogen-containing organic bases (alkyl-, benzyl-, aryl-, and heterocyclic amines) to form sulfite compounds [1, 2].

Sulfur(IV) oxide reacts with water solutions of amides (Am = carbamide, acetamide) to form molecular compounds of the composition $SO_2{\cdot}Am_2{\cdot}(H_2O)_n$ **I** and $SO_2{\cdot}Am{\cdot}(H_2O)_m$ **II**, and also the anionic complexes with hydrosulfite and pyrosulfite ions $Am_2HSO_3^-$ **III**, $Am_4{\cdot}S_2O_5^{2-}$ **IV**, $Am{\cdot}HSO_3^-$ **V**, and $Am_2S_2O_5^{2-}$ **VI**. Equilibria in the SO_2–Am–H_2O system are described by a set of Eqs. (1)–(9) [3].

$$SO_2{\cdot}H_2O \overset{K_1}{\rightleftharpoons} H^+ + HOSO_2^-, \quad (1)$$

$$2\,HOSO_2^- \overset{K^*}{\rightleftharpoons} S_2O_5^{2-} + H_2O, \quad (2)$$

$$HOSO_2^- \overset{K_2}{\rightleftharpoons} H^+ + SO_3^{2-}, \quad (3)$$

$$2Am + SO_2{\cdot}H_2O + (n-1)H_2O \overset{\beta_I}{\rightleftharpoons} SO_2{\cdot}Am_2{\cdot}(H_2O)_n, \quad (4)$$

$$Am + SO_2{\cdot}H_2O + (m-1)H_2O \overset{\beta_{II}}{\rightleftharpoons} SO_2{\cdot}Am{\cdot}(H_2O)_m, \quad (5)$$

$$2Am + HOSO_2^- \overset{\beta_{III}}{\rightleftharpoons} Am_2{\cdot}HOSO_2^-, \quad (6)$$

$$4Am + S_2O_5^{2-} \overset{\beta_{IV}}{\rightleftharpoons} Am_4{\cdot}S_2O_5^{2-}, \quad (7)$$

$$Am + HOSO_2^- \overset{\beta_V}{\rightleftharpoons} Am_2{\cdot}HOSO_2^-, \quad (8)$$

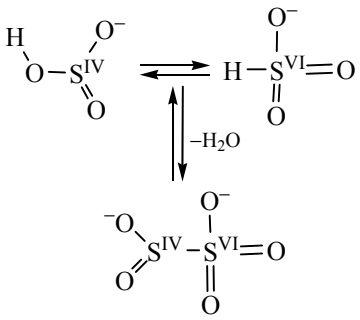
$$2Am + S_2O_5^{2-} \overset{\beta_{VI}}{\rightleftharpoons} Am_2{\cdot}S_2O_5^{2-}. \quad (9)$$

We formerly [4] proposed to use pH-metric and redox-metric methods to control the amount of sulfur(IV) oxide absorbed by a system. Due to formation of sulfites and the products **I**, **II** pH of water solutions of sulfur(IV) oxide in the presence of amines or amides is higher than without these additives at the same content of SO_2 [$Q(SO_2)$]. Formation of anionic complexes **III**–**VI** causes the shift of equilibrium to the right due to higher affinity of amides to hydrosulfite and pyrosulfite ions than to sulfur(IV) oxide leading to the accumulation of free hydrogen ions. Due to that pH in the SO_2–Am–H_2O system is higher than in the SO_2–H_2O one because the acceptor ability of amides to the above-mentioned anions is higher that to protons [3].

Information on the stability constants of complexes formed in the sorption systems may be used for the rational choice of effective absorbents and methods of their regeneration.

Constants of complex formation β_{III}–β_{VI} considered in [3] are just apparent [5] because only on the basis of pH-metric data it is impossible to separate the contributions of hydrosulfite and pyrosulfite ions in the formation of anionic complexes at the equimolar ratio of amide and sulfur in compounds **III**, **IV** and **V**, **VI**.

As is noted [6], the presence of ions with the oxidation degree of sulfur +4 (sulfite and hydrosulfite) and +6 (pyrosulfite) in aqueous SO_2 solutions causes a potential drop in the system.



It must be noted that the hydrosulfite ($HOSO_2^-$) ↔ sulfonate (HSO_3^-) equilibrium is shifted to the side of formation of $HOSO_2^-$ [7].

The above-mentioned potential drop may be described by the Nernst Eq. (10):

$$E = E^0 + (2.3RT/n\mathrm{F})\log([S_2O_5^{2-}]/[HOSO_2^-]). \quad (10)$$

Here E and E^0 are real and standard electrode potential of the $S_2O_5^{2-}/HOSO_2^-$ pair respectively; R is the universal gas constant (8.314 kJ mol^{-1} K^{-1}); T is the absolute temperature, K; n is the variation in charge on the sulfur atom; F is the Faraday constant (96490 C mol^{-1}).

According to the law of mass action connecting the constants with the component composition of water solutions of sulfur(IV) oxide:

$$[HOSO_2^-] = K_1[SO_2{\cdot}H_2O]/[H^+], \quad (11)$$

$$[S_2O_5^{2-}] = K_1^2K^*[SO_2{\cdot}H_2O]^2/[H^+]^2. \quad (12)$$

Substituting the expressions of concentrations of hydrosulfite and pyrosulfite ions [Eqs. (11), (12)] respectively in the Eq. (10) and performing the subsequent transformations we obtain the following equation:

$$E = E^0 + \Theta\log K_1 + \Theta\log K^* + \Theta\log([SO_2{\cdot}H_2O]/[H^+]). \quad (13)$$

Here K_1 and K^0 are the equilibrium constants of Eqs. (1) and (2) respectively; $\Theta = (2.3RT)/(nF)$.

According to the Eqs. (10), (13) the processes of complex formation of amides with SO_2 in water solutions must significantly affect the variation in potential of the system because various oxy-forms ($SO_2{\cdot}H_2O$, $HOSO_2^-$, and $S_2O_5^{2-}$) in which sulfur has different surrounding may take part in the complex formation.

In the work presented an attempt was made to separate the contributions of hydrosulfite and pyrosulfite ions in the equilibrium of formation of anionic complexes in the sulfur(IV) oxide–amide–water systems.

For the achievement of the above-mentioned goal the variation in potential of platinum electrode and pH in the course of titration of water solutions of carbamide and acetamide with gaseous SO_2 at 293 K was studied.

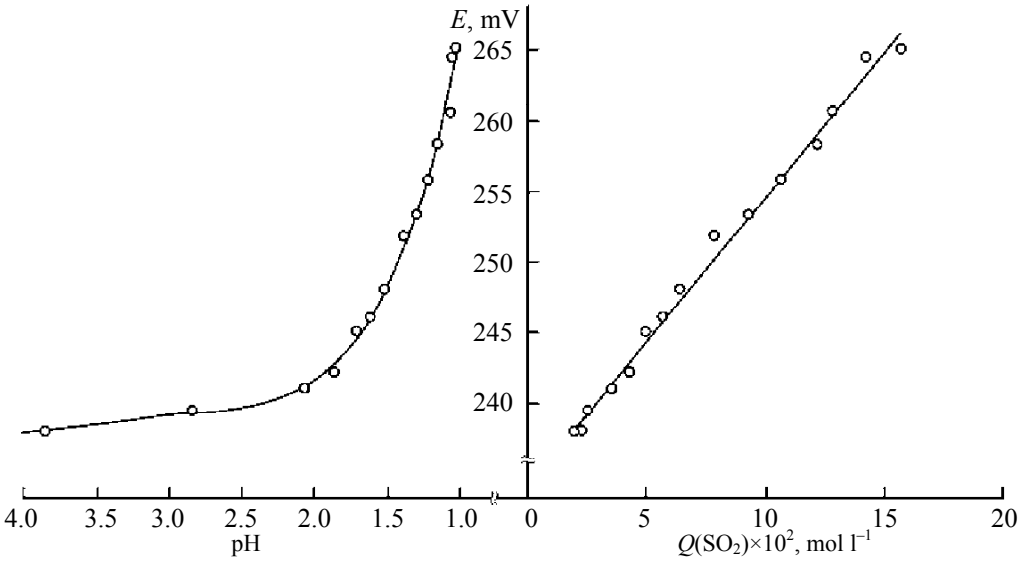


Fig. 1. Dependence of potential of platinum electrode in water on the amount of absorbed sulfur(IV) oxide [$Q(SO_2)$, mol l^{-1}] and pH at 293 K.

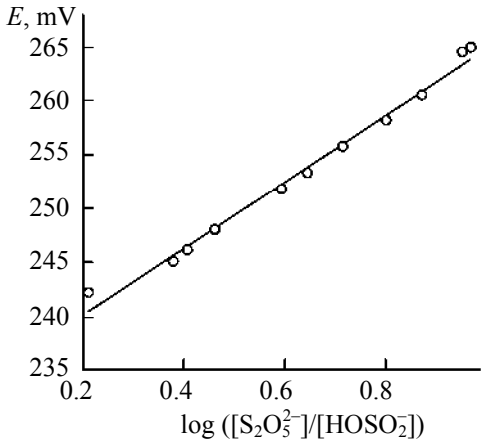


Fig. 2. Dependence of platinum electrode potential in SO_2 water solutions on their composition at 293 K.

Variation in the potential of platinum electrode in aqueous SO_2 solutions depending on pH of the medium during the potentiometric titration of water with sulfur(IV) oxide is presented in Fig. 1.

For the explanation of the character of the $E = f(\text{pH})$ curve we proceeded from the above-mentioned admission that the potential of platinum electrode in aqueous SO_2 solutions (pH < 4) could be described by the Nernst Eq. (10). In as much as in the system under study the processes take place where the oxidation degree of sulfur changes from +4 to +6 {$n = 2$ in the Eq. (10) [6]}, the value $\Theta = (2.3RT)/(nF)$ at 293 K must be equal to 29 mV. For checking the validity of Eq. (10) a procedure [3] of processing the pH-metric curves was used. On the basis of data on the component composition of solutions under study [3] the plot $E = f\log([S_2O_5^{2-}]/[HOSO_2^-])$ (Fig. 2) was obtained.

According to the performed investigations the above-presented dependence may be written in a linear shape:

$$E = A + B\log([S_2O_5^{2-}]/[HOSO_2^-]). \quad (14)$$

Here A = 234 mV; B = 31 mV, the confidence value of the approximation $R = 0.993$.

The comparison of Eqs. (10) and (14) shows that the standard electrode potential of the system $S_2O_5^{2-}$/ $HOSO_2^-$ at 293 K is 234 mV. The value B (31 mV) obtained from the processing of the experimental data is comparable with the theoretical value (29 mV) in the agreement with the data [3].

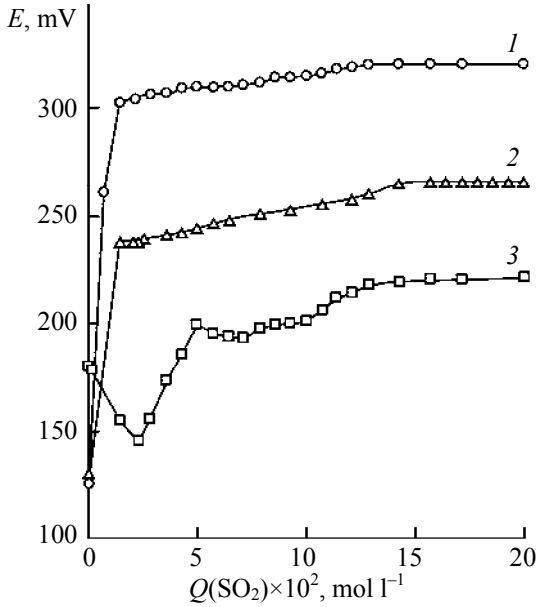


Fig. 3. Dependence of potentials of 0.1 M solutions of (*1, 3*) amides and (*2*) water on the amount of the absorbed sulfur(IV) oxide [$Q(SO_2)$, mol l^{-1}] at 293 K. (*1*) Carbamide and (*2*) acetamide.

For checking the assumption that the processes of complex formation of amides with SO_2 in water solutions must cause the variation in the potential of the system, dependences of the platinum electrode potential on $Q(SO_2)$ and pH in water solutions of carbamide and acetamide in the course of their titration with sulfur(IV) oxide were obtained (Figs. 3–5).

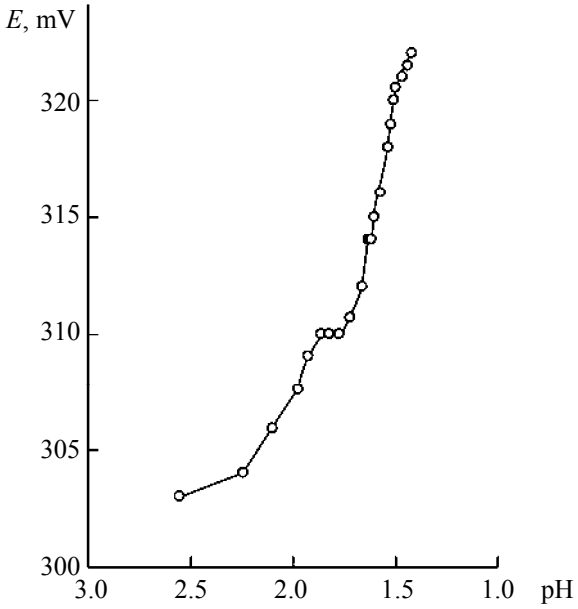


Fig. 4. Dependence of platinum electrode potential on pH of 0.1 M carbamide solution containing SO_2 at 293 K.

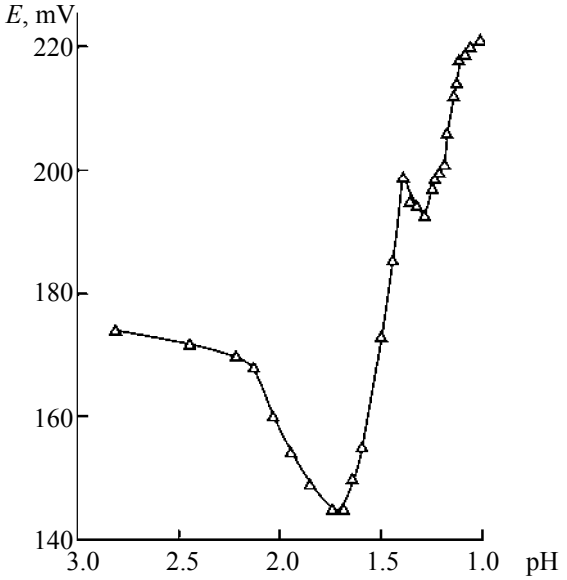


Fig. 5. Dependence of platinum electrode potential on pH of 0.1 M acetamide solution containing SO_2 at 293 K.

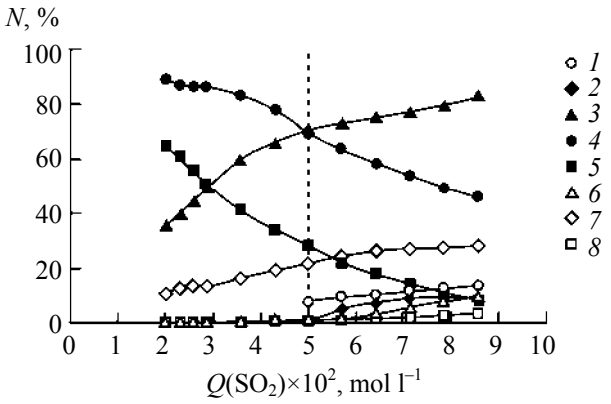


Fig. 6. Diagram of fractional distribution of different complexes in SO_2–CH_3CONH_2–H_2O system depending on $Q(SO_2)$ at 293 K. N is the molar fraction of complexes (*1, 2*) **II,** (*3, 4*) **III**, (*5*) CH_3CONH_2, (*6*) $S_2O_5^{2-}$, (*7*) $SO_2 \cdot H_2O$, (*8*) $HOSO_2^-$, against the total content of (*1, 4, 6–8*) sulfur and (*2, 3, 5*) nitrogen [3].

Analysis of data presented in Fig. 3 shows that platinum electrode potential of 0.1 M carbamide solution is higher than the potential of water solution with the same SO_2 content at 293 K. Introduction of acetamide in water solutions of sulfur(IV) oxide causes a decrease in the potential of the system at 293 K. Such behavior of potential of SO_2 water solutions is connected evidently with the complex formation.

It must be noted that the extremal points and plateau on the plots $E = f[Q(SO_2)]$ and $E = f(\text{pH})$ for 0.10 M acetamide solution (Figs. 3, 5) coincide. For 0.10 M carbamide solution the same dependence confirming complex formation in SO_2–Am–H_2O systems with different component ratio [3, 8] is characteristic.

As it was established recently [3] carbamide and acetamide in water solutions of sulfur(IV) oxide ($0.02 < Q(SO_2) < 0.05$ M) were capable of formation of anionic compounds **III** and **IV** according to Eqs. (6) and (7). Besides, acetamide at $0.05 < Q(SO_2) < 0.10$ M can also form anionic complexes **V** and **VI** according to Eqs. (8) and (9).

Considering that compounds **III** and **V** contain hydrosulfite ions, and the substances **IV** and **VI**, pyrosulfite ones, Nernst equation acquires the shape (15) at $0.02 < Q(SO_2) < 0.05$ M for water solutions of carbamide and acetamide. At $0.05 < Q(SO_2) < 0.10$ M for aqueous acetamide solutions Nernst equation looks like (16).

$$E = E^0 + \Theta\log([S_2O_5^{2-}]/[HOSO_2^-]) + \Theta\log[C(K_{IV})/C(K_{III})], \quad (15)$$

$$E = E^0 + \Theta\log([S_2O_5^{2-}]/[HOSO_2^-]) + \Theta\log[C(K_{IV})/C(K_{III})] + \Theta\log[C(K_{VI})/C(K_V)]. \quad (16)$$

Using the diagrams of partial distribution of different complexes formed in SO_2–CH_3CONH_2–H_2O system depending on $Q(SO_2)$ (Fig. 6 [3]) the concentration dependences $\log \alpha_1 = f[Q(SO_2)]$ and $\log \alpha_2 = f[Q(SO_2)]$ (Fig. 7) where $\alpha_1 = C(K_{IV})/C(K_{III})$ and $\alpha_2 = C(K_{VI})/C(K_V)$ were obtained.

Negative values of $\log \alpha_1$ and $\log \alpha_2$ (Fig. 7) show that in 0.10 M acetamide solution at 293 K mainly the

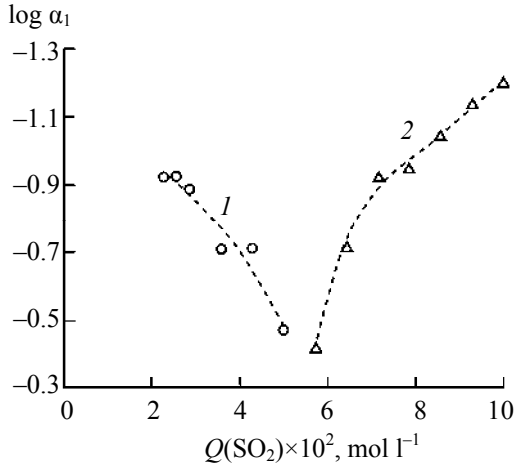


Fig. 7. Concentration dependence of the (*1*) α_1 and (*2*) α_2 values in 0.10 M acetamide solution at 293 K.

compounds **III** and **V** are formed. Formation of complexes **IV** and **VI** under these conditions is also possible. Hence, introduction of acetamide in water solutions of sulfur(IV) oxide at 293 K leads to the formation of anionic compounds with hydrosulfite and pyrosulfite ions. The concentration of complexes **III** and **V** formed by hydrosulfite ions several times exceeds the concentration of complexes **IV, VI** containing pyrosulfite ions, which causes the decrease in potential of the system.

The obtained values of quantitative relationships between α_1 and α_2 were used for calculation of microconstants β_{III}, β_{IV}, β_V, and β_{VI} for acetamide at 293 K.

$$\beta_V = C(K_V)/[Am][HOSO_2^-], \quad (17)$$

$$\beta_{VI} = C(K_{VI})/[Am]^2[S_2O_5^{2-}]. \quad (18)$$

Here $C(K_{II}) = [Am_2HOSO_2^-]$; $C(K_{IV}) = [Am_4{\cdot}S_2O_5^{2-}]$; $C(K_v) = [AmHOSO_2^-]$; and $C(K_{VI}) = Am_2{\cdot}S_2O_3^{2-}]$.

In [3] only the concentration dependences of macroconstants of complex formation as the Eq. (18) were presented. Its parameters for the compounds containing carbamide and acetamide are listed in the table, but the calculation of thermodynamic constants was not carried out.

$$p\beta_i = A_i + B_iQ(SO_2). \quad (19)$$

According to the definition the equilibrium constant of chemical reaction in the ideal solution of compounds taken in standard states is thermodynamical. Under real conditions it relates to the extremely dilutes solutions where the ion force and the concentration of substances in solutions tend to zero [9]. In the SO_2–Am–H_2O systems at $Q(SO_2) \to 0$ the value of ion force also tends to zero because amides are non-electrolytes [10], and under these conditions the value A in the Eq. (18) will correspond conventionally to the thermodynamic constant of complex formation β_i^T.

Using the above procedure the values of thermodynamic microconstants of complex formation β_{IV}^T and β_V^T were calculated. Their exponents are equal respectively to 10.21 and 3.75. Note that these values correspond to the exponents of thermodynamic microconstants which are as large as 10.39 and 3.58 respectively (see the table).

According to the data obtained the values of microconstants β_{IV} practically do not depend on the total SO_2 content in water solutions at 293 K, and log β_{IV} = 5.03±0.122 what is comparable with the value of thermodynamic macroconstant having the exponent equal to 5.57 (see the table).

Values of parameters in the Eq. (18) at 293 K [3]

Complex *i*	Am	A_i	B_i	R	*n*
$Q(SO_2)$ 0.02–0.05 mol l^{-1}					
III	carbamide	–4.40	44.68	0.985	9
III	acetamide	–5.57	12.63	0.964	7
IV	carbamide	–8.42	102.44	0.997	9
IV	acetamide	–10.39	43.85	0.982	7
$Q(SO_2)$ 0.05–0.10 mol l^{-1}					
II	carbamide	–1.29	–15.21	0.996	8
$Q(SO_2)$ 0.05–0.08 mol l^{-1}					
V	acetamide	–3.58	14.83	0.983	6
VI	acetamide	–6.45	34.68	0.985	6

Considering the above the following assumption is possible. Aqueous carbamide solutions as compared to water solutions with the same SO_2 content have higher potential (Fig. 4) caused probably by the fact that the concentration of anionic complexes of carbamide with pyrosulfite **IV** should be higher than the concentration of carbamide complexes **III** with hydrosulfite ions.

To confirm this hypothesis the values of quantitative relationships α_i (Fig. 8) were calculated according to the algorithm analogous to that used for the acetamide-containing systems. According to the results obtained (Fig. 8) the content of complex **IV** in the SO_2–NH_2CONH_2–H_2O system is several orders of magnitude higher than the content of compound **III**.

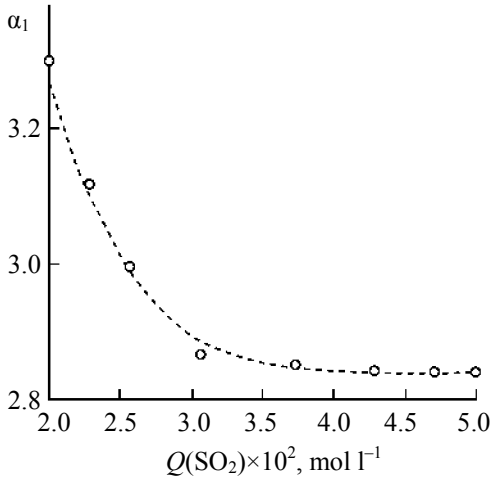


Fig. 8. Concentration dependence of α_i in 0.10 M carbamide solution at 293 K.

The obtained values of thermodynamic β_{IV}^{T} and β_{V}^{T} microconstants with the exponents equal to 4.00 and 8.20 are comparable with the values of the corresponding thermodynamic macroconstants (their exponents are 4.40 and 8.42) (see the table). Increase in the potential of 0.10 M carbamide solution with the increase in $Q(SO_2)$ ($0.05 < Q(SO_2) < 0.10$ M) is connected with the decrease in pH of the medium because the gradient of functional dependence $E = f(\text{pH})$ on this plot remains constant.

Hence, an approach is developed permitting to separate the contributions of hydrosulfite and pyrosulfite ions to the equilibria in the sulfur(IV) oxide–amide–water systems based on the potentiometric procedure of simultaneous mesuring of potentials of platinum and glass electrodes against the chlorosilver one.

EXPERIMENTAL

Gaseous 100% sulfur(IV) oxide and carbamide and acetamide of "pure" grade purified by double crystallization and subsequent drying in a vacuum desiccator according to [11] were used. Procedure of potentiometric experiment is described thoroughly in [12,13]. Measurements were carried out at 293 K.

In the course of the experiment SO_2 concentration was controlled iodometrically at the exit from the reaction solution for each 15–30 s [14]. Quantity of the consumed SO_2 was evaluated experimentally according to the Scheniger method [15].

Each experiment was repeated no less than three times. It was found that the statistic error of the experiment was no more than 2.5% at $Q(SO_2) > 0.01$ mol l^{-1} in all cases.

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