

ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

On Interaction of Sulfur(IV) Oxide with Aqueous Solutions of Ethanolamines

R. E. Khoma^{a,b}, A. A. Shestaka^a, and V. O. Gel'mbol'dt^{a,c}

^a Physico-Chemical Institute of Environmental and Human Protection, Odessa, Ukraine

^b Mechnikov National University, Odessa, Ukraine

^c Odessa National Medical University, Odessa, Ukraine

e-mail: r_khoma@farlep.net

Received July 3, 2011

Abstract—Potentio- and conductometric titration was used to study the interaction in sulfur(IV) oxide–ethanolamines–water systems in comparison with the previously obtained pH-metric data on how the corresponding onium sulfites, hydrosulfites, and pyrosulfites are formed. The ionic and molecular compositions of these solutions were calculated. Correlations between the characteristics of pH-metric titration curves of aqueous solutions of ethanolamines with sulfur(IV) oxide and the relative stability of onium sulfates were revealed.

DOI: 10.1134/S1070427212110067

This study proceeds with the systematic effort aimed to develop the theoretical foundations for catching of acid gases with organic bases [1]. It has been shown that ethanolamines (Am) and aqueous solutions of ethanolamines and their carboxylates are promising SiO₂ chemisorbents [2–6].

According to pH-metric titration data, the interaction in sulfur(IV) oxide–ethanolamines–water systems is accompanied by the formation of the corresponding onium sulfites (at a SO₂ : Am component ratio 1 : 2), hydrosulfites, and pyrosulfites (SO₂ : Am = 9 : 10) [6, 7]. The fact that the second peak in the differential pH-metric curves obtained in titration of aqueous solutions of Am with gaseous sulfur(IV) oxide does not correspond to the expected equimolar ratio (1 : 1) is due to the hydrosulfite–pyrosulfite equilibrium [6, 7]. A qualitative characterization of this equilibrium can be provided by redox potentiometry [8]. A successful experience of joint use of conductometry and redox potentiometry for determining the composition of the compounds being formed is known [9].

It should be noted that only data on the relative stability of ethanolammonium sulfites in aqueous

solutions were reported in [6]. There is no information about the ionic-molecular composition of sulfur(IV) oxide–ethanolamines–water systems.

A topical task in this context is to reveal existence regions of various sulfur-containing molecular and ionic forms in aqueous solutions, the nature of equilibria between these forms, and relative stabilities of the complexes being formed.

To study these aspects of the process of sulfur(IV) oxide chemisorption by aqueous solutions of organic bases, we examined the interaction of SO₂ with aqueous solutions of ethanolamines by independent methods of potentio- and conductometry and subjected previously obtained experimental data [6] to mathematical processing in order to determine the ionic-molecular composition of absorbing systems and to reveal correlations between characteristics of pH-metric titration curves and the relative stability of the complex salts being formed.

EXPERIMENTAL

As starting substances served reagents of for-syn-

thesis grade from Merck: monoethanolamine (MEA), methylmonoethanolamine (MMEA), diethanolamine (DEA), methyldiethanolamine (MDEA), and triethanolamine (TEA). The procedures of potentiometric and chronoconductometric titration were described in detail in [9, 10]. Potentiometric measurements were made with a pH-121 pH-meter. The measurement accuracy of the redox potential was ± 1 mV. Conductometric measurements were made with an Ekspert-002 conductometer (relative error $\leq 0.5\%$).

The measurements were made at 273–313 K. As model solutions served 0.1 M aqueous solutions of the Am specified above.

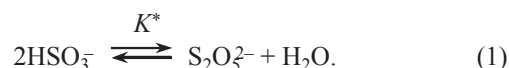
The amount of the reacting SO_2 was determined iodometrically [11] by the Schoniger method [12].

The curves of potentiometric and conductometric titration of 0.1 M solutions of Am with sulfur(IV) oxide are shown in Figs. 1–3. The integral potentiometric titration curves (Figs. 1 and 2a) show two jumps to which correspond dips in the differential curves (Fig. 4).

The nonmonotonic behavior (presence of breaks) of the potio- and conductometric dependences (Figs. 1–3) can be attributed to the formation of compounds with various compositions and structures between SO_2 , sulfur oxyanions, and ethanolamines in water [9].

It should be noted that the dip positions in the differential potentiometric curves (Fig. 4, Table 1) coincide to a first approximation with the peak positions in the corresponding pH-metric curves [6]. According to the data in Fig. 4 and Table 1, the first peak in the differential redox-metric titration curves corresponds to the molar ratio $\text{SO}_2 : \text{Am} \approx 1 : 2$ and to the formation of ethanolammonium sulfites $(\text{AmH})_2\text{SO}_3$ (**I**). The second extremum (dip) corresponds to an $\text{SO}_2 : \text{Am}$ ratio of 1 : 1, and its appearance is due to the formation of ethanolammonium hydrosulfites $(\text{AmH})\text{HSO}_3$ (**II**) and pyrosulfites $(\text{AmH})_2\text{S}_2\text{O}_5$ (**III**) [6]. The binding in these cation-anion complexes occurs due to the electrostatic interaction and ion-ion hydrogen bonds.

According to Raman spectroscopic and UV spectrophotometric data [13], the hydrosulfite ion is dimerized in an aqueous solution into the pyrosulfite ion:



The equilibrium constant K^* is 0.111–0.132. The $[\text{S}_2\text{O}_5^{2-}]/[\text{HSO}_3^-]$ ratio strongly depends on the pH of the medium and SO_2 concentration Q_{SO_2} [14], as well as on the possible presence of additional components (e.g., amides) [8].

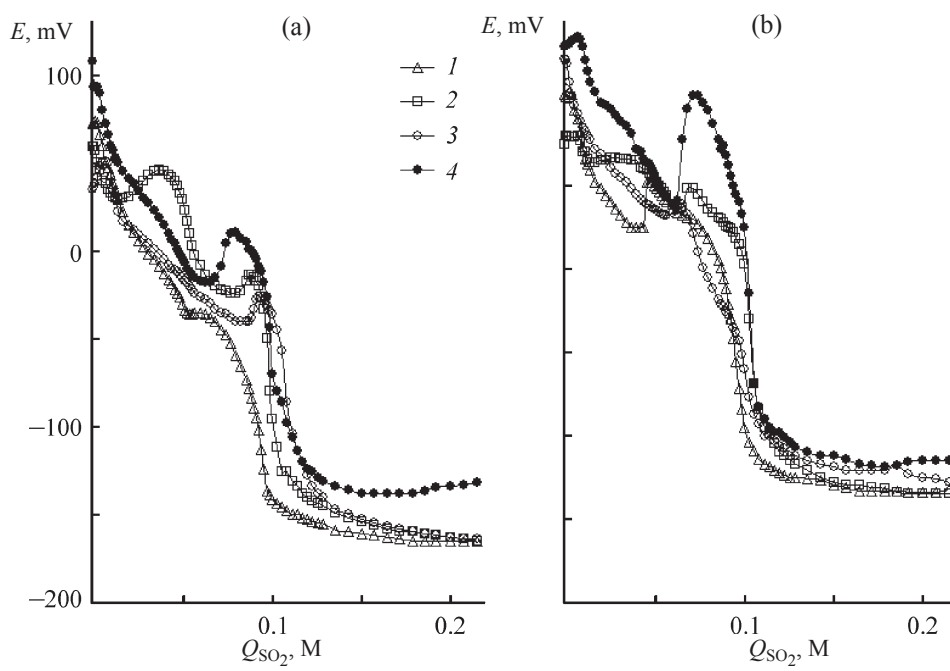
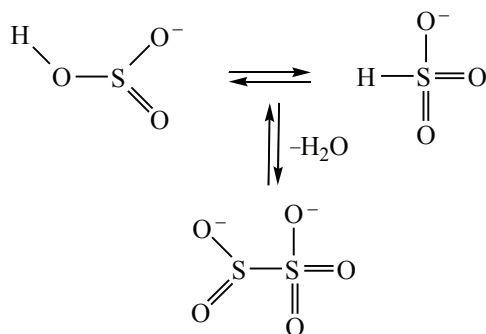


Fig. 1. Potentiometric titration curves of aqueous solutions of (1) MEA, (2) DEA, (3) TEA, and (4) MDEA with gaseous SO_2 at (a) 293 and (b) 313 K. $c_{\text{Am}} = 0.1$ M; the same for Fig. 3. (E) potential and (Q_{SO_2}) concentration; the same for Figs. 2 and 4.

The run of the redox-metric curves (Figs. 1 and 2a) can be understood as follows. Presence of ions containing sulfur in various oxidation states (4 in the case of sulfite and hydrosulfite; 4 and 6 for pyrosulfite) in the $\text{SO}_2\text{-H}_2\text{O}$ system changes the redox potential in the system [14]:



It was noted in [15] that two sulfur atoms in the structure of $\text{S}_2\text{O}_5^{2-}$ are nonequivalent (S–O bond orders dependent on the effective charge of a sulfur atom, are ~ 1.50 and ~ 1.65). Two kinds of S–O bonds having an intermediate nature (between single and double) were discussed in [16]. The structural formula of pyrosulfite acid (nonexistent in free form) [17], which can be used to judge about the structure of the $\text{S}_2\text{O}_5^{2-}$ ion, corresponds to that shown in the scheme.

The content of sulfonate ions in the $\text{SO}_2\text{-H}_2\text{O}$ system is negligible [13], and the above-described change in the

potential must be described by the Nernst equation

$$E = E^0 + \frac{2.3RT}{nF} \log \frac{[\text{S}_2\text{O}_5^{2-}]}{[\text{HOSO}_2^-]}, \quad (2)$$

here E and E^0 are the equilibrium and standard electrode potentials of the $\text{S}_2\text{O}_5^{2-}/\text{HOSO}_2^-$ pair, respectively; R , universal gas constant ($8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$); T , absolute temperature (K); n , change in the oxidation state of the S atom (2); and F , Faraday number (96485 C mol^{-1}).

The $\text{S(IV)} \rightarrow \text{S(VI)}$ transition in the forward reaction (1) is indicated by the calculated value (0.059 V) of the constant Θ [numerically equal to the pre-logarithmic factor $\Theta = (2.3RT)/F$ in the Nernst equation under the standard conditions] according to potentiometric data [14].

With consideration for the fact that compound **II** contains hydrosulfite ions and the protonated form of Am and there are pyrosulfite ions and protonated form of Am in compound **III**, the Nernst equation takes the form (3) at $0.05 \text{ M} \leq Q_{\text{SO}_2} \leq 0.10 \text{ M}$ for the $\text{SO}_2\text{-Am-H}_2\text{O}$ system:

$$E = E^0 + \frac{2.3RT}{nF} \log \frac{[\text{S}_2\text{O}_5^{2-}]}{[\text{HOSO}_2^-]} + \frac{2.3RT}{nF} \log \frac{c_K^{\text{III}}}{c_K^{\text{II}}}, \quad (3)$$

where c_K^{II} and c_K^{III} are the equilibrium concentrations

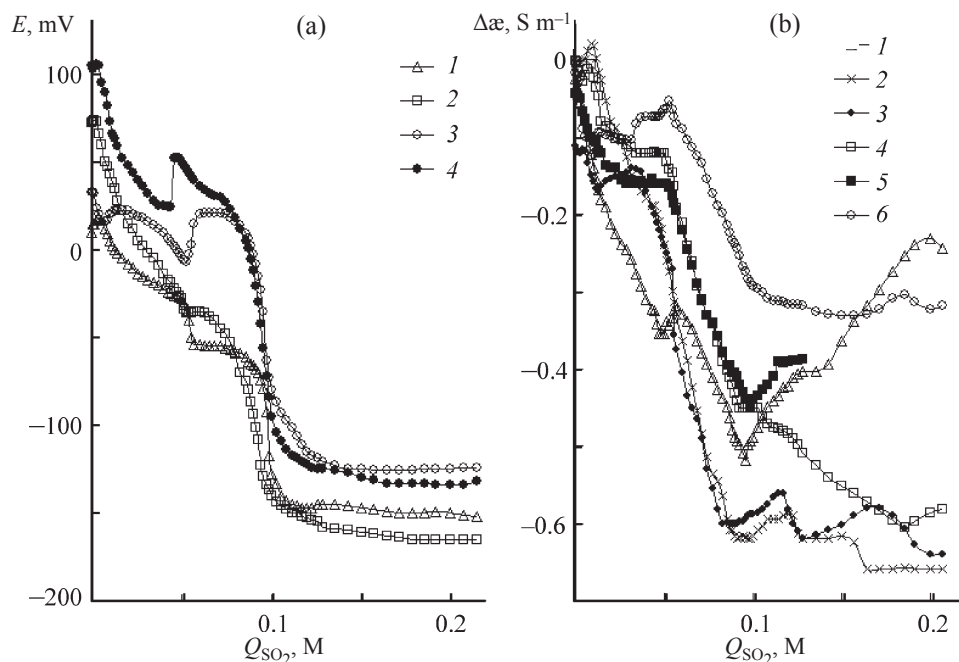


Fig. 2. (a) Potenti- and (b) conductometric titration curves of an aqueous solution of MEA with gaseous SO_2 . ($\Delta\kappa$) Electrical conductivity. T (K): (a) (1) 273, (2) 293, (3) 303, and (4) 313; (b) (1) 273, (2) 278, (3) 283, (4) 293, (5) 303, and (6) 313.

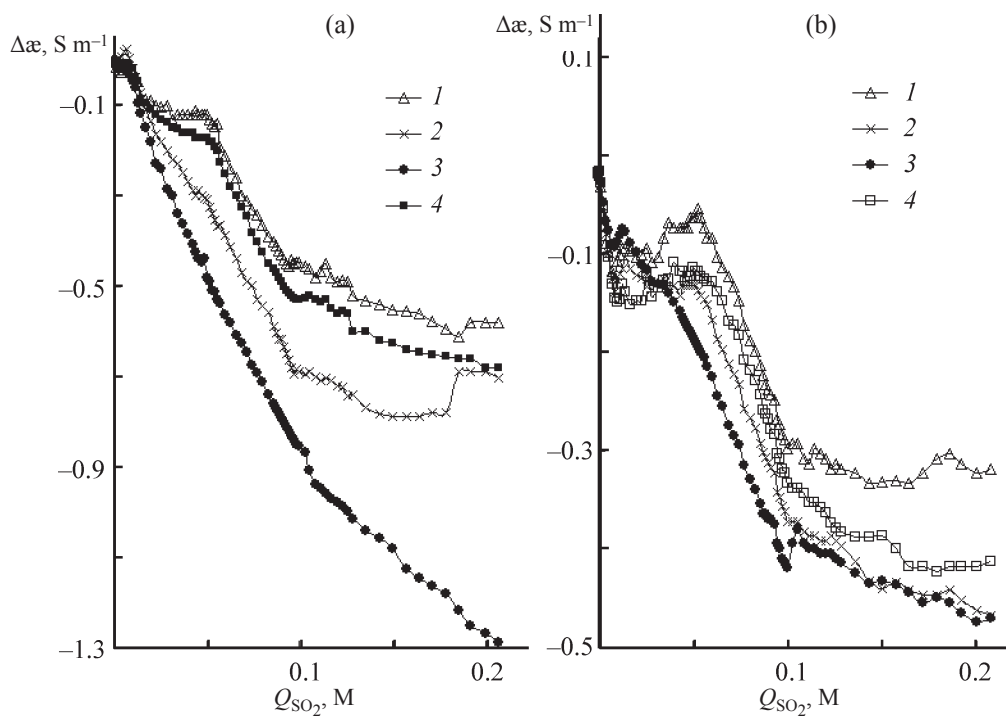


Fig. 3. Conductometric titration curves of aqueous solutions of (1) MEA, (2) DEA, (3) TEA, and (4) MDEA with gaseous SO_2 at (a) 293 and (b) 313 K. ($\Delta\kappa$) Electrical conductivity and (W_{SO_2}) concentration.

of compounds **II** and **III**, respectively.

With consideration for the data from [8], the fact that the redox potential of the system grows as Q_{SO_2} is raised from 0.05 to 0.10 M (pH < 7) (Figs. 1 and 2a) [6] is apparently due to the relative increase in the content

of pyrosulfite ions (or compound **III**), compared with hydrosulfite ions or compound **II**). By contrast, the decrease in E is due to the increase in the content of hydrosulfite ions and compound **II** relative to that of pyrosulfite ions and compound **III**, respectively.

The process of sulfite auto-oxidation in alkaline media [18] by the free-radical mechanism [19] does not occur with aminoalcohols involved. An experiment aimed to assess the oxidation resistance of sulfite compounds in air in sulfur(IV) oxide–ethanolamines–water systems demonstrated that no sulfate ions are formed during a long time (up to three years).

The concentration dependences $\Delta\kappa = f(Q_{\text{SO}_2})$ are shown in Figs. 2b and 3 [$\Delta\kappa = \kappa_3 - \kappa_2 - \kappa_1$, where κ_1 is the electrical conductivity (S m^{-1}) of the Am– H_2O system; κ_2 , conductivity (S cm^{-1}) of the SO_2 – H_2O system; and κ_3 , conductivity (S cm^{-1}) of the SO_2 –Am– H_2O system]. To the positions of extrema in the differential pH- and potentiometric curves (Figs. 1 and 2a) [6] correspond breaks in the $\Delta\kappa = f(Q_{\text{SO}_2})$ curves (Figs. 2b and 3).

The negative values of $\Delta\kappa$ (Figs. 2b and 3) are indicative of the formation of weakly dissociated complexes in SO_2 –Am– H_2O systems [20]. For the system with MEA, the decrease in conductivity, $\Delta\kappa$ (Fig. 2), with

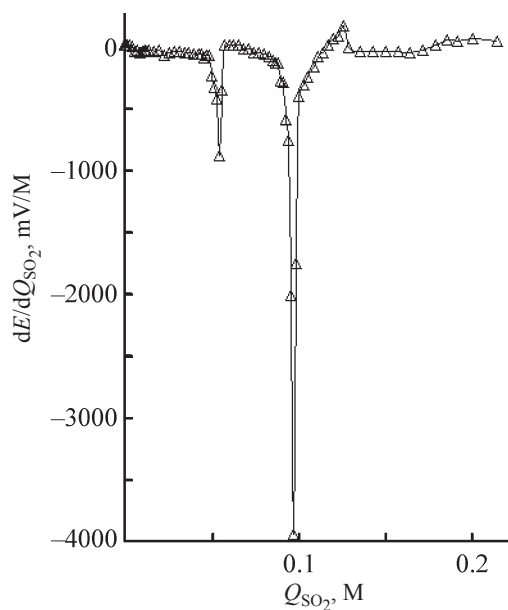


Fig. 4. Differential potentiometric titration curve of an aqueous solution of MEA with gaseous SO_2 at 273 K. $c_{\text{MEA}}^0 = 0.1$ M.

Table 1. Positions of dips in differential potentiometric titration curves of 0.1 M ethanolamine solutions with gaseous sulfur(IV) oxide

T, K	First dip			Second dip		
	$SO_2 : Am$	E, mV	$dE/dpQ(SO_2), mV$	$SO_2:Am$	E, mV	$dE/dpQ(SO_2), mV$
Monoethanolamine (pK_a 9.20)						
273	1.0 : 2.0	-50.0	-886.4	1.0 : 1.0	-128.0	-1760
293	1.0 : 2.0	-30.0	-333.6	1.0 : 1.0	-136.5	-1930
303	1.0 : 2.0	-4.0	-158.7	1.0 : 1.0	-63.0	-4351
313	1.0:2.0	50.0	-158.8	1.0 : 1.0	-72.0	-2490
Diethanolamine (pK_a 8.80)						
293	1.0 : 1.8	-3	-621	1.0 : 1.0	-80	-4732
313	1.0 : 1.8	38	-195	1.0 : 1.0	-69	-3277
<i>N</i> -Methyldiethanolamine (pK_a 8.50)						
293	1.0 : 2.0	-4	-263	1.0 : 1.0	-70	-4160
313	1.0 : 2.0	57	-270	1.0 : 1.0	25	-4538
Triethanolamine (pK_a 7.80)						
293	1.0 : 1.8	-15	-182	1.0 : 1.0	-98	-2503
313	1.0 : 1.8	32	-88	1.0 : 1.0	-60	-1440

the sulfur(IV) dioxide content increasing to 0.050 M at 273 and 278 K (curves 1 and 2) is due to the formation of monoethanolammonium sulfite, and that at $0.057 M < Q_{SO_2} < 0.100 M$ at 273 (curve 1) and $0.050 M < Q_{SO_2} < 0.100 M$ at 278 K (curve 2), to the formation of monoethanolammonium hydro- and pyrosulfite. At other temperatures used in the experiment (283, 293, 303, and 313 K) (Fig. 2b, curves 3–6), the formation of these weakly dissociated compounds or lower mobility ions is accompanied by a decrease in $\Delta\epsilon$. The portions of the curves in Figs. 2b and 3, for which an increase in $\Delta\epsilon$ is observed, correspond to accumulation of compounds characterized by a increased degree of dissociation or mobility [15]. The plateaus in the $\Delta\epsilon = f(Q_{SO_2})$ curves (Figs. 2b and 3) are observed because the accumulation of sulfur(IV) oxide in the SO_2-Am-H_2O systems is not accompanied by any change in the degree of dissociation of the onium complexes being formed or in their mobility.

The peak positions in the differential pH-metric titration curves for MEA, DEA, MDEA, and TEA [6] coincide to a first approximation with the dip positions in the

differential potentiometric curves (Table 1) and those of the breaks in the $\Delta\epsilon = f(Q_{SO_2})$ curves (Figs. 2b and 3).

It is impossible to obtain any unequivocal information about the composition of the compounds being formed from the run of the integral potentiometric curves in (Figs. 1 and 2a), despite their being characterized by certain extrema. The composition of onium sulfates, hydrosulfites, and pyrosulfites being formed is determined by the peak positions in the differential pH-metric titration curves and dip positions in the differential potentiometric curves. It is noteworthy that the conductometric titration data [$\Delta\epsilon = f(Q_{SO_2})$ dependences] on the whole agree with the results furnished by potentiometry.

Noteworthy are the deviation of onium sulfites from stoichiometry (1 : 2) in redox-metric experiments and that of hydrosulfites and pyrosulfites (1 : 1) in pH-metric experiments. In the second case, deviations from the expected composition of the complexes may be due to the attainment of equilibrium (1), which apparently changes the ionic strength of the solution (no supporting electrolytes are used in this study). This results in that the activity of H^+ ions noticeably changes upon

a comparatively small change in the concentration of hydrosulfite and pyrosulfite ions.

Thus, to the extrema in the differential potentiometric curves of titration of aqueous solutions of triethanolamines with gaseous sulfur(IV) oxide correspond breaks in the conductometric curves $\Delta\kappa = f(Q_{\text{SO}_2})$, in agreement with the data of [9]. The use of pH-, potentiometric, and conductometry, whose data confirm and supplement each other, makes it possible to obtain consistent and objective information about the composition of onium compounds formed in sulfur(IV) oxide–ethanolamines–water systems [7].

The equilibria in these systems were calculated using the experimental data [6], as described in [9]. Using the results obtained, we constructed component composition diagrams for the systems under study. Figure 5 shows the fraction distribution diagram for various forms produced in the $\text{SO}_2\text{--HOCH}_2\text{CH}_2\text{NH}_2\text{--H}_2\text{O}$ system, depending on the total content of sulfur(IV) oxide at 293 K. With increasing content of SO_2 in solution (from 5×10^{-3} to 5×10^{-2} M), the molar fractions of onium sulfite (Fig. 5, curve 8) and ethanolammonium cation (curve 6) grow with respect to the total content of nitrogen due to the decrease in pH and to the binding of free MEA (curve 7) into the forms specified. Simultaneously, the relative content of sulfite anions increases (Fig. 5, curve 3) due to the dissociation of onium sulfite: changes in the molar fractions of $(\text{HOCH}_2\text{CH}_2\text{NH}_3)_2\text{SO}_3$ (curve 5) and SO_3^{2-} relative to the total content of sulfur are antipathetic. The molar fractions of SO_3^{2-} (Fig. 5, curve 3)

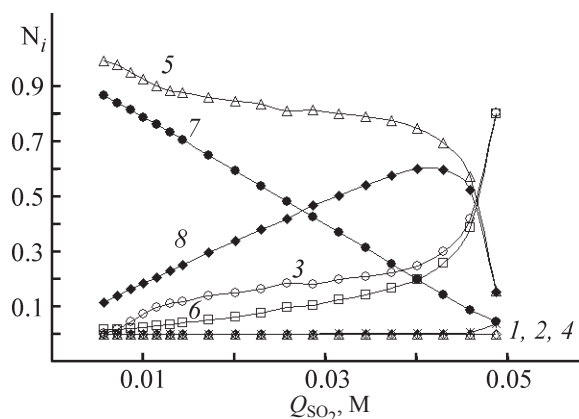
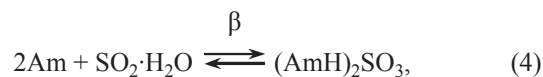


Fig. 5. Dependence of the relative amounts of various forms of the components in the $\text{SO}_2\text{--NH}_2\text{CH}_2\text{CH}_2\text{OH--H}_2\text{O}$ system on Q_{SO_2} at 293 K. (N_i) Molar fraction. $N_1 = [\text{H}_2\text{O}\cdot\text{SO}_2]/Q_{\text{SO}_2}$, $N_2 = [\text{HSO}_3^-]/Q_{\text{SO}_2}$, $N_3 = [\text{SO}_3^{2-}]/Q_{\text{SO}_2}$, $N_4 = (2[\text{S}_2\text{O}_5^{2-}])/Q_{\text{SO}_2}$, $N_5 = [(\text{HOCH}_2\text{CH}_2\text{NH}_3)_2\text{SO}_3]/Q_{\text{SO}_2}$, $N_6 = [\text{HOCH}_2\text{CH}_2\text{NH}_3^+]/Q_{\text{Am}}$, $N_7 = [\text{HOCH}_2\text{CH}_2\text{NH}_2]/Q_{\text{Am}}$, $N_8 = [(\text{HOCH}_2\text{CH}_2\text{NH}_3)_2\text{SO}_3]/Q_{\text{Am}}$.

and $\text{HOCH}_2\text{CH}_2\text{NH}_3^+$ grow symbately. In the Q_{SO_2} concentration range specified above, the content of $\text{SO}_2\cdot\text{H}_2\text{O}$, HSO_3^- , $\text{S}_2\text{O}_5^{2-}$ (Fig. 5; curves 1, 2, and 4) is negligible. The fraction distribution diagrams for various forms in systems with MEA at other temperatures and with other ethanolamines are similar.

The dependences of the negative decimal logarithm of the complexation constants of ethanolammonium sulfites [Eq. (4)] on the ionic strength μ (M) of solutions [21] are linear (Fig. 6) and are described by Eq. (5):



$$p\beta_i = A_i + B_i\mu. \quad (5)$$

The coefficients of Eq. (5) are listed in Table 2.

According to the definition [21], the coefficient A_i in Eq. (5) is a negative decimal logarithm of the thermodynamic complexation constant β . The ethanolammonium sulfates can be arranged in order of decreasing stability in aqueous solutions (Table 2, values of A_i) as follows: MMEA (9.60) > MEA (9.20) > DEA (8.88) > MDEA (8.50) > TEA (7.80).

This order of the ligands is correlated with their basicity. The values in parentheses are those of pK_a , which is the negative decimal logarithm of the ionization constant of the protonated form of a base:



For the sulfite complexes, the variation of the stability

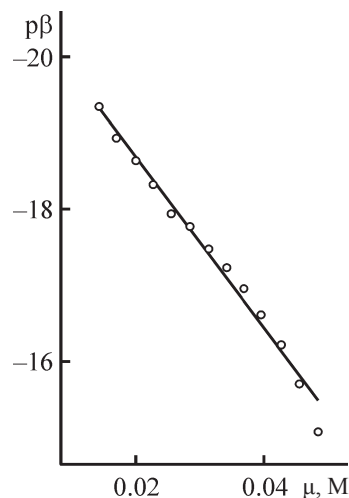


Fig. 6. Dependence of $p\beta$ on the ionic strength μ in the $\text{SO}_2\text{--NH}_2\text{CH}_2\text{CH}_2\text{OH--H}_2\text{O}$ system at 293 K.

and that of temperature are antipate (Table 2) [6].

With increasing total content of SO₂ in the sulfur(IV) oxide–ethanolamines–water systems, the ionic strength grows due to the accumulation of sulfite anions and ethanolammonium cations. In the process, the concentration constants β decrease, which is indicated by the values of B_i in Table 2 (>100). For the systems with MEA, the concentration component B_i of the constant β decreases with increasing temperature.

A comparison of pH-metric titration characteristics: height of the portion of the pH-metric titration curve between the mid-point of the titration jump and its end ($\Delta\text{pH}_{1/2}$) (Fig. 7a), peak value in the differential curve ($\text{dpH}/\text{dp}Q_{\text{SO}_2}$), and area under the portion of the differential curve between the points of the corresponding peak and the following dip in the curve ($S_{1/2}$) (Fig. 7b) with the stability β of the onium sulfates revealed the following correlations (Fig. 8, Table 3).

According to the data obtained (Table 3), the peak

Table 2. Values of the coefficients A_i and B_i in Eq. (5) for ethanolammonium sulfites (r^2 is the correlation coefficient between $\text{p}\beta$ and μr^2 , and N is the number of points)

T, K	$A_i \pm \Delta A_i$	$B_i \pm \Delta B_i$	r^2	N
<i>N</i> -Methylmonoethanolamine ($\text{p}K_a$ 9.60)				
293	-20.43 ± 0.09	100.4 ± 6.2	0.998	12
313	-17.37 ± 0.07	162.8 ± 7.3	0.994	12
Monoethanolamine ($\text{p}K_a$ 9.20)				
283	-20.65 ± 0.08	198.5 ± 6.8	0.998	14
288	-20.31 ± 0.10	193.6 ± 6.5	0.992	14
293	-19.74 ± 0.11	114.5 ± 7.5	0.985	13
303	-18.84 ± 0.12	132.6 ± 7.3	0.984	13
313	-16.63 ± 0.12	117.5 ± 7.1	0.978	14
Diethanolamine ($\text{p}K_a$ 8.80)				
293	-17.38 ± 0.07	143.5 ± 6.5	0.998	13
313	-13.00 ± 0.15	48.9 ± 5.1	0.941	8
<i>N</i> -Methyldiethanolamine ($\text{p}K_a$ 8.50)				
293	-16.28 ± 0.07	136.2 ± 6.3	0.998	14
Triethanolamine ($\text{p}K_a$ 7.80)				
293	-15.23 ± 0.09	190.3 ± 9.2	0.964	13
313	-13.98 ± 0.17	200.2 ± 9.8	0.935	13

values in the differential titration curves vary symbately with the stability characteristics $\text{p}\beta$ of the sulfite compounds; no relationship of this kind is observed between the peak areas in the differential titration curves and $\text{p}\beta$ (Table 3).

The fact that the peak values in the differential titration curves vary symbately with the stability of the onium sulfates being formed and with the basicity $\text{p}K_a$ suggests that, presumably, Coulomb interactions substantially contribute to the stabilization of these ion complexes.

In the given case, the differential curve of the pH-metric acid-base titration is asymmetric near its extrema,

Table 3. Parameters describing the relative stability of ethanolammonium sulfates in aqueous solutions

T, K	$\text{dpH}/\text{dp}Q_{\text{SO}_2}$	$\text{p}\beta$	$\Delta G, \text{kJ mol}^{-1}$	Peak area $S_{1/2}$	$\Delta\text{pH}_{1/2}$
	data of [6]				
<i>N</i> -Methylmonoethanolamine ($\text{p}K_a$ 9.60)					
293	39.6	-20.43	-114.54	0.223	1.64
313	15.5	-17.37	-104.03	0.146	0.98
Monoethanolamine ($\text{p}K_a$ 9.20)					
283	37.3	-20.65	-111.82	0.315	2.16
288	26.7	-20.31	-111.92	0.205	1.32
293	22.8	-19.74	-110.67	0.180	1.19
303	20.2	-18.84	-109.23	0.155	1.02
313	15.1	-16.63	-101.63	0.138	1.01
Diethanolamine ($\text{p}K_a$ 8.80)					
293	15.3	-17.38	-97.44	0.145	1.03
313	7.71	-13.00	-77.86	0.080	0.61
<i>N</i> -Methyldiethanolamine ($\text{p}K_a$ 8.50)					
293	9.53	-16.28	-91.27	0.137	0.98
Triethanolamine ($\text{p}K_a$ 7.80)					
293	14.8	-15.23	-85.39	0.116	0.75
313	3.85	-13.98	-83.73	0.087	0.66

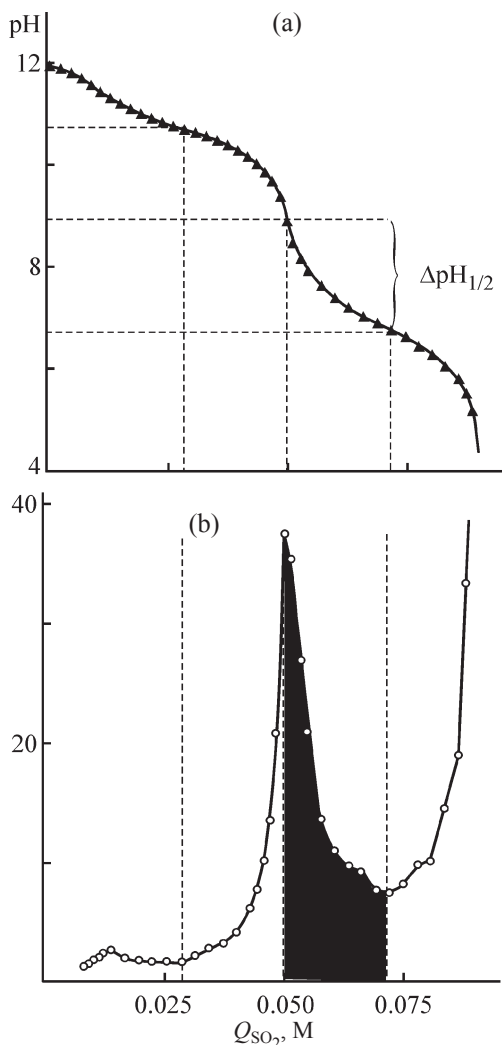


Fig. 7. (a) Integral and (b) differential pH-metric titration curves of an aqueous solution of MEA with gaseous SO_2 [7]. $c_{\text{MEA}}^0 = 0.1 \text{ M}$, $T = 283 \text{ K}$. (Q_{SO_2}) Concentration.

namely, peaks (Fig. 7b). An analysis of the experimental data [6] did not reveal any mutual correlation between the total surface area under the differential pH-metric titration curve and the complexation constant β . Possibly, this is due to the hydrolytic processes occurring in the system, which has been noted previously [6].

At the same time the run of the dependences we obtained (Fig. 8) shows that, with the stability of onium sulfites of ethanolamines increasing within the ranges $13.00 \leq -p\beta \leq 16.28$ and $18.84 \leq -p\beta \leq 20.65$, the pH-metric curve characteristics $\Delta\text{pH}_{1/2}$ and $S_{1/2}$ grow symbately. Within the range $16.28 \leq -p\beta \leq 18.84$, no noticeable changes in $\Delta\text{pH}_{1/2}$ and $S_{1/2}$ are observed. These data (Fig. 8) can be used to develop a procedure for proximate assessment of the relative stability of onium sulfites.

CONCLUSIONS

(1) Redox potentiometry and conductometry were used to confirm previously obtained pH-metric data on the composition of products formed in chemisorption of sulfur(IV) oxide by aqueous solutions of monoethanolamine, *N*-methylmonoethanolamine, diethanolamine, triethanolamine, and *N*-methyldiethanolamine at 273–313 K. This interaction is accompanied by the formation of sulfites, hydrosulfites, and pyrosulfites of the corresponding ethanolammonium cations, with the stability of the sulfites decreasing with increasing temperature.

(2) It was shown that the stability of the sulfite complexes varies symbately with the $\text{p}K_a$ values of ethanolamines.

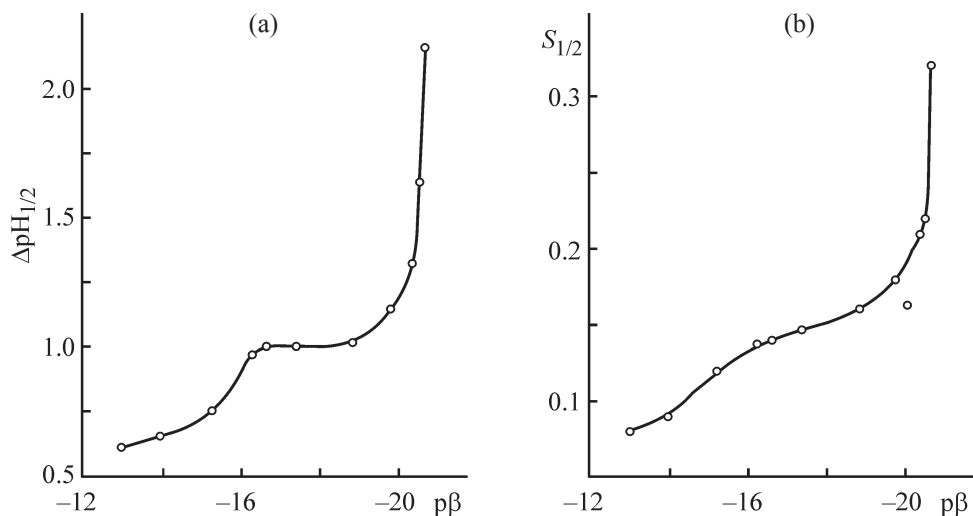


Fig. 8. Dependences of (a) $\Delta\text{pH}_{1/2}$ and (b) $S_{1/2}$ on the stability β of onium sulfites.

(3) The molecular and ionic composition of sulfur(IV) oxide–ethanolamines–water systems was calculated using previously obtained pH-metric data.

(4) It was demonstrated that the revealed mutual correlations between the areas under the differential pH-metric curves of titration of aqueous solutions with sulfur(IV) oxide, on the one hand, and the stabilities of onium sulfates, on the other, enable a qualitative estimate of the efficiency of SO₂ binding into onium sulfates, without making additional calculations on the basis of pH-metric titration data. This circumstance may prove of use in development of methods for sanitary purification of air to remove sulfur(IV) oxide, regeneration of chemisorbents, and utilization of sorption products.

REFERENCES

- Ennan, A.A., Coordination Compounds of Silicon Tetrafluoride and Hydrofluorides of Nitrogen-containing Bases, *Doctoral (Chem.) Sci. Dissertation*, Odessa, 1975.
- US Patent 3904735.
- US Patent 4363791.
- Khoma, R.E., Nikitin, V.I., and Gavrilenko, M.I., *Vestn. Odessa Nats. Univ., Khim.*, 2000, vol. 5, no. 5, pp. 39–44.
- Yavors'kii, V.T., Savchuk, L.V., Bert, E.S., and Olenich, R.R., *SborniknauchnykhtrudovMezhdunarodnoi nauchno–tekhnikeskoi konferentsii "Sovremennye problemy khimicheskoi tekhnologii neorganicheskikh veshchestv"* (Coll. of Sci. Works of Int. Sci.-Techn. Conf. "Modern Problems of Chemical Technology of Inorganic Substances"), Odessa, 2001, vol. 2, pp. 312–315.
- Khoma, R.E., Shestaka, A.A., and Gel'mbol'dt, V.O., *Vopr. Khim. Khim. Tekhnol.*, 2009, no. 5, pp. 86–89.
- Khoma, R.E., Shestaka, O.O., and Gel'mbol'dt, V.O., *Vestn. Odessa Nats. Univ., Khim.*, 2010, vol. 15, no. 12, pp. 34–44.
- Khoma, R.E. and Gavrilenko, M.I., *Zh. Obshch. Khim.*, 2010, vol. 80, no. 5, pp. 729–734.
- Khoma, R.E., Shestaka, A.A., Sokhranenko, G.P., et al., *Zh. Prikl. Khim.*, 2011, vol. 84, no. 1, pp. 18–24.
- Khoma, R.E., Gavrilenko, M.I., and Nikitin, V.I., *Zh. Obshch. Khim.*, 2005, vol. 75, no. 5, pp. 771–777.
- Kel'man, I.N., Brutskus, E.B., and Osherovich, R.Kh., *Metody analiza pri kontrole proizvodstva sernoi kisloty i fosfornykh udobrenii* (Analytical Methods for Monitoring of Manufacture of Sulfuric Acid and Phosphate Fertilizers), Moscow: Khimiya, 1965.
- Klimova, V.A., *Osnovnye metody analiza organicheskikh soedinenii* (Basic Methods for Analysis of Organic Compounds), Moscow: Khimiya, 1975.
- Horner, D.A. and Connick, R.E., *Inorg. Chem.*, 1986, vol. 25, no. 14, pp. 2414–2417.
- Romanenko, S.A., *Component Composition of Aqueous Solutions of Sulfur(IV) Oxide*, *Cand. Sci. Dissertation*, Leningrad, 1986.
- Baggio, S., *Acta Crystal., Section B: Struct. Crystallogr. Crystal Chem.*, 1971, vol. B27, no. 3, pp. 517–522.
- Wiberg, E., Wiberg, N., and Holleman, A.F., *Inorganic Chemistry*, Berlin, 2001, pp. 540–541.
- Cotton, F.A., Wilkinson, G.M., Carlos, A., and Bochmann, M., *Advanced Inorganic Chemistry*, John Wiley & Sons, 1999.
- Travina, O.A., Kozlov, Yu.N., Purmal', A.P., and Travin, S.O., *Kinet. Kataliz*, 1997, vol. 38, no. 2, pp. 242–246.
- Ermakov, A.N., Poskrebyshev, G.A., and Purmal', A.P., *Kinet. Kataliz*, 1997, vol. 38, no. 3, pp. 325–338.
- Khudyakova, T.A. and Kreshkov, A.P., *Konduktometricheskii metod analiza* (Conductometric Analysis), Moscow: Vysshaya Shkola, 1975.
- Hartley, F.R., Burges, C., and Alcock, R.M., *Solution Equilibria*, New York: Ellis Horwood, 1980.