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Complex Formation of Sulfur(IV) Oxide with Ethylenediamine and Its Derivatives in Water

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Abstract—Data of potentiometric, redox, and conductometric studies of interactions in the sulfur(IV) oxide–ethylenediamine (or its analogs)–water systems, being in fair agreement, have showed the formation of onium sulfites, hydrosulfites, and pyrosulfites. The absorbance capacity of aqueous solutions of ethylenediamines with respect to sulfur dioxide depends on the amino groups amount. Ion and molecular compositions of the studied solutions have been computed, and the relative stability of onium sulfites of ethylenediamine and piperazine has been estimated.

Keywords: sulfur(IV) oxide, ethylenediamine, aqueous solution, onium salt

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Earlier studies of the Am–H_2O systems (Am for aminoethanol and its derivatives, hexamethylenediamine, or hexamethylenetetramine) [1–9] have demonstrated that chemosorption of sulfur(IV) oxide with aqueous solutions of N,O-containing organic bases results in onium sulfites, hydrosulfitesand pyrosulfites of protonated forms of the mentioned amines as the major interaction products detected by electrochemical methods (potentiometry, redoxometry, and conductometry) [2–6, 8] as well as isolated in the pure form [7, 9]. Relative stability of the products has been estimated [2, 3, 6, 8].

Ethylenediaminea structural analog of aminoethanol [10]and its derivatives have been recognized as chemosorbents of SO_2 in aqueous solutions [11–14] acting as containers for safe storage and transportation of this gas [15].

Sulfur dioxide forms a monohydrate [Eq. (1)] upon dissolution in water, its dissociation products being hydrosulfite, pyrosulfite, and sulfite ions [Eqs. (2)–(4)] [16].

$$SO_2 + H_2O \rightarrow SO_2{\cdot}H_2O, \quad (1)$$

$$SO_2{\cdot}H_2O \overset{K_1}{\rightleftarrows} H^+ + HSO_3^-, \quad (2)$$

$$2HSO_3^- \overset{K^*}{\rightleftarrows} S_2O_5^{2-} + H_2O, \quad (3)$$

$$HSO_3^- \overset{K_2}{\rightleftarrows} H^+ + SO_3^{2-}. \quad (4)$$

Mono- [Eq. (5)] and diprotonation [Eq. (6)] occurs in aqueous solutions of diamines.

$$Am + H^+ \rightleftarrows AmH^+, K_{a2} = ([Am]{\cdot}[H^+])/[AmH^+], \quad (5)$$

$$AmH^+ + H^+ \rightleftarrows \{AmH_2\}^{2+},$$

$$K_{a1} = ([AmH^+]{\cdot}[H^+])/[\{AmH_2\}^{2+}]. \quad (6)$$

As $K_{a1} >> K_{a2}$, the stepwise formation of onium sulfites, hydrosulfites, and pyrosulfites can be expected.

The nitrogen atoms are not generally equivalent with respect to protonation, undergoing a stepwise protonation [17]. Let us assign H_2NR to the first amino group and H_2NR' to the second one. The stepwise formation of onium sulfites can be described with Eqs. (7) and (8), whereas Eqs. (9) and (10) reflect the hydrosulfites and sulfites formation.

$$2H_2NR + 2H_2NR' + SO_2{\cdot}H_2O \rightleftarrows (H_3NR)_2SO_3 + 2H_2NR', \quad (7)$$

$$(H_3NR)_2SO_3 + 2H_2NR' + SO_2{\cdot}H_2O \rightleftarrows (H_3NR)_2SO_3 + (H_3NR')_2SO_3, \quad (8)$$

$$(H_3NR)_2SO_3 + (H_3NR')_2SO_3 + SO_2{\cdot}H_2O \rightleftarrows 2(H_3NR')HSO_3 + (H_3NR')_2SO_3, \quad (9)$$

$$2(H_3NR)HSO_3 + (H_3NR')_2SO_3 + SO_2{\cdot}H_2O \rightleftarrows 2(H_3NR)HSO_3 + 2(H_3NR')HSO_3. \quad (10)$$

To the best of our knowledge the composition and relative stability of the formed products have not been

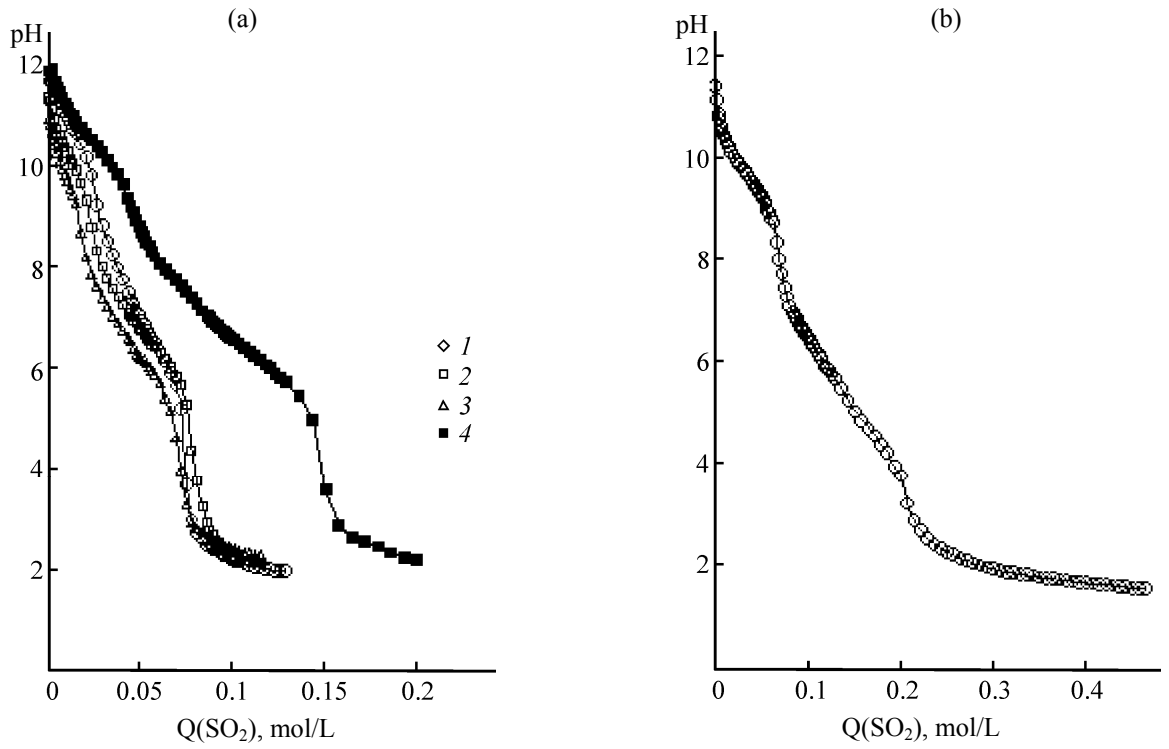

Fig. 1. Curves of potentiometry titration of aqueous solutions of ethylenediamine (a) and diethylenetriamine (b) with gaseous SO_2. c^0_{Am}, mol/L: 0.05 (*1–3*), 0.10 (*4, 5*); *T*, K: 283 (*1*), 293 (*2, 4, 5*), 303 (*3*).

reported so far. In order to check the correctness of the above-stated views we herein report on determination of composition of the formed compounds and the estimation of their relative stability by the independent methods of potentiometry, redox potential measurements, and conductometry. Ethylenediamine, *N*,*N*,*N*',*N*'-tetramethylethylenediamine, piperazine, diethylenetriamine, and polyethylenepolyamine were the tested bases.

Curves of potentiometric and conductometric titration of the aqueous solutions of amines with sulfur dioxide are shown in Figs. 1–5. The integral potentiometric titration curves (Figs. 1 and 2) contained two steps with the two maxima in the differential titration curves (see, for, example, Fig. 3). Hence, the amines behavior was similar to that of animoethanol, hexamethylenetetramine, and hexamethylenediamine [2–4, 6].

In the case of ethylenediamine the positions of the first maxima on the differential potentiometric titration curves (Fig. 3a and Table 1) were identical and corresponded to the SO_2 : amine molar ratio of 1.0 : 2.0 (pH 8.5–9.5 over the whole studied ranges of the amine concentration and temperature), thus confirming the formation of the $[H_2NCH_2CH_2NH_3]_2(SO_3)$ salt [Eq. (7)]. The second maxima on the differential titration curves were observed at the SO_2 : amine ratio of 3.0 : 2.0 (Fig. 3a). Their manifestation was due to the formation of the mixed sulfite-hydrosulfite salt

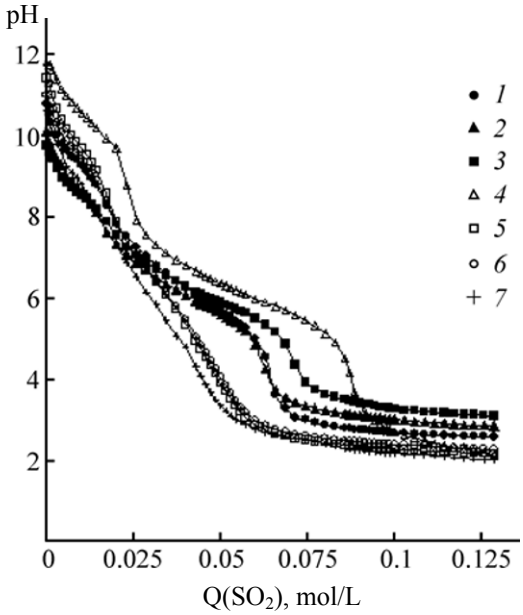

Fig. 2. Curves of potentiometry titration of aqueous solutions of *N*,*N*,*N*'*N*'-tetramethylethylenediamine (*1–3*), piperazine (*4*), and polyethylenepolyamine (*5–7*) (c^0_{Am} 0.1 eq/L) with gaseous SO_2 at 283 (*1*, *5*), 293 (*2*, *4*, *6*), and 303 K (*3*, *7*).

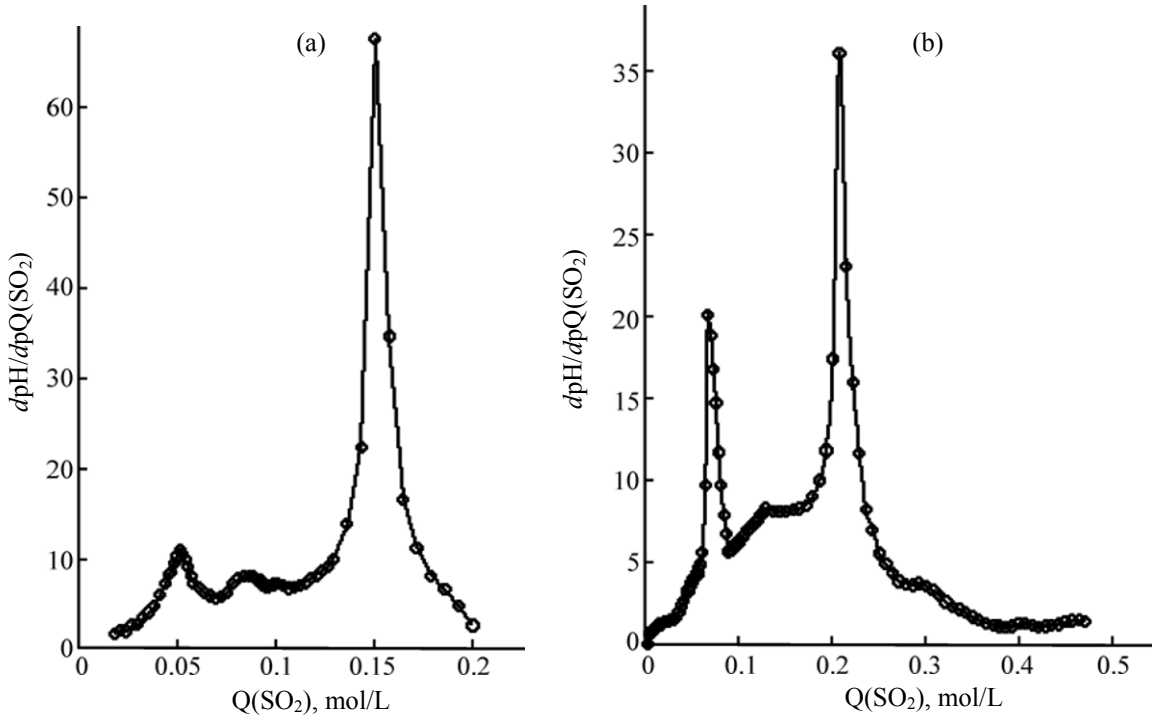

Fig. 3. Differential curves of potentiometry titration of aqueous solutions of ethylenediamine (a) and diethylenetriamine (b) with gaseous SO_2 at 293 K, c^0_{Am} 0.1 mol/L.

Table 1. Parameters of maximum at differential curves (Figs. 1–3) of potentiometry titration of solutions of ethylenediamine and its derivatives with gaseous sulfur(IV) oxide

c^0_{Am}, mol/L	T, K	Effect I		Effect II	
		SO_2 : Am	pH/pQ(SO_2)	SO_2 : Am	pH/pQ(SO_2)
Ethylenediamine (pK_a^1 7.49, pK_a^2 10.17 [17])					
0.10	303	1.0 : 2.0	18.61	3.0 : 2.0	51.9
0.05	283	1.0 : 2.0	11.73	3.0 : 2.0	91.0
0.05	293	1.0 : 2.0	9.58	3.0 : 2.0	57.0
0.05	303	1.0 : 2.0	7.32	3.0 : 2.0	39.3
N,N,N′,N′-Tetramethylethylenediamine (pK_a^1 6.32, pK_a^2 9.44 [17])					
0.05	283	1.0 : 2.0	6.87	3.0 : 2.0	47.7
0.05	293	1.0 : 2.0	6.06	3.0 : 2.0	29.7
0.05	303	1.0 : 2.0	5.00	3.0 : 2.0	28.8
Piperazine (pK_a^1 5.35, pK_a^2 9.73[18])					
0.10	293	1.0 : 2.0	19.02	3.0 : 2.0	57.0
0.05	293	1.0 : 2.0	16.81	3.0 : 2.0	65.1
Diethylenetetramine (pK_a^1 4.42, pK_a^2 9.21, pK_a^3 10.02 [19])					
0.10	293	2.0 : 3.0	20.20	2.0 : 1.0	36.1
Polyethylenepolyamine[a]					
0.10	283	1.0 : 5.0	10.45	1.0 : 2.0	18.3
0.10	293	1.0 : 5.0	8.66	1.0 : 2.0	26.6

[a] The S : N ratio.

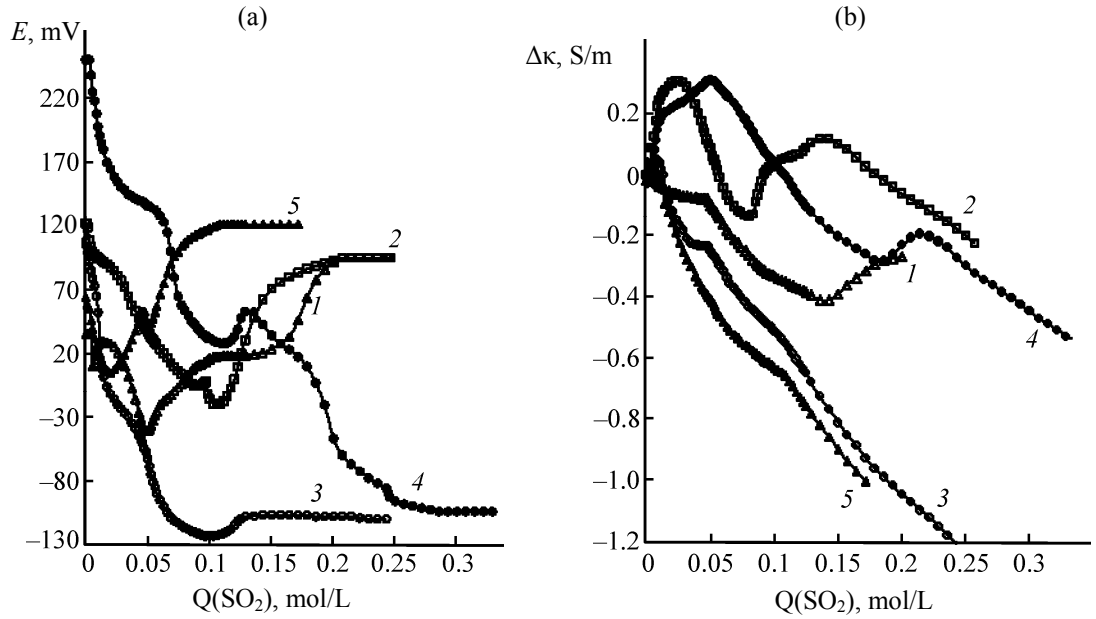

Fig. 4. Curves of redox (a) and conductometric (b) titration of aqueous solutions of ethylenediamine (*1*), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (*2*), piperazine (*3*), diethylenetriamine (*4*), and polyethylenepolyamine (*5*) with gaseous SO_2 at 293 K, c^0_{Am} 0.1 mol/L.

$[H_3NCH_2CH_2NH_3](SO_3)[H_3NCH_2CH_2NH_3](HSO_3)_2$; in other words, one of the nitrogen atoms was bound into the sulfite form and the other was converted into the hydrosulfite form upon protonation [Eq. (9)] at the S : N ratio of 3.0 : 4.0.

The maxima expected at the SO_2 : amine ratio of 4.0 : 2.0 [corresponding to formation of ethylenediammonium hydrosulfite, Eq. (10), or pyrosulfite] were not observed on the differential titration curves.

Hence, the interaction between ethylenediamine and sulfur dioxide in the aqueous solutions resulted in a complete binding of the first amino group into the onium hydrosulfites and pyrosulfites (similarly to the cases of aminoethanol and its derivatives [2, 4]), whereas the second amino group was partially converted into the onium sulfite.

The shape of potentiometric titration curves of other 1,2-diamines was similar (Fig. 2, curves *1–4* and Table 1). The position of the maxima in the differential curves corresponded to the SO_2 : amine ratio of 1.0 : 2.0 and of 3.0 : 2.0.

In the case of diethylenetriamine (Fig. 3b and Table 1) the differential potentiometry curve contained two maxima corresponding to the SO_2 : amine ratios of 0.67 and 2.00 (pH 8.00 and 3.20). Since the amine contained three amine nitrogen atoms, the partial binding occurred to form the onium hydrosulfite $[H_3NCH_2CH_2NH_2CH_2CH_2NH_3](HSO_3)_2$ and pyrosulfite $[H_3NCH_2CH_2NH_2CH_2CH_2NH_3](S_2O_5)$, correspondingly at the S : N ratio of 2.0 : 3.0.

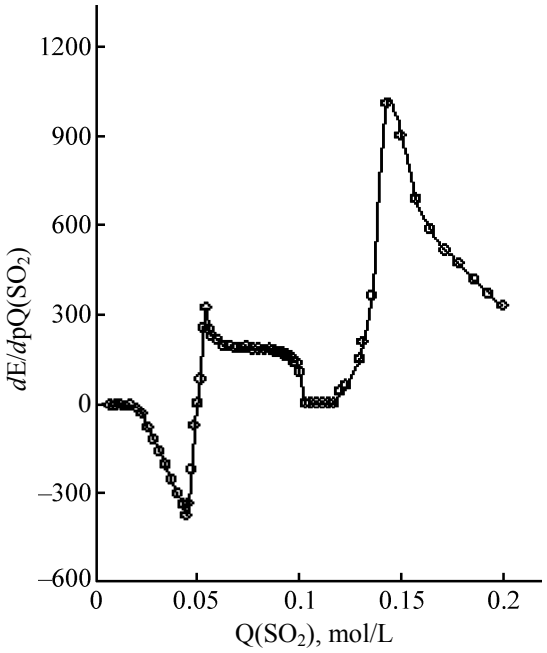

Fig. 5. Differential curve of redox titration of 0.1 mol/L aqueous solution of ethylenediamine with gaseous SO_2 at 293 K.

Table 2. Parameters of curves of redox titration (Figs. 4a and 5) of 0.1 mol/L solutions of ethylenediamine and its derivatives with gaseous SO_2 at 293 K

Effect	SO_2:Am	Integral curve		Differential curve	
		shape	*E*, mV	shape	dE/dpQ(SO_2), mV
Ethylenediamine					
I	1.0 : 2.0	Minimum	–40		0
II	1.0:1.0	Plateau	18		0
III	3.0 : 2.0		24	Maximum	1015
N,*N*,*N*',*N*'-Tetramethylethylenediamine					
I	1.0:1.0	Minimum	–20		0
II	2.0:1.0	Plateau	95		0
Piperazine					
I	1.0 : 2.0	–	–75	Minimum	–520
II	1.0:1.0	Minimum	–125		0
III	3.0 : 2.0	Plateau	–105	Plateau	0
Diethylenetetramine					
I	2.0:3.0	–	80	Minimum	–1130
II	1.0:1.0	Minimum	30		0
III	5.0:4.0	Maximum	53	Maximum	900
IV	2.0:1.0	–	–45	Minimum	–1650
V	3.0:1.0	Plateau	–104	Plateau	0
Polyethylenepolyamine[a]					
I	1.0:5.0	Minimum	5		0
II	1.0 : 2.0	Minimum	40		0
III	1.0:1.0	Maximum	–120		0

[a] The S : N ratio.

In the case of polyethylenepolyamine (Fig. 2, curves *5*–*7*), the integral potentiometry curves contained two steps corresponding to the S–N ratios of 1.0 : 0.5 and 1.0 : 2.0, the latter one evidencing the formation of the onium sulfite $[NH_3(CH_2CH_2NH_2)_nH]_2(SO_3)_{n+1}$ (n = 4–6). Hence, potentiometry data demonstrated that introduc-tion of the additional amino group substituting the OH group of aminoethanol resulted in 1.5 times increased absorption capacity towards SO_2 instead of the expected twofold increase (the S : N ratios being 1.0 : 1.0 for aminoethanol [2] and 3.0 : 4.0 for ethylenediamine, *N*,*N*,*N*',*N*'-tetramethylethylenediamine and piperazine). Further increase in the number of amino groups by introduction of additional amino-ethylene fragment decreased the absorption capacity to the S : N ratio of 2.0:3.0. In the case of commercial polyethylenepolyamine (CAS 29320-38-5, containing 90% of heptamine, the rest being pentamine and hexamine), the S : N ratio at 293 K was only 1.0 : 2.0.

Noteworthily, the positions of the plateau and the extrema in the integral redoxometry curves (Fig. 4aand Table 2) approximately coincided with positions of maxima in the corresponding differential potentiometry curves (Fig. 3 and Table 1). Furthermore, the additional effects were revealed (extrema and plateau) for ethylenediamine, *N*,*N*,*N*',*N*'-tetramethylethylenediamine and piperazine at the S : N ratio of 1.0 : 2.0 corresponding to the formation of ethylenediammonium sulfite [Eq. (7)]. In the case of diethylenetriamine and additional formation of hydrosulfite and pyrosulfite was observed at S : N of 3.0 : 3.0. Redoxometry study of polyethylenepolyamine revealed the formation of the hydrosulfite $[NH_3(CH_2CH_2NH_2)_nH](HSO_3)_{n+1}$ and the pyrosulfite $[NH_3(CH_2CH_2NH_2)_nH]_2(S_2O_5)_{n+1}$ at S : N of 1.0 : 1.0.

The negative Δκ values (Fig. 4b and Table 3) typical of the systems containing ethylenediamine, piperazine and polyethylenepolyamine (Fig. 4b, curves *1*,

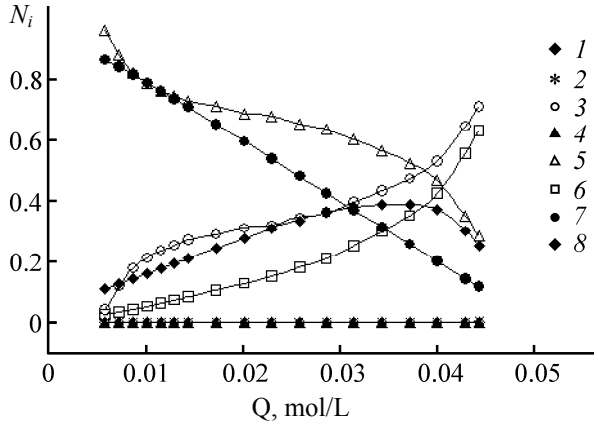

Fig. 6. Ratio of various forms of components N in the SO_2–$NH_2CH_2CH_2NH_2$–H_2O system as a function of $Q(SO_2)$ at 293 K. $N = [H_2O{\cdot}SO_2]/Q(SO_2)$ (*1*), $N = [HSO_3^-]/Q(SO_2)$ (*2*), $N = [SO_3^{2-}]/Q(SO_2)$ (*3*), $N = 2[S_2O_5^{2-}]/Q(SO_2)$ (*4*), $N = [(H_2NCH_2CH_2NH_3)_2SO_3]/Q(SO_2)$ (*5*), $N = [(H_2NCH_2CH_2{\cdot}NH_3^+)]/Q_{Am}$ (*6*), $N = [(H_2NCH_2CH_2NH_2)]/Q_{Am}$ (*7*), and $N = [(H_2NCH_2CH_2NH_3)_2SO_3]/Q_{Am}$ (*8*).

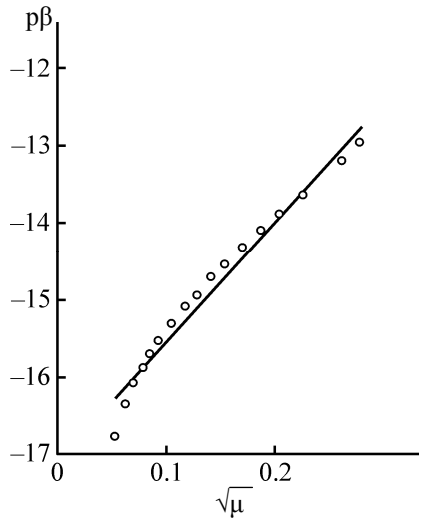

Fig. 7. pβ as a function of ionic strength (μ, mol/L) in the SO_2–$NH_2CH_2CH_2NH_2$–H_2O system at 293 K.

3, *5*) pointed at the formation of weakly dissociated compounds over the whole studied range of SO_2 concentration. The formation of the weakly dissociated sulfite $[H_2NCH_2CH_2NH_3]_2(SO_3)$ and sulfite-hydrosulfite $[H_3NCH_2CH_2NH_3](SO_3)[H_3NCH_2CH_2NH_3](HSO_3)_2$ or ions with lower mobility was accompanied with a relative decrease in the Δκ value up to the SO_2 : ethylenediamine ratio of about 3.0 : 2.0 (Fig. 4b, curve *1* and Table 3). The region of curve *1* (Fig. 4b) with the growing Δκ value corresponded to accumulation of compounds with higher dissociation degree and the formation of H^+ ions (since pH < 3.55; Fig. 1a, curve *4*). Stationary regions of the $\Delta\kappa = f[Q(SO_2)]$ curves (Fig. 4a) likely appeared due to the fact that the accumulation of sulfur dioxide in the studied system was not accompanied with the change in the dissociation degree of the formed onium complexes.

In the cases of the systems containing *N*,*N*,*N*',*N*'-tetramethylethylenediamine and diethylenetriamine, the conductometric titration curves (Fig. 4b, curves *2*, *4*) contained the regions with positive Δκ values and maxima corresponding to the formation of the $[(H_3C)_2N(CH_2)_2N(CH_3)_2H]_2(SO_3)$ and $[H(H_3C)_2NCH_2{\cdot}CH_2N(CH_3)_2H](SO_3)[H(H_3C)_2NCH_2CH_2N(CH_3)_2H]{\cdot}(HSO_3)_2$ salts as well as $[H_2NCH_2CH_2NH_2CH_2{\cdot}CH_2NH_2]_2(SO_3)$ being highly dissociated in contrast to the corresponding complexes with cations of ethylenediamime, piperazine and polyethylenepolyamine. In the case of diethylenetriamine system, the maximum with negative Δκ value corresponded to the formation of the $[H_3NCH_2CH_2NH_2CH_2CH_2NH_3](HSO_3)_2$ and $[H_3NCH_2CH_2NH_2CH_2CH_2NH_3](S_2O_5)$ salts.

Hence, the extrema in the integral and/or differential potentiometric titration curves of aqueous

Table 3. Parameters of curves of conductometry titration (Fig. 4b) of 0.1 mol/L solutions of ethylenediamine and its derivatives with gaseous SO_2 at 293 K

Effect	SO_2 : Am	Δκ, S/m	Shape
Ethylenediamine			
I	1.0 : 2.0	–0.08	Plateau
II	3.0 : 2.0	–0.41	Minimum
N,*N*,*N*',*N*'-Tetramethylethylenediamine			
I	1.0 : 2.0	0.31	Maximum
II	0.8 : 1.0	–0.14	Minimum
III	1.2 : 1.0	0.06	Plateau
IV	3.0 : 2.0	0.12	Maximum
V	2.0 : 1.0	–0.09	Plateau
Piperazine			
I	1.0 : 2.0	–0.25	Plateau
Diethylenetetramine			
I	1.0 : 2.0	0.30	Maximum
II	1.8 : 1.0	–0.28	Minimum
III	2.0 : 1.0	–0.18	Maximum
Polyethylenepolyamine[a]			
I	1.0 : 2.0	–0.64	Knee

[a] The S : N ratio.

Table 4. Parameters A_i and B_i in Eq. (15) for onium sulfites of ethylenediamine and piperazine[a]

c^0_{Am}, mol/L	T, K	$A_i \pm \Delta A_i$	$B_i \pm \Delta B_i$, L/mol	R^2	n
Ethylenediamine					
0.10	293	–16.61±0.05	15.55±0.04	0.972	17
0.05	283	–16.72±0.04	19.99±0.08	0.976	10
0.05	293	–16.34±0.09	17.45±0.07	0.980	9
0.05	303	–17.03±0.06	19.61±0.09	0.9701	9
Piperazine					
0.05	293	–17.20±0.08	18.20±0.06	0.9903	9

[a] R fitting accuracy, n number of points.

solutions of ethylenediamine and its derivatives with gaseous SO_2 corresponded to kinks in the conductometric titration curves $\Delta\kappa = f[Q(SO_2)]$, coinciding with the data in [6, 8]. Combined analysis of potentiometry, redoxometry and conductometry data has given the consistent information on the composition of onium salts formed in the SO_2–organic base–water systems.

As marked above, in the cases of the SO_2–ethylenediamine (piperazine)–H_2O systems, the first stage of the interaction yielded the weakly dissociated onium sulfites: $[H_2NCH_2CH_2NH_3]_2(SO_3)$ and $[HN(CH_2CH_2)_2NH_2]_2(SO_3)$, respectively. Taking into account the mass action law [Eqs. (2)–(6), (11)], the material balance with respect to sulfur [Eq. (12)] and nitrogen [Eq. (13)] as well as the electroneutrality [Eq. (14)], we have derived the following equations set [Eqs. (2)–(6), (11)–(14)].

$$2Am + SO_2\cdot H_2O \overset{\beta}{\rightleftarrows} (AmH)_2SO_3, \quad (11)$$

$$Q_S = [SO_2\cdot H_2O] + [HSO_3^-] + 2[S_2O_5^{2-}] + [SO_3^{2-}] + [(AmH)_2SO_3], \quad (12)$$

$$Q_N = 2[Am] + 2[AmH^+] + 2[\{AmH_2\}^{2+}] + 4[(AmH)_2SO_3], \quad (13)$$

$$[H^+] + [AmH^+] + 2[\{AmH_2\}^{2+}] = [OH^-] + [HSO_3^-] + 2[S_2O_5^{2-}] + 2[SO_3^{2-}]. \quad (14)$$

Solution of the equations using the potentiometry data allowed elucidation of the component (ionic and molecular) composition of the SO_2–ethylenediamine (piperazine)–H_2O system in the region corresponding to the formation of the onium sulfites $[H_2NCH_2CH_2NH_3]_2(SO_3)$ and $[HN(CH_2CH_2)_2NH_2]_2(SO_3)$ at SO_2 : Am ≤ 1.0 : 2.0; pH > 9.00 (Fig. 1a and Fig. 2, curve *4*).

Figure 6 shows the diagram of distribution of the components formed in the SO_2–$H_2NCH_2CH_2NH_2$–H_2O system as a function of the total amount of sulfur dioxide at 293 K. The increase in $Q(SO_2)$ from 5×10^{-3} to 5.0×10^{-2} mol/L resulted in the growing molar fraction of the onium sulfite (curve *8*) and the cation (curve *6*) with respect to the total amount of nitrogen, due to the decrease in pH and to binding of free ethylenediamine (curve *7*) in these forms. Howeverat $Q(SO_2) > 3.7 \times 10^{-2}$ mol/L the relative amount of the onium sulfite decreased, in contrast to the aminoethanol system [8]. Simultaneously the fraction of sulfite anions (curve *3*) increased due to the dissociation of the onium sulfite: the fractions of $(H_2NCH_2CH_2NH_3)_2SO_3$ (curve *5*) and SO_3^{2-} with respect to the total sulfur content change in the opposite directions. Both molar fractions of SO_3^{2-} (curve *3*) and $H_2NCH_2CH_2NH_3^+$ (curve *6*) increased. Amounts of $SO_2\cdot H_2O$, HSO_3^- and $S_2O_5^{2-}$ (curves *1*, *2* and *4*) in the mentioned $Q(SO_2)$ range were negligibly low. The composition diagrams for the systems containing ethylenediamine under other conditions were similar.

The dependence of the complex formation constant of semionium ethylenediamine sulfite [Eq. (11)] on the

Table 5. Parameters of relative stability of onium sulfites of ethylenediamine and piperazine in aqueous solutions[a]

c^o_{Am}, mol/L	T, K	dpH/dp$Q(SO_2)$	pβ	ΔG, kJ/mol	$S_{1/2}$	$\Delta pH_{1/2}$
Ethylenediamine						
0.10	293	10.88	–16.61	–93.12	0.191	1.35
0.05	283	11.73	–16.72	–90.54	0.100	1.00
0.05	293	10.05	–16.34	–91.61	0.151	1.45
0.05	303	7.32	–17.03	–98.74	0.125	1.85
Piperazine						
0.10	293	19.02	–17.20	–89.7	0.117	1.47

[a] $S_{1/2}$ area under the part of the differential curve between the corresponding maximum and the last minimum; $\Delta pH_{1/2}$ is the height of the step in the integral curve of potentiometric titration between the middle and the end of the step.

ionic strength of the solution (for example, Fig. 7) could be fitted with Eq. (15); the corresponding parameters are collected in Table 4.

$$p\beta_i = A_i + B_i\sqrt{\mu}. \quad (15)$$

According to the definition, parameter A_1 of Eq. (15) was the negative common logarithm of the thermodynamic complex formation constant β [20].

From the results (Table 5) it followed that the maxima values in the differential titration curves changed in the opposite direction as compared with the ΔG values, the latter reflecting the stability of the sulfite compounds (in contrast to the aminoethanol derivatives systems [8]). However, the $\Delta pH_{1/2}$ values showed the same trend as the mentioned parameters.

The obtained results may be useful in development of methods of air sanitary purification from sulfur dioxide.

EXPERIMENTAL

Procedures of potentiometric and chronoconductometric titrations have been described elsewhere [6, 21]. Potentiometric measurements were performed using a pH-121 pH-meter. Accuracy of the redox potential determination was ±1 mV. Conductometric titrations were performed using am Ekspert-002 conductometer (relative error below 0.5%). The amount of reacted SO_2 was determined by iodometry [22] and via the Schoeniger method [23]. The measurements were run at 283–303 K.

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