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**Complexing of Sulfur(IV) Oxide
with Hexamethylenetetramine and Hexamethylenediamine
in Aqueous Solutions**

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Abstract—Interaction in the sulfur(IV) oxide–hexamethylenetetramine (hexamethylenediamine)–water systems was studied by pH-, redox-, and conductometric titration techniques. The structure and stability of the resulting molecular and ionic complexes were examined in relation to the nature and concentration of the components in solution, as well as to temperature.

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This study continues a series of systematic research activities that seek to develop efficient methods and tools for capturing sulfur(IV) oxide with organic bases, in particular, hexamethylenetetramine (HMTA) and hexamethylenediamine (HMDA) [1–3]. Using the formerly proposed and commercially tested absorption system based on aqueous solutions of HMTA [4, 5] it is possible to remove co-present SO₂ and HF from process gases. The corresponding flowsheet [4, 5] envisages regeneration of the absorbent and utilization of hydrogen fluoride as cryolite, with sulfur compounds being eliminated from the process cycle as calcium sulfite. It was shown previously [3, 6] that, in aqueous solutions, SO₂ forms onium sulfites, hydrosulfites, and pyrosulfites with HMTA and HMDA.

To refine and supplement the data reported in [1–3, 6], we studied here the interaction of SO₂ with 0.1 M aqueous solutions of polyamines (HMTA and HMDA) by independent pH-, redox- and conductometric techniques.

EXPERIMENTAL

As initial substances we used pharmaceutical-grade HMTA and analytically pure HMDA without prior treatment. For details of the potentiometric experiment, see [7, 8]; chronoconductometric titration of the aqueous solutions of the amines with gaseous sulfur (IV) oxide followed the procedure used in potentiometric titration on a no. 5721 conductometer containing a no. 5981 sensor for measuring the electrical conductivity. The measurements were done at 273–313 K.

During the experiment, the SO₂ concentration was monitored iodometrically at the reaction mixture outlet every 15–30 s [9]. The amount of spent SO₂ was determined experimentally by the Shöniger method [10].

Each experiment was performed at least in three times. The statistical error of the experiment was within 2.5% for the sulfur(IV) oxide content $Q_{\text{SO}_2} \geq 0.01$ M in all the cases.

Figures 1–3 present the pH-, redox-, and

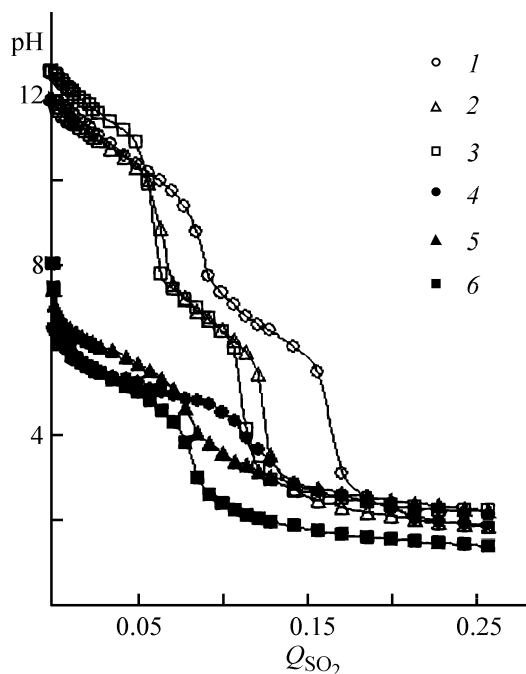


Fig. 1. pH titration curves for the aqueous solutions of (1–3) HMDA and (4–6) HMTA titrated with gaseous SO_2 at (3, 6) 273, (2, 5) 293, and (1, 4) 313 K. $c_{\text{Am}}^0 = 0.1$ M; the same for Figs. 2 and 3. (Q_{SO_2}) Sulfur(IV) oxide content, M.

conductometric curves for titration of 0.1 M HMTA and HMDA solutions with sulfur(IV) oxide. All the integral pH-metric titration curves (Fig. 1) exhibit two jumps. The first jump at pH 10.90–7.60 (HMDA) corresponds to formation of onium sulfites, and the second jump at pH 6.00–2.60 (HMDA) and 5.30–2.30 (HMTA) is associated with formation of onium hydro- and pyrosulfites. For the HMDA-containing system the midpoints of the jumps in the titration curves correspond to the maxima in the differential curves (Table 1). These maxima exhibit significant deviation from the stoichiometry expected for the corresponding onium salts. Monoprotonation of the amine implies the $\text{SO}_2 : \text{Am}$ ratio of 1.0 : 2.0 for sulfites and 1.0 : 1.0 for hydrosulfites (pyrosulfites), and diprotonation, $\text{SO}_2 : \text{Am} = 1.0 : 1.0$ for sulfites, and 2.0 : 1.0, for hydrosulfites (pyrosulfites). The observed deviation is probably associated with the difference in the degrees of involvement of the amino groups in the protonation, which is especially prominent in the case of HMTA (Table 1). Because of major difference in the $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$ values, only one amino group from HMTA is involved in protonation, by contrast to both amino groups in the case of highly basic HMDA.

Monoprotonation of HMTA, resulted from acid-base interaction in the $\text{SO}_2\text{-C}_6\text{N}_4\text{H}_{12}\text{-H}_2\text{O}$ system, deserves

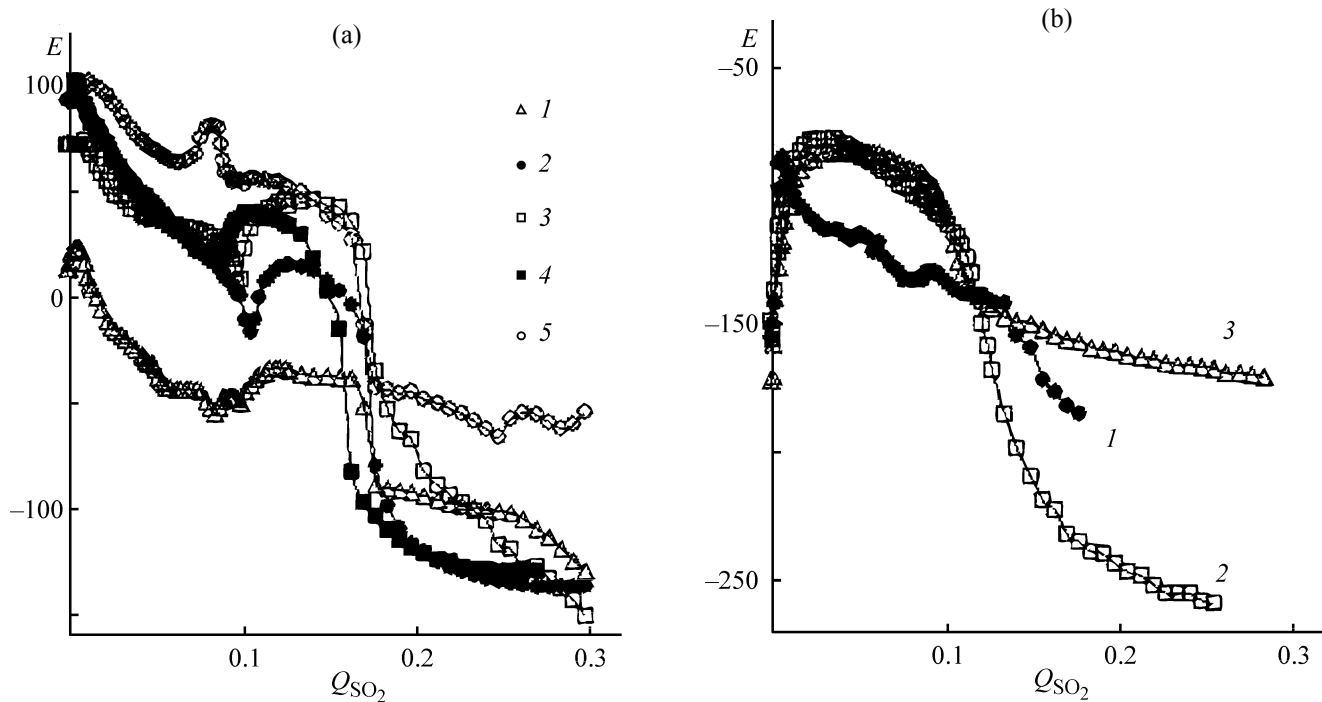


Fig. 2. Redox titration curves for the aqueous solutions of (a) HMDA and (b) HMTA titrated with gaseous SO_2 . (E) Redox potential, mV, and (Q_{SO_2}) sulfur(IV) oxide content, M. T, K : (a): (1) 273, (2) 283, (3) 293, (4) 303, and (5) 313 and (b): (1) 273, (2) 293, and (3) 313.