ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 5, pp. 793–798. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © D.B. Kal'nyi, V.V. Kokovkin, I.V. Mironov, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 5, pp. 705–710.

Sodium Sulfite: A Promising Reagent in the Electrochemical Oxidation of Metallic Silver

D. B. Kal'nyi[a], V. V. Kokovkin[a,b], and I. V. Mironov[a,b]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, pr. Akad. Lavrent'eva, 3, Novosibirsk, 630090 Russia*

[b] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*
e-mail: basil@niic.nsc.ru

Received May 25, 2010

Abstract—Among the complexing agents suitable for the electrochemical silver recovery, a promising one is sodium sulfite forming silver complexes with high stability constants: according to our data, log $\beta_1 \sim 5.3$, log $\beta_2 \sim 8.2$. This reagent is accessible and cheap, but nevertheless it almost never has been used for these purposes. We studied the stability of the sodium sulfite solutions in air and showed a possibility of using them for a long period. Using the methods of potentiodynamic polarization and potentiostatic electrolysis, we have studied characteristics of the process of metallic silver oxidation in the sulfite media. The anodic polarization process of the silver dissolution is shown to occur with 100% yield with respect to the consumed current. Simultaneously, on the cathode deposited up to 90% of dissolved silver.

DOI: 10.1134/S107036321105001X

An urgent problem of chemical technology is the extraction of noble metals, particularly silver, from the electronic and jewelry scrap and similar sources. The traditional methods of the silver extraction [1–3] are based on its dissolution in the presence of oxidants in acid solution (perchloric acid, sulfuric acid, nitric acid) or complexing agents (cyanide, thiocyanate, thiourea). From these solutions, silver is isolated as insoluble salts or is reduced to metal. The main disadvantages of these techniques are the high consumption of reagents and non-selectivity of dissolution: besides silver copper, iron, and other components of the raw material are dissolved.

Significantly less expensive are the methods that use electrolytic anodic oxidation of silver in specially selected electrolytes [4]. Processing a material containing large amount of basic metals (copper, iron, nickel, etc.) should be performed under conditions providing selective transfer of silver in the solution. For this purpose are used the electrolytes containing thiourea [5], thiocyanate [6, 7], amino acids [8], etc. Silver can be deposited and isolated on the cell cathode. Note that the earlier proposed thiourea medium [2] still is widely used in the gold and silver hydrometallurgy. The study of the process of electrolytic oxidation and reduction of silver has been carried out in [9–11].

A promising complexing agent in the processes of electrochemical oxidation of silver is sodium sulfite, the side product in processing of sulfide ores used in the manufacture of chemicals. The stability of the silver(I) sulfite complexes is high enough. According to the handbook data [12], the $Ag(SO_3)_2^{3-}$ stability constants falls to the range log $\beta_2 = 7.7$ to 9.1. The difference in values is due to the difference of the conditions of measuring that do not coincide with our ones. An additional experimental study is therefore required.

Sulfite ion forms stable complexes with much less number of metal ions than cyanide. In addition, in contrast to thiourea, sulfite can be used in alkaline medium, in which many transition metals form insoluble hydroxides. All this allows us to expect a high selectivity at the recovery of silver(I) from a solution in the presence of other metals. However, it is known that the sulfite ions are unstable to the action of atmospheric oxygen. The final product of oxidation is sulfate ion ($SO_3^{2-} + 2OH^- - 2e^- = SO_4^{2-} + H_2O$, $E^0 = 0.90$ V [13]). The widespread view of the rapid oxidation with oxygen was a probable obstacle to the

development of the methods using sulfite ions as the complexing agents, in particular, for the silver recovery. Kinetics of oxidation of SO_3^{2-} in aqueous solutions has been studied [14, 15], but the process mechanism remains unclear. Therefore, one purpose of this study was to obtain quantitative estimates of the stability of sulfite media toward oxidation in the electrochemical experiment at varying different factors.

In [16] has been considered the electrochemical oxidation of silver in thiourea solutions with the addition of sodium sulfite. The study was carried out by potentiodynamic voltammetry. The introduction of sodium sulfite to the thiourea solution was shown to increase the density of the anodic current. However, these data did not allow an unambiguous conclusion that the current density grew due to the oxidation of silver, and not, for example, to the sulfite oxidation on the silver electrode. It is only clear that, since the silver(I) complexes with thiourea are much more stable than with sulfite [12, 17], the observed effect cannot be assigned to an additional complexation in solution. Another result of the addition of sulfite was an increase of the thiourea stability in the alkaline medium.

The aim of our work was to study the characteristics of dissolution of metallic silver in aqueous solutions of Na_2SO_3 on the background of 1 M $NaClO_4$. First, we estimated stability of the sulfite solution in air. Then we measured the silver(I) complexation constants for $Ag(SO_3)_i^{1-2i}$ and protonation constants of sulfite ions by the potentiometry. Using the method of potentiodynamic polarization, we determined the conditions for the silver oxidation. By the method of potentiostatic electrolysis we determined the dissolution rate and the current yield.

Stability of sulfite solutions. Figure 1 shows a typical plot of the sulfite ions concentration in the solution vs. the duration of exposure to the atomsphere. It is seen that during the first 8 h the rate of decrease in the sulfite ion concentration is about 0.005–0.007 M h^{-1}. During this time was spent about a half of the initial ions. However, the rate of the sulfite oxidation decreased markedly over the time, and even after 14 h the total change in concentration of sulfite ion did not exceed 60%.

Figure 2 shows the changes in concentration of sulfite ion vs. the ratio of the air–solution contact area to the volume of solution (*S/V*) at stirring and without it for the same period (6 h). These dependencies are nearly linear. As seen, the effect of stirring is not very significant, the difference is on the average 20%. Minimizing the contact area to 1 cm^2 (volume 50 cm^3) practically excludes the effect of stirring, the rate of the sulfite ions oxidation is so low that after 6 h the total decrease does not exceed 4% of the initial concentration.

Effect of pH on the oxidation of sulfite ion is shown in Fig. 3. Here, the concentration of sulfite was reduced to one tenth compared with the above experiments to ensure more sharp results at its variations in acidic medium. As one can see, the rate of oxidation of sulfite ions in the acidic medium is much lower than in alkali (in these particular conditions approximately 3–4 times). This is due to increasing concentration of the HSO_3^- form which is much more resistant to oxidation compared with SO_3^{2-}.

The results obtained allow us the estimation of the time intervals during which the Na_2SO_3 concentration decrease due to oxidation by the oxygen air remains within certain range. So, if the initial relative concentration of the solution was 0.1 M Na_2SO_3, then at S/V = 0.3 cm^{-1} (the usual conditions of electrochemical measurements) it decreased by 10% in about 70 min, therefore measurements can be performed without a protection against air. At the minimization of the contact area with the atmosphere the sodium sulfite solution can be used for a long time.

Determination of equilibrium constants. The protonation constants of sulfite ion and the stability constants of the silver complexes with sulfite ions were determined by potentiometric titration with simultaneous measuring the circuit EMF (with a pH-meter/ionometer Anion 410 device):

$$Ag \mid AgCl \mid 1\ M\ NaClO_4,\ 2\times10^{-4}\ M\ NaCl \parallel 1\ M.\ NaClO_4 \parallel W \mid \text{test electrode}, \quad (1)$$

where W is the test solution.

To determine the protonation constants of sulfite ion, from the analytical composition of the solutions and the EMF of the circuit (1) the values of the functions of formation were calculated that were used to find the values K_{1H} and K_{2H} applying a weighted nonlinear least-squares method.

$$H^+ + SO_3^{2-} = HSO_3^- \ (K_{1H}),$$
$$H^+ + HSO_3^- = H_2SO_3 \ (K_{2H}), \quad (2)$$

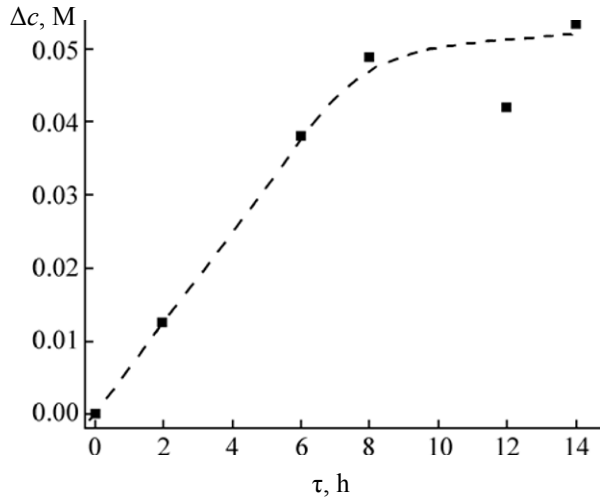

Fig. 1. Variation of the sodium sulfite solution concentration vs. the contact time with atmosphere: c_{init} = 0.1 M, pH = 9.5, V = 50 cm^3, S = 15 cm^2, T = 20°C, stirring.

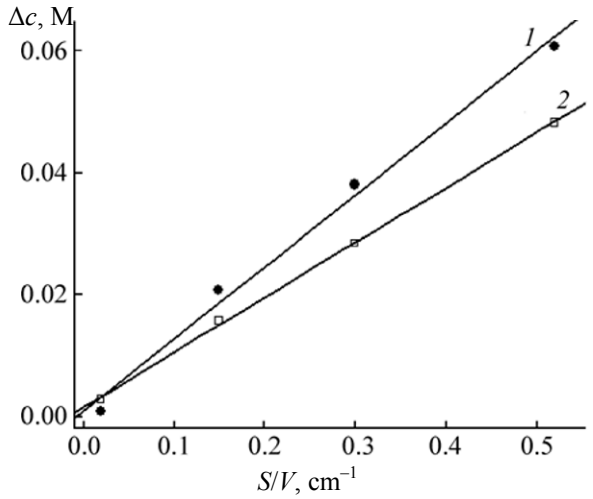

Fig. 2. Dependence of the sulfite concentration change for 6 h vs. the S/V ratio. c_{init} = 0.1 M, pH = 9.5, T = 20°C; (*1*) with stirring, (*2*) without stirring.

$$n_H = \frac{c_{H^+} - [H^+]}{c_{SO^{2-}}} = \frac{K_{1H}\cdot[H^+] + 2K_{1H}\cdot K_{2H}\cdot[H^+]^2}{1 + K_{1H}\cdot[H^+] + K_{1H}\cdot K_{2H}\cdot[H^+]^2} \quad (3)$$

The protonation constants values log K_{1H} = 6.34± 0.07 and log K_{2H} = 1.47±0.10 obtained for I = 1 M ($NaClO_4$) are well consistent with the published data [12]. They were used further to calculate the formation constants of the silver sulfite complexes **I**.

To determine the formation constants of the complexes $Ag(SO_3)_i^{1-2i}$ [Eq. (4)], from the circuits [Eq. (1)] EMF with silver electrode were calculated the values of the Leden function [Eq. (5)]:

$$Ag^+ + iSO_3^{2-} = Ag(SO_3)_i^{1-2i}\ (\beta_i), \quad (4)$$

$$\Phi = c_{Ag}/[Ag^+] = 1 + \beta_1[SO_3^{2-}] + \beta_2[SO_3^{2-}]^2. \quad (5)$$

The equilibrium concentrations of sulfite $[SO_3^{2-}]$, necessary for determining stability constants β_1 and β_2, were calculated iteratively using expressions (6)–(9):

$$[SO_3^{2-}] = \alpha_0\cdot c'(SO_3^{2-}), \quad (6)$$

$$\alpha_0 = 1/(1 + K_{1H}\cdot[H^+] + K_{1H}\cdot K_{2H}\cdot[H^+]^2), \quad (7)$$

$$c'(SO_3^{2-}) = c(SO_3^{2-}) - n_{Ag}\cdot c_{Ag}, \quad (8)$$

$$n_{Ag} = \frac{[AgSO_3^-] + 2[Ag(SO_3)_2^{3-}]}{[Ag^+] + [AgSO_3^-] + [Ag(SO_3)_2^{3-}]} = \frac{c_{Ag} - [Ag^+]}{c_{Ag}} + \frac{[Ag(SO_3)_2^{3-}]}{c_{Ag}}. \quad (9)$$

In the first phase, the contribution of the $Ag(SO_3)_2^{3-}$ complex was suggested to be negligibly small, and from the expression (9) were calculated the average ligand numbers n_{Ag} and then the overall concentrations of the sulfite ions $c'(SO_3^{2-})$ [Eq. (8)] not involved in the complexes, and finally, the equilibrium concentrations $[SO_3^{2-}]$ [Eq. (6)] and the constant β_1 and β_2 [Eq. (5)] in the first approximation. Taking Eq. into account, in the next phase were calculated the n_{Ag} values using $[SO_3^{2-}]$, β_1 and β_2 of the first approximation, and the iteration cycle was continued.

$$n_{Ag} = \frac{\beta_1[SO_3^{2-}] + 2\beta_2[SO_3^{2-}]^2}{1 + \beta_1[SO_3^{2-}] + \beta_2[SO_3^{2-}]^2} \quad (10)$$

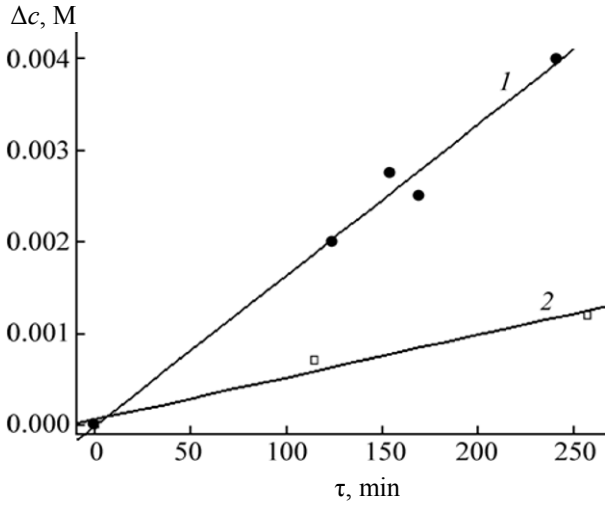

Fig. 3. Changes in the sulfite concentration in time at different pH: (*1*) 8.9, (*2*) 4.0. c_{init} = 0.1 M, V = 50 cm^3, S = 15 cm^2, T = 20°C, without stirring.

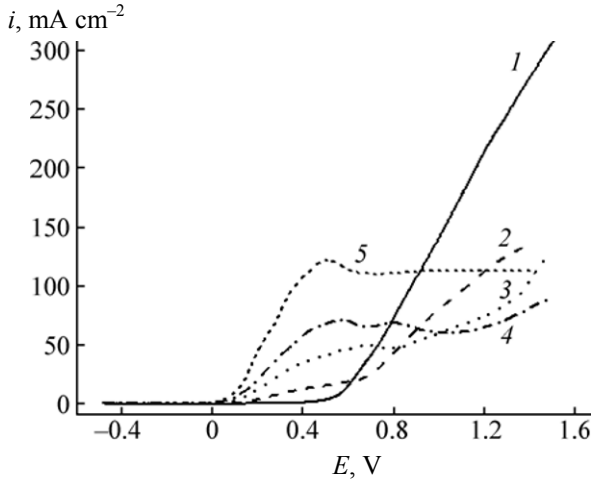

Fig. 4. Effect of Na_2SO_3 concentration and temperature on the current of the silver oxidation at a rate of potential sweep 20 mV s^{-1}: (*1*) without Na_2SO_3, (*2*) 0.1 M Na_2SO_3, (*3*) 0.25 M Na_2SO_3, (*4*, *5*) 0.5 M Na_2SO_3; temperature: (*1, 2, 3, 4*) 18°C, (*5*) 50°C. Supporting electrolyte: 1 M $NaClO_4$. $c(AgClO_4) = 10^{-5}$ M, pH = 9.0–9.6.

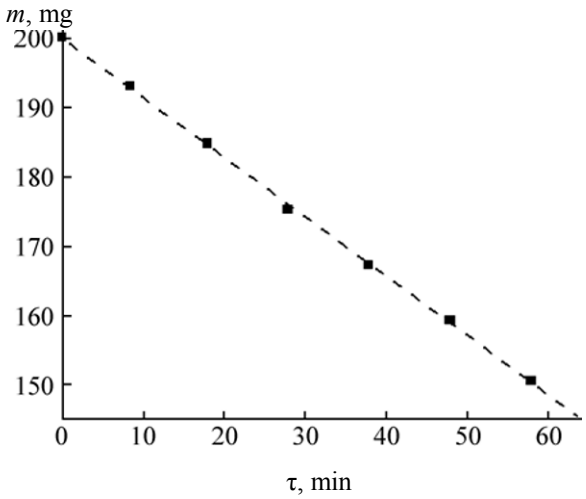

Fig. 5. Dependence of the mass of silver electrode on the electrolysis duration. E = 0.30 V, the composition of the solution: 0.1 M Na_2SO_3, 1 M $NaClO_4$; pH = 9.2.

Since in almost all experiments the total concentration of sulfite was significantly higher than the c_{Ag}, the iteration process converged rapidly. The obtained values of the formation constants are as follows: $\log \beta_1 = 5.3\pm0.2$; $\log \beta_2 = 8.2\pm0.1$. These values we used further for interpreting the potentiodynamic voltammograms.

Potentiodynamic voltammetry. Figure 4 shows the dependences on the sodium sulfite concentration and temperature obtained by the potentiodynamic polarization method. The curve *1* is obtained for a silver electrode in the supporting solution. As seen, it is shifted relatively to the curves *2–5* registered for the solutions with the sodium sulfite additive. The value of the shift is 0.30–0.47 V for different sulfite concentrations, which is close to the calculated values: $\Delta E \approx (RT/F)\ln \beta_2[SO_3^{2-}]^2) = 0.36$–$0.44$ V.

Curves *2–5* (Fig. 4) can be arbitrary divided in two segments in the region of shifting the current–voltage curve, differing by the rate of the current growth with the potential. In the first segment fast rise of current occurs in the range of 0.1–0.4 V. In the second section (above 0.4 V) the rate of the current growth reduced considerably. Increasing the solution temperature also leads to the current growth (curves *4* and *5*).

The nature of the *2–5* plots that include reaching a limiting current indicates apparently a steady process of the sulfite ions diffusion to the electrode surface, where silver is oxidized. The potentiodynamic curves of similar shape obtained in [9], where has been studied the silver oxidation in thiourea media with the sodium sulfide additives, were explained analogously. Bek et al. [9] suggest that thiourea reaches electrode under the diffusion control.

Potentiostatic electrolysis. To determine the current yield at the oxidation of silver in the region of the shift of the current–voltage curve potential caused by the complex formation we carried out electrolysis at a constant potential of 0.30 V. The data obtained are shown in Fig. 5. The dependence of the change in the electrode mass in time is linear. The total loss of mass of the silver electrode at the electrolysis was 49.5± 0.2 mg in 1 h. The mass of dissolved silver calculated from the amount of electric current spent is 48.7± 0.5 mg. Comparison of this value with the experimental data indicates almost 100% current yield at the silver dissolution. In the course of electrolysis, a white film soluble in nitric acid formed on the cathode. Analysis of the resulting nitric acid solution by atomic absorption spectrometry gave the total content of silver 45 mg. Consequently, taking into account the errors of analysis, we can argue that on the cathode deposited about 90% of the dissolved silver.

Thus, our experiments showed that sodium sulfite is a promising agent for the electrochemical silver dissolution. The anodic oxidation of silver in aqueous

solution of Na_2SO_3 is shown to proceed at lower potentials due to formation of the silver(I) sulfite complexes. This correlates with the estimation of the potential shift using the obtained stability constants. Note that the values of the constants β_1 and β_2 are of independent interest for the chemistry of silver. The oxidation of Ag occurs with 100% current yield.

Consequently, the sulfite ions consumption is due only to the process of the oxidation by air, and can be controlled. We found that in acidic media the oxidation of sulfite proceeds slower. The sulfite consumption in an alkaline medium can also be minimized by reducing the *S*/*V* factor. The dissolved silver is reduced on the cathode to the metal, thus the steps of the silver extraction into the solution and concentrating can be combined. Currently we study oxidation of silver in the presence of other metals.

EXPERIMENTAL

For the preparation of solutions were used the following reagents: perchloric acid (reagent grade), anhydrous sodium sulfite (analytical grade), silver nitrate (analytical grade).

The silver perchlorate solution was prepared from silver nitrate. First, by the action of alkali on the $AgNO_3$ solution Ag_2O precipitate was obtained, which was carefully washed with the bidistilled water using decantation procedure. Then to the resulting precipitate perchloric acid was gradually added till its dissolution (pH = 3).

In the voltammetric experiments, the ionic strength was maintained at 1 M ($NaClO_4$). The measurements were performed at room temperature, 20±2°C. At determining the formation constants of silver(I) complexes and the sulfite ion protonation constants, the temperature was maintained at T = 25.0±0.1°C using a thermostat.

As the electrode for voltammetry was used the silver wire (purity 99.9%) of the diameter 0.50 and 2.00 mm. For potentiometric measurements were used "pasted" silver electrodes, which are characterized by good reproducibility of measurements [18]. They were produced by thermal decomposition of the silver(I) oxide paste on a platinum wire.

In all experiments, for the contact of electrode with the working solution was used a liquid bridge filled with 1 M $NaClO_4$ to prevent contamination of the tested solutions with the chloride ions.

Potentiometric measurements. As the indicator electrode were used the "pasted" silver electrode for determininig the equilibrium concentration [Ag^+] and an ESL-43-07 glass electrode to measure pH. Concentrations were calculated from the Nernst equation: $E_H = E_H^{\varnothing} + 0.05916\log [H^+]$ and $E_{Ag} = E_{Ag}^{\varnothing} + 0.05916\times \log [Ag^+]$, where the electrode calibration (determination of $E_H^{\varnothing}$ and $E_{Ag}^{\varnothing}$) was performed using the data obtained for solutions with known concentrations of $HClO_4$ or $AgClO_4$ in the medium of 1 M $NaClO_4$. The concentration of the investigated forms was low (< 0.1 M), therefore changes in the medium (that is, in the activity coefficients) and diffusion potential were neglected [19]. The protonation constants were determined by measuring the potential of glass electrode in a W solution containing 1 M $NaClO_4$, 2.00×10^{-2} M Na_2SO_3, and varied amounts of $HClO_4$. In the study of the complex forming agent, the W solution included 1 M of $NaClO_4$, 9.00×10^{-3} M of $HClO_4$, varied amounts of $AgClO_4$ (10^{-3}–10^{-2} M) and Na_2SO_3 (< 0.1 M). In these experiments the potentials of both silver and glass electrodes were measured. The data were analyzed using a nonlinear least squares procedure.

Potentiodynamic measurements. The measurements were performed using a three-electrode cell with nonseparated cathode and anode spaces. As working electrode platinum or silver 0.6 cm^2 electrodes were used. Before measurements, they were preconditioned for 10 s in concentrated nitric acid and washed with distilled water. Auxiliary electrode was a platinum grid 6×6 cm, as the reference was used a silver chloride electrode EVL-1M3 filled with 1 M NaCl. To determine the pH of solutions was used a glass electrode ESL-43-07 and the same reference electrode. The solution in the cell was stirred with a magnetic stirrer.

The voltammetric experiments were performed with a PI-50-1.1 potentiostat and a PR-8 programmer. Voltammograms were recorded in the potential range –0.50–1.50 V at the potential scan rate 20 mV s^{-1}. The obtained dependences were passed to a computer with a built-in L-154 card. All results obtained are shown in the potential scale relative to the used reference electrode.

Potentiostatic measurements. The experiments were performed in the same cell as for the potentiodinamic measurements. The auxiliary electrode was platinum grid, the working electrode was a silver wire of 0.50 mm diameter, coiled into a spiral. The

dissolution process was carried out at room temperature for 1 h while stirring the solution. The change in the mass was monitored gravimetrically by weighing the electrode with an analytical balance every ten minutes during the electrolysis. In addition, the silver content in the final working solution and in the precipitate formed was determined by atomic absorption spectrometry.

Investigation of the stability of solutions of sodium sulfite. Experiments on the stability of the Na_2SO_3 solutions were carried out as follows. Aliquots of freshly prepared solution [$c(Na_2SO_3)$ = 0.1 M, pH = 9.4–9.6] were placed in a container with a given volume and area of the contact with the atmosphere, and stored in air for a specified time (2–14 h). Concentration of sulfite in the solutions during the experiments was determined by iodometric titration [20]. In some experiments, the initial solution was acidified with perchloric acid to a desired pH.

In the kinetic experiments the contact area between the sodium sulfite solution and air (S = 1, 15, and 26 cm^2), solution volume (V = 50 and 100 cm^3), pH, magnetic stirrer rotation rate were varied. The maximum stirring rate was taken to provide flat contact surface of the solution with the atmosphere. This corresponded to approximately 200 rpm of the magnetic stirrer bar.

ACKNOWLEDGMENTS

This work was supported by the Foundation for the assistance to development of small innovative enterprises in the scientific and technical sphere.

REFERENCES

1. Maslenitskii, I.N. and Chugaev, L.V., *Metallurgiya blagorodnykh metallov* (Noble Metal Metallurgy), Moscow: Metallurgiya, 1972.
2. Plaksin, I.N. and Kozhukhova, M.A., *Dokl. Akad. Nauk SSSR*, 1941, vol. 31, p. 671.
3. Meretukov, M.A. and Orlov, A.M., *Metallurgiya blagorodnykh metallov. Zarubezhnyi opyt* (Noble Metal Metallurgy. Foreign Experience), Moscow: Metallurgiya, 1991.
4. Tomilov, A.P., *Prikladnaya elektrokhimiya* (Applied Electrochemistry), 3 ed., Moscow: Khimiya, 1984.
5. Kakovskii, I.A. and Potashnikov, Yu.M., *Kinetika protsessov rastvoreniya* (Kinetics of the Dissolution Processes), Moscow: Metallurgizdat, 1975.
6. Potashnikov, Yu.M., Kakovskii, I.A., and Chursanov, Yu.V., *Izv. Akad. Nauk SSSR, Metally*, 1985, p. 39.
7. Bersirova, O., Tsesiulis, G., and Kublanovskii, V., *Zh. Prikl. Khim*., 2009, vol. 82, p. 1126.
8. Tarasevich, M.R., Chernyshova, L.S., Bogdanovskaya, V.A., and Kudaikulova, G.A., *Elektrokhimiya,* 2001, vol. 37, p. 510.
9. Bek, R.Yu., Shuraeva, L.I., Ovchinnikova, S.N., and Vais, A.A., *Elektrokhimiya*, 2007, vol. 43, p. 305.
10. Bek, R.Yu., Shuraeva, L.I., Ovchinnikova, S.N., and Kenzin, V.I., *Elektrokhimiya*, 2007, vol. 43, p. 1329.
11. Nikolaeva, V.A., Kharin, A.N., and Plugotorenko, V.I., *Issledovaniya po elektroosazhdeniyu i rastvoreniyu metallov* (Research on Electrical Deposition and Dissolution of Metals), Moscow: Nauka, 1971, p. 140.
12. Sillén, L.G., Martell, A.E., and Bjerrum, J., *Stability Constants of Metal–Ion Complexes*, 2 ed., London: The Chemical Society, 1964, p. 231
13. Dobosh, D., *Electrochemical Data. A Handbook for Electrochemists in Industry and Universities*, Moscow: Mir, 1980.
14. Gladkii, A.V., *Zh. Prikl. Khim*., 1984, vol. 57, p. 2121.
15. Khasanov, V.V., Ryzhova, G.L., and Mal'tseva, E.V., *Khimiya rastitel'nogo syr'ya* (Chemistry of the Raw Material from Plants), 2004, p. 77.
16. Liyuan Chai, Masazumi Okido, and Wanzhi Wei, *Hydrometallurgy*, 1999, vol. 53, p. 255.
17. Mironov, I.V. and Tsvelodub, L.D., *Zh. Neorg. Khim.,* 1996, vol. 41, no. 2, p. 240.
18. Ives, D.J. and Janz, G.J., *Reference Electrodes. Theory and Practice*, New York: Academic Press, 1961, pp. 198, 651.
19. Mironov, I.V., *Vliyanie sredy i kompleksoobrazovanie v rastvorakh elektrolitov* (Medium Effect and Complexation in Electrolite Solutions), Novosibirsk: INKh Sib. Otd. Ross. Akad. Nauk, 2003.
20. Kolthoff, I.M., Belcher, R., Stenger, V.A., and Matsuyama, G., in *Volumetric Analysis, part III*, Moscow: GNTI Khim. Literatura, 1961, pp. 347–349.