*Chemistry for Sustainable Development* **15** (2007) 313–318

# Effect of the Acidity of the Medium on the Cathode Reactions of Sulphite and Thiosulphate Anions during Silver Extraction from Fixing Solutions

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(Received July 13, 2006; revised September 25, 2006)

## Abstract

Dependence of the processes involving reduction of the main components of fixing solutions (silver ions, thiosulphate and sulphite) on silver, graphite and platinum cathodes on pH is investigated. It is established that the pH value has the strongest effect on the reduction of sulphite ion; in the medium with pH $\geq$ 7 it does not get reduced. Quite contrary, the reduction of thiosulphate and silver is only weakly dependent on this parameter. The optimal electrolysis conditions (potentiostatic mode at the cathode potential equal to 0.85 V, and pH $\geq$ 7) were chosen so that they allow one to recover the worked out fixing solutions using the flow voluminous porous cathodes and to decrease the residual silver content down to 0.5–1.0 mg/l.

## INTRODUCTION

Worked out fixing solutions belong to the reagents incorporating precious metals along with toxic components. This feature complicates processing of these solutions because it is necessary to meet ecological and economical requirements at the same time. These problems are solved in the most complete form by means of the recovery of fixing solutions: after silver extraction to the acceptable level (0.2–0.5 g/l) [1]), these solutions may be directed to repeated use. At the same time, it is necessary to conserve the concentrations of the main components of fixing solutions: thiosulphate and sulphite ions. For a single use of the fixing solution, it is necessary not only to extract silver from it to a level allowed for disposal into sewerage system (0.5–1.0 mg/l) but also to neutralize other components (for example, to transform $S_2O_3^{2-}$ and $SO_3^{2-}$ ions into less toxic $SO_4^{2-}$ ions) or to decrease their content to the corresponding standards. The necessity of neutralization is due to the fact that thiosulphate and sulphite ions, even without silver, bring about essential ecological danger. Since these ions are strong reducing agents, they are distinguished by the high chemical and biological oxygen demand; they decompose in water reservoirs to form toxic sulphur-containing compounds.

The most promising method of processing worked out fixing solutions, both from the viewpoint of regeneration and in the aspect of neutralization, is electrolysis including that with flow voluminous porous cathodes [1–6]. As we have already indicated, an optimal electrolysis mode should provide, on the one hand, sufficiently complete conservation of the main components of solution, on the other hand, the high rate of extraction and the low residual concentration of silver in solution. In the case of a more negative side cathode reaction, the residual silver content in solution is in fact determined by the potential of this reaction. According to the data of [2], a minimal silver content in solution after electrolysis, assuming the side reaction of thiosulphate reduction to hydrosulphide
($S_2O_3^{2-} + 8H^+ + 8\bar{e} \rightarrow 2HS^- + 3H_2O$)
is 23 mg/l, which is much more than the standard value allowing disposal into sewerage system.

One of the important factors affecting the electrode reactions of sulphur compounds is the solution pH [7–11]. The goal of the present work was to investigate the effect of pH on the cathode reactions of sulphite and thiosulphate anions with respect to the electrolysis of fixing solutions.

## EXPERIMENTAL

The cathode behaviour of thiosulphate and sulphide ions was studied in the solutions of $Na_2S_2O_3$ (200 g/l) and $Na_2SO_3$ (15 g/l) within the pH range 3–9.5 at a temperature of (20±1) °C. The chosen concentrations of thiosulphate and sulphite correspond to their concentrations in the most widespread compositions of fixing solutions [12]. To estimate the rate of silver recovery, we used a mixture of these solutions containing 200 mg/l silver. The concentrations of $SO_3^{2-}$ and $S_2O_3^{2-}$ ions were determined by means of iodometry [13]; silver concentration was measured by means of atomic absorption.

The cathode reduction of the components of fixing solutions was investigated using the graphite, silver and platinum electrodes by means of the direct DC voltammetry with the help of a unit including the sensor with the mechanical renewal of the surface of indicator electrode [14], programmable potentiostat IPC-micro and a computer controlling the measurement process and processing the results. The potentials were measured with respect to the silver chloride reference electrode. Silver recovery from solution was carried out with a laboratory electrolyser without separation of electrode spaces; the electrolyser was equipped with a graphite anode and a flow voluminous porous cathode with the overall area of 0.3 $dm^2$ [15] in the potentiostatic mode with the solution circulation rate about 12 l/h. The efficiency of electrolysis process was estimated on the basis of the degree and rate of silver recovery, as well as on the basis of silver yield as a function of current. The fibrous carbon materials with high and low electrical conduction like VNG-30 and KNM [16] and a metallized polymeric material like syntepon [7] were used as the cathode.

## RESULTS AND DISCUSSION

### Cathode behaviour of $S_2O_3^{2-}$ ion

The cathode polarization curves recorded with a graphite electrode in the background solution of $Na_2SO_4$ and with the addition of $Na_2S_2O_3$ for two pH values (5.8 and 9.5) are presented in Fig. 1, *a*. One can see that all the three curves almost coincide with each other, that is, thiosulphate does not get reduced on graphite in the region of potentials before the start of hydrogen reduction (φ ≈ −1.5 V). Similar results were also obtained for a platinum cathode; however, the start of hydrogen evolution in this case occurs at more positive potentials (φ ≈ −1 V).

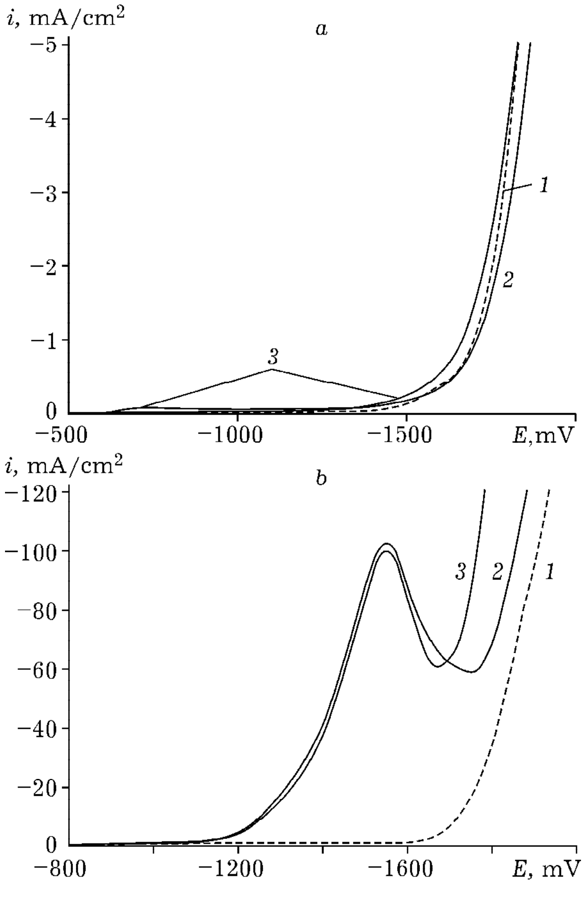

Fig. 1. Cathode reduction of thiosulphate ion on graphite (*a*) and silver (*b*) electrodes. The potential scan velocity 20 mV/s: *1* – background, 1 M $Na_2SO_4$, pH values: 5.8 (*a*), pH 9.5 (*b*); *2*, *3* – solution of 200 g/l $Na_2S_2O_3$ + 1 M $Na_2SO_4$, pH values: 9.5 (*2*) and 5.8 (*3*).

Unlike for platinum and graphite, the wave of the cathode reduction of thiosulphate ions is observed on silver. One can see in Fig. 1, *b* that the reduction starts at $\varphi$ = −0.8...−0.9; at $\varphi \approx -1.5$V we observe a clear peak of the limiting current density of $S_2O_3^{2-}$ ion reduction. One can see that the current density of thiosulphate reduction is weakly dependent on the solution pH because its peak decreases by 3–5 % while pH increases from 5.8 to 9.5. It should be noted that the potential of the start of thiosulphate ion reduction on silver (−0.85 V with respect to the silver chloride reference electrode) is more negative than that indicated in [2]. This is likely to be connected with the fact that thiosulphate reduction occurs according to reaction $S_2O_3^{2-} + 2e \rightarrow SO_3^{2-} + S^{2-}$ which is known to be accompanied by the formation of reduction products – sulphite and sulphide anions in the solution [18, 19]. Qualitatively, the formation of sulphide ions for the potential more negative than −1.2 V is confirmed visually: when silver ions are present in the solution, a black silver sulphide precipitate is formed, and a rapid development of the cathode surface is observed. The transition from metal silver deposition to the deposition of a mixture of Ag and $Ag_2S$ with an increase in the cathode current density or with a decrease in silver concentration was described in a number of works [3, 16]. With the potential more positive than −0.85 V, metal silver may be deposited without any danger of the cathode decomposition of thiosulphate.

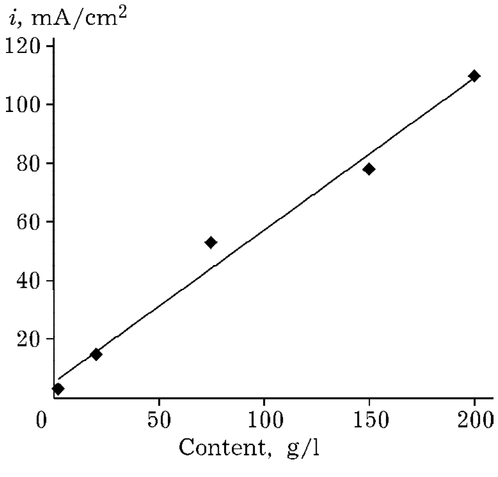

Fig. 2. Dependence of the limiting current density of thiosulphate ion reduction at a silver cathode on the concentration of $Na_2S_2O_3$. Potential scan velocity: 20 mV/s.

One can see in Fig. 2 that the height of the peak of current density at $\varphi = -1.5$ V is proportional to the concentration of thiosulphate, which allows us to consider the density of the current of thiosulphate reduction on a silver cathode as a promising analytical signal for the voltammetric determination of thiosulphate ions in fixing solutions.

### *Cathode behaviour of $SO_3^{2-}$ ion*

The cathode polarization curves in the solution of 15 g/l $Na_2SO_3$ + 1 M $Na_2SO_4$ at pH 5.8 and 9.5, on the mechanically renewed electrodes made of platinum, graphite and silver are shown in Fig. 3. A comparative analysis of these curves with similar dependencies for thiosulphate allows us to reveal thee essential differences.

1. The $SO_3^{2-}$ ion is easily reduced on all the electrodes involved in the investigation. The process starts at substantially more positive potentials (about −500 mV) and under further cathode polarization is masked by the process of hydrogen evolution which occurs on platinum much earlier in comparison with silver and graphite (the potential values are −1, −1.5, and −1.7 V, respectively).

2. A detailed shape of the cathode curve of sulphite ion reduction is essentially dependent on the electrode material: one cathode wave is observed on platinum and on graphite; the height of the limiting current density on plat-

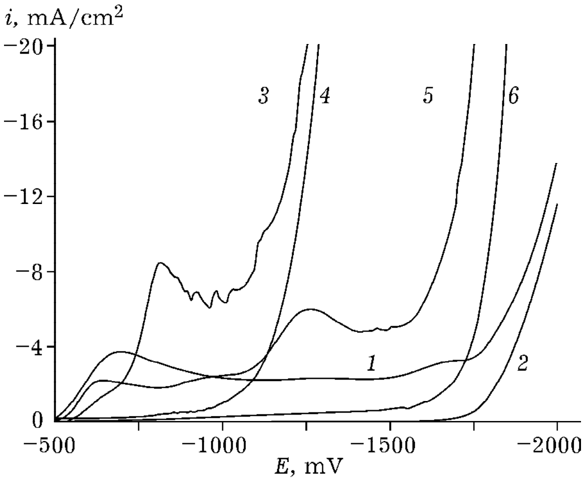

Fig. 3. Cathode reduction of sulphite ion on graphite (*1*, *2*), platinum (*3*, *4*) and silver (*5*, *6*). Potential scan velocity: 20 mV/s; solution: 15 g/l $Na_2SO_3$ + 1 M $Na_2SO_4$; pH values: 5.8 (*1*, *3*, *5*), 9.5 (*2*, *4*, *6*).

inum is twice as large as that on graphite. Two consequent cathode waves are observed on the silver cathode; the limiting current density of the first wave is close to the limiting current density of $SO_3^{2-}$ ion reduction on graphite, while the peak of the second wave corresponds to the limiting current density of sulphite ion reduction on platinum. This is likely to be an evidence of the stage character of sulphite ion reduction on silver. The possible products of reduction (for example, dithionite *etc.*) were considered in [7, 9]. In the case under our consideration, it is necessary to stress that no limiting reduction of $S^{4+}$ in sulphite into $S^{2-}$ ion occurs, which is confirmed by the absence of turbidity in solution after its treatment within the investigated potential range with the addition of silver ions.

3. Unlike for thiosulphate, the cathode reduction of $SO_3^{2-}$ ion on all the electrodes is essentially dependent on pH value. The dependence of limiting current density of $SO_3^{2-}$ reduction on silver (at $\varphi \approx -1.2$ V) on pH is shown in Fig. 4. One can see that variation of this parameter within the limits pH 3–6 has almost no effect on the process; however, further alkalisation of the solution to pH ≥ 7 leads at first to a sharp (about a factor of 5) then to a slower decrease in the limiting current density of $SO_3^{2-}$ reduction. Such a character of the curve may be explained by the fact that sulphite ion exists in different forms in aqueous solutions depending on pH [23]: $SO_2$ (pH < 3), $HSO_3^-$ (pH 3–6) and $SO_3^{2-}$ (pH > 7). It is also known that at least on mercury cathode sulphite ion relates to the difficultly reducible anions while $SO_2$ and $HSO_3^-$ get reduced rather easily [9]. Our results show that a similar situation is observed also for the reduction of sulphite on silver.

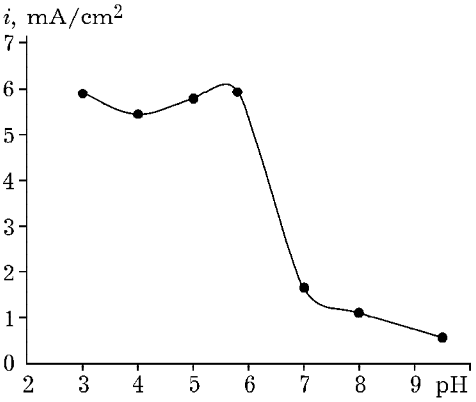

Fig. 4. Dependence of the limiting current density of sulphite ion reduction ($\varphi \approx -1.2$ V) at a silver electrode on pH value. Potential scan velocity: 20 mV/s; solution: 15 g/l $Na_2SO_3 + 1$ M $Na_2SO_4$.

When investigating silver recovery processes, it is necessary to carry out a comparative analyse of the region of potentials of silver and sulphite ion reduction. Measurement of the cathode polarization curves in fixing solutions with different silver content showed that in the case if the latter is 2 g/l, silver starts to get deposited on a silver electrode at $\varphi \approx -0.35$ V. With an increase in silver content up to 17.8 g/l, the potential of the start of reduction shifts to approximately −0.2 V, while for decreased content 0.2 g/l it becomes more negative (to −0.5 V). Therefore, in the initial fixing solutions (pH 5.8) the regions of reduction potentials of silver and sulphite overlap. So, to provide deep silver recovery and avoid reduction of $SO_3^{2-}$ ions, it is necessary to carry out preliminary preparation of solutions. Otherwise, while silver gets recovered from the fixing solution, the concentration of sulphite in this solution would decrease and the products of its reduction would get accumulated.

At the final stage of electrolysis, the determined current density in the potential region before the start of thiosulphate reduction ($\varphi \approx -0.85$ V) will be determined not by silver discharge but by a side process of sulphite reduction (because of the component concentration ratio, because the concentration of Ag ions is much lower than that of $SO_3^{2-}$ ions). Such a relation between the current densities of the target and side processes can not only lead to a decrease in the yield as a function of current but also to decrease the effective depth of penetration of the target reaction into the porous electrode (due to an increase in ohmic losses in the liquid and solid phases) [22]. Under these conditions, it is difficult to achieve low residual content of silver ions by the one-stage electrochemical treatment of fixing solutions. Nevertheless, taking into account the above-described high sensitivity of the side process of $SO_3^{2-}$ ion reduction to solution pH, it is possible to suppress the side reaction of the cathode reduction of $SO_3^{2-}$ due to small alkalisation of the initial fixing solution to pH > 7. This will allow, on the one hand, to decrease substantially the consumption of sulphate during the electrochemical regeneration of fixing solutions, on the other hand, to eliminate the effect of side processes and, as a consequence, to increase the rate of silver recovery and decrease its residual content.

Our assumption was tested in the investigation of the effect of pH value on the degree of silver recovery from fixing solutions (initial silver content: 200 mg/l) on voluminous porous cathodes made of carbon fibre materials of VNG-30 and KNM grades and of metallized syntepon. Starting from the obtained data that the ion is not get reduced on silver cathode at φ more positive than −0.85 V at any pH value, while sulphite ion gets reduced at pH 5.8 and does not do so under alkalisation to pH ≥ 7, we chose the following conditions to test the effect of pH value on silver recovery from fixing solutions: potentiostatic electrolysis mode at φ ≈ −0.85 V, pH 5.8 and 9.5.

It was established that the nature of the materials of the cathodes involved in the investigation has only a slight effect on the kinetics of silver recovery. As an example, Fig. 5 shows the data obtained with the cathode made of VNG-30. One can see that the major part of silver is removed from solution within the first 15−20 min, then the recovery process slows down sharply; the residual metal content at pH 5.8 turns out to be much higher than that at pH 9.5 (1.8 and 0.6 mg/l, respectively).

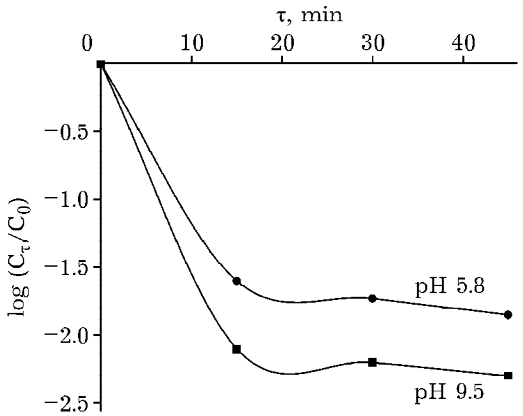

Fig. 5. Effect of solution pH on silver recovery at the cathode made of VNG-30. $C_0$ and $C_τ$ are initial and current silver concentrations, mg/l; electrode potential φ = −0.85 V; solution volume: 0.65 l.

At pH 5.8, silver recovery is almost completely suppressed by side reactions, that is why the yield as a function of current is only 3−5 %. Preliminary alkalisation of the solution to pH 9.5 causes an increase in the yield as a function of current to 34−58 %, the recovery degree to 99.2−99.4 %, average rate of silver recovery increases to 275−327 mg/(h · $dm^2$). The highest values of these electrolysis parameters were obtained with the cathode made of metallized syntepon.

So, the investigation showed that pH value has a diverse effect on the cathode reduction of the main components of fixing solutions. The strongest dependence is observed for sulphite ions; the process of their reduction on silver, platinum and graphite is almost completely suppressed at pH ≥ 7. The pH value has almost no effect on the reduction of silver and thiosulphate ions. The obtained results allowed us to choose an optimal mode of electrolysis for the regeneration of worked out fixing solutions with the help of flow voluminous porous cathodes providing minimal losses of thiosulphate and sulphite, high efficiency of silver recovery, and the return of recovered matter for repeated use. Recycling of the fixing solution allows one to decrease or even prevent disposal of toxic compounds into the environment, to increase silver saving and to improve the ecological characteristics of chemical photographic works.

## CONCLUSIONS

1. The ability of thiosulphate ions to get reduced is strongly dependent on the nature of the cathode material: on platinum and on graphite, reduction almost does not proceed (at least before the potential of the start of hydrogen evolution), while on silver the $S_2O_3^{2-}$ ion gets reduced at the potentials more negative than −0.85 V with the formation of sulphide and sulphite ions. The peak current density of thiosulphate ion oxidation on silver is proportional to its content in solution. Variation of pH value within the pH range 6−9 has almost no effect on the current strength of thiosulphate reduction.

2. Sulphite ion is easily reduced on all the investigated cathodes. The potential regions of silver reduction and silver deposition overlap.

The rate of sulphite reduction decreases sharply when the solution is acidified to pH ≥ 7.

3. Elimination of the side reactions of cathode reduction of thiosulphate and sulphite ions (in the first case, by means of choosing the potential value at approximately −0.85 V, in the second case, by alkalisation to pH ≥ 7) allows one to enhance the rate of silver recovery and yield as a function of current. In addition, with the use of flow voluminous porous cathodes made of fibrous carbon materials and metallized syntepon for the electrolysis of fixing solutions, one may reduce the residual silver content to about 1 mg/l.

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