Evolution of Anolyte Composition in the Oxidative Electrolysis of Sodium Bromide in a Sulfuric Acid Medium

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Abstract—The oxidation of a 10 mM aqueous solution of sodium bromide in a sulfuric acid medium on the surface of a platinum electrode in a cell with separated spaces was studied. The process is important in view of the use of the bromine—bromide redox couple in redox flow batteries. The study was performed by cyclic voltammetry, potentiostatic chronoamperometry with optical absorption spectrum recording, and measurements of the potential of the redox reference electrode. A numerical procedure for processing the experimental spectra of the solution was developed to separate them into the spectrum of molecular bromine and the residual signal. The latter was attributed to the absorption of the tribromide anion based on the literature data.

The experimental dependences of the Br_2 and Br_3^- concentrations for the oxidative electrolysis of the NaBr solution in the sulfuric acid medium agreed well with the theoretical predictions. The current efficiency of bromine formation was evaluated.

Keywords: electrooxidation of bromide ion, tribromide anion, indicator electrode, spectroelectrochemistry **DOI:** 10.1134/S1023193518130335

INTRODUCTION

Bromine and its compounds are widely used in various fields, for example, in the production of flame retardants [1] and pesticides [2] and in water and air cooling systems [3]. In view of recent growth of interest in electrochemical power sources, studies on hydrogen bromine redox flow batteries (RFBs) with a bromine-bromide redox couple have appeared [4, 5].

The best samples of hydrogen bromine RFBs show power densities of up to 1.5 W/cm² [5] and are well suited for various stationary power applications in future, for example, as reserve power sources or for storing the electric energy produced in the nonpermanent mode by solar and wind power plants. However, the use of hydrogen bromine flow batteries is limited by the corrosivity of bromine, degradation of the platinum catalyst on the surface of the hydrogen electrode due to bromine crossover, and relatively high cost of bromine.

The recently proposed hydrogen bromate RFBs [6]

in which the BrO_3^- anion is used as a high-energy multielectron oxidant are free from these drawbacks. It was shown that the six-electron reduction of bromate anions to bromide anions [7], which occurs in the autocatalytic mode, corresponds to the high theoretical discharge current densities and to the maximum power density among all flow batteries. However, only the operation of hydrogen bromate flow batteries in the current generator mode [8] has been demonstrated until now, while for the full energy cycle, it is necessary to additionally provide an efficient mode of electric energy regeneration, that is, battery charging.

It was shown that the hydrogen bromate flow battery operating in the discharge mode gives acid bromide-containing solutions as the main product, which should be oxidized back to the bromate anion during regeneration [8]. As is known, the bromide anion spontaneously transforms into the bromate anion at high pH [9]. There are some other ways of converting the bromide ion into the bromate ions, for example, by chlorination and ultraviolet treatment [10, 11] or by ozonation combined with treatment with hydrogen peroxide H_2O_2 [12]. From the viewpoint of the closed energy cycle of a flow battery, however, it would be most advantageous and convenient to convert the bromide ion into the bromate ion by electrooxidation without correcting pH if possible.

The electrooxidation of the bromide anions to the bromate anions or bromine compounds of even higher oxidation states was described in [13-18]. However, they are not suitable for fuel regeneration in hydrogen bromate batteries because the electrolysis of alkaline or neutral bromide-containing solutions in these batteries [14–18] is performed using expensive electrode materials such as boron-doped diamond (BDD) [13, 14, 16], while the electrooxidation of the bromide ion in the regeneration reactor is most effective when performed in its acidic solutions, i.e., without pH correction. In addition, many of these studies were performed only at low concentrations of bromide ions [13, 14, 16, 17], and the electrolysis of bromide-containing solutions was carried out at potentials beyond the limits of the electrochemical window of stability of aqueous electrolytes [14, 16-18], which leads to concomitant reactions of water electrolysis and hence to inevitable energy loss.

Several publications described the electrooxidation of the bromide ion to bromine performed on platinum electrodes in acidic aqueous media [19-22]. Some of them suggest the possibility of further electrooxidation to compounds of higher oxidation states, for example, the hypobromite anions BrO⁻. Two pairs of redox peaks were observed in the anodic region of the cyclic voltammograms [19, 20]: one at 0.94 V relative to SCE (which is associated with the Br_2/Br^- redox couple) and the other at 1.29 V relative to SCE (Br⁻/BrO⁻ transition). These data are of great interest from the viewpoint of the electrochemical regeneration of spent fuel from a hydrogen-bromate flow battery because the hypobromite anion BrO⁻ is one of the essential intermediates in a series of reductions of the bromate ions [23]. However, the hypothesis about the electrochemical formation of BrO⁻ hypobromite was not tested in [20, 21], while other authors interpreted similar data obtained by electrooxidation of bromide ions in nitrobenzene and acetonitrile as the peaks of the

Br^{-}/Br_{3}^{-} and Br_{3}^{-}/Br_{2} redox couples [24, 25].

The goal of this study was to develop a method for quick determination of the composition of a brominecontaining medium suitable for investigating the electrolytic oxidation reactions of bromide anions under various reaction conditions. For this purpose, a series of experiments were performed in a flow cell of special design capable of simultaneously recording the optical spectra in the visible and near-UV ranges, evaluating the total redox capacity of the system, and determining the equilibrium potential of the indicator platinum electrode in a bromine-containing medium located in the anode chamber of a three-electrode electrochemical cell with separated spaces.

The applicability of the new technique was tested on the electrolysis oxidation of 10 mM NaBr in an acidic medium (0.7 M H_2SO_4) at a potential of 1.1 V relative to Ag/AgCl; the concentrations of Br₂ and Br₃⁻, which depended on the amount of the transmitted charge, were compared with the theoretical predictions based on the thermodynamic data from the literature.

EXPERIMENTAL

Sample Preparation

The following substances were used to prepare the electrolyte solution: sulfuric acid (H₂SO₄, reagent grade), Khimmed, mass concentration 95%), sodium bromide (NaBr, \geq 99%, Sigma Aldrich), sodium sulfate (Na₂SO₄, 99%, Sigma Aldrich), and sodium bromate (NaBrO₃, \geq 99%, Sigma Aldrich). The pH of the system was measured on an ANION 4100 stationary pH meter using the ESK-10601/7 electrode; the result was 0.41.

To prepare the reference aqueous solution of bromine (5 mM Br₂), exact volumes of 0.3 M NaBr, 0.15 M NaBrO₃, and 2 M H₂SO₄ solutions were mixed to provide a stoichiometric ratio of sodium bromide and bromate (5 : 1) in reaction (1) in an excess of sulfuric acid:

$$5NaBr + NaBrO_{3} + 3H_{2}SO_{4}$$

$$= 3Br_{2} + 3H_{2}O + 3Na_{2}SO_{4}.$$
(1)

Cyclic Voltammetry

For cyclic voltammetry (CV) measurements, a three-electrode circuit was used with a silver chloride reference electrode (SCE, Ag/AgCl in 3.5 M KCl), platinum wire as an auxiliary electrode, and a platinum electrode with a diameter of 1 mm as a working electrode. Hereinafter, the potentials are given relative to the Ag/AgCl electrode in 3.5 M KCl. The measurements were performed on an ELINS-50-Pro potentiostat in a Faraday cage shielded from the external electromagnetic fields. The solution used was deoxygenated before the experiment, and the measurements were performed in an inert argon atmosphere.

The cyclic voltammograms were measured in the range from -220 to 1500 mV; the scan rate was 100 mV/s.

Oxidative Electrolysis of Sodium Bromide with Recording of the Evolution of the Optical Absorption Spectrum of Anolyte

The electrolysis of 10 mM bromide-containing solutions was performed in an argon atmosphere in a hermetically sealed quartz optical cell of special design with a stirrer immersed to the bottom. The Teflon lid of the cell had holes for four electrodes: a platinum counter electrode, silver chloride reference electrode (Ag/AgCl electrode in 3.5 M KCl), platinum working electrode in the form of a square mesh with a side of 1.5 cm and a step of 1.5 mm, and indicator electrode in the form of platinum wire with a length of 3 cm and a diameter of 1 mm. The volume of the solution V inside the cell was 2.3 mL.

The potentiostatic mode was used with a potential of 1.1 V relative to Ag/AgCl applied for 90 min using an Autolab PGSTAT302N potentiostat, which recorded the experimental dependences of the current on the transmitted charge.

The optical absorption spectra of the solution were recorded intermittently during the electrolysis using an Avantes StarLine AvaSpec2048 fiber optic spectrophotometer. The interval between successive recordings was 10 s. The optical path length was 10 mm. The spectrum of a quartz cell with tridistilled water was recorded as a reference spectrum. All measurements were performed with a stirrer turned on for uniform distribution of all the components of the solution throughout its volume; the operation of the potentiostat and spectrophotometer was synchronized using a PC.

The indicator electrode (platinum wire) and silver chloride reference electrode were connected to the input channel of the Autolab 302N potentiostat AD converter via a differential subtracting repeater, which provided high input resistance without any effect of the measuring current on the recorded potential difference.

Mathematical Processing of the Optical Absorption Spectra

The program algorithm (proposed and described in detail in [26]) is implemented in Mathcad software. It allows the decomposition of the experimental optical spectrum recorded at a certain moment during the electrolysis into the contribution of absorption by dissolved molecular Br_2 and the residual spectrum.

The spectrum $A_{exp}(\lambda)$ (absorption depending on the wavelength) can be represented as the sum of two components

$$A_{\rm exp}(\lambda) = XA_{\rm ref}(\lambda) + A_{\rm res}(\lambda), \qquad (2)$$

where λ is the wavelength, $A_{ref}(\lambda)$ is the reference optical absorption spectrum of 5 mM Br₂ (for the synthesis, see above) preliminarily measured under the same conditions, $A_{res}(\lambda)$ is the residual optical spectrum, and X is the coefficient form 0 to 1 at which the sum

$$\sum \left[A_{\exp}(\lambda_{t}) - XA_{\mathrm{ref}}(\lambda_{t})\right]^{2}$$
(3)

is maximum (for the wavelengths λt in the range from 380 nm to 430 nm, i.e., in a narrow neighborhood of the absorption maximum of dissolved bromine). Thus, the determined X value makes it possible to calculate the conversion of the bromide Br⁻ anion into molecular bromine Br₂ at the moment of spectrum recording. At X = 0, Br₂ is absent in the system; at X = 1, all Br⁻ is converted by oxidation into Br₂, and $XA_{ref}(1)$ is shown by the spectrum of bromine accumulated in solution by the given moment of time. For

each moment of time during the measurement of $A_{exp}(l)$, Eq. (2) can be used after finding the corresponding value of X to calculate the residual optical spectrum $A_{res}(l)$.

Theoretical Dependences of the Concentrations of Solution Components on the Transmitted Charge

The theoretical dependences of the concentrations of bromine compounds on the equilibrium potential of the system were calculated by analogy with [27]. For the given initial concentrations of the bromide anion c_{tot} and the equilibrium potential *E*, the following set of equations is solved:

$$\frac{[Br_2]}{Br^{-}]^2} = 10^{2A(E-E_1^\circ)},$$
(4)

$$\frac{[Br_3^-]}{[Br^-]^3} = 10^{2A(E-E_2^\circ)},$$
(5)

$$\left[\mathbf{Br}^{-}\right] + \left[\mathbf{Br}_{3}^{-}\right]/3 + \left[\mathbf{Br}_{2}\right]/2 = c_{\text{tot}},\tag{6}$$

where [Br⁻], [Br₂], and [Br₃⁻] are the concentrations of the corresponding compounds; E_1° is the standard potential of the Br⁻/Br₂ redox couple; E_2° is the standard potential of the Br⁻/Br₃, redox couple; and $A = F/RT \ln 10 = 16.92$. In addition, for each *E* and c_{tot} we can calculate the charge *Q* transmitted during the electrooxidation of the initial amount of the bromide anion to molecular bromine and tribromide anion in the concentrations found using (4)–(6). For this, we use the equation

$$Q/FV = \left(\left[\mathbf{Br}_{3}^{-} \right] + 2\left[\mathbf{Br}_{2} \right] \right), \tag{7}$$

where F is the Faraday constant equal to 96485 C/mol. Thus, based on the thermodynamic predictions, it is possible to find not only the dependences of the concentrations of various bromine compounds on the equilibrium potential, but also the dependences of the concentrations on the charge transmitted during the electrolysis, which will be compared here with experimental data.

RESULTS AND DISCUSSION

CV Analysis

Figure 1 shows the cyclic voltammogram for the electrooxidation of an acidic solution of NaBr on a platinum electrode. In the range of negative potentials, the voltammogram contains the peaks of hydrogen adsorption/desorption on the platinum surface characteristic of a sulfate medium [28]. In the range of positive potentials, there are three groups of waves: (1) a pair of oxidation/reduction peaks with a halfwave potential $E_{1/2} = E_{pa} + E_{pc} = 0.952$ V correspond-



Fig. 1. Cyclic voltammogram of the Pt electrode in 10 mM NaBr + 0.3 M Na₂SO₄ + 0.7 M H₂SO₄. pH 0.41. Scan rate: 100 mV/s.

ing to the Br_2/Br^- redox couple; (2) a weak cathode wave at -0.55 V corresponding to the reverse reduction of the surface platinum oxide Pt–OH that formed in the process competing with the oxidation of the bromide ion [20]; (3) an oxidation peak at 1.40 V with a poorly resolved reverse reduction peak at 1.33 V.

The literature gives different interpretations of the latter pair of redox peaks. Some authors interpreted it as the electrooxidation of Br_2 into bromine compounds at higher degrees of oxidation, for example, the hypobromite BrO^- anion [21]. The absence of a pronounced reverse peak of the reduction of BrO^- in this case can be explained by the high rate of the homogeneous reaction of counter-proproportionation (8) in an acidic medium [23]:

$$HOBr + Br^{-} + H^{+} = Br_{2} + H_{2}O.$$
 (8)

In other studies, however, the similar data were interpreted differently. In [29] the peak similar in shape and position was associated with the electrooxidation of the bromide Br^- anion adsorbed on the surface into HOBr; in [24, 25], where the electrooxidation of bromide ions in nonaqueous media was studied, two waves with a similar shape in the range of positive potentials were attributed to the Br^-/Br_3^- and

 Br_3^-/Br_2 redox couples.

Oxidative Electrolysis of the Bromide Anion

In further experiments, the electrolysis of the bromide anion was performed in a potentiostatic mode at a potential E = 1.1 V. This value was chosen in accordance with the CV data based on the following considerations: (1) It lies in the electrochemical stability window of aqueous electrolytes when platinum is used as a working electrode material. (2) The potential E = 1.1 V lies between two anode waves on the CV curve (Fig. 1), so the process responsible for the second anode wave near the potential of 1.4 V should not occur under these conditions; therefore, an analysis of the solution composition during the electrolysis can provide information about the processes for both anode waves.

Note that the thermodynamic and kinetic data for reactions (1) and (8) suggest that the solution contains no bromate and hypobromite ions, at least until the amount of bromide ions decreases in solution due to the fast counter-proportionation reactions. At the same time, based on the thermodynamic data, the accumulation of significant quantities of the tribromide anion was not excluded due to the reaction

$$Br_2 + Br^+ = Br_3^-.$$
 (9)

Figure 2a shows the experimental dependences I(t) and Q(t) obtained during the oxidative electrolysis of the 10 mM sulfuric acid solution of NaBr for 90 min. It can be seen that Q = 2.20 C passes through the system during the experiment.

This charge should be compared with the charge required for complete single-electron oxidation of Br^- to molecular bromine Br_2 :

$$Q_{\rm eq} = Fc_{\rm tot}V.$$
 (10)

Having substituted F = 96485 C/mol, $c_{tot} = 10$ mM, and V = 2.3 mL, we obtain that $Q_{eq} = 2.219$ C (called an equivalent charge here); and let us designate Q/Q_{eq} as Y (relative charge).

The absorption spectra of the system were recorded during the electrolysis (Fig. 2b). At the start of electrolysis (the curve for t = 30 s), the peak at 265 nm in the spectrum begins to grow rapidly; it can be attributed to the tribromide Br_3^- anion [30]. The molar extinction coefficient of Br_3^- at a wavelength of 260 nm $\epsilon(Br_2)$ is very large: 37200 M⁻¹ cm⁻¹ [31]; i.e., it is more than two orders of magnitude larger than that of Br₂ in the region of its absorption maximum: $\varepsilon(Br_2) =$ 167 M⁻¹ cm⁻¹ at 400 nm [32, 33]. An increase in the concentration of the bromide anion during the electrolysis quickly leads to exceeded sensitivity threshold of the device (the curves for t = 100, 250, and 500 s). At the same time, a broad absorption peak at 400 nm corresponding to molecular bromine Br₂ becomes clearly visible in the optical spectra [30]. During further electrolysis, the contribution of the tribromide anion starts to decrease in the optical spectra (the

curve t = 1000 s, where the contribution of Br_3^- is still clearly pronounced, can be compared with the curves for t = 2500 and 5400 s, whose form is already close to the optical spectra of pure Br_2 with a broad peak at 400 nm and a sharp rise in the short-wave region starting from 290–300 nm); the intensity of the Br_2







Fig. 2. (a) Chronoamperogram (solid line) and chronocoulogram (dashed line) recorded during potentiostatic electrolysis (E = 1.1 V) of the solution of 10 mM NaBr + 0.3 M Na₂SO₄ + 0.7 M H₂SO₄ on a platinum electrode. The arrows indicate the ordinate axes corresponding to the curves. (b) Absorption spectra of anolyte during the electrolysis (Fig. 1) at different moments of time *t*, s: (*I*) 1, (*2*) 10, (*3*) 100, (*4*) 250, (*5*) 500, (*6*) 1000, (*7*) 2500, and (*8*) 5400.

absorption band is stabilized (the curves for t = 1000, 2500, and 5400 s; a slight decrease in the peak height for t = 5400 compared with that at t = 2500 s will be considered below).

Results of the Decomposition of the Experimental Optical Spectra

Figure 2b is suitable for qualitative analysis of the behavior of the system, but quantitative analysis based on these data is difficult because the optical spectra of various bromine compounds overlap each other in certain ranges of wavelength. Therefore, we used the sep-



Fig. 3. Illustration of the use of the algorithm for the decomposition of the experimental absorption spectrum of anolyte $(A_{exp}(\lambda), \text{ curve } I)$ into the spectrum of bromine $(XA_{ref}(\lambda), \text{ curve } 2)$ and the residual spectrum $(A_{res}(\lambda), \text{ curve } 3)$. For decomposition, the reference spectrum of bromine was used (5 mM Br₂, curve 4). The experimental spectrum corresponds to t = 1070 s (relative charge Y = 0.9), X = 0.837.

aration of the experimental spectra $A_{exp}(\lambda)$ into two components: the contribution due to absorption by molecular bromine $XA_{ref}(\lambda)$ and the residual spectrum $A_{res}(\lambda)$. The contribution of molecular bromine was determined as the product of the reference spectrum by the coefficient X, selected according to the algorithm described in the section "Mathematical Processing of Absorption Spectra" and converted into the current bromine content in the anolyte. A typical example of processing the graphical data using the proposed algorithm is shown in Fig. 3. After the separation procedure, the spectrum of the tribromide anion remains as the residual spectrum [30], which confirms that the chosen procedure is correct.

According to Fig. 2b, the optical absorption spectra have no characteristic signals of bromine compounds other than molecular bromine Br_2 and tribromide anion Br_3^- , for example, the bromate BrO_3^- anion with a characteristic rise in the short-wave region starting at 270 nm [33].

The absence of other bromine compounds in significant concentrations relative to the total analytical concentration of bromine was expected in the system with the chosen experimental conditions. In an acidic medium, the equilibrium of counter-proportionations (8) and (1) involving HOBr and BrO_3^- is strongly shifted toward the formation of Br_2 [34], which precludes the formation of significant amounts of bromine compounds at higher degrees of oxidation than zero (Br_2) by homogeneous chemical reactions [23].



Fig. 4. (a) Dependence of the Br_3^- concentration on the relative charge. Circles: the result of the processing of spectrophotometric data; solid lines: calculation by Eqs. (4)–(6) at different values E_2^0 , V: (1) 1.053, (2) 1.052, and (3) 1–1.051. (b) Dependence of the Br_2 concentration on the relative charge. Circles: the result of the processing of the spectrophotometric data; solid line: calculation by Eqs. (4)–(6) $E_2^0 = 1.052$ V; dashed line: hypothetical situation when molecular bromine is the sole product of electrooxidation of bromide with 100% current efficiency.

Therefore, within the transmitted charge, up to Q_{eq} , the system has significant amounts of only three bromine compounds in the system: Br⁻, Br₂, and Br₃⁻. The concentration of Br₂ can be evaluated from the spectrum $X^*A_{ref}(\lambda)$ obtained after the decomposition of the experimental optical spectrum of the system from the optical absorption at a wavelength of 396 nm (corresponding to the maximum optical absorption of

Br₂); the concentration of Br₃⁻ can be evaluated from the residual spectrum $A_{res}(\lambda)$ from the optical absorption at a wavelength of 310 nm (this wavelength was chosen to remain within the sensitivity range of the instrument).

Dependence of the Concentrations of Various Bromine Compounds on the Transmitted Charge. Comparison with the Thermodynamic Predictions

The molar extinction coefficients $\epsilon_{Br_2}^{396} = 167 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{Br_3}^{310} = 7400 \text{ M}^{-1} \text{ cm}^{-1}$ [23] were used to calculate

the experimental concentrations of Br_2 and Br_3^- . The calculated data are shown in Fig. 4 in comparison with the results of thermodynamic predictions made by analogy with [28]. Two parameters were used as the free parameters of the model described above in the "Theoretical Dependences" section: the standard

potential E_1° of the Br⁻/Br₂ redox couple and the standard potential E_2° of the Br⁻/Br₃⁻ redox couple; $E_1^{\circ} =$ 1.0874 [34], and E_2° was chosen such that the best agreement could be achieved between the experimental data and the thermodynamic predictions for the form of the dependence of [Br₃⁻] on the relative charge Y (Fig. 4b).

Figure 4a shows that the best agreement with the experimental data is observed for $E_2 = 1.052$ V, which coincides well with the tabulated value $E_2 = 1.0503$ [34]. The thermodynamic constant of formation of the tribromide anion $K = [Br_3^-]/[Br_2][Br^-]$ can also be calculated from the values of E_1° and E_2° using (4), (5). Taking that $E_1 = 1.0874$ V and $E_2 = 1.052$ V, we obtained $K = 10^{2A(E_1^{\circ}-E_2^{\circ})} = 16$ M⁻¹, which is in good agreement with the literature value of K = 18 M⁻¹ [35, 36]. For thermodynamic calculations, $E_1^{\circ} = 1.0874$ V and $E_2^{\circ} = 1.052$ V were used. According to Fig. 4b, the dependences predicted based on these constants also agree with the experimental data: the concentration of the tribromide anion Br_3^- reaches a maximum of 0.2 mM in the range of $Y = Q_{eq} = 0.45 - 0.5$ and then decreases to zero at Y = 1.0.

Figure 4b shows the theoretical and experimental dependences of the concentration of molecular bromine on the charge that passed during the electrolysis. The concentration of molecular bromine Br₂ gradually increases during the electrolysis up to the point Y = 0.97, after which it begins to decrease. Three main regions can be isolated in the plot. In the first region from Y = 0 to Y = 0.1, the experimental concentration of bromine (circles) (according to the spectrophotometry data) is slightly lower than the concentration obtained from the thermodynamic predictions (solid curve). In this case, 0.1 equivalent charge passes through the system already within the first 50 s of elec-

trolysis (the total electrolysis time is 5400 s). This deviation of experimental data from predictions may be explained by several factors. Firstly, on small time scales, the equilibrium concentrations do not set in the system; the bromine that formed during the electrolysis in the near-electrode layer is not yet distributed over the system and not hit by the beam of the spectrophotometer. Secondly, at the initial moments of electrolysis, a significant portion of energy is spent on the formation of the surface platinum oxides and, possibly, on accumulation of adsorbed bromine.

At the stage of electrolysis from Y = 0.1 to Y = 0.8, the experimentally (spectrophotometrically) observed concentration of molecular bromine gradually begins to exceed the thermodynamic predictions and is compared with the maximum possible concentration calculated on condition that the system has no tribromide anions (dashed curve). The deviation of the experimental data from predictions, in turn, may be explained by the systematic experimental errors associated, for example, with the preparation of a solution of the required concentration.

Finally, at the final stage of electrolysis, from Y = 0.8 to Y = 1.0, the increase in the concentration of molecular bromine in the anolyte again begins to gradually lag behind the thermodynamic predictions. This may be explained by the gradual evaporation of volatile bromine from the spectral cell, which in this area already has a significant influence on the system composition due to the relatively longer duration of the final stage of the process: the electrolysis at Y = 0.8-1.0 equivalent charge takes 4700 s, while the electrolysis at Y = 0.8 takes only 700 s.

At Y = 0.97, the concentration of molecular bromine reaches its maximum of 4.5 mM, which is close to the maximum concentration of 5 mM achieved in the full single-electron oxidation of 10 mM of the bromide anion to molecular bromine Br₂. After Y = 0.97, a sharp decrease in the concentration is observed, which may be explained by the fact that all bromide anions in the system were already oxidized to bromine and Br₂ in the system starts to be gradually converted into HOBr.

Evaluation of Current Efficiency for the Electrooxidation of the Bromide Anion Br⁻ to Molecular Bromine Br₂

The current efficiency for the electrooxidation of the bromide anion to molecular bromine Br_2 over the period from the start of the process to an arbitrary moment of electrolysis (N_{eff}) can be estimated by the equation

$$N_{\rm eff} = 2[Br_2]FV/Q.$$
(11)

Figure 5 shows the experimental dependence of the current efficiency on the amount of transmitted

Current efficiency, arb. units 1.0 0.8 0.6 0.4 0.2 0 0.2 0 0.2 0.4 0.2 0.2 0.4 0.2 0.4 0.2 0.4 0.2 0.4 0.2 0.4 0.4 0.2 0.4 0.4 0.2 0.4 0.4 0.2 0.4 0.4 0.2 0.4 0.4 0.2 0.4 0.4 0.2 0.4 0.4 0.2 0.4 0.4 0.2 0.4 0.4 0.2 0.4 0.4 0.2 0.4 0.2 0.4 0.2 0.4 0.2 0.4 0.2 0.4 0.2 0.4 0.2 0.4 0.2 0.4 0.2 0.4 0.4 0.5 0.4 0.5 0.4 0.6 0.81.0

Fig. 5. Dependence of the current efficiency N_{eff} for the electrooxidation of the bromide anion to molecular bromine Br_2 on the relative charge. Circles: the result of the processing of the spectrophotometric data; solid line: cal-

culation by Eqs. (4)–(6) at $E_2^{\circ} = 1.052$ V.

charge in equivalent units in comparison with a similar dependence based on the thermodynamic predictions.

For the theoretical dependence, it can be seen that the integrated current efficiency gradually increases during the electrolysis, reaching 100% at Y = 1.0; that is, all the transmitted charges were spent on the electrooxidation of the bromide anion to molecular bromine and there are no significant amounts of tribromide in the system. At the same time, at the beginning of electrolysis (up to Y = 0.1), the theoretical current efficiency is no more than 90%; that is, a significant part of the transmitted charge (no less than 10%) is spent on the formation of the tribromide anion.

The same three regions can be distinguished on the experimental dependence as in Fig. 4a. In the range of Y from 0 to 0.1 equivalent charges, there is a sharp increase from 0 to ~0.85 in the current efficiency. The experimental current efficiency everywhere in this region remains smaller than that obtained by thermo-dynamic predictions; this may be explained by the nonuniform distribution of bromine formed during the heterogeneous reaction over the system and by the formation of platinum surface oxide and bromine adsorption.

In the second region, from Y = 0.1 to Y = 0.8, the experimental current efficiency begins to exceed the corresponding value calculated on the basis of thermodynamic predictions, gradually reaching the maximum possible value of 1.0. This anomalous behavior may be explained by the experimental errors associated with the preparation of initial solutions; i.e., initially the system had a slightly higher concentration of bromine atoms than 10 mM in thermodynamic calculations.

Y. arb. units



Fig. 6. Dependence of the indicator electrode potential on the relative charge. Circles: the result of the measurement during the electrolysis; solid line: calculation by Eqs. (4)–(7) at $E_2^{\circ} = 1.052$ V.

Finally, in the third region from Y = 0.8 to Y = 1.0, the experimental current efficiency begins to lag behind the thermodynamic predictions, gradually decreasing to $N_{\text{eff}} = 0.9$, and at the point Y = 0.97 it decreases sharply to ~0.8. This behavior may be explained by a combination of two factors: the increased role of bromine evaporation on large time scales and the appearance of HOBr in the system after complete electrooxidation of bromide anions to bromine in the system.

Dependence of the Indicator Electrode Potential on the Transmitted Charge. Comparison with the Results of Calculation

Based on the thermodynamic predictions it is also possible to obtain the dependence of the equilibrium potential in the bromine–water system during the electrooxidation of the bromide anion on the transmitted charge. In Fig. 6 the dependence is given in comparison with the experimental dependence of the potential of the indicator electrode brought in contact with the solution inside the spectroelectrochemical cell. The presented dependences are in good agreement with one another, which confirms the possibility of using the indicator electrode to determine the equilibrium potential of the system during the oxidative electrolysis of bromide ions.

Thus, it is possible to construct the experimental dependences of the concentrations of bromine atoms in various bromine compounds (i.e., taking into account their stoichiometric coefficients: Br^- , $2Br_2$, and $3Br_3^-$) on the indicator electrode potential and compare them with the thermodynamic predictions



Fig. 7. Distribution of bromine atoms over various bromine compounds with allowance for their stoichiometric

coefficients: (1) [Br⁻], (2) 2[Br₂], and (3) 3[Br₃⁻] on the equilibrium potential of the system. Circles: the result of the processing of the spectrophotometric data; solid line: calculation by Eqs. (4)–(7) at $E_2^\circ = 1.052$ V.

(Fig. 7). The experimental dependence for Br_3^- repeats the theoretical one at the qualitative and quantitative levels (except for a small shift of the maximum of the tribromide anion concentration toward lower potentials).

The curve for $[Br_2]$ has characteristic areas similar to those in Figs. 5 and 6: before E = 0.89 V, the experimental dependence lags behind the theoretical one, then it starts to exceed it, this behavior persisting up to E = 0.95 V. In the region of E = 0.97 V, the experimental dependence starts to lag far behind the thermodynamic predictions; after reaching the plateau $2[Br_2] =$ 0.9 M in the region of E = 1.04 V, it begins to decay sharply, which can again be explained by the gradual accumulation of HOBr in the system after the bromide anions (previously involved in counterproportionation (4) with HOBr molecules) vanished.

A more precise elucidation of the nature of this deviation and a study of the possibility of formation of HOBr and bromine compounds in higher oxidation states during the electrolysis oxidation of bromide anions in acidic media will be the subject of a separate study, which is especially important in the context of the problem of regeneration of spent fuel in the hydrogen—bromate flow battery [25]. This study showed that spectroelectrochemistry with subsequent algorithmic decomposition of the optical absorption spectra into components is suitable for effective determination of the composition of the bromine-containing medium during the electrolysis oxidation of the bromide anion to molecular bromine.

CONCLUSIONS

The oxidative electrolysis of acid bromide-containing solutions with simultaneous recording of absorption spectra and the equilibrium potential of the system using an indicator electrode has been performed. The dependences of the concentrations of various bromine compounds were evaluated using the spectrum decomposition. The results agree well with the thermodynamic predictions, which shows the possibility of using the absorption spectra for evaluating the composition of the system.

The dependence of the equilibrium potential of the system measured with the aid of the indicator electrode on the transmitted charge coincides with the thermodynamic predictions. This shows that potentiometry is also suitable for monitoring the composition of the system.

The current efficiency for complete electrooxidation of the bromide anion to molecular bromine was evaluated: $N_{\rm eff} = 0.85$.

The thermodynamic constant of formation of the tribromide anion K = 16 was evaluated. Its value agrees well with the literature data.

The obtained indirect evidence (CV and spectroelectrochemistry data) showed the possibility of formation of HOBr during the oxidative electrolysis of the bromide anion in an acidic medium.

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