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Theoretical Analysis of Changes in the Solution Composition during Anodic Electrolysis of Bromide[1]

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Abstract—The changes in indicator-electrode potential and (quasi)equilibrium solution composition in the anodic compartment of a model electrolyzer initially filled with aqueous electrolyte containing 0.5 M concentration of bromide anions are calculated under the condition that pH 2 is maintained constant in this compartment. The theoretical analysis is carried out for three different hypotheses concerning the possible depth of electrolysis and the nature of processes involved: (1) no bromine compounds with positive degree of oxidation are formed; (2) bromine compounds with the degree of oxidation not higher than +1 are formed; (3) the process can involve the formation of both bromate ions and bromine compounds with the lower degrees of oxidation (Br_3^-, Br_5^-, Br_2, BrO^-, HBrO) in solution as well as the liquid phase of bromine $\left(Br_2^{liq}\right)$. All electrochemical and chemical reactions involving bromine-containing species taken into account within the framework of hypotheses of system evolution 1, 2, and 3 are assumed to be (quasi)equilibrium, and the electric current through the cell separator is assumed to be provided by supporting electrolyte ions. Methods are proposed for experimental determination of the version of evolution of Br-containing anolyte during electrolysis.

Keywords: bromide-ion electrooxidation, equilibrium composition, tribromide anion, pentabromide anion, liquid bromine

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INTRODUCTION

The process of electrochemical oxidation of bromide anion Br^- was actively studied experimentally in both aqueous solutions [1–14] and nonaqueous media [15–17]. Attention was focused on the initial stage of this process which when carried out in dilute solutions produces dissolved molecular bromine [2, 3, 9, 10, 13–17]

$$2Br^- - 2e \rightleftarrows Br_2. \qquad (1)$$

Raising the concentration of Br^- ions in the initial solution increases the number of possible products of this process due to the formation of both compounds with intermediate degrees of oxidation (particularly, tribromide anion Br_3^- and pentabromide anion Br_5^-) and the phase of liquid bromine Br_2^{liq} [18, 19]:

$$Br_2 + Br^- \rightleftarrows Br_3^-, \qquad (2)$$

$$Br_2 + Br_3^- \rightleftarrows Br_5^-, \qquad (3)$$

$$Br_2 \rightleftarrows Br_2^{liq}. \qquad (4)$$

At the same time, certain authors demonstrated the possibility of electrochemical oxidation of bromide to the higher degrees of oxidation, particularly, to bromate $\left(BrO_3^-\right)$ [4–8, 12] and even perbromate $\left(BrO_4^-\right)$ [4]. Insofar as, based on the general principles of electrochemistry, one can expect that an electrochemical process involving transfer of several electrons and, at the same time, accompanied by the break and formation of strong chemical bonds can hardly proceed with a noticeable rate, the formation of bromine com-

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[1] This paper is dedicated to the 80th anniversary of Professor V.V. Malev who has made a considerable contribution into modern directions of electrochemistry.

pounds with positive degrees of oxidation should apparently be initiated by the reaction of disproportionation of molecular bromine and its scheme should depend on the solution pH:

$$Br_2 + H_2O \rightleftarrows HBrO + Br^- + H^+ \quad \text{(acidic and neutral media)}, \tag{5}$$

$$Br_2 + 2OH^- \rightleftarrows BrO^- + Br^- + H_2O \quad \text{(alkaline media)}. \tag{6}$$

In turn, the compounds with the degree of oxidation +1 can undergo a series of disproportionation stages to form short-lived compounds with the higher degrees of oxidation to the point of accumulation of more stable compounds bromates and even perbromates [20–22], in particular, by the overall reaction

$$3HBrO \rightleftarrows BrO_3^- + 2Br^- + 3H^+, \tag{7}$$

$$3BrO^- \rightleftarrows BrO_3^- + 2Br^-. \tag{8}$$

When writing these reaction schemes, we took into account that HBr and $HBrO_3$ are strong acids, i.e., dissociate completely, and Br_3^- and Br_5^- are not protonated, at least at pH ≥ 0 [23].

The compounds with the degree of oxidation +7 (perbromates) are not considered in this study, because they cannot be formed in noticeable amounts in the potential interval under consideration (below +1.6 V vs. SHE) in acidic and neutral media.

The processes of formation of compounds with positive degrees of bromine oxidation depend both on the parameters of the electrochemical process (the chosen mode, potential or current) and on the cell design (particularly, the material of electrode and separating membrane). Moreover, the overall electrooxidation often proceeds above the equilibrium potential of oxygen evolution for a given pH value, which leads to superposition of the latter side process and also to involvement of its intermediates in the homogeneous reactions of bromine-containing species.

For these reasons, flowing anodic current through a solution originally containing bromide anions is accompanied by the formation and interconversion of multiple bromine compounds. The occurrence of these processes is determined by both thermodynamic factors and the rates of processes involved. The latter, in turn, depend intricately on the solution pH and the total concentration of Br atoms in all possible bromine-containing compounds c_{tot} (which, in the absence of losses, coincides with the initial bromide concentration). This is why, on the basis of general knowledge, we cannot predict which processes will be sufficiently fast under experimental conditions (on the time scale of electrolysis), i.e. will be quasi-equilibrium, and which will not occur at all.

This is why, in this study, the evolution of working electrode potential E and solution composition was calculated for three different assumptions on which stages are sufficiently fast for the thermodynamic equilibrium to be attained, while all the other stages are totally ignored.

Version 1. The electrolysis involves only reactions (1)–(4) to produce bromine compounds with the negative or zero degrees of oxidation, i.e., no oxygen-containing compounds of bromine are formed.

Version 2. Reactions (1)–(4) and the subsequent chemical transformations (5) and/or (6) to produce bromine compounds with the degree of oxidation +1 have time enough to occur, whereas the subsequent processes (7) and/or (8) do not occur during the electrolysis.

Version 3. All reactions (1)–(8) proceed sufficiently fast so that the electrolysis produces the aforementioned bromine compounds with oxidation degree up to +5.

The analysis shown below assumes that the thermodynamic equilibrium is established in all reactions considered within the framework of a given version.

THE METHOD USED FOR CALCULATING THE CHARACTERISTICS OF THIS SYSTEM

The method used here is an outgrowth of the approach used in our study [18] in which for version 3 (see above) we calculated the equilibrium characteristics of this system (the ***total redox charge*** of bromine-containing compounds Q and the composition of the system, i.e., the amounts of each bromine-containing compound N_i) as a function of ***total amount of Br atoms*** (in moles) in the system N_{tot} and solution pH. In contrast to [18], below we ignore the transition of Br_2 molecules to the gas phase above the solvent, because for hermetically closed cells with commensurable volumes of liquid and gas phases, the amount of bromine in the latter is negligible as compared with N_{tot}.

In analogy with [18], we assume that bromine-containing compounds do not cross the boundaries of the anodic compartment in electrolyzer (i.e., their loss due to transfer through separator or due to evaporation of Br_2 from solution is ruled out) so that the total amount of Br atoms in all components of the system (N_{tot}) remains unchanged during the electrolysis and, hence, is equal to the number of moles of Br^- ions in the original solution, i.e. known.

In the analysis within the framework of version 3, we take into account 8 bromine-containing compounds with degrees of oxidation from –1 to +5 (Table 1). For each of these compounds, Table 1 shows the number of bromine atoms n_i and the parameter x_i which is

Table 1. The number of bromine atoms and the total degree of oxidation for bromine atoms in the composition of various bromine-containing compounds

i	1	2	3	4	5	6	7	8
	Br^-	Br_3^-	Br_5^-	Br_2	HBrO	BrO^-	BrO_3^-	Br_2^{liq}
n_i	1	3	5	2	1	1	1	2
x_i	−1	−1	−1	0	+1	+1	+5	0

called [18] ***the total degree of oxidation*** of Br atoms in the compound of type i, being determined as the number of electrons which should be withdrawn from the required number (one or several) of neutral Br atoms in order to obtain compound A_i of type i: $n_i\,Br(0) - x_i e \rightarrow A_i$, for instance, $n_{BrO^{3-}} = 1$, $x_{BrO^{3-}} = +5$, or $n_{Br^{3-}} = 3$, $x_{Br^{3-}} = 1$, or $n_{Br^{5-}} = 5$, $x_{Br^{5-}} = -1$ (see Table 1), as a result of the following transitions: $Br(0) - 5e \rightarrow BrO_3^-$, $3\,Br(0) + e \rightarrow Br_3^-$, $5\,Br(0) + e \rightarrow Br_5^-$.

Then, the total number of moles of Br atoms in the system N_{tot} and its total redox charge Q satisfy the following balance conditions:

$$N_{tot} = \sum n_i N_i, \tag{9}$$

$$Q = F\sum x_i N_i, \tag{10}$$

where summation is carried out over all compounds (Table 1), N_i is the number of moles of type-i compound, the values of parameters n_i and x_i are shown in table, and F is the Faraday constant.

The charge Q_{elchem} consumed in changes in the degree of oxidation of Br atoms involved in all bromine-containing components of this system from the beginning of electrolysis to a given moment t is assumed to be known. This means that either the current efficiency of the corresponding electrochemical stages is equal to 100% (then Q_{elchem} coincides with the electrolysis charge up to this moment) or (if the current efficiency is lower than 100%) the current efficiency of a given process is known and the charge Q_{elchem} can be calculated based on the known charge of electrolysis.

The change in the total redox charge of the system from its initial value Q_{ini} to its value Q in moment t as a result of changes in the degree of oxidation of Br atoms in bromine-containing compounds is directly related to the passed charge of electrolysis Q_{elchem}:

$$Q = Q_{ini} + Q_{elchem}, \tag{11}$$

where $Q_{ini} = -FN_{tot}$, because Br^- was the only bromine-containing compound in the initial state.

Thus, the total redox charge of the system Q can be found by measuring Q_{elchem} in any moment of electrolysis.

Below, in graphical illustrations, in place of the total redox charge of the system Q, we used the corresponding specific characteristic—***the average degree of oxidation*** x in this state of the system

$$x = Q/FN_{tot}\sum x_i N_i\Big/\sum n_i N_i\,. \tag{12}$$

According to Eq. (11), $x_{ini} = -1$ in the initial state of the system.

The conditions of thermodynamic equilibria (see below) contain not the amounts of substances N_i, but their concentrations c_i determined by the relationships

$$c_i = N_i/V^{sol}, \tag{13}$$

where V^{sol} is the solution volume (in a given moment of electrolysis, if it changes). Note that the definition (13) for $i = Br_2^{liq}$ (for liquid bromine phase) is totally formal because this component of the system forms its own phase, i.e. is not dissolved in the aqueous solution; however, this definition is convenient for simplifying formulas.

For concentrations, the balance condition (9) takes the form

$$c_{tot} = \sum n_i c_i, \tag{14}$$

where the formally introduced total concentration of Br atoms in this system is given by the following relationship: $c_{tot} = N_{tot}/V^{sol}$. Its value is considered here as a known parameter of the system.

The set of independent thermodynamic relationships for electrochemical and chemical transitions in this system for *version 3*, i.e., under an assumption that all reactions (1)–(8) are equilibrium, were formulated in [18]. This publication also gives solution for the corresponding system of equation for concentrations c_i of all components shown in Table 1 for the cases where the liquid bromine phase is absent and where it forms.

In the latter study, the following three components of the system were assumed to be known: the total concentration of Br atoms in the system c_{tot}, the solution pH, and the equilibrium potential E, whereas the total redox charge Q and the concentration of all bromine-containing compounds c_i were found in calculations.

Insofar as at electrolysis, it is the charge Q that serves as the standard controlled parameter rather than the potential E (although the latter can also be measured by the indicator electrode the potential of which is determined by the redox transitions between compounds with different degrees of Br oxidation), it was of interest to predict the dependences of E and concentrations c_i on Q which can be found from the preceding calculations based on the $Q(E)$ dependence.

The calculations in versions 1 and 2 were carried out by exactly the same principal procedure but with the smaller number of bromine-containing compounds and, correspondingly, the smaller number of conditions of thermodynamic equilibrium related to the discarded compounds. Thus, in version 2 where reactions of formation (7) and (8) do not occur during the electrolysis, it is sufficient to eliminate BrO_3^- from the list in Table 1 and omit the thermodynamic Eq. (15) for its concentration (shown in [18]) from relationships (9), (10, (12), (14). For version 1, we eliminated also HBrO and BrO^-, as well as Eqs. (16) and (22) [18] for their concentrations.

The goal of these calculations was to consider three different scenarios of variation of solution composition as a function of processes entailing changes in the degree of oxidation of bromine in its compounds. These scenarios correspond to ***two limiting cases*** for certain processes where their rates ***are so fast that their concentrations strictly obey the thermodynamic relationships*** or ***so slow that these processes do not occur at all.*** It seems evident that the real situation is intermediate and depends on multiple parameters of the system. In the future, the analysis of limiting cases performed here will allow the characteristics measured during the electrolysis to be compared with those calculated, which will allow drawing ***qualitative*** conclusions on the processes that have time enough to proceed in this system.

DISCUSSION

Below, the results for versions 1, 2, and 3 are presented in the graphical form. The calculations were carried out for an aqueous solution initially containing 0.5 M bromide. It was assumed that the total concentration of Br atoms during the electrolysis remains equal to this value $c_{tot} = 0.5$ M. The solution pH 2 was assumed to be constant despite the presence of processes involving protons.

Relationship between the Potential E and the Redox Charge Q

Figure 1 shows how the potential E which can be measured by the indicator electrode depends on the degree of oxidation of Br atoms in the system x, i.e., on the normalized total redox charge of the system Q (which changes with the electrolysis charge Q_{elchem}) in the course of evolution of the system according to versions 1, 2, and 3.

Note that as follows from Eq. (11), the beginning of electrolysis (bromide solution) corresponds to $x = -1$ and the maximum degree of oxidation depends on the assumed direction of evolution: $x = 0$ (Br_2 in its dissolved and, probably, liquid states) for version 1, $x = +1$ (HBrO and BrO^-) for version 2, and $x = +5$ $\left(BrO_3^-\right)$ for version 3. As the redox charge approaches the corresponding maximum value, the calculated potential of the indicator electrode begins to increase infinitely (Fig. 1) according to the Nernst equation due to the decrease in the concentration of compounds with the lower degrees of oxidation.

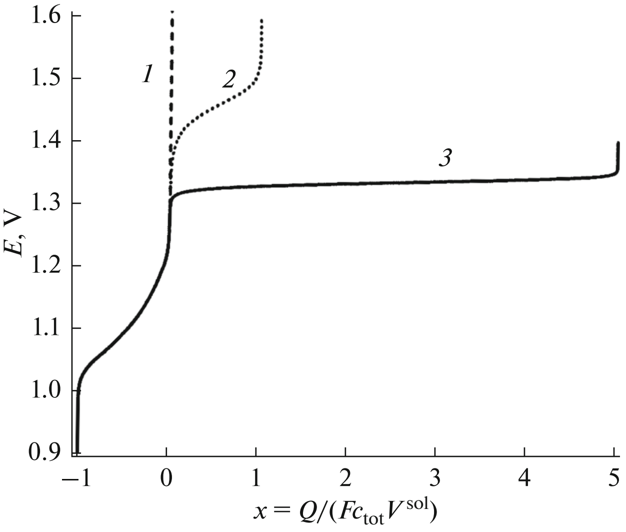

Fig. 1. Dependence of the equilibrium potential of the system E (vs. SHE) on the changes (determined by the changes in the electrolysis charge Q_{elchem}) in its average degree of oxidation x, i.e., the total redox charge Q normalized to the number of Br atoms in the system $N_{tot} = c_{tot}V^{sol}$ (see Eq. (12)). Curves: (*1*) calculation 1, (*2*) calculation 2, (*3*) calculation 3.

It seems that the presence of such increase of the potential at the corresponding value of normalized redox charge can serve as a convenient diagnostic criterion for finding which of versions is realized in a system studied experimentally.

This conclusion appears to be substantiated for version 2 where the potential should remain in the expected interval up to x values close to +1 (which allows excluding version 1), whereas in the vicinity of +1, the potential starts to increase sharply (which contradicts the predictions of version 3).

The possibility that x values higher than +1 are reached is the clear indication in favor of version 3, provided the contribution to the electrolysis charge Q_{elchem} made by the processes that have nothing to do with changes in the degree of oxidation of Br are excluded. The fulfillment of the latter condition is checked by the presence (or absence) of the rapid potential growth when approaching x close to +5 (Fig. 1).

The most complicated task is to check the correspondence of system to version 1. Figure 1 shows that as the charge approaches its value corresponding to $x = 0$, the segment of virtually vertical potential growth is observed in ***all*** curves *1, 2,* and *3*, so that the difference between them lies in the value of potential E at which this rapid growth stops. When we observe a deviation from the vertical region of an experimental curve in the potential region corresponding to predictions of curve *2* or curve *3*, we can draw a ***tentative*** conclusion that the corresponding processes of formation of bromine oxocompounds are sufficiently fast (see reactions (5)–(8)). At the same time, the deviation from the vertical line $x = 0$ at the higher potentials cannot be considered as indication in favor of exclusion of versions 2 and 3, because curves *2* and *3* in Fig. 1 are calculated for the ***equilibrium*** state of mentioned reactions of formation of bromine compounds with the positive degrees of oxidation. In a real system, the electrode reactions can occur with a considerable overpotential which can shift the corresponding curve *2* or *3* to the top.

This is why, one should keep himself from making the final choice between versions 1, 2, and 3 based only on the potential vs. charge curves (Fig. 1) but use also the data on the solution composition in these versions (see below).

Note that at the potential of formation of bromine in positive degrees of oxidation (above 1.3 V vs. SHE in Fig. 1), the reaction of oxygen evolution becomes ***thermodynamically*** possible. However, on all electrode materials known, the oxygen reaction proceeds with a considerable overpotential [24, 25]. Particularly, even on platinum, a considerable current of oxygen evolution can be observed only at potentials above 1.6 V vs. SHE. This allows us to assume that under the conditions of this study, the current efficiency of the reaction of anodic evolution of oxygen should be sufficiently low; and, hence, the curves in Fig. 1 will not change at least ***qualitatively***. Were the contribution made by oxygen reaction to the total charge of electrolysis considerable, then its value should be taken into account when calculating the experimental values of the charge Q_{elchem} in Eq. (11) associated with changes in the degree of oxidation of bromine atoms.

Yet another side process which can be observed at so high potentials (up to 1.6 V vs. SHE) is corrosion of the electrode metal. To minimize its effect, stable materials such as platinum, conducting oxides (RuO_2, IrO_2, PbO_2), or boron-doped diamond (BDD) should be used. Only then we can assume that the value Q_{elchem} is close to the electrolysis charge.

Relationship between the Distribution of Concentrations c_i and the Total Redox Charge Q

Figure 2 shows the changes in solution composition as a function of the electrolysis charge Q_{elchem}, i.e., the changes in the total redox charge of the system Q recalculated to the average degree of oxidation of Br x (Fig. 1). Figures 2a, 2b, and 2c show the results of calculations for versions 1, 2, and 3, respectively. The interval of x variation in each of these figures (and in Fig. 1) is chosen to be suitable for version under consideration. At the same time, the scale of the x axis remains the same in all these figures, which makes easier their comparison.

In Fig. 2, the concentration of each compound c_{i} is replaced by the concentration of atoms in this compound, i.e., the values $n_i\ c_i$ are considered, where n_i is taken from Table 1. The advantage of such choice is the fact that, according to Eq. (14), this value reflects the ***relative contribution of this compound to the total concentration of Br atoms in the system*** c_{tot}, i.e., at each x value the sum of concentrations in Fig. 2 is equal to c_{tot}.

Comparing Figs. 2a, 2b, and 2c shows the coincidence of evolution of solution composition in the x interval between −1 and 0. This region is also shown in Fig. 3a by superposition of results for versions 1 and 2. First of all, the concentration of Br^- gradually decreases (line *1*) mainly due to formation of Br_3^- (taking into account the presence of 3 Br atoms in each ion) and also of Br_2 and Br_5^-. In the second part of this interval, we observe a decrease, first, in the content of tribromide and then in the content of pentabromide, while the concentration of dissolved bromine molecules quickly increases.

Shortly before the attainment of $x = 0$, this concentration (Br_2) reaches its maximum value of 0.185 M corresponding to the saturated solution of Br_2 in water. As x increases further, the Br_2 concentration remains unchanged whereas the remaining part of formed Br atoms (0.5 M − 2 × 0.185 M = 0.13 M) pass to the phase of liquid bromine Br_2^{liq} (Fig. 3a).

Figure 3b shows the evolution in the vicinity of $x \cong 0$ in more detail and one can distinguish even the very small difference between the curves for liquid bromine in version 1 (the slightly higher dashed curve that ends at $x = 0$) and version 2 (the solid curve that continues to $x > 0$). This difference between the predictions for Br_2^{liq} is associated with the beginning of formation of HBrO at the low negative values of x for version 2.

Thus, within the $-1 < x < 0$ interval, the electrolysis leads only to the transition between the original compound with the degree of oxidation −1 (bromide ion) and the neutral bromine molecules in the dissolved or liquid states (degree of oxidation 0) via the

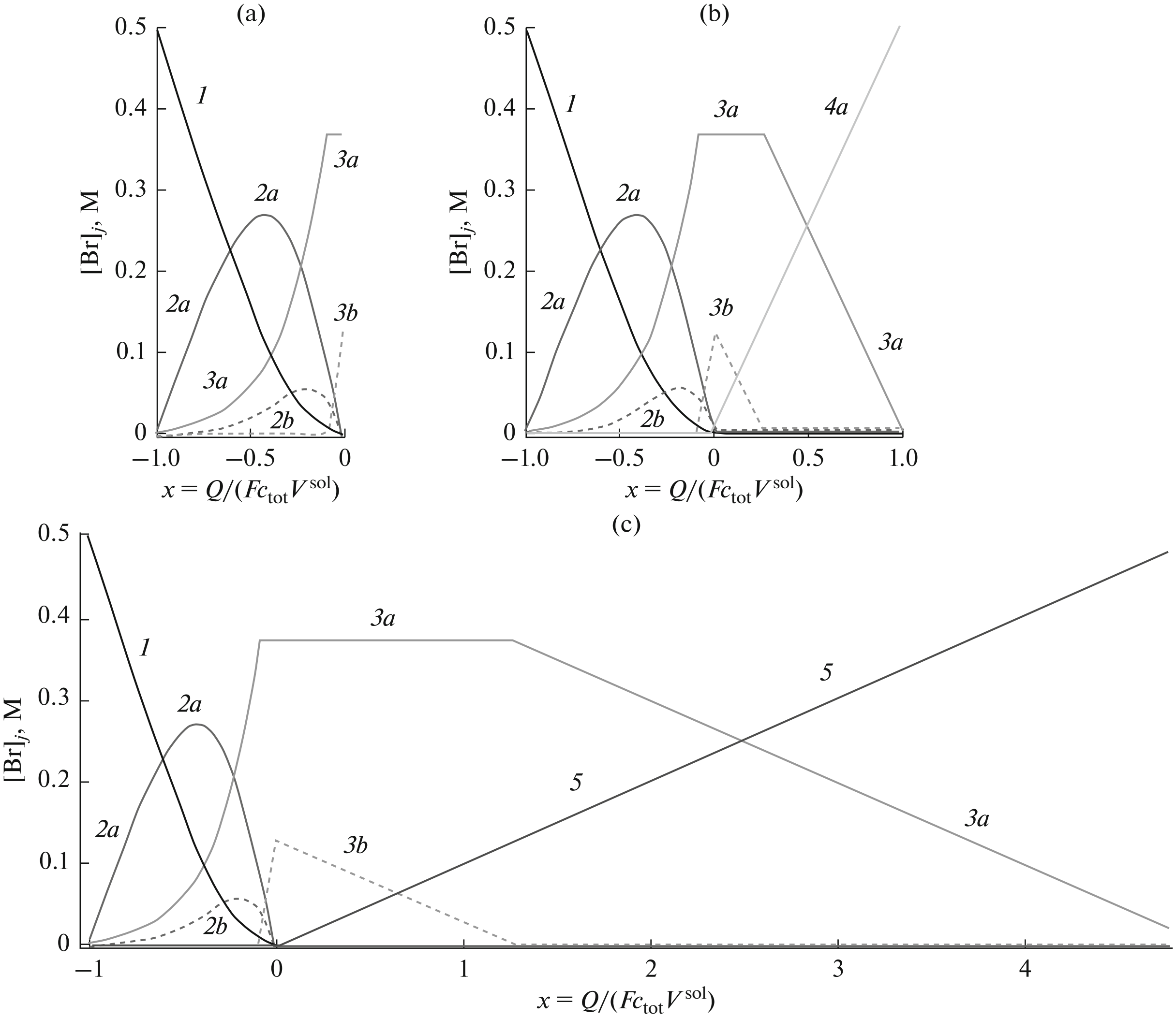

Fig. 2. Changes in the solution composition (concentrations $n_i c_i$ in Eq. (14)) as a function of the average degree of oxidation of Br atoms x during the electrolysis (see legend to Fig. 1) for versions (a) 1, (b) 2, and (c) 3. The curves in Figs. (a)–(c) correspond to compounds: (*1*) Br^-, (*2a*) Br_3^-, (*2b*) Br_5^-, (*3a*) Br_2, (*3b*) Br_2^{liq}, (*4a*) HBrO, (*5*) BrO_3^-. For each compound i, the molar concentration of Br, i.e., $n_i c_i$, is given (see Table 1).

compounds with intermediate degrees of oxidation (tribromide and pentabromide anions), whereas the formation of oxocompounds of bromine with the positive degree of oxidation is virtually impossible due to the higher standard potentials of the corresponding reactions.

The prediction on the equilibrium composition of anolyte at positive x can be realized only for versions 2 (Fig. 2b) and 3 (Fig. 2c). Comparing the calculated concentrations of compounds in this interval shows their ***total difference*** for these versions.

The probability of formation of only compounds with the degree of oxidation +1 (version 2, Fig. 2b) suggests that the as x exceeds 0, the concentration of HBrO (line 4a) rapidly increases according to the linear law (concentration of BrO^- is very low due to the low solution pH), as a result of disappearance of, first, the phase of liquid bromide (line 3b) and, then, its dissolved form (line 3a), so that at $x = +1$ virtually only HBrO remains in the system.

The absolutely different type of evolution is predicted by version 3 (Fig. 2c). In this case, the oxidation of molecular bromine (first, from its liquid phase and, then, from its solution: curves *3b* and *3a*) leads to nonlinear increase in the bromate concentration (line *5*), whereas HBrO and BrO^- with the intermediate degree of oxidation +1 are virtually absent. The electrolysis

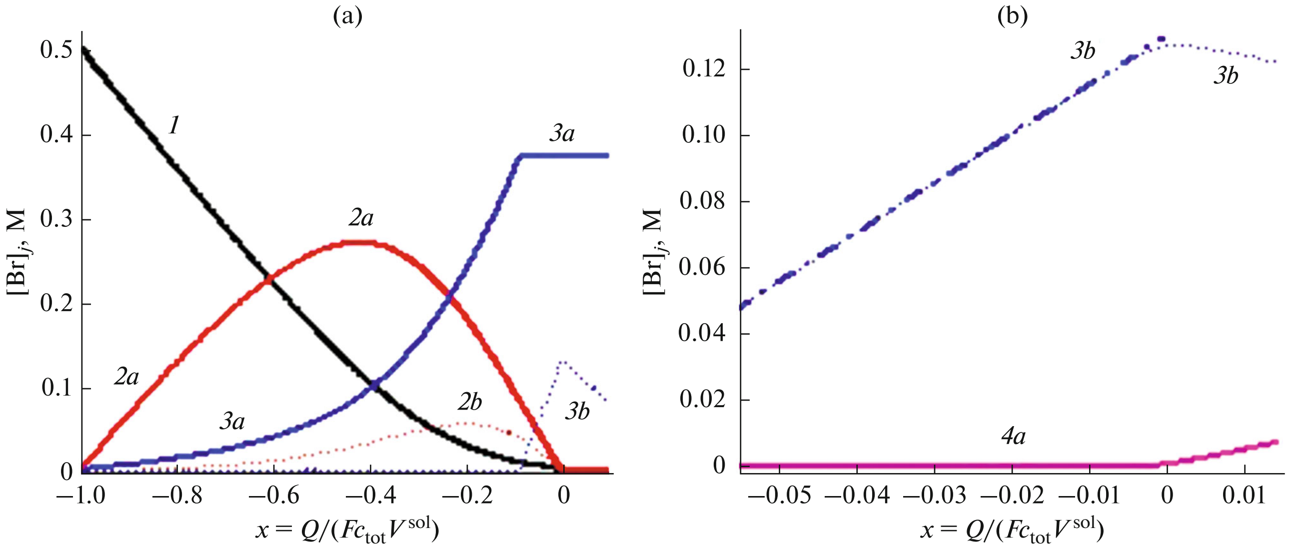

Fig. 3. Comparison of the evolution of solution composition (concentrations n_ic_i in Eq. (14)) for the initial stage of electrolysis in versions (dashed curves) 1, and (solid curves) 2. The curves in figures a and b correspond to compounds: (*1*) Br^-, (*2a*) Br_3^-, (*2b*) Br_5^-, (*3a*) Br_2, (*3b*) Br_2^{liq}, (*4a*) HBrO, (*5*) BrO_3^- (all according to calculation 1); (*3b'*) Br_2^{liq} (calculation 2). (a) The region—1 < x < 0 in which the corresponding solid and dashed curves merge together. (b) The region near $x = 0$ in which a slight difference between curves for Br_2^{liq} (*3b*' and *3b*) in versions 1 and 2 can be distinguished.

ends at $x = +5$ where bromate is the only component of the system.

Thus, by monitoring the changes in solution composition (for example, by changes in the solution spectra in UV-visible wavelength range [13]) during the electrolysis in the interval $x > 1$, it is possible to unambiguously distinguish the different stages of evolution 1, 2, and 3. In version 1, bromine remains in their zero degree of oxidation (bromine molecules); in version 2, the transition between molecular bromine and HBrO takes place; and, finally, in version 3 the loss of molecular bromine is accompanied by an increase in the concentration of bromate anion.

Relationship between the Distribution of Concentrations c_i and the Potential E

To make our consideration completer, in Fig. 4, we show the evolution of solution composition during the electrolysis as a function of the indicator electrode potential.

The virtual coincidence of curves in Fig. 1 for versions 1, 2, and 3 in the interval $-1 < x < 0$ means that the conclusions made when analyzing the evolution of solution composition as a function of the redox charge of the system (Figs. 2 and 3) are directly transferred to the composition vs. electrode potential dependences in the corresponding interval below 1.3 V, which, naturally, is confirmed by the analysis of data in Fig. 4.

At the same time, there is substantial difference in the ways the concentration changes in Figs. 2 and 4, which is explained by the fact that the potential interval in Fig. 1 corresponding to this charge region is very wide. Thus, the transition of bromide to molecular bromine (dissolved and liquid) turns out to be extended widely as compared with the Nernstian interval because it actually consists of ***two*** successive transitions: (1) Br^- to $Br_3^- + Br_5^-$; (2) $Br_3^- + Br_5^-$ to $Br_2 + Br_2^{liq}$. For the total concentration c_{tot} equal to 0.5 M, the fraction of pentabromide in the transition potential region is several times lower than the fraction of tribromide, despite the larger number of Br atoms in this ion. The accumulation of molecular bromine begins from its dissolved form and, when saturation is reached ($c_{Br_2} = 0.185$ M), its concentration stops to increase while the contribution of the liquid phase Br_2^{liq} increases.

To the end of these transitions, the concentrations of Br_2 and Br_2^{liq} within the framework of version 1 stop to change due to the absence of processes producing bromine oxocompounds (Fig. 4a). On the other hand, the evolution of system's composition continues in versions 2 and 3 but in totally different ways.

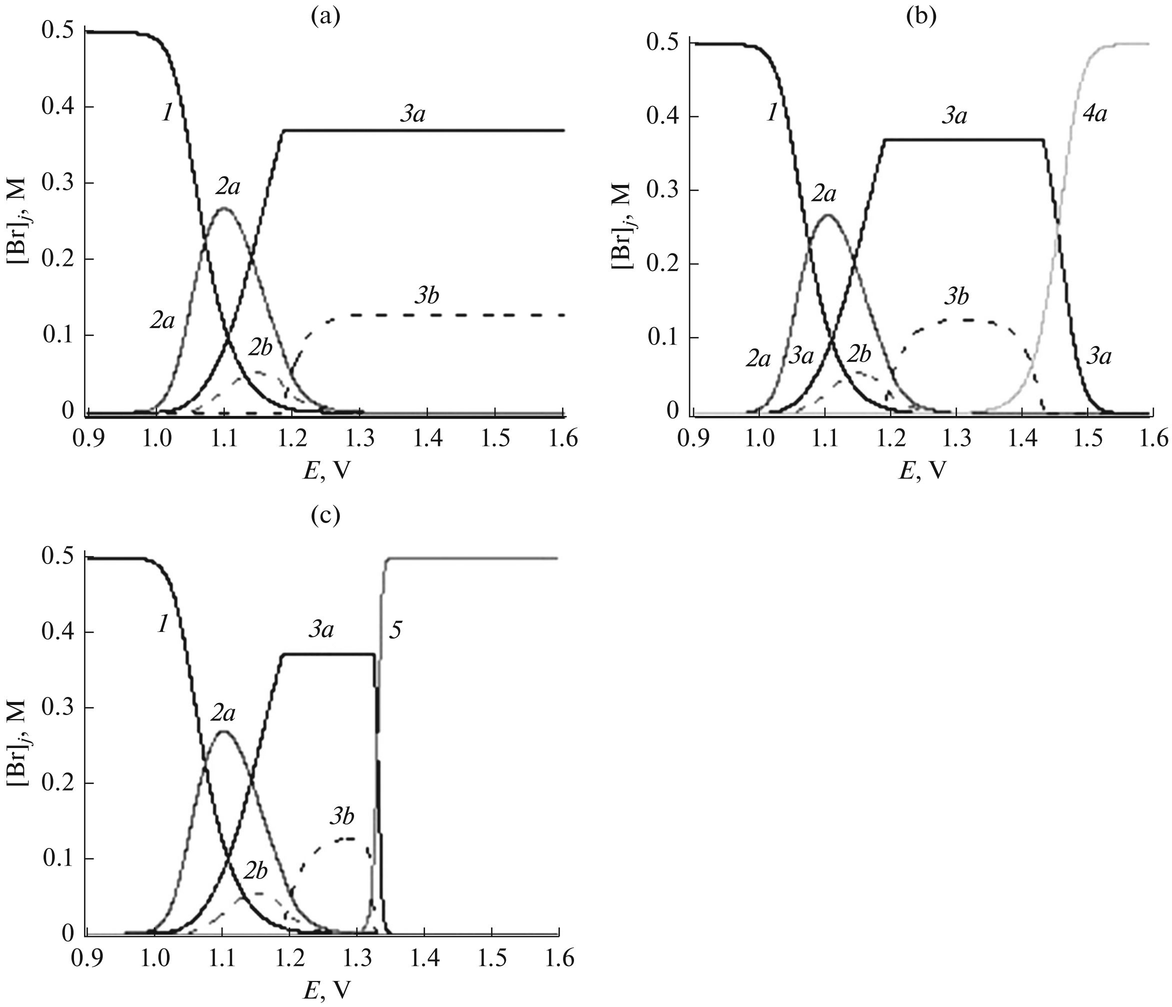

Fig. 4. Changes in solution composition during the electrolysis (concentrations n_ic_i in Eq. (14)) as a function of potential E (vs. SHE) for versions (a) 1, (b) 2, and (c) 3. The curves in Figs. a–c correspond to compounds (*1*) Br^-, (*2a*) Br_3^-, (*2b*) Br_5^-, (*3a*) Br_2, (*3b*) Br_2^{liq}, (*4a*) HBrO, (*5*) BrO_3^-.

In version 2 (Fig. 2b), above potential of 1.35 V, the transformation of molecular bromine begins (first from its liquid phase and then from solution) to form HBrO in the potential interval of ca. 200 mV wide, after which the evolution stops. In contrast, no compounds with the degree of oxidation +1 are formed conceptually in version 3, and molecular bromine transforms to BrO_3^- in a very narrow potential region (ca. 50 mV wide). It should be stressed once more that these predictions are made under the assumption that the corresponding stages (5)–(8) are fast and thus remain quasi-equilibrium during the electrolysis.

For versions 1, 2, and 3 (Fig. 4), the evolution of solution composition as a function of potential E is also shown in semilogarithmic coordinates (Fig. 5). The Nernst equation (in its logarithmic form) for any equilibrium between bromine compounds in different degrees of oxidation represents a linear relationship between the potential E and logarithms of their equilibrium concentrations. Hence, when a single bromine-containing compound (or several compounds with the same degrees of bromine oxidation) makes the predominate contribution to the total concentration c_{tot}, for the other compounds we obtain linear dependences of logarithm of concentration on the potential with the slope determined by ratios x_i/n_i between predominant and “trace” compounds (Fig. 5).

Yet another characteristic feature of plots in Fig. 5 is that they clearly demonstrate both the transition regions from one dominating compound to another and the behavior of concentrations of compounds that make a relatively small contribution to the total concentration.

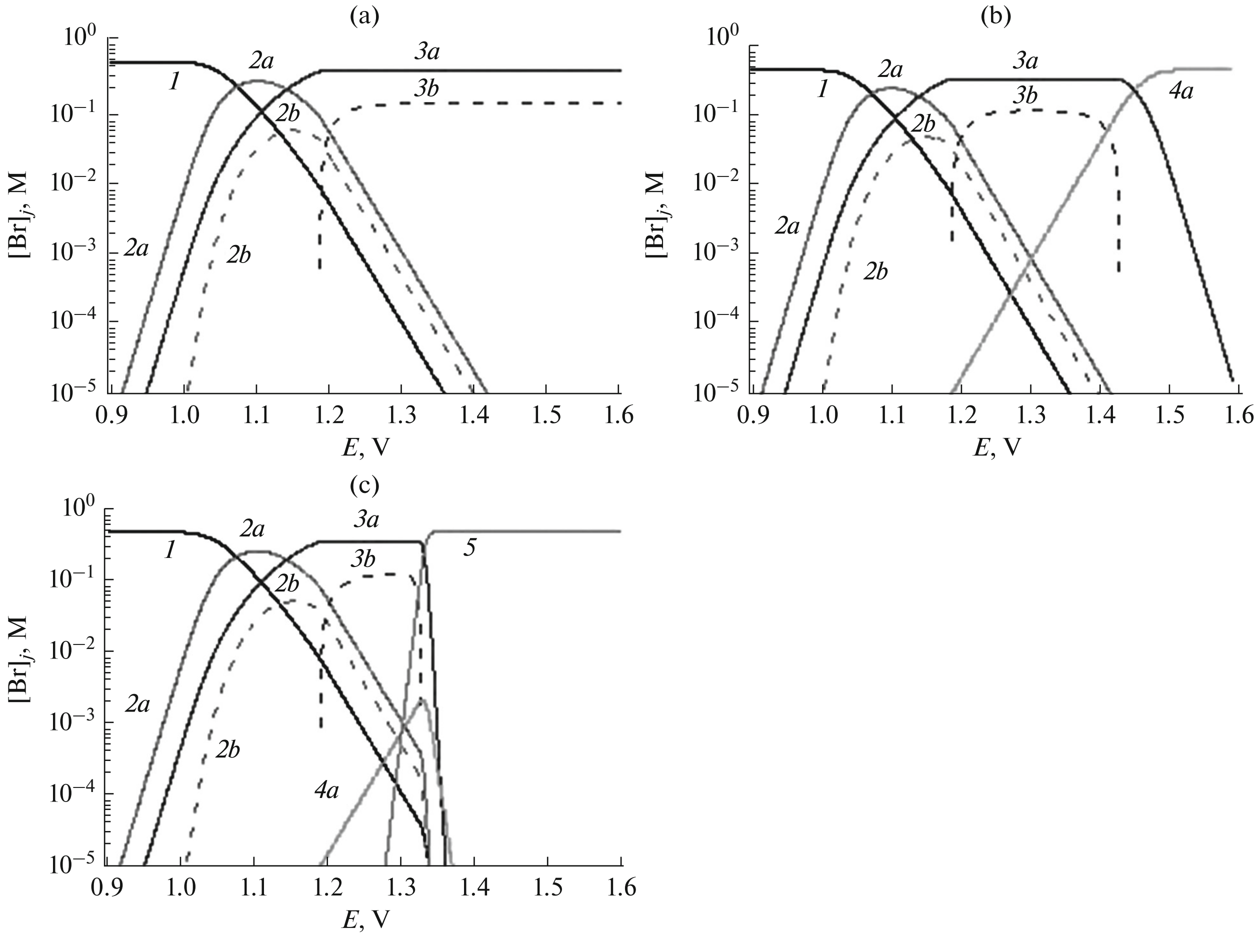

Fig. 5. Changes in solution composition during electrolysis (logarithmic scale: $\log n_i c_i$) as a function of potential E (vs. SHE) for versions (a) 1, (b) 2, and (c) 3. Curves in all figures (a–c) correspond to compounds: (*1*) Br^-, (*2a*) Br_3^-, (*2b*) Br_5^-, (*3a*) Br_2, (*3b*) Br_2^{liq}, (*4a*) HBrO, (*5*) BrO_3^-.

CONCLUSIONS

The above theoretical investigation is aimed at predicting the changes in system's characteristics during the oxidative electrolysis of a bromide-containing solution for three different scenarios of processes that occur in this system: version 1 in which no oxobromine compounds are formed during the electrolysis; version 2 in which the compounds with the degree of oxidation +1 have time to form; and version 3 where, in addition, the processes leading to formation of bromate anions are also sufficiently fast. Under the condition that all processes involved are quasi-equilibrium, for these three versions of system evolution, the changes in both the concentrations of all bromine-containing compounds and the indicator-electrode potential are analyzed as a function of the electrolysis charge consumed in redox transformations of Br atoms involved in these compounds. The spectroscopic method is proposed for monitoring the state of the system and also for elucidating by which version it evolves.

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CONFLICT OF INTERESTS

The authors state the absence of any conflict of interests.

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