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Article

Analysis of the Composition of Bromide Anion Oxidation Products in Aqueous Solutions with Different pH via Rotating Ring-Disk electrode Method

Roman Pichugov [1,*], Dmitry Konev [2], Ivan Speshilov [1], Lilia Abunaeva [1], Mikhail Petrov [1] and Mikhail Vorotyntsev [1,2,3]

[1] Mendeleev University of Chemical Technology of Russia; rompich90@gmail.com
[2] Institute of Problems of Chemical Physics (Russian Academy of Sciences); dkfrvzh@gmail.com
[3] Frumkin Institute of Physical Chemistry and Electrochemistry (Russian Academy of Sciences); mivo2010@yandex.com
* Correspondence: rompich90@gmail.com

Abstract: We measured the ring collection coefficient of bromide anion oxidation products in a neutral and slightly alkaline medium on a rotating ring-disk electrode (glassy carbon disk, platinum ring) varying the following parameters: disk electrode rotation velocity, sodium bromide concentration, pH of the medium (in the range of 6 – 12), anode current on the disk and the electroreduction potential of the bromide anion oxidation products on the ring. The data obtained is presented via dependences of the cathode ring current to the disk current ratio vs the ring electrode potential. The analysis of the results was carried out by comparing the experimental polarization curves of the ring electrode with the data of cyclic voltammetry in model solutions to determine the electrical activities of various bromine compounds in positive oxidation states. We claim that RRDE method could be used to obtain quantitative and qualitative data on the electrooxidation of bromide ion in neutral and alkaline solutions. For the most effective regeneration of the spent oxidizer the values of pH > 10 and moderate concentrations of NaBr should be used.

Keywords: ring rotating disk electrode (RRDE); voltametric analysis; flow battery; bromide oxidation)

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1. Introduction

The world's demand for high-energy power sources is growing annually due to the general tendencies for the development of stationary and mobile electrical devices whose production volume is increasing rapidly. To meet the growing demands for energy sources in the vast row of different applications various energy storage devices were recently developed to compete with fossil fuels. Among them redox flow batteries (RFB) are one of the most promising candidates for stationary energy storage purposes, where energy is stored in reduced or oxidized form of liquid chemical substances in the flowing media. The principal profit of the RFB operation in contradistinction to solid state systems (e.g. lithium-ion batteries), allows one to vary the energy capacity and the power density of energy system in independent way: varying the volume of posolyte (positive electrolyte) and negolyte (negative electrolyte) tanks and the electrode area inside the membrane-electrode assembly (MEA), correspondingly. Moreover, the low cost of RFB devices, their prominent stability upon storage, fire and explosion safety, no need in toxic electrolytes or hazardous materials usage, as well as the absence of precious metal catalysts at the electrodes makes these systems perfect to outperform the competitors as energy storage devices for stationary applications.

A fundamental drawback of most proposed flow batteries up to recent advances was their low power density (~ 0.2-0.4 W/cm^2, for all-vanadium and iron-chromium redox flow batteries) which leads to a high cost of power and consequently arising trend for searching

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new high energy density electrolytes. With the advent of hydrogen-bromine (H_2-Br_2) flow batteries concept with power density 1-1.5 W/cm^2 and round-trip efficiency of 91% at 1.6 A/cm^2 reported, this restriction was removed resulting in the attempts of their commercialization in the USA and Israel as grid-scale energy storage solutions [1-6]. Nevertheless, several fundamental problems remained unsolved up to now: their moderate energy density as well as the toxicity and corrosive activity of bromine. For further increase of energy density, the substantial progress was made exploring new multi-electron oxidizers. Recently proposed bromate oxidizer is currently attracting interest to replace bromine due to the extremely high charge density and energy densities owing to a very high solubility of bromate lithium salts and multi-electron reduction process: 6 electrons for its rapid transition to bromide in strong acidic conditions [7-9]. E.g. the reported bromate RFB reaches specific power of 1 W/cm2 for 1 M H2SO4 [10], although there is an evident lack of studies for the regeneration process of the utilized oxidizer in a form of acidic bromide solution to initial bromate one. Therefore, today is of great interest to realize a complete energy cycle for such a system. The general reaction of bro-mate formation can be written as [11]:

$$Br^- + 3H_2O = BrO_3^- + 6H^+ + 6e^-, \quad (1)$$

There are two known ways to perform this conversion:

- Heterogeneous oxidation of bromide (through the stage of formation of bromine) to bromate, which can be realized in an acid medium;
- Homogeneous reaction of disproportionation of bromine in a slightly alkaline medium.

The formation of bromate in neutral or slightly alkaline medium was experimentally demonstrated. Pavlovic et al. states that in case of electrochemical formation of bromates the current efficiency cannot be above 67 % since one third of current is used for oxygen evolution [12]. The systematic study of bromide oxidation with bromate formation on boron doped diamond electrodes (BDD) was performed by Bergman [13]. Vacca et al. indicated that the main mechanism of bromate formation is the oxidation mediated by hydroxyl radicals and oxygen radicals [14]. Cettou and coworkers obtained contradictory results of current efficiency for bromate formation. They reported 90 % of current efficiency for primary reaction. However, from the point of view of thermodynamics, favored reactions should proceed at lower potential. According to Cettou [11], the standard potentials for the anodic formation of bromate is around 1.45 V when the standard potential for bromine discharge is only 1.1 V. In addition, in many studies on the electrolysis of bromide to bromate low concentrations of bromide are used and electrolysis is carried out at potentials beyond the electrochemical stability window of aqueous electrolytes [13].

Therefore, in slightly alkaline solutions the oxidation of hydroxyl ion and the formation of bromate from hypobromite and bromide are thermodynamically preferred. When all bromate is formed by the chemical reaction the resulting current efficiency can reach 100 %. To favor this approach, the neutral or alkaline solutions should be preferred when the main way of bromate formation is the reaction of hypobromous acid disproportionation [15]. Several research groups demonstrated this, e.g. in the paper by Cettou [11] it is demonstrated on Ti/RuO_2 electrodes that the bromate is formed upon the oxidation of hypobromite by hypobromous acid. Pavlovic et al. stated that the current efficiency of bromate formation reaches 98-99 % in the pH range between 8.5 and 9.5 on DSA electrodes [12]. Nevertheless, the overall reaction is of the third order, it is ten times faster than the chlorate formation at the same temperatures [11].

To form a closed energy cycle of the bromate RFB it is required to carry out the regeneration of the spent oxidizer considering another optimization parameter – round trip energy efficiency. To obtain sufficient values of cycle efficiency the optimal way of regeneration (electrooxidation) should be determined. The key issues in the bromide oxidation in neutral and alkaline media is the current yield of the desired product and the composition of near-electrode layer. A traditional electrochemical method for solving this issue is a rotating ring-disk electrode (RRDE). For example, in the work by Johnson RRDE was used to study the oxidation of bromide on a platinum electrode in 1 M sulfuric acid [16]. On one of the electrodes (on the Pt disk) bromine was generated after the application of anode current on it and on the second electrode (Pt ring) products of bromide oxidation were registered in the cathode part of this process. It was shown that the oxidation of bromide at these conditions results in the formation of not only bromine but also hypobromous acid. However, no references exist about the application of RRDE method for neutral and alkaline media with high bromide concentrations.

Therefore, the existing experimental data is not enough to analyze the combination of electrochemical and chemical stage of bromate regeneration. As a result, it became necessary to determine whether it is possible to obtain the data for a combination of stages by the rotating ring-disk electrode method. There is a lot of information on the oxidation of bromide to bromate, although the rigorous analysis of the data was not carried out. Since the voltammetric analysis on the ring allows to study the rate of disproportionation of bromine and its various products, to achieve this goal we performed a thorough analysis of the bromide oxidation in buffer solutions with different pH using rotating ring-disk electrode.

2. Experimental

2.1. Chemicals

Sodium bromide (99%, Laverna, Russia) and triply distilled water were used for electrolytes preparation. The required amount of sodium bromide powder was added to the prepared buffer solution at a predetermined pH. All experiments were performed for two concentrations of bromide: 0.5 M and 1 M. High concentrations of bromide ion are studied due to the potential use in RFB.

Sodium bromate (99%, Labteh, Russia) was used as received. Solutions of HOBr were prepared by the reactions of bromine disproportionation in alkaline medium, i.e. acidic bromine solution was neutralized by 2.5 M NaOH (99%, Laverna, Russia).

Buffer solutions were prepared according to the procedure described in the literature [17]. Buffer solutions with pH 10.5, 10, 9.5 were prepared by mixing different amounts of 0.1 M aqueous sodium hydroxide solution (NaOH) and 0.05 M aqueous sodium tetraborate solution ($Na_2B_4O_7 \cdot 10H_2O$) (Labteh, Russia) to give required pH. Buffer solutions with pH 7.5, 7, 6.5, and 6 were prepared by mixing different amounts of 1/15 M of an aqueous solution of KH_2PO_4 (Labteh, Russia) and 1/15 M of an aqueous solution of Na_2HPO_4 (Labteh, Russia) to give required pH 0.1 M NaOH, that was used as a buffer solution with pH = 12.5.

Once the buffer solution was prepared, a pH meter ANION 4100 was used to determine pH.

2.2. Procedures

Electrochemical measurements were performed at room temperature using an Autolab PGSTAT302N potentiostat/galvanostat. Rotating ring-disk electrode with a rotation speed control Pine MSRX (Pine Research Instrumentation, USA) in a double-walled three-electrode cell (volume 200 mL) was used for all electrochemical measurements. A working electrode RRDE consisted of glassy carbon (GC) disk (diameter 5 mm) and Pt ring (outer diameter 7.5 mm and 6.5 mm inner diameter), Pt wire used as a counter electrode and Ag/AgCl as a reference electrode filled with saturated KCl solution in electrical contact with solution through salt bridge filled with 1 M H2SO4.

To prepare for each measurement the working electrode was gradually polished by SiC paper of decreasing abrasive grain size and diamond suspension of ¼ mm (Escil, France).

2.3. Ring Collection Coefficient Measurements

For systematic studies of the bromide anion oxidation process kinetics and its products composition qualitative and quantitative the following experimental procedure was employed.

Prior to the measurements of ring collection coefficient, for each composition cyclic voltammograms were recorded to determine the range of potentials and currents when the primary reaction of bromide oxidation occurs without simultaneous intensive oxygen evolution. Among studied solutions this value was defined in the most alkaline solution. Maximum current was determined to be 10 mA in 0.1 M NaOH and was used for all buffer solutions.

The following procedure was used for all studied NaBr solutions with different pH from 6 to 13. A constant current of 10 mA was applied to the GC disk. GC electrode was selected due to the ten times lower current densities compared to Pt ring recorded by scanning CVs of buffer solutions in case of neutral and alkaline pH.

Under the application of current the electrochemical oxidation of bromide to bromine on the surface of GC disk occurred. The potential of Pt ring took specific values. In this case, the curve of the current decay was registered on the ring. Each value of ring potential remained unchanged for 20 s to obtain steady-state value of current. The integration value for two last seconds was recorded as a current value on the Pt ring corresponding to this potential. The ring potential values were varied from +0.65 V to – 0.9 V. The potential range of the ring was chosen to be far from the equilibrium potential of the bromide-bromine redox couple (i.e. bromine generated on the disk would be reduced on the ring close enough to diffusion limited regime). Such wide range of potentials is studied due to the possibility of reduction of other bromine containing products, for example HOBr (or BrO^-), as described in several articles [16].

Similar dependencies were measured for other bromine containing species to determine the applicability of the proposed experimental setup.

The ratio of the value of the measured current on the Pt ring to the applied current on the disk is called the "ring collection coefficient". This value was measured for two different rotation speed – 200 rpm and 5000 rpm – modeling extremely low and high rates of solution supply to the electrochemical reactor and, consequently, the transfer rates of reaction products on the disk to the ring.

To determine the maximum value of ring collection coefficient and control the conditions of its constancy an experiment of electrochemical bromide oxidation was performed in 1 M H_2SO_4 solution where the oxidation product of bromide (bromine) is thermodynamically stable according to Pourbaix diagram [18-19]. The obtained value of ring collection coefficient in this case was 0.25 ± 0.1. Estimation by the theoretical formula [20] for this geometry of RRDE gives 0.26 indicating an agreement of the experimental data.

Moreover, to eliminate the effect of side reaction on the ring electrode – electroreduction of dissolved oxygen the experimental algorithm was also supplied with the measurement and substraction of the background currents on the Pt ring obtained under the application of zero current on GC disk.

3. Results and Discussion

3.1. Electrochemical Activity of Various Bromine containing Species

To study the oxidation of bromide process in neutral and alkaline solutions, it's current efficiency and composition of the near-electrode layer via the rotating disk electrode method, the electrochemical properties of bromine-containing compounds were studied at first.

3.1.1. Electrochemical Oxidation of Bromide Anion

To determine the range of potentials and currents when the primary reaction of bromide oxidation occurs without simultaneous intensive hydrogen or oxygen evolution cyclic voltammograms of NaBr solutions were recorded for different pH of electrolytes (see Figure 1).

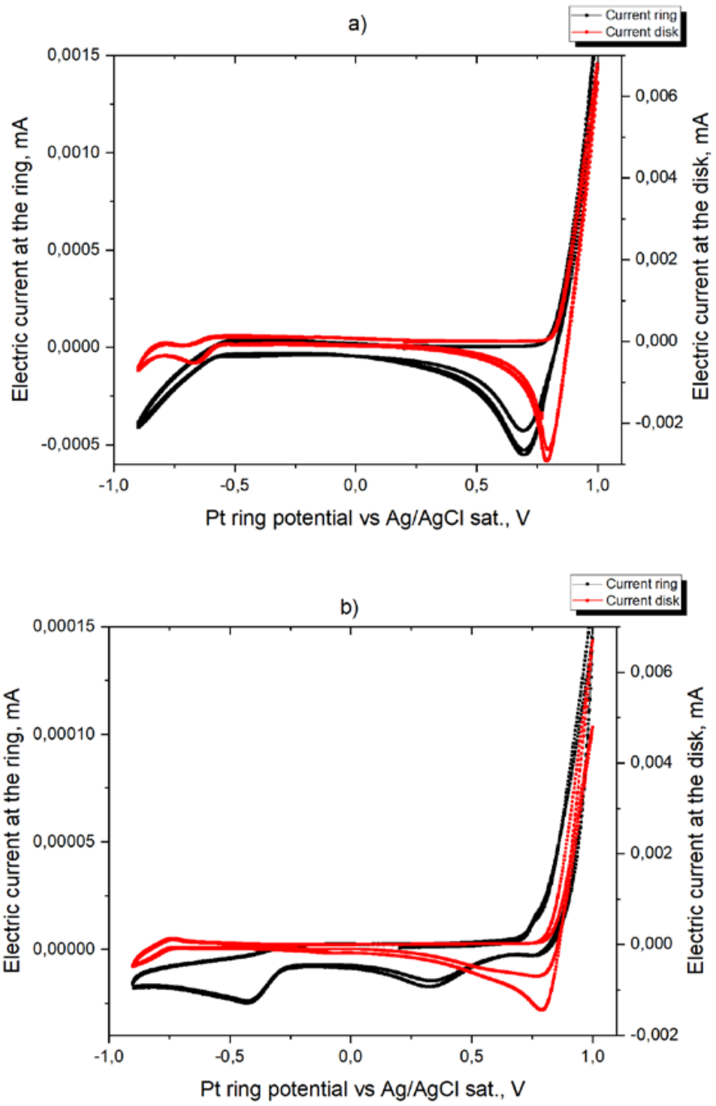

Figure 1. Cyclic voltammograms of 0.5 M NaBr solutions measured at scan rate 50 mV/s at different pH values of buffer solutions at rotating disc and ring: a) pH = 7; b) pH = 10.

Since the process of bromide electrooxidation

$$Br_2 + 2e^- = 2\,Br^- \tag{2}$$

doesn’t involve protons, therefore one can observe the redox peak that doesn’t depend on pH value and is at cathodic area near + 0.8 V. Since there is no hydrogen evolution at the left part of the Figure 1 until at least 0.8 V, the availably potential window for the experimental setup is approximately from -0.8 V till 0.8 V.

Additionally imposing the constant 10 mA value of the disk current we produced the chemically equivalent amount of bromine to collect it at the Pt ring registering dependencies of the current values at the ring vs its potential for alkaline (pH = 10) and for neutral conditions (pH = 7). Such setup allows one to examine the possible occurrence of homogeneous chemical step, e.g. bromine disproportionation in alkaline medium:

$$Br_2 + 2OH^- = BrO^- + Br^- + H_2O \tag{3}$$

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According to Figure 2 in neutral solution the constancy of the collected current in the whole interval of potentials witnesses the absence of chemical transformation while bromine species move from the disk to the ring surface, therefore the diffusion limited regime takes place.

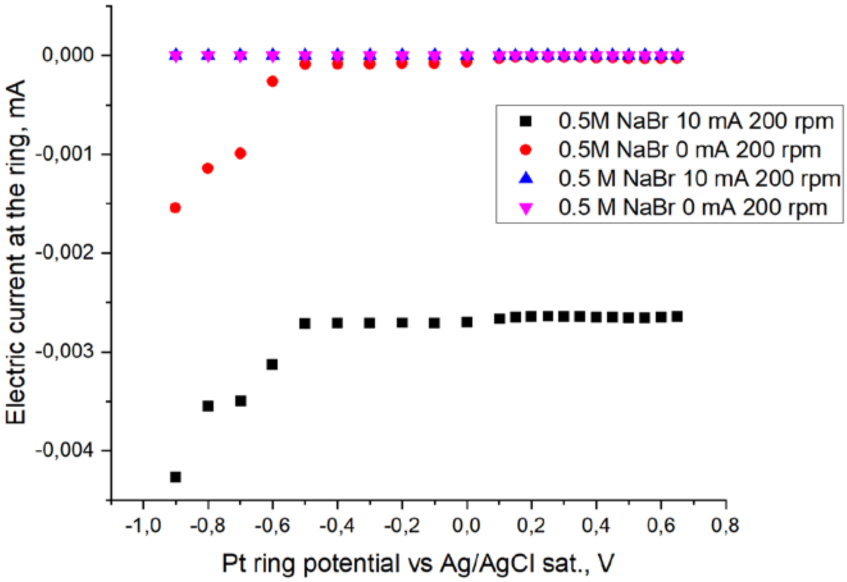

Figure 2. The Pt ring collected current dependencies on the potential under stationary conditions for 0.5 M NaBr at different pH of solutions. Rpm = 200.

For alkaline solution vice versa, no current is observed since the bromine disproportionation via homogeneous reaction. To verify the experimental setup for both cases control experiments were performed with no current imposed at the disk witnessed the absence of the current at the ring.

3.1.2. Electrochemical Activity of $NaBrO_3$ on Pt Ring in Solutions with Various pH

To determine the electrochemical activity of bromate anion the potential range was limited in the anodic region by 0.8 V limit to prevent the formation of bromide/bromine redox couple. Figure 3 demonstrates CVs of $NaBrO_3$ in the solutions with different pH indicating that bromate anions exhibit electrochemical activity at much more negative potentials than the bromide/bromine redox couple and the process is independent on pH of electrolyte.

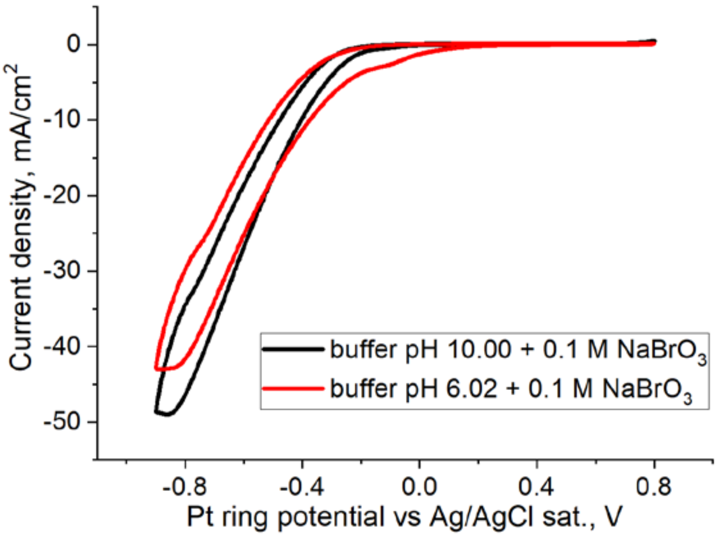

Figure 3. Cyclic voltammograms of NaBrO3 in buffer solutions with pH = 6 and pH = 10 recorded on a stationary platinum electrode at a scan rate of 50 mV/s.

For $NaBrO_3$ the ring current vs potential dependence is shown at Figure 4 for different pH and rotation rates of the RRDE (while no current is imposed at the disc). In the potential range from 0.6 V to 0 V no current on the ring was registered. Further the cathode current on the ring increases proportionally as the potential shifts to more negative values.

Polarization curves clear similarities on Figure 3 and Figure 4 are noteworthy. In the negative potential region under 0 V the observed cathodic waves are attributed to the discharge of bromate anion on the platinum electrode. These observed currents are apparently associated with the direct bromate anion reduction. Besides one should exclude the possibility of redox mediated bromate electroreduction (EC′′ mechanism) due to the absence of the strongly acidic medium which is a must for such an autocatalytic process [21-22], so that the observed current is apparently associated with the discharge of bromate anion.

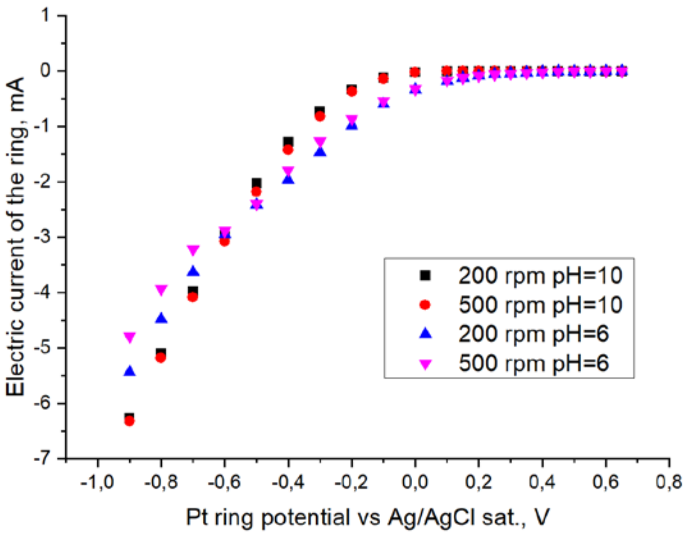

Figure 4. The Pt ring collected current vs the potential dependence under stationary conditions for 0.1 M $NaBrO_3$ in various buffer solutions at RRDE different rotation velocities.

3.1.3. Electrochemical Activity of HOBr (OBr^-) on Pt Ring

Electroreduction of bromine (+1) compounds on platinum has been widely studied [16]. The equilibrium potential of this process in solutions of 1 M H_2SO_4 (pH = 0) was found to be 1.34 V vs standard calomel electrode. Since our experimental conditions are different, we performed our control estimation of this value.

Figure 5 shows cyclic voltammograms of HOBr in solutions of alkali pH. Different pH values were obtained depending on the amount of alkali added to neutralize the initial acidic bromine solution. Comparing the previously obtained curves for bromates a peak at + 0.3 V region is presumably associated with the electroreduction of HOBr to Br^-.

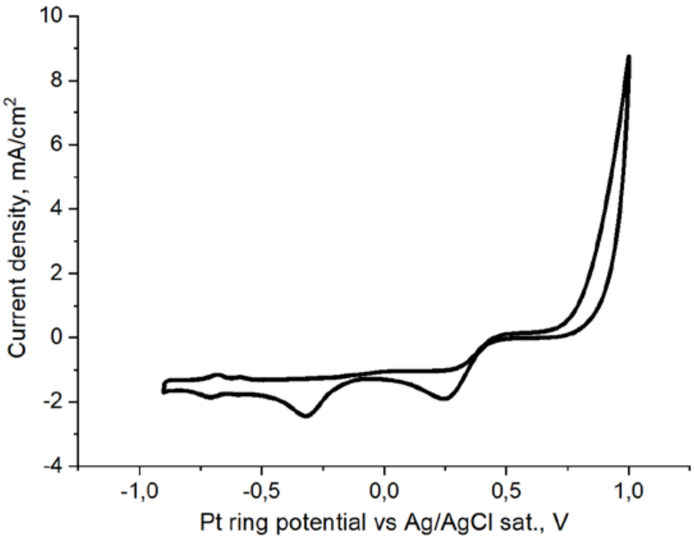

Figure 5. Cyclic voltammograms of 0.1 M OBr- recorded at 50 mV/s on the stationary platinum electrode. pH = 11.66.

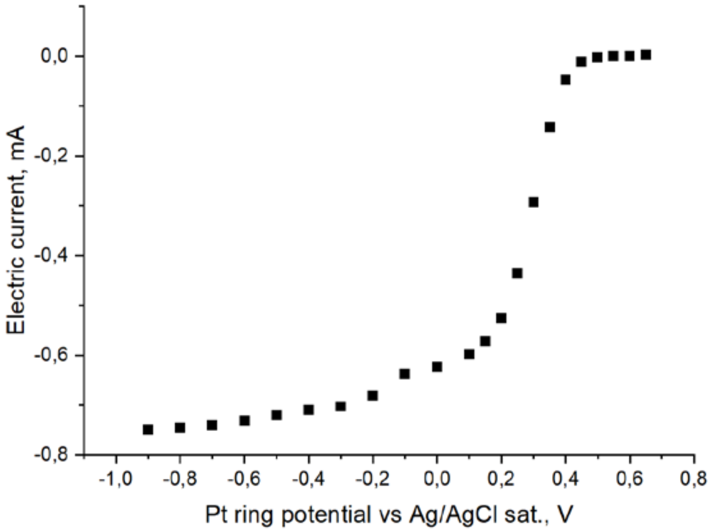

Figure 6. The Pt ring collected current vs the potential dependence under stationary conditions for 0.1 M OBr^-. pH = 11.66, rpm = 200.

Figure 6 shows the dependence of the collected current on the potential on the platinum ring for BrO^-. This dependence shows that at a potential value below 0.4 V there is a noticeable increase in the current on the ring indicating the electroreduction of the hypobromite anion at this potential. The current increase continues reaching a certain limiting value at - 0.1 V and then increases slightly due to the superposition of two processes occurring simultaneously in accordance with the peak points at Figure 5 – one starting from the 0.1 V, another from -0.3 V.

The presented experimental data suggest the possibility of using RRDE method for electrooxidation reaction of bromide ion to obtain quantitative information on the kinetics of this complex process. In particular, the conversion rate of primary product of bromide oxidation (molecular bromine) into oxygen-containing bromine compound (hypobromite ion) (or its undissociated form HOBr) and bromate ion BrO_3^- can be estimated based on experimental dependencies of current collection coefficients from potential on Pt ring electrode. This possibility is based on the difference in potentials of electroreduction waves of these components:

- Br_2 reacts in the whole potential range including the region above + 0.5 V in the diffusion-limited regime;
- BrO^- ion is reduced in potential range near + 0.5 V reaching the diffusion limit near +0.1 V;
- Finally, BrO_3^- begins to react near +0.1 V with a gradual increase of the reaction at more negative potentials.

3.2. Ring Collection Coefficients at Different pH

As it was shown in the previous sections the obtained experimental data of collected current values on the Pt ring would present an integral characteristic since both molecular bromine and products of bromine disproportionation with a higher oxidation state can be reduced on the ring. In addition, the charge balance may be maintained by the constancy of the ring current (and, consequently, collected current values) regardless of the occurrence of disproportionation reaction and its rate in case of identical electrochemical activity of all bromine forms (0, +1, +5) on the ring electrode. However, the obtained experimental data and several experimental works in literature [23] indicates the significant overvoltage for the electroreduction of bromine compounds with oxidation states +1 and +5, which should lead to the separation of corresponding products reduction waves making possible to monitor near-electrode concentration of molecular bromine in the certain range of potentials. To verify this, the following studies were performed.

In this section we compare the dependencies of current collection efficiencies on the ring potential at different parameters of the studied system to evaluate their effect on the composition of the oxidation products of the bromide ion considering the subsequent chemical stages. The following dependences are present for specific NaBr concentration, current on the GC disk and rotation speed of RRDE. The presented data allows to analyze the effects of pH solution, the concentration of bromide passed through GC disk and rotation speed of the RRDE.

The ring collection efficiency was determined as follows:

$$N = \frac{I_{(\mathrm{ring})} - I_{0(\mathrm{ring})}}{I_{(\mathrm{disc})}} \tag{4}$$

Where $I_{(\mathrm{ring})}$ – is a current registered on the Pt ring when the current is applied to the GC disk, $I_{0(\mathrm{ring})}$ – current registered on the Pt ring in case of zero current applied to the GC disk, $I_{(\mathrm{disc})}$ – value of current applied to the GC disk.

Figures 7 and Figures 8 demonstrate the dependencies of the ring collection efficiencies for 0.5 M NaBr and 1 M NaBr, respectively.

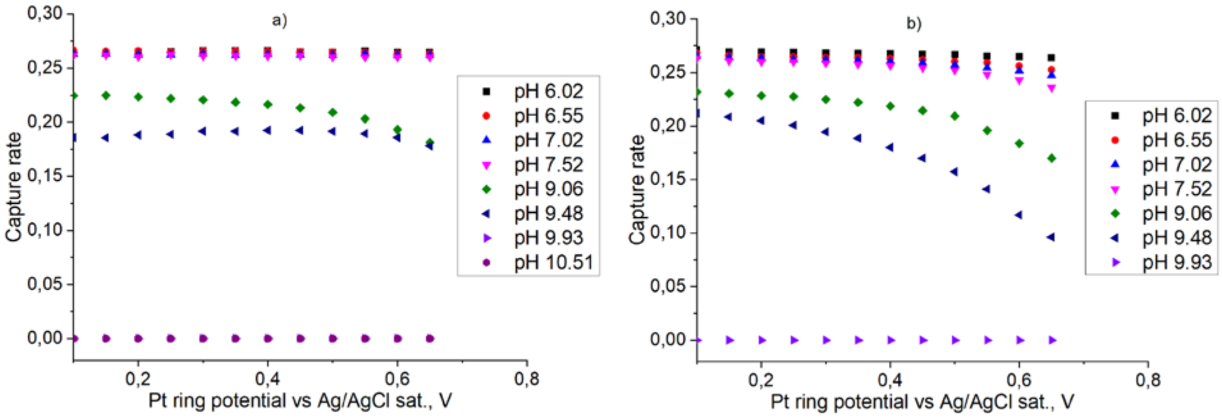

Figure 7. Ring collection efficiencies on the Pt ring under the applied 10 mA on the GC disk for 0.5 M NaBr solutions at different pH. The graphs are presented for two rotation rates of the RRDE: a) 200 rpm, b) 5000 rpm.

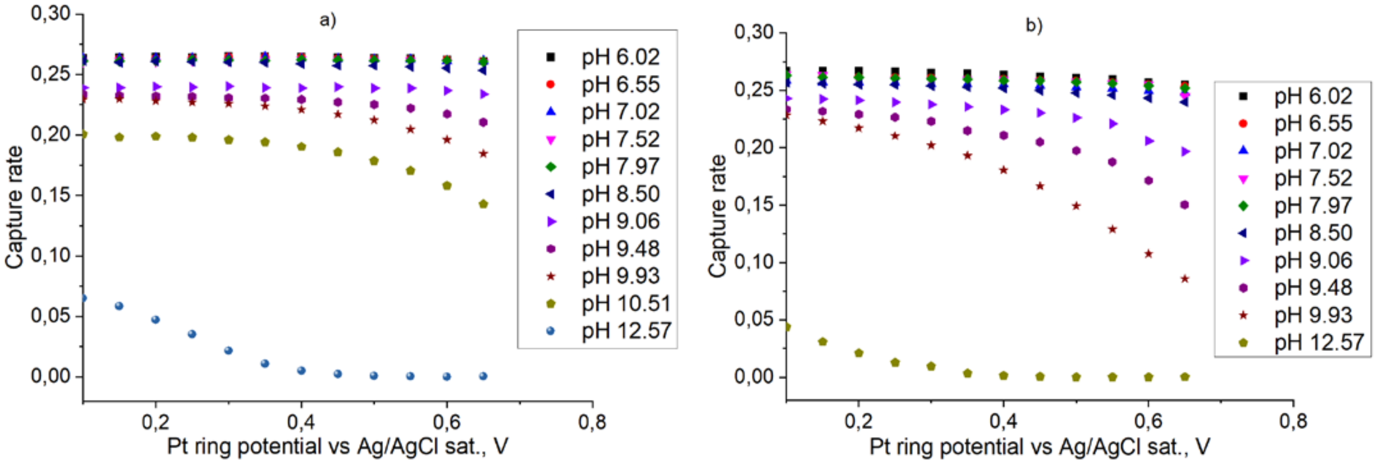

Figure 8. Ring collection efficiencies on the Pt ring under the applied 10 mA on the GC disk for 1 M NaBr solutions at different pH. The graphs are presented for two rotation rates of the RRDE: a) 200 rpm, b) 5000 rpm.

From the presented data one can conclude that RRDE method allows to obtain quantitative information on the kinetics of the complex process, which includes electrochemical oxidation of bromide to bromine and subsequent chemical stages involving bromine disproportionation in a neutral and alkaline medium. As it was demonstrated in previous sections, the bromine is reduced in the whole range on Pt ring potential on Figures 7-8. Moreover, the reduction of BrO$^-$ (or undissociated form HOBr) occurs in the potential region from +0.5 V reaching the diffusion limit at + 0.1 V. Since then, the current collection efficiency in the potential region from 0 V to 0.7 V should be equal its maximum value if other bromine-containing compounds are not formed.

In some cases, the current collection efficiency does not reach its maximum value of 0.26 indicating the bromate formation in alkaline media (pH > 9). Based on this assumption, we demonstrated that at specific values of pH only bromate is formed in the system revealing striking disagreement with the reported experimental data by [11,16].

For high concentrations of NaBr the disproportionation reaction occurs at pH > 9. With the increase of NaBr concentration the rate (degree) of bromine disproportionation decreases at the same pH values due to the possible formation of Br3-. Comparing two different rotation rates of RRDE we can state that the bromate is not formed at high rotation rate (5000 rpm) of RRDE.

As a result, the obtained experimental data indicate that chemical reaction of bromine disproportionation in alkaline medium is rather fast. Therefore, the reaction of disproportionation can be used for a regeneration of the spent oxidizer.

4. Conclusions

RRDE method could be used to obtain quantitative and qualitative data on the electrooxidation of bromide ion in neutral and alkaline solutions. We showed experimentally that the chemical reaction of bromine disproportionation in alkaline medium leads to bromate formation and the reaction proceeds quickly enough, which does not correspond to the known literature data. Thus, the disproportionation reaction can be used to regenerate the spent oxidizer in a hydrogen-bromate redox flow battery. For the most effective regeneration of the spent oxidizer the values of $pH > 10$ and moderate concentrations of NaBr should be used.

Supplementary Materials: Not applicable.

Author Contributions: Conceptualization, R. Pichugov and M. Petrov; methodology D. Konev and L. Abunaeva; validation, I. Speshilov; investigation M. Petrov; writing—original draft preparation, L. Abunaeva.; writing—review and editing, M Vorotyntsev. All authors have read and agreed to the published version of the manuscript.

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