

## Bromate Reaction on a Rotating Disc Electrode: A New Method of Obtaining Approximate Analytical Solutions for Stationary Regime

M. A. Vorotyntsev<sup>a,b,c,d,\*</sup>, A. E. Antipov<sup>a,b, \*\*</sup>,  
M. M. Petrov<sup>a,b</sup>, R. D. Pichugov<sup>a,b</sup>, E. I. Borisevich<sup>b</sup>,  
E. M. Antipov<sup>a,b</sup>, and Academician S. M. Aldoshin<sup>b,c</sup>

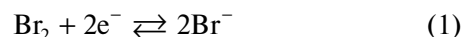
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**Abstract**—A new method (AA approximation) is proposed for obtaining approximate analytical solutions of a system of equations describing the transport of the basic reagents for the electroreduction process of the  $\text{BrO}_3^-$  anion on a rotating disc electrode in an acid medium in the presence of very small additions of molecular bromine. This process is of significant interest both from the fundamental point of view (as an example of a new electrochemical EC" mechanism with autocatalytic properties) and from the applied point of view in the context of prospects to create, on its basis, innovation power sources—bromate redox flow batteries. Since the previously proposed method for solving the system of kinetic transport equations for this system turned out to be inapplicable for very large diffusion layer thicknesses and very strong currents, here a new method of obtaining approximate analytical expressions for concentration profiles and maximum current is proposed. It has been shown that its predictions are in good agreement with the results of the numerical solution of the same problem in a wide range of system parameters, including the region of very large diffusion layer thicknesses, which confirms the validity of the used analytical approximations.

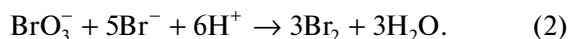
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In recent years, interest in electrochemical current sources based on redox flow batteries (RFBs) has increased due to the extensive prospects for their use as stationary energy storage devices: recently, hybrid hydrogen–bromine redox batteries have been proposed that have outstanding power densities [1], and a few years ago, hydrogen–bromate RFBs have been developed where bromates (in particular, lithium and sodium bromates) are used as an oxidizing agent, which show huge energy densities [2, 3]. Despite the non-electroactivity of bromate anions at the cathode at potentials negative with respect to the SHE poten-

tial, the electroreduction of bromate anions on a catalytically inactive (for example, carbon) rotating disk electrode (RDE) in an acidic medium in the presence of trace amount of molecular bromine has been realized under stationary conditions [2]. This appeared to be possible due to the new electrochemical EC" mechanism, where the reaction occurs due to the presence of the redox mediator cycle, consisting of a reversible transformation on the electrode:



in combination with the stage of comproportionation into the solution:



Earlier, we obtained for the first time approximate analytical solutions (A0 approximation) of the system of ordinary differential kinetic transport equations for the key reagents ( $\text{BrO}_3^-$ ,  $\text{Br}^-$ ,  $\text{Br}_2$ ,  $\text{H}^+$ ) within the framework of the Nernst diffusion layer model, under

<sup>a</sup>Mendeleev University of Chemical Technology of Russia, Moscow, 125047 Russia

<sup>b</sup>Moscow State University, Moscow, 119992 Russia

<sup>c</sup>Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

<sup>d</sup>Institute of Molecular Chemistry, University of Burgundy, Dijon, France

\*e-mail: mivo2010@yandex.com

\*\*e-mail: 89636941963antipov@gmail.com

the condition of an excess of both protons compared to bromate ions [2], and bromate ions compared to protons. Comparison of analytical predictions and the results of numerical integration of the same equations confirms the validity of analytically performed approximations for a wide range of system parameters, in particular, the ratio of the diffusion-to-kinetic layer thicknesses:  $x_{dk} = z_d/z_k$ . At the same time, a significant discrepancy was found between the results of the A0 approximation and numerical calculation at very large values of this parameter (substantially more than 10) [4]. This paper proposes a new method (AA approximation) for obtaining approximate analytical solutions of this system of equations (exemplified by the Nernst diffusion layer model), which is in good agreement with numerical calculations in a wider range of system parameter values, including for very large values of the parameter  $x_{dk}$ .

### SYSTEM DESCRIPTION

Since the same assumptions as in [4] are here used, they are briefly formulated below.

The components of the system are denoted as follows: A ( $\text{BrO}_3^-$ ), B ( $\text{Br}^-$ ), C ( $\text{Br}_2$ ), and H ( $\text{H}^+$ ). Their concentrations  $A(z)$ ,  $B(z)$ ,  $C(z)$ , and  $H(z)$  depends on the only spatial variable  $z$  normal to the RDE surface ( $z = 0$  corresponds to the electrode surface). Volume concentrations— $A^\circ$ ,  $B^\circ = 0$ ,  $C^\circ$ , and  $H^\circ$ —meet the conditions  $H^\circ \gg A^\circ \gg C^\circ$ ; i.e., the protons are in excess to bromate ion and act as a supporting electrolyte, whereas the bromine concentration in the solution volume is many orders of magnitude lower than these concentrations. Due to an excess of protons, we can neglect the migration component of the transport of ions A and B.

The local rate of comproportionation reaction (2) per solution volume unit  $V(z)$  depends on the local reagent concentrations  $A(z)$ ,  $B(z)$ , and  $H(z)$  [5]:

$$V(z) \equiv -\frac{d[\text{BrO}_3^-]}{dt} = kA(z)B(z), \quad (3)$$

where the rate constant  $k$  depends on the proton concentration  $H(z)$  ( $H(z) \cong H^\circ$ ) [6].

In the Nernst layer model [7], concentrations change only into the diffusion layer:  $0 < z < z_d$ , whereas beyond this layer ( $z > z_d$ ) the concentrations are equal to their volume values.

Transition to dimensionless variables is performed by analogy with [4] by introducing the kinetic layer

thickness (at weak currents)  $z_k$  and limiting diffusion current densities of bromate  $j_A^{\text{lim}}$  and bromine  $j_C^{\text{lim}}$ :

$$z_k \equiv \left[ \frac{D_B}{5kA^\circ} \right]^{1/2}, \quad j_A^{\text{lim}} \equiv \frac{5FD_A A^\circ}{z_d}, \quad (4)$$

$$j_C^{\text{lim}} \equiv \frac{2FD_C C^\circ}{z_d},$$

where  $F$  is the Faraday constant;  $D_A$ ,  $D_B$ , and  $D_C$  are the diffusion coefficients of the corresponding components; the diffusion layer thickness  $z_d$  is given by the Levich equation

$$z_d = 1.61D_A^{1/3} \nu^{1/6} \Omega^{-1/2}, \quad \Omega = \frac{2\pi}{60} f \text{ [rpm]}. \quad (5)$$

Dimensionless variables for spatial coordinate  $z$ , cathodic current density  $j$  (which is considered to be a given parameter in the galvanostatic mode of the process), and the concentration distributions of components A, B, and C, as well as dimensionless combinations of parameters are introduced by Eqs. (6)–(8):

$$x \equiv z/z_k, \quad x_{dk} \equiv z_d/z_k, \quad (6)$$

$$a(x) \equiv \frac{A(z)}{A^\circ}, \quad b(x) \equiv \frac{D_B B(z)}{D_A A^\circ}, \quad c(x) \equiv \frac{D_C C(z)}{D_A A^\circ}, \quad (7)$$

$$J \equiv \frac{j}{j_A^{\text{lim}}}, \quad J_{CA} \equiv \frac{j_C^{\text{lim}}}{j_A^{\text{lim}}} = \frac{2D_C C^\circ}{5D_A A^\circ} = 0.4c^\circ, \quad (8)$$

$$c^\circ \equiv \frac{C^\circ D_C}{D_A}, \quad A^\circ = \frac{5}{2} J_{CA}.$$

Inside the Nernst layer, the following transport equations for the reagents can be written:

$$\frac{d^2 a}{dx^2} = \frac{1}{5} a(x)b(x), \quad \frac{d^2 b}{dx^2} = a(x)b(x), \quad (9)$$

$$\frac{d^2 c}{dx^2} = -\frac{3}{5} a(x)b(x),$$

at the electrode surface, balance laws taking into account the stoichiometry of reaction (2)

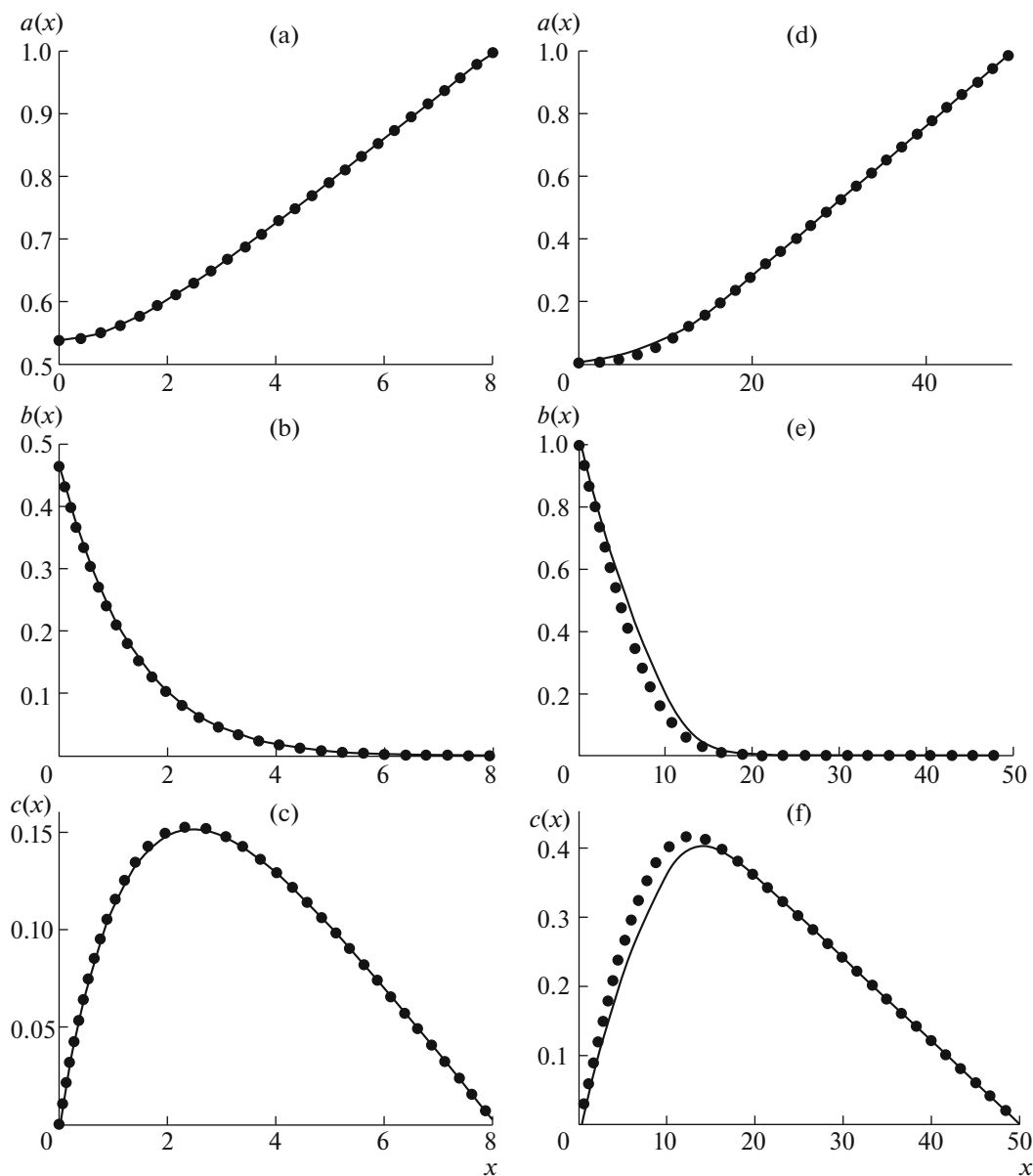
$$\frac{da}{dx} = 0, \quad \frac{db}{dx} = -\frac{5J}{x_{dk}}, \quad \frac{dc}{dx} = \frac{5J}{2x_{dk}} \quad \text{at} \quad x = 0 \quad (10)$$

and, finally, conditions at the outer boundary of the diffusion layer:

$$a(x) = 1, \quad b(x) = 0, \quad c(x) = c^\circ = \frac{5}{2} J_{CA} \quad (11)$$

at  $x = x_{dk}$ .

From these expressions, relationships between concentration distributions can be derived by twofold integration [5]:



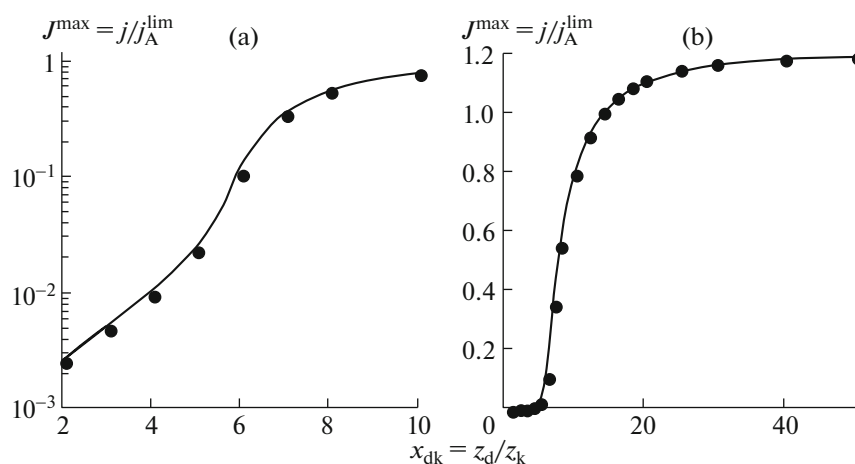
**Fig. 1.** Dimensionless concentration profiles  $a(x)$  for bromate anion (a, d),  $b(x)$  for bromide anion (b, e), and  $c(x)$  for bromine (c, f) at the diffusion-to-kinetic layer thickness ratio (a–c)  $x_{dk} = 8$  and dimensionless current density  $J = J_{\max} = 0.6$  and (d–f)  $x_{dk} = 50$  and  $J = J_{\max} = 1.19$ ;  $J_{CA} = 10^{-3}$ . Here and in Fig. 2, data points denote numerical modeling results, and the solid line shows analytical predictions in the framework of the AA approach.

$$\begin{aligned}
 1 - a(x) &= J \left( 1 - \frac{x}{x_{dk}} \right) - \frac{1}{5} b(x) \\
 &= \frac{5}{6} \left( 1 - \frac{x}{x_{dk}} \right) J + \frac{1}{3} [c(x) - c^o].
 \end{aligned}
 \quad (12)$$

Equations (9)–(11) in combination with in combination with the conditions of continuity and non-negativity of all concentration distributions inside the entire diffusion layer, determine the only solution for each set of values specified (in the galvanostatic mode)

combinations of system parameters:  $x_{dk}$ ,  $J_{CA} \left( J_{CA} = \frac{2}{5} c^o \right)$ , and  $J$ , the last of which is limited above by the  $J^{\max}$  value, at which the condition of positivity of all concentrations is violated, namely,  $c(0) = 0$ .

Thus, the problem of the theory consists in (1) finding the distribution of concentrations  $a(x)$ ,  $b(x)$ , and  $c(x)$  for all admissible sets of parameters  $x_{dk}$ ,  $J_{CA}$ , and  $J$  ( $0 < J < J^{\max}$ ); (2) in finding the maximum current density  $J^{\max}$  for all sets of parameters  $x_{dk}$  and  $J_{CA}$ .



**Fig. 2.** Dependence of the dimensionless maximal current density  $J_{\max}$  on  $x_{dk}$ : (a) logarithmic scale for the current and (b) linear scale for the current,  $J_{CA} = 10^{-3}$ .

## RESULTS AND DISCUSSION

Previously [2], we have obtained an approximate analytical solution for the case of weak current ( $j \ll j_A^{\lim}$ , i.e.,  $J \ll 1$ ) for any values of the  $x_{dk}$  and  $J_{CA}$  ( $J_{CA} \ll 1$ ). It has been shown that, at  $x_{dk} < x_{dk}^* \cong 6$ , all possible values of current density  $J$ , including its maximal value  $J^{\max}$  (at a given  $x_{dk}$ ), meet the weak current condition. Therefore, strong current ( $J \sim 1$ ) can flow

only at rather large  $x_{dk}$  values:  $x_{dk} > x_{dk}^* \cong 6$ , i.e., for a thin kinetic layer when its thickness is very small as compared with the diffusion layer thickness  $z_d$ .

An iteration algorithm of finding approximate analytical solutions for distributions of concentrations  $a(x)$ ,  $b(x)$ , and  $c(x)$  has also been suggested for the thin kinetic layer mode [2]:  $x_{dk} \gg 1$ , i.e.,  $z_d \gg z_k$ . Within the zero approximation, the bromate concentration  $a(x)$  inside the entire diffusion layer was taken to be constant and equal to its value  $a(0)$  at the electrode surface:  $a(x) \cong a(0)$  (A0 approximation). The substitution of this  $a(x)$  approximation into Eq. (9) for  $b(x)$  gives the analytical solution of the first order for  $b(x)$ , which makes it possible to calculate  $a(0)$  and the corresponding profiles of the other concentrations by Eq. (12).

The numerical solution [4] of the same Eqs. (9)–(11) showed that the results of the A0 approximation are inapplicable at very large  $x_{dk}$  values (significantly more than 10). Therefore, here we suggest a new method (AA approximation) in which different zero approximations are used for  $a(x)$  in two intervals “sewn” together at a priori unknown point  $x^*$ :

$$a(x) \cong \begin{cases} a(0) & \text{at } 0 < x < x^* \\ 1 - J \left( 1 - \frac{x}{x_{dk}} \right) & \text{at } x^* < x < x_{dk}. \end{cases} \quad (13)$$

These expressions for  $a(x)$  are substituted into the right-side of Eq. (9), and for both intervals of the  $x$  variable, analytical first-order solutions are found. The coordinates of the point  $x^*$  can be found from the condition of continuity of concentration profiles in both the zero and first approximations. From Eqs. (12), the other concentration profiles can be obtained, and the maximal current  $J^{\max}$  can be obtained from the condition  $c(0) = 0$ .

The calculated analytically  $a(x)$ ,  $b(x)$ , and  $c(x)$  concentration profiles are presented in Fig. 1 in comparison with the results of numerical integration of the same system of equations solved without any approximations. As the  $x_{dk}$  parameter increases to very large values, at which the A0 approximation deviates from the numerical solution more than two times, the coincidence of the analytical predictions of the new AA approximation and numerical data does not exceed 5%. A smaller deviation (no more than 2%) demonstrates the dependence of the maximum value current density from the parameter  $x_{dk}$  (Fig. 2).

## CONCLUSIONS

Thus, a new method of calculation (AA approximation) of diffusion transport of reagents for the electroreduction process of the  $\text{BrO}_3^-$  anion on a rotating disc electrode in an acid medium in the presence of very small additions of molecular bromine is presented. It has been shown that its predictions are in good agreement with the results of numerical solution of the same problem in a very wide range of system parameters  $x_{dk}$  and  $J$ , including the region of very large diffusion layer thicknesses, for which an analytical solution was previously unknown.

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