DEPENDENCE OF THE RATE OF REDUCTION OF BrO_4^- ON THE NATURE OF THE ELECTRODE

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UDC 541.138

It was shown in [1, 2] that the kinetics of BrO_4^- discharge on a mercury drop electrode can be described in the framework of the elementary theory of retarded discharge [3, 4]. We have investigated the reduction of BrO_4^- anion on drop electrodes of Hg and In – Ga eutectic alloy and on rotating disk electrodes of Sb and Bi. Part of the experimental data was presented in [5, 6] and the experimental method was described in [7, 8]. The potentials in the present paper are given with respect to the normal calomel electrode.

On all of the electrodes investigated, except for the In – Ga alloy electrode, the i – E polarization curves for BrO_4^- reduction have the same form (Fig. 1) [1, 5, 6]: On going from a positive ($q > 0$) to a negative surface charge, a decrease in the rate of discharge is observed. With further increase in the cathodic potential, the rate of BrO_4^- reduction grows. An increase in the supporting electrolyte concentration c_S leads to an increase in the rate of BrO_4^- reduction at $q < 0$. At the potential of zero charge (p. z. c.) on Hg and Bi, the reaction rate is independent of solution composition and all the i – E curves intersect. In the case of an antimony electrode at p. z. c. and more negative surface charge, dissolution of the electrode is observed. As a result, the kinetics of BrO_4^- discharge can only be studied at $q < 0$. To calculate the kinetic currents, the experimental values of the current at the mercury drop electrode were corrected for concentration polarization according to [9] and by the theory of steady-state diffusion during BrO_4^- discharge on rotating disk electrodes. The charge of the reacting particles z_0 for various potentials was calculated from data on the dependence of log i on log c_S by

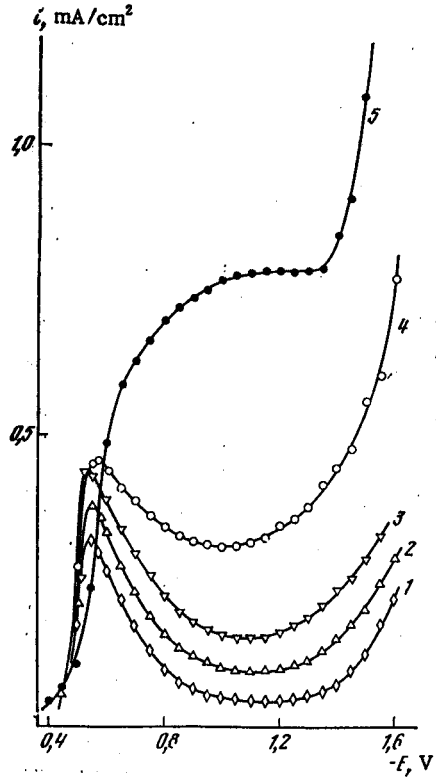

Fig. 1. Polarization curves of the reduction of $2 \cdot 10^{-4}$ N $NaBrO_4$ in water on a rotating disk electrode of antimony in the presence of NaF of concentration $5 \cdot 10^{-3}$ (1), $1 \cdot 10^{-2}$ (2), $2 \cdot 10^{-2}$ (3), 0.1 N (4), and in the presence of 2 N KCl (5).

M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 15, No. 4, pp. 587-590, April, 1979. Original article submitted August 29, 1978.

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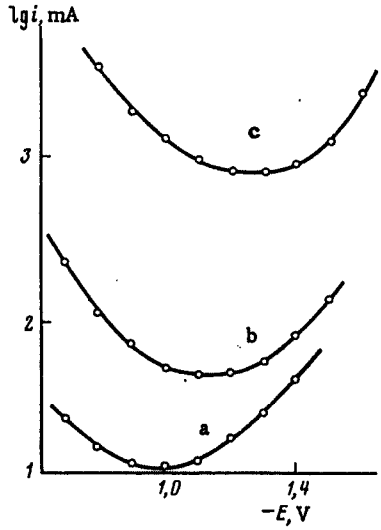

Fig. 2

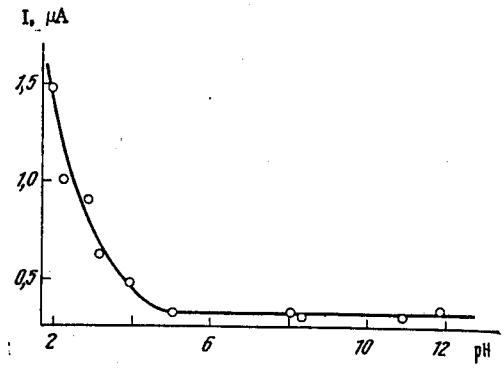

Fig. 3

Fig. 2. Kinetic current of the reduction of $2 \cdot 10^{-4}$ N $NaBrO_4$ in the presence of $5 \cdot 10^{-3}$ N NaF on a mercury electrode (a), an antimony electrode (b), and a bismuth electrode (c).

Fig. 3. Rate of reduction of $2 \cdot 10^{-4}$ N $NaBrO_4$ on a mercury drop electrode in the minimum polarization curve (E = −1.0 V) as a function of the pH of the solution in the presence of 10^{-2} N NaF.

the method described in [10]. A linear relationship between log i and log c_S at q = const was found for all of the electrodes. The average value of z_0 calculated from the slope was 0.85 ± 0.05, which is close to the theoretical value of the charge of a BrO_4^- anion. It follows from a comparison of the log i, E curves of BrO_4^- reduction on various electrodes (Fig. 2) that the rate of discharge on Sb is significantly higher than on Hg, even though the p. z. c. of antimony is somewhat less negative than the p. z. c. of mercury. In agreement with the theory of retarded discharge, the rate of reduction of persulfate anion (first group anions [5]) is higher on a mercury electrode than on an antimony electrode [11] because, on going from electrodes with a less negative value of p. z. c. to electrodes with a more negative p. z. c., the negative value of the ψ_0-potential at E = const decreases. Unlike the reduction of $S_2O_8^{2-}$, the reduction of BrO_4^- has a rate that depends on the nature of the electrode. This can be explained if it is assumed that electron transfer is the slow step in the discharge of BrO_4^- and that solvent molecules, which are proton donors (second group anions [5, 6]), participate in the elementary process. The nature of the proton donors can vary; however, in that pH region where the rate of BrO_4^- discharge does not depend on the pH of the solution (Fig. 3), it is natural to assume that the proton donors are adsorbed solvent molecules.

The overall reduction of BrO_4^- in aqueous solutions proceeds according to the equation

$$BrO_4^- + 2\bar{e} + H_2O \rightarrow BrO_3^- + 2OH^-$$

and the reaction rate i is, according to [5, 6], equal to

$$i = Kc_a \exp\frac{\alpha F}{RT}\left(-E - \frac{z_0 - \alpha}{\alpha}\psi_1\right)\exp\frac{G}{RT}, \qquad (1)$$

where K is the rate constant of the reaction, c_a is the concentration of the anion being reduced, α is the transfer coefficient, and ψ_1 is the average value of the potential in the plane in which the centers of the reacting particles are concentrated in the transition state of the reaction. It is assumed that in the absence of specific adsorption of the ions $\psi_1 \approx \psi_0$ (ψ_0 is the potential of the outer Helmholtz plane). The quantity G is the sum of nonelectrostatic, specific, standard free energies of the reacting particles, of the reaction products, and of the change in the standard, electrochemical potential of the solvent, the molecules of which are proton donors, when it is transferred from solution in the reaction zone $\bar{g}_{H_2O}$. For the reaction being studied

$$G = (1-\alpha)g_{BrO_4^-} + (1-\alpha)\bar{g}_{H_2O} + \alpha g_{BrO_3^-} + 2\alpha g_{OH^-}.$$

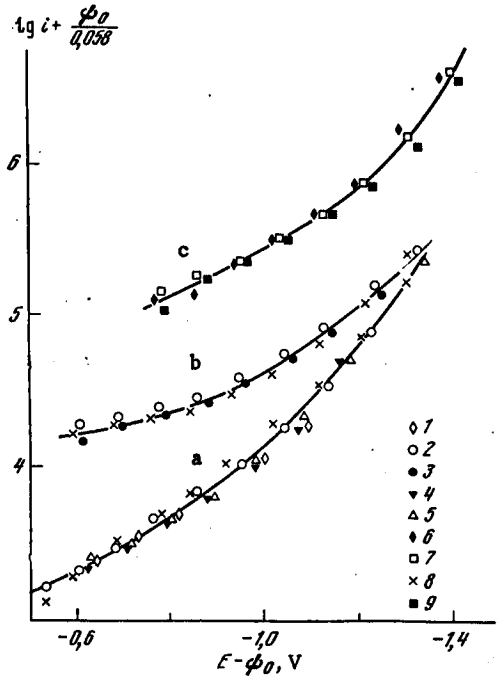

Fig. 4. Corrected Tafel dependences of the reduction of $2 \cdot 10^{-4}$ N $NaBrO_4$ in water in the presence of NaF on a mercury electrode (a), an antimony electrode (b), and a bismuth electrode (c). c_{NAF}, N: 1) 0.1; 2) $1 \cdot 10^{-2}$; 3) $2 \cdot 10^{-2}$; 4) $3 \cdot 10^{-2}$; 5) $5 \cdot 10^{-2}$; 6) $1.2 \cdot 10^{-3}$; 7) $2.8 \cdot 10^{-3}$; 8) $5.0 \cdot 10^{-3}$; 9) $5.2 \cdot 10^{-3}$.

With negative charges of the surface $q < 0$ the specific adsorption of BrO_4^-, BrO_3^-, and OH^- can be neglected and then $G \approx (1 - \alpha)\bar{g}_{H_2O}$.

From Eq. (1) it follows that the rate of reaction in the region of $q < 0$ at $E = \text{const}$ increases with a decrease in the negative value of the ψ_1-potential and with an increase in the adsorption energy of water, i.e., with an increase in the degree of hydrophilicity of the metal. Inasmuch as the hydrophilicity of Sb is significantly greater than that of Hg [12] and the p.z.c. of these metals are close [11], then in accordance with Eq. (1) the rate of reduction of BrO_4^- on Sb must be higher than on Hg. This is supported by the data obtained (Fig. 2). The hydrophilicity of In – Ga alloy is greater than the hydrophilicity of Bi or Sb [12] and so the rate of BrO_4^- discharge on an electrode of In – Ga is so great that at $q < 0$ the limiting diffusion current is observed. This distinguishes this process from the reduction reactions of anions in the first group where solvent molecules do not participate in the discharge process ($S_2O_8^{2-}$, $Fe(CN)_6^{3-}$ [8]).

It follows from Eq. (1) that the discharge rate of BrO_4^- on different electrodes will be described by one and the same linear function in the coordinates $\log i + (z_0F/2.3RT)\psi_1 - [(1 - \alpha)/2.3RT]\bar{g}_{H_2O}$, $-(E - \psi_1)$ (CTD-2).* However, the value of $\bar{g}_{H_2O}$ which enters into Eq. (1) is unknown and the CTD of BrO_4^- discharge can only be constructed in the same coordinates as for the first group anions (CTD-1 [5, 6]). In this case, the CTD for the BrO_4^- discharge does not coincide for different electrodes and the difference in reaction rates on different electrodes is determined by the change in the value of $[(1 - \alpha)/2.3RT]\bar{g}_{H_2O}$ on going from one metal to another (Fig. 4). In a specific approximation, one can assume that $\bar{g}_{H_2O}$ is close to the energy of adsorption of water and then the change in this value on going from Hg to Bi amounts to ~0.5 kcal/mole at the p.z.c. This value is close to the change in the energy of adsorption of water on these electrodes which was determined from other data [13].

Thus, the effect of the nature of the electrode on the rate of reduction of anions of the second group at a constant electrode potential is determined not only by the change in the structure of the electrical double layer but also by the change in the degree of hydrophilicity of the metal.

*CTD = corrected Tafel dependence.

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FORMATION OF THE ELECTRIC DOUBLE LAYER ON BISMUTH IN ALIPHATIC ALCOHOLS

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UDC 541.138

The present work is a continuation of our studies [1-3] of the formation of the electric double layer on bismuth in alcoholic solvents. It investigates the formation of the electric double layer in 1-butanol. This work also includes some additional measurements and calculations for methanol and ethanol which were thoroughly studied earlier [1, 2]. According to the literature, the formation of the electric double layer in 1-butanol has been studied so far only on the mercury electrode [4].

The structure of the boundary bismuth/1-butanol was investigated by measuring the differential capacitance C as function of the potential E of the bismuth electrode in $LiClO_4$ solutions. As in the case of 1-propanol [3], measurements were taken at several frequencies f of the alternating current and the equilibrium values of C obtained by extrapolation of the experimentally determined capacities to f = 0. The electrode potential was measured against the aqueous saturated calomel electrode (s.c.e.) by means of a chain which was analogous to that used in other alcohols:

$$\mathrm{Bi}\left|\begin{matrix}c\,M\ \mathrm{LiClO_4}\\ \mathrm{C_4H_9OH}\end{matrix}\right|\begin{matrix}0.005\,M\ \mathrm{LiClO_4}\\ \mathrm{C_4H_9OH}\end{matrix}\left|\begin{matrix}0.005\,M\ \mathrm{LiClO_4}\\ \mathrm{H_2O}\end{matrix}\right|\begin{matrix}\text{sat. KCl}\\ \mathrm{H_2O}\end{matrix}\Big|\ \text{s.c.e.} \qquad (1)$$

The concentration c of $LiClO_4$ in the test solution was varied over the range 0.005-0.5 M (8 values). The diffusion potential at the boundary of the solutions c M $LiClO_4$/0.005 M $LiClO_4$ was assessed as described in [3].

The 1-butanol used in the tests was of the "pure" grade. It contained less than 0.1% water and was redistilled on a fractionating column under vacuum (60 mm Hg). Additional drying of the solvent over CaO had no effect on the C, E curves. The main criteria for the purity of the solvent were the stability of capacitance with time and the absence of peaks or jumps on the capacitance curves. The purification of methanol, ethanol, and $LiClO_4$ has been described earlier [1-3]. In the present work C, E curves were taken in 0.005 M solutions of $LiClO_4$ in methanol and ethanol using the chain (1) with the aim to obtain data comparable to data obtained in

Tartu State University. Translated from Élektrokhimiya, Vol. 15, No. 4, pp. 591-594, April, 1979. Original article submitted September 12, 1978.

0038-5387/79/1504-0499$07.50