EFFECT OF THE NATURE OF THE METAL UPON THE RATE OF REDUCTION OF THE $Fe(CN)_6^{3-}$ ANION

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The studies of the reduction of the $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$ anions at thallium [1] and indium [2] amalgam electrodes as well as the studies of the reduction of the $S_2O_8^{2-}$ and $S_4O_6^{2-}$ anions at solid electrodes [3] have shown that the effect of the nature of the electrode upon the rate of discharge of electrons in the absence of specific adsorption is governed solely by the structure of the electrical double layer. Paper [4] has been devoted to a study of the reduction of $Fe(CN)_6^{3-}$ at rotating disk lead and cadmium electrodes. It has been found that the dependence of the rate of discharge of the anion on the electrode potential and on the nature and concentration of the base electrolyte can be explained as due to the slow rate of the electrochemical step of the discharge process. However, because no data concerning the dependence of the ψ_0 potential on the electrode potential φ were available, the authors of [4] were not able to quantitatively compare the rates of discharge at these metals. At the present time, data have become available on the dependence of the differential capacity on the electrode potential and the composition of the solution and sufficiently accurate zero-charge potentials have been determined for bismuth [5], lead [6], and cadmium [7]. In connection with this, we have studied the reduction of $Fe(CN)_6^{3-}$ at rotating disk electrodes made of bismuth, lead, and cadmium, and have compared the discharge rates of $Fe(CN)_6^{3-}$ at these metals.

Apparatus used in the study has been described in [8]; the rate of rotation used was 10,000 rpm. Metals of the following purity were used for the construction of the electrodes: bismuth-000, ultrapure, contained less than $5 \cdot 10^{-4}\%$ impurities; lead, 99.9998%; cadmium, 99.99999%. The surface of lead and cadmium electrodes was polished prior to each experiment using previously described techniques (for lead, see [6], for cadmium, see [9]). The bismuth electrode was mechanically polished using specially prepared glass powder similarly as in [3]. The $i-\varphi$ curves obtained after such a treatment were the same as the $i-\varphi$ curves obtained with bismuth electrode polished by the technique described in [10].

After anodic polishing or treatment with glass powder, the electrodes were subject to a 3-hour cathodic polarization at potentials which were by 0.4 V more negative than $\varphi_{\varepsilon=0}$, in a solution of supporting electrolyte from which the air oxygen had been removed. All reagents used in the work were recrystallized several times, and the solutions were prepared using triply distilled water treated with activated charcoal in order to remove organic admixtures [11]. The polarization $I-\varphi$ curves were recorded using a P-5827 potentiostat and were corrected for the residual current. All the potentials are given with respect to a nce.,

Figure 1 shows the $i-\varphi$ reduction curves of $Na_3Fe(CN)_6$ at the bismuth electrode in the presence of different concentrations of sodium fluoride. Analogous curves were obtained for lead and cadmium electrodes. The shape of the curves coincides with the data obtained in [4]. In the region of negative charges of the surface, the $i-\varphi$ curves exhibit a drop of current characteristic of the reduction of anions. However, in contrast to the reduction of the $S_2O_8^{2-}$ and $S_4O_6^{2-}$ anions, the reduction of $Fe(CN)_6^{3-}$ does not change significantly with increasing negative value of the potential which is due to considerably stronger repulsion of the triply charged anion from the negatively charged surface. The rate of reduction of the $Fe(CN)_6^{3-}$ anion increases (Fig. 1) with increasing concentration of the cation of the supporting electrolyte, i.e., Na^+, because the negative value of the ψ_0 potential decreases.

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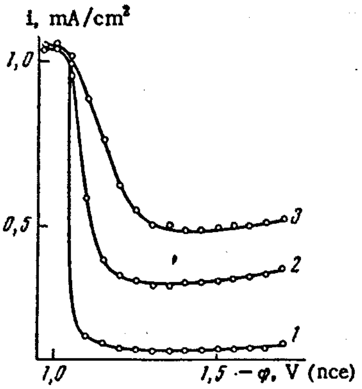

Fig. 1

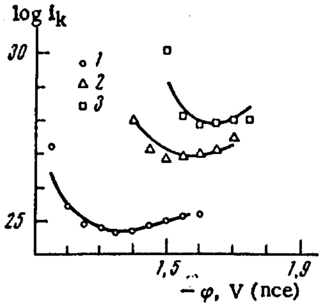

Fig. 2

Fig. 1. Polarization reduction curves of $3 \cdot 10^{-3}$ N $Na_3Fe(CN)_6$ at the rotating bismuth electrode in the presence of NaF (N): 1) 0; 2) $1.5 \cdot 10^{-3}$; 3) $3 \cdot 10^{-3}$. Rotation rate m = 10,000 rpm.

Fig. 2. Dependence of the rate of reduction of $3 \cdot 10^{-3}$ N $K_3F2(CN)_6$ on the electrode potential: 1) Bi; 2) Pb; 3) Cd. Full lines – calculated curves; points – experimental data.

From the data concerning the dependence of the reduction rate on the concentration of the cations of the supporting electrolyte, it was possible to calculate the charge of the reacting particle n_1, using Eq. (1):

$$\left(\frac{\partial \ln i_k}{\partial \ln c}\right)_{\varphi - \frac{RT}{n_2F} \ln c} = -\frac{n_1}{n_2}, \tag{1}$$

where i_k is the kinetic discharge current of the anion and n_2 is the charge of the cations of the supporting electrolyte. Equation (1) was derived in [1] under the assumption that the absolute magnitude of the adsorption of all anions in the solution, Γ_A, is small at negative charges of the surface when compared with the adsorption of the cations, Γ_C. The charge n_1 was calculated using experimental points i corrected for concentration polarization according to the theory of concentration polarization in stationary conditions. The determination was carried out for $3 \cdot 10^{-3}$ N $Na_3Fe(CN)_6$ and $3 \cdot 10^{-3}$ N $K_3Fe(CN)_6$ solutions in the presence of varying concentrations of sodium fluoride and potassium chloride, respectively. When $\varphi - (RT/n_2F) \ln c = \text{const}$, all electrodes exhibit a linear dependence of log i_k on log c and the mean values of n_1, calculated from the slope, $n_1 = -2.8 \pm 0.1$, are close to the theoretical value, $n_1 = -3$.

From the dependence of the rate of the process on the electrode potential φ, the concentration, and the nature of the supporting electrolyte, one can conclude that the electrochemical step of the discharge process of $Fe(CN)_6^{3-}$ at bismuth, lead, and cadmium electrodes is the slow step in the overall reduction process. In such a case, when the electron transfer is a slow process, the discharge rate of anions increases when going from metals with a less negative $\varphi_{\varepsilon=0}$ to metals with more negative $\varphi_{\varepsilon=0}$ [1-3]. The data shown in Fig. 2 confirm this conclusion: the rate of reduction of $Fe(CN)_6^{3-}$ increases at all potentials when going from bismuth to lead and cadmium whose zero-charge potentials are −0.67 [5], −0.84 [6], and −1.02 V [7], respectively. The corrected Tafel plots [1, 12], i.e., plots using coordinates

$$\left(\lg i_k - \frac{\psi_0 n_1 F}{2.3RT}\right), \quad -(\varphi - \varphi_0)$$

for the reduction of $Fe(CN)_6^{3-}$ at the bismuth electrode in the presence of varying concentrations of sodium fluoride, derived on the basis of slow-discharge theory (cf. Eq. (10) in [1]), coincide for all three concentrations of NaF studied (Fig. 3). The corrected Tafel plots were constructed using the potential of the outer Helmholtz surface calculated according to the diffusion double layer theory, i.e., under the assumption that $\psi_1 = \psi_0$. The surface charges necessary for the calculation of the ψ_0 potentials were obtained by numerical integration of the differential capacity vs electrode potential curves using the data from [5-7, 9]. The Tafel corrected plots for the discharge of $Fe(CN)_6^{3-}$ at various electrodes calculated for $3 \cdot 10^{-3}$ N

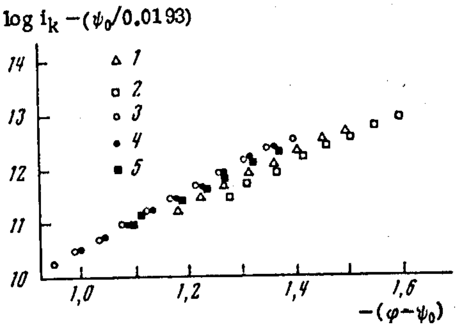

Fig. 3

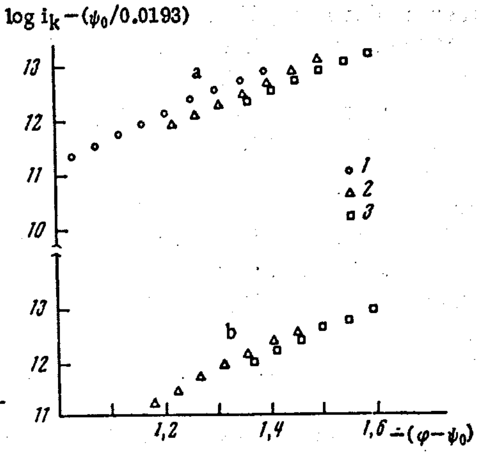

Fig. 4

Fig. 3. Corrected Tafel plots for the reduction of $3 \cdot 10^{-3}$ N $Na_3Fe(CN)_6$ at the following electrodes: 1) Pb; 2) Cd B; in the presence of NaF (N): 3) 0; 4) $1.5 \cdot 10^{-3}$; 5) $3 \cdot 10^{-3}$.

Fig. 4. Corrected Tafel plots for the reduction of $K_3Fe(CN)_6$: a) $3 \cdot 10^{-3}$ N $K_3Fe(CN)_6$ at the following electrodes: 1) Bi; 2) Pb; 3) Cd; b) 10^{-3} N $K_3Fe(CN)_6 + 2 \cdot 10^{-3}$ N KCl.

$Na_3Fe(CN)_6$ (Fig. 3), $3 \cdot 10^{-3}$ N $K_3Fe(CN)_6$ (Fig. 4a), and 10^{-3} N $K_3Fe(CN)_6 + 2 \cdot 10^{-3}$ N KCl (Fig. 4b) are practically the same, and the difference in plots at high negative potentials on the $(\varphi-\psi_0)$ axis is about 70 mV (Fig. 4) whereas the difference for log $i_k-\varphi$ curves is ~500 mV in the same potential range (Fig. 2).

When going from $Na_3Fe(CN)_6$ to $K_3Fe(CN)_6$ solutions (Figs. 3 and 4a), the rate of discharge of $Fe(CN)_6^{3-}$ increases at all electrodes under study. However, this increase is smaller than at a mercury electrode which can be explained as due to a decreased difference in the adsorption of Na^+ and K^+ ions at the solid electrodes used in this work when compared with a mercury electrode [5-7]. Somewhat more pronounced differences in Tafel corrected plots for different electrodes in the case of $Fe(CN)_6^{3-}$ than in the case of the reduction of $S_2O_8^{2-}$ and $S_4O_6^{2-}$ [3] may be due to much higher sensitivity of the discharge of $Fe(CN)_6^{3-}$ toward changes of the ψ_0 potential.

In order to obtain a full coincidence of the log $i_k-\psi_0 n_1 F/RT$ curves for different metals, it is necessary that the differences of the ψ_0 potentials be not higher than 5-8 mV which is within the limits of accuracy of determining the $C-\varphi$ curves. The α values determined from the Tafel corrected plots for bismuth, lead, and cadmium are all within 0.24 ± 0.02. The obtained α values are close to $\alpha = 0.2 \pm 0.02$ for the discharge of $Fe(CN)_6^{3-}$ at the indium amalgam [2], this value being different from $\alpha = 0.16$ for mercury [13]. The reasons for these discrepancies are not clear. Using α obtained from the Tafel corrected plots, we were able to calculate the theoretical log $i_k-\varphi$ curves and to compare them with the experimental curves. The constant in the equation for slow discharge [1] was determined from the experimental values of the reduction rate using the minimum on the log $i_k-\varphi$ curves and was found to be $4.4 \cdot 10^6$ A-cm-mole^{-1}. Figure 2 presents a comparison of the calculated and experimental curves; the agreement is good for all electrodes studied.

The obtained data show the applicability of the slow-discharge theory in the case of the reduction of $Fe(CN)_6^{3-}$ at bismuth, lead, and cadmium electrodes. The results of the present work confirm the basic conclusion of the slow-discharge theory according to which the differences in the rate of reduction of $Fe(CN)_6^{3-}$ at different electrodes depend only on the differences in the structure of the electrical double layer. It is worth noting that, in a series of recently published papers [14], a different mechanism treatment of the mechanism of discharge of the $Fe(CN)_6^{3-}$ ion has been proposed. We shall discuss a comparison of these different points of view in a subsequent publication using new experimental data.

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