THE MECHANISM OF THE REDUCTION OF FERRICYANIDE AT A DROPPING MERCURY ELECTRODE

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The $Fe(CN)_6^{3-}$ anion was first reduced at a dropping mercury electrode by Lingane and Kolthoff[1], who established that the anion can be determined polarographically in 0.1 N KCl solution in the presence of methyl red. Frumkin and Florianovich[2] observed, however, in an investigation of the reduction of $Fe(CN)_6^{3-}$ in dilute solutions with a total electrolyte concentration less than 10^{-2} N that the reaction is inhibited in the range of potentials more negative than the zero-charge point of the electrode.

With increase in the total concentration, the reaction rate increased and the usual limiting diffusion current was attained when the concentration of the KCl added to the $K_3Fe(CN)_6$ was as low as $10^{-3}-10^{-2}$ N. When instead of KCl, salts of polyvalent cations were added, the limiting current was attained at much lower concentrations of the additives. This relation between the reaction rate and solution composition was analogous to that observed in the reduction of the $S_2O_8^{2-}$ anion and suggested that the rate of reduction of $Fe(CN)_6^{3-}$, as in the case of $S_2O_8^{2-}$, is determined by the slow electron capture by the anion. However, in contrast to the reduction of $S_2O_8^{2-}$, there was no increase in the reaction rate at strongly negative potentials. To explain $I-\varphi$ curves of such a form in terms of the equation derived by Frumkin and Florianovich[2],

$$i = kc_a \exp\frac{\alpha F}{RT}\left(-\varphi + \frac{3+\alpha}{\alpha}\psi_1\right), \quad (1)$$

where c_a is the bulk concentration of the anion and k is a constant, it was necessary to suppose that $\alpha \simeq 0.1$, and even then the theoretical curves were not completely identical with the experimental. The shape of the $I-\varphi$ curves for the reduction of $Fe(CN)_6^{3-}$ can also be explained in terms of other hypotheses, for example the slow penetration of the anion into the field of the double layer[7] or a chemical reaction within the double layer preliminary to discharge.. The experimental data obtained by Frumkin and Florianovich do not permit an unambiguous conclusion as to the reaction mechanism.

Frumkin and Florianovich[2] established that the electrochemical reduction of $Fe(CN)_6^{3-}$ depends much more strongly on the concentration of foreign cations than does the reduction of $S_2O_8^{2-}$. Furazhkova[4] noted that the sensitivity of the reduction of $Fe(CN)_6^{3-}$ is so great that even traces of polyvalent cations, which can enter the solution from certain types of insufficiently inert glass, can suppress the fall in the current on $I-\varphi$ curves. Kivalo and Laitinen[5] and Kivalo[6] have asserted that the reduction of $Fe(CN)_6^{3-}$ takes place without inhibition and that the data of Frumkin and Florianovich are erroneous. However, in the first paper quoted above the authors reached this conclusion from measurements in 0.01 N NaOH, where in fact the reaction is not inhibited[6], and in the second the investigations were made at high total electrolyte concentrations. Furthermore, it is possible that Kivalo's solutions contained traces of polyvalent cations.

The present work, some of the results of which have already been published[9], concerns a detailed investigation of the electrochemical reduction of the $Fe(CN)_6^{3-}$ anion at a dropping mercury electrode.

EXPERIMENTAL

The Jena glass[4] cell used to obtain the polarisation curves was similar to that described earlier[10]. The measurements were made in an atmosphere of nitrogen purified from traces of oxygen by passage through a furnace at 220° containing reduced copper deposited on Kieselguhr. The circular-section capillaries employed had the following constants: rate of flow of mercury $m_1 = 1.4$ and $m_2 = 1.25$ mg sec^{-1}; drop times $\tau_1 = 5.5$ and $\tau_2 = 6.1$ sec; the constants were determined in 10^{-3} N $Li_3Fe(CN)_6 + 6 \times 10^{-2}$ N LiCl solution at a potential $\varphi = -0.5$ V. The potential of the mercury drop was measured by means of the usual compensation circuit relative to the normal calomel electrode (n.c.e.), to which all the potentials quoted in this work have been referred.

The current was determined by means of an M-21 galvanometer with a sensitivity of 1×10^{-9} A mm^{-1}. All the experiments were carried out at room temperature, 20° ± 2°. The temperature coefficient of the reaction was measured in an air thermostat. Results which were satisfactorily reproducible were obtained only up to 30° – 35°. Under the experimental conditions the composition of the solution probably changed somewhat at higher temperatures, for reasons which we have not elucidated.

All the curves for the electrochemical reduction of $Fe(CN)_6^{3-}$ have been corrected for the charging currents. The $I-\varphi$ curves obtained in the electrochemical reduction of 10^{-3} N $K_3Fe(CN)_6$ either alone or in the presence of additives were corrected for the charging currents measured in the corresponding solutions. Those obtained for 10^{-3} N $Li_3Fe(CN)_6$ and 10^{-3} N $Cs_3Fe(CN)_6$ solutions containing various amounts of LiCl and CsCl respectively were corrected for the charging currents measured in LiCl and CsCl solutions of the corresponding concentrations.

All the reagents employed were thoroughly purified. The salts were twice recrystallised from doubly-distilled water and KCl and Na_2SO_4 were also ignited. $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ were recrystallised four times from doubly-distilled water. $Li_3Fe(CN)_6$ and $Cs_3Fe(CN)_6$ were obtained from $K_3Fe(CN)_6$ by Meyer's method[11]. A solution of $K_3Fe(CN)_6$ was treated with aqueous $AgNO_3$, and the precipitate of $Ag_3Fe(CN)_6$ was thoroughly washed by decantation and then shaken with LiBr or CsI solutions. The $Li_3Fe(CN)_6$ or $Cs_3Fe(CN)_6$ solutions were evaporated until crystallisation; the crystals were filtered off, recrystallised from doubly-distilled water, and dried in a vacuum at 30°. The purity of the salts was established by the identity of the curves obtained for the following solutions: 10^{-3} N $K_3Fe(CN)_6 + 10^{-3}$ N LiCl and 10^{-3} N $Li_3Fe(CN)_6$ (synthetic salt) + 10^{-3} N KCl in the case of $Li_3Fe(CN)_6$; and 10^{-3} N $K_3Fe(CN)_6 + 10^{-3}$ N CsCl and 10^{-3} N $Cs_3Fe(CN)_6$ (synthetic salt) + 10^{-3} N KCl in the case of $Cs_3Fe(CN)_6$.

All the solutions were prepared from doubly-distilled water. The mercury used was chemically purified and then twice distilled in a vacuum. Only the sections of the $I-\varphi$ curves referring to negative surface charges are quoted, since those for the positive surface charges are distorted by polarographic maxima of the first kind.

RESULTS

A normal polarisation curve (Fig. 1 in ref. 9) was obtained in the reduction of $Fe(CN)_6^{3-}$ at a dropping mercury electrode in 10^{-3} N $K_3Fe(CN)_6$ + 3×10^{-2} N KCl solution. The limiting current, 0.94 μA at 25°, agrees satisfactorily with the value calculated by the Ilkovič equation (which is based on the Nernst[9] equation) for $D = 8.9 \times 10^{-6}$ cm² sec⁻¹. The limiting current does not depend on the potential after it has been corrected for the variation in the drop time with potential.

At lower total electrolyte concentrations the curves for the electrochemical reduction of the ferricyanide anion exhibit a current drop (Fig. 1 in ref. 9) near the zero-charge potential of mercury, in agreement with Frumkin and Florianovich's data[2]. With increasingly negative potentials, the current attains a minimum value and then remains practically constant. Measurements made in 10^{-3} N $K_3Fe(CN)_6$ solution have shown that the minimum current is independent of the height of the mercury column and consequently is determined by purely kinetic factors. We observed similar curves with a current drop for 2×10^{-3} N and 3×10^{-3} N $K_3Fe(CN)_6$ solutions, as well as in 10^{-3} N $Li_3Fe(CN)_6$ and 10^{-3} N $Cs_3Fe(CN)_6$ solutions containing added LiCl and CsCl respectively (Figs. 1 and 2). After the current has passed through a minimum in 10^{-3} N $Li_3Fe(CN)_6$ solutions containing added LiCl, it increases somewhat at potentials more negative than -2.0 V. The increase in the current is small and becomes smaller still when increase in the concentration of added LiCl leads to a higher reaction rate and the diffusion of the anion towards the electrode surface begins to exert an ever increasing effect on the overall rate of the process.

To determine the relation between the rate of reduction of $Fe(CN)_6^{3-}$ and the potential, the polarisation curves were corrected for the concentration polarisation with allowance for the dependence of the drop time τ and the rate of flow of mercury m on the potential. The corrections were made by means of the equation of the precise polarisation concentration theory for first-order reactions at a dropping electrode, developed by Meiman and Bagotskii[12]. In this theory an allowance is made for the fact that during irreversible electrode reactions the rate of decrease of the reacting-species concentration at the electrode surface

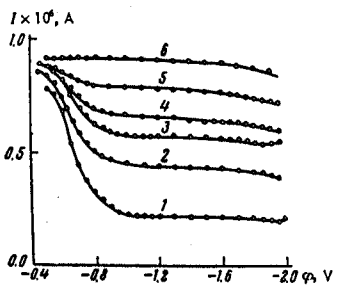

Fig. 1. Polarisation curves for the reduction of 10^{-3} N $Cs_3Fe(CN)_6$ in the presence of CsCl at various concentrations, N:
1) 0; 2) 3×10^{-4}; 3) 5×10^{-4}; 4) 10^{-3}; 5) 2×10^{-3}; 6) 5×10^{-3}.

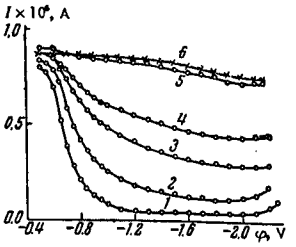

Fig. 2. Polarisation curves for the reduction of 10^{-3} N $Li_3Fe(CN)_6$ in the presence of LiCl at various concentrations, N:
1) 0; 2) 10^{-3}; 3) 2×10^{-3}; 4) 3×10^{-3}; 5) 10^{-2}; 6) 3×10^{-2}.

with increase in the drop size depends on the reaction rate and the rate of supply of new species from the bulk of the solution through diffusion. Meiman's calculation shows that, for first-order reactions, *i.e.* reactions obeying the equation $i = (1/\beta)c_a$ (where i is the current density and $1/\beta$ the reaction rate constant, which in the general case depends on the potential), the concentration of the discharging species at the electrode surface is a function of the dimensionless parameter μ, which includes time, the diffusion coefficient D, and $1/\beta$. At the moment of separation of the drop this parameter is given by

$$\mu_0 = \frac{\tau^{1/6}}{\sqrt{\frac{7}{3}} nFD^{1/6}\beta},$$

whence

$$\frac{1}{\beta} = \frac{\sqrt{\frac{7}{3}} nFD^{1/6}\mu_0}{\tau^{1/6}}. \qquad (2)$$

Relation (2) makes it possible to calculate the reaction rate constant corrected for concentration polarisation. Since $i = (1/\beta)c_a$,

$$i = \frac{\sqrt{\frac{7}{3}} nFD^{1/6}\mu_0 c_a}{\tau^{1/6}}. \qquad (3)$$

For the practical application of Eqn. (3), $nFD^{1/2}c_a$ has been replaced by $\bar{I}_d/0.627\, m^{2/3}\tau^{1/6}$ ($\bar{I}_d$ is the average limiting diffusion current). Then

$$i = \frac{\bar{I}_d\mu_0}{0.41 m^{2/3}\tau^{1/6}}. \qquad (4)$$

In the calculation by Eqn. (4) of curves corrected for concentration polarisation, it is necessary, for each test solution, to find the values of m, τ, $\bar{I}_d$, and μ_0 at various potentials.

The values of m and τ were determined directly by experiment. $\bar{I}_d$ for curves with current drop can be established experimentally only for $\varphi = -0.5$. The limiting currents at other potentials, *i.e.* the values of $\bar{I}_d$ which would be observed if the electrochemical reduction at these potentials in solutions with the given total electrolyte concentration took place without inhibition, were calculated from the limiting diffusion current $\bar{I}_d'$ in the solution

with the minimum foreign electrolyte concentration necessary for inhibition not to be observed, from $\bar{I}_d''$, *i.e.* the limiting current at $\varphi = -0.5$ in this solution, and from the limiting current $\bar{I}_d'''$ at $\varphi = -0.5$ in the test solution, by means of the relations†

$$\frac{\bar{I}_d}{\bar{I}_d} = \frac{\bar{I}_d'''}{\bar{I}_d''}. \quad (5)$$

Thus in the calculation an allowance was made both for the change in $\bar{I}_d$ with potential due to variation in τ and for the differences in the limiting current in solutions with different electrolyte concentrations, caused by the migration effect. Finally, the value of μ_0 was determined from the "reduced" concentration polarisation curve, calculated by Meiman and Bagotskii; this was done by finding the ratio $\bar{I}/\bar{I}_d$ from the experimental data, where $\bar{I}$ is the average current and $\bar{I}_d$ is the calculated limiting current in the test solution at a potential such that the reaction current is $\bar{I}$. Calculations made by Eqn. (4) (Figs. 3*a* and 8*a*) show that, after the minimum has been attained, the rate of the electrochemical reduction of $Fe(CN)_6^{3-}$ increases by 30–40% with further increase in the potential. The absence of a rise in the experimental curves is due to the fact that the rate of reduction of $Fe(CN)_6^{3-}$ only slowly increases with the potential, whereas the surface of the mercury drop, to which the kinetic current is proportional, rapidly diminishes with increase in the negative charge on the electrode.

Plots of the logarithms of the corrected electrochemical-reduction currents in 10^{-3} *N* $Li_3Fe(CN)_6$, $K_3Fe(CN)_6$, and $Cs_3Fe(CN)_6$ containing LiCl, KCl, and CsCl respectively against the logarithms of the corresponding cation concentrations are linear with the slope 3.0 in the case of $Li_3Fe(CN)_6$ + LiCl solutions and 3.2 for $K_3Fe(CN)_6$ and $Cs_3Fe(CN)_6$ containing KCl and CsCl respectively (Fig. 4*a*).

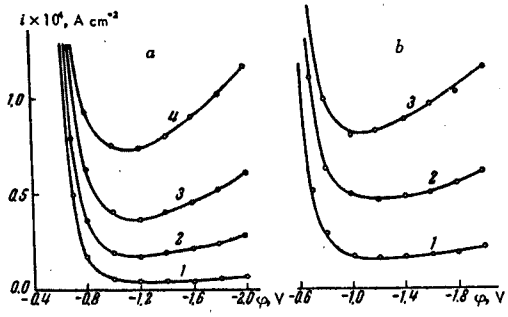

Fig. 3. Curves for the electrochemical reduction of the $Fe(CN)_6^{3-}$ anion, corrected according to Eqn. (4): *a*) 10^{-3} *N* $K_3Fe(CN)_6$ with added KCl, *N*: 1) 0; 2) 5×10^{-4}; 3) 10^{-3}; 4) 1.5×10^{-3}. *b*) 10^{-3} *N* $Cs_3Fe(CN)_6$ with added CsCl, *N*: 1) 0; 2) 3×10^{-4}; 3) 5×10^{-4}.

† The applicability of relation (5) follows from the fact that the potential drop in dilute solutions is equivalent to a decrease in the diffusion coefficient of the anion[2].

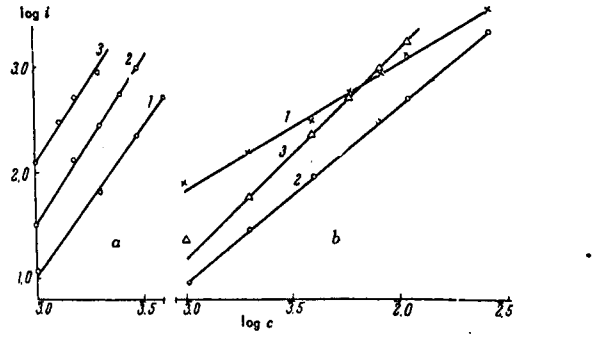

Fig. 4. *a*) Variation of the rate of the electrochemical reduction of $Fe(CN)_6^{3-}$ with the concentration of various cations: 1) Li^+; 2) K^+; 3) Cs^+. *b*) Variation of the rate of the electrochemical reduction of $S_2O_8^{2-}$ anion with the K^+ concentration at various potentials, V: 1) 0.8; 2) 1.05; 3) 1.35.

This means that the rate of reduction of $Fe(CN)_6^{3-}$ increases in proportion to the concentration of foreign cations raised to the power 3.0–3.2. It is seen from Fig. 4*a* that the rate of reduction of $Fe(CN)_6^{3-}$ increases in the series $Li^+ < K^+ < Cs^+$. When Li^+ is replaced by K^+, at the same concentration, the rate of the reaction increases by a factor of 2, and following replacement of K^+ by Cs^+, also at the same concentration, by a factor of 4.

In the reduction of the $S_2O_8^{2-}$ anion the dependence of the reaction rate on the concentration c of foreign cations changes with the potential. In 10^{-3} *N* $K_2S_2O_8$ solutions containing KCl the reaction rate is proportional to $c^{1.3}$ at $\varphi = -0.8$ V, to $c^{1.7}$ at $\varphi = -1.05$ V, and to $c^{2.0}$ at $\varphi = -1.35$ V (Fig. 4*b*). In 10^{-3} *N* $K_2S_2O_8$ solutions containing CsCl the variation of the reaction rate with the concentration of the foreign cation was determined only approximately since the test solutions always contained K^+. It was found that the reaction rate varied as $c^{1.2}$ at $\varphi = -0.75$ V, and as $c^{1.9}$ at $\varphi = -1.3$ V. The ratio of the rates of $S_2O_8^{2-}$ reduction in the presence of equal concentrations of Cs^+ and K^+ is 7.

The rate of the electrochemical reduction of $Fe(CN)_6^{3-}$ increases with increasing charge on the cation in the supporting electrolyte. The removal of the inhibition in the presence of K^+ takes place when the concentration of KCl is 3×10^{-2} *N*, whereas the concentration of La^{3+} sufficient to remove the inhibition is 5×10^{-5} *N*.

All the organic cations tested, $[(CH_3)_4N]^+$, $[(C_2H_5)_4N]^+$, $[(C_4H_9)_4N]^+$, $[(C_5H_{11})_4N]^+$, and $[(C_6H_{13})_4N]^+$, enhance the rate of reduction of $Fe(CN)_6^{3-}$ throughout the range of their absorption potentials (Figs. 5*b* and 6*b*). Their effectiveness becomes greater with increase in the concentration and carbon chain lengths. There is an increase in the effect of $[(C_6H_{13})_4N]^+$ cation on the reaction rate at strongly negative potentials (Fig. 6*b*). An enhancement of the effect of $[(C_5H_{11})_4N]^+$ and $[(C_6H_{13})_4N]^+$ on the rate of reduction of $S_2O_8^{2-}$ was also observed in spite of the fact that the degree of coverage of the electrode surface by the organic cations diminishes with increase in the negative potential (Fig. 6*a*). These effects are probably analogous to those observed earlier in the investigation of the influence of $[(C_4H_9)_4N]^+$ on the reduction of $PtCl_4^{2-}$ and may be explained in terms of

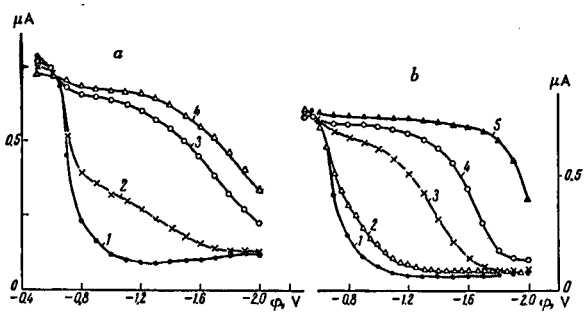

Fig. 5. Curves for the electrochemical reduction of 10^{-3} N $K_3Fe(CN)_6$ in the presence of additives:
a) $[(CH_3)_4N]_2SO_4$, N: 1) 0; 2) 10^{-4}; 3) 5×10^{-4}; 4) 10^{-3}.
b) $[(C_2H_5)_4N]_2SO_4$, N: 1) 0; 2) 10^{-5}; 3) 4×10^{-5}; 4) 10^{-4}; 5) 10^{-3}.

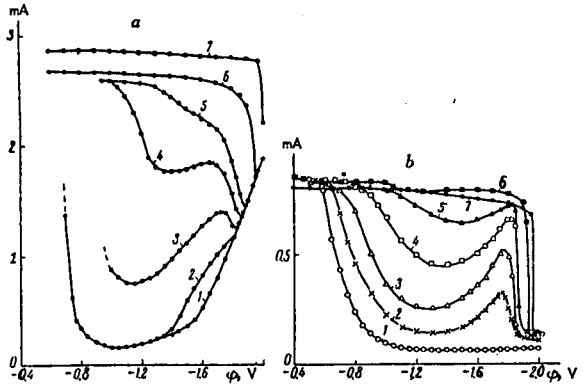

Fig. 6. *a*) Polarisation curves for the reduction of 10^{-3} N $K_2S_2O_8$ in the presence of $[(C_5H_{11})_4N]Br$ at various concentrations, N: 1) 0; 2) 2×10^{-5}; 3) 3×10^{-5}; 4) 4×10^{-5}; 5) 5×10^{-5}; 6) 10^{-4}; 7) 10^{-3}. *b*) Polarisation curves for the reduction of 10^{-3} N $K_3Fe(CN)_6$ in the presence of $[(C_6H_{13})_4N]Br$ at various concentrations, N: 1) 0; 2) 5×10^{-6}; 3) 10^{-5}; 4) 1.5×10^{-5}; 5) 2×10^{-5}; 6) 5×10^{-5}; 7) 10^{-4}.

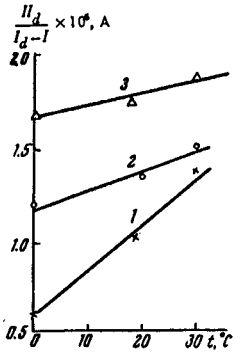

Fig. 7. Temperature dependence of the rate of the electrochemical reduction of $Fe(CN)_6^{3-}$ in various solutions:
1) 10^{-3} N $Li_3Fe(CN)_6$ + 3×10^{-3} N LiCl;
2) 10^{-3} N $K_3Fe(CN)_6$ + 1.5×10^{-3} N KCl;
3) 10^{-3} N $CsFe(CN)_6$ + 10^{-3} N CsCl.

the hypothesis that large organic cations are deformed at high negative surface charges, which leads to a change in the relative position of the centre of the activated complex of the anion undergoing discharge and the positive charge of the cation[14]‡.

‡ The electrochemical reduction of the planar $PtCl_4^{2-}$ anion in the presence of $[(C_4H_9)_4N]^+$ was found to be accelerated by the cation in the potential range where, according to differential-capacity measurements, it was deformed[14]. The enhanced effect of the large organic cation $[(C_5H_{11})_4N]^+$, due to its deformation, was observed in the reduction of $S_2O_8^{2-}$. The reduction of $Fe(CN)_6^{3-}$ is influenced only by the deformation of a cation at least as large as tetrahexylammonium. It is thus possible to conclude that the distance from the electrode surface to the centre of the activated complex of the anion undergoing discharge appears to increase in the series $PtCl_4^{2-} < S_2O_8^{2-} < Fe(CN)_6^{3-}$.

The halide anions Cl^- and Br^- have no effect on the rate of reduction of $Fe(CN)_6^{3-}$ at negative surface charges. Increase in the charge of the supporting-electrolyte anions in the series $Cl^- < SO_4^{2-} < Fe(CN)_6^{4-}$ lowers the reaction rate (Fig. 3 in ref. 9). An analogous, but much weaker, effect was observed also in the reduction of $S_2O_8^{2-}$§.

The temperature coefficient of the reduction of $Fe(CN)_6^{3-}$ is positive and depends on the nature of the supporting-electrolyte cations (Fig. 7).

DISCUSSION

Detailed investigation of the reduction of $Fe(CN)_6^{3-}$ has revealed that this reaction is in many respects analogous to the electrochemical reduction of the $S_2O_8^{2-}$ anion which has been shown to obey quantitatively the slow-discharge theory[2]. On the assumption that the rate of reduction of $Fe(CN)_6^{3-}$ is determined by the slow addition of electrons to the $Fe(CN)_6^{3-}$ species within the double layer, we calculated the $Fe(CN)_6^{3-}$ electrochemical-reduction curves by Eqn. (1), as has been done earlier in the case of $S_2O_8^{2-}$ reduction, but with the difference that allowance for concentration polarisation was made according to the exact Meiman–Bagotskii theory. The value of α was determined from the ascending portion of the corrected curves and proved to be 0.16. In comparing the theoretical and experimental curves, the zero-charge point was taken as 0.48 V and k proved to be 1.25×10^{12} A cm mole^{-1}. As can be seen from Fig. 8, the theoretical curves reproduce the general shape of the experimental, but there are differences, reaching approximately 20% in the potential range 1.2–2.0 V.

§ The decrease in the cation concentration in $K_4Fe(CN)_6$ solutions due to the formation of $KFe(CN)_6^{3-}$ [18] is much too small to have a marked effect on the rate of reduction.

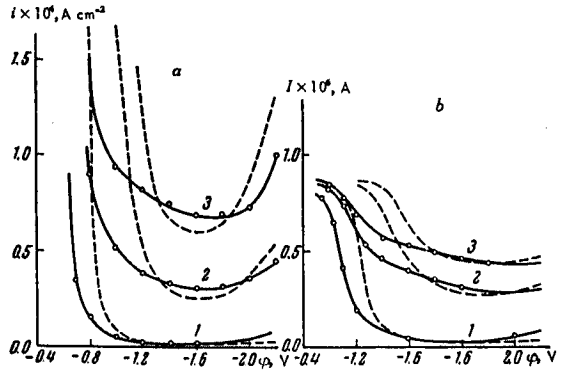

Fig. 8. *a*) Experimental (continuous line) and calculated (broken curve) [by Eqn. (1)] variation of the rate of the electrochemical reduction of $Fe(CN)_6^{3-}$ with potential in 10^{-3} *N* $Li_3Fe(CN)_6$ solutions with various concentrations of LiCl, *N*: 1) 0; 2) 2×10^{-3}; 3) 3×10^{-3}. *b*) Comparison of the experimental (continuous line) and calculated (broken curve) polarisation curves for the reduction of 10^{-3} *N* $Li_3Fe(CN)_6$ in the presence of LiCl at various concentrations, *N*: 1) 0; 2) 2×10^{-3}; 3) 3×10^{-3}.

It follows from Eqn. (1), allowing for the logarithmic dependence of the ψ_1 potential on the electrolyte concentration, that the rate of reduction of a triply-charged anion should increase with increase in the concentration of a singly-charged supporting-electrolyte cation raised to the power $3 + \alpha$ and of a doubly-charged cation raised to the power $2 + \alpha$¶. This has been found to apply to the electrochemical reduction of the $Fe(CN)_6^{3-}$ anion. The rate of $S_2O_8^{2-}$ reduction, at potentials sufficiently negative for the logarithmic relationship between the ψ_1 potential and the cation concentration to apply, is proportional to $c^{2.0}$, whereas in fact it should be proportional to $c^{2+\alpha}$. The discrepancy may be explained, first, in terms of the considerations set out in the preceding footnote and, second, by the fact that during the reduction of $S_2O_8^{2-}$ there is a negative potential drop in the bulk of the solution at low electrolyte concentrations[2]. As a result of this drop the concentration of cations in the solution layer around the electrode exceeds its equilibrium value in solutions with the same content of cations but without a bulk potential drop. This is equivalent to saying that when the reaction rate is plotted against the cation concentration, the solution concentrations, for low currents, should be taken as somewhat greater than the actual. During the reduction of the triply-charged $Fe(CN)_6^{3-}$ anion the potential drop in the bulk of the solution is much smaller than in the case of $S_2O_8^{2-}$ and does not cause such a pronounced change in the relation between the reaction rate and the cation concentration.

It should be noted that the relation between the reduction rate and the supporting-electrolyte concentration cannot be used as a criterion of the correctness of the chosen reaction mechanism. Thus if it is assumed that the rate of $Fe(CN)_6^{3-}$ reduction is determined by the formation of $MFe(CN)_6^{2-}$, $M_2Fe(CN)_6^{-}$, or $M_3Fe(CN)_6$ species within the double layer, the reaction rate should be proportional to $c^{3.0}$. If it is supposed, however, that the reduction of $Fe(CN)_6^{3-}$ takes place according to the equations $M^+ + Fe(CN)_6^{3-} + e \rightarrow$ or $2M^+ + Fe(CN)_6^{3-} + e \rightarrow$, as in Gierst's[13] explanation of the ascending branch of the $S_2O_8^{2-}$ reduction curve, and that the $MFe(CN)_6^{2-}$ or $M_2Fe(CN)_6^{-}$ species at the electrode surface and in the bulk of the solution are in equilibrium, then the reaction rate should be proportional to $c^{3+\alpha}$. Analogous examination of the reduction of $S_2O_8^{2-}$ shows that its rate, depending on the mechanism, can be proportional either to $c^{2+\alpha}$ or $c^{2.0}$.

It has been shown that Eqn. (1) gives an approximate description of the shape of $I-\varphi$ curves for the reduction of $Fe(CN)_6^{3-}$ and explains the relation between the reaction rate and the concentration and charge of the supporting-electrolyte cations. To explain the dependence of the reaction rate and the temperature coefficient of the reaction on the radius of the supporting-electrolyte cation and the way it is influenced by the anions which are not specifically adsorbed, it is necessary to take into account the fact that the ψ_1 potential at a certain distance from the electrode surface is not constant but changes in the immediate vicinity of the cations around which the anions must be concentrated. Thus we arrive at the conclusion that cationic bridges are formed in the surface layer. This suggestion was first made in earlier work to explain the temperature coefficient of the reduction of $S_2O_8^{2-}$ and the influence of the radius of the supporting-electrolyte cations on its rate[15,3].

The correctness of the conclusion that the rate of $Fe(CN)_6^{3-}$ reduction is determined by the slow addition of an electron to the $Fe(CN)_6^{3-}$ species and the necessity to allow for interaction with cations within the limits of the double layer also follow from the considerations set out below. Let us assume that the $Fe(CN)_6^{3-}$ ions are reduced, without allowing for the non-uniformity of the distribution of potential along the electrode surface. The concentration of anions at the electrode surface in 10^{-3} *N* solution is $c_a e^{3\psi_1 F/RT}$, which at $\varphi = -2.0$ V ($\psi_1 = -0.245$ V) amounts to $\sim 10^{-19}$ mole cm^{-3}. Consequently the quantity of discharging material in a layer 10^{-7} cm thick at the electrode surface is $\sim 10^{-26}$ mole cm^{-2}, *i.e.* we find that there is less than 1 molecule of reactant per unit surface. Thus, under the given conditions reduction of the triply-charged anion should not take place at all. Furthermore, Levich's calculation of the rate of penetration of anions into the field of the double layer[7] shows that even in the case of the doubly-charged anion the currents calculated for strongly negative potentials are much lower than the experimental.

Finally we may retain the classical double-layer structure and assume, after Gierst[13], that $MFe(CN)_6^{2-}$ or even $M_2Fe(CN)_6^{-}$ ions are reduced. Adopting 4×10^{-8} cm as the effective diameter of the $MFe(CN)_6^{2-}$ species and assuming that the reaction

$$M^+ + Fe(CN)_6^{3-} \rightleftarrows MFe(CN)_6^{2-} \qquad (6)$$

proceeds from left to right without energy of activation, we may calculate, from collision theory, the rate constant for

¶ This is true when the distance between the electrode surface and the centre of the activated complex of the anion undergoing discharge is equal to the radius of the cation. In the general case when the plane containing the charge centres of the activated complexes is closer to the electrode surface than the plane containing the charges of the foreign cations, the dependence of the reduction rate on the cation concentration should be less than indicated in the text.

the recombination of M and $Fe(CN)_6^{3-}$ at 293° as 1.3×10^{11} litre mole^{-1} sec†. The equilibrium constant of the above reaction may be estimated on the assumption that 10^{-3} N $M_3Fe(CN)_6$ solution contains approximately 1% of $MFe(CN)_6^{2-}$ ion pairs, although this quantity appears to be somewhat too high. The equilibrium constant of reaction (6) is then found to be 3×10^{-2} mole litre^{-1}. On the basis of these quantities, calculation of the thickness of the layer in which reaction (6) takes place yields a value of the order of 5×10^{-8} cm, assuming the diffusion coefficient to be 10^{-5} cm^2 sec^{-1}. Thus the thickness of the reaction layer is much lower than that of the diffusion layer which in 10^{-3} N solution is $\sim 10^{-6}$ cm. Thus the assumption that reaction (6) takes place is equivalent to postulating the formation of cationic bridges involving cations adsorbed on the mercury surface‡. Finally, if it is supposed that the $M_2Fe(CN)_6^-$ species are reduced, it is necessary to resort to the improbably small value of $\alpha \simeq 0.05$ to explain the observed shape of the curve.

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SUMMARY

1. A study has been made of the effect of solution composition and temperature on the rate of the electrochemical reduction of $Fe(CN)_6^{3-}$ at a dropping mercury electrode.
2. The polarisation curves for the reduction of $Fe(CN)_6^{3-}$ have been corrected for concentration polarisation according to the equation of Meiman and Bagotskii's exact concentration–polarisation theory for first-order reactions at a dropping mercury electrode, with allowance for the variation of m and τ with potential. Calculation shows that, with increasing potential, the rate of the electrochemical reduction of $Fe(CN)_6^{3-}$ falls to a minimum and then increases again by 30–40%. Thus the polarisation curve for the reduction of $Fe(CN)_6^{3-}$ is similar in shape to that for the electrochemical reduction of the $S_2O_8^{2-}$ anion.
3. It has been shown that as the concentration of the indifferent electrolyte increases, the rate of $Fe(CN)_6^{3-}$ reduction rises in proportion to the concentration of singly-charged cations raised to the power 3.0–3.2, and the rate of $S_2O_8^{2-}$ reduction, at strongly negative potentials, rises in proportion to this concentration raised to the power 2.0.
4. On the basis of the experimental results obtained and an examination of various current mechanisms for the electrochemical reduction of anions, it has been concluded that the rate of reduction of $Fe(CN)_6^{3-}$ is determined by the slow addition of an electron to the $Fe(CN)_6^{3-}$ species, within the double layer.

† If an allowance is made for the volume occupied by the solvent molecules, the value of the rate constant obtained is approximately 10 times greater.

‡ The thickness of the reaction layer may exceed that of the diffusion layer only if it assumed that recombination of M^+ and $Fe(CN)_6^{3-}$ requires an activation energy > 4 kcal.

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PHOTOIONISATION OF ORGANIC VAPOURS IN THE VACUUM ULTRA-VIOLET†

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Ionisation potentials are widely employed for the solution of a number of problems[1]. In particular, they lead to a deeper understanding of molecular structure since they are one of the principal characteristics of the electronic shell of isolated molecules.

Until recently the first ionisation potentials, corresponding to the fundamental ionisation process

$$AB + E \rightarrow AB + e,$$

were determined by two methods: by electron impact using a mass-spectrometric technique and from electronic absorption spectra in the vacuum ultra-violet[2]. In view of a number of defects in the above methods, a new procedure,

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