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Edited by

P. ZUMAN
Polarographic Institute,
Czechoslovak Academy of Science, Prague

with the collaboration of

I. M. KOLTHOFF
Department of Chemistry,
University of Minnesota, Minneapolis

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CHAPTER IX

THE ELECTROREDUCTION OF ANIONS

ALEXANDER N. FRUMKIN

Institute of Electrochemistry, Academy of Sciences of the U.S.S.R., Moscow

and

NINA NIKOLAEVA-FEDOROVICH

Chair of Electrochemistry. Faculty of Chemistry, Moscow State University

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I. Introduction

The electroreduction of anions has attracted the attention of electrochemists for a long time in connection with the use of cyanide electrolytes in electroplating. Haber (27) pointed out that the concentration of Ag^+ ions in a cyanide solution is so small that these ions cannot be considered as an intermediate product in the process of electroreduction; according to Haber a direct participation of $Ag(CN)_3^{2-}$ ions in the electrode process on the surface of the Ag electrode must be therefore assumed. Haber's conclusion was fundamentally correct, although, as has

been shown recently, in the case of complex cyanide solutions which contain ions with a different number of CN groups in equilibrium, the negative charge of the reacting particles is often smaller than the negative charge of the preponderant constituent (21, 34).

The later development of this problem was stimulated by the use of the polarographic method. Heyrovský and his collaborators (28, 52, 53) discovered the strong dependence of the rate of anion reduction on the concentration and the valency of the cations of the supporting electrolyte.

Krjukova (35) showed that the anomalous form of the current–voltage curve of the persulfate anion is caused by the repulsion between the anion and the negatively charged electrode surface. It thus became evident that the study of anion electroreduction might be helpful for the understanding of the relations between electrochemical kinetics and adsorption phenomena. The purpose of this communication is to give an account of the present development of this line of research.

The process of anion electroreduction is characterized by two peculiarities: (*a*) the ohmic drop of potential in the bulk of the solution hinders the approach of the reducible anion to the electrode surface; (*b*) if the reduction occurs at potentials more negative than the potential of zero charge, a second still more important hindrance arises from the electric field of the double layer, which impedes the penetration of the reacting particle in the Helmholtz layer and its adsorption on the electrode surface.

II. The Influence of the Ohmic Potential Drop

As a result of the first hindrance the limiting current of the electroreduction of anions in the absence of a foreign electrolyte is lower than in the presence of an excess of a supporting electrolyte, as was pointed out by Heyrovský (29). The quantitative evaluation of this effect in the general case presents some difficulties. For the particular case of an electroreduction not accompanied by a change in the number of charges of the anions, i.e. one which proceeds according to

$$A_1^{n-} + n(p-1)e^- \rightarrow pA_2^{n-} \qquad (1)$$

Florianovich and Frumkin (9) carried out the calculation on the

assumption of a constant thickness of the diffusion layer. It was shown that the ratio of the limiting current in a solution of an electrolyte of the K_nA_1 type, $(i_d)'$, to the limiting current in the presence of an excess of a supporting electrolyte, $(i_d)''$, is equal to

$$\frac{(i_d)'}{(i_d)''} = \frac{(n+1)\left[p\left(\frac{D_{A_1}}{D_{A_2}}\right)^{1/n+1} - 1\right]}{p\frac{D_{A_1}}{D_{A_2}} - 1} \qquad (2)$$

where D_{A_1} and D_{A_2} denote the diffusion coefficients of A_1 and A_2. In the case of the reduction of $S_2O_8^{2-}$ ($n=p=2$, $D_{A_1}/D_{A_2}=1.08$) it follows from equation (2) that $(i_d)'/(i_d)''=0.76$. Thus, under usual conditions of the experiment, the electric field in the bulk of the solution causes a noticeable, but not a very substantial, slowing down of the reaction rate [cf. (54)].

III. The Electroreduction of Anions of the XO_3^- Type

Peculiarities of anion electroreduction connected with the elementary act itself were observed for the first time by Heyrovský (28) and his collaborators (50, 52, 53), who investigated the behavior of such anions as NO_3^- or BrO_3^- at the dropping mercury electrode. They found that the reduction potentials are shifted to more positive values with increase of the charge of the cation, for instance in the series K^+, Ba^{2+}, La^{3+}. This was explained by the formation of ion pairs, as for instance $La(NO_3)^{2+}$, facilitating the approach of the anion to the electrode surface. The concept of ion-pair formation was later repeatedly used in order to interpret the behavior of anions of the XO_3^- type, often together with the additional assumption of an increased reactivity resulting from the deformation of the anion by the electric field of the cation (8, 41, 48, 57).

One of the authors (10) made an attempt to deal with these phenomena, taking into account the influence of the structure of the double layer on the kinetics of irreversible electrode processes. From this point of view, primarily worked out for the case of the hydrogen evolution reaction, the acceleration of the reduction of NO_3^- anions in the presence of multivalent cations is explained by the shift of the ψ_1-potential, i.e. the potential at a distance of

one ionic radius from the electrode surface, to more positive values. This shift causes an increase in the surface concentration of the anions as well as in the effective potential difference in the Helmholtz layer, both changes tending to accelerate the reaction. It was pointed out that the effects observed are too large to be explained on the basis of taking into account only the average values of the potential at a distance of one ionic radius from the electrode surface, and that values of the ψ_1-potential in the immediate neighborhood of multivalent cations ought to be considered.

It was later shown that the equilibrium properties of the double layer also, at least in the case of specific anion adsorption, cannot be understood without considering its discrete structure (5, 6, 7, 24, 25, 38a).

A more detailed study revealed the complexity of the NO_3^- reduction process in the presence of La^{3+}. If the reduction is carried out on a dropping electrode in an unbuffered medium, at a definite potential a discontinuous transition from low to high values of the current strength is observed (29, 33, 41). As was shown by Frumkin and Zhdanov (19, 20), these abrupt changes of current strength, accompanied by the appearance of a hysteresis loop on the polarogram, can be explained without considering the elementary act itself by taking into account two effects, namely the dependence of the pH in the neighborhood of the electrode surface on the reaction rate and the catalysis of the reduction process by the OH^- ions produced during the reaction. The molecular nature of this autocatalytic effect has not, however, been completely elucidated until now. It was first supposed that an increase of the pH leads to a formation of more easily reducible anion orthoforms, but this view could not be substantiated by experimental evidence. It is more probable that, as a result of the interaction of La^{3+} ions with OH^- ions in the neighborhood of the electrode surface, products of the hydrolysis of La^{3+} which exert a stronger catalytic action than normal La^{3+} ions are formed. This idea, suggested during a discussion of the problem by Dr. Grabowski, is seemingly supported by measurements of the differential capacity of mercury in slightly alkalized solutions of $LaCl_3$ (3). At pH values exceeding 7 the equilibrium value of the differential capacity is but slowly established; the change in

the dependence of differential capacity on applied voltage with time elapsed after drop formation points to the appearance of ions more strongly adsorbed than normal La^{3+} ions, perhaps lanthanum polycations. The slow rate of formation of the substance accelerating the NO_3^- reduction in the presence of La^{3+} becomes evident when current–voltage curves are taken in solutions containing La^{3+} in a low and NO_3^- in a relatively high concentration (39). Under these conditions, a minimum is observed on the polarogram in the neighborhood of which the current decreases strongly with decrease of drop time (Fig. 1; the

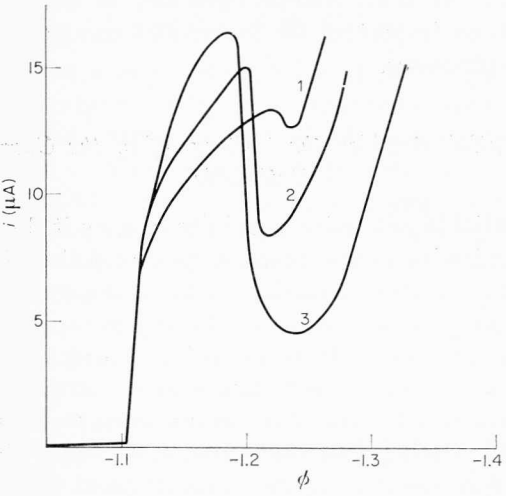

FIG. 1. Dependence of the current–voltage curve of an 0.1N KNO_3 + 2.1×10^{-3}N $LaCl_3$ solution on the height of the mercury column, h. $m = 2.3$ mg s^{-1}, $t = 4.2$ sec ($h = 30$ cm, $\varphi = 0$ *vs* N.C.E.). (1) $h = 20$ cm; (2) $h = 30$ cm; (3) $h = 60$ cm.

potentials in this and subsequent figures are referred to a N.C.E.). The nature of the minimum has not yet been completely elucidated; it is probable that the falling off of the current with increase of the negative potential is caused by a change in the conditions of adsorption of either the NO_3^- ion or the product of the interaction of the La^{3+} and OH^- ions, which acts as a catalyst.

IV. Anomalous Current–Voltage Curves

Interesting conclusions concerning the mechanism of anion electroreduction could be drawn from the study of the reduction

of multivalent anions, as for instance $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, $PtCl_4^{2-}$, $PtCl_6^{2-}$, $Pt(NO_2)_4^{2-}$, $S_4O_6^{2-}$, $Hg(CN)_4^{2-}$. This line of research was initiated by Krjukova (35), who found on the current–voltage curves of the reduction of persulfate a minimum due to the repulsion of the reacting particle by the negatively charged electrode surface. Similar phenomena have been later observed and studied in a considerable number of anion-reduction processes at mercury, thallium amalgam, lead, cadmium, copper and platinum electrodes. It is not the object of this paper to discuss all the data obtained, which have, besides, recently been reviewed (11–14, 16, 17); we shall confine ourselves to a résumé of those results which are important for the understanding of the mechanism of these processes.

A. The Potential at which the Falling off of the Current Becomes Noticeable

This potential is not quite a definite one, as it depends on the relative magnitudes of the reaction rate and the diffusion rate, and therefore changes somewhat with a change in the factors determining the diffusion process (drop time or angular velocity of a rotating electrode). It would be interesting to determine the current–voltage curve of these anions after complete elimination of the diffusion control, but this has not been realized so far. In the case of the $S_2O_8^{2-}$ ion, the potential at which the falling off of the current is observed at low concentrations of the supporting electrolyte lies in the neighborhood of the point of zero charge; it shifts with change of the electrode material, following the shift of the point of zero charge (11, 31, 43). With other anions, which are probably more strongly adsorbed, as for instance $PtCl_4^{2-}$ or $Cd(CN)_4^{2-}$, the falling off of the current occurs at potentials which are more negative than the potential of zero charge.

B. The Charge of the Anion

Anomalous current–voltage curves have so far been obtained with many di- and some trivalent anions. Under definite conditions minima appear on polarograms of NO_3^-, ClO_2^-, BrO_3^- and IO_3^- anions as well, but the mechanism of the corresponding

electrode process has not yet been completely elucidated. Dips on the current–voltage curves are also observed in the case of the reduction of a few neutral molecules, as for instance $Pt(NH_3)_2Cl_2$ and $Pt(NH_3)_2(OH)_2Cl_2$ (17, 32) and of some cations, as for instance $[Co(NH_3)_4Cl_2]^+$ (47a). Although in these cases there is no repulsion by the negatively charged electrode surface of the reacting molecule as a whole, it is probable that a repulsion which modifies the conditions for adsorption is exerted on negatively charged groups contained in the molecule.

C. The Rôle of the Cations

At potentials at which the repulsion of the anion by the electrode surface manifests itself, the current increases with the concentration of the cations of the supporting electrolyte. The efficiency of the cations increases with increase of the charge (9, 15, 35, 48), and at constant charge, with increase of the radius ($H_3O^+ < Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$; $Ca^{2+} < Sr^{2+} < Ba^{2+}$) (11, 16, 18a, 46, 55). The sensitivity of the reduction process towards the action of cations varies greatly according to the anions involved. Thus the falling off of the current in the case of $Fe(CN)_6^{3-}$ disappears altogether in the presence of 5×10^{-3}N K^+, whereas in the case of $PtCl_4^{2-}$ the minimum on the current–voltage curve is preserved even in the presence of supporting electrolytes in a high concentration (36), although it becomes much less deep in a N CsCl solution (47). Surface-active organic cations, as for instance $N(C_4H_9)_4^+$ or $N(C_5H_{11})_4^+$, accelerate the reduction of the $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, $Hg(CN)_4^{2-}$ and $Cd(CN)_4^{2-}$ ions. On addition of these cations even at low concentrations the normal value of the diffusion current is restored, but their action vanishes at their desorption potential, as shown in Figure 2 (13, 34, 46, 46a, 49, 51). An utterly different effect is observed with NO_3^-, BrO_3^- and IO_3^- anions. In these cases the addition of the organic cations strongly inhibits the electroreduction processes. At potentials at which it is adsorbed on the Hg surface the $N(C_4H_9)_4^+$ cation completely suppresses the accelerating action of Ba^{2+} and La^{3+} on the reduction of these anions; as a result a nearly discontinuous rise of the current is observed at the desorption potential of $N(C_4H_9)_4^+$ (Fig. 3) (56). The behavior of the $PtCl_4^{2-}$ ion is in

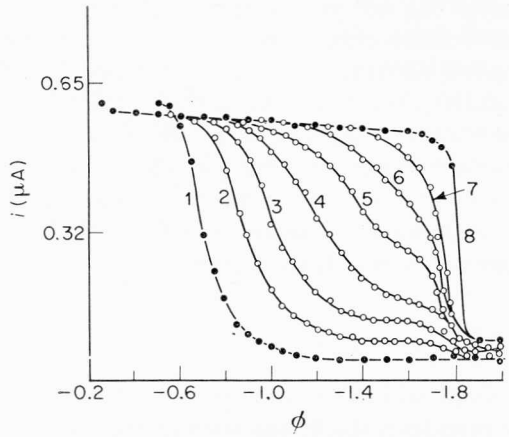

FIG. 2. Current–voltage curves of 10^{-3}N $K_3Fe(CN)_6 + x$N $N(C_5H_{11})_4Br$ solutions. (1) $x = 0$; (2) $x = 1 \times 10^{-5}$; (3) $x = 2 \times 10^{-5}$; (4) $x = 2.2 \times 10^{-5}$; (5) $x = 2.5 \times 10^{-5}$; (6) $x = 3 \times 10^{-5}$; (7) $x = 5 \times 10^{-5}$; (8) $x = 1 \times 10^{-4}$, $m = 1.36$ mg s^{-1}, $t = 5.4$ sec.

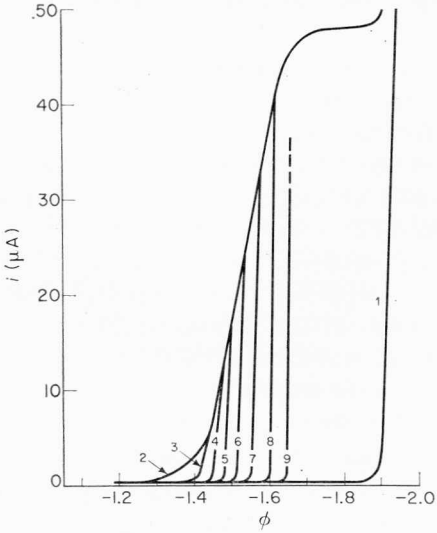

FIG. 3. The influence of $N(C_4H_9)_4I$ additions (denoted as TBI) on the reduction of BrO_3^- in the presence of Ba^{2+}. (1) 0.2N $BaCl_2$; (2) $+ 1.96 \times 10^{-3}$N $KBrO_3$; (3) $+ 1.57 \times 10^{-4}$N TBI; (4) $+ 3.14 \times 10^{-4}$N TBI; (5) $+ 4.70 \times 10^{-4}$N TBI; (6) $+ 9.23 \times 10^{-4}$N TBI; (7) $+ 2.4 \times 10^{-3}$N TBI; (8) $+ 3.62 \times 10^{-3}$N TBI; (9) $+ 1.20 \times 10^{-2}$N TBI.

this respect an intermediate one. At small negative potentials, the $N(C_4H_9)_4^+$ cation inhibits its reduction, the inhibition being more pronounced if the supporting electrolyte is a Cs salt, than if it is a Na salt. At more negative potentials, however, at which, judging from the value of the differential capacity, the organic cation is somewhat flattened, the reduction of $PtCl_4^{2-}$ is strongly accelerated in its presence. The acceleration disappears at the desorption potential of the cation (47). By measuring the dependence of the current on the drop age it could be shown that the action of the $N(C_5H_{11})_4^+$ cation is a dual one: it accelerates the reduction of the $PtCl_4^{2-}$ ion at small coverages and inhibits it at larger ones (18b).

D. The Influence of the pH *of the Solution in the Presence of Multivalent Cations*

The rate of the reduction of $S_2O_8^{2-}$ in the presence of La^{3+} (as well as of cations with a smaller charge) remains unchanged if the solution is acidified; in the presence of thorium salts acidification even enhances the accelerating action of thorium ions, probably causing an increase of their charge (suppression of hydrolysis) (16, 55a). The dependence of the reaction rate on the pH in the presence of multivalent cations in the case of the $S_2O_8^{2-}$ anion is therefore quite different from the dependence observed with anions of the XO_3^- type. It should, however, be mentioned that the $S_2O_8^{2-}$ reduction has not yet been investigated under conditions where OH^- ions are formed during the electrolysis process, as in the case of the NO_3^- reduction, in which the interaction between La^{3+} and OH^- ions occurs at the electrode surface.

E. The Rôle of the Anions of the Supporting Electrolyte

If the $S_2O_8^{2-}$ reduction is carried out at a positively charged electrode surface, the anions of the supporting electrolyte exert an inhibiting action which increases in the sequence $SO_4^{2-} < Cl^- < Br^- < I^-$, that is with rising adsorbability of the anion (30). At potentials more negative than the point of zero charge, the sequence in the case of univalent anions is inverted, the reaction rate increasing on transition from Cl^- to I^-. This effect is

especially noticeable with Cs salts and practically disappears if the supporting electrolyte is a Na salt (18).

The reduction of anions at a negatively charged surface is slowed down in the presence of the divalent SO_4^{2-} anion; in the case of the $S_2O_8^{2-}$ reduction this effect is small and can perhaps be explained by a decrease in the activity of the cations in the solution, but in the case of the reduction of NO_3^- or BrO_3^- in the presence of La^{3+}, the SO_4^{2-} ions strongly inhibit the reaction, as shown in Figure 4, even at concentrations which are much lower than the concentration of the La^{3+} ions (39).

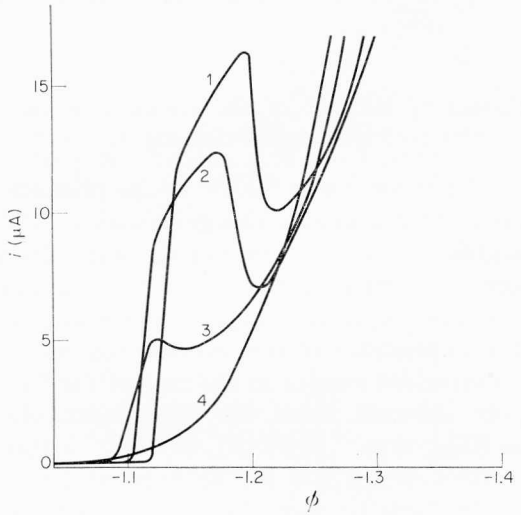

FIG. 4. The influence of K_2SO_4 additions on the reduction of NO_3^- in the presence of La^{3+}. (1) 0.1N $KNO_3 + 2.1 \times 10^{-3}$N $LaCl_3$; (2) $+ 4 \times 10^{-5}$N K_2SO_4; (3) $+ 10^{-4}$N K_2SO_4; (4) $+ 3 \times 10^{-4}$N K_2SO_4 (m and t as in Fig. 1).

The inhibiting action exerted by surface-active anions (Cl^-, Br^-, I^-) on the $S_2O_8^{2-}$ reduction process at potentials corresponding to the positive branch or to the beginning of the negative branch of the electrocapillary curve increases greatly in the presence of surface-active cations of the NR_4^+ type. As a result, minima on the current–voltage curve appear at those concentrations of the supporting electrolyte at which, in the absence of surface-active cations, a diffusion-controlled limiting current is observed (12, 13, 40, 45).

Finally, in considering the rôle of the anions of the supporting electrolyte, it should be kept in mind that in some cases the reducible anion can interact slowly with the anions of the supporting electrolyte, the resultant change of its constitution considerably influencing its reactivity. Thus, the $Pt(NO_2)_4^{2-}$ anion in the presence of Cl^- is first transformed into the much more easily reduced $Pt(NO_2)_2Cl_2^{2-}$ complex, whereas a further introduction of chlorine into the coordination shell decreases the reaction rate (44).

F. Surface-active Neutral Molecules

The formation of dense adsorbed layers of neutral molecules, for instance $C_8H_{17}OH$, inhibits the reduction of anions as it inhibits other electrode processes (31, 40, 45); it is noteworthy that the especially simple electron transfer reaction $Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$ does not present an exception in this respect (23). The repulsion of the anions by the negative charges of the electrode surface manifests itself in the presence of adsorbed layers of neutral molecules too.

G. The Temperature Coefficient

The temperature coefficient of the rate of anion reduction depends on the cation of the supporting electrolyte (16, 57). Thus on increase of the temperature from 5 to 45°C the rate of reduction of $S_2O_8^{2-}$ approximately doubles in the presence of 0.01N Na^+, remains practically unchanged in the presence of 0.01N K^+, and decreases ca 5 times in the presence of 0.01N Cs^+.

V. The Mechanism of the Reduction of Anions

The existence of an intimate connection between the peculiarities of the electroreduction of anions and the repulsion of anions by the negatively charged electrode surface is beyond doubt, but the working out of a quantitative theory, embracing the problem from all sides, is still far from being completed. Frumkin and Florianovich (9, 15), assuming that the anions A^{n-} in the electric double

layer and the anions in the bulk of the solution are in equilibrium, and that the rate-determining step is the electron transfer from the electrode to the anion, have deduced the relation

$$\frac{J}{1-J/J_d} = Kc_A \exp \frac{\alpha F}{RT}\left(-\varphi+\frac{\alpha+n}{\alpha}\psi_1\right) \qquad (3)$$

(J = current strength, J_d = limiting diffusion current, c_A = concentration of the anions in the bulk of the solution, φ = electrode potential, K and α = constants; $0<\alpha<1$). If the reaction is carried out at the dropping mercury electrode the correction for concentration polarization can be applied in a more exact form, using the method of calculation given by Meiman (42) and Bagozky (1). With the help of equation (3) which contains only two arbitrary constants, the current–voltage curves obtained on $S_2O_8^{2-}$ reduction with KCl solutions of different concentrations as supporting electrolyte can be approximately reproduced. The ψ_1 values used by Frumkin and Florianovich were average values of the ψ_1-potential, calculated according to the classical double-layer theory. However, on confronting equation (3) with experimental data some difficulties cannot be avoided. The derivation of equation (3) implies the assumption that the energy of activation of the reduction process at the minimum of the current–voltage curve has a fairly large positive value, which contradicts the results of measurements of the dependence of the reaction rates on temperature. Moreover, the dependence of the reaction rate on the radius of the cation is more pronounced than would be expected on the basis of equation (3) and the extent to which the hydrogen overvoltage at mercury electrodes in acid solutions is dependent on the same parameter.

These facts make it necessary to take into account the interaction between the reacting anion and the next neighboring cation in the Helmholtz layer, leading to the formation of some kind of a cationic bridge which links the anion to the electrode surface. With temperature rise, these cationic bridges dissociate, which explains the anomalous values of the temperature coefficient of the reaction rate. As the appearance of cationic bridges is determined mainly by coulombic forces, it is evident that taking into account the formation of these bridges is to a certain extent equivalent to the introduction into equation (3) of local

ψ_1- potential values instead of average ones. A treatment in many respects similar to that given above has been applied by Delahay and Mattax to the reduction of IO_3^- anions in solutions of different ionic strength (4).

The introduction of the concept of cationic bridges diminishes the divergency between the theory of Frumkin and Florianovich and the original theory of Heyrovský. We should, however, like to emphasize that what we consider as the most important point is the stress laid on interactions within the limits of the double layer and not in the bulk of the solution. To make this point clear, let us consider in somewhat more detail the inhibiting action of SO_4^{2-} ions on the reduction of NO_3^- in the presence of La^{3+}, discovered by Heyrovský. As ion pairs formed by La^{3+} and NO_3^- ions certainly exist in the bulk of the solution, it could be supposed that the inhibiting effect is a result of the displacement of NO_3^- ions from these ion pairs by SO_4^{2-} ions. However, as can be seen from Figure 4, the rate of the reduction of NO_3^- ions is decreased several times on addition of SO_4^{2-} ions, even when the concentration of the latter remains so small that they cannot exert a substantial influence on the composition of ion pairs in the bulk of the solution (39). This can be explained only by a displacement of the NO_3^- ions by SO_4^{2-} ions from the surface layer, although the composition of ion pairs in the bulk of the solution is doubtless also changed when a higher concentration of SO_4^{2-} ions is reached. The study of the influence of SO_4^{2-} ions on the reduction of BrO_3^- in the presence of La^{3+} leads to similar conclusions (56). Of great interest for the elucidation of the mechanism of anion reduction are the effects observed in the presence of large organic cations. As the adsorption of these cations shifts the ψ_1-potential to more positive values, an increase of the reduction rate should be expected, which is actually observed in the case of the reduction of $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$ and other anions. The inhibition of the reaction observed in the case of the reduction of NO_3^-, BrO_3^- and IO_3^- appears at first sight to contradict the concept according to which the reaction rate can be correlated with the ψ_1-potential. This contradiction can be removed on considering that the transition from an inorganic cation to an organic one with a larger radius, for instance from La^{3+} to $N(C_4H_9)_4^+$, causes an increase of the distance between

the electrode surface and the outer Helmholtz layer. It is therefore possible that a shift of the average ψ_1-potential to more positive values in the outer Helmholtz layer, where the centers of the cations are located, is accompanied by a shift of the ψ_1-potential at a distance equal to the effective radius of the reacting anions (inner Helmholtz layer) in the opposite direction. Moreover, the difference between the local more positive values which the ψ_1-potential acquires in the neighborhood of cations and its average value at the distance of the radius of the cations from the electrode surface must be much larger in the case of multivalent inorganic cations than in the case of the bulky organic cations. It is evident that the closer the approach of the center of the reacting anion to the electrode surface in the transition state of the reaction the more unfavorable the conditions become for the reduction of the anion in the presence of large organic cations. This explains why the inversion of the normal accelerating action of the NR_4^+ cations is observed only in the case of anions with a flat or nearly flat configuration (14).

The necessity of taking into account the location of the center of the reacting particle when discussing the influence of the double layer structure on reaction rates, was pointed out also by Breiter, Kleinerman and Delahay (2). It is important to stress once more that all effects depending on organic cations are observed only at potentials at which these are adsorbed on the electrode surface and, as has already been mentioned in considering the reduction of $PtCl_4^{2-}$, the deformation of the adsorbed cation by the electric field of the double layer can cause a change from an inhibition to an acceleration of the reaction.

In discussing the electroreduction of anions we have considered until now only changes in the concentration of the reacting particles. It is probable that, at least in the case of anions which are specifically adsorbed, another effect might be of importance—that is, the change of the bonding between the anion and the electrode surface. Thus, it is probable that the $PtCl_4^{2-}$ anion is linked to a positively or slightly negatively charged electrode through Cl atoms, whereas at a strongly negatively charged interface a deformation of the anion becomes possible, facilitating a closer approach to the electrode surface of the positively charged central Pt atom.

It was assumed in the derivation of equation (3) that the anions in the surface layer and those in the bulk of the solution remain in equilibrium in the course of the reaction; the refinements discussed above do not bear on this point of the theory. A radically different point of view is, however, possible, and this was worked out in a quantitative form by Levich (37). He supposed that an equilibrium between the surface layer and the bulk of the solution does not establish itself in the reacting system, the rate-determining step being the penetration of the anion into the electric field of the double layer. A quantitative evaluation showed that the retardation of the approach of a divalent anion to the electrode surface caused by electrostatic repulsion is not only sufficient to account for the falling off of the current observed in the case of the $S_2O_8^{2-}$ reduction, but should provoke a still larger decrease in the reaction rate. This led Levich to the conclusion that the reacting substance is transported to the electrode surface in the form of ion pairs with a smaller negative charge than the $S_2O_8^{2-}$ ion, as for instance $KS_2O_8^-$. Another way of removing this difficulty would of course be to take into account the discrete structure of the double layer. The theory of Levich explains the falling off of the current with the increase of the negative potential, but not its subsequent rise, which was hitherto observed in all cases, with the sole exception of the $Fe(CN)_6^{3-}$ reduction. To explain this second rise of the current, it could be assumed that at very negative potentials the transfer of electrons from the electrode to the anion is effected by a tunneling mechanism which transports the electrons over distances exceeding the thickness of the Gouy layer. The realization of such a process would make it unnecessary for the anion to overcome the electrostatic repulsion. *A priori*, the occurrence of electron tunneling appears much more probable in the case considered here than in the case of the discharge of hydrogen ions, for which this mechanism was primarily suggested by Gurney (26). However, the strongly pronounced dependence of the reaction rate on the radius of the cation may be advanced as an argument against the existence of tunneling at distances which are large compared with the dimensions of inorganic cations.

Levich has recently deduced a relationship between current strength and potential, taking into account both the slow

penetration of the anion in the electric field of the double layer and the slow electron transfer:

$$J = \frac{Kc_A \exp\{(n+\alpha)\psi_1 - \alpha\varphi\}}{1 + \frac{2\lambda K}{(2n-1)D_A nF} \exp\{(\alpha - \frac{1}{2})\psi_1 - \alpha\varphi\}} \qquad (4)$$

where D_A is the diffusion coefficient of the anion and λ the thickness of the Gouy layer (38).

It should be noted that current–voltage curves of the form predicted by equation (4), on which a second falling off should be observed after the second rise of the current strength, have not so far been obtained.

Finally, we shall discuss the possibility of a rate-determining step consisting in the formation of an ion pair or of some other similar association of ions.* This possibility has apparently been suggested for the first time by Gierst (22). If the ion pair is formed in the bulk of the solution, that is if the thickness of the reaction layer considerably exceeds the thickness of the double layer, the rate of the process should be independent of the electrode potential,† as well as of the changes of the ψ_1-potential caused by adsorption phenomena, as long as a new rate-determining step or a new reaction path is not created. The great sensitivity of the reactions considered in this paper to adsorption phenomena seems to show that in these cases the rate-deter-

* Besides ion-pair formation the rate-determining step may consist in any other reaction leading to a decrease of the negative charge of the anion, as for instance partial hydrolysis in the case of a chlorocomplex or a reaction of the type $Cd(CN)_4^{2-} \rightarrow Cd(CN)_3^- + CN^-$. We shall not discuss these reactions in this paper.

† Gierst assumes (*op. cit.* p. 49) that at potentials corresponding to the descending branch of the current–voltage curve of the $S_2O_8^{2-}$ reduction the rate-determining step is the formation of an ion pair in the bulk of the solution:

$$S_2O_8^{2-} + Me^+ \rightarrow MeS_2O_8^-$$

At more negative potentials, according to Gierst, the rate-determining step is an electrochemical reaction with the simultaneous participation of electrons and of $S_2O_8^{2-}$ and Me^+ ions. The hypothesis of two different mechanisms at potentials at both sides of the minimum of the current–voltage curve is hardly compatible with the fact of an identical dependence of the reaction rates on the radius of the cation in both cases.

mining step cannot consist in a chemical reaction in the bulk of the solution.

At the negative end of the current–voltage curve of the $Fe(CN)_6^{3-}$ reduction, the current strength within certain potential limits depends only slightly on the potential, although the sensitivity towards the adsorption of surface-active cations is preserved (Fig. 2). Within these potential limits, the current strength, corrected for concentration polarization, is proportional to the third power of the concentration of K^+ and Cs^+ (14, 49). It has appeared to us for some time that the experimental data obtained are compatible with the assumption that the rate-determining step is the formation of a neutral complex from the trivalent anion and three univalent cations within the limits of the double layer. Recently, however, the determination of current–voltage curves of $Li_3Fe(CN)_6 + LiCl$ solutions and the introduction of a correction taking into account the dependence of the drop time on the potential showed that at more negative potentials a second rise of the current just as in the case of the $S_2O_8^{2-}$ anion reduction is observed (49). It is therefore probable that there exists no fundamental difference between the mechanism of the process in the two cases, the repulsion effects being more pronounced in the case of $Fe(CN)_6^{3-}$ only on account of the higher charge of the anion.

We have tried to show that the investigation of the anion reduction, which was started by Prof. J. Heyrovský and his collaborators, has made it possible to establish a series of interesting relations between reaction rates and the structure of the double layer. This investigation is yet far from being brought to an end, and its further development may still lead to many essential conclusions.

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