INFLUENCE OF CATION ADSORPTION ON THE KINETICS OF ELECTRODE PROCESSES

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The influence of cation adsorption on the rate of the electroreduction and formation of cations as well as on the electroreduction of anions is discussed. The effects observed are correlated with changes of the ψ_1-potential, but whereas in reactions with the participation of cations average values of the ψ_1-potential can be used, in the anion electro-reduction the dependence on the ψ_1-potential on the distance between the reacting anion and the cation which is its next neighbour must be taken into account. The electro-reduction of the $PtCl_4^{2-}$ anion which has a flat configuration shows a much smaller sensitivity towards cations than the electroreduction of the $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$ anions.

Measurements of reaction rates and differential capacities in the presence of Cs^+ ons indicate a certain specific adsorbability of the Cs^+ ion. If both the cation and the anion are surface-active, that effect of the adsorption on reaction rates which prevails at a definite potential is still enhanced.

Herasymenko and Slendyk [1] observed that the presence of cations in solution influences the hydrogen overvoltage on mercury, which rises with the increase of the cation concentration. They found that the effectiveness of the cations increases with increasing charge and for univalent cations in the order $Li^+ < Na^+ < K^+ < Rb^+$. The largest rise of the overvoltage was observed in the presence of La^{3+} and Th^{4+}. The author made an attempt [2] to correlate these phenomena with the distribution of the potential within the electric double layer. Let c be the bulk concentration of the reacting particles, n their charge and ψ_1 the potential at the point of the surface layer where the centre of the charge of the reacting particle is situated. The surface concentration of the reacting particle is proportional to $c \exp(-\psi_1 nF/RT)$; and the velocity of the electron transfer from the electrode surface to the reacting particle, i.e. the current density i, is equal to

$$i = kc \exp(-\psi_1 Fn/RT) \exp[-\alpha(\phi - \psi_1 F/RT] = kc \exp(-\alpha\phi F/RT)$$
$$\exp[(\alpha - n)\psi_1 F/RT], \quad (1)$$

where ϕ denotes the potential difference between the electrode and the solution, and α is a constant $(0 < \alpha < 1)$. If the backward reaction is considered, $-\beta = -(1 - \alpha)$ must be substituted for α and $(n - 1)$ for n. The velocity of the backward reaction must be therefore proportional to $\exp[(1 - \alpha)\phi F/RT] \exp[(\alpha - n)\psi_1 F/RT]$. The factor containing ψ_1 has the same influence on the forward and backward reactions, as would be expected.

The coefficient $(\alpha - n)$ is negative, if $n \geqslant 1$, and positive if $n \leqslant 0$. Therefore, in cation discharge or formation the adsorption of another cation (whether coulombic or specific), which shifts ψ_1 to more positive values, must inhibit the reaction, whereas in reactions with the participatiom of anions, cation adsorption must increase the reaction rate.

When applying eqn. (1) to the discharge of the hydrogen ion, we suppose that the value of ψ_1 at a distance from the electrode surface equal to one atomic radius

can be found using the classical double-layer theory, i.e. on the assumption, that the ψ_1-potential depends on the distance from the electrode surface only, but not on the position of the reacting particle in the transition state relative to the ions constituting the ionic side of the double layer. Eqn. (1) gives a correct quantitative expression of the slowing-down of the discharge of hydrogen ions in dilute solutions of HCl caused by an addition of KCl.[3, 4] The slowing-down of reactions with the partici- pation of cations is specially great in the presence of organic cations, for instance $N(C_4H_9)_4{}^+$, which are specifically adsorbed, as was shown by Jofa and Kabanov for the hydrogen ion discharge on a mercury electrode.[5] The decrease of the exchange current between amalgams of Zn, Cd and others and the corresponding ions in the solution was investigated by electrochemical methods as well as with the help of radioactive indicators.[6, 7] This decrease may amount in some cases to four orders
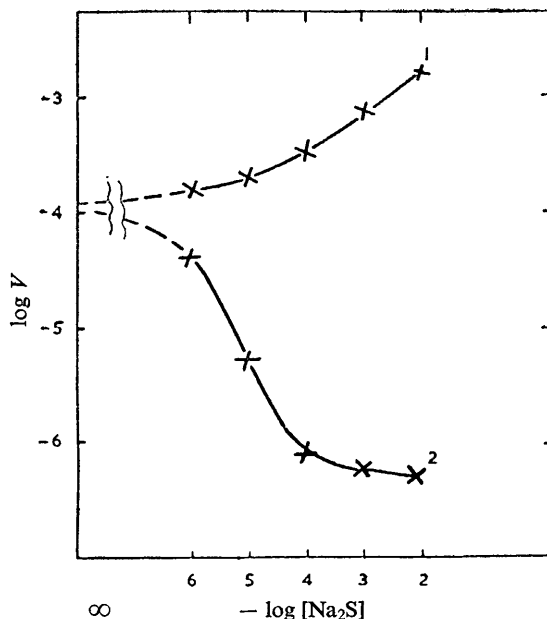

FIG. 1.—Dependence of the velocity V of the dissolution of iron in sulphuric acid on the concentration of Na_2S added.
1, N H_2SO_4; 2, N H_2SO_4 + 5 × 10^{-3} N $[N(C_4H_9)_4]_2 SO_4$.

of magnitude or even more. Of particular interest are phenomena observed in the corrosion of iron in acid solutions. As it was shown by Jofa,[8] organic cations of the $N(C_4H_9)_4{}^+$ type cause only a small increase of the hydrogen overvoltage as well as a small slowing-down of the anodic process in H_2SO_4 solutions at the stationary potential in the absence of external polarization and are apparently not adsorbed on the metal under these conditions, but in the presence of Br^- or still better I^- or SH^- ions the inhibiting action of the organic cations is shown to a full extent (fig. 1). This enhancement of the adsorption of organic cations due to anions was shown to be connected with the chemisorption of anions on the electrode surface. Anion chemisorption, like the formation of surface oxide layers, causes a shift of the zero-charge potential towards more positive values, the charge of the electrode surface at the stationary potential of the metal dissolution becoming thus negative.[9] More- over it appears that the chemisorption process in some way makes the metal surface more hydrophobic.[10] These results present some interest for the understanding of the behaviour of corrosion inhibitors.

CATION ADSORPTION AND ANION ELECTROREDUCTION

The increase of the rate of anion electroreduction under the influence of cation adsorption was observed for the first time by Heyrovsky and Tokuoka, who investigated the behaviour of anions of the XO_3^--type (NO_3^-, BrO_3^-) at the dropping mercury electrode.[11]   They found that the half-wave potential of these anions is shifted to more positive values when the charge and the concentration of the non-reducible cations in the solution increases and explained this phenomenon by the formation of ionic pairs which facilitates the approach of the anion to the negatively charged electrode surface.   It was also assumed that the polarization of the anion by the electric field of the cation enhances its reactivity.   The author expressed the opinion that the increase of the rate of anion electroreduction in the presence of multivalent cations could be correlated according to eqn. (1) with changes of the ψ_1-potential.[12]   But, whereas in the discharge of H^+ions, when the cations of the double layer repel the reacting particle, average values of the ψ_1-potential—for instance those calculated with the help of the Stern theory of the double layer—can be used, this is not admissible in the case considered.   As the attraction between the cations of the double layer and the anions to be reduced brings them close together, the dependence of the ψ_1-potential on the distance between the reacting anion and the cation which is its next neighbour must be taken into account.   It is evident that these local ψ_1-potential values may differ considerably from the average ones and, the metal surface being negatively charged, must be shifted to more positive potentials.   The electroreduction of anion of the XO_3^- type, accompanied by the formation of OH^- ions, presents some peculiarities which shall be mentioned later on.   It appears to the author that we can obtain more information for the understanding of the mechanism of cationic action by considering the behaviour of another group of anions.

The current density-voltage curves of di- and tervalent anions, whose reduction begins at sufficiently positive potentials, show a falling-off of the current with increasing cathodic polarization in the potential region where the electrode bears a negative charge.   This was observed for the first time by Krjukova,[13] who investigated the electroreduction of the $S_2O_8^{2-}$ anions. This effect, caused by the repulsion between the anion and the negatively charged electrode surface disappears or becomes at least less pronounced on increasing the concentraion of the electrolyte in the solution, the results obtained depending in the first instance upon the nature of the cation.[9, 14]   In many cases ($S_2O_8^{2-}$, $PtCl_4^{2-}$) at still higher cathodic polarization a new rise of the current-voltage curve is observed which will not be discussed here in detail.   Fig. 2 gives the dependence of the current-voltage curve of the $Fe(CN)_6^{3-}$ reduction on a dropping mercury electrode on the concentration of KCl added.[15] The part of the curve referring to potentials more positive than the zero-charge potential is not reproduced on the drawing as it is strongly distorted by a polarographic maximum of the first kind.   With $[KCl] = 5 \times 10^{-3}N$, the limiting value of the diffusion current is reached.   The potentials throughout this paper are referred to the normal calomel electrode.

The suppression of the minimum on the current-voltage curve can be considered as a measure of the effectiveness of the cationic action.   According to their sensitivity towards the presence of cations, as it was shown by Nikolajeva-Fedorovich and others, the electroreducible polyvalent anions may be divided in two groups.

A. ANIONS OF THE $S_2O_8^{2-}$ AND $Fe(CN)_6^{3-}$ TYPE.   The anomalies of the current-voltage curves disappear altogether on increasing the concentration of the non-reducible electrolyte.   The effectiveness of the action of cations strongly increases in the sequence $K^+ < Ba^{2+} < La^{3+}$, and for univalent cations in the sequence $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.[9]   At the minimum of the current-voltage curve, the current corrected for the concentration polarization, i.e. the magnitude $\dfrac{i}{1 - i/i_d}$, rapidly rises with increasing cation concentration especially [15] for the tervalent

anion $Fe(CN)_6^{3-}$ (fig. 3).   With $S_2O_8^{2-}$ the temperature coefficients of the current at the minimum of the current voltage curve have been determined.   The temperature coefficients are very small and decrease in the order $Na^+ > K^+ > Cs^+$.[16,17]   In the presence of Cs^+ the temperature coefficient of the $S_2O_8^{2+}$ electroreduction is negative.

FIG. 2.—Current-voltage curves of 10^{-3} N $K_3Fe(CN)_6$ + x KCl solutions.

1, $x = 0$;
2, $x = 5 \times 10^{-4}$N;
3, $x = 10^{-3}$N;
4, $x = 2 \times 10^{-3}$N;
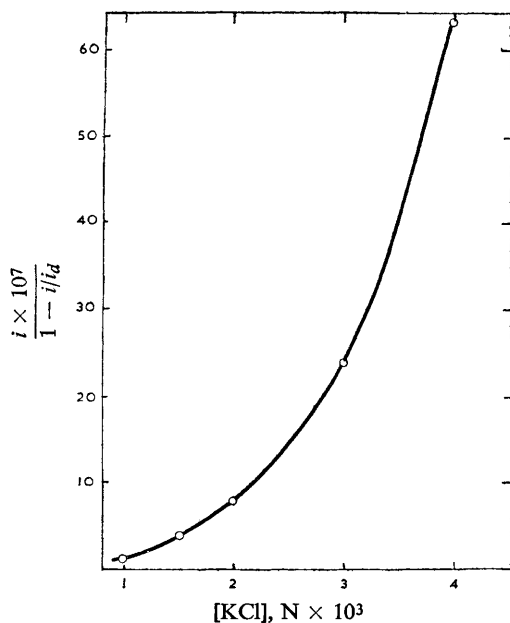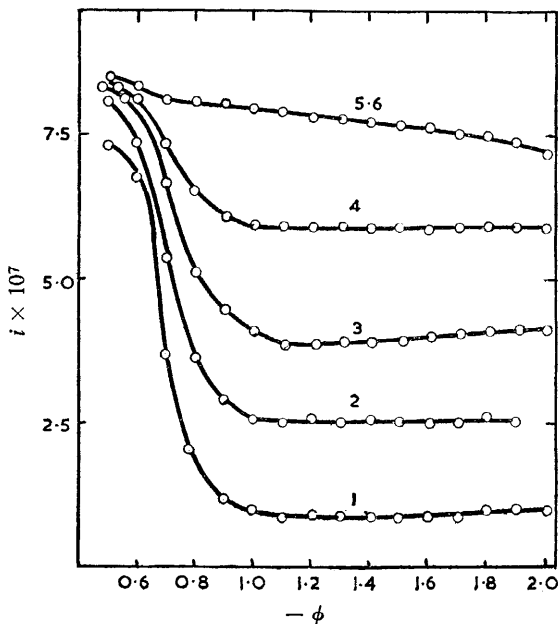5, $x = 5 \times 10^{-3}$N;
6, $x = 10^{-2}$N.

FIG. 3.—Dependence of the current strength at the minimum of the current-voltage curve in $K_3Fe(CN)_6$ + KCl solutions on the concentration of KCl; current corrected for concentration polarization.

Surface-active cations like $N(C_4H_9)_4^+$ restore the normal diffusion-controlled value of the current in the region of potentials in which they are adsorbed at the mercury-solution interface, but their action disappears at high cathodic

polarizations, when the large organic cations are displaced by smaller inorganic ones and water molecules (fig. 4). [15, 16, 18]   The desorption potential of $N(C_4H_9)_4^+$ can be determined independently from measurements of differential capacity.[18]   The $Hg(CN)_4^{2-}$ anion which was investigated by Siekerski [19] behaves in a similar manner.
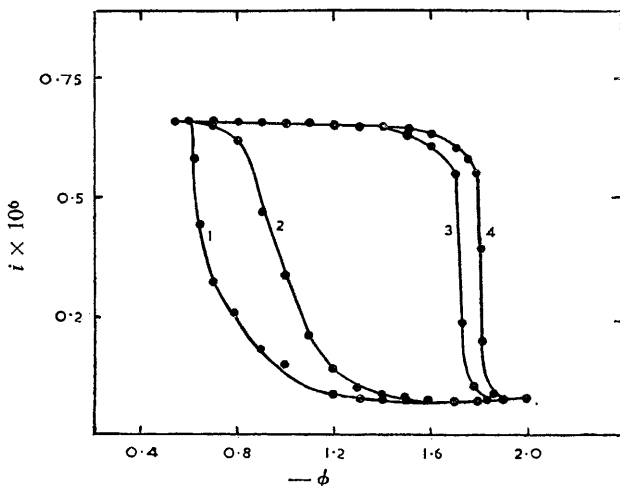

FIG. 4.—Current-voltage curves of $10^{-3}N$ $K_3Fe(CN)_6 + x[(C_4H_9)_4N]_2SO_4$ solutions.
1, $x = 0$; 2, $x = 10^{-5}N$; 3, $x = 5 \times 10^{-5}N$; 4, $x = 10^{-4}N$.

B. The behaviour of the $PtCl_4^-$ anion is markedly different.   The dip on the current-voltage curve of $PtCl_4^{2-}$ discovered by Laitinen and Onstott [20] does not disappear on increasing the concentration of the non-reducible electrolyte, although it becomes narrower and less deep.[21]   The greatest suppressing action is exerted by Cs^+ cations (fig. 5).   In contradistinction to what is observed with $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$, the addition of $N(C_4H_9)_4^+$ does not increase, but actually decreases the current density if the potential is not too negative (fig. 6).   The current under these conditions drops to a value independent of the nature of the cation which was present in the solution before the addition of $N(C_4H_9)_4^+$.   It is therefore natural to suppose that the slowing-down of the current is caused by the expulsion of Na^+ or Cs^+ from the ionic sheet of the double layer by the $N(C_4H_9)_4^+$ cations, and that the approach of the anions to the latter gives rise to conditions unfavourable for the electrochemical process at the given potential.   However, at more negative potentials in the presence of $N(C_4H_9)_4^+$, a large increase of the current is observed, which is followed by a new decrease [21] at the desorption potential of $N(C_4H_9)_4^+$.   It is remarkable that the potential corresponding to the increase of the current approximately coincides with the potential at which a hump on the differential capacity-voltage curve of dilute $N(C_4H_9)_4^+$ solutions is observed.   This hump suggests a deformation, perhaps a flattening of the adsorbed cation.

The behaviour of the $PtCl_6^{2-}$ ion is noteworthy.[22]   On the current-voltage curve of this anion a very pronounced decrease of the current is observed (fig. 7).   For a small increase of the concentration of the non-reducible cation (or on addition of $N(C_4H_9)_4^+$) the current in this potential region increases until it reaches a limit equal to the current corresponding to : (the $PtCl_4^{2-}$ electroreduction process) $+ \frac{1}{2}$(the limiting diffusion current of $PtCl_6^{2-}$ electroreduction).   A further increase of the concentration of the non-reducible electrolyte effects the current-voltage curve of $PtCl_6^{2-}$ only to the same extent as it affects the $PtCl_4^{2-}$ electroreduction.   This shows that during the first step of the electroreduction of $PtCl_6^{2-}$,

$$PtCl_6^{2-} + 2e \rightarrow PtCl_4^{2-} + 2 Cl^-,$$
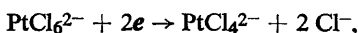
the influence of cations manifests itself in a manner similar to that observed with $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$ electroreduction and is much more pronounced than during the second step,

$$PtCl_4^{2-} + 2e \rightarrow Pt + 4\ Cl^-.$$
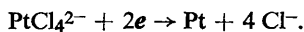
Although the experimental data available are too few for a generalization, attention should be pointed to the fact that anions whose electroreduction is not markedly influenced by the positive charge of the large organic cation $N(C_4H_9)_4^+$ have a flat configuration, whereas anions with a three-dimensional configuration are
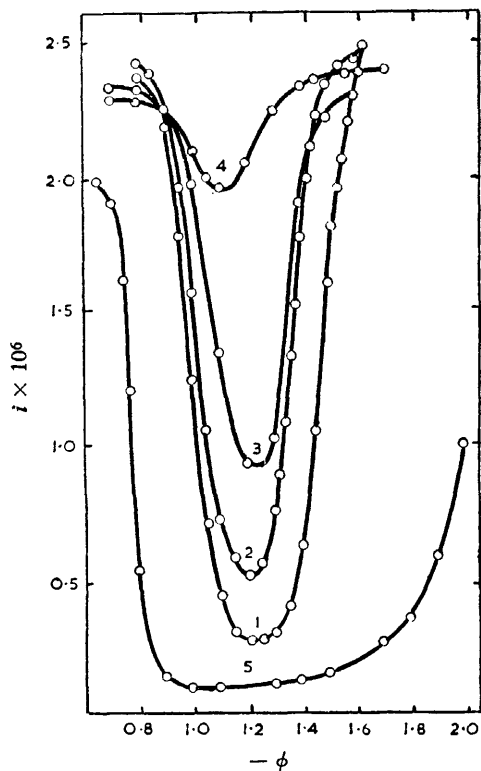

FIG. 5.—Current-voltage curves of K_2PtCl_4 solutions in the presence of foreign electro-lytes,

1, $10^{-3}N\ K_2PtCl_4 + N\ NaCl$;
2, $10^{-3}N\ K_2PtCl_4 + N\ KCl$;
3, $10^{-3}N\ K_2PtCl_4 + NBaCl_2$;
4, $10^{-3}N\ K_2PtCl_4 + N CsCl$;
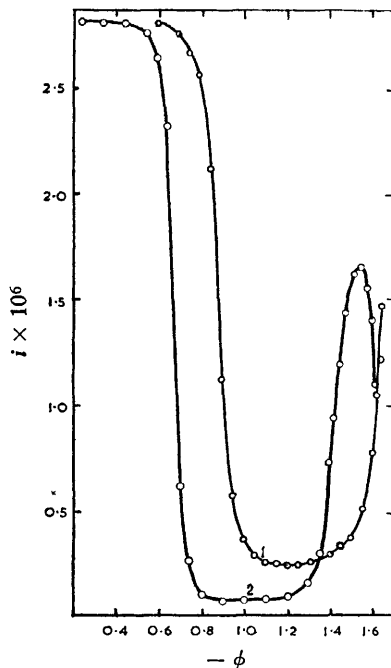5, $10^{-3}N\ K_2PtCl_4$ without additions.

FIG. 6.—Current-voltage curves of $10^{-3}N\ K_2PtCl_4 + 0.1\ N\ Na_2SO_4 + x[(C_4H_9)_4N]_2\ SO_4$ solutions.

1, $x = 0$;
2, $x = 10^{-3}N$.

sensitive to the presence of this cation. Apparently, for anions of the $PtCl_4^{2-}$ type, the transition state of the reaction is situated very close to the electrode surface, at least at potentials which are not too negative, and the positive charge of the $N(C_4H_9)_4^+$ ion has only a small influence on the local, rate-determining, value of the ψ_1-potential. At very negative potentials, in the region of the second rise of the current-voltage curve of the $PtCl_4^{2-}$ electroreduction a close approach of the reacting anion to the electrode surface is impeded and the difference between the behaviour of anions of the $S_2O_8^{2-}$ and $PtCl_4^{2-}$ types becomes less pronounced. The behaviour of the $PtBr_4^{2-}$ anion is similar to that of $PtCl_4^{2-}$.

Delahay and Mattax [23] found that the rate of the electroreduction of iodate ions is approximately proportional to the concentration of cations.

The rate of the electroreduction of BrO_3^- anions in the presence of univalent cations, as shown by Zykov and Shdanov,[24] increases in the order $Na^+ < K^+ < Cs^+$, and in the same order the temperature coefficient of the current strength is shifted towards more negative values.
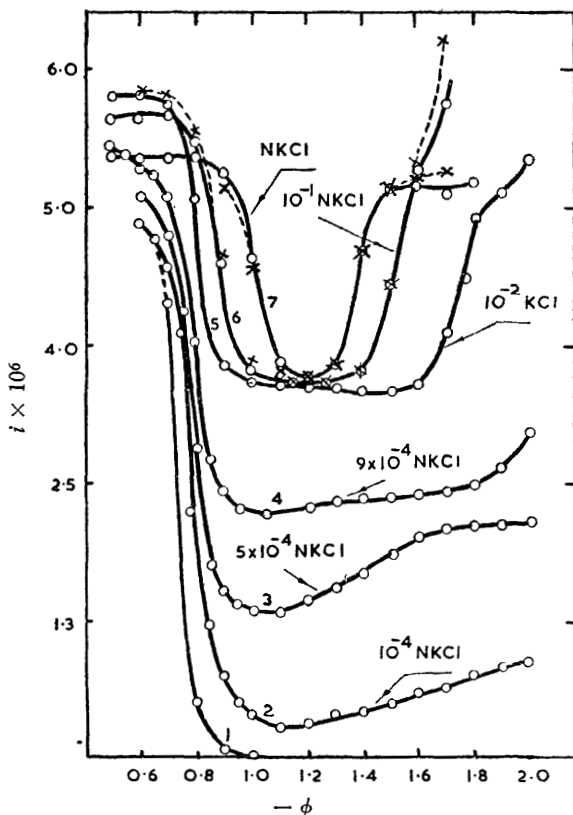

FIG. 7.—Full curves 1, 2, 3, 4, 5, 6, 7—current-voltage curves of $10^{-4}N$ K_2PtCl_6 solutions with various additions of KCl;

$$6 — x — x — 10^{-4}N \ K_2PtCl_4 + 0 \cdot 1 \ N \ KCl;$$
$$7 — x — x — 10^{-4}N \ K_2PtCl_4 + N \ KCl.$$

The ordinates of the two dotted curves are increased by half the limiting diffusion current of the $PtCl_6^{2-}$ electroreduction.

The electroreduction of these anions in the presence of La^{3+} ions discloses some peculiarities, as the OH^- ions which are formed during this process, (which increase according to the reaction

$$BrO_3^- + 3H_2O + 6e \rightarrow Br^- + 6 \ OH^-)$$
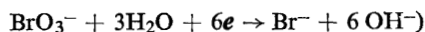
reinforce the influence exerted by the La^{3+} ion on the kinetics of the reaction. The reaction acquires therefore an autocatalytic character, which leads to the appearance of discontinuous transitions from low to high current densities at definite potentials.[25] The formal theory of these phenomena which was given by the author and Shdanov [26] does not present particular difficulties, but the reason for the enhancing of the La^{3+} effect by OH^- ions is not quite clear. It appears possible that on increase of the

pH, polycations with a higher positive charge are formed from La^{3+} ions,[27] which catalyze the reduction of XO$^-$ anions more strongly than normal La^{3+} ions, but this question needs further investigation. An addition of N(C$_4$H$_9$)$_4$$^+$ ions which expel the La^{3+} ions from the double layer causes a shift of the discontinuous rise of the current to much more negative potentials, possibly to the desorption potential of the N(C$_4$H$_9$)$_4$$^+$ ion (fig. 8). The negative catalytic action of the N(C$_4$H$_9$)$_4$$^+$ ion in this case is still more pronounced than for the PtCl$_4$$^{2-}$ electroreduction.
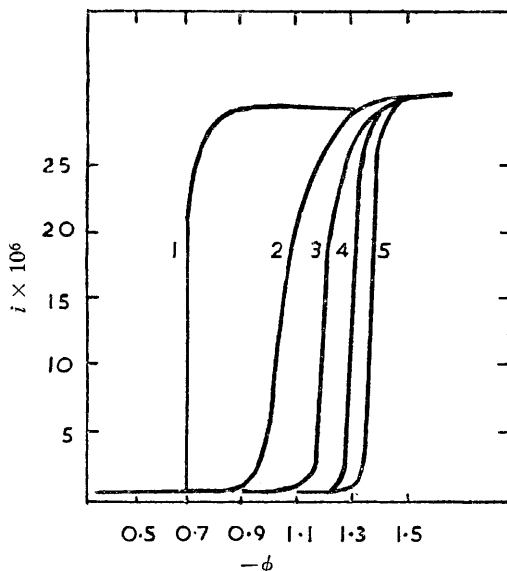

FIG. 8.—Current-voltage curves of $1 \cdot 2 \times 10^{-3}$N KBrO$_3$ + $0 \cdot 013$ M LaCl$_3$ + x N(C$_4$H$_9$)$_4$ Br solutions.
1, $x = 0$; 2, $x = 4 \times 10^{-4}$N; 3, $x = 8 \times 10^{-4}$N; 4, $x = 1 \cdot 56 \times 10^{-3}$N; 5, $x = 3 \cdot 43 \times 10^{-3}$N.

THE MECHANISM OF THE ANION ELECTROREDUCTION

Frumkin and Florianovich [14] have shown that the current-density against voltage curve of the S$_2$O$_8$$^{2-}$ anions electroreduction in the presence of varying concentrations of KCl, corrected for concentration polarization, i.e. the quantity $\dfrac{i}{1 - i/i_d}$, may be fairly well represented by eqn. (1) assuming $\alpha = 0 \cdot 28$. This expression for the reaction rate was deduced assuming that there exists an equilibrium between the anions in the ionic side of the double layer and those in the bulk of the solution and that electron transfer from the electrode to the anions in the double layer is the rate-determining step. Neither the specific adsorbability of the anions, nor the discrete structure of the double layer was taken into account. On the basis of this theory the explanation of the second increase of the current-voltage curve is as follows : at sufficiently negative potentials the ψ_1-potential changes with increasing polarization but slowly, whereas the decrease of the activation energy given by $\alpha\phi F/RT$ continues, which leads to a rise of the factor containing $- \alpha\phi F/RT$ in the exponent. For the Fe(CN)$_6$$^{3-}$ electroreduction, no current increase on further rise of the negative potential after the falling-down of the current is observed. This makes it probable that the rate-determing step for this tervalent anion is the penetration through the electric field of the double layer and not the discharge of the anions of the double layer, i.e. that equilibrium between the anions in the double layer and in the bulk of the solution does not exist. A quantitative theory of the

anion electroreduction taking into account both the finite rates of the penetration and of the electron transfer was developed recently by Levich.[28]

Independently of our conclusions as to the nature of the rate-determining step, it is clear that the ψ_1-potentials appearing in the expression for the reaction rate should be interpreted not as average but as local values of the ψ_1-potential. The pronounced dependence of the 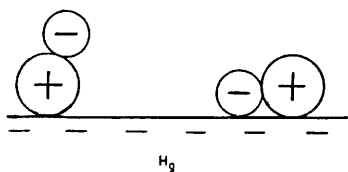reaction rate on the radius of the cation, the negative values of the temperature coefficient of the current strength, and finally, the retardation of the electroreduction of $S_2O_8^{2-}$ by divalent non-reducible anions [14]—all these facts cannot be explained except by assuming that the anions discharged must be located in the immediate neighbourhood of one of the cations of the double layer, or to express it otherwise, that the anions which are discharged are linked with the electrode surface by cationic bridges [17, 16] (fig. 9). Delahay and Mattax [23] drew a similar conclusion from the study of the iodate electroreduction. This assumption makes it also possible to understand the difference in the sensitivity towards cations of the anions of the $S_2O_8^{2-}$ and $PtCl_4^{2-}$ types.

FIG. 9.—Schematic diagram of the formation of cationic bridges at the mercury-solution interface.

As it follows from what has been written above, the rate-determining step may be the electron transfer to the anions linked with the surface by cationic bridges as well as the formation of these bridges within the double layer which necessitates the penetration of the anion through its electric field.

Nothing definite can yet be stated as to the nature of the elementary act itself and in particular as to the possible role of electron-tunnelling. At any rate, if electron-tunnelling, whose probability should increase with increase of the negative potential of the electrode, is realized, it occurs only at distances of the magnitude of the ionic radii.

The rapid increase of the reaction rate on passing from Li^+ to Cs^+ leads to the conclusion that the ψ_1-potential in the neighbourhood of the Cs^+ cation is markedly (by *ca.* 40 mV) more positive than in the neighbourhood of the Li^+ ion. From the electrocapillary data of Gouy [29] and differential capacity measurement of Grahame,[30] it was known that the charge of the double layer at negative potentials in the presence of caesium salts is larger than in the presence of other cations. According to Grahame the effects observed could be accounted for by the increased capacity of the inner Helmholtz layer when formed by Cs^+ ions,[31] although he expressed some doubts about the sufficiency of this assumption.[32]

In order to explain the difference in the reaction rates mentioned above we carried out measurements of differential capacity in solutions of CsF and CsI [33] and compared the results obtained with data referring to NaF and NaI. It was found that in the presence of Cs^+ the adsorption potential of I^- is shifted towards more negative values which proves independently of kinetic data that the interaction between anions and cations in the double layer is more pronounced with Cs^+ than with other cations. It is perhaps still more significant that the differential capacity of a positively charged mercury surface in fluoride solutions markedly increases on substituting CsF for NaF (fig. 10). As it was shown by Grahame [34] that F^- ions are not specifically adsorbed on a Hg surface (ψ_1-potential thus positive, if $\epsilon > 0$), this clearly suggests a specific adsorbability of the Cs^+ ion. Moreover, a definite, although small, shift of the zero-charge potential to more positive values is observed in CsF solutions.

The ideas presented have certain points in common with Heyrovsky's theory of ionic pairs, [11,35] but there is also a marked difference between the two concepts, as Heyrovsky referred to the formation of ionic pairs in the bulk of the solution, whereas it is here assumed that what really matters is the interaction between anions and cations within the double layer. An attempt could be made to interpret the

currents of the anion electroreduction observed at negative potentials as kinetic currents whose magnitude is determined by the rate of formation of ionic pairs in the bulk of the solution, but this assumption could hardly be reconciled with the observed dependence of these currents on the concentration and the radius of the cations.

In electron-exchange reactions between anions occurring in the bulk of the solution, as for instance the exchange between MnO_4^{2-} and MnO_4^- studied by Sheppard and Wahl,[36] or the $S_2O_3^{2-}+BrAc^-$ reaction,[37] cationic bridge formation plays probably a role too, but the difference between the accelerating action of Na^+ and
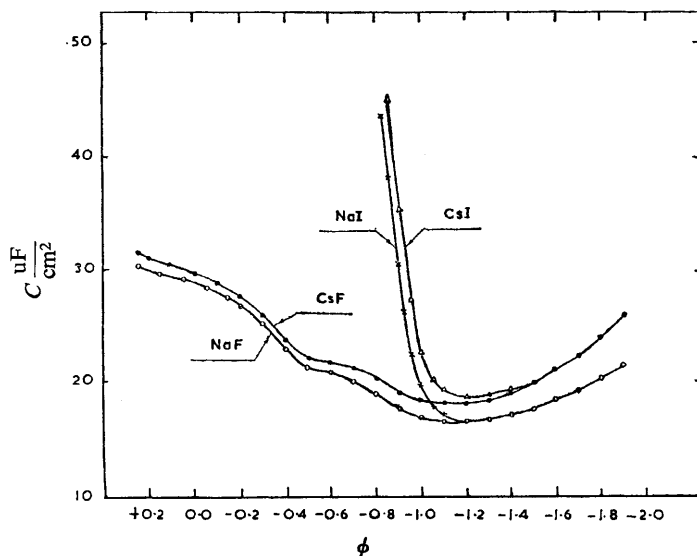

FIG. 10.—Differential capacity-voltage curves of mercury in 0·1 N solutions of sodium and caesium salts.

Cs^+, although it has the same sign as in electrode processes, is much less pronounced. It must, however, be acknowledged that to explain the nearly complete independence of the current on the potential which is observed over a wide potential range with $Fe(CN)_6^{3-}$ electroreduction a more thorough study of the ψ_1-potential distribution in the double layer is necessary than that which has been carried out at present.

COMBINED ACTION OF SURFACE-ACTIVE ANIONS AND CATIONS

It could be expected that if two surface-active ions with opposite signs of the charge are simultaneously present in the solution they mutually weaken their action. In practice, as a rule just the opposite is observed. The effect of the adsorption of the ion which prevails at a definite potential is still enhanced if the ion of opposite sign is specifically adsorbed at the same potential, even if this adsorption is small. Let us consider the following case as an example. If the electrode surface bears a positive or a small negative charge, surface-active anions somewhat inhibit the $S_2O_8^{2-}$ electroreductiom. On introducing $N(C_4H_9)_4^+$ ions in a solution containing for instance Br^- anions this inhibition is enhanced to such an extent that a dip appears on the current-voltage curve in the neighbourhood of the zero-charge potential.[18, 38] This shows that the $N(C_4H_9)_4^+$ cation, which by itself accelerates the $S_2O_8^{2-}$ electroreduction under definite conditions, may act as an inhibitor of the same reaction by enhancing the adsorption of anions. Similar effects are observed in the hydrogen ion discharge on mercury if both I^- and $N(C_4H_9)_4^+$ ions are present in the solution. As already mentioned, the adsorption of $N(C_4H_9)_4^+$ exerts in this

case a strong inhibiting action, whereas at potentials at which the I$^-$ ion is adsorbed, it increases the reaction rate and lowers the hydrogen overvoltage. As has been shown by Jofa and Tsa Chuan Sin,[39] this decrease is somewhat enhanced on addition of N(C$_4$H$_9$)$_4^+$ ions to the solution. Current-voltage curves of an unusual shape are observed in this case (fig. 11).
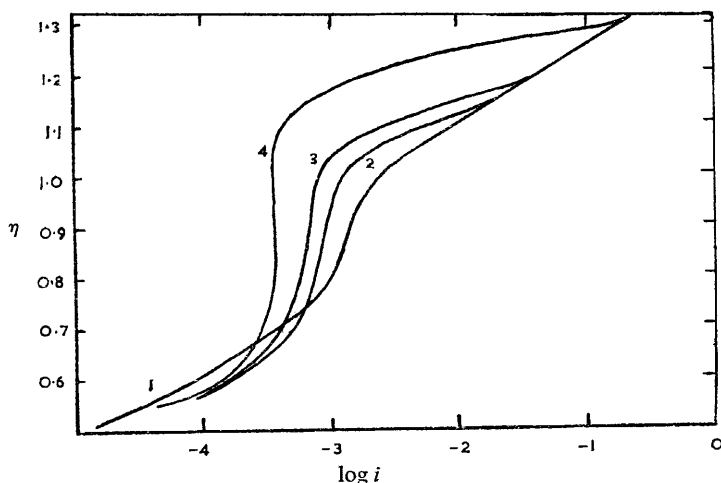

FIG. 11.—Hydrogen overvoltage on mercury in 2N HCl + 2N KI + xN (C$_4$H$_9$)$_4$Br solutions.

1, $x = 0$; 2, $x = 4 \cdot 9 \times 10^{-5}$N; 3, $x = 1 \cdot 2 \times 10^{-4}$N; 4, $x = 4 \cdot 6 \times 10^{-4}$N.

THE ROLE OF CATIONS IN THE ELECTROREDUCTION OF NEUTRAL MOLECULES

According to eqn. (1) the adsorption of cations should increase the rate of electroreduction with $n = 0$. The experimental data available are insufficient to draw conclusions as to the correctness of this conclusion. Ashworth [40] who studied the kinetics of benzophenone electroreduction in an alkaline medium observed relations between the reaction rate and the radius of the cations which are very similar to those which we found in anion electroreduction, but gave them a quite different interpretation. As it has been shown by Loshkarev,[41] in the electro-reduction of neutral molecules, the displacement of the reacting molecules from the electrode surface by large organic cations, which leads to an inhibition of the reaction, plays a very significant role. It is probable that the effects observed by Ashworth must be referred to anions which are formed as intermediates of the process.

In this communication I have tried to show the diversity of the relations between adsorption phenomena and electrochemical processes. It appears that the study of these relations might be helpful for the understanding of the mechanism of ionic reactions, heterogeneous catalysis and some other phenomena too.

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