1 The Adsorption of Ions at the Metal-Solution Interface and Its Influence on Electrode Kinetics*

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INTRODUCTION

A close relationship exists between the kinetics of electrode processes and the structure of the electric double layer. The transition from a diffuse to a nondiffuse structure of the double layer as well as the specific adsorption of ions must therefore exert a pronounced influence on the rate of electrochemical reactions (1, 2, 3). These problems, examined for a number of years in our laboratory, have attracted the attention of other investigators, among whom Delahay (4), Gierst (5), and Kolthoff (6) ought to be mentioned. It is the aim of this chapter to give a review of some of our results obtained in this field during the last few years.

A DIRECT METHOD FOR THE DETERMINATION OF ADSORPTION POTENTIALS

The change of the potential difference between metal and solution which occurs when ions are adsorbed at an uncharged metal surface can be defined as an adsorption potential; it is in many respects similar to the adsorption potentials arising in the presence of surface active ions at the gas-solution interface. Adsorption potentials at the metal-solution interface should not be identified with the potential difference between the plane where the centers of the adsorbed ions are located and the interior of the solution. Adsorption potentials are a measure of the electric effect produced by ionic adsorption. We shall also apply the term "adsorption potential" to the shifts of the electrode potential caused by the adsorption of ions at a charged metal surface under conditions of a constant charge density ξ, although these shifts do not depend only on the specific adsorption of ions but also on changes of the double layer capacity. For the mercury-solution interface the adsorption potentials can be deduced without difficulty from electrocapillary data, measurements of differential capacity, or measurements with the help of a dropping electrode. If an electrode is practically an ideal polarizable one, that is, if the constancy of an arbitrary potential value imposed on the electrode is preserved for a sufficiently long time, adsorption potentials can be directly determined by substituting a solution containing a surface active ion for an initial inactive one, for instance $1N$ H_2SO_4, and measuring the resulting shift of potential. To minimize effects depending on changes in the structure of the diffuse part of the double layer, the ionic strength of the solutions used should not be too low or

*This Chapter is drawn from a paper which was not presented orally at the Symposium because the author was unable to attend.

markedly influenced by the introduction of the adsorbed ions (7, 8). Carrying out these measurements becomes possible only after a thorough removal from the system of electrochemically active gases or other depolarizers. A large surface area for the electrode per unit volume of the solution is necessary as well. Platinized-platinum electrodes are therefore especially convenient. For smooth platinum reliable results can be obtained with an electrode with an apparent surface of ca. 20 cm^2, the volume of the solution being ca. 1 cc. Before carrying out the experiments, smooth platinum electrodes should be preheated in a quartz tube to 1000-1100°C. Some experiments have been carried out with gold electrodes.

When interpreting the results obtained with solid electrodes, we should keep it in mind that if the measurements are carried out with adsorbed hydrogen present on the electrode surface, the quantity whose constancy can be secured by the elimination of depolarizers is not the surface charge ξ, but $(\xi - AF)$, where A denotes the amount of hydrogen adsorbed per cm^2 of metal surface and F is the Faraday. Similar complications can arise in the presence of adsorbed oxide layers.

As seen from Fig. 1, the adsorption potentials of anions decrease if the initial potential of the electrode is shifted to the negative. The adsorption potentials of the halogen ions on platinum are analogous to those obtained with mercury as far as the dependence on concentration and on the radius of the ion is concerned, although their absolute values are larger.

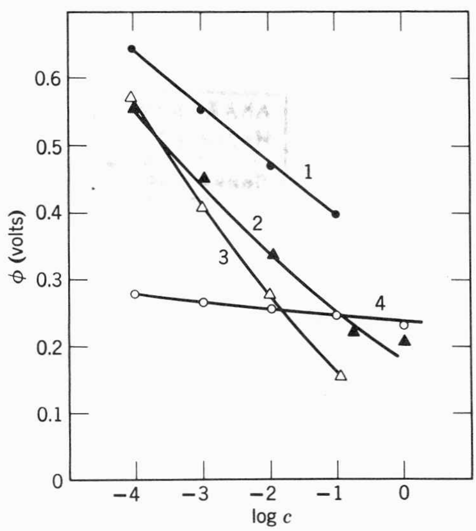

Fig. 1. Dependence of the shift of the potential $(\Delta\phi)$ on the initial concentration of the adsorbed ion c. 1. KCl, initial electrode potential 0.7 v; 2. KBr, initial electrode potential 0.7 v; 3. KI, initial electrode potential 0.7 v; 4. KBr, initial electrode potential 0.3 v. Platinized Pt electrode. Potentials referred to the hydrogen electrode in $1N$ H_2SO_4.

THE SPECIFIC ADSORPTION OF INORGANIC CATIONS

This method has made it possible to demonstrate the existence of a strong specific adsorption of some inorganic cations at the surface of a platinum electrode (8). If the initial potential of the platinum is 0.3 v vs. N.H.E., the shifts of the potential to more positive values caused by the adsorption of Tl^+, Pb^{+2}, Cd^{+2}, and Zn^{+2} ions from $0.1N$ solutions with $1N$ H_2SO_4 or $1N$ $HClO_4$ as the supporting electrolyte amount respectively to 0.56, 0.46, 0.32, and 0.12 v. As shown earlier (9, 10), Tl^+ ions are noticeably adsorbed at the mercury-solution interface as well, and the shift of the point of zero charge on substitution of a $1N$ KNO_3 + $0.1N$ $TlNO_3$ solution for $1N$ KNO_3 amounts to 0.265 v (Fig. 2). Specific adsorption at the mercury-solution interface is also observed with Pb^{+2} ions and, according to our data, a certain specific adsorbability, probably increasing with increasing negative charge of the electrode, can be detected even with Cs^+ ions, although the shift of the point of zero charge with Cs^+ ions amounts only to 1-3 mv (11). This last point was contested by the late Professor Grahame, whose untimely death I profoundly regret. To me it does not appear possible to account for the differences between the differential capacity-voltage curves of mercury in CsF and NaF solutions, especially with a positive surface charge, without resorting to this assumption.

We must conclude that the frequently quoted statement that inorganic cations are never specifically adsorbed is incorrect.

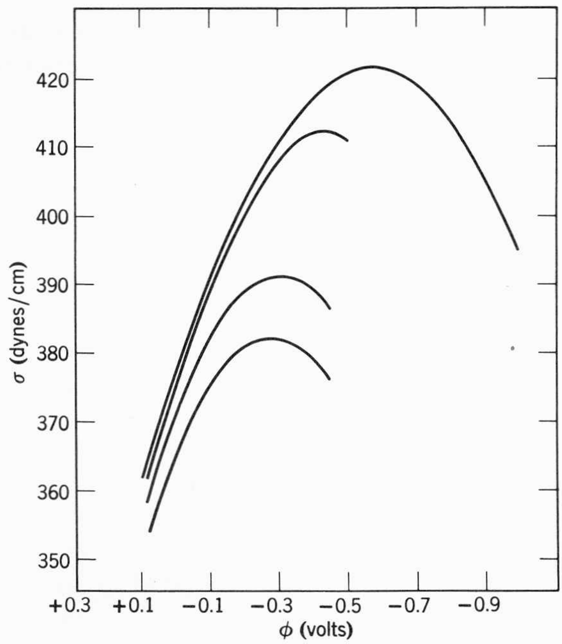

Fig. 2. Electrocapillary curves of mercury in $1N$ $KNO_3 + 0.01N$ $HNO_3 + x$ $TlNO_3$. ϕ vs. N.C.E. Curves from top to bottom: $x = 0$; $0.01N$; $0.1N$; $0.2N$.

As in anion adsorption, the nature of the forces which determine the adsorption of cations may vary within wide limits. The adsorption of the cesium ion is certainly caused by van der Waals' forces, whereas the adsorption of thallium or cadmium ions on platinum appears to be a chemisorption process leading to the formation of some surface compound or surface alloy. The adsorption of these ions changes the chemical properties of the platinum surface, as seen for example from Fig. 3, which shows some charging curves obtained with a platinum electrode before and after adsorption of Cd^{+2}.

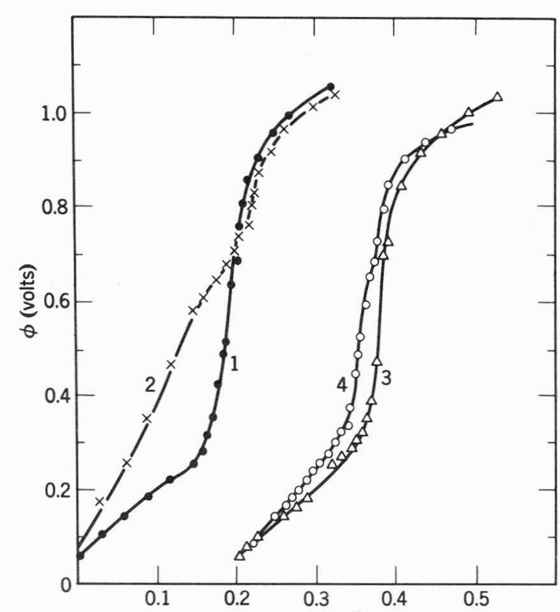

Fig. 3. Effect of Cd^{+2} ions adsorption on the anodic charging curves of platinized Pt. Charging curves: 1. In $1N$ H_2SO_4; 2. In $1N$ $H_2SO_4 + 0.1N$ $CdSO_4$; 3. In $1N$ H_2SO_4 after adsorption of Cd^{+2} from $1N$ H_2SO_4 + $0.1N$ $CdSO_4$ (initial potential 0.3 v) and a repeated washing of the electrode with $1N$ H_2SO_4 that restored the initial form of the curve; 4. In $1N$ H_2SO_4 after the cleaned electrode has been kept in this solution for 80 hr. Curve 4 shows that some Cd reappears on the surface, diffusing back from deeper layers. Curves 3 and 4 are shifted along the abscissas by 0.2 v. The potential ϕ is referred to the hydrogen electrode in $1N$ H_2SO_4.

It was sometimes assumed in earlier works that if ions which can be exchanged between the metal electrode and the solution are absent, adsorption processes may become potential determining. The experiments described here show that this conception is incorrect, inasmuch as the final potential attained by the electrode, when adsorption equilibrium is reached, depends not only on the adsorbability of the ions present in the solution but also on the initial potential of the electrode, which can be fixed independently.

It is possible that the pronounced specific adsorption of some inorganic cations on solid metallic surfaces may play a considerable role in electrodeposition processes.

THE DESORPTION POTENTIAL AND THE KINETICS OF ELECTRODE PROCESSES

At sufficiently negative potentials, surface active inorganic anions are desorbed from the electrode surface; at the desorption potential their action on electrode processes must disappear. The investigation of the action of the adsorption of halogen ions on the hydrogen overvoltage on mercury has so far led to contradictory results. It was found in an earlier work (12) that the potentials at which a deviation of the Tafel line from its rectilinear course caused by the adsorption of anions becomes noticeable are definitely (by 0.14-0.29 v) more negative than the desorption potentials of the anions determined from electrocapillary data. Measurements of hydrogen overvoltage and differential capacity recently carried out by Tsa Chuan-sin and Jofa on dropping mercury electrodes in 1*N* HCl + 2*N* KCl, 1*N* HCl + 2*N* KBr and 1*N* HCl + 2*N* KI have removed this contradiction (13). The authors determined the dependence of the surface charge ξ as well as that of the hydrogen overvoltage η on the composition of the solution and found that the η vs. log i curves of the solutions containing Br^- and I^- begin to diverge from the Tafel line for 1*N* HCl + 2*N* KCl at the same potentials at which differences between the corresponding ξ values become noticeable (Fig. 4, 5). On the basis of the equation of the slow discharge theory

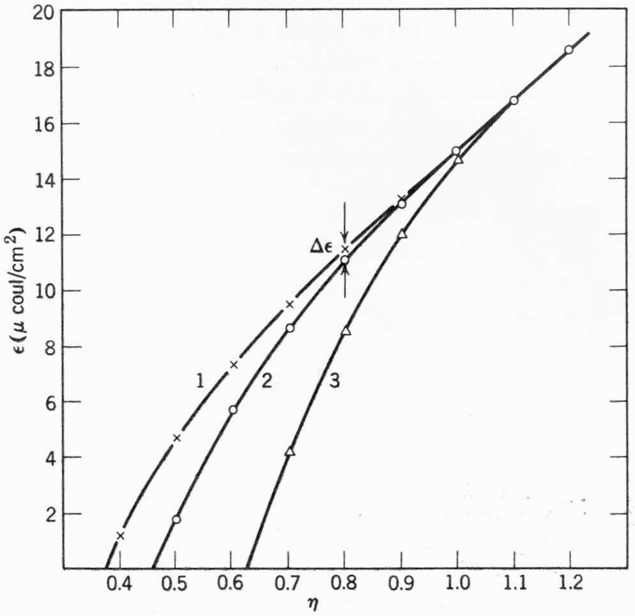

Fig. 4. Dependence of the charge density of mercury ϵ on overvoltage η. 1. 1*N* HCl + 2*N* KCl; 2. 1*N* HCl + 2*N* KBr; 3. 1*N* HCl + 2*N* KI.

$$\eta = \frac{RT}{\alpha F} \ln i - \frac{1-\alpha}{\alpha} \frac{RT}{F} \ln [H_3O]^+ + \frac{1-\alpha}{\alpha} \psi_1 + \text{constant} \tag{1}$$

and of the relation

$$\xi = C(\phi - \psi_1) \tag{2}$$

(i = current density, ϕ = electrode potential, ψ_1 = potential in the plane where the centers of the hydrogen ions are situated, C = capacity of the Helmholtz layer), a simple relation can be established between the lowering of the hydrogen overvoltage and the change of the surface charge $\Delta\xi$ resulting from the specific anion adsorption:

$$\left(\frac{\partial \ln i}{\partial \xi}\right)_\eta = \frac{(1-\alpha)\,F}{RTC} \tag{3}$$

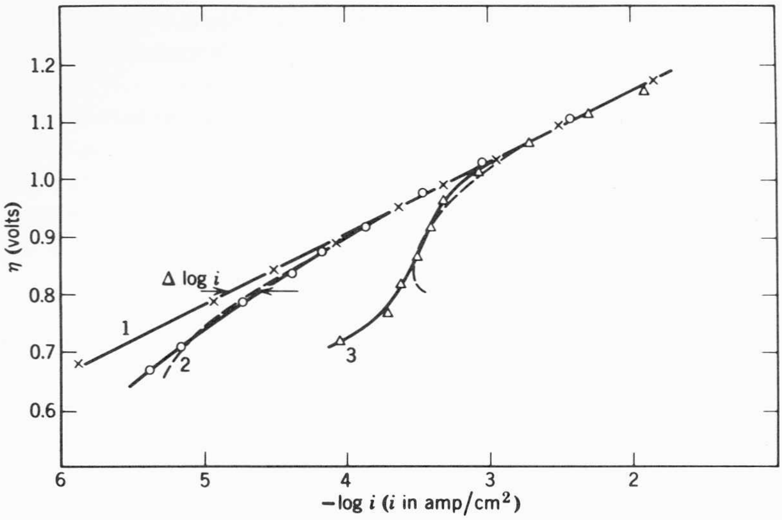

Fig. 5. Dependence of the overvoltage η on the log of the current density i. 1. $1N$ HCl + $2N$ KCl; 2. $1N$ HCl + $2N$ KBr; 3. $1N$ HCl + $2N$ KI. The dotted curves were calculated according to eq. 3.

Equation 3 is only a roughly approximate one because when it was deduced, no distinction was made between the distances of the inner and outer Helmholtz planes from the electrode surface, but the error committed is probably not very great if the negative charge of the electrode is high and the amount of specifically adsorbed anions small. With the help of eq. 3 and by using experimental $\Delta\xi$ values, it is possible to calculate from the current-voltage curves obtained in $1N$ HC1 + $2N$ KC1 the current-voltage curves in solutions containing surface active Br^- and I^- ions. The dotted curves of Fig. 5 have been obtained in this way. If we consider that the calculation has been carried out without introducing any arbitrary constants, there is remarkable agreement between the calculated and the experimentally observed overvoltages, as long as $\Delta\xi$ remains small enough. This shows conclusively that the changes of overvoltage caused by the specific adsorption of anions on mercury depend only on changes in the structure of the double layers.

If the adsorbed anions are bound to the surface by strong covalent bonds, their adsorption must influence the kinetics of electrode reactions in yet another way, that is, by changing the energies of adsorption of the reacting particles or the reaction products. This may lead to an inversion of the effect observed in the adsorption of anions on mercury, that is, to an increase of the hydrogen overvoltage in the presence of surface active anions (1, 14, 15). I shall not dwell further on this point since it is considered in the chapter by Professor Kolotyrkin (Chapter 9), but I should like to emphasize that the relationship between the adsorption of anions and their action on electrode processes is also preserved when the anions are bound to the surface by strong covalent bonds. The electrochemical behavior of the β-phase of the Pd–H system can be quoted as an example. It was shown that the ionization of hydrogen dissolved in palladium proceeds with a great velocity in an acid medium, for instance in $1N$ H_2SO_4, whereas in alkaline solutions a marked overvoltage (16, 17) is observed. L. Shanina has recently found that I^- ions strongly inhibit the reaction

$$\mathrm{Pd{-}H} \rightarrow \mathrm{H^+} + e^- \tag{4}$$

and cause a big increase of the overvoltage when the β-phase saturated with hydrogen at atmospheric pressure is polarized anodically in $1N$ H_2SO_4, whereas for an alkaline solution in which the electrode potential is shifted to negative values and the iodide anions are not adsorbed on the palladium surface I^- anions do not seem to exert any influence on the rate of the ionization process.

It must be kept in mind, however, that although a general parallelism between adsorption and variation of reaction rate is preserved, the relationship between the two groups of phenomena on solid electrodes with an inhomogeneous surface might become more complex. Thus, the adsorption potential of Br^- anions on a Pt electrode reaches a practically constant value after 10-15 minutes, whereas the rate of the ionization of molecular H_2 on active platinum continues to decrease after the electrode has been immersed in this solution for 8 hr (1). This kind of result is not wholly unexpected as the kinetic activity of the platinum electrode may be determined by the conditions on a small but very active part of the electrode surface, which does not markedly influence the adsorption properties of the whole of the electrode surface.

At sufficiently negative potentials, not only anions but such large organic cations as $N(C_4H_9)_4^+$ are desorbed from the electrode surface, which leads to a large increase of the electrode capacity. The desorption of organic cations, unlike the desorption of inorganic anions, does not depend on an electrostatic repulsion but depends on the energy gain resulting from this capacity increase. In this respect there is no pronounced difference between the behavior of organic cations and that of neutral molecules, although the desorption of cations occurs at more negative potentials.

The question of the influence of the double layer electric field on the adsorption of organic molecules has attracted much attention. When dealing with this problem, however, it is usually assumed that Langmuir's adsorption isotherm can be applied to these processes. In fact this isotherm, which can be regarded as a first approximation for the adsorption of small molecules on an uncharged surface, is completely inapplicable to the adsorption of larger molecules at negative potentials.

Figure 6 shows the dependence of the mercury surface coverage θ on the concentration of $N(C_4H_9)_4I$ in the presence of 1*N* KI as determined by B. Damaskin. The measurements were carried out on a growing mercury drop after 4 sec of drop growth ($m = 1.68$ mg/sec). The coverage was estimated from measured differential capacity values as was done by Delahay and Trachtenberg (18), but it was taken into account that in the neighborhood of the desorption potential the measured differential capacity differs somewhat from the capacity at constant coverage which must be used in the calculations. This correction for the conditions of the experiments (low concentrations of the substance adsorbed and an a-c frequency of 10 kc/sec) was small. The dotted curve on the left-hand side of Fig. 6 has been calculated using Ilkovic's equation with the assumption that the area occupied by each adsorbed ion equals 76.7 Å^2 and the diffusion coefficient of $N(C_4H_9)_4^+$ equals $5.2 \cdot 10^{-6}$ cm^2/sec (19). The solid curve 1 was obtained at $\phi = -1.0$ v (vs. N.C.E.), that is, at a potential corresponding approximately to the maximum adsorbability of the organic cation in a 1*N* KI solution. It nearly coincides with the dotted curve, which shows that the coverage is determined here by the diffusion rate. At more negative potentials, to which the curves 2 - 6 refer, the adsorbability of the cation gradually decreases and the determination of the coverage can be carried out by using $N(C_4H_9)_4I$ solutions of a higher concentration. For these conditions, the amount of the surface active substance, which could be supplied by the diffusion process, exceeds the amount that can be adsorbed by a factor of several units; the coverage must therefore approach the equilibrium value. At sufficiently negative potentials and a definite concentration depending on the potential as shown in Fig. 6, the coverage θ is observed to suddenly increase discontinuously from small values to a value close to $\theta = 1$. The formation of the adsorbed layer of tetrabutylammonium iodide at negative potentials and consequently its destruction must therefore be considered as two-dimensional changes of state, the sharpness of the transition increasing with the shift of the potential to negative values.

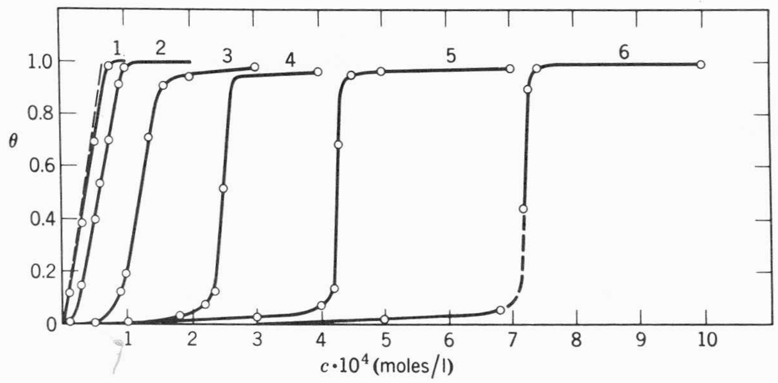

Fig. 6. Dependence of the coverage of a growing mercury drop with an adsorbed layer (θ) on the concentration c of $N(C_4H_9)_4I$ (in the presence of 1*N* KI). 1. $\phi = -1.0$ v; 2. $\phi = -1.3$ v; 3. $\phi = -1.4$ v; 4. $\phi = -1.47$ v; 5. $\phi = -1.5$ v; 6. $\phi = -1.53$ v. The dotted curve was calculated according to the equation of Ilkovic. The potential ϕ is vs. N.C.E.

I should like to add that more than 30 years ago, I worked out a theory for the dependence of the adsorption isotherm shape on the potential drop at the electrode surface (20), which may explain why condensation phenomena in the surface layer appear preferably at very negative potentials. Figure 6 shows that the desorption potential is shifted to more negative values with an increase of the concentration of $N(C_4H_9)_4^+$. The quantitative theory of this phenomenon, also given in the paper quoted, leads to a relationship wholly confirmed by B. Damaskin's measurements. Two-dimensional phase transitions do not occur with substances of a lower molecular weight, but even with a molecule as small as that of *tert*-amyl alcohol the adsorption isotherms at sufficiently negative potentials have a pronounced S-shaped form and strongly deviate from the classical Langmuir type (20).

Adsorbed organic cations exert great influence on electrode processes, either accelerating them, as in the reduction of $S_2O_8^{-2}$ and $Fe(CN)_6^{-3}$, or retarding them, as in the reduction of NO_3^- or BrO_3^- in the presence of Ba^{+2} or La^{+3}. It can be shown that the effects of both signs disappear at the desorption potential of the organic cations (2, 3). Since the desorption potential of large organic cations is sharply defined, the verification of the relationship between adsorption and kinetic effects can be carried out here with a higher degree of accuracy than can a study of inorganic anions which have been discussed.

THE SIMULTANEOUS ADSORPTION OF SURFACE ACTIVE ANIONS AND CATIONS

The specific adsorption of anions on a negatively charged surface is suppressed if the potential drop in the double layer is sufficiently great. This conclusion, however, does not hold if surface active cations are present in the solution. Thus, the interfacial tension at the mercury-solution interface σ is lowered at a transition from a solution of tetrapropylammonium chloride to a solution of tetrapropylammonium iodide of the same concentration not only in the case of a positive surface charge but also in the case of a negative charge (21) (Fig. 7).

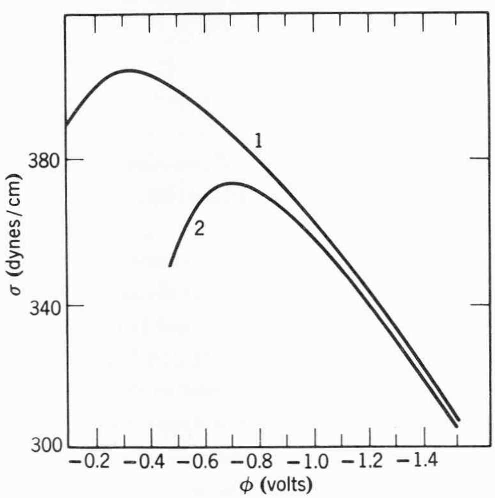

Fig. 7. Electrocapillary curves of mercury. 1. $0.1N\ N(C_3H_7)_4Cl$; 2. $0.1N\ N(C_3H_7)_4I$.

In the presence of the $N(C_4H_9)_4^+$ cations, anions enter the composition of the surface layer even at potentials as negative as the desorption potential. This follows from the fact that the shape of the differential capacity-voltage curves of tetrabutylammonium salts in the neighborhood of the desorption potential depends on the nature of the anion (21) (Fig. 8). It is noteworthy that whereas in solutions containing inorganic cations a substitution of I^- for Cl^- always leads to an increase of the capacity, the opposite effect, that is, a lowering of the capacity, is observed at negative potentials in the presence of $N(C_4H_9)_4^+$. This inversion of the effect of I^- anions can be explained by the assumption that at very negative potentials the $N(C_4H_9)_4^+$ cations approach the electrode surface closer than I^- anions, which are adsorbed on the layer of cations, and that the main result of the presence of I^- anions is to enhance the adsorption of $N(C_4H_9)_4^+$ cations. The presence of I^- anions probably leads to an increase of the attractive forces acting in the adsorbed layer and facilitates the two-dimensional condensation quoted previously.

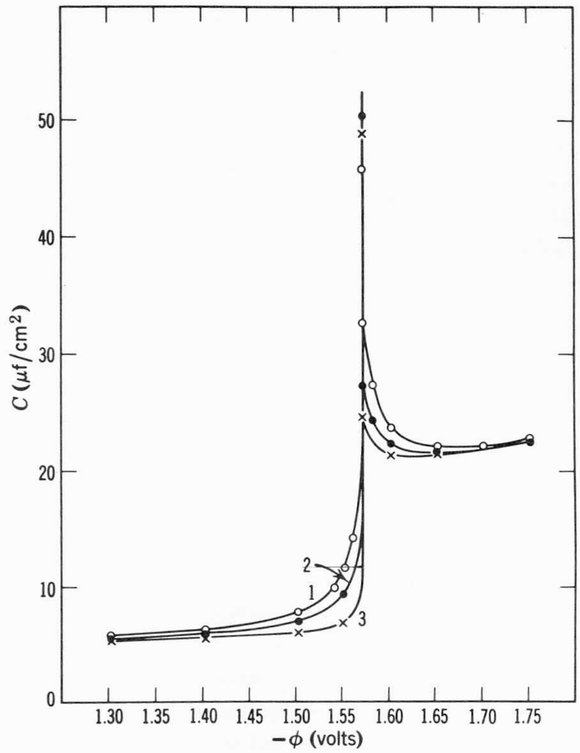

Fig. 8. Dependence of the differential capacity C on the potential in the neighborhood of the desorption potential. 1. $1N$ KCl + $10^{-3}N$ $[N(C_4H_9)_4]_2SO_4$; 2. $1N$ KBr + $10^{-3}N$ $[N(C_4H_9)_4]_2SO_4$; 3. $1N$ KI + $10^{-3}N$ $[N(C_4H_9)_4]_2SO_4$. A-c frequency 1000 cycles/sec.

From differential capacity measurements (22), it follows that at a somewhat less negative potential, the order of the positions of the I^- and $N(C_4H_9)_4^+$ ions relative to the electrode surface changes and the I^- anions come in immediate contact with mercury.

The promoting action of surface-active cations on the adsorption of anions is also manifested in the field of electrode kinetics. In the presence of tetrabutyl- or tetraamylammonium salts, bromine and chlorine anions are drawn into the double layer and inhibit the electroreduction of persulfate at a negatively charged electrode if the negative charge is not too high, whereas in the absence of organic cations this inhibition does not occur (2). In the presence of tribenzylamine, even SO_4^{-2} anions at high concentrations inhibit the reduction of $S_2O_8^{-2}$ on a dropping mercury electrode (23). In the simultaneous adsorption of surface active anions and cations, the sign of the effect exerted on the rate of the electrode reaction depends on their position in relation to the electrode surface (Fig. 9). At potentials more negative than that corresponding to the point "δ," the introduction of I^- in a solution containing $N(C_4H_9)_4^+$ causes an increase of the hydrogen overvoltage on mercury (instead of the usually observed lowering), whereas at potentials more positive than that corresponding to point "a" on addition of $N(C_4H_9)_4^+$ to a solution of I^- anions, a decrease of η instead of the normal increase occurs (22).

A mutual promotion of the adsorption processes is also observed, although to a lesser degree, with inorganic ions. Thus the iodine ion is desorbed from the mercury-solution interface at more negative potentials in the presence of cesium than in the presence of sodium cations. The promotion of the anion adsorption in the presence of specifically adsorbed cations may cause a change of the sign of the adsorption potential. In CsF solutions, that is, in the presence of an inactive anion, the point of zero charge is shifted somewhat to more positive values as compared with a NaF solution. The substitution of a CsI solution for a NaI solution of equal concentration, however, causes a shift of the point of zero charge towards negative potentials since the adsorption of iodine is enhanced in the presence of Cs^+ (11). The promotion of the adsorption of organic cations in the presence of surface active halogen anions or of SH^- may prove of importance in the practical application of corrosion inhibitors (1, 3, 24).

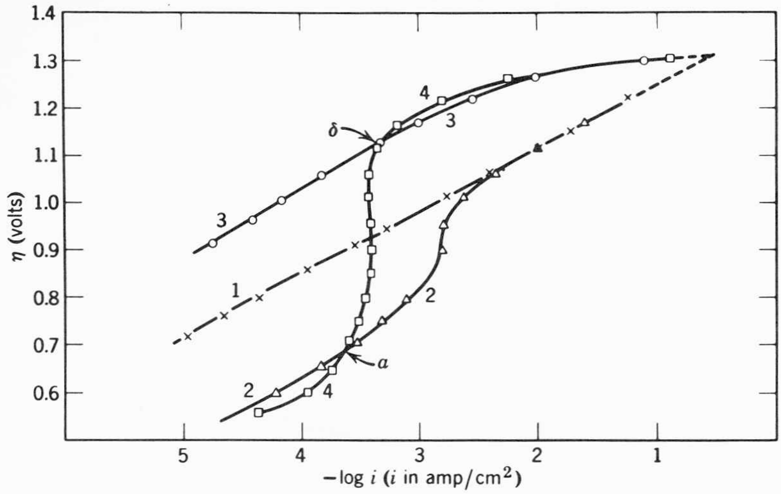

Fig. 9. Dependence of the overvoltage on the log of the current density with a dropping mercury electrode. 1. $2N$ HCl + $2N$ KCl; 2. $2N$ HCl + $2N$ KI; 3. $2N$ HCl + $2N$ KCl + $4.5 \cdot 10^{-4} N$ $N(C_4H_9)_4Br$; 4. $2N$ HCl + $2N$ KI + $4.5 \cdot 10^{-4} N$ $N(C_4H_9)_4Br$.

THE CATALYSIS OF THE ELECTROREDUCTION OF THE XO_3^- TYPE ANIONS BY La^{+3} IONS

The action exerted by inorganic electrolytes on the rate of electrode processes is determined in the cases considered so far by the adsorption of ions present in the electrolytic solution. The phenomena observed in the reduction of NO_3^-, BrO_3^- or IO_3^- ions in the presence of lanthanum salts are more complex. The rate of reduction process is known to strongly increase under these conditions on alkalization of the solution, which is the cause of the autocatalytic character of this process when carried out at a dropping electrode in an unbuffered medium and of the appearance of discontinuous changes of current density and of hysteresis loops in the polarograms (25). If the solution contains La^{+3} at a low concentration, the current density in a certain potential region rapidly diminishes with the increase of the height of the mercury column (26). This anomalous dependence points to a slow rate of the formation of the catalytically active substance in the vicinity of the electrode surface. It is possible that the actual catalyst is some form of lanthanum polycations, appearing as a result of the interaction between La^{+3} ions and OH^- ions produced by the reduction of NO_3^-. Measurements of the differential capacity of the mercury electrode in an alkaline solution of $LaCl_3$ also show that the equilibrium in the surface layer is slowly established (27). The concept according to which the enhancing of the catalytic action of the La^{+3} cations in the presence of OH^- ions is connected with the hydrolysis of lanthanum ions was formulated for the first time by Z. Grabowski (28).

THE MECHANISM OF THE REDUCTION OF $Fe(CN)_6^{-3}$ ANIONS

The influence of the double-layer structure on electrode kinetics is most pronounced in the case of the electroreduction of anions at electrodes with a negatively charged surface. I shall not try to give here a review of this problem already treated in a number of publications (1, 2, 3, 21, 29, 30, 31), but shall restrict myself to one particularly interesting problem, the electroreduction of the $Fe(CN)_6^{-3}$ anion.

In the polarograms of dilute solutions of ferricyanides, such as $10^{-3}N$ $K_3Fe(CN)_6$, a falling off of the current is observed at negative potentials (32). As the current density shows only a small dependence on the potential in the potential interval from −1.12 to −2.0 v (vs. N.C.E.), it could be assumed that in this region the rate-determining step is a chemical reaction in the bulk of the solution or in the surface layer preceding the electron transfer. More exact determinations of the dependence of the reaction rate on the potential, carried out quite recently by O. Petrij, do not confirm this assumption however. They have shown that the apparent independence of the current on the potential disappears if a correction for the variation of the drop time with the potential is introduced, the latter being very pronounced at these negative potentials. This correction transforms the horizontal part of the current-voltage curve to a flat minimum with a considerable rise of the current density at the negative end of

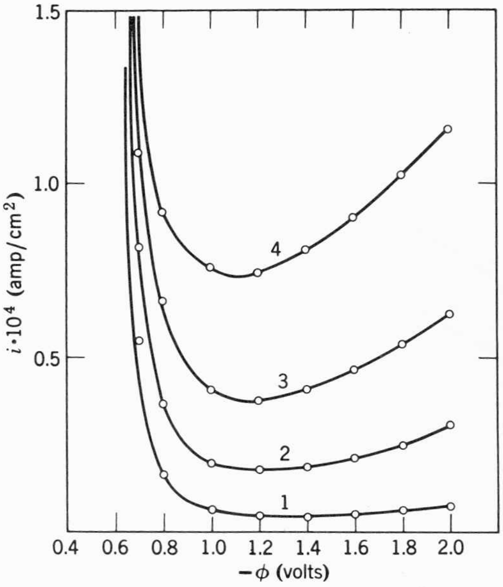

Fig. 10. Dependence of the rate of the electroreduction of $Fe(CN)_6^{-3}$ on the potential (vs. N.C.E.). The rates are given per cm^2. 1. $10^{-3}N$ $K_3Fe(CN)_6$; 2. $10^{-3}N$ $K_3Fe(CN)_6 + 0.5 \cdot 10^{-3}N$ KCl; 3. $10^{-3}N$ $K_3Fe(CN)_6 + 10^{-3}N$ KCl; 4. $10^{-3}N$ $K_3Fe(CN)_6 + 1.5 \cdot 10^{-3}N$ KCl.

the curve. Figure 10 represents the dependence of the rate of the reduction of $Fe(CN)_6^{-3}$ anions on the potential in the presence of different concentrations of KCl. The rates per cm^2 have been calculated from experimental values of the current on a dropping electrode with a correction for concentration polarization applied on the basis of Meiman's exact theory (33) and the variation of drop time with the potential taken into account (the usual correction for the charging current, of course, was applied as well).

In Figure 11, similar curves are given for solutions containing $Li_3Fe(CN)_6$ + LiCl; the measurements here could be extended to a somewhat more negative potential, that is, to −2.2 v. The dependence of the rate of the reduction of the $Fe(CN)_6^{-3}$ anion on the potential in the presence of K^+ ions at sufficiently negative potentials can be represented approximately with the help of the relation

$$i = K[A]\,\phi_a^{-(6+2\alpha)} \exp -\left(\frac{\alpha\phi_a F}{RT}\right) \tag{5}$$

where the transfer coefficient α equals 0.16 and the potential ϕ_a is referred to the point of zero charge. $[A]$ denotes the concentration of the anion in the solution. Equation 5 can be deduced from the relation

$$i = K_1 \exp\left\{[-\alpha\phi + (3+\alpha)\psi_1]\frac{F}{RT}\right\} \tag{6}$$

(which expresses the rate of the reduction of a trivalent anion in the absence of concentration polarization according to the slow discharge theory in its most elementary form) by substituting the approximate expression for ψ_1:

$$\psi_1 = \text{constant} + \frac{2RT}{F}\ln(-\phi_a) + \frac{RT}{F}\ln c \tag{7}$$

where c denotes the concentration of the univalent cation in the bulk of the solution.

It follows from eq. 6 and 7 that the rate of the reaction must be proportional to $c^{3+\alpha}$. This conclusion is in full agreement with experimental data. The current densities, calculated with the help of eq. 5, agree with experimental values within 20% at potentials more negative than −1.15 v. It should be added that in the presence of $K_4Fe(CN)_6$ the rate of the $Fe(CN)_6^{-3}$ reduction is lower than in the presence of KCl of the same normality. A similar relation is observed if we compare the reduction rates of $S_2O_8^{-2}$ with K_2SO_4 and KCl as supporting electrolytes.

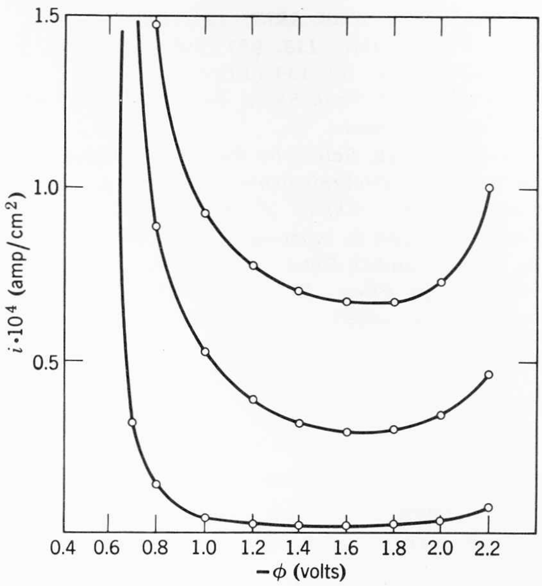

Fig. 11. Dependence of the rate of the electroreduction on the potential (vs. N.C.E.). 1. $10^{-3}N$ $Li_3Fe(CN)_6$; 2. $10^{-3}N$ $Li_3Fe(CN)_6 + 2 \cdot 10^{-3}N$ LiCl; 3. $10^{-3}N$ $Li_3Fe(CN)_6 + 3 \cdot 10^{-3}N$ LiCl.

The experimental facts accumulated so far show that there exists no fundamental difference between the mechanisms of the reduction of $Fe(CN)_6^{-3}$ and $S_2O_8^{-2}$ anions. In both reductions the strong dependence of the reaction rate on the radius of the cation (the rate of $Fe(CN)_6^{-3}$ reduction increasing ca. 4 times on substituting Cs^+ for K^+) as well as the value of the temperature coefficient point to the great importance of the interaction between the anion and the next neighboring cation in the double layer. It is possible that for the trivalent ferricyanide anion the simultaneous interaction with two or three neighboring cations has to be taken into account. Since these interactions have not been considered while deducing eq. 5, such calculations can give only roughly approximate results.

I have tried to show that the close connection between the adsorption of ions and their participation in electrode processes can be demonstrated with the help of many independent methods. I think that the results obtained may help to solve similar problems in other branches of electrochemical kinetics where the role of the adsorption of the reacting substance has not been sufficiently elucidated up to now. An example of this lack of clarification is the irreversible reduction of many organic compounds.

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DISCUSSION

Professor P. Delahay (communicated): In connection with Professor Frumkin's work on the reduction of ferricyanide, I should like to report briefly on some recent work Mr. Kleinerman did in our laboratory on the reduction of chromicyanide on the dropping mercury electrode. This is a fast electrode reaction which was originally studied by Randles and Somerton.[1] Our preliminary results on the effect of the double layer structure on the exchange current density are given in Fig. *D*-1. The transfer coefficient was also determined and found equal to 0.57. Measurements were not made for concentrations below $0.1M$ potassium cyanide because of the danger of decomposition of chromicyanide.

The slope of the line log i_0 against ψ for the higher electrolyte concentrations agrees with the theoretical value (no specific adsorption) $(\alpha + 3)F/RT$ with $\alpha = 0.57$ and without consideration of the effect of current on the distribution of chromi- and chromocyanide in the double layer. The latter effect is relatively small in the present case. The exchange current density, however, is appreciably larger than expected for the lower electrolyte concentrations. This difference may be related to the cation effect discussed by Professor Frumkin, or there may be some spurious effect (impurities, etc.). Further work is now in progress.

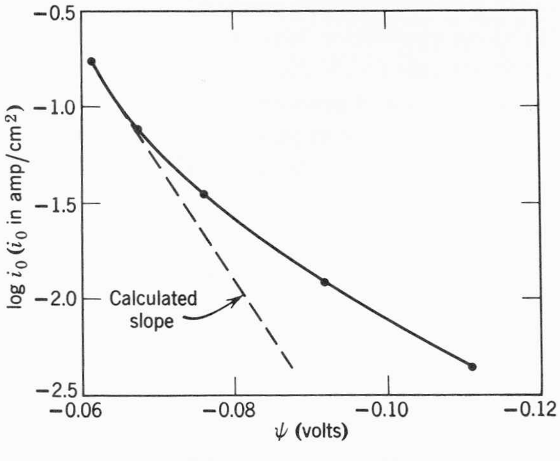

Fig. *D*-1. Variations of the exchange current density with the difference of potential ψ across the diffuse double layer at 30°C for the reaction $Cr(CN)_6^{-3} + e^- = Cr(CN)_6^{-4}$ on mercury. Equal concentrations of potassium chromi- and chromocyanide ($2.5 \times 10^{-3}M$), $0.1M$ potassium cyanide, and varying concentration of potassium chloride (0, 0.1, 0.3, 0.5, and $0.7M$).

I also should like to discuss briefly minima that were observed by Mr. Kleinerman in our laboratory for the reduction of chromate on a dropping thallium amalgam electrode. Results are summarized in Fig. *D*-2. Minima are not observed with the dropping mercury electrode. Reference is made to my comments on Dr. Gierst's paper (Chapter 5) for a discussion of the dropping thallium electrode.

Further work is now in progress, and only the *very tentative* conclusion can be advanced that this type of minimum is similar to those obtained in the reduction of some other anions (cf. the work of Frumkin and his school).

[1] J. Randles and K. Somerton, *Trans. Faraday Soc., 48,* 937 (1952).

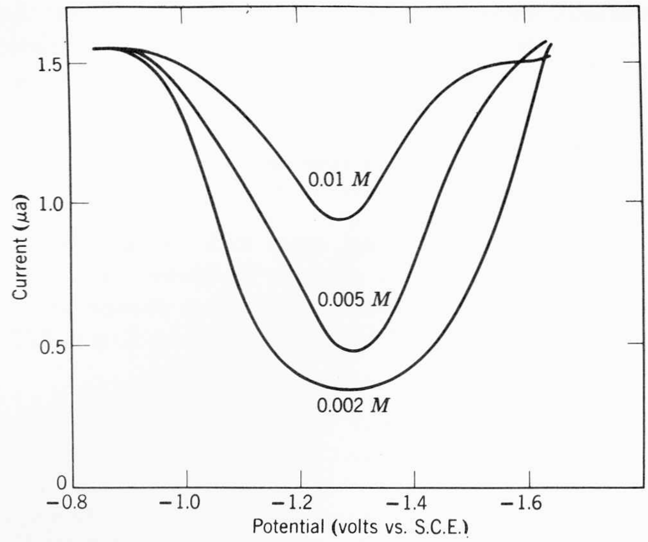

Fig. D-2. Current-potential curves for the reduction of sodium chromate ($10^{-4}M$) on a dropping thallium amalgam electrode (3.4% Tl) at 30°C in sodium hydroxide of varying concentration. Rate of amalgam flow, 0.98 mg/sec; drop time at − 1.3 v, 5.48 sec.

Dr. P. Rüetschi (communicated): Professor Frumkin points out that "adsorption potentials at the metal-solution interface can be considered as a measure of the electric effect produced by ionic adsorption, although they should not be identified with the potential difference between the plane where the centers of the ions adsorbed are situated and the interior of the solution." In another paper presented at the same meeting of the Society (1) I have arrived at identical conclusions. The electrochemical interface (double layer) can be treated as a condenser. Adsorption of foreign species will change the charge of this condenser, and therefore, its voltage. In this manner the influence of foreign adsorbed species on hydrogen overvoltage can be explained quantitatively. Anions will compensate the charge of accumulation protons in the interface, decrease the positive charge on the solution side of the interface, and decrease hydrogen overvoltage. Adsorbed cations will add to the positive charge of accumulating protons and increase hydrogen overvoltage.

The electrostatic energy E of a condenser is given by $E = \frac{1}{2} CV^2 = \frac{1}{2} qV$ where C = capacity, q = charge, and V = voltage. It is interesting to note that the integrated Lippmann equation for the relation between surface energy and electrode potential has for constant capacity C exactly this form. The energy per unit charge is then $E/q = V/2$ and per charge $Z_i e_o$ (where Z_i is the valence and e_o the electronic charge) is $\frac{1}{2} Z_i e_o V$. The energy E of a species in the double layer (and thus in the "initial" state of the electrode reaction) varies therefore with potential according to

$$E = (\tfrac{1}{2} Z_i e_o \, \Delta V) + E_o$$

If now Boltzmann statistics are used for the distribution of the energy states between the bulk and double layer, the term in the bracket becomes the exponent over RT of an exponential, and the Volmer equation is recovered immediately with $\alpha = 1/2$. The voltage change ΔV is the one produced by the reacting species only (in the case of hydrogen evolution by accumulating protons). If foreign adsorbed species like anions contribute to (or rather subtract from) the total voltage variation of the double layer, then ΔV must be replaced by $\Delta V_{\text{total}} - \Delta V_{\text{foreign}}$. This then immediately explains the ψ_1 −potential term in Frumkin's theory of overvoltage. These considerations are given in more detail in my paper.[1]

It is interesting to note that the factor 1/2 in the integrated Lippmann equation and in the Volmer equation have the same origin. It stems from the energetic considerations on the basis of a condenser model. The charges in the double layer (in the "initial" state of the electrode reaction) are subject to the field in the double layer and their energetic state changes with the field (or voltage) in the manner indicated above.

Finally, I would like to point out that the relation between changes in adsorption energy on solid-gas interfaces and changes in work function with coverage as discovered by Boudart and Mignolet also have their origin in electrostatic interaction like in a condenser. One finds that the change in adsorption energy ΔE with coverage is related to the change in electronic work function $\Delta\phi$, according to $\Delta E = \frac{1}{2} Z_i e_o (\Delta\phi)$ where $Z_i e_o$ is the charge of the dipole formed. The energetic considerations for a condenser apply here also.

[1] P. Rüetschi, Paper 189, National Meeting, Electrochemical Society, Philadelphia, May 1959. (*Enlarged Abstracts, Theoretical Division*, p. 79.)

Professor A. Frumkin (communicated): I cannot agree with the explanation of the appearance of the coefficient 1/2 in the slow discharge theory given by P. Rüetschi in his contribution to the discussion. The electrostatic term in the expression for the energy change per unit charge occurring on the discharge of a hydrogen ion is given by $\partial E/\partial q = V$ and not by $E/q = V/2$ as assumed by P. Rüetschi.

Dr. R. Parsons (communicated): There appears to be a discrepancy between the calculation presented by Professor Frumkin in his Fig. 5 and the claim made in my paper that Professor Frumkin's eq. (1) is only semiquantitave when ions from the base solution are specifically adsorbed. I believe that this arises from differences in the method of calculating the outer Helmholtz potential ϕ_2. If we use my eq. (23) together with Grahame's results for $0.9N$ NaF[1] and $1N$ KI,[2] we find that the greatest difference in ϕ_2 between these solutions in the hydrogen overvoltage region is about 35 mv which should lead to an overvoltage in $1N$ KI lower by this amount than in a solution in which there is no specific adsorption. This should be directly comparable with the results of Jofa et al.[3] where a lowering of up to 300 mv was observed. A detailed comparison is shown in Fig. *P*-1.

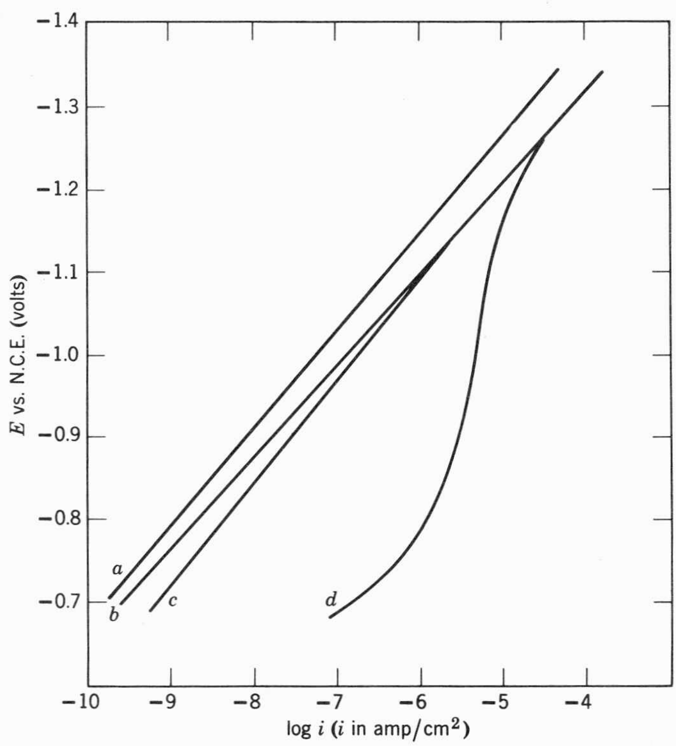

Fig. *P*-1. Tafel lines for hydrogen evolution: *a*. calculated with $\alpha = 1/2$ and $\phi_2 = 0$; *b*. calculated with $\alpha = 1/2$ and ϕ_2 for $0.9N$ NaF; *c*. calculated with $\alpha = 1/2$ and ϕ_2 for $1N$ KI; *d*. experimental for $1N$ KI + $0.1N$ HCl from ref. 3.

This suggests that the error in Professor Frumkin's "roughly approximate" method of estimating ϕ_2 is greater than he expected and that his eq. 1 does not account quantitatively for this effect if the hydrogen ion is assumed to be in the outer Helmholtz plane. It seems likely that the specifically adsorbed anion pulls the hydrogen ion closer to the electrode, or as Professor Frumkin has previously suggested,[4] there are considerable local variations in the potential.

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Professor A. Frumkin (communicated): The errors resulting from the approximations introduced in the derivation of eq. 1 are probably of minor importance in the case of a small adsorption of anions on a negatively charged surface, which is considered in my paper.