DOUBLE LAYER ADSORPTION:

DISCUSSION

Interpretation of Differential-Capacity Curves Obtained on a Metal-Solution Interphase by D. Grahame

J. O'M. Bockris. The resistance of the double layer of a mercury electrode varies with frequency over quite a wide range; at the same time the capacity is independent of frequency (at least up to 10^5 cps). This effect has been observed by different authors and on cells with different arrangements of the electrodes so that it can hardly be caused by experimental errors.

Let us assume that τ is the relaxation time of water adsorbed in the double layer. It is readily shown that in the double layer appear a pseudocapacity and a pseudoresistance, which may be expressed approximately by the following relations:

$$\Delta C = \frac{C_0 \Delta\varepsilon \omega^2 \tau^2}{1 + \omega^2 \tau^2}, \tag{1}$$

$$R = \frac{1}{C_0 \Delta\varepsilon}\left[1 + \frac{1}{\omega^2 \tau^2}\right], \tag{2}$$

where C_0 is a constant, $\Delta\epsilon$ is the change in dielectric constant, and ω is the frequency.

From these relations it follows that at low frequencies the pseudocapacity is small; it begins to change with the frequency of the order of $1/\tau$, and at very high frequencies the capacity of the double layer will be less than the capacity at low frequencies by the value $C_0\Delta\epsilon$. The pseudoresistance has a high value at low frequencies and at high frequencies it tends to $1/C_0\Delta\epsilon$. From this it follows that the double layer on a mercury electrode surface does not represent a pure capacity, but should be represented by a capacity and a resistance connected in parallel. The problem of the need for allowing for this resistance depends on its relative value (i.e., on the frequency used). For mercury in 1 N KI good agreement between theory and experiment is obtained if it is assumed that τ equals 10^8 sec. We should note in passing that at this value of τ, the effect of frequency on the capacity could be detected only at frequencies of the order of 10^8 cps and above.

The physical meaning of this phenomenon is that the adsorbed water molecule may be on the surface in two (mirror opposite) positions; in both positions the direction of the dipole moment is not perpendicular to the surface. The action of an electrical field consists of the fact that it tends to turn the dipole so that it is perpendicular to the surface. A detailed calculation on this model will be published elsewhere.

D. Grahame. It is possible to raise one objection to the theory proposed by Bockris. It concerns the relation of the dispersion of resistance, which this theory attempts to explain, to the solution concentration. Experimental data show that this dispersion is approximately proportional to the specific resistance of the solution. Moreover, according to the theory proposed the dispersion should be almost independent of the solution concentration as it is determined mainly by the water concentration. It should be emphasized that this dispersion of the resistance may be caused by the fact that it is impossible to attain an alternating current density which is completely identical on all sections of the surface of the electrode studied.

DISCUSSION

Kinetics of Electrochemical Reactions and the Electrocapillary Zero of Metals

by L. I. Antropov

J. O'M. Bockris. In connection with the opinion of L. I. Antropov that in the electrodeposition of metals the limiting stages may be either the discharge of ions or the crystallization of the metal, I would like to note the value of calculating the curve of the change in free energy during these reactions. The position of maximum energy on such a curve characterizes the nature of the limiting stage. These curves were calculated for various metals by Conway and Bockris. The general nature of these curves was identical for different metals: In the first stage, the discharge of the metal ion, the free energy increases to a maximum and then falls sharply. The deep energy minimum corresponds to the state of partial binding of the discharging ion by the metal surface. There are then two stages with two very slight energy maxima, which correspond to diffusion processes of the discharge particle along the surface and crystallization of the metal. In the reaction studied the fall in free energy after the discharge was so great that subsequent maxima were still much less than the maximum value of the free energy in the transition stage of the discharge act. This effect was expressed so sharply that it confirms the statement that the slow stage in the electrodeposition of metals is the discharge stage.

S. V. Gorbachev. Bockris stated that when we are considering the liberation of metals, in all cases the limiting stage must be the discharge of ions. I recall that this conclusion was drawn on the basis of energy calculations. Bockris' conclusion will be correct when thermodynamics apply, but thermodynamics apply when there is no process. Energetics determine the equilibrium, but when there is a process another factor may be the limiting one. This may be seen if the relation of activation energy to potential is followed. At low potentials, the activation energy is large. At very high process rates, the limiting factor may be yet another one, which in energy effect is third order and less effective, diffusion, for example.

In conclusion I would like to say that at the present time the theory of slow discharge lays claim to the role of universal theory of electrolysis processes, although it is quite clear that the whole complexity of electrochemical reactions cannot be embraced by a single theory.

V. V. Krasnoyarskii. In connection with the report of L. I. Antropov I wish to consider the problem of the kinetics of electrode processes in the cathodic protection of metals from corrosion. By considering the rules of the kinetics of electrode processes it is possible to derive quantitative relations between the rate of corrosion under stationary conditions (i_{corr}), the magnitude of the polarizing current (i_p), the displacement of the potential in a negative direction, and the degree of protection. In accordance with A. N. Frumkin's theory of conjugated electrochemical reactions, all the reactions that are possible under the given conditions (discharge and ionization of hydrogen and metal and reduction of oxygen) proceed on the surface of the metal immersed in an electrolyte. However, the rate of solution of the metal is frequently determined by a single cathode reaction. Thus, for metals of the iron group in acid media, the rate of ionization of the metal is determined largely by the discharge of hydrogen ions, while in neutral and alkaline electrolytes, oxygen depolarization is of decisive importance. In these cases the change in the rates of the anode and cathode processes with a displacement of the electrode potential in a negative direction, may be expressed in the following way:

$$\Delta\varphi = \varphi_{dir} - \varphi' = b_a \lg \frac{i_{corr}}{i_a} = b_c \lg \frac{i_c}{i_{corr}} \qquad (1)$$

where b_a and b_c are the slopes of the anode and cathode polarization curves in the semilogarithmic system of coordinates $\Delta\varphi$, $\lg i_p$ $\left(b = \frac{2RT}{nF} \cdot 2.303\right)$, while i_a and i_c are the rates of the true anode and cathode processes during cathode polarization of the electrodes by a current i_p.

Since $i_p = i_c - i_a$, then the degree of protection $P = \frac{i_{corr} - i_a}{i_{corr}} \cdot 100$, reached at given values of i_p or $\Delta\varphi$, may be calculated by substituting the value of i_p in equation (1). It is no less interesting to evaluate the efficiency of protection $E = \frac{i_{corr} - i_a}{i_p} \cdot 100$.

The relation of P and E, calculated in this way, to $\Delta\varphi$ and i_p/i_{corr} is given in the table.

Degree of Protection P and Efficiency of Protection E of a Metal from Corrosion at Various Values of i_p/i_{corr} and $\Delta\varphi$

i_p/i_{corr}	$\Delta\varphi$, v	P	E	i_p/i_{corr}	$\Delta\varphi$, v	P	E
		%				%	
0,16	0,00267	10	62,5	2,02	0,0404	80	39,6
0,31	0,00545	20	64,5	3,06	0,0580	90	29,4
0,49	0,0093	30	61,2	5,02	0,0708	94	23,4
0,688	0,0127	40	58,2	9,99	0,116	99	19,9
0,91	0,0174	50	55,0	14,135	0,133	99,5	7,04
1,00	0,0193	53,5	53,5	31,599	0,174	99,9	3,16
1,18	0,0230	61	50,8	99,999	0,232	99,99	1,00
1,52	0,0310	70	46,0	315,999	0,290	99,999	0,32

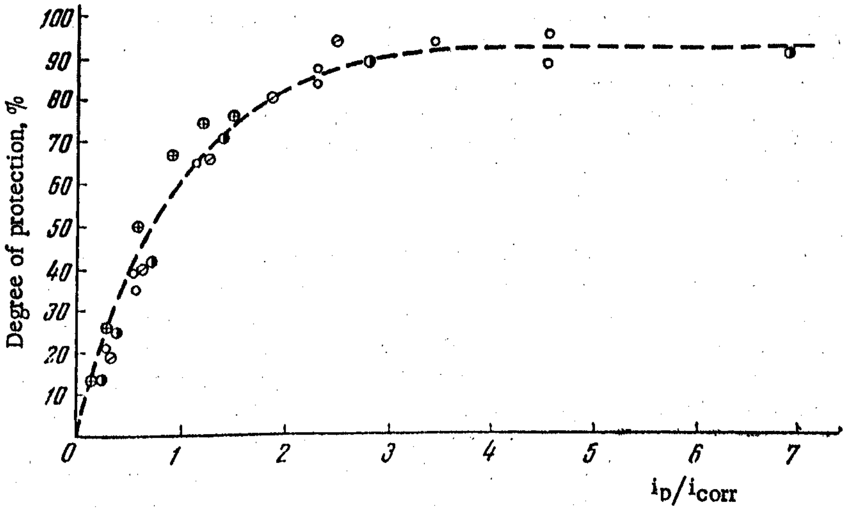

Fig. 1. Relation of degree of protection of steel to cathode current density (from the data of Clement and Walker) in 10^{-3} N H_2SO_4 in an oxygen atmosphere with the solution stirred at the following rates: 0(⊕); 35(◐); 110(∅); 450(○) rev/min.

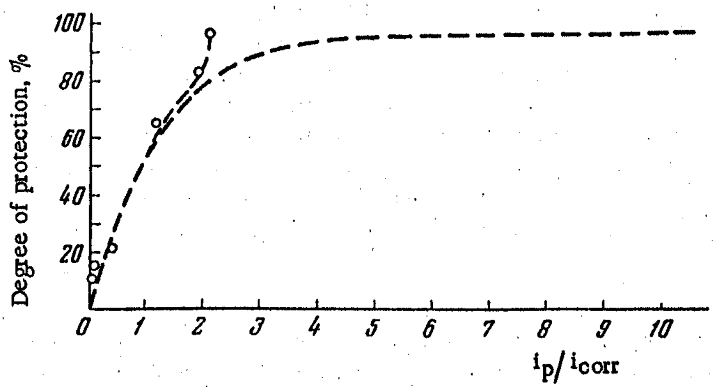

Fig. 2. Effect of concentration polarization on the degree of protection when the limiting density of the oxygen diffusion current is reached (according to the data of Bannister).

DISCUSSION

Good agreement is observed in a comparison of experimental data with a theoretical curve, which is shown, for example, for one particular case in Fig. 1. Analogous treatment of the results of Ken and Wilhelm, Caldwell and Albano, and other authors showed that the experimental conditions (electrolyte composition, electrolyte stirring rate, composition of the gas phase over the electrolyte, etc.), determining the corrosion rate, did not affect a plot of P against i_p/i_{corr}. In this connection, it is interesting to examine the mechanism of combined protection by the action of inhibitors and cathode polarization. In the presence of an inhibitor there is an increase in the overvoltage of the cathode and anode processes and, correspondingly, a fall in the corrosition rate. Under these conditions, the protecting current, which is lower in absolute value, cannot serve as an index of the increase in the efficiency of electrochemical protection, as was stated by L. I. Antropov. In actual fact, the ratio i_p/i_{corr} necessary to attain a given degree of protection remains constant if the change in the corrosion conditions does not lead to the formation of multilayer absorption films with a high electrical resistance or to the appearance of concentration polarization. As a result of concentration polarization a high degree of protection is attained at lower values of the ratio i_p/i_{corr}. As the limiting diffusion current is approached in cathode polarization of the protected object, there is a sudden approach to practically complete protection (Fig. 2). In treatment of the data of I. N. Frantsevich, V. F. Negreev, A. A. Farkhadov, V. P. Saraev, and others, in whose experiments concentration polarization was not eliminated, analogous deviations from the theoretical curve are observed. The relations examined were applied successfully in the planning of electrochemical protection.

M. A. Gerovich. Even in 1928 A. N. Frumkin observed the anomalous behavior of some derivatives of aromatic compounds, such as mono- and polyhydric phenols, in adsorption at a mercury--solution boundary which appeared as a displacement of the electrocapillary zero of the surface toward more negative potentials and as a higher adsorbability in comparison with the solution--air boundary. A. N. Frumkin considered that the reason for this behavior of aromatic compounds was more planar orientation of the molecules of the latter at the mercury-solution boundary, which facilitated the interaction of negatively charged polar groups, in particular, OH groups, with the metal surface.

In further development of this work in the electrochemistry department of the M. V. Lomonosov Moscow State University, a study was made of the electrocapillary behavior of aromatic hydrocarbons, such as benzene, naphthalene, anthracene, etc., which have no polar properties. In this work we observed a qualitatively analogous displacement of the electrocapillary zero and their predominant adsorption on a positively charged mercury surface. The displacement of the maximum of the electrocapillary zero curve toward negative potentials and the predominant adsorption on a positively charged mercury surface increased with an increase in the number of benzene rings. These observations indicate that the appearance of negative jumps in potential during the adsorption of aromatic hydrocarbons does not require the presence of a polar group and is evidently caused by the properties of the benzene ring itself, in which the bond between carbon atoms is affected by means of π electrons. A comparison of electrocapillary curves for aromatic and the corresponding hydroaromatic compounds, which do not have π electrons, for example, benzene--cyclohexane and naphthalene--decalin, shows that hydroaromatic hydrocarbons, which do not have an aromatic nature, are not adsorbed on a positively charged metal surface and behave similarly to aliphatic compounds displacing the maximum of the electrocapillary curve toward positive potentials.

This gave grounds for putting forward the hypothesis that the predominant adsorption on a positively charged mercury surface is caused by interaction between the π electrons of the benzene ring, which effect the bond between the carbon atoms, and the positive charges of the metal surface. As follows from recent literature data, a similar interaction plays a substantial role in a number of chemical conversions of the acceptor--donor type, involving aromatic hydrocarbons. As Andrews and Keefer showed, this type of reaction includes the interaction between aromatic hydrocarbons and Ag^+ ions, leading to the formation of molecular complexes of the type $AgAr^+$ in which the positive charge of the silver is transferred to the aromatic nucleus. It may be imagined that in our case there is an analogous interaction in which the charge of the metal is partially transferred to the benzene ring.

This idea on the nature of the adsorption effect of aromatic hydrocarbons was also confirmed by the electrocapillary behavior of compounds without an aromatic nature, but having π electrons. Thus, for example, unsaturated cyclic hydrocarbons, cyclohexene and cyclohexadiene are adsorbed on a positively charged mercury surface. The unsaturated hydrocarbons may be arranged in the following series with respect to increasing adsorbability: cyclohexene < cyclohexadiene < benzene. The relation between the adsorbability of these compounds, expressed through the depression of surface tension, and the number of double bonds or π electrons is linear in the first approximation. Unsaturated aliphatic hydrocarbons, such as 1,5-hexadiene and 2,4-hexadiene behave analogously.

Finally, an investigation was made of the adsorption properties of compounds of the ionic type in which the aromatic ring is a cation. Electrocapillary curves of a solution of tropylium perchlorate, a compound consisting of a seven-membered ring with three double bonds, forming the cation, and a perchlorate anion, showed that despite the positive charge, the cation is strongly adsorbed on a positively charged mercury surface which is undoubtedly connected with the predominating effect of the π-electron interaction.

A. G. Stromberg. The literature contains a statement that in the case of molecular substances, the penetration of depolarizer ions through the film of these substances is of prime importance to the kinetics of the electrode process, while for ionic substances, their effect on the discharge--ionization process itself, which is normally characterized by the φ_1 potential, is recognized. In this connection I would like to say a few words on our recent study on the effect of camphors, typical molecular substances, on the discharge of Cd^{2+} ions, from which it follows quite clearly that this effect is connected largely with the change in the φ_1 potential. We carried out experiments on a cadmium amalgam electrode, studied the effect of camphor concentration on the electrode process, and compared these data with electrocapillary curves. The maximum on the electrocapillary curve was displaced by the addition of camphor by 0.3 v; this indicates that despite the absence of excess charge camphor has a high dipole moment, which produces the displacement in the φ_1 potential. From the theory of slow discharge--ionization it may be shown that the relation between the anode half-wave potential of the cadmium amalgam and the φ_1 potential should be linear with a slope of unity, while for the cathode wave there should be an analogous linear wave relation but with a slope equal to β/α. When we compared these values, a plot of the anode half-wave potential against the φ_1 potential at the same potential at which we measured the half-wave potential, gave a straight line with a slope of about unity for the anode wave and close to β/α for the cathode wave. This fact and a number of others on which I will not dwell show that in the case of molecular substances, the change in φ_1 potential may play a decisive role.

Our study of the effect of tetrabutylammonium on the discharge of Cd^{2+} ions also lead to interesting results. In the case of this typical organic cation one might have expected the effect of the φ_1 potential in the pure form. However, it was found that there, together with slow discharge--ionization, there was still depression of the limiting current.

We considered that by covering part of the surface, tetrabutylammonium cations decrease the surface on which discharge proceeds and thus decrease the limiting current. If the surface density of tetrabutylammonium ions is denoted by G and that for complete filling of the surface by G_∞, then the fraction of free surface will equal $1 - G/G_\infty$. Calculation showed quantitative agreement with experiment. Thus, it is also necessary to consider screening of the surface by large organic molecules.

Z. Ch. Grabowski. L. I. Antropov put forward the hypothesis that the adsorption of organic compounds on the electrode surface is a necessary condition of the reduction. However, the vast experimental material on the polarographic reduction of organic compounds on mercury shows that reduction proceeds even at very negative potentials (-2.5 v) at which there is no appreciable adsorption of neutral molecules and particularly molecules of a completely nonpolar character, e.g., unsaturated hydrocarbons. If this hypothesis is correct, then reduction should cease at the desorption potentials of the organic substances. I know of two cases of a fall in current strength with an increase in negative potential (phenolphthalein and benzophenone oxime), but for these cases there is evidence of a chemical reaction preceding the true electrode stage. From the work of Siekierski it follows that the rate of the process may be a complex function of the potential in this case. On the other hand, there are some regular connections between the electrochemical behavior of organic compounds and their structure. Thus, for example, the half-wave potential is linearly connected with a structural factor, which is the so-called substituent constant σ in the Hammett equation. This linear relation is obeyed well for a number of aromatic compounds with the same reacting group and with different substituents, regardless of the effect of the charge of the mercury on the adsorption of these compounds, even if the molecule is charged positively or negatively. (E. T. Bartel, Z. R. Grabowski, Prace Konferencji Polarografiznej, Warszawa, 1956, p. 323; Z. R. Grabowski, ibid., p. 100).

There are many such arguments and therefore, in principle, adsorption is not necessary for reduction. Reduction may proceed with thermal collisions of depolarizer molecules with the electrode. Obviously there are cases where adsorption accelerates the reduction process or changes its mechanism. However, this does not indicate that it is essential.