EFFECT OF METAL ELECTRODE SURFACE STATE ON THE MECHANISM OF ELECTROCHEMICAL SOLVATED-ELECTRON GENERATION IN HEXAMETHYLPHOSPHORAMIDE

L. I. Krishtalik, N. M. Alpatova, and E. V. Ovsyannikova

UDC 541.13

It is shown that the mechanism of electrochemical solvated-electron generation in hexamethylphosphoramide depends on the state of the surface. On a passive surface, the electrons are generated by thermionic emission, they escape into the solution in delocalized form, and are then thermolyzed and solvated. On an active surface, the electrons pass into solution by an electrochemical dissolution mechanism, i.e., localized electrons are formed in the vicinity of the electrode surface.

In recent years, researchers have started to study the mechanism of a peculiar electrochemical process, viz., the cathodic generation of solvated electrons, the solvent used being hexamethylphosphoramide [1-8].

The experimental results on the kinetics of this process obtained by different authors are contradictory. Thus, it was found in the work of Avaca and Bewick [5] and in our works [1-4] that the process is described by a Tafel equation with a slope of 60 [1-4] or 83-93 mV [5] and is not diffusion controlled. According to the hypothesis of Kanzaki and Aoyagui [6, 7], who obtained a polarization curve corresponding to a Tafel equation with a slope of 60 mV, the process is diffusion controlled and the electron-transfer coefficient of the electrochemical step, determined by nonsteady-state methods, is 0.25-0.30 [6]. It would be of interest to find out the reasons for these discrepancies.

The measurements were made on a platinum or electropolished-copper electrode in a hermetically sealed cell with a stirrer. The construction of the cell has been described in [8]. We used 0.3-0.4 M LiCl solutions in hexamethylphosphoramide (5.5°) containing solvated electrons generated electrochemically at an auxiliary cathode. The potentials were measured relative to an aqueous calomel electrode. The applicability of such a reference electrode was verified in [8]. The methods used to purify the solvent and prepare the solutions are described in [9]. The exchange currents were determined using a technique analogous to that used in [4].

The polarization curves were plotted as follows: We measured the equilibrium electrode potential φ_0 corresponding to a given concentration of the solvated electrons generated at the auxiliary cathode, then we set a predetermined cathodic current and recorded the corresponding potential φ and then we determined the limiting anodic current $I^a_{\lim}$ and again monitored φ_0. If the measured values of the equilibrium potential φ_0 coincided and $I^a_{\lim}$ was constant, this indicated that the concentration of solvated electrons remained constant in the time taken to plot the polarization curve. Then, a new value was set for the concentration of solvated electrons generated at the auxiliary electrode, and a new series of measurements was taken.

In the course of these experiments it was found that the character of the cathode process depends on the state of the surface. It was found that the generation characteristics which we obtained in [1-4] apply to a passive surface state [2, 8]. Dubois and co-workers [10] have also pointed out the possibility of a passive film being formed on a cathode in alkali-metal salt solutions. On the basis of the generation characteristics obtained with

---

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Elektrokhimiya, Vol. 12, No. 10, pp. 1493-1498, October, 1976. Original article submitted February 7, 1975.

such an electrode, we can postulate that the process goes by a thermionic-emission mechanism under these conditions [2, 4].

Short-term anodic polarization with large currents leads to an active surface state. Due to the presence of solvated electrons in the bulk of the solution, this state can be maintained without appreciable variations over long periods (of the order of several hours). On activation, the rate of solvated-electron generation increases by a factor of 1.5-2 and becomes dependent on mixing. The effect of mixing on the generation rate indicates that the process is dependent on the reverse reaction, i.e., the oxidation of the solvated electrons. To study the kinetics of the electrochemical generation step proper, it is necessary to introduce corrections for the concentration changes and the reverse reaction into the experimental values of the cathodic current. If, as has been suggested in [4], we assume that, in the general case, the cathodic generation current is the sum of the currents corresponding to thermionic emission into the solution and electrochemical dissolution of the electrons, we can write the following expression for the currents:

$$I=k_1e^{-\varphi}+k_2e^{-\alpha\varphi}-k_1'c_s-k_2'c_se^{(1-\alpha)\varphi}, \tag{1}$$

where k_1 is the rate constant for thermionic emission, k_1' is the product of the rate constant for delocalized-electron oxidation and the equilibrium constant for the transition of the electrons from the localized to the delocalized state, k_2 is the rate constant for electrochemical dissolution of the electrons to form localized electrons, k_2' is the rate constant for solvated-electron oxidation, α is the electron-transfer coefficient of the electrochemical electron-dissolution reaction, and φ is the electrode potential expressed in units of RT/F.

If we bear in mind that under steady-state conditions, the cathodic current is

$$I=DF\frac{c_s-c_0}{\delta}=k(c_s-c_0),$$

where D is the diffusion coefficient of the solvated electrons, F is the Faraday number, δ is the thickness of the diffusion layer, and c_0 and c_s are the bulk and surface concentrations of the solvated electrons, and that the anodic limiting diffusion current $I^a_{\lim} = kc_0$, then the corrected cathodic current can be expressed by the formula

$$I_{\text{corr}}=\frac{I_{\text{obs}}}{1-(I_{\text{obs}}+I^a_{\lim})e^{-\eta}/I^a_{\lim}}, \tag{2}$$

where η is the overvoltage in units of RT/F.

Thus, using our method of measurement, which makes it possible to determine $\eta = \varphi_0 - \varphi$ and $I^a_{\lim}$, we can perform the necessary calculations.* In the case of purely concentration polarization, the equation of the cathodic polarization curve is of the form

$$I_{\text{obs}}=I^a_{\lim}(e^{\eta}-1). \tag{3}$$

The latter equation is valid at high exchange currents and not very high η. Equations (2) and (3) are applicable not only to the mechanism expressed by formula (1) but also for any other one-electron process.

Curve 1 in Fig. 1 is an experimental cathodic curve for an active surface without mixing. At not very low overvoltages, curve 1 is described by a Tafel equation with a slope of 55 mV. Since, as noted above, stirring has a great effect on polarization on an active surface, the slope of 55 mV indicates that the process is totally diffusion controlled in the absence of mixing. The diffusive nature of the process is confirmed by the agreement between the observed exchange currents, anodic limiting diffusion currents, and the extrapolated cathodic currents (Fig. 1, curve 2).

A diffusion mechanism is observed on activated surfaces in the absence of mixing irrespective of the degree of activation of the surface. With mixing, the character of the cathode process depends on the degree of activation. With strong activation, the generation rate is also diffusion-controlled. In Fig. 1, the experimental cathodic curve (curve 3) is com-

---

*The calculations on the basis of formula (2) were performed on a Mir-1 computer using a program set up by R. G. Érenburg, to whom the authors are grateful.

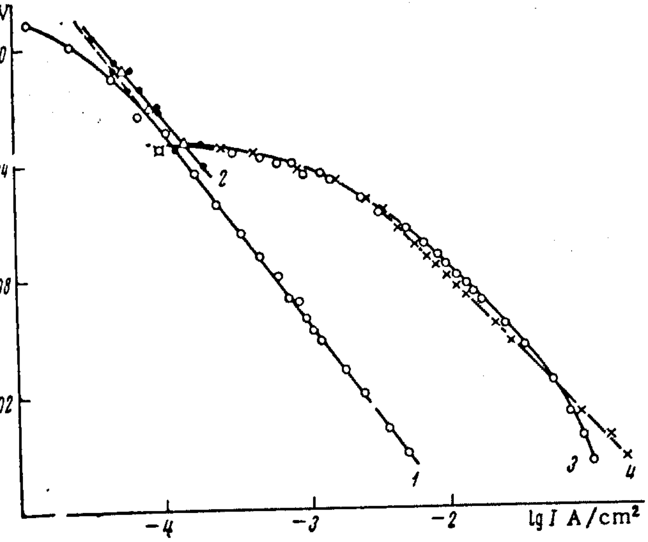

Fig. 1. Potential dependence of cathodic currents (1), exchange currents (2), and anodic limiting currents (2) in hexamethylphosphoramide at 55°C: 1, 2) platinum electrode after anodic activation, 0.33 M LiCl, without mixing; 3) cathodic polarization curve for a copper electrode after anodic activation, 0.38 M LiCl, stirrer speed 1700 rpm; 4) cathodic polarization curve under the same conditions calculated from equation for purely concentration polarization.

pared with the curve (4) calculated from Eq. (3) for a completely reversible process. The curves coincide over a considerable range of current densities.

With mixing on a less active surface, we observe an appreciable degree of irreversibility, as indicated by the lack of agreement between the experimental cathodic curve (curve 1, Fig. 2) and the curve calculated from Eq. (3) for an equilibrium process (curve 2, Fig. 2). When we use relation (2) to correct the experimental values of the cathodic current, the polarization curve corresponds to curve 3. Curve 3 is described by a Tafel equation with a slope of 122 ± 6 mV (average value from five experiments). This form of the true cathodic polarization curve shows that the generation of the solvated electrons proceeds by an electrochemical dissolution mechanism [4]. The transfer coefficient of the cathode reaction (α) is 0.45 ± 0.05, but the accuracy with which α is determined is low because the introduction of corrections in the basis of Eq. (2) gives on large error at very low current densities and low overvoltages, and the value of the potential may be distorted at high current densities by ohmic voltage drops. To determine α independently, we investigated the dependence of the equilibrium potential φ_0 on the exchange current (curve 4, Fig. 2). The exchange currents I°_{obs} measured from the slopes of the polarization curves in the vicinity of the equilibrium potential were corrected for diffusion variations.

According to the results obtained by Érenburg [11], these corrections can be introduced using the formula

$$\frac{1}{I^\circ_{obs}}=\frac{1}{I^\circ_{true}}+\frac{1}{I^\circ_{diff}}, \tag{4}$$

where I°_{obs} is the exchange current determined experimentally from the slope of the polarization curve in linear coordinates close to equilibrium; I°_{true} is the exchange current of the electrochemical step; and I°_{diff} is the effective exchange current in the diffusion step, equal to the diffusion-limited anodic electron-oxidation current at a given equilibrium potential φ_0. Equation (4) is valid for one-electron processes including two successive steps with stoichiometric numbers equal to unity. In the present case, these steps comprise the electrochemical dissolution of the electrons and the diffusion of the solvated electrons from the electrode into the bulk of the solution. The α value determined from the dependence of φ_0 on log I°_{true} is 0.55 ± 0.04 (average from five experiments), which practically coincides with the value determined from the slope of the corrected cathodic curve. There is close agreement between the corrected exchange currents and the extrapolated cathodic currents (curves 3 and 4), which is to be expected on the basis of the proposed generation mechanism, i.e., the mechanism of electrochemical dissolution of the electrons to form solvated electrons in the vicinity of the electrode surface. In this case, the rates of the cathode and anode processes without allowance for the reverse reactions are expressed by the relations

$$I_c=\vec{k}e^{-\alpha\varphi}, \tag{5}$$

$$I_a=\overleftarrow{k}ce^{(1-\alpha)\varphi}. \tag{6}$$

In accordance with Eq. (5), the rate of the cathode process will be independent of the concentration of solvated electrons at large deviations from equilibrium (curves 1, 5 and

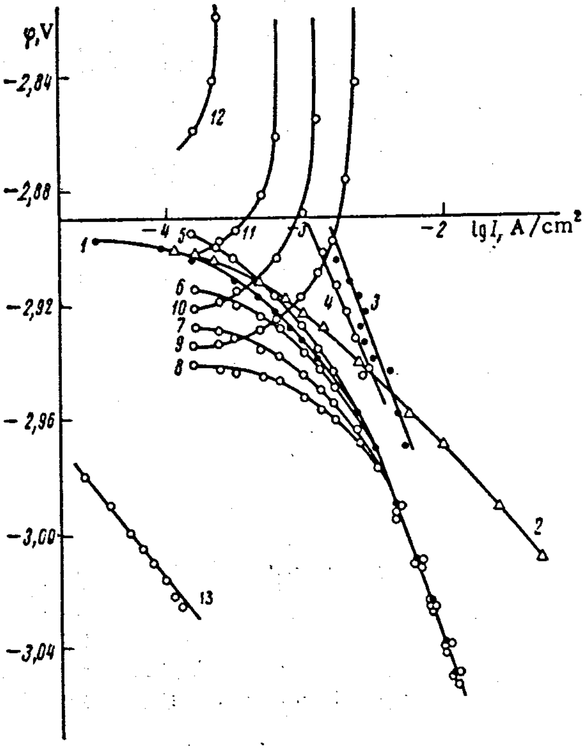

Fig. 2. Potential dependence of cathodic and anodic currents and exchange currents at 5.5°C in a LiCl solution on a copper electrode at a stirrer speed of 1700 rpm: 1) experimental curve, $\varphi_0 = -2.896$ V; 2) cathodic curve calculated from concentration-polarization equation for curve 1; 3) cathodic curve calculated from Eq. (2) corresponding to curve 1; 4) potential dependence of corrected exchange currents; 5-12) cathodic and anodic curves for φ_0 values of −2.885 V (5, 12), −2.909 V (6, 11), −2.924 V (7, 10), −2.939 V (8, 9); 13) cathodic curve for a passive copper surface in 0.3 M LiCl.

6-8, Fig. 2, which correspond to different equilibrium potentials, i.e., different solvated-electron concentrations, coalesce at high currents). In accordance with Eq. (6), the rate of anodic oxidation of the solvated electrons will depend on the concentration of solvated electrons (curves 9-12, Fig. 2).

On the basis of the data obtained, we can conclude that the lack of agreement between the results obtained by different authors [1-7] is due to the use of electrodes with different degrees of passivity, the latter depending considerably on the previous history of the electrode. Kanzaki and Aoyagui [6, 7] were evidently working with a fairly active platinum electrode, the electrode surface being activated by anodic polarization in the presence of solvated electrons formed by dissolution of metallic sodium in the bulk of the solution. Processes proceeding by a mechanism in which electrons are electrochemically dissolved to form electrons localized around the electrode, are similar to normal electrochemical reactions in which the activation energy is determined by the solvent-reorganization energy.

Although the characteristics of solvated-electron generation on a passive surface studied in [1, 3] gave us reason to propose a thermionic emission mechanism, the presence of a passive film on the surface makes the evidence obtained inadequate. When there is considerable passivation, the generation process takes place at individual points on the free surface, while the diffusion of the solvated electrons takes place in the narrow pores of the passive film. If the pore diameter is small compared with the thickness of the film, the rates of the cathode and anode processes will be independent of mixing at sufficiently great film thicknesses, although the rate of the process is diffusion-controlled. We therefore attempted to obtain additional evidence for the validity of the thermionic emission mechanism. Curve 13 in Fig. 2 represents the cathodic polarization curve for a passive surface at various stirring speeds. In accordance with the data obtained in [1, 3], the generation rate is independent of the stirring speed. Under the same conditions, however, the limiting anodic currents increase with increasing stirring speed. This shows that the hypothesis concerning the decisive role of diffusion in the narrow channels is invalid, so that we can regard the hypothesis of a thermionic emission mechanism as being valid. Several estimates also confirm this mechanism.

According to photoelectrochemical data, the work function of a mercury electrode at the zero-charge potential is 3.6 V [12]. As is known, the work function determined from photoemission data applies to the formation of a delocalized electron, i.e., to the same primary product as is formed by thermionic emission. The work function calculated on the basis of Sommerfeld's formula for thermionic emission, viz., $I = AT^2\exp(-W/RT)$, where $A = 120$ A·cm^{-2}·deg^{-2} and W is the work function [13], gives $W = 0.58$ V for a current of 10^{-3} A/cm² and a temperature of 25°C. Bearing in mind that a generation current of 10^{-3} A/cm² corresponds to a potential of −2.78 V (she) [1, 3]), and that the zero-charge potential of mercury in hexamethylphosphoramide is 0.17 V (she) [14], we obtain a value of 3.53 V for the work function of a mercury electrode at the zero-charge potential, which is practically the same as the value of 3.6 V determined by photoemission experiments [12].

Thus, the results obtained show that the generation of solvated electrons in hexamethylphosphoramide is a more complex phenomenon than was suggested in [1-3]. The generation mechanism changes when the conditions are changed, especially when the state of the surface changes.

The rate of generation of solvated electrons by the electrochemical dissolution mechanism, like the rate of a normal electrochemical process, may be highly dependent on the degree of passivation. Passivation will have less effect on the rate of generation by the thermionic emission mechanism.

Indeed, the height of the barrier to the tunneling of electrons in a delocalized state is less than that of localized electrons, since the energy of the latter is lower. Consequently, the formation of a passivating film, which can be described as an increase in the thickness of the barrier, has less effect on thermionic emission. In principle, it is possible to have a case where film formation does not retard thermionic emission at all.*

On the basis of this difference in the effect of passivation on the rate of processes proceeding by different mechanisms, we can explain the fact that the generation mechanism changes when the surface state changes. On passing from an active to a passive surface, the rate of generation by the electrochemical dissolution mechanism decreases sharply and the cathode process will be determined mainly by thermionic emission, the rate of which is relatively weakly dependent on the state of the surface.

LITERATURE CITED

1. N. M. Alpatova, L. I. Krishtalik, and M. G. Fomicheva, Élektrokhimiya, 8, 535 (1972).
2. L. I. Krishtalik, M. G. Fomicheva, and N. M. Alpatova, Élektrokhimiya, 8, 629 (1972).
3. N. M. Alpatova, M. G. Fomicheva, E. V. Ovsyannikova, and L. I. Krishtalik, Élektrokhimiya, 9, 1234 (1973).
4. N. M. Alpatova, L. I. Krishtalik, E. V. Ovsyannikova, and S. E. Zabusova, Élektrokhimiya, 9, 884 (1973).
5. L. A. Avaca and A. Bewick, J. Electroanal. Chem., 41, 395 (1973).
6. Y. Kanzaki and S. Aoyagui, J. Electroanal. Chem., 36, 297 (1972).
7. Y. Kanzaki and S. Aoyagui, J. Electroanal. Chem., 51, 19 (1974).
8. E. V. Ovsyannikova, L. I. Krishtalik, and N. M. Alpatova, Élektrokhimiya, 12, 1032 (1976).
9. M. G. Fomicheva, Yu. M. Kessler, S. E. Zabusova, and N. M. Alpatova, Élektrokhimiya, 11, 163 (1975).
10. J.-E. Dubois, A. Monvernay, and P.-C. Lacaze, J. Chim. Phys., 39 (1973).
11. R. G. Érenburg, Élektrokhimiya, 10, 457 (1974).
12. R. R. Dogonadze, L. I. Krishtalik, and Yu. V. Pleskov, Élektrokhimiya, 10, 507 (1974).
13. L. N. Dobretsov and M. V. Gomoyunova, Emission Electronics [in Russian], Nauka, Moscow (1966).
14. R. V. Ivanova and M. G. Fomicheva, Élektrokhimiya, 8, 1259 (1972).
15. A. M. Brodskii, Yu. Ya. Gurevich, Yu. V. Pleskov, and Z. A. Rotenberg, Modern Photoelectrochemistry. Photoemission Phenomena [in Russian], Nauka, Moscow (1974).

---

*This, however, does not rule out the possibility of passivation having some effect in the case of a thermionic emission mechanism. When thick films are formed, a surface-blocking effect will occur. Visual observation shows that in some cases, the electrons are generated at individual points on the surface of an electrode with a high degree of passivation, these points occupying only a small proportion of the working surface.