EXCHANGE CURRENTS OF THE "ELECTRON" ELECTRODE IN HEXAMETHYLPHOSPHORAMIDE

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Previously we have studied the kinetics of electrochemical generation of solvated electrons in a solution of lithium chloride in hexamethylphosphoramide [1-4]. An attempt was made in the present work to use for this purpose an electrode which is reversible with respect to the solvated electrons in the solution. Such a reversible "electron" electrode in a solution of metallic sodium in liquid ammonia was suggested by Kraus [5] as early as 1914, later also by Laitinen and Nyman [6] and by Dye [7]. Platinum and tungsten were employed as electrode materials.

Recently, after completion of the experimental part of the present work, the realization of the reversible electron electrode in a solution of sodium in hexamethylphosphoramide was reported [8].

A bare platinum wire or a platinum wire electrolytically coated with copper (0.17 cm^2) were used as the electron electrodes in the present work. The electrodes were dipping into a solution of lithium chloride (0.17-0.20 mole/liter) in hexamethylphosphoramide containing solvated electrons. The technique of solvent purification and of preparing lithium chloride solutions in this solvent has been described previously [2]. The solvated electrons in the bulk of the solution were obtained by electrochemical generation at an auxiliary cathode. The cathode compartment was fitted with an arrangement for passing purified argon and with a magnetic stirrer, and was separated from the anode compartment by a stopcock with glass frit. The measurements were made at 5.5°C. The lower temperature enhances the chemical stability of the solvated electrons, and leads to a higher stationary concentration of these electrons. When during cathodic polarization of the auxiliary electrode the solvated electrons accumulate in the solution, the potential of the indicator electrode shifts toward negative values, and remains constant for some time after the auxiliary polarization current has been switched off; this time is sufficient for recording the cathodic and anodic polarization curves near the equilibrium potential. These curves were taken pointwise under galvanostatic conditions, and the potential at zero current was measured after every point. In addition, cathodic polarization curves were recorded over a wider range of currents, so that the shape of the cathodic polarization curve far from the equilibrium potentials could be defined, and this curve extrapolated into the region of the equilibrium potentials. The curves were recorded, both point by point and with automatic current scan, for which purpose a P-5827 potentiostat together with an LPM-60M pH-meter and a KSP-4 recorder was used. A PHM-52 pH-meter from Radiometer was used for measuring the potentials. The input impedance for dc is higher than 10^{12} ohm with this instrument. The potential of the indicator electrode was measured relative to a sodium-sensitive glass electrode dipping into a solution of sodium bromide (0.18-0.20 mole/liter) in hexamethylphosphoramide. Electrodes of the types ÉSL-51-04 and ÉSL-51-05 with the standard aqueous filling were used. These electrodes were shown to be suited for the hexamethylphosphoramide medium by measuring the emf of a concentration cell with transference consisting of two glass electrodes dipping into sodium bromide solutions of different concentration (Fig. 1) at 25 and 5.5°C. At 25°C one observes a practical coincidence of the measured values with those calculated from the equation $E = 2t_-(RT/nF) \ln c_0/c$.

The transport number for Br^-, which is 0.73, was calculated from the experimental value $\lambda^\infty_{Br^-} = 15.9\ \Omega^{-1} \cdot cm^2 \cdot eq^{-1}$ [9] and from the value $\lambda^\infty_{Na^+} = 5.9\ \Omega^{-1} \cdot cm^2 \cdot eq^{-1}$, which was calculated from Walden's

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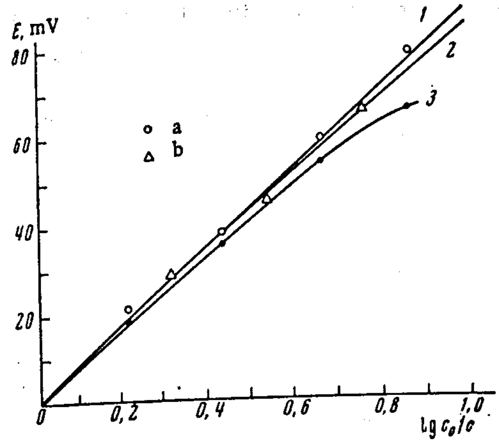

Fig. 1. The emf (in mV) of a concentration cell consisting of two sodium glass electrodes, as function of the concentration c (in mole/liter) of sodium bromide solutions, at c_0 = const. 1) Experimental curve, at 25°C: a) $c_0 = 0.202$; b) $c_0 = 0.208$. 2) Theoretical curve, at 25°C; 3) experimental curve, at 5.5°C, $c_0 = 0.163$.

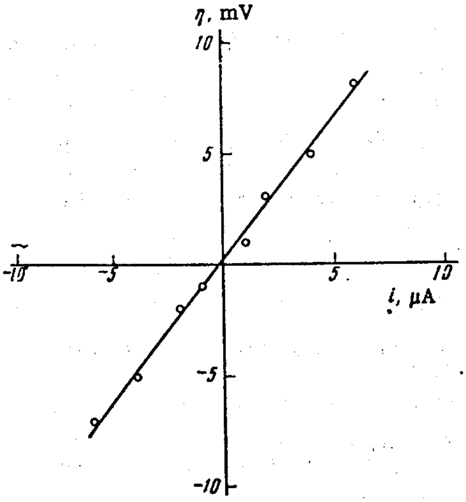

Fig. 2. The overpotential η (in mV) as a function of the current i (in μA); $\varphi_0 = -3.003$ V, 5.5°C.

rule for a series of amide-type solvents [10]. Such close agreement between calculated and experimental values is, to a certain extent, unexpected, inasmuch as the calculation is approximate in nature.

We have also measured the asymmetry potentials of a few glass electrodes dipping into 0.20 mole/liter sodium bromide solution. They are no higher than 2 mV at 25°C. Potentials which were stable to within 1 mV were established at the sodium glass electrodes within 10 min or less at 25°C, and within 40-50 min at 5.5°C.

For comparison with the data from preceding papers, we determined the emf of a cell consisting of a sodium glass electrode in 0.20 mole/liter sodium bromide solution and the lead reference electrode which we had employed before [1-4]. At 25°C this emf was 840 ± 4 mV.

A typical polarization curve in linear coordinates that was obtained at the indicator electrode is shown in Fig. 2. It is a smooth curve going through the coordinate origin without any break, and comes close to being a straight line near the equilibrium potential. From the slope of the polarization curve near the equilibrium potential one can determined the exchange currents, provided that one makes certain assumptions about the mechanism by which the equilibrium or stationary state becomes established at the electrode. We have suggested previously [1-4] that two mechanisms may be responsible for the electrochemical generation of solvated electrons in hexamethylphosphoramide, which can be described by a polarization curve having a Tafel slope of 60 mV: thermoelectronic emission or barrierless electrochemical dissolution.

Thermodynamic equilibrium at the electron electrode can be established by three mechanisms.

1. Thermoelectronic emission of electrons into the solution/return of delocalized electrons from the solution to the electrode.

The reaction rates are described by the equations

$$I_{\text{cath}} = \vec{k}_1 \cdot e^{-\frac{\varphi F}{RT}} \tag{1}$$

and $I_{\text{an}} = k_1' \cdot c'$, where c' is the concentration of delocalized electrons. Since $c' = c \cdot e^{-\Delta E/RT}$, where c is the concentration of solvated electrons and ΔE is the energy difference between delocalized and solvated electrons,

$$I_{\text{an}} = \overleftarrow{k}_1 \cdot c. \tag{2}$$

The initial segments of the polarization curves correspond to the equations

$$I = I_{01}\eta; \tag{3}$$

where I_{01} is the exchange current, η is the overvoltage in units of RT/F, and the dependence of the equilibrium potential φ_0 on the exchange current is described by the equation

$$\varphi_0 = \text{const} - \frac{RT}{F} \ln I_{01}. \tag{4}$$

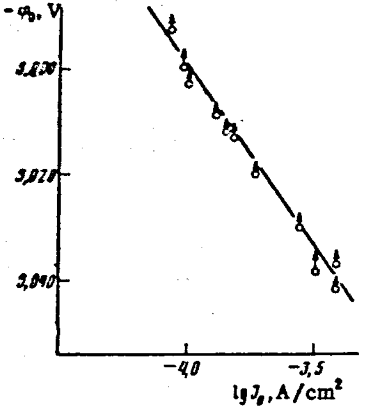

Fig. 3. The equilibrium potential φ_0 as a function of the exchange current I_0, in A/cm², at 5.5°C.

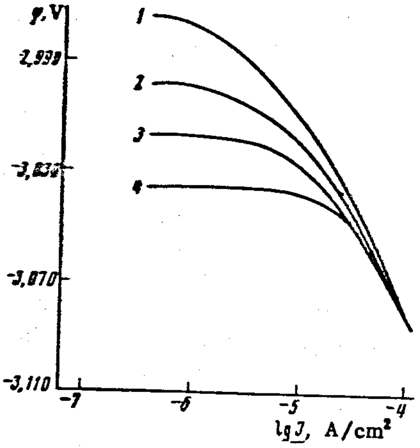

Fig. 4. The rate of electrochemical generation of solvated electrons I (A/cm²) as a function of potential φ (in V) at various values of the equilibrium potential φ_0 (in V): 1) −2.979; 2) −3.002; 3) −3.018; 4) −3.036; t° = 5.5°C.

2. Barrierless electrochemical dissolution of electrons/nonactivational oxidation of electrons (the transition from the state of a solvated electron into the metal). The kinetic equations of this process formally coincide with those describing thermoemission.

3. Ordinary electrochemical dissolution of electrons/ordinary oxidation of electrons.

Such a mechanism is described by the equations

$$I_{\text{cath}} = \vec{k}_2 \cdot e^{-\frac{\alpha\varphi F}{RT}}, \tag{5}$$

$$I_{\text{an}} = \overleftarrow{k}_2 \cdot c \cdot e^{\frac{\beta\varphi F}{RT}}, \tag{6}$$

where α and β are the transfer coefficients of the corresponding reactions.

The initial segments of the polarization curve are described by an equation which is similar to Eq. (3), while the dependence of equilibrium potential on exchange current is

$$\varphi_0 = \text{const} - \frac{RT}{\alpha F} \ln I_{02}. \tag{7}$$

When there is equilibrium at the electrode, one or two out of these processes can take place. Processes 1 and 2 and their sum correspond to one set of equations (1)-(4). The parallel existence of processes 1 and 3 must correspond to the following equations: the cathodic curve far from the equilibrium potential is described by Eq. (1) under the condition $I_{01} \cdot e^{b\eta_{\text{cath}}F/RT} \gg I_{02}$, the anodic curve far from the equilibrium potential (with $I_{02} \cdot e^{b\eta_{\text{an}}F/RT}$) by Eq. (6).

Near equilibrium the polarization curve is of the form

$$I = I_{01}\left(1 + \frac{I_{02}}{I_{01}}\right)\eta = I_0\eta, \tag{8}$$

where I_0 is the combined exchange current.

Under the condition $I_{02}/I_{01} < 1$, one has $I_{01} \simeq I_0$, and the dependence of the equilibrium potential on the combined exchange current I_0 is similar to Eq. (4):

$$\varphi_0 = \text{const} - \frac{RT}{F} \ln I_0. \tag{4a}$$

An example for the dependence of equilibrium potential on the exchange currents calculated by Eq. (8) is shown in Fig. 3. The results of the measurements are reported in Table 1. All of the experimental dependences of equilibrium potentials on exchange currents are described by Eq. (9):

$$\varphi_0 = (-3.302 \pm 0.030) - (0.060 \pm 0.004) \lg I_0 \tag{9}$$

It can be seen from Eq. (9) that potential and exchange current are related by an equation having a slope of 60 mV. This is in harmony with the above Eqs. (4) and (4a). The data obtained cannot be reconciled with the results of Kanzaki and Aoyagi [8], viz., that the kinetics of cathodic electron generation in hexamethylphosphoramide corresponds to a transfer coefficient of 0.15–0.20. These authors explain the slope of the cathodic polarization curve (60 mV) by slow diffusion of solvated electrons away from the cathode. We have previously shown [1] that concentration polarization in the present system actually is not important.

TABLE 1. Dependence of the Equilibrium Potential on the Exchange Current, and Comparison between Experimental and Extrapolated Values for the Latter

№ n/n	Electrode material	Str. line $\varphi_0 = A - B \lg I_0$		Slope of the Tafel section of cathodic curve, mV	$\Delta \lg I_0$
		B, mV	max. scatter of φ_0, mV		
1	Pt	63	±4	53	+0,29 — +0,22
2	Pt	63	±4	75	0,00 — −0,11
3	Cu*	49	±7	57	+0,03 — −0,13
4	Cu	59	±5	55	+0,05 — +0,04
5	Cu	58	±2		
6	Cu	58	±6	72	+0,14 — +0,10
7	Cu	65	±2		
8	Cu	66	±2		

*Numbers 3-8: copper-plated platinum.

It was of interest to compare the exchange currents determined from the slope of the curve near the equilibrium potential with those obtained by extrapolation of cathodic polarization curves recorded far from equilibrium (Fig. 4). Table 1 also presents a comparison between the exchange currents, in addition to data characterizing the experimental measuring uncertainties. These data on the exchange currents are presented in the last column as differences between the logarithms of "equilibrium" exchange currents [i.e., those determined from Eq. (8)] and of those extrapolated. Since the curves are not quite parallel, two values for the $\log I_0$ difference are reported, which correspond to the start and end, respectively, of the experimental straight line of φ_0 against $\log I_0$. It can be seen that there is a rather significant scatter in the data, which is due to the large experimental difficulties encountered when working with hexamethylphosphoramide. The average value for the differences calculated from the data of the table is +0.06. These currents are thus quite similar. Their small difference, if it is taken to be real, may be due to the fact that the exchange current extrapolated from the cathodic region represents I_{01}, i.e., refers to electron emission only, while the equilibrium φ_0 is determined by the sum of two parallel pathways. From the magnitude of $\Delta \log I_0$ one can estimate that the ratio $I_{02}/I_{01} \simeq 0.15$. However, more definite conclusions cannot be drawn in view of the insufficient accuracy of the experimental data.

Figure 4 presents typical cathodic polarization curves for various values of the equilibrium potential. The portions of the stationary polarization curves which are at potentials far from the equilibrium values coincide with the curves obtained by automatic recording at different scan rates. This, and the shape of the curves, strengthen the earlier conclusion that the rate of electrochemical electron generation is independent of solution composition. Curves corresponding to different concentrations of solvated electrons merge far from the equilibrium potential.

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