ANODIC OXIDATION OF SOLVATED ELECTRONS IN HEXAMETHYLPHOSPHORAMIDE

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During the anodic oxidation of solvated electrons (s.e.) generated electrochemically in a solution of lithium chloride in hexamethylphosphoramide one observes diffusion-limited currents which are porportional to s.e. concentration. The Nernst equation is shown to hold for the "electron" electrode. This indicates that thermodynamic equilibrium with respect to the s.e. is established at the electrode. In studies of the anodic oxidation of s.e. in sodium bromide solutions, evidence was obtained for the existence of complexes containing the bielectron; in particular, the appearance of kinetic currents caused by the slow dissociation of the complex yielding monoelectrons.

When inert electrodes are immersed into solutions containing solvated electrons, a negative stationary potential is established at them. It had been suggested for solutions in liquid ammonia that this potential is an equilibrium potential [1-3]. An electrode reversible with respect to the solvated electrons was realized in hexamethylphosphoramide with solutions of lithium chloride [4] and sodium perchlorate [5].

Fulfillment of the Nernst equation must be the criterion of reversibility of the "electron" electrode. Previously we had studied the exchange currents of the "electron" electrode [4], but observance of the Nernst equation had not been verified.

The analysis of results obtained for solutions of sodium salts is complicated by the presence of $Na^+...e_2^{2-}$ aggregates [6, 7]. This had not been taken into account in [5-9], where the equilibrium at the electrode and the reaction of anodic oxidation of solvated electrons had been studied.

In the present work the equilibrium at the "electron" electrode was studied in solutions of lithium chloride and sodium bromide.

The tendency toward formation of $M^+...e_2^{2-}$ aggregates is much smaller for lithium ions that it is for sodium ions [6, 7]; therefore in solutions of lithium salts, the anodic limiting currents of the oxidation of electrons can serve as a measure of the concentration of solvated electrons in the bulk.

By using solutions of sodium bromide one can examine the effect of bielectron formation on the features of the oxidation of solvated electrons.

The measurements were done in two types of sealed cell. In the first type of cell, a rotating platinum or copper disc pressed intoTeflon served as the working electrode. The electrode design with magnetic drive was analgous to the design used by Tarasevich, Shepelev, and Burshtein [10] *. The speed of rotation was regulated by varying the supply voltage to the dc motor, and determined with a strobotac.

In the second type of cell, a stationary copper or platinum wire served as the working electrode. Mixing was achieved with a four-blade glass stirrer which was set in rotation with the same drive as used for the rotating electrode of the first cell.

With the cell of the first type we could determine the anodic limiting currents of oxidation of solvated electrons under defined hydrodynamic conditions. The design of the second type of cell made it possible to

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make measurements with a Luggin capillary brought up closely to the electrode surface, which served to reduce the distorting influence of ohmic losses on the potential values.

The solvated electrons were obtained by electrochemical generation at an auxiliary platinum electrode in the working compartment of the cell. Otherwise the cell design was close to that described before [4].

Stationary polarization curves were recorded using a P-5827 potentiostat in the potentiostatic mode. The potential was set relative to the auxiliary platinum electrode which was present in the working compartment of the cell, the current was noted and the potential of the working electrode read against the reference electrode. As reference electrodes we used an electrode of sodium glass ÉSL-51-04 with standard aqueous filling in the lithium chloride solution in hexamethylphosphoramide at 5.5°C or an aqueous saturated calomel electrode at room temperature. A system of one-way stopcocks and intermediate vessels served to prevent access of water traces to the working compartment. The emf of a cell consisting of these reference electrodes is 71 ± 9 mV, the calomel electrode being the positive pole. The main uncertainty of the measurements was due to fluctuations in the glass electrode potentials for different electrodes, whereas the reproducibility of the potential drop at the boundary between the aqueous and nonaqueous solution was ± 2 mV. The potentials reported in the paper were measured or recalculated against the potential of the aqueous saturated calomel electrode.

For the measurements we used lithium chloride and sodium bromide solutions having a concentration of 0.3-0.4 mole/liter. Solution purification and the technique of preparation of the solutions have been described before [11].

In lithium chloride solutions, the anodic polarization curves have one wave with a limiting current. The shape of the curve in the region of the limiting current depends on the surface state.

A platinum electrode which after cathodic and anodic treatment in aqueous H_2SO_4 solution and drying in vacuum is immersed into hexamethylphosphoramide solution containing solvated electrons is passive. A similar surface state is also found on an electrode which was dried at 200°C in a drying oven. The passivity is mainly affecting the kinetics of generation of solvated electrons; surface passivation decreases the rate of the process. This problem will be discussed in a separate communication. Partial activation of the surface occurs while the anodic polarization curves are recorded. Such a surface will be called semipassive in the following. The anodic polarization curve in the region of the limiting current is not strictly horizontal. Such a shape of the curve is typical for a nonuniform surface [12], and indicates that passivity is partly retained. Further activation of the surface takes place after brief anodic polarization with currents of 0.5 to $1 \cdot 10^{-1}$ A/cm^2. Such a surface will be called active below. The limiting-current plateau becomes horizontal. However, the limiting currents are similar in value when for the semipassive surface the currents at an overpotential of + 700 mV are taken. Such accord between the currents indicates that the degree of surface blocking on the semipassive surface is low. The values of the limiting currents depend on the rate of rotation of the stirrer. Similar results had been obtained for a platinum electrode of different geometry and also for an electrode of electropolished copper (Fig. 1). It follows from Fig. 1 that the values of potential and limiting current are connected via the equation $\varphi_0 = \varphi_0^0 + A - (0.055 \pm 0.001) \lg I_{\text{lim}}$ (the average value of ten experiments), where A is determined by the proportionality factor between the concentration of solvated electrons and the current, i.e., depends on the stirring conditions. One can suggest that with an excess of salt, the main part of the solvated electrons will exist in the form of noncontacting ion pairs. The limiting anodic oxidation current is proportional to the concentration of such pairs. With an excess of salt, i.e., of lithium ions, the equilibrium $Li^+ + e_s^- \rightleftharpoons [Li^+ \ldots e_s^-]$ is displaced to the right, and with $[Li^+] = \text{const}$, one has $[e_s^-] = \text{const}' \, [Li^+ \ldots e_s^-]$ and $[e_s^-] = \text{const}'' \, I_{\text{lim}}$. Thus, the Nernst equation at 5°C for an electrode which is reversible with respect to the solvated electrons in the solution will be of the form $\varphi_0 = \text{const} - 0.055 \lg I_{\text{lim}}$, and this is found by experiment.

Curves similar to the ones shown in Fig. 1 were obtained for rotating disc electrodes of copper and platinum. Their slope in the similogarithmic plot is 58 ± 3 mV (the average value from 10 experiments). The diffusional nature of the limiting currents is confirmed by their dependence on the rate of rotation of the electrode (Fig. 2). From these data one can estimate the order of magnitude of the concentration of solvated electrons being obtained electrochemically. The values of the diffusion coefficient D of solvated electron in lithium chloride solutions at 5°C are not known. In [13] the value of D was determined for the free electron in pure solvent, and was found to be $1.4 \cdot 10^{-5}$ cm^2/sec at room temperature. In the presence of dissolved salt, the value of D should decrease because of interaction between the solvated electrons and the salt's cations. As the lowest value of D we took the diffusion coefficient of the strongly solvated lithium ion, which is $2.7 \cdot 10^{-6}$ cm^2/sec as calculated from the limiting mobility of this ion which was determined in [14]. The results of calculations with $D = 1.4 \cdot 10^{-5}$ and $2.7 \cdot 10^{-6}$ cm^2/sec using the data of Fig. 2 are reported below. The values of the viscosity

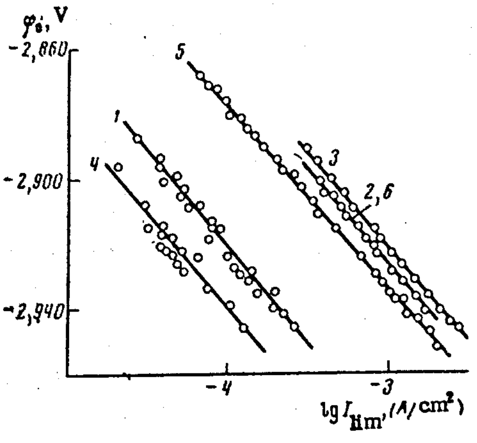

Fig. 1

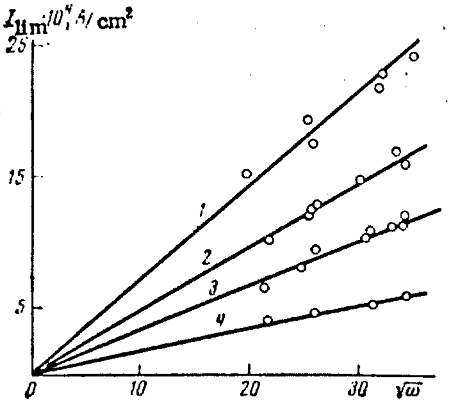

Fig. 2

Fig. 1. The equilibrium potential φ_0 (in V) as a function of the logarithm of the limiting oxidation current of solvated electrons I_{lim} in 0.33-0.40 mole/liter lithium chloride solutions at 5.5°C. Curves 1 and 4 without stirring, for the other curves: rate of rotation of the stirrer 1700 min^{-1}. 1) Platinum, the semipassive and active surface state; 2) platinum, semipassive surface, 3) platinum, active surface, 4) electropolished copper, the semipassive and active surface state, 5) electropolished copper, semipassive surface, 6) electropolished copper, active surface.

Fig. 2. The limiting anodic oxidation current of solvated electrons I_{lim} (in A/cm^2) as a function of the rate of rotation ω (min^{-1}) of the platinum disc electrode in 0.36 mole/liter lithium chloride solution at 5.5°C. 1) $\varphi_0 = -2.91$ V, 2) $\varphi_0 = -2.90$ V, 3) $\varphi_0 = -2.39$ V, 4) $\varphi_0 = -2.88$ V.

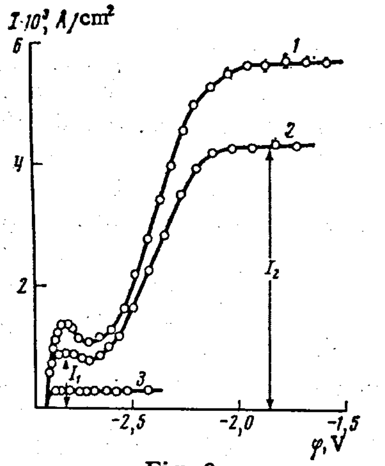

Fig. 3

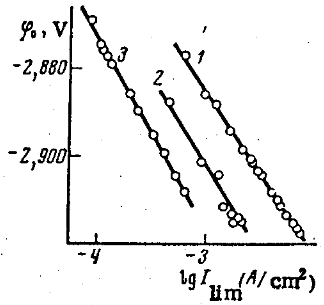

Fig. 4

Fig. 3. The current I_1 (in A/cm^2) as function of the potential φ (in V) for anodes of electropolished copper in 0.32 mole/liter sodium bromide solution at 5.5°C at different rates of rotation of the stirrer and a constant concentration of solvated electrons corresponding to $\varphi_0 = -2.916$ V. Rates of rotation of the stirrer: 1) 1750, 2) 540 min^{-1}, 3) without stirring.

Fig. 4. The equilibrium potential φ_0 (in V) as a function of the logarithm of the limiting oxidation currents of solvated electrons I_{lim} (in A/cm^2) in 0.32 mole/liter sodium bromide solution at 5.5°C. Rate of rotation of the stirrer 1750 min^{-1}. 1) $\varphi_0 - \lg I_2$ with anodic preactivation of the surface prior to each point and without activation; 2) $\varphi_0 - \lg I_1$ with anodic preactivation prior to each point, 3) $\varphi_0 - \lg I_1$ without anodic preactivation.

(9.6 cP) and specific weight (1.046 g/cm^3) were obtained by extrapolating to t = 5°C the corresponding data for 0.3 mole/liter lithium chloride solution at 25 and 10°C which had been obtained in our laboratory by M. G. Fomicheva.

These estimates yield the concentration of solvated electrons as a function of the equilibrium potential of the "electron" electrode in 0.36 mole/liter lithium chloride solution at 5.5°C:

$-\varphi_0$, V:	$c \cdot 10^3$, mole/liter	$c \cdot 10^3$, mole/liter
2,91	4,3 *	13
2,90	2,9 *	8,7
2,89	1,9 *	5,9
2,88	1 *	2,9

*Here D = $1.4 \cdot 10^{-5}$ cm^2/sec, in the other cases D = $2.7 \cdot 10^{-6}$ cm^2/sec.

Thus, it has been established that during the anodic oxidation of solvated electrons electrochemically generated in lithium chloride solutions one sees diffusion-limited currents which are proportional to the concentration of the solvated electrons. It has been shown that the behavior of the electrode in such a system obeys the Nernst equation, i.e., thermodynamic equilibrium is established on the electrode with respect to the solvated electrons. The anodic oxidation curve of solvated electrons in sodium bromide solutions at 5.5°C is presented in Fig. 3. There are two limiting-current plateaus on the curve. An analogous shape of the anodic curve was obtained by Kanzaki and Aoyagi [9] for sodium perchlorate solution. Figure 4 shows as an example (curve 1) the equilibrium potential as function of the logarithm of the limiting current I_2. At a given rate of stirring the values of the current I_2, which is diffusional in nature, are connected with the values of potential via the equation $\varphi_0 = \text{const} - (0.035 \pm 0.001) \lg I_2$ (the average value from four experiments). In contrast to lithium chloride solutions where noticeable stationary concentrations of the solvated electrons and reversibility of the "electron" electrode can be obtained only when the temperature is lowered to 5.5°C, the "electron" electrode can be realized in sodium bromide solutions at higher temperatures as well. Results similar to those shown in Figs. 3 and 4 were obtained for sodium bromide solution at 25°C, too. The slope of the $\varphi_0 - \lg I_2$ curve is 36 mV. In explaining the results obtained one must keep in mind that in NaBr solutions in addition to the solvated electrons there exist $[\text{Na}^+ \ldots e_2^{2-}]$ aggregates containing the bielectron. The association constant K of the reaction $\text{Na}^+ + 2e_s^- \rightleftharpoons [\text{Na}^+ \ldots e_2^{2-}$ where $[e_s^-]$ are the solvated electrons in the free state or in the form of noncontacting ion pairs is $2.8 \cdot 10^4$ mole^{-2}liter^2 at room temperature [6, 7]. The most positive values of the equilibrium potential in sodium bromide solution containing the lowest $[e_s^-]$ concentration are −2.88 to 2.86 V. It follows from the data reported (cf. the conclusion) that a concentration of solvated electrons of about $1 \cdot 10^{-3}$ mole/liter should correspond to this potential. Estimates show that for a sodium bromide concentration of 0.3–0.4 mole/liter at room temperature, more than 90% of the total amount of solvated electrons will exist in the solution in the form of the $\text{Na}^+ \ldots e_2^{2-}$ complex. The limiting diffusion current I_2 is the combined oxidation current of mono- and bielectrons. If the equilibrium $\text{Na}^+ + 2e_s^- \rightleftharpoons \text{Na}^+ \ldots e_2^{2-}$ is shifted toward the side of aggregate formation, then at a given rate of stirring one has $I_2 = \text{const}\, [\text{Na}^+ \ldots e_2^{2-}]$, and the Nernst equation at 5.5°C should have the form $\varphi_0 = \text{const} - 0.028 \lg I_2$. The slope of the $\varphi_0 - \lg I_2$ curve should increase as the equilibrium is shifted toward the side of formation of monoelectrons, and upon complete dissociation of the complex should assume the value of 55 mV. In the experiment one finds the intermediate value of 35 mV, which implies comparable contributions of mono- and bielectrons to the diffusion current. Generally speaking this should have been expected, considering the higher mobility of the monoelectrons. However, within the limits of this explanation it remains obscure why the slope of the experimental $\varphi_0 - \lg I_2$ curve does not depend on potential. This possibly is due to the fact that the measurements can only be performed over a narrow potential range.

The limiting diffusion current I_2 on the anodic polarization curve is preceded by the limiting current I_1 (Fig. 3). The dependence of the electrode's equilibrium potential on this current is presented in Fig. 4 (curves 2 and 3). At a given rate of stirring and the temperature of 5.5°C, the values of potential and of the logarithm of current are connected via the equation $\varphi_0 = \text{const} - (0.036 \pm 0.003) \lg I_1$ (the average value from five experiments). For 25°C the slope of the $\varphi_0 - \lg I_1$ curve is 39 mV.

Kanzaki and Aoyagi [9] believe that the current I_1 is kinetic and due to slow dissociation of $\text{Na}^+ \ldots e_s^-$ pairs. However, the data obtained by us do not agree with this mechanism and allow us to suggest that the current I_1 is a kinetic current caused by slow dissociation of the complex $\text{Na}^+ \ldots e_2^{2-}$ yielding e_s^-. In this case the limiting kinetic current can be expressed as

$$I_1 = 2F \cdot 10^{-3} \sqrt{D k_d c_1 c_2}, \tag{1}$$

where D is the diffusion coefficient of the solvated electron, k_d is the rate constant of dissociation of the complex $Na^+ \ldots e_2^{2-}$ into $Na^+ + 2es^-$, c_1 is the concentration of solvated electrons, and c_2 is the concentration of $Na^+ \ldots e_2^{2-}$ aggregates. If this equation is used to express c_1 in terms of I_1, if it is remembered that $c_2/c_1 = K$, and if the c_1 value found is substituted into the Nernst equation, then one finds that at 5.5°C the values of the equilibrium potential and of the limiting kinetic current must be connected via the expression $\varphi_0 = \text{const} - 0.037 \lg I_1$. Just such a dependence is observed in experiment. This indicates that the current I_1 is due to slow dissociation of a complex containing bielectrons rather than monoelectrons. Were the current I_1 the kinetic dissociation current of the complex $Na^+ \ldots e_S^-$ as suggested by Kanzaki and Aoyagi [9], then the slope of the $\varphi_0 - \lg I_1$ plot would have to be 55 mV, since such a kinetic current would be proportional to the concentration of $Na^+ \ldots e_S^-$ pairs which, with an excess of sodium ions, is linearly related to the concentration of monoelectrons.

It follows from Fig. 3 that the current I_1 is not completely independent of the rate of rotation, even through the effect of the rate of stirring is not as strong as in the case of the currents I_2 (with stirring $I_2 > I_1$, without stirring $I_2 < I_1$). Equation (1) can be rewritten as $I_1 = \text{const } c_2^{1/3}$. If it is remembered that the diffusion current I_2 is proportional to c_2, then a correction for diffusional limitations can be introduced into the I_1 values according to the relation

$$I_1^{\text{corr}} = \frac{I_1}{(1 - I_1/I_2)^{3/4}}.$$

However, introduction of this correction cannot alter the character of the $\varphi_0 - \lg I_1$ dependence. It follows from Fig. 4 that the ratio I_1/I_2 is practically independent of potential, so that the correction factor represents a constant quantity. In the case of curve 2 (Fig. 4) the factor $1/(1 - I_1/I_2)^{3/4}$ is 1.4, and cannot substantially alter the absolute values of I_1.

The different nature of the currents I_1 and I_2 is also manifest in the different effects exerted by the electrode's surface state on the size of these currents. As in the case of lithium chloride solutions, the values of the currents I_2 for a surface which was specially activated by a brief anodic polarization with a current of 10^{-1} A/cm² prior to each point, and for a surface which had not experienced such treatment and was merely activated during the process of recording the anodic curves are practically the same (curve 1, Fig. 4). For currents I_1, surface activation prior to each point causes an increase in current (curves 2 and 3 of Fig. 4). The influence of spontaneous surface passivation on the current I_1 is also seen from the drop in current which occurs on an anodic polarization curve recorded on an electrode which was activated only prior to starting the recording of the curve (curves 1 and 2 of Fig. 3).

The thickness of the diffusion layer is substantially larger than that of the reaction layer which is caused by the magnitude of the kinetic current I_1. At low passivity, the size of the blocked or passive sections can be less than the diffusion layer thickness, and will therefore not influence the diffusion current, but the size of the passive sections will have a noticeable effect on the kinetic current, owing to the small thickness of the reaction layer.

Thus, in sodium bromide solutions containing solvated electrons one can also realize the reversible "electron" electrode. The anodic oxidation of the solvated electrons under these conditions is importantly influenced by the presence of equilibrium in the solution between solvated electrons and complexes containing the bielectron.

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