THE PRIMARY NATURE OF SOLVATED-ELECTRON GENERATION IN HEXAMETHYLPHOSPHORAMIDE

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Solvated electrons are generated during cathodic polarization of inert electrodes in solutions of alkali metal halides and perchlorates in hexamethylphosphoramide (HMP) [1-5].

Like liquid ammonia, HMP is capable of dissolving the alkali metals under formation of solvated electrons [6], so that two fundamentally different processes could be adduced to explain the formation of solvated electrons at the cathode in solutions of metal salts: a primary process, where an electron escapes directly from the electrode into the solution, or a secondary process, where the alkali metal is electrolytically deposited and then chemically dissolved.

The rate of the process is independent of salt cation and electrode metal [3]; this points to the primary nature of generation. Previously we had attempted to investigate this question by comparing the cathodic polarization curves in dilute lithium chloride solutions at copper and amalgamated copper electrodes [2]. At the amalgamated electrode, limiting diffusion-migration currents of lithium ion discharge with amalgam formation are observed. Previously [2] we had regarded the absence of limiting diffusion-migration currents at the copper electrode as one argument against the secondary electron generation mechanism. This conclusion is not unambiguous, however, because the processes of material transport are highly complex in this system, particularly because of Stefan flow which is produced by the considerable changes in solution density accompanying the electrode reaction. We propose to discuss this question in a separate communication. Direct experimental proof for the primary nature of solvated-electron generation can be realized by performing the generation in solutions which do not contain any metal ions. If the generation is a primary process, a rise in current must be found on the polarization curve in dilute acid solutions following the limiting discharge current of the proton donors at potentials which are typical for electron generation in solutions of alkali metal salts.

The measurements were carried out in solutions of $HClO_4$ and HCl in HMP. The techniques of solvent purification and of preparation of the HCl solutions have been described before [7, 8]. Perchloric acid was used in the form of the distilled hydrate $HClO_4 \cdot 2.4H_2O$. The perchloric-acid solutions were prepared by adding small quantities of acid to a large volume of solvent while carefully mixing in order to avoid decomposition of the solvent, which is unstable against acids [9].

The polarization curves were recorded by the methods described before [7]. Platinum, electropolished copper, and mercury were used as cathode materials; the mercury was used as dropping electrode. The potentials were measured relative to the lead reference electrode in HMP [2] or to an aqueous saturated calomel half-cell. The EMF of a cell made up of these electrodes is 0.84 V. The potentials reported in Fig. 1 refer to the calomel electrode. Reproducible results could not be obtained at acid concentrations above 0.1 mole/liter. This evidently is due to electrode passivation by the products of solvent decomposition which occurs by the action of the acid.

The results of the measurements in dilute $HClO_4$ and HCl solutions are presented in Fig. 1. It can be seen that at the stationary copper and platinum electrodes and at the dropping mercury electrode there is a limiting discharge current of the proton donors followed by a current rise corresponding to a new elec-

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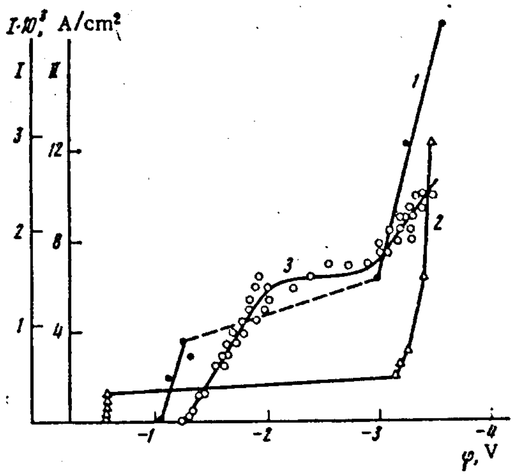

Fig. 1. The current I (in A/cm²) as function of potential φ in acidic solutions in hexamethylphosphoramide at 25°C: 1) $HClO_4$, 0.05 mole/liter, copper electrode, ordinate II; 2) HCl, 0.03 mole/liter, platinum electrode, ordinate II; 3) $HClO_4$, 0.02 mole/liter, dropping mercury electrode, ordinate I.

trode process. Because of the absence of a base electrolyte and of the low conductivity of the dilute solutions, ohmic losses distort the values of potential, especially in the case of the dropping mercury electrode where the Luggin capillary is not very close. However, this electrode with its continuously renewed surface allows one to avoid surface contamination. It can be seen from the figure that the limiting currents are between 1 and 6 mA/cm². Therefore, the lowest generation currents corresponding to the onset of the current rise are 0.1 to 1 mA/cm². Potentials of 2.9 to 3 V correspond to such values of current in the generation of solvated electrons in lithium chloride solution; within the limits of experimental accuracy this coincides with the potentials of the current rise.

In solutions of perchloric acid, which is highly dissociated in HMP [10], the discharge of molecules of the water introduced together with the acid might be the reaction observed following hydrogen ion discharge. However, in low concentrations water is very tightly bound to the solvent [8, 11]. In particular, it is reduced by solvated electrons only at a concentration of 0.5 mole/liter [11], and at the dropping mercury electrode it gives kinetic currents of low magnitude [12]. It therefore appears that the current rise in $HClO_4$ solutions cannot be attributed to the discharge of water molecules.

The results obtained thus demonstrate that the generation of solvated electrons in HMP can occur in the absence of alkali-metal cations, and therefore is not tied to their electrodeposition and subsequent dissolution but is a primary process.

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