ELECTROCHEMICAL GENERATION OF SOLVATED ELECTRONS AND LIBERATION OF HYDROGEN AT CADMIUM IN HEXAMETHYLPHOSPHORAMIDE

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As established by ESR studies [1,2], optical absorption spectra [3], and dynamic polarization of solvent protons [4], solvated electrons are formed during cathodic polarization in solutions of lithium chloride and sodium bromide in hexamethylphosphoramide. From studies of the kinetics of this process the hypothesis was put forard and, to a definite extent, substantiated that the process was primary in character [5, 6]. However, it is of interest to obtain additional proofs of this hypothesis.

By comparing the regularities of the electrochemical generation of solvated electrons with the regularities of normal electrochemical reactions it has been shown [6] that the hydrogen liberation process occurs by direct discharge of the protons of the donor, and not by chemical reaction of these donors with solvated electrons. This result was obtained at platinum and copper cathodes, i.e., metals with a low and an average hydrogen overvoltage. In this work the validity of the proposition for cadmium, a metal with a high hydrogen overvoltage, has been examined.

The stationary galvanostatic polarization curves were measured for a cadmium cathode in solutions of lithium chloride and lithium chloride with added HCl in hexamethylphosphoramide by the method developed earlier [6]. The electrode of grade KD-000 cadmium was chemically polished by the method proposed by Leikis and coworkers [7]. In addition polarization measurements for a platinum electrode in a solution of sodium bromide with solvated electrons present were carried out by the procedure given in [8]. Measurements were made at 25°C.

The results of the measurements are given in Fig. 1. The upper curve, having a Tafel slope of ~60 mV, corresponds to the electron generation process. The broken lines denote the region of scatter of the experimental data, which relates to the electrochemical generation of solvated electrons at Cu and Pt cathodes according to the data of [5, 6] (curve 1).

The lower branches of the polarization curves correspond to the hydrogen liberation process.

The points corresponding to the generation process for cadmium, platinum, and copper in LiCl and LiCl + HCl solutions, as well as for platinum in a solution of NaBr + solvated electrons* lie practically on a single curve. These data confirm and supplement the conclusion reached previously that the rate of the electrochemical generation of electrons is independent of the composition of the solution and the electrode material. This fact indicates that generation of solvated electrons is a primary process and is not linked with electrode-position of the alkali metal and its subsequent "chemical" dissolution with formation of solvated electrons. In the latter case coincidence of the polarization curves would scarcely be expected for the three different cathode materials. This conclusion is even more clearly confirmed by the independence

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*Measurements for platinum in sodium bromide solution with solvated electrons absent did not give reproducible results.

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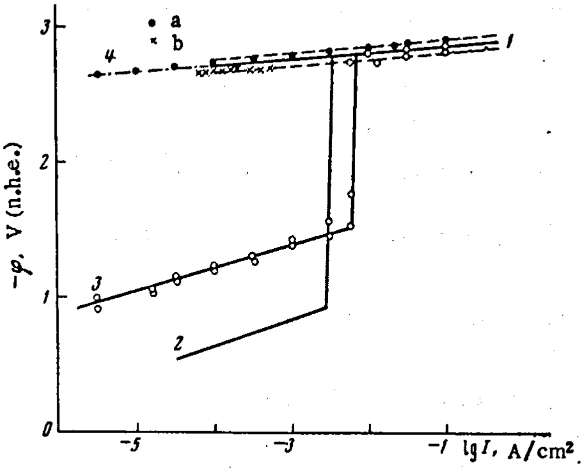

Fig. 1. Dependence of the potential φ on the current density I at 25°C in hexamethylphosphoramide: 1) for copper and platinum in 0.20 M LiCl [5, 6]; 2) for copper in 0.20 M LiCl + 0.15 M HCl [6]; 3) for cadmium in 0.20 M LiCl + 0.17 M HCl; 4a) for cadmium in 0.20 M LiCl; 4b) for platinum in 0.20 M NaBr + solvated electrons.

of the results on the nature of the alkali metal cation – the cathodic polarization curves for the lithium chloride and sodium bromide solutions coincide.

The curve for the cadmium electrode in a LiCl + HCl solution is similar in form to the corresponding curves for copper and platinum obtained previously [6]. The lower section corresponding to liberation of hydrogen has a slope of 150 mV and is shifted ~600 mV towards negative potential values compared with the corresponding curve for copper (curve 2). The difference in hydrogen overvoltage for copper and cadmium in hexamethylphosphoramide is practically identical with that in aqueous solution ($\Delta\eta = 0.63 \pm 0.05$ V [9]), which is understandable since this value is mainly determined by the difference in the hydrogen adsorption energies. As is the case for platinum and copper, for cadmium, a metal with a high hydrogen overvoltage, the electron generation potentials are strongly shifted towards negative values compared with the region of hydrogen liberation potentials (for cadmium at 1.3-1.6 V). This indicates that hydrogen liberation at a metal with a high hydrogen overvoltage also is a primary process at least for acid solutions. Apparently this is also true for alkaline solutions since it is doubtful whether by change of pH it is possible to cover the interval of potentials 1.3-1.6 V.

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