POSSIBILITY OF ELECTROCHEMICAL GENERATION OF SOLVATED ELECTRONS IN CERTAIN APROTIC SOLVENTS

N. M. Alpatova, S. E. Zabusova, and L. I. Krishtalik

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The possibility of electrochemical generation of solvated electrons (SE) has been reliably demonstrated for a number of solvents, where the stability of the SE is rather high. Such solvents include, for example, liquid ammonia and hexamethylphosphorus triamide. In these systems it was established that SE are actually formed on the cathode [1]. It was of interest to determine the possibility of electrochemical generation of SE in other aprotic solvents, which, however, are incapable of dissolving the alkali metals with the formation of solvated cations and electrons.

The electrochemical generation of SE occurs at very negative potentials, and therefore generation might be expected only in a system, the basic components of which will not be reduced on the cathode, i.e., in aprotic solvents. The chemical stability of SE in most aprotic solvents is low, and the direct identification of SE is difficult. However, the process of generation can be recognized according to the characteristic principles established for the generation of SE in hexamethylphosphorus triamide as an example.

The measurements were performed by the method of static polarization curves, taken in a galvanostatic system with a P-5827 potentiostat in a hermetic cell with a mixer on copper and amalgamated copper electrodes. The design of the cell is described in [2]. Solutions of $(C_4H_9)_4NI$ in dimethyl sulfoxide and propylene carbonate were used as the medium. The salt was recrystallized twice from double-distilled water and dried under vacuum. Dimethyl sulfoxide was purified by freezing out, by treatment with calcium oxide, and redistillation under vacuum. Propylene carbonate was redistilled under vacuum. The potentials were measured relative to a saturated aqueous calomel reference electrode (SCE). The measurements were performed in an atmosphere of purified argon.

The results of the measurements for dimethyl sulfoxide are cited in Fig. 1a. Analogous results were also obtained in propylene carbonate. As can be seen, after a small diffusion wave of reduction of the impurity (probably water), a rise in the current is observed at potentials of about −2.8 V. This rise may be due to several processes: reduction of the solvent, discharging of cations or nonsolvated molecules of the supporting electrolyte, and generation of solvated electrons.

The hypothesis of reduction of the solvent is contradicted by the independence of the rate of the process from the material of the electrode (such catalytically varied materials as copper and copper amalgam were used). The rate of discharging of the $(C_4H_9)_4N^+$ cations or $(C_4H_9)_4NI$ molecules should depend on the nature of the electrode, and in measurements in a dilute salt solution, on the mixing, which is not observed experimentally (Fig. 1a). The results obtained permit us to assume that the rise in the current is due to the generation of SE. This hypothesis is supported by a number of arguments, primarily the high negative values of the potentials of this process. In values the potentials are close to the potentials of generation of SE in hexamethylphosphorus triamide, measured relative to the same aqueous reference electrode [1, 2]. The interfacial jumps of the potential at the water–dimethyl sulfoxide and water–hexamethylphosphorus triamide interfaces should not differ too much. This is indicated by the small difference of the half-wave potentials of the discharging of weakly solvated Rb^+ and Cs^+ cations with the formation of an amalgam in these solvents relative to an aqueous SCE (for hexamethylphosphorus triamide $E_{1/2}^{Rb^+} = -1.97$ and $E_{1/2}^{Cs^+} = -1.94$ V,

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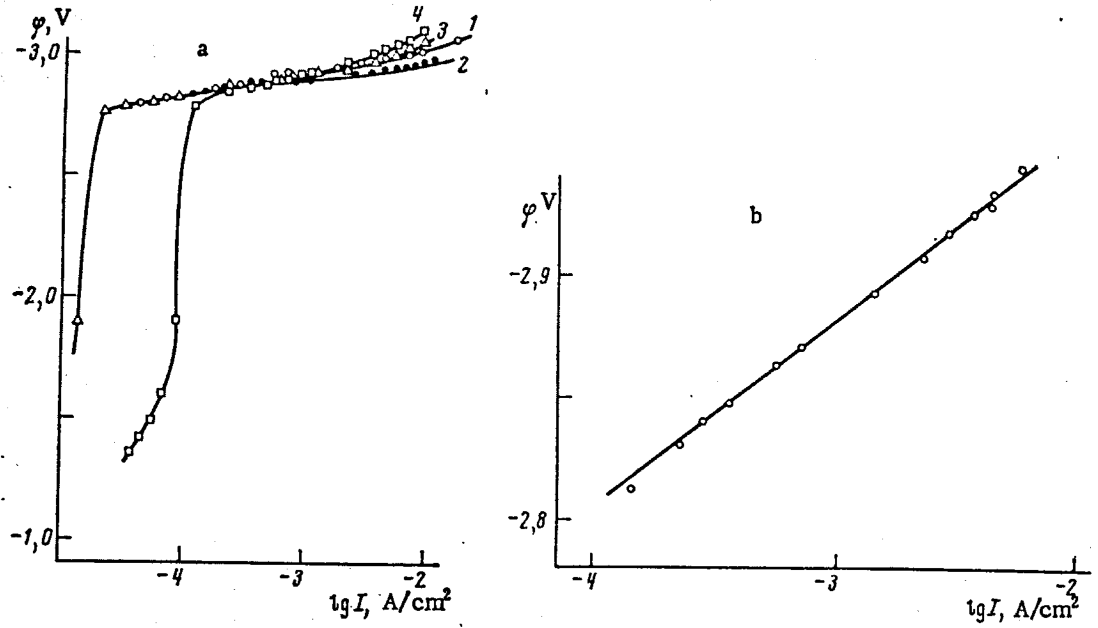

Fig. 1. Dependence of the potential φ on the logarithm of the current density I in a solution of tetrabutylammonium iodide in dimethyl sulfoxide on copper (a, curve 1) and on amalgamated copper (a, curves 2-4; b) electrodes. Salt concentration, M/liter; a) 0.07 (1, 2); 0.013 (3, 4); b) 0.14; a: 1-3) taken without mixing; 4) rate of rotation of the mixer 1700 rpm; b) without mixing. Temperature of the solution 22 ± 2°C (a) and 25°C (b).

for dimethyl sulfoxide $E_{1/2}^{Rb^+} = -2.06$ and $E_{1/2}^{Cs^+} = -2.03$ V) [3, 4]. For the liberation of delocalized electrons from the electrode in two solvents, we might expect close values of the electrode potential jumps. The values of the energy of interaction of the delocalized electrons with the medium, determined by the inertialess portion of the polarization of the solvent, in dimethyl sulfoxide and hexamethylphosphorus triamide, should not differ too greatly, since the optical dielectric constants ε_{opt} of these solvents are close. The indices of refraction, the square of which determines ε_{opt}, are equal to 1.4742 and 1.4564 for dimethyl sulfoxide and hexamethylphosphorus triamide, respectively [4, 5].

The assumption of generation of SE also agrees with the fact that the rate of the process does not depend on the electrode material and the rate of mixing. This corresponds to the patterns established previously for the generation of SE in hexamethylphosphorus triamide on passive electrodes [1].

The results presented in Fig. 1a were obtained in salt solutions with a concentration no more than 0.07 M. To determine the true form of the polarization curves, we took the polarization curve in a more concentrated solution (Fig. 1b). As can be seen from Fig. 1b, the curve corresponds to a Tafel equation with a slope close to 60 mV, which is also characteristic of the process of generation of SE according to the mechanism of thermionic emission [1].

Thus, the results obtained permit us to hypothesize that in aprotic solvents — dimethyl sulfoxide and propylene carbonate — the process of electrochemical generation of solvated electrons can be carried out.

LITERATURE CITED

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