TWO MECHANISMS OF THE GENERATION OF SOLVATED ELECTRONS IN APROTIC SOLVENTS

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The cathodic processes occurring at metal electrodes in solutions of tetrasubstituted ammonium salts in dimethyl sulfoxide and hexamethylphosphoric triamide have been studied. From the rules of behavior obtained one can suggest that in a number of systems, the cathodic process is generation of solvated electrons via two parallel reactions. One of these follows the mechanism of electrochemical dissolution of electrons, the other that of thermal electron emission.

The electrochemical generation of solvated electrons (s.e.) in media that dissolve alkali metals with the formation of s.e. and are chemically stable toward these electrons has been studied in rather great detail [1]. Attempts have been made recently to detect this process in aprotic solvents reacting chemically with the s.e.. Preliminary results [2] gave rise to the suggestion that s.e. can be generated cathodically in solutions of tetrabutylammonium salts in dimethyl sulfoxide (DMSO) and propylene carbonate.

Results of a more detailed examination of the possible generation of solvated electrons in systems where they lack chemical stability are presented in this paper. Solutions of tetrasubstituted ammonium salts in hexamethylphosphoric triamide (HMP) and DMSO were used as systems meeting this requirement.

The method of steady-state polarization curves recorded under galvonostatic conditions with a P-5827 potentiostat was used for the investigation. The potentials were measured at 25 ± 0.1°C relative to an aqueous saturated calomel electrode (sce). It had been shown previously [3] that this electrode can be used for such measurements. For a determination of the state of the electrode surface, the capacitance was determined with an R-5021 ac bridge. The data were obtained as series equivalents in the region of potentials where marked faradaic currents are absent.

Solutions of $(C_4H_9)_4NI$, $(C_4H_9)_4NBF_4$, $(C_2H_5)_4NBF_4$, and $(CH_3)_4NI$ in DMSO and HMP were used with amalgamate , opper, copper, stationary mercury, gallium, cadmium, and lead cathodes. Tetrabutyl- and tetramethylammonium iodide of "pure" grade were twice recrystallized from twice-distilled water. Recrystallization of tetrabutylammonium iodide from benzene did not yield a sufficiently pure material.

There are indications in the literature [4] that iodide solutions in DMSO are decomposing chemically; therefore, tetrabutylammonium tetrafluoroborate was used in addition to the iodide. Tetrabutylammonium tetrafluoroborate was obtained by neutralization: $(C_4H_9)_4NOH + HBF_4 \rightarrow (C_4H_9)_4NBF_4 + H_2O$, in aqueous medium. All salts were carefully dried in vacuum at 50 to 60°C. Solvent purification and the preparation of HMP solutions were carried out following the methods described previously [2, 5]. The solutions in DMSO were prepared in air. The copper electrode was polished electrochemically, the cadmium and lead electrode were polished chemically. The design of the sealed cell with stirrer was described in [3]. This cell was used for the measurements with all electrodes other than the stationary mercury electrode. The latter was formed by the end of a glass tube fused into the cell bottom and filled with mercury. A gallium drop suspended at a short platinum wire fused into glass served as the stationary gallium electrode. The platinum surface had been etched in aqua regia and plated electrochemically with a thin layer of gallium [6] before the gallium drop was suspended.

Some of the polarization curves obtained in solutions of tetrasubstituted ammonium salts in HMP and DMSO are presented in Fig. 1. Curves 1 to 4 refer to the copper electrode in solutions of $(C_2H_5)_4NBF_4$ in HMP at two salt concentrations. The curves correspond to an extreme scatter of ± 50 mV in the experimental data. Similar curves located between curves 1 to 4 were obtained for the copper electrode in 0.04 M $(CH_3)_4NI$ and 0.04 to 0.10 M $(C_4H_9)_4NBF_4$ in HMP.

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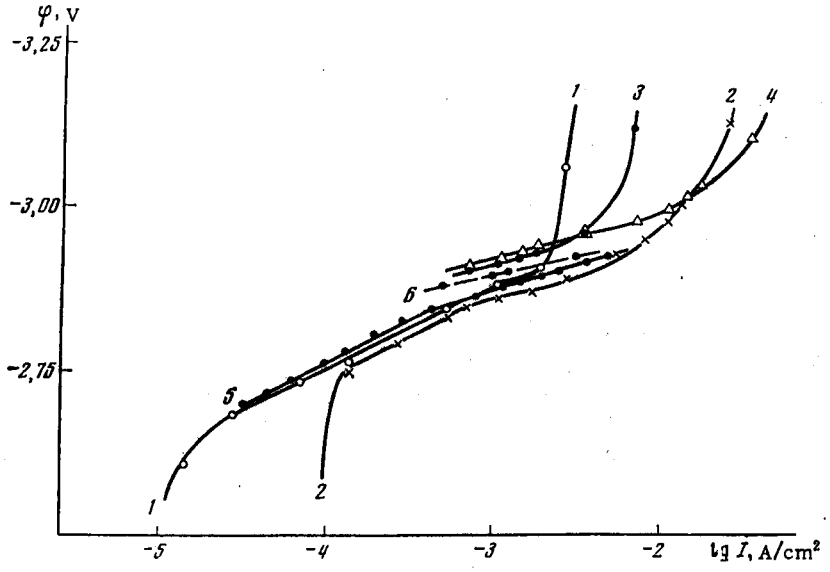

Fig. 1. The potential as a function of cathodic current density (I, in A/cm^2) at 25°C. 1) to 4) Electropolished copper in 0.10 (1, 2) and 0.20M (3, 4) tetraethylammonium tetrafluoroborate solutions in HMP without (1, 3) and with stirring (2, 4); 5) amalgamated copper in 0.23M tetrabutylammonium iodide solution in DMSO; 6) the upper section of curve 5 after correcting the currents by amounts corresponding to the extrapolated currents of the lower branch of curve 5.

Curve 5 of Fig. 1 refers to the amalgamated copper electrode in $(C_4H_9)_4NI$ solution in DMSO. Similar curves coinciding with curve 5 to within ± 20 mV were obtained for DMSO at the same electrode in $(C_4H_9)_4NBF_4$ solution and at electropolished copper in $(C_4H_9)_4NI$ solution. The curves obtained at the stationary mercury and gallium electrode in $(C_4H_9)_4NBF_4$ solutions in DMSO fall into the same potential range, but the slopes of the curves are strongly altered, due to solution penetration between the walls and the mercury in the case of the mercury electrode, and due to high impurity reduction currents in the case of the gallium electrode.

Reproducible values of potential could not be obtained when recording the polarization curves at the amalgamated copper and the mercury electrode in $(CH_3)_4NI$ solutions in HMP and DMSO, $(C_2H_5)_4NBF_4$ solutions in HMP and DMSO, and $(C_4H_9)_4NBF_4$ solution in HMP. Black films of varying thickness formed on the electrode surfaces. The films could be removed by high anodic polarization, but reformed even at low cathodic current densities.

Cathodic polarization of the lead and cadmium electrode with currents of 10^{-3} to 10^{-2} A/cm^2 in tetrabutylammonium tetrafluoroborate solution in DMSO was attended by dispersion of the cathode material. A black tarnish formed at the walls of the cathode compartment when lead was used. The lead and cadmium electrode disintegrated. The potentials of cathodic dispersion were between −2 and −2.4 V.

It follows from Fig. 1 that the cathodic processes occurring in solutions of tetrasubstituted ammonium salts in DMSO and HMP are subject to the same rules of behavior.

1. The processes occur at very negative potentials. It was of interest to compare the values of potential obtained in the two solvents. According to [7], the equilibrium potentials for poorly solvated ions should only slightly depend on the nature of the solvent. The half-wave potentials of the reversible discharge of rubidium and cesium ions with amalgam formation in HMP and DMSO which were measured relative to the aqueous nce differ by no more than 100 mV, and depend only slightly on the nature of the base solution [8, 9]. One can suggest, therefore, that the potential drops at the interfaces water/DMSO and water/HMP are similar, and roughly compare to the potentials measured in DMSO and HMP in a direct fashion. One can see from Fig. 1 that the cathodic processes examined occur at practically the same potentials.

2. The rate of the process is independent of stirring (curves 1 to 4) in the central part of the polarization curves. The most complete picture can be obtained when the curves without stirring are recorded going from

high to low currents, since under these conditions the distorting effect of the limiting diffusion current of impurity reduction is less pronounced at low currents (curves 1 and 2).

3. Within the limits of experimental accuracy, the rate of the process is independent of the electrode material (copper, amalgamated copper, mercury, or gallium in tetrabutylammonium salt solution in DMSO) and of the length of the radicals in the tetrasubstituted ammonium cation (the copper electrode in solutions of tetramethyl-, tetraethyl-, and tetrabutylammonium salts).

4. The polarization curves have two sections, in general: a lower one with a slope of 120 to 140 mV, and an upper one with a slope of 80 to 90 mV. This shape of the curves is most clearly developed for the systems with DMSO, but is retained in the case of HMP.

The shape of the polarization curves of Fig. 1 (decreasing Tafel slope with increasing current density) indicates that two processes with different transfer coefficients are occurring in parallel.

If the currents of the second branch of the polarization curve (curve 5 of Fig. 1) are corrected by amounts corresponding to the extrapolated values of current of the lower branch, a corrected polarization curve is obtained (curve 6 of Fig. 1) which has a Tafel slope of 60 mV.

The suggestion that the cathodic process in solutions of tetrasubstituted ammonium salts in HMP and DMSO is the electrochemical generation of solvated electrons is the most likely explanation for the rules of behavior found. The behavior of the cathodic process in these systems is similar to that of the cathodic reaction in solutions of alkali metal salts in HMP. It has been shown reliably [10-12] that electrochemical generation of solvated electrons is the cathodic process in the latter case.

By analogy with the solutions of alkali metal salts in HMP, the suggestion can be made that the process responsible for the first section of the polarization curve (slope 120 to 140 mV) is generation of solvated electrons via the electrochemical dissolution mechanism [13]. The second process, which is responsible for the section of the polarization curve with slope 60 mV, is generation of solvated electrons via the thermionic emission mechanism [13]. Generation via this mechanism occurs in parallel to the electrochemical dissolution of electrons. Comparing the potentials at which solvated electrons are generated via the two mechanisms in solutions of alkali metal halides [13] with the potentials for the corresponding processes presented in Fig. 1 one finds that they are similar. The earlier suggestion concerning primacy of the generation process [14] is confirmed by the similarity of the potentials at which solvated electrons are generated in solutions of lithium, sodium, tetramethylammonium, tetraethylammonium, and tetrabutylammonium salts. This means that electrons are the primary products of the cathodic process; they are not produced upon dissolution of alkali metal or $R_4N^{\cdot}$ radicals first formed at the electrode.

Limiting currents are seen in the polarization curves obtained in solutions of tetrasubstituted ammonium salts in DMSO and HMP. In HMP, the limiting currents increase with the salt concentration (see Fig. 2) and stirring intensity, i.e., they are due to diffusion and migration. This can be explained by considering that the solvent is chemically stable toward the solvated electrons, while the tetraalkylammonium ions are reacting with them to yield electrically neutral species. At sufficiently high current densities, this causes the solution layer next to the electrode to become impoverished in current carriers, and a limiting diffusion–migration current arises. In cases where the diffusion layer is substantially thicker than the layer where the chemical reaction between the tetrasubstituted ammonium ions and the solvated electrons is taking place, the behavior of the electrode near the limiting current will be similar to that of electrodes in systems with the usual diffusion–migration currents. The suggestion that the solvated electrons are reacting chemically with the tetraalkylammonium ions in HMP is in harmony with the negative results obtained in attempts to detect solvated electrons by EPR during cathodic polarization in tetrabutylammonium chloride solution [15].

Limiting currents are seen as well in the polarization curves obtained in DMSO. But in contrast to the limiting currents in HMP, these do not depend on stirring, and not much on salt concentration. In dilute solutions, the currents are substantially higher than the diffusion–migration currents found in this solvent during the discharge of hydrogen or lithium ions at similar concentrations [2]. The absence of limiting diffusion–migration currents in solutions of tetrasubstituted ammonium salts in DMSO can be explained by assuming that in this system, the solvent molecules are effective scavengers for the electrons [16] generated at the cathode, while the reaction products of the electrons and DMSO apparently do not react with the tetrasubstituted ammonium ions to yield neutral species. This prevents an impoverishment of the solution layer next to the electrode with respect to ionic current carriers which would give rise to limiting diffusion–migration currents.

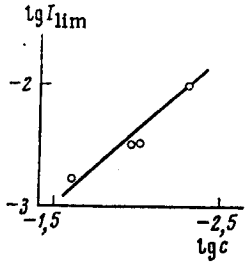

Fig. 2. The limiting current (I_{lim}, in A/cm^2) as a function of the tetraethylammonium tetrafluoroborate concentration (c, in mole/liter) in HMP at an electrode of electropolished copper, at 25°C without stirring.

The limiting currents occurring in DMSO can be suggested to be passivation-related, i.e., due to blocking of the electrode surface by reaction products of the solvent molecules and the electrons generated at the cathode.

It has been demonstrated previously [13, 17] that the state of the electrode surface has great influence on the electrochemical generation of s.e. The capacitance of the amalgamated copper electrode was measured in 0.06 to 0.11 M $(C_4H_9)_4NBF_4$ solutions in DMSO in order to determine the state of the electrode surface in the systems examined. Measurements were made over the range of potentials from −1.0 to −2.6 V, where practically no faradaic current is flowing as yet, but the most negative potentials are close to the potentials of s.e. generation. It was found that over the above range of potentials, the capacitance is 6.3 to 6.5 μF/cm^2, practically independently of potential, salt concentration, and ac frequency (7 to 20 kHz). On account of the lack of frequency dependence, this capacitance can be regarded as a double-layer capacitance. One can conclude when comparing this value of capacitance for the amalgamated copper electrode with the corresponding value for the mercury electrode in DMSO [18] that the surface of the amalgamated copper electrode is free of screening oxide or other layers during the generation of s.e.

The capacitance of the copper electrode in 0.06 M $(C_4H_9)_4NBF_4$ solution in HMP is 5 μF/cm^2 over the range of potentials from −1 to −2.0 V. This value of capacitance is somewhat higher than the value of 3.5 μF/cm^2 obtained earlier [17] for the active surface of a copper electrode in lithium chloride solution in HMP, and substantially higher than the value of 1.6 μF/cm^2 found for the passive copper electrode in the same solution. Thus, one can infer that the generation of s.e. in $(C_4H_9)_4NBF_4$ solution at the copper electrode proceeds while screening layers are practically absent from the surface.

The results obtained show that the generation of solvated electrons is a rather general cathodic process occurring at negative potentials in aprotic solvents. In HMP, generation occurs in salt solutions, both of the alkali metals and of tetrasubstituted ammonium. In some other aprotic solvents, e.g., DMSO, generation evidently can only be accomplished in salt solutions of tetrasubstituted ammonium, where a surface free of screening layers can be realized. Alkali metal is evolved during cathodic polarization in the solutions of alkali metal salts in certain aprotic solvents. This is typical in particular for lithium salt solutions, where the reversible lithium electrode can be realized. The potentials exhibited by such an electrode in lithium salt solution are more negative than those of solvated-electron generation, which, however, does not occur at such electrodes. In explaining this effect one has to remember that the lithium electrode in aprotic solvents is covered with an oxide film which possibly does not interfere with the cathodic deposition and anodic dissolution of lithium but inhibits the generation of solvated electrons and prevents chemical reaction of the lithium with the solvent. Potassium and sodium can vigorously react with DMSO [4]; their oxide or hydroxide films usually are more readily soluble in nonaqueous solvents. It is an interesting fact that the electrochemical generation of s.e. in a solvent such as HMP (HMP solutions have become the classical example of media where such reactions will occur) can be suppressed, despite the potential having sufficiently negative values. Avaca and Bewick [19] have shown that the lithium electrode is chemically stable in saturated lithium chloride solution in HMP, and apparently reversible with respect to lithium ions; the generation of s.e. does not occur at this electrode, even though its potential is more negative than the potentials required for s.e. generation at an inert electrode. One can suggest that the cathodic formation of s.e. is suppressed by the formation of a lithium hydroxide film on the electrode.

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ELECTROSTATIC FREE ENERGY OF ADSORPTION LAYERS FORMED BY COMPLEX IONS

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A statistical—thermodynamic method is presented which can be used to determine the composition of the adsorption layers forming at the interface between a metal and an electrolyte solution containing charged and neutral metal complexes. The method rests on calculations of the electrostatic free energy of the adsorption layer which include the discreteness-of-charge effect of the adsorbed species. It is shown that at a given mean density of adsorbed charge, structures with different discrete charges can be realized, and that this difference must have a substantial effect on the kinetics of electrochemical reactions taking place in the adsorbed state.

The heavy use of polarographic techniques in electroanalytical chemistry, particularly for the determination of metal ions in solutions, has provided the stimulus for the formulation and realization of detailed experimental research into the adsorption of complexes of different metals on mercury [1-15]. One of the most interesting and important features discovered in these studies is the so-called anion-induced adsorption. This effect is a very sharp rise in the adsorbability of complex species (which exist as ions or molecules) which occurs when surface-active anions are present. Thus, specific adsorption of iodide ions on mercury gives rise to the adsorption of cadmium, which does not exhibit surface activity of its own [6]. A similar effect of induced adsorption is seen in solutions containing Pb^{2+} and Cl^-. Lead, which is not adsorbed on mercury in the absence of surface-active anions, can be detected in the adsorption layer at the interface between mercury and aqueous chloride solution [10]. Anion-induced adsorption has the practically important effect that electrode reactions involving the cations of complex-forming metals can be accelerated significantly (by several orders of magnitude) [12, 15].

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