

ANION REDUCTION IN NONAQUEOUS SOLVENTS

II. DIMETHYL SULFOXIDE

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UDC 541.138.3:546

In the modern theory of the elementary act of charge transfer, the activation process is associated with a redistribution of the solvent molecules in the reaction zone. Hence for the development of this theory experimental data are required on the kinetics of electrode reactions as function of the solvent. Convenient for these purposes are the reduction reactions of certain anions, e.g., $S_2O_8^{2-}$, since at negative values of surface charge there is no specific adsorption of reacting species or reaction product, and the influence of the solvent on the discharge rate is determined only by its effect on the heat of the reaction's elementary act and on solvent dipole reorientation.

It has been established in [1] that the reaction rate of $S_2O_8^{2-}$ reduction at mercury in sodium salt solutions in dimethyl sulfoxide (DMSO) is much lower than that in water. The literature is lacking data on the reduction of anions in aprotic solvents at different electrodes. We therefore examined the kinetics of persulfate ion reduction at dropping electrodes of mercury and of eutectic gallium-indium alloy (indium "gallam"). Part of the data on the kinetics of persulfate ion reduction at mercury in DMSO has been published in [1].

Unlike indium amalgam, one does not find negative indium adsorption for indium gallam at negative surface charge of the electrode [2]. The zero-charge potential ($\varphi_{\epsilon=0}$) of indium gallam is 0.7 V more negative than $\varphi_{\epsilon=0}$ of mercury in DMSO [3]. The technique of working with indium gallam and the purification of DMSO are reported in [4] and [1], respectively. Capillary and cell were dried before they were filled with indium gallam and with the electrolyte solutions in DMSO.

All potentials in the paper are stated relative to an aqueous normal calomel electrode connected with the cell via a vessel containing saturated KCl solution in water. The salt bridge was entirely filled with electrolyte in DMSO.

The $I-\varphi$ curves for the electroreduction of 10^{-3} N $K_2S_2O_8$ at the dropping mercury electrode in DMSO in the presence of various concentrations of KPF_6 are presented in Fig. 1. Persulfate ion reduction begins at positive values of surface charge. As the zero-charge potential is approached, the discharge rate is drastically inhibited, and the region where the reaction is practically completely inhibited is about 0.7 V. The rate of persulfate ion reduction increases when the cathodic potential is rising further (Fig. 1, curve 1). With increasing KPF_6 concentration the rate of $S_2O_8^{2-}$ reduction becomes larger at negative values of surface charge but smaller at positive values. At the $\varphi_{\epsilon=0}$ of mercury in DMSO, which is -0.31 V, the anion reduction rate is independent of base-electrolyte concentration, and all the $I-\varphi$ curves are intersecting practically at one point (Fig. 1). Such dependence of the rate of anion electroreduction on electrode potential and base-electrolyte concentration can be explained with a slow electrochemical step of anion discharge. In this case the discharge rate is determined by the equation

$$i = zFk_s^0 c_A \exp \left\{ -\alpha \left(\varphi + \frac{n_1 - \alpha}{\alpha} \psi_1 \right) F/RT \right\}, \quad (1)$$

where z is the number of electrons involved in the reaction; F is the Faraday constant; φ is the electrode potential as measured against some reference electrode; ψ_1 is the mean potential in the plane where the centers of charge of the reacting species are located in the transition state of the reaction; n_1 and c_A are the charge and concentration of the reacting species in the bulk of the solution; k_s^0 and α are constants. Equation (1) had been derived under the assumption that the distribution of potential and ionic concentration within the diffuse

M. V. Lomonosov State University, Moscow. Translated from *Élektrokimiya*, Vol. 13, No. 1, pp. 89-92, January, 1977. Original article submitted December 10, 1975.

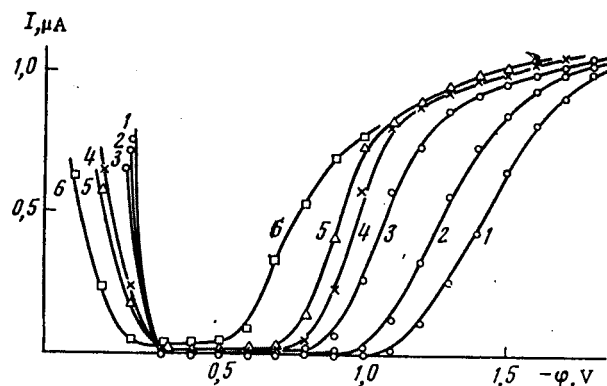


Fig. 1. Polarization curves for the reduction of 10^{-3} N $K_2S_2O_8$ in DMSO at the dropping mercury electrode in the presence of different concentrations of KPF_6 : 1) $5 \cdot 10^{-3}$ N; 2) 10^{-2} N; 3) $2.5 \cdot 10^{-2}$ N; 4) $5.0 \cdot 10^{-2}$ N; 5) 10^{-1} N; 6) $5.0 \cdot 10^{-1}$ N.

part of the electric double layer retains its equilibrium character while the electrode reaction is taking place (static ψ_1 -effect) [5].

On indium gallam, persulfate ion reduction in DMSO can only be studied at negative values of surface charge, where the minimum of current is found on the $I-\varphi$ curve and the discharge rate increases with the concentration of base-electrolyte cations. At positive values of surface charge of the indium-gallam electrode, $S_2O_8^{2-}$ ion reduction could not be studied since the alloy dissolves anodically at these potentials (Fig. 2). From the data on the reaction rate on indium gallam as function of the concentration of base-electrolyte cations at negative values of surface charge we calculated the charge n_1 of the reacting species in the bulk of the solution by the method of [6]. The average value of n_1 in 10^{-3} N $Na_2S_2O_8 + NaClO_4$ solutions was -1.3 , that in 10^{-3} N $K_2S_2O_8 + KPF_6$ solution was -1.9 . The deviation of n_1 from the value -2.0 found in the presence of sodium ions indicates that ionic aggregates are formed in the bulk of the solution [7].

The possibility of ion pair formation in DMSO is associated with the dielectric constant of DMSO, which with a value of 47 is lower than that of water. In harmony with this idea [5], corrected Tafel plots (cTp) for the reduction of $S_2O_8^{2-}$ in the presence of different concentrations of sodium ions coincide provided that in calculating these cTp one uses the approximate integer value of charge $n_1 = -1.0$ determined from the kinetic data. In solutions of potassium salts, the cTp are found to coincide when $n_1 = -2.0$. Here it has been assumed that the ψ_1 potential equals the potential of the outer Helmholtz plane, ψ_0 , and the values of surface charge required to calculate the ψ_0 potential were found by numerical integration of the differential capacity curves for mercury [8] and indium gallam [3] in DMSO. Let us extrapolate the cTp obtained on mercury and indium gallam (assuming here that they are linear) to the potential range where the discharge currents on the $I-\varphi$ curves, e.g., on mercury, are so low that it would be impossible to calculate cTp from the experimental data. We then shall calculate the polarization curves using the dependence of ψ_0 potential on electrode potential. The $\log i - \varphi$ dependences thus found for the $S_2O_8^{2-}$ reduction in DMSO on indium gallam and on mercury are similar in shape to the $\log i - \varphi$ dependence for the same reaction in aqueous solutions (Fig. 3). It can be seen from the figure that in accordance with the difference that exists between the zero-charge potentials, the rate of $S_2O_8^{2-}$ reduction in DMSO increases at all potentials as one goes from mercury to indium gallam.

The difference in reaction rate decreases with increasing negative potential, but differences in the reaction rates remain even at the most negative values of surface charge of the electrode.

The heterogeneous rate constants k_s^0 of persulfate ion reduction have been calculated from Eq. (1). For mercury in 10^{-3} N $Na_2S_2O_8 + 10^{-2}$ N $NaClO_4$ solution, $k_s^0 = 5.0 \cdot 10^{-3}$ cm/sec in water and $6.5 \cdot 10^{-7}$ cm/sec in DMSO; for indium gallam the values are $4.0 \cdot 10^{-3}$ and $4.1 \cdot 10^{-7}$ cm/sec, respectively. These data confirm the results following from slow discharge theory that k_s^0 is independent of electrode material, but indicate that this quantity depends on the solvent. When comparing the k_s^0 values obtained in water and DMSO we must keep in mind, however, that in going from one solvent to another we could not rigorously satisfy the condition of keeping φ constant, since in the measurements in DMSO we could not take into account the potential difference existing at the interface between aqueous and nonaqueous phase, which is an integral part of the φ value being measured. The decrease in rate constant found to occur when one goes from water to DMSO may depend both

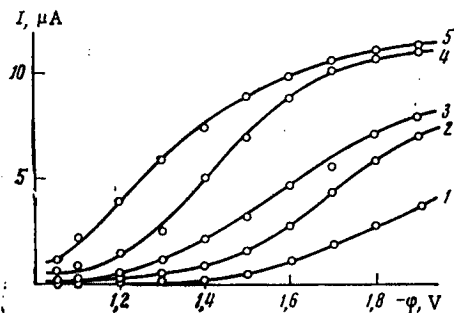


Fig. 2

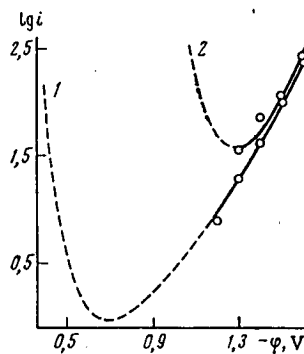


Fig. 3

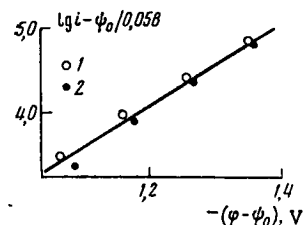


Fig. 4

Fig. 2. Polarization curves for the reduction of 10^{-3} N $\text{Na}_2\text{S}_2\text{O}_8$ in DMSO at the dropping indium-gallam electrode in the presence of different concentrations of NaClO_4 : 1) $2.0 \cdot 10^{-3}$ N; 2) $5.0 \cdot 10^{-3}$ N; 3) $1.5 \cdot 10^{-2}$ N; 4) $2.5 \cdot 10^{-2}$ N; 5) $5.0 \cdot 10^{-2}$ N.

Fig. 3. The rate of $\text{S}_2\text{O}_8^{2-}$ ion reduction as function of potential in 10^{-3} N $\text{K}_2\text{S}_2\text{O}_8 + 0.5 \cdot 10^{-2}$ N KPF_6 solution in DMSO: 1) mercury; 2) indium gallam. Points: experimental data; dashed lines: calculation.

Fig. 4. Corrected Tafel plots for the reduction of 10^{-3} N $\text{Na}_2\text{S}_2\text{O}_8 + 2.5 \cdot 10^{-2}$ N NaClO_4 at mercury (1) and indium-gallam (2) electrodes.

on the weaker solvation of the anions in DMSO [9] and on differences in surface layer structure in these two solvents. The observation that k_s^0 changes by approximately the same factor for mercury and for indium gallam as one goes from water to DMSO can be attributed both to prevalence of the bulk factor, i.e., solvation energy of the anion, and to the fact that any differences in the chemisorption of solvent dipoles between mercury and indium gallam have already been leveled at potentials negative enough to measure the reaction rate at indium gallam [3, 10].

Using the calculated values of ψ_0 potential we obtained cTp for mercury and indium-gallam electrodes in DMSO. The cTp for persulfate ion reduction at mercury and indium gallam in DMSO are linear, and coincide for solutions having the same composition (Fig. 4). The transfer coefficient α for this reaction is the same at all electrodes, and has a value of 0.27 ± 0.02 in the presence of NaClO_4 . Corrected Tafel plots which are independent of electrode metal show that the rate of persulfate ion reduction at the electrodes studied in DMSO is determined only by the structure of the electric double layer, and that the electronic work function from these metals into electrolyte solution in DMSO is the same at a given potential.

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