THE ELECTROREDUCTION OF $S_2O_8^{=}$ ANION AT A DROPPING GALLIUM – INDIUM ALLOY ELECTRODE

A. N. Frumkin, N. V. Fedorovich,
S. I. Kulakovskaya, and M. D. Levi

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An investigation of the reduction of $S_2O_8^{=}$ and $S_4O_6^{=}$ anions at solid bismuth, tin, lead, and cadmium electrodes has shown that the dependence of the reaction rate on the electrode's nature is determined only by the structure of the electric double layer, i.e., by the value of the ψ_1 potential whose magnitude and sign are determined by the position of the point of zero charge $\varphi_{\varepsilon=0}$ [1]. In that there is some difficulty in determining the true area for measurements at solid electrodes, liquid electrodes are more suitable for elucidating the reasons for change in reduction rate with change in the nature of the electrode. In connection with the investigation of the mechanism, $S_2O_8^{=}$ reduction was carried out at a dropping electrode made of the eutectic alloy of gallium and indium which freezes at 15°C. In contrast with indium amalgam [2], negative adsorption of indium at negative electrode surface charges is not observed for the gallium–indium alloy; the potential of zero charge of the Ga–In alloy is 0.49 V more negative than $\varphi_{\varepsilon=0}$ for mercury [3]. There are no data in the literature for the electroreduction of anions at the Ga–In alloy.

Ga–In alloys were obtained by dissolving indium (99.999%) in gallium (99.999%) under a solution of specially purified NaOH with gentle heating. Immediately before recording the current–voltage curves, the alloy was washed once with a 0.1 N solution of NaOH, and then poured into the reservoir to which was attached a capillary 2.5 cm long with a 0.1 mm diameter. The characteristics of the capillary were: flow rate, $m = 8$ mg/sec; drop time, $\tau = 2.5$ sec in twice distilled water. Potentials were measured relative to a normal calomel electrode.

On reducing $S_2O_8^{=}$ at a dropping indium–gallium alloy a slowing of the reaction at negative surface charges is observed in dilute solutions just as was the case at mercury, thallium, and indium amalgam [4], and also solid electrodes [1] (Fig. 1). With further increase in cathodic polarization, the reaction rate increases again. An increase in discharge rate for $S_2O_8^{=}$ is observed on increasing the concentration of the base electrolyte cation (Fig. 1) and on increasing its radius on going from Na^+ to K^+ (Fig. 2). From experimental data on the dependence of reaction rate on base electrolyte cation concentration, the charge on the reacting particle, n_1, in the bulk of the solution was determined using the relation

$$\left(\frac{\partial \ln i}{\partial \ln c}\right)_{\varphi-\frac{RT}{n_2F}\ln c} = -\frac{n_1}{n_2}, \qquad (1)$$

where i is the Faradaic current for anion reduction and n_2 is the charge on the base electrolyte cation. This relationship was derived [5] from the electrocapillary equation assuming that the adsorption of all anions in the solution, Γ_A, at negative surface charges is small in comparison with the adsorption of cations, Γ_K, and that the relation $\varphi - (RT/n_2F)\ln c = \text{const}$ is fulfilled for solutions having the same concentration of reducing anion but different concentrations of base electrolyte. To calculate the Faradaic currents, the experimental currents were corrected for concentration polarization [6] taking into consideration changes in τ and m with potential. Log i versus log c relationships calculated for various potentials in solutions of 10^{-3} N $Na_2S_2O_8 + NaClO_4$ were linear; n_1 was determined from the slope. For the $S_2O_8^{=}$ reduction reaction the value of n_1 was determined in the potential interval −1.4 to −1.55 and was shown to be −1.8; that is, the values of n_1 obtained are close to the theoretical value $n_1 = -2$.

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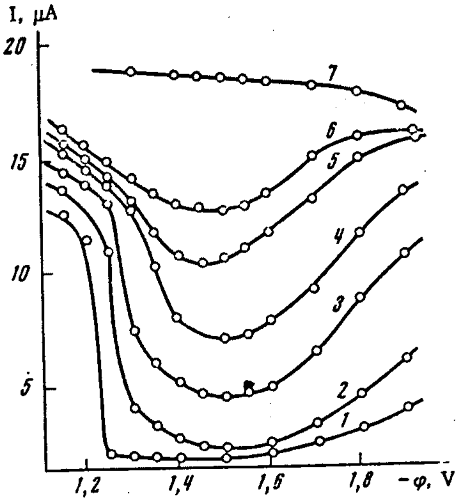

Fig. 1

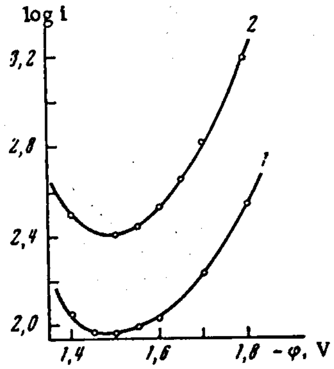

Fig. 2

Fig. 1. Polarization curves of the reduction of 10^{-3} N $Na_2S_2O_8$ at a dropping electrode of gallium indium alloy with additions of $NaClO_4$ at concentrations of: 1) (0; 2) 10^{-3}; 3) $2.5 \cdot 10^{-3}$; 4) $4 \cdot 10^{-3}$; 5) $6 \cdot 10^{-3}$; 6) $9 \cdot 10^{-3}$; 7) $5 \cdot 10^{-2}$ M.

Fig. 2. Polarization curves for the reduction of $S_2O_8^=$ at a gallium–indium alloy electrode in the following solutions: 1) 10^{-3} N $Na_2S_2O_8$ + $2.5 \cdot 10^{-3}$ N $NaClO_4$; 2) 10^{-3} N $K_2S_2O_8$ + $2 \cdot 10^{-3}$ N $KClO_4$.

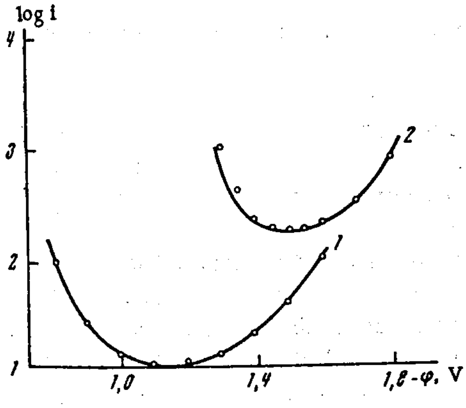

Fig. 3. Dependence of the rate of $S_2O_8^=$ reduction on potential in the following solutions: 1) 10^{-3} N $Na_2S_2O_8$ + $4 \cdot 10^{-3}$ N NaF at mercury; 2) 10^{-3} N $Na_2S_2O_8$ + $4 \cdot 10^{-3}$ N NaF at gallium–indium alloy. The continuous curve 2 was calculated according to Eq. (1) [7].

The dependence of $S_2O_8^=$ reduction rate at the gallium–indium alloy on electrode potential, nature, and concentration of base electrolyte can be explained by the slowness of the electrochemical step in anion discharge, the rate of discharge being given by Eq. (1) [7], which was derived on the assumption that the equilibrium character of the potential distribution and ion concentrations was maintained within the diffuse part of the double layer when an electrode reaction took place (the static ψ_1 effect according to Gierst). According to a conclusion of the theory of slow discharge [1, 4] the reaction rate increases with increase in the negative value of $\varphi_{\varepsilon=0}$, that is, on going from mercury to indium–gallium alloy whose $\varphi_{\varepsilon=0}$ is -0.96 V [2]. Insofar as differences in the values of ψ_0 potentials (ψ_0 is the potential on the outer Helmholtz plane) for different electrodes is largest near $\varphi_{\varepsilon=0}$, then differences in $S_2O_8^=$ discharge rates are largest in this potential region, and these differences decrease with increase in the negative value of the electrode potential (Fig. 3).

Calculation of the ψ_0 potential was carried out according to the theory of the equilibrium diffuse layer, the necessary charge values for the calculation being found by the integrating differential capacity curves for the indium–gallium alloy in $NaClO_4$ solutions obtained by Kaliuzhna. On using the calculated values of ψ_0, corrected Tafel plots (CTP) were obtained for $S_2O_8^=$ discharge at the indium–gallium alloy and compared with CTP for this reaction at mercury. As is apparent from Fig. 4, CTP for the $S_2O_8^=$ discharge reaction at the gallium–indium alloy coincide for different base electrolyte concentrations and with extrapolated values of CTP for the mercury electrode. CTP at the gallium indium alloy are linear over the whole potential range, a very small deviation from linearity being observed near the point of zero charge ($\varphi_{\varepsilon=0}$). The transfer coefficient α, found from the slope of the CTP at high negative charges, is equal to 0.22 ± 0.02 for the gallium–indium alloy. A log i, φ curve was calculated according to the equation for slow discharge [4] using the value of α found

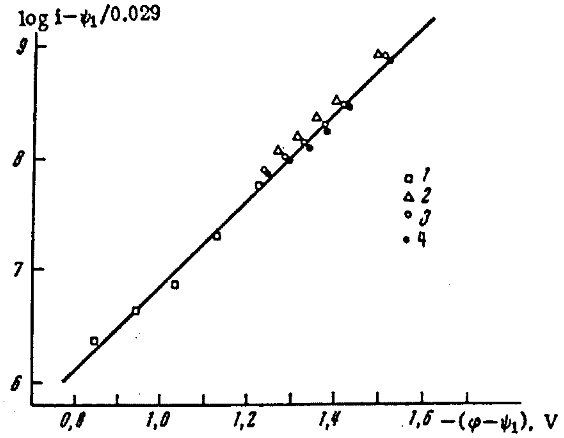

Fig. 4. Corrected Tafel plots for the reduction of 10^{-3} N $Na_2S_2O_8$ at electrodes of: 1) Hg in the presence of $4 \cdot 10^{-3}$ N NaF; 2) Ga–In in the presence of 10^{-3} N $NaClO_4$; 3) Ga–In in the presence of $2.5 \cdot 10^{-3}$ N $NaClO_4$; 4) Ga–In in the presence of $4 \cdot 10^{-3}$ N $NaClO_4$.

from the slope of the CTP ($\alpha = 0.23$). The constant in the equation was determined from the experimental value of the reduction rate of $S_2O_8^{=}$ at the minimum in the log i, φ curve and was found to be $1.2 \cdot 10^{+3}$ A·cm·mole^{-1}. The calculated log i, φ curve is compared with the experimental curve in Fig. 2, from which it is apparent that the calculated and experimental curves are in satisfactory agreement.

As was already stated above, the equation for the theory of slow discharge in its simplest form stating the linear relationship between ($\log i - n_1\psi_1F/RT$) and $-(\varphi-\psi_1)$ was used in constructing the CTP. The method of calculating ψ_1 used here assumes that this quantity can be considered as the average value of the potential on the outer Helmholtz plane. The legitimacy of such an assertion has been examined several times in the literature (see, for example [8]). The assumption that the divalent, and consequently, relatively strongly hydrated anion is located on the outer Helmholtz plane in the transition state does not give rise to any particular doubts; however, the correctness of using the average rather than the local value of ψ_1 is not clear inasmuch as the dependence of the reaction rate on the nature of the cation is evidence for the localization of the reacting anion in the transition state in the immediate vicinity of the cation found in the outer part of the electric double layer, an ion pair perhaps being formed with it. This proximity should result in an increase in the calculated local ψ_1 potential above its average value at the same distance from the metal surface. This can be called the electrostatic effect of forming a cation bridge (see also [1]). The fact that a sufficiently linear dependence of log i on φ exists after introduction of a correction based on ψ_0, in spite of this effect, is evidence that the difference between the average and local values of the ψ_1 potential probably depends very little on φ for the range of values of φ examined. In this case, exchange of the local value of ψ_1 for the average value only effects the value of the rate constant.

The existence of a cation bridge can also result in a quantum-mechanical effect by changing the mechanism of electron transfer from the metal to the anion [9], which probably should result in a decrease in the ψ_1 effect. However, we do not have sufficient evidence that the quantum-mechanical bridging mechanism of electroreduction actually is realized in the present case.

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