DETERMINATION OF THE CHARGE AND REACTION ORDER IN THE ELECTROREDUCTION OF THE $S_2O_8^{2-}$ ION IN ETHYLENE GLYCOL

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In [1] it was proposed that the inverse dependence of the activation energy of the discharge of $S_2O_8^{2-}$ on the radius of the cation in ethylene glycol and in water may be due predominantly to a temperature dependent change in the stability of the ion pair in the bulk of the solution relative to the change in adsorption effects in ethylene glycol. Since the formation of ion pairs in the bulk of the solution must be manifested by the effective charge of the reacting particles, our aim was to determine this charge in ethylene glycol solutions using the method of Frumkin and Petrii [2]. The charge was determined from the rate of the process as a function of the concentration of the cation of the base electrolyte at constant electrode potential. The charge thus found for the reacting particles is correct, provided that the adsorption of anions on the negatively charged surface is negligible relative to the adsorption of cations.

In determining the charge of the reacting particles the experimental current was corrected for concentration polarization by the method described in [3]. The purification of reagents and the experimental procedure were described in [1]. The charge of the $S_2O_8^{2-}$ anion was determined in $NaClO_4$, KCl, and CsCl solutions, containing $Na_2S_2O_8$, $K_2S_2O_8$, and $Cs_2S_2O_8$, respectively. Figures 1 and 2 show the experimental curves obtained after correcting for concentration polarization. It was found that the charge of the reacting particles, n_1, in ethylene glycol was always considerably less than 2, while in water [2] and formamide [4] it approached 2. For $NaClO_4$ and KCl in ethylene glycol $n_1 = 1.1$, for CsCl $n_1 = -1.45$. This result is not surprising since in nonaqueous solutions of low dielectric constant association of the individual ions and the probability of ion pair formation is considerably greater than in aqueous solutions.

This is also in agreement with results on the temperature dependence of the rate constant of reduction of the $S_2O_8^{2-}$ anion as a function of the radius of the cation. The least solvated Cs^+ cations form the most stable ion pairs in the bulk of the solution and, consequently, show the greatest activation energy in the reduction process. This appears to be the cause of the reduced dependence of the reaction rate on the radius of the cation. The effect of the increased stability of the bond between adsorbed cations and $S_2O_8^{2-}$ anions on the reaction rate in going from Na^+ to Cs^+ is largely compensated by the enhanced stability of ion pairs in the bulk of the solution and the corresponding decreased activity of the reacting anion. It should be noted, however, that a decreased charge on the $S_2O_8^{2-}$ anion makes it more difficult to explain the minimum exhibited by the $I-\varphi$ curves. Repulsion between particles of low charge and the surface should have less effect on the form of polarization curves than if the particles have a high negative charge.

However, because of the formation of ion pairs between ions of the electrolyte, ethylene glycol solutions behave as if their concentration were lower at a given stoichiometric composition than the concentration in the corresponding aqueous solution. This would contribute to deepening the minimum. This is even more clearly manifested in pyridine solutions, as noted by Damaskin and co-workers [5], where the minimum in the reduction curve of $S_2O_8^{2-}$ is retained up to 1 N base electrolyte concentration. The much reduced width of the minimum in ethylene glycol relative to aqueous solutions is possibly due to the fact that adsorption of the cations of the base electrolyte in ethylene glycol solutions occurs at much less negative electrode potentials [6].

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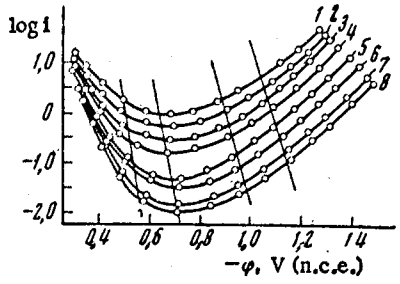


Fig. 1

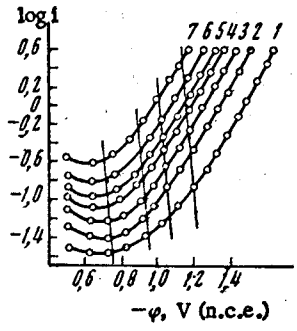


Fig. 2

Fig. 1. Polarization curves of the reduction of 10^{-3} N $Na_2S_2O_8$ at the following concentrations of $NaClO_4$: 1) $3 \cdot 10^{-1}$; 2) $2 \cdot 10^{-1}$; 3) 10^{-1}; 4) $6.9 \cdot 10^{-2}$; 5) $2.9 \cdot 10^{-2}$; 6) $1.9 \cdot 10^{-2}$; 7) $9 \cdot 10^{-3}$; 8) $7 \cdot 10^{-3}$.

Fig. 2. Polarization curves of the reduction of 10^{-3} N $Cs_2S_2O_8$ at the following concentrations of CsCl: 1) 0; 2) 10^{-3}; 3) $2 \cdot 10^{-3}$; 4) $3 \cdot 10^{-3}$; 5) $4 \cdot 10^{-3}$; 6) $5 \cdot 10^{-3}$; 7) $6 \cdot 10^{-3}$.

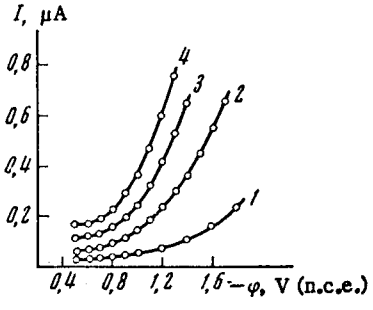


Fig. 3

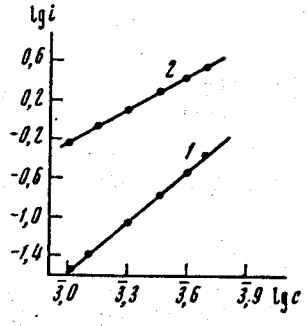


Fig. 4

Fig. 3. Polarization curves for $K_2S_2O_8$ solutions without base electrolyte: 1) $1 \cdot 10^{-3}$; 2) $2 \cdot 10^{-3}$; 3) $3 \cdot 10^{-3}$; 4) $4 \cdot 10^{-3}$.

Fig. 4. The reaction rate as a function of the concentration of the reducible anion in $K_2S_2O_8$: 1) in the presence of 0.1 N KCl; 2) without adding an inert electrolyte.

As was shown in [7], in accordance with the presumed slowness of the charging stage, the reaction order p for the discharge of $S_2O_8^{2-}$ in aqueous solutions depends on the structure of the electric double layer. When $\psi_1 \simeq 0$ the reaction rate is $i = kc$ and $p = 1$. In dilute base electrolyte solutions where the effect of ψ_1 on the electrode process is large $i = kc^{n_1+\alpha+1}$ and $p = n_1 + \alpha + 1$. For the discharge reaction of $S_2O_8^{2-}$ in dilute solutions in water $p = 2.7$ which is close to the theoretical value, $p = 3.2$.

Polarization curves in ethylene glycol solutions of $K_2S_2O_8$ without base electrolyte are shown on Fig. 3. After correcting the polarization curves for concentration polarization according to [5], log i was plotted against log c and the reaction order was determined from the slopes (Fig. 4).

As expected, in concentrated ethylene glycol solutions a first-order reaction was observed. In dilute ethylene glycol solutions, where the effect of the electric field of the double layer on the rate of the electrode process is especially pronounced, the reaction order was found to be 1.8.

The agreement between experimental and theoretical values is satisfactory when the charge of the reacting particles is equal to 1, which is close to the value obtained in this work.

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