# EFFECT OF THE RADIUS OF BASE ELECTROLYTE CATIONS ON THE REDUCTION OF PERSULFATE ANION ON A MERCURY ELECTRODE

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The effect of the radius of base electrolyte cations on the rate of electrochemical reduction was first investigated in the work of Herasymenko and Slendyk [1] and N. N. Izgaryshev and Kh. M. Ravikovich [2]. In a study of the effect of alkali and alkaline earth metal cations on the reduction of hydrogen, Herasymenko and Slendyk found that the rate of hydrogen liberation in the presence of alkali metal chlorides decreased by a factor of approximately one and a half with a change from lithium to cesium. The same type of effect was described in the work of N A. Izgaryshev and Kh. M. Ravikovich on the effect of alkali metal cations on the electrodeposition of nickel and in the work of R. M. Vasenin and S. V. Gorbachev [3] on the effect of the same cations on the electrodeposition of copper.

From experimental data on the structure of the electrical double layer it follows that the adsorbability of alkali and alkaline earth metal cations on an electrode surface depends somewhat on their radius. The surface tension of mercury in 1N solutions of alkali metal chlorides and in 0.5 N solutions of alkaline earth metal chlorides is practically the same [4] and the difference in capacity calculated from electrocapillary curves hardly exceeds the limits of experimental error. However, by direct measurement of the capacity of a mercury electrode Grahame [5] found that both the differential and the integral capacities increased with a change from $Li^+$ to $Cs^+$ and form $Ca^{2+}$ to $Ba^{2+}$.

In connection with the work of Grahame it might have been expected that the change in the ionic radius of the base electrolyte cations would affect the rate of reduction of both cations and anions. As follows from the theory of slow discharge, this effect should be considerably greater for anions than for cations [6]. By a study of the electroreduction of anions, especially in dilute solutions, in recent years many authors [7] have observed an anomalous dependence of the current density on the electrode potential, in the region of the electrocapillary zero potential. With a change from positive to negative charges,the current falls sharply and again increases only at strongly negative potentials. In the case of the anion $S_2O_8^{2-}$, the retardation of the reaction disappears with an increase in the total concentration of ions in the solution and, especially, with the introduction of multiply charged cations into the solution.

The polarization curves observed in the reduction $K_2S_2O_8$ may be explained quantitatively if it is assumed that during reduction there is equilibrium between anions in the double electrical layer and anions in the volume of the solution, and that the rate of reduction of the anion is determined by the rate of addition of an electron to an adsorbed anion. Starting from these assumptions, A. N. Frumkin and G. M. Florianovich [8] derived an equation for the relation of current density to electrode potential.

We investigated the effect of the radius of alkali and alkaline earth cations on the electrical reduction of $K_2S_2O_8$. Figure 1 gives polarization curves of $10^{-3}$ N $K_2S_2O_8$ in the presence of 0.01 N solutions of alkali metal chlorides.* Figure 2 shows polarization curves of the reduction of $K_2S_2O_8$ at the same concentration but in the presence of $2 \cdot 10^{-4}$ N alkaline earth metal chlorides. The figures presented show that the increase in ionic radius from $Li^+$ to $Cs^+$ and from $Ca^{2+}$ to $Ba^{2+}$ leads to an increase in the rate of electroreduction of $S_2O_8^{2-}$. The clearest effect of the cation radius appears in the case of monovalent cations. Thus, with an alkali metal chloride concentration of $10^{-2}$ N, the rate of the reaction increases by a factor of 40 with a change from lithium to cesium at a potential of -1 v (relative to a saturated calomel electrode). The magnitude of this effect is considerably greater

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* The first approximate data on the effect of alkali metal cations on the reduction of $S_2O_8^{2-}$ were obtained in the diploma work of R. M. Akopyan.

than that of similar effects described for other reactions. Experiment shows that in the presence of 0.001 N solutions of a foreign electrolyte, the effect of the cation radius becomes less noticeable. In this case the decrease in the effect is connected with the fact that in the solution there is a mixture of identical amounts of potassium ions (from persulfate) and base electrolyte cations. Potassium cations at the same concentration ($10^{-3}$ N) as base electrolyte cations smooth out the observed effect. The same relation is observed in the presence of divalent cations of alkaline earth metals.

The same effect of alkali and alkaline earth metal cations was observed by Žežula [9] in the electroreduction of $S_4O_6^{2-}$ and $S_5O_6^{2-}$. The rate of reduction of $K_2S_4O_6$ at the minimum of the polarization curve increased by a factor of approximately 20 with the addition of 0.2 N solutions of alkali metal chlorides.

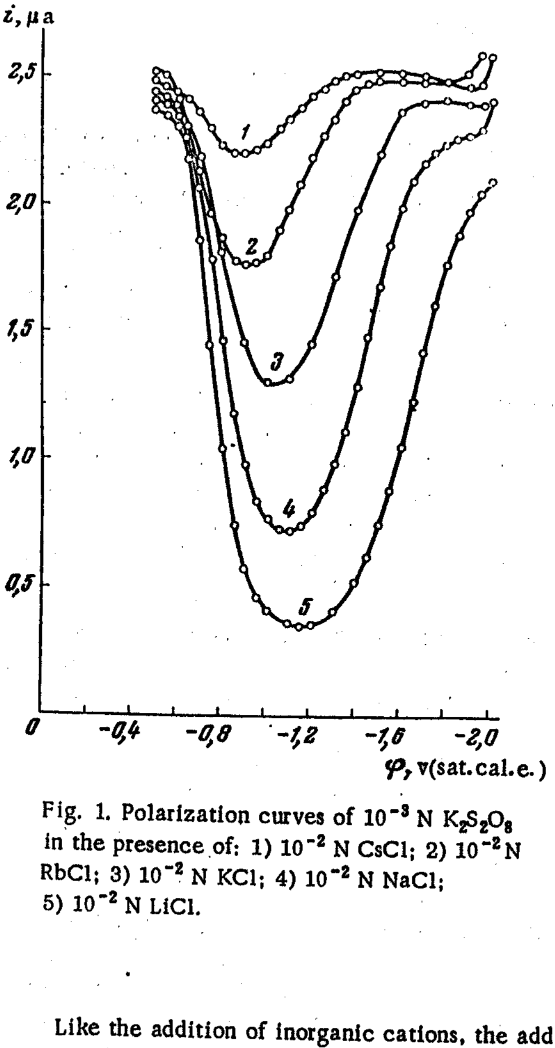

Fig. 1. Polarization curves of $10^{-3}$ N $K_2S_2O_8$ in the presence of: 1) $10^{-2}$ N CsCl; 2) $10^{-2}$ N RbCl; 3) $10^{-2}$ N KCl; 4) $10^{-2}$ N NaCl; 5) $10^{-2}$ N LiCl.

The effect of the radius of cations on electrochemical reduction may be explained by the difference in the distribution of potential in the electrical field of the double layer in the presence of cations of different radii. The processes examined occur at the boundary between the solution and the metal, which bears a negative charge. In the presence of more weakly hydrated cations, for example, $Cs^+$, the double layer should have a less diffuse structure than in the presence of other alkali metal ions at the same concentration. According to experiment, from the theory of slow discharge it follows that a decrease in the diffuseness should lead to an increase in the rate of discharge of negatively charged ions. The difference in distribution of potential in the double layer in the presence of cations of different radii is also shown by the values of differential capacity.

We measured the capacity of a mercury electrode [10] in 0.01 N solutions of alkali metal chlorides, i.e., in solutions where the effect of the base electrolyte cation radius on the reduction rate is greatest. As Fig. 3 shows, in the case of a potential of −1.7 v, the capacity increases by 3.5 μf/cm² with a change from lithium to cesium. It is very important that, in 0.01 N solutions, the difference in the values of the differential capacity for cations with different radii is observed not only at considerably negative polarizations but also at the electrocapillary zero of mercury where the double layer has the most diffuse structure. With a change from $Li^+$ to $Cs^+$, the difference in the capacities at the electrocapillary zero was 0.9 μf/cm² and at a potential of -0.7 v, where there is a maximum on the capacity curve, this difference reached 1.3 μf/cm².

Like the addition of inorganic cations, the addition of organic cations, for example $[(CH_3)_4N]^+$ and $[(C_4H_9)_4N]^+$, increased the rate of $K_2S_2O_8$ reduction; observed differences were of only a quantitative character. The addition of $[(CH_3)_4N]_2SO_4$ at a concentration of $10^{-2}$ N completely eliminated the retardation of the reaction (Fig. 4), while in the presence of the same concentration of cesium ions (the most effective of the alkali metal cations), a fall in current was still observed (Fig. 1).

The effect of the quaternary salts increased with an increase in the chain length. Thus, when $[(C_4H_9)_4N]_2SO_4$ was added even at a concentration of $5 \cdot 10^{-6}$N the fall in current disappeared completely. However, the action of this additive appeared only in the potential region in which this compound is adsorbed; $[(C_4H_9)_4N]_2SO_4$ is desorbed from the electrode surface at strongly negative potentials, and the curves with additives merge with the curve for a pure solution of $K_2S_2O_8$ (Fig. 5).

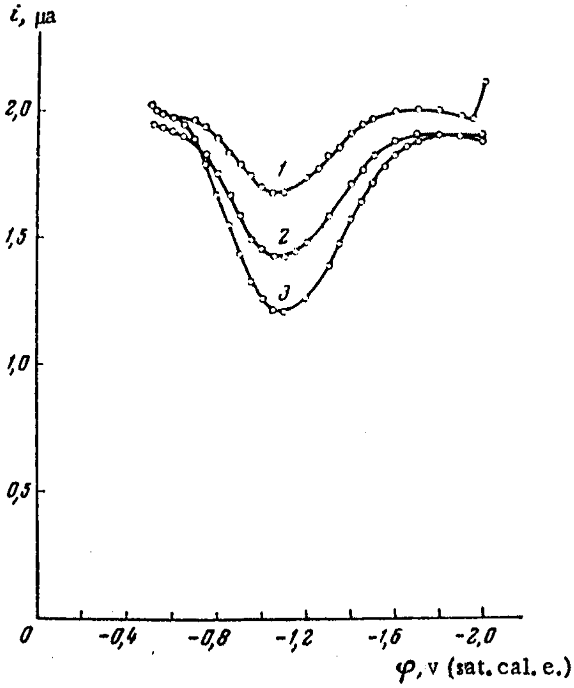

Fig. 2. Polarization curves of $10^{-3}$ N $K_2S_2O_8$ in the presence of: 1)$2\cdot10^{-4}$ N $BaCl_2$; 2)$2\cdot10^{-4}$ N $SrCl_2$; 3)$1\cdot10^{-4}$ N $CaCl_2$.

This explanation was confirmed by measurements of the capacity of a mercury electrode in solutions with $[(C_4H_9)_4N]_2SO_4$ added. Figure 6 gives polarization curves of $10^{-3}$ N $K_2S_2O_8$ +0.01 N $Na_2SO_4$ with additions of $[(C_4H_9)_4N]_2SO_4$. Figure 7 presents capacity curves, plotted in 0.01 N $Na_2SO_4$ with additions of $[(C_4H_9)_4N]_2SO_4$ present in corresponding concentrations. These data show that the cation $[(C_4H_9)_4N]^+$ is adsorbed on a mercury surface over a wide range of potentials, but at strongly negative potentials it is desorbed from the electrode surface and the differential capacity increases from 5–6 μf to normal values for inorganic electrolytes. The desorption potential of $[(C_4H_9)_4N]^+$, determined from capacity curves, agrees well with the potential of the current fall on the polarization curve of $S_2O_8^{2-}$ in the presence of this salt (Figs. 6 and 7). Thus, the introduction of organic cations into the solution and their adsorption leads to an increase in the rate of reduction of persulfate anions.

The experimental data on the accelerating action of organic cations on the reduction rate of $K_2S_2O_8$ do not confirm the hypothesis of M. A. Loshkarev and A. A. Kryukova[11] that the action of organic cations is similar to that of molecular additives and differs from the latter only in the region of adsorption potentials.

Figure 8 gives polarization curves of $K_2S_2O_8$ with the addition of $10^{-3}$ N $[(C_4H_9)_4N]_2SO_4$ in the presence of 1 N $Na_2SO_4$, KCl and KBr. As this graph shows, in the presence of $Cl^-$ and $[(C_4H_9)_4N]^+$ ions, there is retardation of the reduction of $S_2O_8^{2-}$, which is even greater in the presence of $Br^-$ ions. The introduction of $SO_4^{2-}$ anions at the same concentration does not produce retardation of the the reaction. This effect may be explained by an increase in the adsorption of anions in the presence of the surface-active cation $[C_4H_9)_4N]^+$, which naturally leads to a retardation of the reduction of $S_2O_8^{2-}$. An analogous effect was described in the work of A. P. Martirosyan and T. A. Kryukova [12].

As has been pointed out, the retardation of $K_2S_2O_8$ reduction is connected with the change in the sign of the charge on the surface of the mercury electrode [7]. However, the nature of the elementary act in the reduction of anions on a strongly negatively charged surface is not clear. The second rise in current density with an increase in the negative charge of the surface be explained by the transfer of an electron at relatively high distances, i. e., tunnel transfer. It seemed that this hypothesis is confirmed by the low values of the activation energy of $K_2S_2O_8$ reduction in the presence of 0.01 NKCl, calculated from data on the temperature coefficient [13]. The experimental data presented in this work on the effect of the base electrolyte cation radius on the rate of $K_2S_2O_8$ reduction (Figs. 1 and 2) cannot be explained by a tunnel mechanism as the nature of the cation should not be important in a tunnel transfer if the latter occurs at large distances.

In addition, measurement of the temperature dependence of $S_2O_8^{2-}$ reduction in the presence of alkali metal cations showed that the temperature coefficient of the rate of this reaction depends on the nature of the base electrolyte. Figure 9 gives data on the temperature dependence of the current strength at $\varphi = -1.1$ v (relative to a saturated calomel electrode), corrected for concentration polarization, in the presence of base electrolyte cations. As this figure shows, the rate of $K_2S_2O_8$ reduction in the presence of 0.01 N NaCl increases with an increase in temperature; replacement of NaCl by CsCl at the same concentration leads to retardation of the reaction with temperature. The reduction was practically independent of temperature in the presence of 0.01 N KCl.

The experimental data on the effect of the base electrolyte cation on the rate of reduction of the $S_2O_8^{2-}$ anion and the dependence of the apparent activation energy on the radius of the base electrolyte cations compels us to assume that the reduction of anions at strongly negative potentials occurs through the formation of cation bridges, which facilitate the approach of the anion to the cathode.

The literature contains reports on the formation of a similar type of bridge. Thus, from data of electrocapillary measurements in KCl and KI solutions in the presence of the polyvalent cation $Al^{3+}$, L. M. Shtifman [14] came to the conclusion that iodine anions are drawn into the electrical double layer in the presence of aluminum with the surface negatively charged. We obtained analogous data with the cation $La^{3+}$ present in the same solutions. M. A. Vorsina and A. N. Frumkin [15] came to the same conclusions in work on the measurement of the capacity of a mercury electrode in the presence of multiply charged cations.

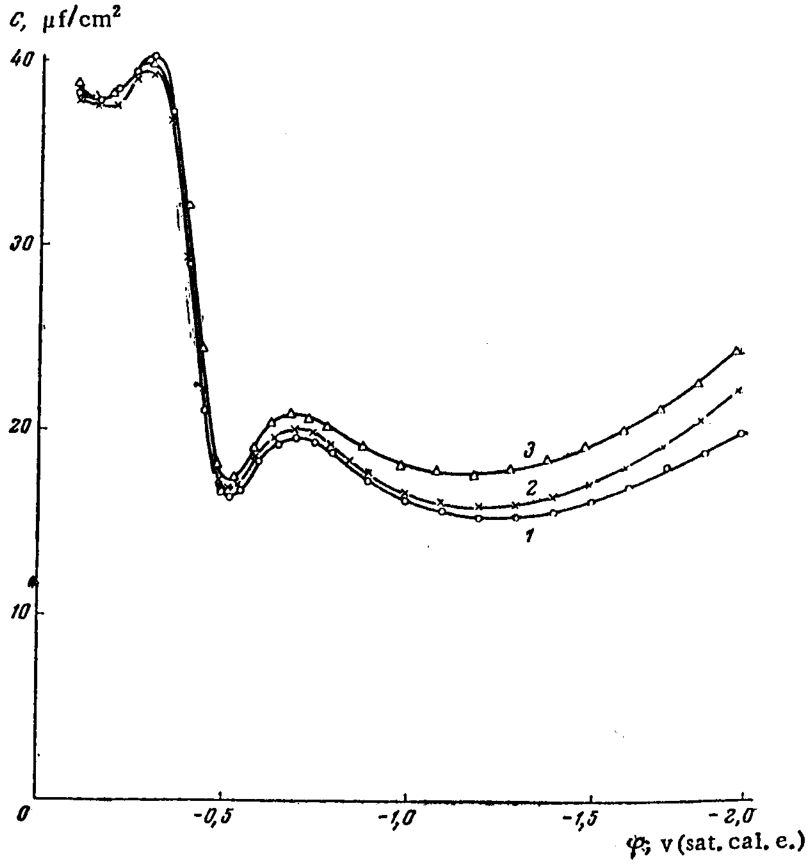

Fig. 3. Differential capacity curves in the following solutions:
1) 0.01 N LiCl; 2) 0.01 N KCl; 3) 0.01 N CsCl. Frequency 400 cps.

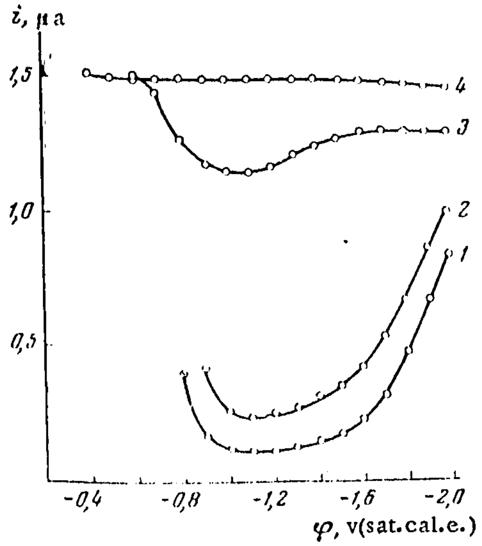

Fig. 4. Polarization curves of $10^{-3}$ N $K_2S_2O_8$: 1) Without additives; 2)$10^{-4}$ N $[(CH_3)_4N]_2SO_4$; 3)$10^{-3}$ N $[(CH_3)_4N]_2SO_4$; 4)$10^{-2}$ N $[(CH_3)_4N]_2SO_4$.

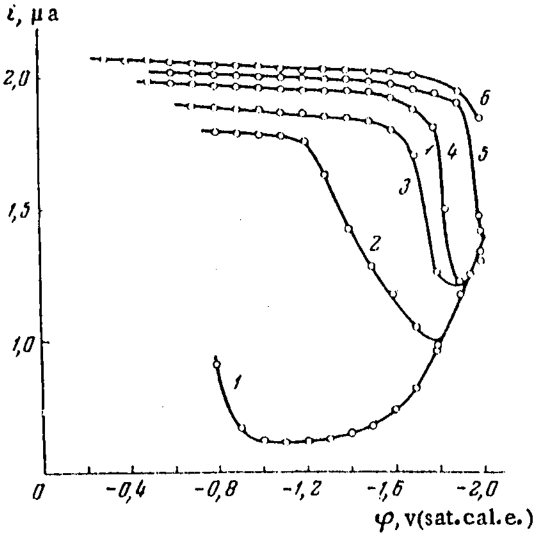

Fig. 5. Polarization curves of $10^{-3}$ N $K_2S_2O_8$: 1) Without additives; 2)$5\cdot10^{-6}$ N $[(C_4H_9)_4N]_2SO_4$; 3)$10^{-5}$ N $[(C_4H_9)_4N]_2SO_4$; 4)$2.5\cdot10^{-5}$ N $[(C_4H_9)_4N]_2SO_4$; 5)$5\cdot10^{-4}$ N $[(C_4H_9)_4N]_2SO_4$; 6)$10^{-3}$ N $[(C_4H_9)_4N]_2SO_4$.

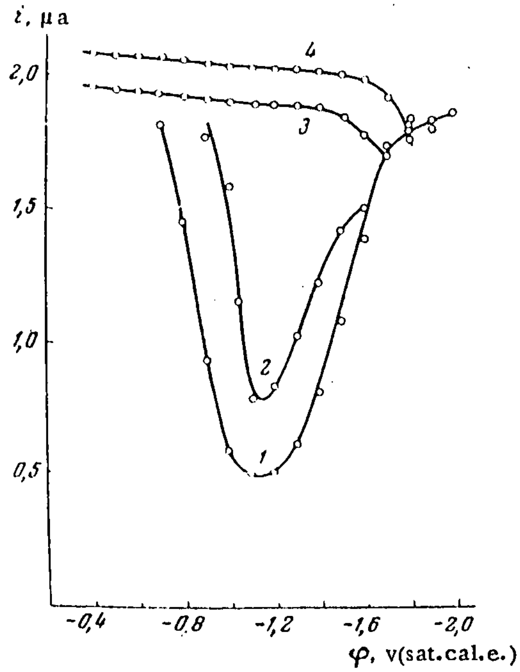

Fig. 6. Polarization curves of $10^{-3}$ N $K_2S_2O_8$ in the presence of $10^{-2}$ N $Na_2SO_4$: 1) Without additives; 2)$5\cdot10^{-6}$ N $[(C_4H_9)_4N]_2SO_4$; 3)$10^{-5}$ N$[(C_4H_9)_4N]_2SO_4$; 4)$5\cdot10^{-4}$ N$[(C_4H_9)_4N]_2SO_4$.

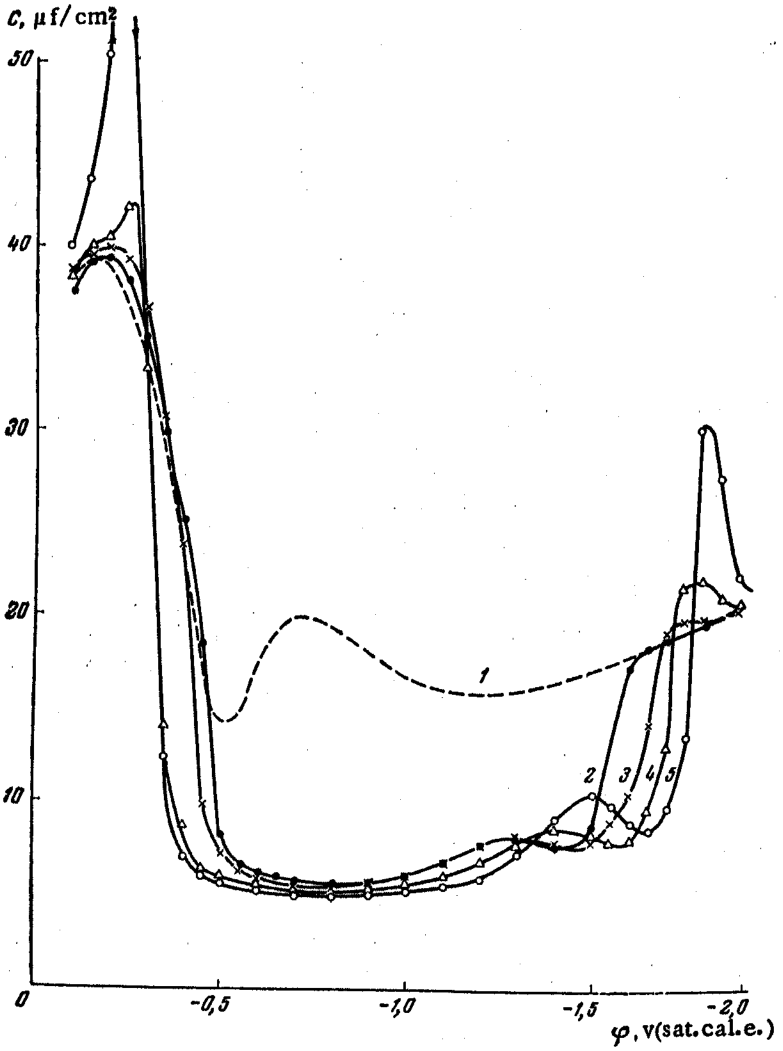

Fig. 7. Differential capacity curves of $10^{-2}$ N $Na_2SO_4$: 1) Without additives; 2) $5 \cdot 10^{-6}$ N $[(C_4H_9)_4N]_2SO_4$; 3) $10^{-5}$ N $[(C_4H_9)_4N]_2SO_4$; 4) $5 \cdot 10^{-5}$ N $[(C_4H_9)_4N]_2SO_4$; 5) $5 \cdot 10^{-4}$ N $[(C_4H_9)_4N]_2SO_4$. Frequency 400 cps.

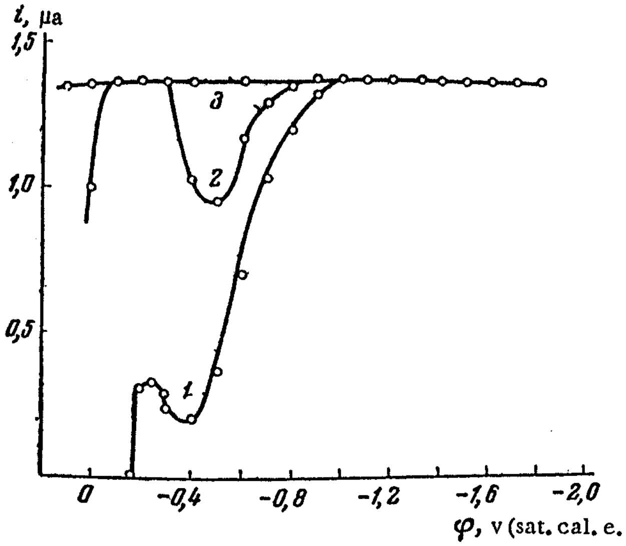

Fig. 8. Polarization curves of $10^{-3}$ N $K_2S_2O_8$ in the presence of: 1)1 N KBr and $10^{-3}$ N $[C_4H_9)_4N]_2$ $SO_4$; 2)1 N KCl and $10^{-3}$ N $[(C_4H_9)_4N]_2$ $SO_4$; 3)1 N $Na_2SO_4$ and $10^{-3}$ N $[(C_4H_9)_4N]_2$ $SO_4$.

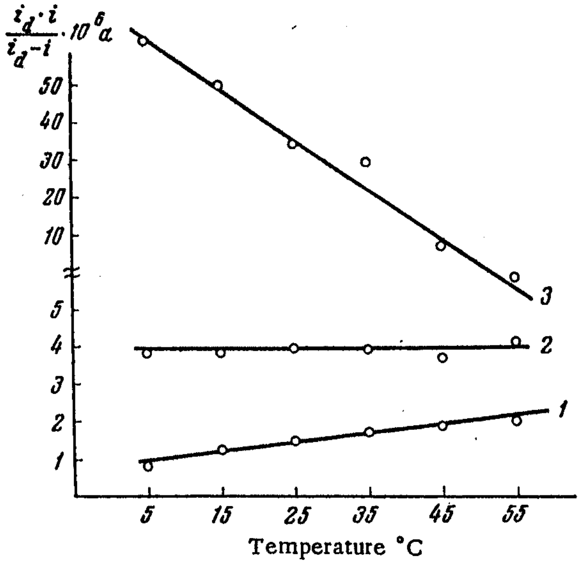

Fig. 9. Temperature dependence of the reduction current of $10^{-3}$N $K_2S_2O_8$, corrected for concentration polarization at $\varphi = -1.1$ v in the presence of: 1)0.01 N NaCl; 2)0.01 N KCl; 3)0.01 N CsCl.

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