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THE ELECTROREDUCTION OF THE $S_2O_8^{2-}$ ANION*

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INTRODUCTION

The $S_2O_8^{2-}$ anion was the first to be studied with the purpose of investigating the mechanism of anionic electroreduction under conditions of a sharp deviation of the polarization curve from the classical Tafel equation, caused by electrostatic interaction between the anionic charge, the electrode surface and the ions of the electrical double layer[1-3].

To date, the persulfate anion, along with the $S_4O_6^{2-}$ ion, which is in many respects similar to it, remains one of the most convenient subjects for investigation of this group of phenomena[4-6]. This communication is concerned with data obtained recently or not hitherto published on the electro-reduction of $S_2O_8^{2-}$.

The elementary theory of anionic electroreduction[2] leads to eqn. (1) between the electrode potential φ and the current density i:

$$i = kc_i \exp\left\{-\alpha\left(\varphi + \frac{n_i-\alpha}{\alpha}\psi_1\right)F/RT\right\} \tag{1}$$

where α is the transfer coefficient, n_i, c_i are respectively the charge and the concentration of the reacting particles in the bulk solution, and ψ_1 is the mean value of the potential in the plane in which are located the centers of the charges of reacting particles in the transition state of the reaction. This theory was based on the following assumptions: the reacting particle in the transition state of the reaction is in equilibrium with the particles in the bulk solution in accordance with the Boltzmann equation; the electrical double layer structure can be described by the Gouy-Stern theory; the noncoulombic interactions of the reacting particles and of the reaction products, both with the electrode surface and with other double layer ions, do not depend on φ; the dependence of the rate of the electrochemical reaction in which the adsorbed particle participates, upon the effective potential difference, is expressed by the classical Tafel equation with a constant coefficient α; no account is taken of the discreteness-of-charge effects in the double layer.

Gierst[3] proposed the term "static" ψ_1 effect for phenomena conforming, even if approximately, with the above concepts. Equation (1) leads to the conclusion that the dependence of log i on φ should be expressed by a curve with a maximum

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* Dedicated to Dr. J. E. B. Randles on the occasion of his retirement from the Chemistry Department, University of Birmingham.

at positive surface charges and with a minimum at negative ones, and terminating in a current rise with further increase in the negative values of ψ_1. Such curves for the $S_2O_8^{2-}$ anion have not yet been given in the literature, and cannot be obtained at a dropping mercury electrode on account of the diffusion limitations, and because of the distortion of the curve in the case of a positive surface charge by a polarographic maximum of the first kind[7]. In the case of the BrO_4^- ion reduction at the dropping mercury electrode, for which k seems to be less than for $S_2O_8^{2-}$, an i, φ curve with a maximum and a minimum was obtained, distorted however, by a polarographic maximum at positive surface charges★. When the measurements for the $S_2O_8^{2-}$ anion were carried out using a rotating disc electrode[2], diffusion limitations also prevented observation of the current maximum at positive surface charges.

EXPERIMENTAL

In order to eliminate the diffusion limitations in the region of positive surface charges, the reduction of $S_2O_8^{2-}$ was studied at a rotating amalgamated copper electrode at high rotation rates, under both laminar and turbulent stirring

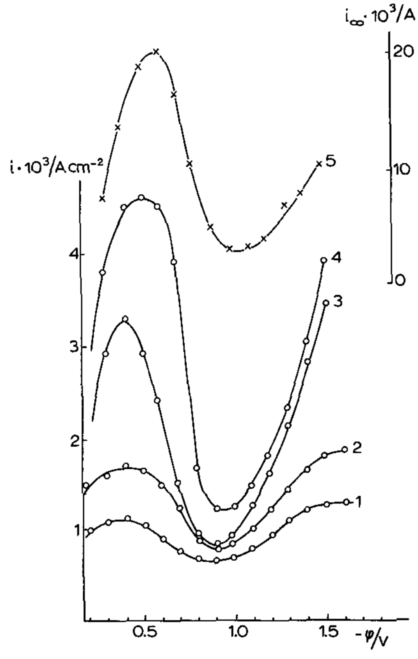

Fig. 1. Dependence of current density on potential in 5×10^{-4} M $K_2S_2O_8$+0.05 M KCl solution at an amalgamated copper electrode. (1,2) The i, φ curves under laminar stirring conditions at 5400 and 7000 r.p.m., respectively; (3,4) the i, φ curves for the same rotation rates under turbulent stirring conditions; (5) i_∞, φ curve in the absence of diffusion limitations (see text).

★ According to information which came to the authors' notice after this paper had been written, the maximum is suppressed by the small addition of any surface-active anion[49].

conditions; the experimental procedure is described in ref. 9. Turbulent stirring was effected with the aid of the L-shaped Teflon electrode holder. The working surface of the electrode was an amalgamated copper Hg(Cu) disc 1 mm in diameter, moving during rotation of the electrode along its circumference. The rotation rate was adjusted to 28000 r.p.m. The limiting diffusion current of $S_2O_8^{2-}$ under turbulent stirring conditions is about three times as high as the limiting diffusion current under laminar conditions at the same rotation speed; this corresponds to an electrode rotation rate under laminar conditions of 300000 r.p.m. (Fig. 1). All potentials are referred to the normal calomel electrode. At varying rates of rotation m, but in excess of 9000 r.p.m. and at positive surface charges, the dependence of the current density on $m^{0.9}$ deviates from the linear requirements of purely diffusion kinetics[10]. This shows that the reaction passes into the mixed kinetics region. However, even at the maximum rotation rates used in this study, the diffusion limitations could not be completely eliminated. As the reduction of the $S_2O_8^{2-}$ anion is a first order reaction, the transition from the diffusion current to the kinetic one occurs in a wide range of rotation rates. Therefore, for calculation of the kinetic current i_∞ the dependence of the current density i on the rotation rate was given in the coordinates i^{-1} *versus* $m^{-0.9}$ and the kinetic current density values were determined by extrapolation of m to infinity. The result for 5×10^{-4} M $K_2S_2O_8+0.05$ M KCl solution is shown in Fig. 1, curve 5. With the supporting electrolyte concentration increasing to 0.1 M KCl, in accordance with eqn. (1), the current density at a positive surface charge decreased, and at a negative one increased.

DISCUSSION

The data obtained so far for the turbulent stirring conditions are to be treated as preliminary because the reproducibility of measurements was no greater than 5% and the accuracy of the extrapolated results was 15%. For this reason, we shall not consider them here in greater detail. It should be noted however, that the possibility of a transition into the mixed kinetics region in the case of electroreduction of the $S_2O_8^{2-}$ anion at a positively charged solid electrode surface is of interest, since it can be used as a basis for a method of determination of the p.z.c. from kinetic data. Namely, at the p.z.c. the current density should not depend on the supporting electrolyte concentration, so that the i, φ curves plotted at different supporting electrolyte concentration should intersect at this point. Due to the high value of the coefficient before ψ_1 in eqn. (1) (in the case of $S_2O_8^{2-}$ $\alpha\simeq0.22$, $n_i=-2$ and hence $(n_i-\alpha)/\alpha\sim10$), the value of i is very sensitive to the change of ψ_1 and thus to the supporting electrolyte concentration. The applicability of this method does not depend on the assumptions on which the deduction of eqn. (1) is based, and requires only the absence of the specific adsorption of the supporting electrolyte ions, a small concentration of the reduced anion as compared to the supporting electrolyte ions, and (in the case of oxidizable metals) a negligible value of the current of anodic dissolution of the electrode metal at the p.z.c. as compared to the current of the electroreduction of the $S_2O_8^{2-}$ anion. It should be also borne in mind that measurements on an electrode with small surface area in a vigorously stirred solution require a very high degree of solution purity and removal of traces of organic impurities.

The experimental data obtained so far are not sufficient to make measurements of the i, φ dependence an independent quantitative method of p.z.c. determination, and only semiquantitative estimates of this kind have been carried out. However, the p.z.c. values found from the position of the differential capacity minimum in diluted solutions, have been correlated with the polarization curves for anionic electroreduction. A more detailed analysis of the assumptions underlying the derivation of eqn. (1) is necessary for assessment of the reliability of the results obtained.

According to the theory developed by Levich, it is possible that the slow step in anionic electroreduction at a negatively charged surface, is the rate of anionic diffusion within the electrical double layer, rather than the electrochemical process[11]. In its original form, this theory lead to the conclusion that the reaction rate gradually decreases with increasingly negative values of φ (dynamic ψ_1-effect according to Gierst[3]). In this case the total polarization curve should have only one maximum at a positive surface charge. In a later publication, in order to fit the theoretical conclusions to the experimental results obtained with $S_2O_8^{2-}$ and other anions, Levich suggested that both steps occur at commensurable rates[11]. This suggestion, with the assumption that $|\psi_1| \gg RT/F$ leads to the following equation of the polarization curve at a negatively charged surface.

$$i = \frac{kc_i \exp\{(-n_i+\alpha)\psi_0-\alpha\varphi\}F/RT}{1+(k\lambda/D_i)\exp\{(\alpha+\frac{1}{2})\psi_0-\alpha\varphi\}F/RT} \tag{2}$$

where ψ_0 is the mean potential value on the outer Helmholtz plane (it is assumed that $|\psi_0| > RT/F$), λ the Gouy length, D_i the diffusion coefficient of the reduced anion: errors in sign occurring in the original paper are corrected in eqn. (2). The analysis of eqn. (2) shows that upon transition to increasing negative surface charges, i passes through a minimum, then increases as in the case of the applicability of eqn. (1), but with further increase of the negative values of φ passes through a maximum and begins to decrease. Thus, the total polarization curve should show a minimum and two maxima, as well as a descending branch at very negative potentials. Such polarization curves have not been obtained so far with singly- and doubly-charged anions, so that we can conclude that the dynamic ψ_1 effect is not rate determining in the measurable potential range in the case of the reduction of these anions and we shall not take it into account in what follows*.

This is not the case with another effect, which was also not taken into consideration in the deduction of eqn. (1), *viz.* the discreteness-of-charge effect. The necessity of taking into account the discrete structure of the electric double layer and the local, rather than the mean, value of the ψ_1 potential was pointed out apparently for the first time in ref. 15, when discussing the influence of multivalent cations on the electroreduction of the NO_3^- anion at the dropping mercury electrode. With a change of the cation of the supporting electrolyte

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* The conclusion is less unambiguous in the case of the $Fe(CN)_6^{3-}$ anion. In some experiments the i, φ curve after passing through a minimum and a slight rise of i with increasing φ shows a section on which i is almost independent of φ (see *e.g.* ref. 13), which was considered as a transition to a descending branch of the i, φ curve[11]. In ref. 14 it is assumed that during the electroreduction of $Fe(CN)_6^{3-}$, account should be taken of the dynamic ψ_1 effect.

at given value of φ, the rate of anion reduction increases in the sequence[4,5,12] $Li^+ < Na^+ < K^+ < Cs^+$; a somewhat slighter increase is observed also in the sequence $Ca^{2+} < Sr^{2+} < Ba^{2+}$[18]. The specific adsorption of cations increases in the same sequence[16]. Increase of the specific adsorption should lead to increase of the reduction rate, but as shown by calculation[17], without allowance for the double layer discreteness, this effect is not sufficient to account for the experimentally observed differences between the i, φ curves measured in the presence of different cations. Another reason for the necessity of taking into account the discrete structure of the double layer during anionic discharge at a negatively charged surface, is the fact that the observed rates of discharge are higher than the limiting rate of the permeation of a doubly-charged anion through the electrostatic barrier of the double layer calculated[11] in a unidimensional approximation. Hence it follows that the variation in the reduction rate with change in the cation radius, is associated with some kind of interaction between the reacting particles with charges of opposite sign; this can be formulated as a manifestation of the local (micro) potential due to formation of cationic bridges or of ion-pairs[6,11,19,20,26]. The ability for forming ion-pairs changes in parallel with the increase of adsorbability with increasing cation radius; thus, according to Hindman[21], the n.m.r. method registers the formation of ion-pairs in 1 *M* CsCl and 1 *M* RbCl solutions, but not in 1 *M* KCl and 1 *M* NaCl. Consequently these two effects should be additive. A greater firmness of the bond between anion and electrode surface in the transition state of the reaction in the presence of the Cs^+ cation, is confirmed by measurement of the temperature coefficient of electroreduction of the $S_2O_8^{2-}$ anion at the minimum of the i, φ curve. The formal activation energy of the reaction, which is positive in the presence of Na^+, is negative in the presence of Cs^+[6,18,22]. The decrease in reaction rate with increasing temperature in the case of the Cs^+ ion can be explained only by the breaking of some bond between the electrode surface, the caesium ion and the anion. Another explanation of the difference in the accelerating effect of cations of unequal radii was proposed by Fawcett[23,24]. According to Fawcett, the electrostriction of hydrated cations is of decisive importance. Greater electrostriction of the more polarizable caesium ion reduces repulsion because at large $-\varphi$ values the center of the reacting anion becomes located beyond the outer Helmholtz plane, whereas in the case of more rigid Na^+ and Li^+ ions, the outer Helmholtz plane does not approach the electrode surface and the transition state of the reaction remains localized in the dense part of the double layer. This theory, however, cannot explain the observed dependence of the activation energy and even of its sign, on the cation radius.

The question arises, whether in spite of the formation of cationic bridges or ion-pairs thus decreasing the anionic charge in the double layer, the quantity n_i in eqn. (1) should retain the value it has in the bulk of the solution. In ref. 5 a criterion was proposed for determination of n_i from the dependence of i on φ and on the concentration of the supporting electrolyte cations c, namely

$$-n_i = n\left(\frac{\partial \ln i}{\partial \ln c}\right)_{\varphi-(RT/nF)\ln c\, c_i} \tag{3}$$

where n denotes the cationic charge of the supporting electrolyte. Equation (3) was derived on the basis of an unidimensional model of the double layer under the assumption that the surface excess of anions Γ_A in the double layer is negligible as compared to that of the cations Γ_K, but independently of the suppositions concerning the mechanism of the electrochemical reaction itself. It is based on the conclusion that when both the conditions $\varphi-(RT/nF)\ln c=\text{constant}$ and $\Gamma_A \ll \Gamma_K$ are fulfilled, the distribution of the cations in the double layer at distances which are small compared with the Gouy length is independent of c. The conclusion is compatible with a certain specific adsorption of the cation.

It follows from the derivation of eqn. (3) that the value of n_i refers to the charge of the reacting particle in the bulk of the solution. Ion pair formation can diminish the charge value in the bulk solution[11,35,45] and in ref. 25 the possible influence of this circumstance on the polarization curves of anionic electroreduction was analyzed.

The calculations support the conclusion that in the investigation of the reduction of $S_2O_8^{2-}$ and probably of $Fe(CN)_6^{3-}$ ions from aqueous solutions, the decrease of the mean value of the charge due to ion-pair formation in the bulk solution can be neglected. This conclusion, however, is not valid for nonaqueous solutions, *e.g.* solutions in ethylene glycol[29].

Equation (3) was tested in a series of experiments on the reduction of the $S_2O_8^{2-}$, $S_4O_6^{2-}$ and $Fe(CN)_6^{3-}$ anions at liquid and solid electrodes[5,6,27,28]. It was found that as $-\varphi$ rises (n was unity) the value of n_i thus determined actually approaches -2 in the case of doubly-charged and -3 in that of triply-charged anions. This approach takes place at less negative surface charges and is better realized the larger the cationic radius and therefore the lower the supporting electrolyte concentration at which the measurements are carried out.

From eqn. (3) taking into account that according to the theory of the diffuse double layer, at sufficiently negative potentials the values of the mean potential at the outer Helmholtz plane ψ_0 satisfy the condition

$$\psi_0=(RT/nF)\ln c+\text{const}, \tag{4}$$

at $\varphi-\psi_0=\text{const}$, it is easy to obtain

$$\left\{\frac{\partial[\ln i+n_iF\psi_0/RT]}{\partial \ln c}\right\}_{(\varphi-\psi_0),\,c_i}=0 \tag{5}$$

whence for a reaction of the first order

$$\ln i+n_iF\psi_0/RT=\ln kc_i+\mathrm{f}(\varphi-\psi_0) \tag{6}$$

where $\mathrm{f}(\varphi-\psi_0)$ represents some function of $(\varphi-\psi_0)$.

Equation (6) can be considered as a generalization of eqn. (1). If we assume that the electroreduction of the adsorbed anion follows the classical Tafel equation with the potential difference $(\varphi-\psi_0)$ in the exponential, instead of eqn. (6) we can write

$$\ln i+n_iF\psi_0/RT=\ln kc_i-\alpha(\varphi-\psi_0)F/RT \tag{7}$$

This is the form which Delahay *et al.*[19] gave to eqn. (1) and which is very convenient for the processing of experimental data. It follows from eqn. (7) that the polarization curve in the coordinates

$$\log i+n_i\psi_0F/2.3\,RT,-(\varphi-\psi_0)$$

should be expressed by a straight line with the slope $\alpha F/RT$ usually called the corrected Tafel plot (c.T.p.).

The assumption that ψ_1 is equal to ψ_0 in eqns. (5)–(7) is not obligatory, as a relation similar to eqn. (4) must hold for the ψ_1 values at distances from the electrode surface somewhat exceeding that of the outer Helmholtz layer as well, provided that they remain small compared with the Gouy length. However the choice of the value $\psi_1=\psi_0$ is to be preferred, taking into account that according to Krishtalik[34], small deviations in the position of the centers of charge of reacting particles from the outer Helmholtz plane in the direction of the inner part of the double layer do not affect significantly the value of ψ_1.

It follows from eqn. (7), that the c.T.p. should not depend on the supporting electrolyte concentration c. It was shown[5] that in the case of the dropping mercury electrode, the conclusions from the elementary theory, both as regards the linearity of c.T.p. and its independence of the value of c, are best obeyed, the more negative the potential and the larger the cationic radius. In the presence of Li^+ and to some extent of Na^+ the correction for the ψ_1 effect proved to be clearly insufficient and did not eliminate the characteristic minimum on the log i, φ curve; this could be due to a certain specific adsorption of the $S_2O_8^{2-}$ anion. As is clearly shown by Fig. (3) in ref. 5, eqn. (6) holds, at least approximately, even when large deviations from eqn. (7) are observed. The approximation is however better in the cases of Cs^+ and K^+ than with Na^+ and Li^+.

The experimental verification[5] of the criterion, shows that the electrochemical reaction is preceded by the transfer of the reacting anion from the bulk solution to the double layer region, in which at a sufficiently negative charge the condition $\Gamma_K \gg \Gamma_A$ is valid. In all other respects, this criterion is however not diagnostic because, as was already pointed out[5], the slow discharge mechanism is also valid in the case when anion transfer from the bulk solution to the interface is effected by means of the ion pair $MS_2O_8^-$ (M^+ is a singly-charged cation of the supporting electrolyte), provided that in the bulk solution the ion-pair is in equilibrium with the $S_2O_8^{2-}$ anions and $[MS_2O_8^-] \ll [S_2O_8^{2-}]$*.

In fact in this case, in eqn. (6) $c_i=[S_2O_8^{2-}]$ and $n_i=-2$ should be substituted by $c_i=[MS_2O_8^-]$ and $n_i=-1$, but under the assumptions made $[MS_2O_8^-]=k'c[S_2O_8^{2-}]$. From this relation and eqn. (4) it follows that in eqns. (6) and (7) it is possible to retain the former values of n_i and c_i when changing the supporting electrolyte concentration in spite of the fact that in reality the transfer is effected by the ion pair $[MS_2O_8^-]$. Thus the explanation of the dependence of c.T.p. on the nature of the cation by means of the ion-pair concept and within the framework of the elementary theory leads to eqn. (1) with n_i retaining its bulk value, provided that we use the c.T.p. obtained at the same electrode at different supporting electrolyte concentrations.

This is not the case, however, when we compare the c.T.p. obtained with electrodes made from different metals at a constant supporting electrolyte concentration c. Thus, for instance, if we assume that it is not the $S_2O_8^{2-}$ anions which are reduced, but the ion pairs $MS_2O_8^-$, then in eqns. (1) and (7) we should put $n_i=-1$. With this substitution also, it follows from the deduction of eqn. (1) that

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* This criterion is valid also if the process rate is determined by slow penetration[5].

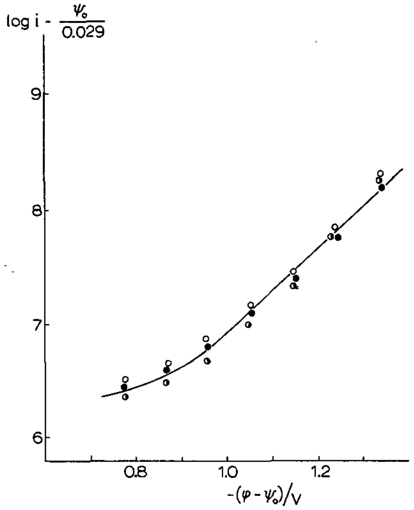
the coincidence of the c.T.p. measured at different metals, is possible only if the states of the adsorbed anion at the same values of ψ_0, but with different electrode materials, can be considered to be approximately identical. The difference between the results of the comparison of the c.T.p. on the same electrode at differing values of c, and those for electrodes from different metals, can be accounted for as follows. The value of $(\varphi-\psi_0)$ in eqn. (7) deduced for the former case gives the potential difference within the limits of the inner layer or differs from it by a constant depending on the reference electrode. In the latter case this is not so owing to the difference in the values of p.z.c. of the metals being compared, as well as to the different orientation of water molecules at p.z.c. To eliminate the difficulty caused by this circumstance we could try to substitute the quantity $(\varphi-\psi_0)$ in the right hand side of eqn. (7) by $(\varphi-\varphi_\varepsilon-\psi_1)$, where φ_ε are the potentials of zero, or rather of equal negative charge, of the electrodes being compared[43]. However, it is easy to see that this change cannot lead to the coincidence of the c.T.p.

Now let us consider the experimental data which permit us to compare the c.T.p. obtained by means of electrodes from different metals.

The kinetics of anionic electroreduction at mercury and nonmercury electrodes were compared for the first time by Delahay and Kleinerman[38], but the validity of the argument that the c.T.p. of mercury and thallium amalgams[5,19,38], as well as that of indium amalgams[27], coincide, is somewhat decreased by the fact that due to negative adsorption of thallium and of indium dissolved in mercury, the uncorrected Tafel plots also come closer together with increasing cathodic polarization. The most comprehensive experimental evidence is available on the c.T.p. of the $S_2O_8^{2-}$, $S_4O_6^{2-}$ and $Fe(CN)_6^{3-}$ anions obtained by the rotating disc electrode method with electrodes from Bi, Sn, Pb, Cd, Sb, In and Hg(Cu)[6,36,37,40] and by the dropping electrode method with Hg and the eutectic Ga + In alloy[41].

The deviations from the conclusions based on eqn. (7) were not observed for the electroreduction of the $S_2O_8^{2-}$ and $S_4O_6^{2-}$ anions at solid electrodes assuming $n_i = -2$. The reasons for this difference are not quite clear. Possibly, the supposed specific adsorption of the $S_2O_8^{2-}$ anion on the solid metals investigated is less pronounced than on mercury. However, in comparing the data obtained at not very negative potentials at a dropping mercury electrode and at the rotating disc solid electrodes, some sources of error should be taken into account. Namely, in the case of the dropping electrode the correction for the concentration polarization becomes unreliable when the current being measured approaches the limiting diffusion current, whereas in the case of solid electrodes the anodic dissolution which sets in in many cases does not allow us to carry out the measurements of the electroreduction rate in the neighborhood of the p.z.c., though differential capacity measurements in this potential range are still possible. Figure 2 shows the degree of coincidence of the data obtained for liquid mercury by means of the dropping electrode, and correcting for the concentration polarization according to Meiman and Bagotzky[51], with that obtained by means of rotating disc electrodes of amalgamated copper and amalgamated gold.

Figure 3 shows the i, φ curves corrected as usual for concentration polarization, for $S_2O_8^{2-}$ anion reduction in the presence of KF at rotating disc electrodes.



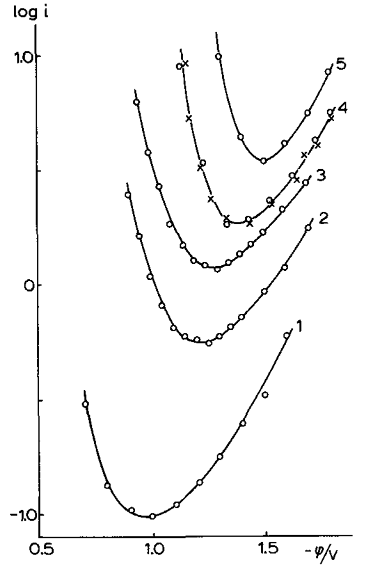


Fig. 2. Corrected Tafel plots of the $S_2O_8^{2-}$ anion reduction in 5×10^{-4} *M* $Na_2S_2O_8 + 4 \times 10^{-3}$ *M* NaF. (◑) dropping mercury electrode; (○) rotating disc electrode, amalgamated copper; (●) rotating disc electrode, amalgamated gold.

Fig. 3. Dependence of the reduction rate of the $S_2O_8^{2-}$ anion in 5×10^{-4} *M* $K_2S_2O_8 + 9 \times 10^{-3}$ *M* KF on potential at rotating disc electrodes from (1) Sb, (2) Bi, (3) Sn, (4) Pb (o), In (x), (5) Cd.

Figure 4 shows the c.T.p. for solid electrodes in the presence of fluorides (in the case of the Sn electrode, perchlorates were used since the F^- ion is apparently specifically adsorbed on tin). Some of the data in Fig. 4, *viz.* for Bi, Sn, Pb and Cd with NaF as supporting electrolyte have been published[6]; the technique of measurements and the sources used for calculation of ψ_0 are also given there. In ref. 28 the ψ_0 values were equated with the corresponding values obtained for Hg at potentials equidistant from the p.z.c., which leads to errors[42]. Detailed data on indium are given[37]. Information on the application of differential capacity measurements in diluted solutions to the investigation of the electric double layer structure is available[42].

Considering the marked differences between the p.z.c. of Pb and In (-0.84 and -0.93 V respectively[42]), the practical coincidence of the uncorrected i, φ curves for these metals should lead to a difference between the c.T.p. However this is not the case as the anomaly in the position of the uncorrected i, φ curves is compensated for by the somewhat higher capacity of the dense part of the double layer at indium at negative potentials as compared to that at Pb[42,43]. As can be seen from Fig. 4, the c.T.p. values calculated assuming $n_i = -2$ coincide in a wide potential range within the accuracy of the measurements presently possible. If the value $n_i = -1$ is used, the c.T.p. values of different metals draw nearer only at very negative potentials, at which the very difference in the values of ψ_0 of different metals is already not large and the choice of the value of n_i does not affect much the dependence of the c.T.p. on the nature of the metal. In the light of the foregoing, this result shows that the decrease of the effective charge of the

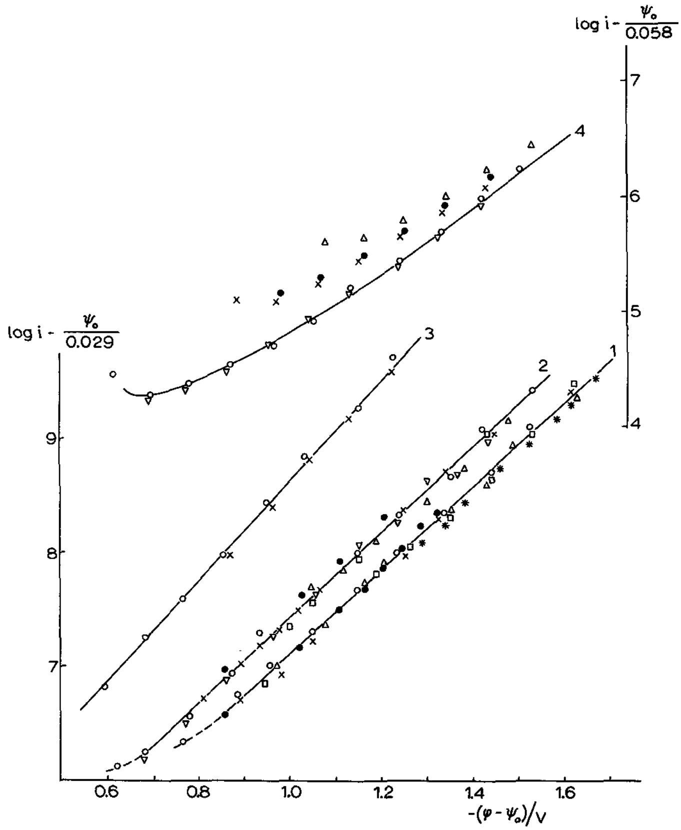


Fig. 4. Corrected Tafel plots of the $S_2O_8^{2-}$ anion reduction, calculated on the assumption $n_i = -2$. (1) 5×10^{-4} *M* $Na_2S_2O_8 + 9\times10^{-3}$ *M* NaF at electrodes of Sb (▽), Hg(Cu) (○), Bi (×), Sn (-·-), Pb(△), Cd (□), In (*); (2) 5×10^{-4} *M* $K_2S_2O_8 + 9\times10^{-3}$ *M* KF at electrodes of Sb (▽), Hg(Cu) (○), Bi (×), Sn (-·-), Pb (△), Cd (□); (3) 5×10^{-4} *M* $Cs_2S_2O_8 + 9\times10^{-3}$ *M* CsCl at electrodes of Hg(Cu) (○), Bi (×). Curve 4, corrected Tafel plots using the same data as for curve 2, but calculated on the assumption $n_i = -1$.

reacting particle localized within the limits of the double layer, and resulting from interaction with the supporting electrolyte cations, is much less than would be expected in the case of formation of a stable ion pair. Moreover, for the c.T.p. of different metals to coincide it would be necessary, as has been pointed out above, that the microdielectric characteristics of the medium near the reacting particle in the transition state of the reaction within the electric double layer should be independent of the nature of the metal, and that the reaction probability should depend only on the value of $(\varphi - \psi_0)$ and not on the field gradient within the dense layer in the case of differences in its capacity.

As it seems to us, the conclusions drawn from the comparison of the c.T.p. of different metals favor the following picture of the electroreduction process.

It is the at least partially hydrated anion $S_2O_8^{2-}$ localized at such a distance from the physical interface, that the nature of the electrode metal can no longer affect significantly the microdielectric characteristics of the medium surrounding the anion at given ψ_0, which undergoes reduction. This condition can be approximately fulfilled if in the transition state of the reaction the anion does not approach the physical interface nearer than the outer Helmholtz plane; Grahame's theory of the diffuse double layer contains a similar assumption. According to this assumption in the initial, or transition states of the reaction, the anion is localized in a medium containing cations in a relatively high concentration, which form an ionic atmosphere near the anion. This ionic atmosphere can affect both the distribution of the anion between the solution bulk and the surface layer and also the reorganization energy of the solvent, and hence the activation energy of the electroreduction reaction. The structure of this atmosphere depends both on the anion charge and on the value of ψ_0, and the nature of the supporting electrolyte cations. It seems probable that in the presence of more weakly hydrated cations, such as caesium cations, the transition of the anion from the bulk to the surface is facilitated, and the reorganization energy of the solvent is decreased, which leads to acceleration of the reaction. The applicability of the Tafel equation for the electroreduction of an already adsorbed anion requires special consideration. However, the obscure points encountered here probably do not differ from those arising in the quantum-mechanical treatment of the constancy of α in a wide range of φ in the case of other electroreduction reactions, *e.g.* that of the hydrogen ion discharge reaction.

Undoubtedly, these considerations, which differ somewhat from the concepts previously used, of the decisive role of the formation of the cationic bridges or ion-pairs in the double layer, will raise objections. They should be treated only as a certain tentative outline of a possible theory requiring further quantitative development.

Some papers have been published recently[30–33], in which attempts are made at a more rigorous quantitative treatment of the problem of anionic electroreduction. These works, however, do not consider the difficulties arising in interpreting the coincidence of the c.T.p. obtained for different metals.

Further more accurate experimental studies are necessary of the influence of the nature of the metal on the kinetics of electroreduction of the anion $S_2O_8^{2-}$ and other anions, in wide concentration range of the supporting electrolyte, and as close as possible to the p.z.c.

If we assume $n_i = -2$, in the presence of Na^+ and K^+ ions α becomes equal to 0.22 ± 0.02. As would be expected, considering that in both cases the elementary act of the electrochemical reaction is accompanied by breaking of the O–O bond, the value of α for electroreduction of the $S_2O_8^{2-}$ anion is close to that for the reduction of H_2O_2 ($\alpha \simeq 0.25$). This makes doubtful the concept according to which we have the value of $\alpha = 0.22$ (instead of $\alpha = 0.5$) because the process rate is determined not only by the slow discharge, but also by slow penetration. Moreover, if the slow penetration affected significantly the shape of the polarization curve, as is clear, in particular, from eqn. (2), the c.T.p. of different metals should not coincide. This has been pointed out by Fawcett[14]. An interpretation of the α value in the case of H_2O_2 reduction has been given by Krishtalik[50].

It is clear from Fig. 4, that in the case of a supporting electrolyte containing Cs^+ ions, the value of α is somewhat higher. A marked increase of α when passing from Na^+ to K^+ and Cs^+ was observed for the PtF_6^{2-} anion[44].

The coincidence of c.T.p. for metals, for which the work function into vacuum

W_e varies within 0.5 V, proves conclusively that W_e should not figure in the equations of electrochemical kinetics[44–48].

The c.T.p. of the $Fe(CN)_6^{3-}$ anion reduction at Bi, Pd, Cd and In electrodes[37,40] coincide approximately ($\alpha \simeq 0.24$), the differences observed being within the accuracy of calculation by means of eqn. (7), for the triply charged anion. However, so far it has not been possible to bring into exact conformity the data on the reduction of the ferricyanide anion at the dropping mercury electrode[5], indium amalgam and solid electrodes; the theoretical interpretation of the α values also remains controversial in this case[32]. This problem requires further investigation.

SUMMARY

It has been shown that extrapolating the dependence of the i, φ curves for the electroreduction of the $S_2O_8^{2-}$ anion in the presence of 0.05 M KCl on the r.p.m. of a rotating electrode under turbulent stirring conditions, an i, φ curve undistorted by concentration polarization at positive surface charges can be obtained.

The corrected Tafel plots (c.T.p.) for the electroreduction of the $S_2O_8^{2-}$ anion at antimony, amalgamated copper, bismuth, tin, lead, cadmium and indium rotating disc electrodes have been compared. The c.T.p. depend on the cation of the supporting electrolyte, but are practically independent of the nature of the electrode metal if the value -2 is ascribed to the charge of the reacting particle in the double layer. The coincidence of the c.T.p. shows that the work function does not appear in the equations of electrochemical kinetics and that, at least for the $S_2O_8^{2-}$ anion, the slow penetration (dynamic ψ_1 effect) does not markedly affect the i, φ dependence in the measurable section of the polarisation curve.

No coincidence of the c.T.p. obtained with different metals is observed if the effective charge of the reacting particle in the double layer is equated with -1. The implications of this result are discussed.

Additional measurements are required in the case of the $Fe(CN)_6^{3-}$ anion.

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