

THE ELECTROREDUCTION OF ANIONS
IN FORMAMIDE AND WATER;
A COMPARISON OF THE DOUBLE LAYER CATION EFFECT*

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Current-potential data showing a large double layer effect for the electroreduction of peroxydisulphate and trioxalatocobaltate(III) anions at a mercury electrode in formamide are presented and compared with the corresponding data in water. These data are then discussed with respect to three different explanations of the double layer cation effect, namely, variations in the properties of the inner layer with the specific cation at the Outer Helmholtz Plane, interaction between the reacting species and the double layer cation, and the specific adsorption of cations.

The effects of interfacial structure on electrode kinetics are most pronounced when polyvalent ions react at a similarly charged electrode. In the case of anion electroreduction at potentials cathodic of the electrocapillary maximum it has been shown that the current depends markedly on the nature of the base electrolyte, on whether ions or neutral molecules are specifically adsorbed at the electrode, and on the nature of the electrode¹. Until recently², detailed examination of kinetic data in terms of Frumkin's theory³ has largely been limited to results at the mercury — and mercury amalgam — aqueous solution interfaces¹ where precise thermodynamic data for interfacial structure were available.

An anomalous result of the above studies was the pronounced specific effect of the double layer cation for reduction of polyvalent anions. In this case a change in base electrolyte cation in the series Li^+ to Cs^+ caused a marked change in the observed current. Several explanations have been offered for this effect including cation specific adsorption⁴, interaction between the reacting ion and cations either in the bulk of the solution or in the double layer at the reaction site⁵, and differences in the distance of closest approach to the electrode for the reacting species and the various cations⁶.

In the hope that a better understanding of double layer effects could be achieved, a study of electroreduction reactions was undertaken in the amide solvents. These solvents possess a wide range of bulk physical properties^{7,8}. In addition, considerable variation in the structure of the mercury-solution interface with the nature of the solvent has been found in differential capacity studies⁹. Formamide is a reasonably good solvent for inorganic salts and therefore

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was chosen for the initial experiments. The physical properties of formamide and water are such that significant differences in ionic solvation and the extent of ion pairing in the bulk of the solution are expected. From interfacial capacity studies⁹⁻¹¹, several pertinent differences in the structures of the mercury-solution interface have been found. In aqueous solution¹², the capacity of the inner layer for solutions of the alkali metal chlorides at far cathodic potentials increased in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$, whereas in formamide^{9,10}, the order was $\text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{Cs}^+$. In addition, it was concluded¹¹ that formamide was strongly adsorbed on mercury with the negative end of the molecular dipole oriented towards the metal such that reorientation of the solvent molecules at the interface did not occur until the charge density on mercury was about $-7 \mu\text{C} \cdot \text{cm}^{-2}$. In contrast, reorientation of the water dipoles at the mercury-aqueous solution interface occurred close to the point of zero charge¹³.

In the present paper polarographic data for the electroreduction of peroxydisulphate and trioxalatocobaltate (III) anions are presented and compared with data for the corresponding aqueous systems.

EXPERIMENTAL

The apparatus, experimental procedure, methods of reagent and solvent purification, and sources of double layer data have been described elsewhere^{16,17}.

Kinetic data were obtained at a dropping mercury electrode by measuring the current at the end of drop life, and the drop time as functions of electrode potential, the depolarizer concentration being $5 \cdot 10^{-4} \text{M}$ in all cases. The alkali metal perchlorates at low concentration were used as base electrolytes in formamide, the corresponding fluorides being used in water. It was assumed that specific adsorption of perchlorate anion was negligible at potentials cathodic of the electrocapillary maximum (ecm) in formamide¹⁷. The rate of charge transfer was calculated at 50 mv intervals from the measured current, drop time, and flow rate, and calculated diffusion limited current at the same potential using Koutecký's theory for diffusion controlled¹⁸ and irreversible polarographic currents¹⁹ with consideration of the effects of electrode sphericity²⁰. The potential of the working electrode was measured with respect to an aqueous saturated calomel electrode, the liquid-liquid junction being designed so that contamination of formamide solutions with water was negligible¹⁷. This potential scale was converted to a rational one by measuring the ecm potential with respect to the same reference electrode in the corresponding base electrolyte solution using the streaming mercury electrode technique of Grahame¹⁶.

Tables of differential capacity, Outer Helmholtz Plane potential, Φ_2 , and electrode potential on the rational scale, Φ_m were calculated as a function of base electrolyte concentration from tabulated values of the differential capacity of the inner layer, C_1 and surface charge density on the electrode, q . The Gouy-Chapman theory was applied in the calculation of the differential capacity of the diffuse layer and the OHP potential.

Both of the above calculations were carried out on an IBM Model 360 digital computer.

RESULTS AND DISCUSSION

Current-potential data for the electroreduction of peroxydisulphate anion in formamide are presented in Fig. 1. Current minima with characteristics similar to those for the corresponding aqueous system were observed. At potentials cathodic of the ecm the current decreased from its diffusion limited value i_d , the magnitude of the depression depending on the base electrolyte cation in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ >$

> Cs^+ . The results in formamide differed from those in water in that the current ratio i/i_d and its change from the Cs^+ to the Li^+ system were considerably less in formamide for a given base electrolyte concentration and electrode potential on the rational scale.

The charge on the reacting species was determined from rate constant-potential data at a single base electrolyte concentration by applying the finite difference method described earlier¹⁶. For the case that electron transfer is the rate determining step in the reaction mechanism and for potentials sufficiently cathodic of the equilibrium potential, then, according to the Frumkin equation

$$\Delta[(\ln k)/f]/\Delta(\Phi_2 - \Phi_m) = \beta - z \Delta\Phi_2/\Delta(\Phi_2 - \Phi_m), \quad (1)$$

where k is the rate of electron transfer, β , the Tafel slope, z , the charge on the reacting anion, and Δ , an operator indicating a small but finite increment in the given function. Thus the charge was determined from the slope of a plot of the data according to equation (1). This value of charge was then used to construct corrected Tafel plots (CTP).

The results for peroxydisulphate anion reduction have been discussed in detail elsewhere¹⁷ and are only summarized here. The charge on the reacting anion was

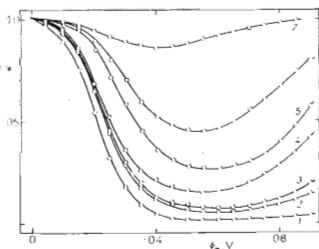


FIG. 1

Ratio of the Current to the Diffusion Limited Current, i/i_d , as a Function of the Electrode Potential on the Rational Scale, Φ_m , for the Electroreduction of Peroxydisulphate Anion at Mercury in Various 0.01M Base Electrolyte Solutions

1 LiClO_4 , 2 NaClO_4 , 3 KClO_4 , 4 CsClO_4 in formamide, 5 NaF , 6 KF , 7 CsF in water.

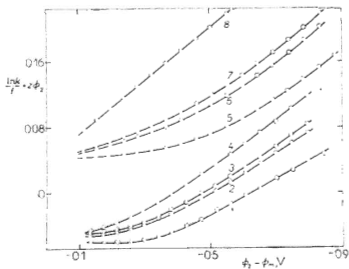


FIG. 2

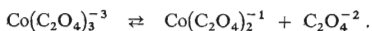
Corrected Tafel Plots for the Electroreduction of Peroxydisulphate Anion at Mercury in Various 0.01M Base Electrolyte Solutions

1 LiClO_4 , 2 NaClO_4 , 3 KClO_4 , 4 CsClO_4 in formamide; 5 LiF , 6 NaF , 7 KF , 8 CsF in water.

found to be -2 . The differential plots were linear in the limit of low Φ_m but were curved for high Φ_m . The shape of the differential plots was qualitatively similar to those obtained for kinetic data in aqueous systems⁶. It is significant that the intercept on the ordinate axis (β) of the straight line drawn through the linear section depended on the nature of the solution cation for both the formamide and water cases. The change in the limiting value of β , β_0 was such that β_0 increased with increase in the cation's atomic number. CTP for peroxydisulphate data in both solvents constructed with the charge equal to -2 are shown in Fig. 2. The qualitative similarities for results in the two solvents are striking. In both cases the corrected reaction rate increases with increase in atomic number of the base electrolyte cation. In addition the CTP are curved for low values of $\Phi_2 - \Phi_m$ and approach an approximately constant slope at higher values (0.28 in formamide and 0.34 in water). The degree of curvature at lower potentials is dependent on the nature of the base electrolyte cation.

Current-potential data for the electroreduction of trioxalatocobaltate(III) anion in the potential region immediately cathodic of the ecm are presented in Fig. 3. The double layer effect for this system in aqueous solution has been described previously by Nikolajeva-Fedorovich and co-workers¹⁵. Briefly, the anion is reduced at mercury in two steps, the first involving the one electron reduction of Co(III) to Co(II), and the second, the two electron reduction of Co(II) to the metal. The data presented here correspond to the first step and show a double layer effect similar to that observed for other polyvalent anions¹. The cation effect in both solvents was in the same order and similar to that for the peroxydisulphate reaction. However, it is significant that the current did not fall below its diffusion limited value until the electrode potential was about 100 mV cathodic of the ecm (as determined in the base electrolyte alone). This suggests that the reacting particle is specifically adsorbed on mercury at not too negative potentials; this interpretation is supported by the fact the oxalate anion is itself adsorbed on mercury²¹.

Differential plots of the kinetic data were constructed according to equation (1), and the charge on the reacting particle found to be -1 in water and -3 in formamide. However, these results are tentative for the following reasons. The differential method of charge determination relies heavily on kinetic data in the potential region where Φ_2 is changing rapidly with $\Phi_2 - \Phi_m$, that is, just cathodic of the ecm. If, in fact, the reacting anion is significantly specifically adsorbed in the same potential region, the Frumkin equation (Eq. (1)) is not valid. If specific adsorption is only significant for values of $\Phi_m > -0.2$ V. The above results are probably valid. Using a different method Nikolajeva-Fedorovich and co-workers¹⁵ found the charge on the reacting anion to be -1 when the base electrolyte was dilute aqueous KCl. They postulated that the trioxalatocobaltate(III) anion was somewhat unstable in the absence of excess oxalate so that a mononegative species was produced in the equilibrium



It is interesting that the differential analysis results in a higher charge on the reacting anion in formamide. Presumably this is due to a lower dissociation constant for the above equilibrium in this solvent and the lower absolute value of Φ_2 for a given ionic strength and electrode potential. The higher charge on the reacting species undoubtedly accounts for the sharper decrease in current with increase in potential in formamide (Fig. 3).

Finally, a cation effect similar to those described above has been observed for the reduction at mercury of hexacyanoferrate(III) anion in formamide²².

As described previously⁶, the cation effect can be rationalized in terms of a model in which the reacting particle is in the inner layer in the transition state, its distance from the OHP depending on the specific cation at that plane and on the potential drop across the inner layer. For a given inner layer potential difference, the average potential at a reaction site whose distance from the electrode is constant will increase in absolute value with increase in inner layer thickness. This thickness is assumed to increase with increase in the solvated radius of the cation at the OHP²³, that is, according to the series $\text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$. New experimental evidence supporting the latter assumption has recently been obtained by Damaskin and co-workers²⁴. The change in inner layer thickness with potential drop across it is due to electrostriction²⁵.

For the above conditions the Frumkin equation may be written

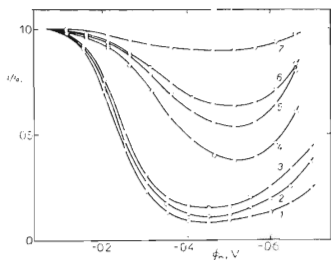


FIG. 3

Ratio of the Current to the Diffusion Limited Current, i/i_d , as a Function of the Electrode Potential on the Rational Scale, Φ_m , for the Electroreduction of Trioxalatocobaltate (III) Anion at Mercury in Various 0.01M Base Electrolyte Solutions

1 LiClO_4 , 2 NaClO_4 , 3 CsClO_4 , 4 LiF , 5 NaF , 6 KF , 7 CsF in water.

$$\ln k = \ln k_0 - zf\Phi_2 + [\alpha n - \lambda(\alpha n - z)] f(\Phi_2 - \Phi_m), \quad (2)$$

where k_0 is the reaction rate at the ecm, α , the transfer coefficient, n , the number of electrons involved in the reaction, and $\lambda = (x_2 - x_r)/x_2$, x_2 being the thickness of the inner layer and x_r , the distance of the charge centre of the reacting particle in the transition state from the electrode. As the thickness of the inner layer decreases, λ decreases, and the Tafel slope increases. This prediction is confirmed by the CTP of Fig. 2 in that the Tafel slope increases at constant $\Phi_2 - \Phi_m$ in the series $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$, and for a given cation with increase in $\Phi_2 - \Phi_m$. The constancy of the Tafel slope at higher values of $\Phi_2 - \Phi_m$ and for the peroxydisulphate reaction in aqueous CsF over the whole potential range can also be accounted for if it is assumed that the inner layer possesses regions of different dielectric properties, that closer the electrode having a low dielectric constant and that nearer the OHP a higher value²³. Then, when the particle is in the second region, a situation which apparently holds when the inner layer thickness is relatively small, the potential experienced by the particle is approximately constant and equal to Φ_2 (*i.e.* $\lambda = 0$).

It is interesting to note that the order of the cation effect in the kinetic data is different from that in the capacity data whereas in water they are the same. According to the above model, the thickness of the inner layer increases in the order $\text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$ in both solvents. The capacity of the inner layer can be considered as approximately proportional to the ratio of the dielectric constant of the inner layer to its thickness. From capacity studies it has been concluded that the inner layer thickness in the two solvents is about the same (3.3 Å in water²⁶ and 3.9 Å in formamide¹¹), so that the inner layer contains fewer solvent molecules in the case of formamide. In the latter case ionic solvation will be more important in determining the orientation of solvent molecules than in water; thus the inner layer dielectric constant will be more dependent on the nature of the cation at the OHP in formamide. The dielectric constant will be highest in the case of strongly solvated ions such as Li^+ and will decrease in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$. This order is opposite to that for the thickness. Thus, the relative values of the inner layer dielectric constant and thickness could be such that their ratio, that is the inner layer capacity, increases in the order $\text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{Cs}^+$. This order of inner layer capacity is observed at far cathodic potentials where Cs^+ is specifically adsorbed. The position of Cs^+ in the series could well be different if it were not specifically adsorbed.

According to the above model the Tafel slope can be related to the thickness of the inner layer region of low dielectric constant by the equation

$$\beta - z = (\alpha n - z)(1 - \lambda_0) = (\alpha n - z)x_r/x_2. \quad (3)$$

From the data presented in Fig. 2, it follows that the increase in inner layer thickness

from Cs^+ to Li^+ is smaller in the case of formamide. This is undoubtedly due to the fact that formamide is a larger molecule than water so that the change in solvation number with ionic radius is smaller.

According to an alternative explanation⁵, the cation effect is due to interaction between the reacting species and the cations in the double layer in the vicinity of the reaction site. Although a simple quantitative theory for this effect does not exist, a model proposed recently by Parsons²⁷ to account for the effect of specifically adsorbed ions on electrode kinetics might also be applicable in an approximate way to this case. In this model, changes in the ionic atmosphere of the reacting particle with electrode potential were related to changes in the activity coefficient of the activated complex through the adsorption isotherm for the adsorbed ions. If it is assumed that the reacting particle is at the OHP or in the inner layer region of high dielectric constant in the transition state, the Frumkin equation with explicit inclusion of the activity coefficient of the activated complex becomes

$$\ln k = \ln k_0 - zf\Phi_2 + \alpha n f(\Phi_2 - \Phi_m) - \ln \gamma_*, \quad (4)$$

where γ_* is the stated activity coefficient. By analogy with Parsons' treatment²⁷, $\ln \gamma_*$ can be expressed as a function of the reacting particle - cation interaction and the concentration of the double layer cation at the OHP. For the case of attractive interaction $\ln \gamma_*$ is negative and increases in absolute value with increase in cation concentration. In addition it is reasonable to expect the interaction to be greater for more polarizable, weakly hydrated cations like Cs^+ so that $\ln \gamma_*$ would increase in the series $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ for constant cation concentration at the OHP. However, quantitative testing of such a model must await the development of a more sophisticated model for the diffuse layer which reliably estimates the concentration of the double layer ion at the OHP. Qualitatively, according to this explanation, it follows that the change in reacting anion-cation interaction in the series Li^+ to Cs^+ is less in formamide than in water. As above, this could be attributed to differences in solvation in the two solvents. It is difficult, however, to account for the constancy of the Tafel slope at high values of $\Phi_2 - \Phi_m$ by this model. This implies that $\ln \gamma_*$ remains constant with potential under these conditions.

It should be pointed out that when the charge on the reacting particle is determined by the differential method formation of ion pairs between the reaction ion and base electrolyte cations in the bulk of the solution is detected. This conclusion follows in that the value for the charge obtained is independent of the reactant concentration in this case. When the charge is determined by comparing reaction rates for varying base electrolyte concentration at constant electrode charge density, the value obtained is that of the anionic species whose stoichiometric concentration is held constant. This is not necessarily equal to the charge on the species transported through the double layer^{4,14}. Thus, there is no difficulty in distinguishing between ionic

interaction in the double layer and in the bulk of the solution when the differential method is used.

The final explanation of the cation effect considered here is cationic specific adsorption. There does not seem much doubt that Cs^+ is significantly adsorbed on mercury in both water^{24,28} and formamide^{9,10} at sufficiently cathodic potentials. However, from the data of Parsons and Stockton²⁸, specific adsorption of this cation is negligible at potentials anodic of $-15 \mu\text{C} \cdot \text{cm}^{-2}$ and for concentrations less than 0.02M. Thus, it would be difficult to quantitatively account for the cation effect over the whole potential range by cation specific adsorption. Furthermore, if cationic specific adsorption were a significant influence, one would expect a noticeable concentration effect with CTP. As the base electrolyte concentration increases, so would the amount of specific adsorption. Thus the value of Φ_2 estimated ignoring this adsorption would be too negative by an amount which would increase with base electrolyte concentration. As a result CTP constructed with the incorrect value of Φ_2 would lie above one another in order of increasing base electrolyte concentration. A small concentration effect has been observed in both water⁴ and formamide¹⁷ but in the opposite direction. This concentration effect can be attributed to a decrease in the activity coefficient of the reacting anion with increase in ionic strength.

In summary, the details of the cation effect in both water and formamide can be ascribed to changes in inner layer properties with the nature of the cation. Interaction between the reacting anion and the double layer cation at the reaction site can also account for the results in a qualitative fashion but quantitative testing of the data with a model based on interaction does not seem possible as yet. However, it is clear that the cation effect cannot be entirely attributed to cationic specific adsorption. It is hoped that current studies of the cation effect in other solvents will further elucidate this problem.

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