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IONIC ASSOCIATION AND CORRELATION BETWEEN DOUBLE LAYER STRUCTURE AND ELECTRODE KINETICS

by

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The possibility of ion pair formation *solely in the double layer* region at the electrode in charge transfer reactions was suggested in a previous paper[2] from this Laboratory. It was discussed in some detail by Frumkin[3] to account for certain features of current-potential curves for the reduction of anions. Ion pair formation outside the double layer was not considered. Formation of ion pairs in the bulk of the solution was discussed recently by Joshi and Parsons[4], together with other interpretations, to account for the properties of the electrical double layer at the interface between mercury and mixtures of barium chloride and hydrochloric acid. The influence of ion pair formation in the bulk of solution in the correlation between double layer structure and electrode kinetics does not appear to have been considered thus far and is investigated here. Results are given for the reduction of iodate on mercury in alkaline solutions of varying composition. This electrode reaction is advantageous because it occurs in a range of potentials in which there is very little specific adsorption of the ions involved. Application is made of the corrected Tafel plot recently mentioned in a previous paper from this Laboratory.[5]

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(1) Graduate student since September 1960.

(2) P. Delahay and C.C. Mattax, *J. Am. Chem. Soc.*, *76*, 5314 (1954).

(3) (a) A.N. Frumkin, *Trans. Faraday Soc.*, *55*, 156 (1959). (b) A.N. Frumkin, *Transactions of the Symposium on Electrode Processes*, E. Yeager, ed., Wiley, New York, N.Y., 1961, p.1.

(4) K.M. Joshi and R. Parsons, *Electrochim. Acta*, *4*, 129 (1961).

EXPERIMENTAL

Experimental methods were quite conventional and have been reported previously[5]. Adsorbable impurities (organic) were removed by treatment with activated charcoal as noted before[5]. The solution of KOH was titrated. The $K_4Fe(CN)_6$ solution was prepared from the dehydrated salt and was titrated for verification[6].

A five-compartment cell was used with the following electrodes: hydrogen electrode in I; D.M.E. or capillary of Lippmann electrometer and platinum cylinder for differential capacity measurements in III; a high-resistance saturated calomel electrode inserted in IV; and a mercury pool in V. Junctions between compartments were: a bridge with fritted glass disks for I-II; a 1 mm.-bore capillary for II-III; and fritted glass disks for III-IV and IV-V. Solutions in the compartments were: the solution being studied in II, III and IV; this solution, but without potassium iodate, in I and the bridge; and KOH in V. All potentials were measured against the hydrogen electrode in I, the electrode in V being the anode of the electrolysis circuit. The potential of the hydrogen electrode was verified against the S.C.E.: E = -0.964 V. for 5 mM KIO_3 + 20 mM KOH; -0.960 V, for the same solution with 0.4 M KCl; -0.963 V. for the solution with

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(5) K. Asada, P. Delahay and A.K. Sundaram, J. Am. Chem. Soc., **83**, 3396 (1961).

(6) I.M. Kolthoff and R. Belcher, "Volumetric Analysis", Vol. III, Interscience Publishers, Inc., New York, N.Y., 1957, p.135.

0.2 M K_2SO_4 instead of KCl; and -0.966 V. for the solution with 0.1 M $K_4Fe(CN)_6$ instead of KCl or K_2SO_4.

Currents did not exceed 10% of the diffusion current and were corrected for mass transfer polarization by use of the factor $\left[1 - (i/i_d)\right]$. This correction factor is sufficiently accurate for maximum currents during drop life at the foot of a polarographic wave[7].

DESCRIPTION AND DISCUSSION OF RESULTS

Parallel linear Tafel plots were obtained in the current density range, I = 20 to 800 μA.cm^{-2}, for the reduction of potassium iodate in the electrolytes of Table I. These plots yielded αn_a = 0.75 (α, transfer coefficient; n_a number of electrons in the activated step) in good agreement with the previously reported[8] value of 0.77. Corrected Tafel plots were prepared according to

$$\ln I + \frac{zF}{RT}\Delta\varphi = \ln I^{\circ} + \frac{\alpha n_a F}{RT} E_e - \frac{\alpha n_a F}{RT}\left(E - \Delta\varphi\right) \qquad (1)$$

where I is the current density, I^{o} the exchange current density, E the electrode potential, E_e the equilibrium electrode potential, $\Delta\varphi$ the difference of potential across the diffuse double layer

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(7) J. Koutecky and J. Cizek, Coll. Czechoslov. Chem. Communs., 21, 836 (1956).

(8) M. Breiter, M. Kleinerman and P. Delahay, J. Am. Chem. Soc., 80, 5111 (1958).

from the plane of closest approach to solution, z the ionic valence with sign of the reduced species (iodate), and F, R and T have their usual significance[9]. Values of $\Delta\varphi$ were calculated by a previously described method[5] from the theory of the diffuse double layer, experimental differential capacities[10] and the point of zero charge. Parallel linear plots were obtained which yielded $\alpha n_a = 0.89$ and the intercepts in Table I . The lines without and with 0.4 M KCl are essentially identical within the experimental error of 3-5 mV but the double layer correction is less satisfactory for 0.2 M K_2SO_4 and, especially, 0.1 M $K_4Fe(CN)_6$. Disagreement for K_2SO_4 was previously noted[8] (without the use of corrected Tafel plots).

Several causes can be invoked for the disagreement between theory and experiment: variation of activity coefficient, ion pair formation in the double layer, influence of ion size, etc. (cf. ref.4). Further, the calculation of $\Delta\varphi$ is based on the Gouy-Chapman theory, i.e. on a very simplified model not unlike that of the Debye-Hückel model for electrolytes. It is surprising, in this respect, that the double layer correction holds so well for concentrations as high as 0.4 M KCl[11]. Ionic association in the bulk of the solution, which

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(9) See ref.5 for a discussion.

(10) Capacities were measured with KIO_3 present as the reaction is so irreversible that the faradaic impedance is very large in comparison with the double layer impedance.

(11) P. Delahay, "Transaction of the Symposium on Electrode Processes", E. Yeager editor, John Wiley and Sons, New York, 1961, p.138.

is not negligible for K_2SO_4 and $K_4Fe(CN)_6$, is also to be reckoned with. One has $\log K = 0.96$[12a], for formation of $K\,SO_4^-$, and $\log K = 2.3$[12b] for formation of $K^+Fe(CN)_6^{3-}$. Ionic association seems negligible for KOH and KCl[12c]. The corresponding error on ionic concentrations, if ionic association is not considered, is significant, especially for K^+ ions which are non-specifically adsorbed in the diffuse double layer at the potentials considered here. The corrected Tafel plots of Fig.1 were obtained after allowance was made for ionic association. The discrepancy for K_2SO_4 noted above disappears and, in fact, there seems to be a slight overcorrection. Results for KOH alone, KOH + KCl, and KOH + K_2SO_4 are nearly the same within experimental error. The discrepancy for $K_4Fe(CN)_6$ is decreased but not entirely eliminated. This discrepancy, as given by Fig.1, is greater than it actually is because formation of the triple ion $(K_2^+)Fe(CN)_6^{2-}$ was not considered. There is evidence for the formation of this ion[13] but no quantitative datum is available. Further, other effects, and particularly the influence of ionic size could be invoked to explain the remaining small departure from theory. This matter will not be taken here, though it is being studied at the present in this Laboratory.

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(12) (a) J. Bjerrum, G. Schwarzenbach and L.G. Sillen, "Stability constants, Part II", The Chemical Society, London, 1958, p.80. (b) Ibid., p.32. (c) Ibid., pp.2 and 93.

(13) S.R. Cohen, Thesis, Cornell University, Ithaca, 1956, p.34.

Ionic association of the reactant, KIO_3 (K = -0.25 for formation[14] of $K^+IO_3^-$) should also be considered since the faradaic current is the sum of the currents for the reduction of IO_3^- and $K^+IO_3^-$. These two parallel electrode processes undoubtedly have different exchange densities. Further, kinetics of dissociation of $K^+IO_3^-$ complicates matter. Double layer corrections for this type of process were discussed semi-quantitatively[8, 15], and theoretical analyses have been worked out[16, 17]. This effect is probably minor here because of the weak association between K^+ and IO_3^-.

In conclusion, correction for ionic association of the supporting electrolyte and/or ionic reactants appears in order in the correlatopn between double layer structure and electrode kinetics. However, one would do well to remember the words of caution of Robinson and Stokes[18] when using equilibrium constants for ionic association.

ACKNOWLEDGMENT.- This investigation was supported by the Office of Naval Research.

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(14) Cf. ref.12, p.124.

(15) L. Gierst, ref.11, pp.109-138.

(16) H. Matsuda, J. Phys. Chem., 64, 336 (1960).

(17) H. Hurwitz, Z. Elektrochem., 65, 178 (1961).

(18) R.A. Robinson and R.H. Stokes, "Electrolyte Solutions", 2nd edition, Academic Press, Inc., New York, N.Y., 1959, pp.421-423.

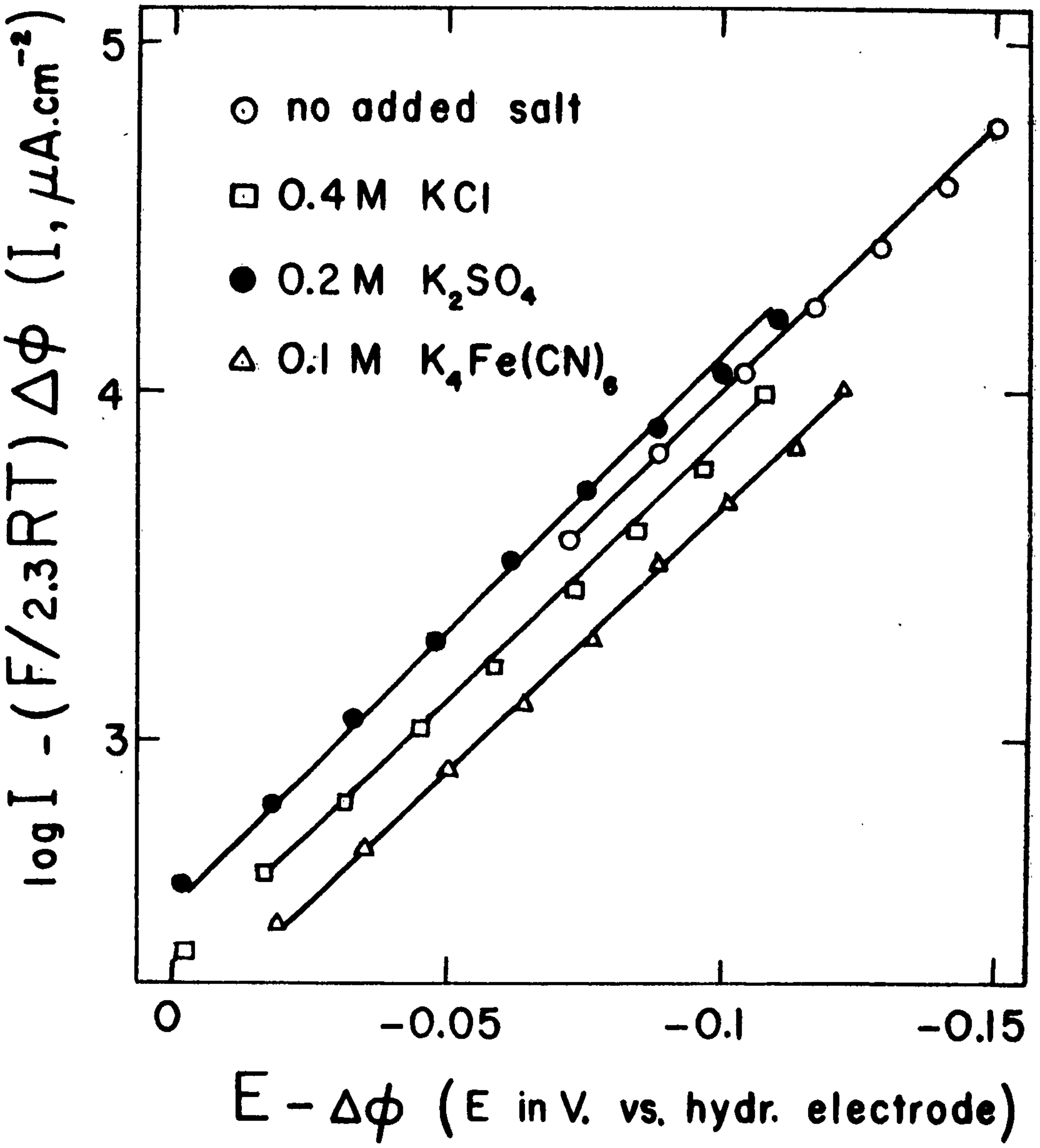
TABLE I

REDUCTION OF 5 mM KIO_3 IN 20 mM KOH ON MERCURY AT 25°

Added salt	E at $I = 100 \mu\cdot cm^{-2}$ for Tafel plot V. vs. H.E. [a]	$E - \Delta\varphi$ for corrected Tafel plot [b] V. vs. H.E.
none	-0.247	-0.036
0.4 M KCl	-0.105	-0.042
0.2 M K_2SO_4	-0.121	-0.050
0.1 M $K_4Fe(CN)_6$	-0.132	-0.070

(a) H.E. ≡ hydrogen electrode in identical solution as for electrolysis but without KIO_3. (b) For $\log I + (zF/2.3\ RT)\Delta\varphi = 10^3$ (I in $\mu A\cdot cm^{-2}$).

Fig.1 - Corrected Tafel plots for the solutions of Table I. Correction for ionic association was made for K_2SO_4 and $K_4Fe(CN)_6$.



○ no added salt
□ 0.4 M KCl
● 0.2 M K_2SO_4
△ 0.1 M $K_4Fe(CN)_6$
5
4
3
0
-0.05
-0.1
-0.15
$\log I - (F/2.3RT)\Delta\phi$ (I, $\mu A.cm^{-2}$)
$E - \Delta\phi$ (E in V. vs. hydr. electrode)

FIG. 1

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