

ELECTRODE KINETICS AND DOUBLE-LAYER STRUCTURE.
THE $Zn^{2+}/Zn(Hg)$ ELECTRODE REACTION IN MIXED POTASSIUM HALIDE
SOLUTIONS

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INTRODUCTION

Specific rate constants of electrode reactions are strongly influenced by the nature and concentration of the base electrolyte used. In some cases (see for example, DELAHAY¹) the concentration effect has been interpreted quantitatively by taking into account the potential difference across the diffuse double layer (Frumkin-theory). The effect of the nature of the supporting electrolyte has only qualitatively been correlated to the specific adsorption of the anions, especially in the case of halide solutions. For example, GIERST AND CORNELISSEN² measured the half-wave potentials of the Eu^{3+}/Eu^{2+} couple as a function of composition in 1 *M* mixtures of perchlorate and halides. They found the reaction rate to increase in the series $Cl^- < Br^- < I^-$ in the presence of perchlorate. Specific adsorption on mercury, exhibited by the anions, varies in the same sequence. TAMAMUSHI *et al.*³ observed the same trend for the $Zn^{2+}/Zn(Hg)$ electrode in mixtures of $NaClO_4$ with halides. On the other hand, BLACKLEDGE AND HUSH⁴ ascribed the results of their experiments on the same electrode in similar base electrolyte mixtures to a mechanism in which complexes of Zn^{2+} with the added anions take part.

In this connection it seemed worthwhile to make a quantitative study of the relation between the rate constant and the specifically adsorbed amount of anions in mixtures of base electrolytes. We chose the $Zn^{2+}/Zn(Hg)$ reaction in mixtures of KCl, KBr and KI with a total concentration of 1 *M*, for the following reasons: (a) the rate constant values of the zinc reaction in the pure base electrolytes differ greatly⁵; (b) the rates can easily be measured with an alternating current method; (c) double-layer data of at least chloride and iodide are known from the literature^{6,7}; (d) the $Zn^{2+}/Zn(Hg)$ reaction mechanism has been investigated many times; it appears that the rate-determining step is likely to be a two-electron transfer⁸. In addition, the presence of Zn^{2+} ions in millimolar concentration has no detectable effect upon the double-layer capacity in 1 *M* solution⁹, and it may therefore be assumed that the double-layer structure is not significantly changed by the addition of Zn^{2+} .

EXPERIMENTAL

The measurements of the kinetic parameters were made using the oscilloscopic

square-wave method developed in this laboratory^{10,11}, which allows the direct reading of the activation overvoltage from the screen of an oscilloscope at the moment of zero diffusion polarization, t_0 , occurring in each half period of the applied square-wave current. The effect of the double-layer capacity is minimized by measuring at frequencies sufficiently low to allow an accurate extrapolation to zero frequency. Recently, we discussed the applicability and the limitations of this method¹¹ and in that communication it is erroneously stated that the upper limit depends on the error in the activation overvoltage measured at low frequency (16 Hz).

However, if k_{sh} is large, the application of much higher frequencies is permissible, as the effect of the double-layer capacity is smaller in this case*. The highest frequencies at which the double-layer charging current is negligible have been estimated earlier as a function of k_{sh} for the oscilloscopic sine-wave method¹². Approximately the same frequency limits will be valid for the square-wave method and it can be calculated that both methods are now limited by the ohmic resistance and the double-layer capacity to k_{sh} -values of *ca.* 0.2 cm sec⁻¹.

Solutions were made from analytical-grade salts dissolved in doubly-distilled tap-water. The cell solutions consisted of mixtures of KCl, KBr, KI and KNO₃ with a total concentration of 1 M, and 5 mM ZnSO₄. It was necessary to acidify the solutions (with perchloric acid) to pH 3 in order to avoid precipitation of zinc hydroxide on the electrode. Solutions were de-aerated with nitrogen which had been passed through vanadous sulphate solution.

Zinc amalgam was prepared electrolytically and kept in a nitrogen atmosphere. An amalgam pool could not be used as a counter electrode—the indicator electrode being an amalgam drop—because of spontaneous dissolution of zinc from the pool in the acid solution. Therefore *two amalgam drops* served as electrodes; they were *both* renewed before a new measurement. A mercury pool was placed at the bottom of the cell in order to minimize dissolution of zinc from the discarded drops on strong dilution.

The surface area of the electrodes was determined by the usual drop weight method. The radius of the drops was about 0.05 cm, which allows the application of the current-voltage relation in terms of linear diffusion. An electrode distance of 1.2–1.3 cm was adopted. With distances down to 1 cm, no deviations were noticed as a result of distortion of the lines of force between the drops.

Capacitance-potential curves of mercury in mixtures of 1 M KCl and 1 M KI were carried out using the impedance bridge described earlier⁹. Electrocapillary curves of the same mixtures were recorded with the drop-time method.

The kinetic parameters of the zinc reaction in various supporting electrolytes

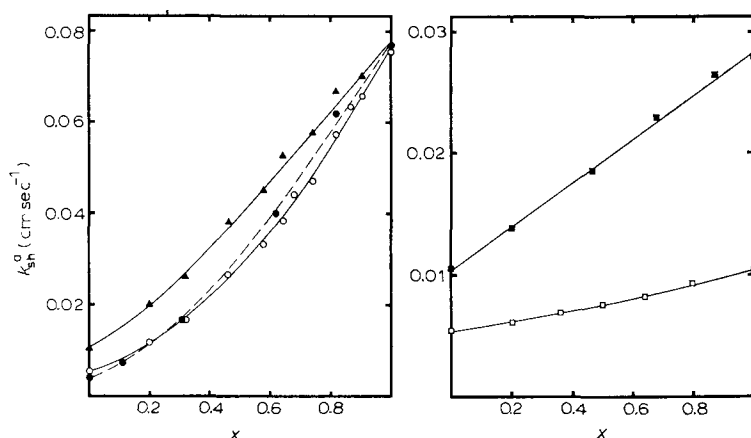
From the measured charge transfer resistances, θ , apparent formal rate constants, k_{sh}^a , were calculated using RANDELS' equation¹³

$$k_{sh}^a = (RT/n^2 F^2) \{ (C_{ox}^*)^\alpha (C_{red}^*)^\beta \theta \}^{-1}$$

in which $C_{ox}^* = C_{red}^* = 5 \cdot 10^{-6}$ mole cm⁻³ was introduced for the bulk concentrations. In Fig. 1, the rate constants thus obtained, have been plotted against composition for 1 M mixtures of KCl + KI, and KNO₃ + KI, with almost identical results. Similar curves were obtained for KCl + KBr, and KBr + KI mixtures (Fig. 2).

* This fact was brought to our attention by Mr. D. J. KOOLJMAN.

Our k_{sh}^a -values are in good agreement with literature data³⁻⁵. The transfer coefficient, β , of the zinc reaction has frequently been found to be close to 0.3, regardless of the nature of the base electrolyte, except for the value 0.00 in 1 M KI, observed by BLACKLEDGE AND HUSH⁴. However, we found $\beta = 0.32 \pm 0.08$ for the zinc reaction in 1 M KI, which is quite close to the values in the other media. In 0.5 M KCl + 0.5 M KI a similar result, $\beta = 0.27 \pm 0.06$, was obtained (Fig. 4).



Figs. 1 and 2. Apparent rate constants, k_{sh}^a , of $Zn^{2+}/Zn(Hg)$ electrode reaction as a function of x in mixed solns. (○), $(1-x)$ M KCl + x M KI; (●), $(1-x)$ M KNO₃ + x M KI (dashed curve); (▲), $(1-x)$ M KBr + x M KI; (□), $(1-x)$ M KCl + x M KBr; (■), $(1-x)$ M KBr + 0.5 x M KCl + 0.5 x M KI.

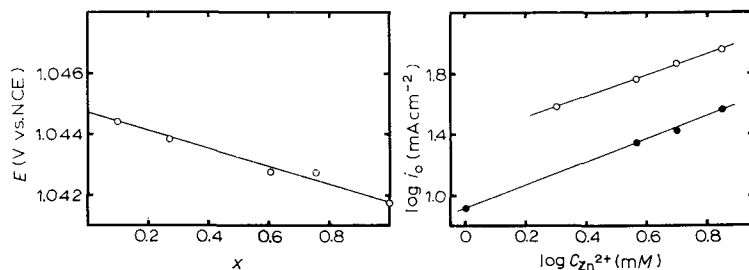


Fig. 3. Equilibrium potentials of $Zn^{2+}/Zn(Hg)$ electrode ($C_{Zn} = C_{Zn^{2+}} = 5$ mM) in $(1-x)$ M KCl + x M KI solutions.

Fig. 4. Determination of the transfer coefficient, α , of $Zn^{2+}/Zn(Hg)$ electrode reaction, in (○), 1 M KI; (●), 0.5 M KCl + 0.5 M KI. $C_{Zn} = 5$ mM. The slopes are $\alpha = 0.68$ and $\alpha = 0.73$, respectively.

In order to evaluate the double-layer parameters, the equilibrium potential of a 5 mM zinc amalgam electrode in 5 mM Zn^{2+} solution was measured as a function of the molar ratio in KCl + KI mixtures. The results are shown in Fig. 3.

Specific adsorption and ϕ_2 -potentials in halides at the equilibrium potential of the zinc reaction

The double-layer parameters needed for our investigation are not directly

available in the literature. We can use only the data on pure KCl and KI solutions of varying ionic strength reported by GRAHAME AND PARSONS⁶, from which we obtained the specifically adsorbed quantities, $q_{Cl}^1 = -0.5 \mu C \text{ cm}^{-2}$ and $q_I^1 = -5.9 \mu C \text{ cm}^{-2}$ in 1 M solution at the equilibrium potentials given in Fig. 3. The ϕ_2 -potentials are -0.046 V and -0.056 V in KCl and KI, respectively. For 1 M KBr we applied GRAHAME's procedure to the interfacial tension data given by DEVANATHAN AND PERIES¹⁴, which resulted in an approximate value for $q_{Br}^1 = -1 \pm 0.5 \mu C \text{ cm}^{-2}$ and $\phi_2 = -0.047 \pm 0.001 \text{ V}$.

Specific adsorption studies in mixed electrolytes have, to our knowledge, been carried out only with mixtures of one specifically adsorbing anion (e.g., KI⁷ or NH_4NO_3 ¹⁵) with fluoride, which is assumed to be not specifically adsorbed. On this assumption, the specifically adsorbed charge is obtained by an elegant method developed by DUTKIEWICZ AND PARSONS⁷. These authors showed also that a plot of the specifically adsorbed charge against the salt activity of KI at constant surface charge density, q , for KF + KI solutions is identical with the same plot for pure KI solutions at the same q . This means that values of q_I^1 pertaining to the mixtures can be derived from the data available⁶ on pure KI solutions.

When both anions of a binary electrolyte, e.g., KCl + KI, are subject to specific adsorption, the separate values of q_{Cl}^1 and q_I^1 can be determined, in principle, by a combination of the procedures of GRAHAME⁶ and DUTKIEWICZ AND PARSONS⁷. However, at the potential of interest, -1.04 V vs. NCE , chloride is only slightly adsorbed in the inner layer and, as a first approximation, the structure of the double layer in $(1-x) \text{ M KCl} + x \text{ M KI}$ may be assumed to be identical with that of $(1-x) \text{ M KF} + x \text{ M KI}$. This is supported by the fact that the capacity-potential curves for KCl + KI, measured by us for $x=0, 0.01$ and 0.1 , proved to be identical with the corresponding curves in KF + KI at potentials below -1.0 V vs. NCE .

We therefore used GRAHAME's data on pure KI solution to prepare plots of

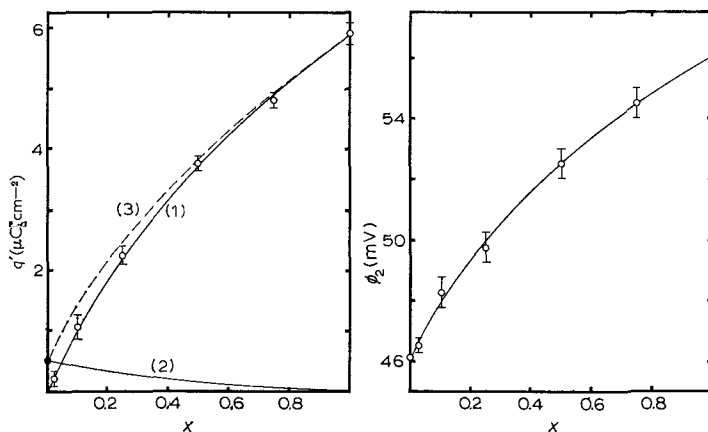


Fig. 5. (Curve 1), charge due to specific adsorption of anions at the equilibrium potential of $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$ electrode ($C_{\text{Zn}} = C_{\text{Zn}^{2+}} = 5 \text{ mM}$) in solns. of $(1-x) \text{ M KF} + x \text{ M KI}$; (curve 2), analogous plot, estimated for $(1-x) \text{ M KCl} + x \text{ M KF}$; (curve 3), sum of 1 and 2 (see text).

Fig. 6. Potentials of the outer Helmholtz plane at the equilibrium potential of $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$ electrode ($C_{\text{Zn}} = C_{\text{Zn}^{2+}} = 5 \text{ mM}$) in mixed solns. of $(1-x) \text{ M KCl} + x \text{ M KI}$.

q_1^{-1} vs. the salt activity, $a_{K^+}a_{I^-}$, at some integral values of q (-10 to $-12 \mu\text{C cm}^{-2}$). Following DUTKIEWICZ AND PARSONS⁷, such plots are easily transformed into plots of q_1^{-1} vs. x , the mole fraction of KI in KF + KI mixtures, after calculation of $a_{K^+}a_{I^-}$ in 1 *M* solutions as a function of x (the mean activity coefficient is taken as constant). Then, only the proper values of q are needed to obtain q_1^{-1} at the equilibrium potential of the zinc reaction as a function of x . These values were calculated from the above-mentioned capacity-potential curves by back integration from -1.54 V vs. NCE, where $q = -20 \mu\text{C cm}^{-2}$ for both 1 *M* KI and 1 *M* KCl⁶. The resulting "specific adsorption isotherm at the zinc equilibrium potential" is shown in Fig. 5 (curve 1). In addition, a curve is given, that represents an estimation of the variation of $q_{Cl^-}^{-1}$ with x , calculated in a similar way from Grahame's data on pure KCl solutions (curve 2). It seems reasonable to assume that the presence of chloride in the inner layer has only a minor effect on the total specifically adsorbed charge, except for low values of x . The attribution of Cl^- might be accounted for by adding together curves 1 and 2 (curve 3), although this is a rather debatable procedure.

However, as will be shown in the discussion, Fig. 5 is sufficiently useful for the comparison of k_{sh} -values with q^1 . Since the specific adsorption of NO_3^- is of the same order of magnitude as that of Cl^- , it may also be applicable to KNO_3 -KI mixtures, in particular for $x > 0.2$.

Finally, the ϕ_2 -potentials at the zinc equilibrium potential can be calculated as a function of x in the usual way⁶ from q and q^1 (Fig. 6).

DISCUSSION

The data represented in Figs. 1 and 2 are "apparent" rate constants, k_{sh}^a , calculated from the measured exchange current density, i_0 , by

$$i_0 = nFk_{sh}^a [Zn^{2+}]_a^\alpha [Zn]^\beta \quad (1)$$

in which $n=2$, $[Zn]$ is the concentration of zinc in the amalgam, and $[Zn^{2+}]_a$ the concentration of the total amount of zinc ions introduced into the solution. A "true" rate constant, k_{sh} , may be defined in the usual way by introduction of the Frumkin correction and activities instead of concentrations:

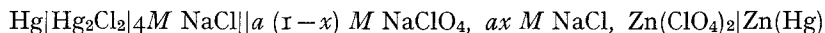
$$i_0 = nFk_{sh}^f [Zn^{2+}]_t^\alpha [Zn]^\beta \exp \{ -(\alpha nF/RT) \phi_2 \} \quad (2)$$

where $[Zn^{2+}]_t$ is the true concentration of non-complexed Zn^{2+} present in the solution, and the exponential term represents the Frumkin correction ($z=n$). In a first approximation, the "activity factor", $f = (f_{Zn^{2+}})^\alpha (f_{Zn})^\beta$, may be considered as a constant in solutions of varying composition at constant ionic strength, and we will therefore calculate a "true formal rate constant" k_{sh}^f , given by

$$k_{sh}^f = fk_{sh} = k_{sh}^a \frac{[Zn^{2+}]_a^\alpha}{[Zn^{2+}]_t^\alpha} \exp \left(\frac{\alpha nF}{RT} \phi_2 \right) \quad (3)$$

Among the anions concerned in our investigation, NO_3^- and I^- are known to show little tendency to complex formation¹⁶, so that we may take $[Zn^{2+}]_t \approx [Zn^{2+}]_a$ for solutions of these ions. If chloride is present, however, complex formation is appreciable¹⁷, the dominant species being probably $ZnCl^+$ and $ZnCl_3^-$. Unfortunately, unambiguous evaluation of the correction factor $[Zn^{2+}]_a/[Zn^{2+}]_t$ is hardly feasible,

because the study of complex formation involves variation of the composition of the solution, which also causes changes in other quantities. For example, SILLÉN AND LILJEQUIST¹⁷ measured the e.m.f.'s of the cell



$a = 3$ or 0.5

from which the stability constants of the zinc-chloride complexes can be derived if one neglects the changes in the activity coefficients and in the liquid junction potential. In $3 M$ solution they found $K_{\text{Cl},1} = 0.65$ and $K_{\text{Cl},3} = 1.4$ for the complexes ZnCl^+ and ZnCl_3^- , respectively. In $0.5 M$ solution, only the first constant could be obtained: $K_{\text{Cl},1} = 0.45$.

The equilibrium potential measurements in $\text{KCl} + \text{KI}$ mixtures, described in the present paper, are similar to SILLÉN'S experiments and, again neglecting the changes in $f_{\text{Zn}^{2+}}$ and the liquid junction potential, the observed change in e.m.f. can be interpreted as the consequence of the presence of ZnCl^+ and ZnCl_3^- with stability constants $K_{\text{Cl},1} = 0.5$ and $K_{\text{Cl},3} = 0.08$. As this is in reasonable agreement with SILLÉN'S results, it seems justified to use the e.m.f. values of Fig. 3 for the estimation of the correction factor from

$$\Delta E = E_{x=1} - E_x = 29.58 \log \frac{[\text{Zn}^{2+}]_a}{[\text{Zn}^{2+}]_t} \quad (4)$$

The error introduced by the approximation, will not be very serious, because the correction itself is of minor importance compared to the large variation of k_{sh}^a with composition in $\text{KCl} + \text{KI}$ mixtures. This can be seen in Fig. 7 where the effects

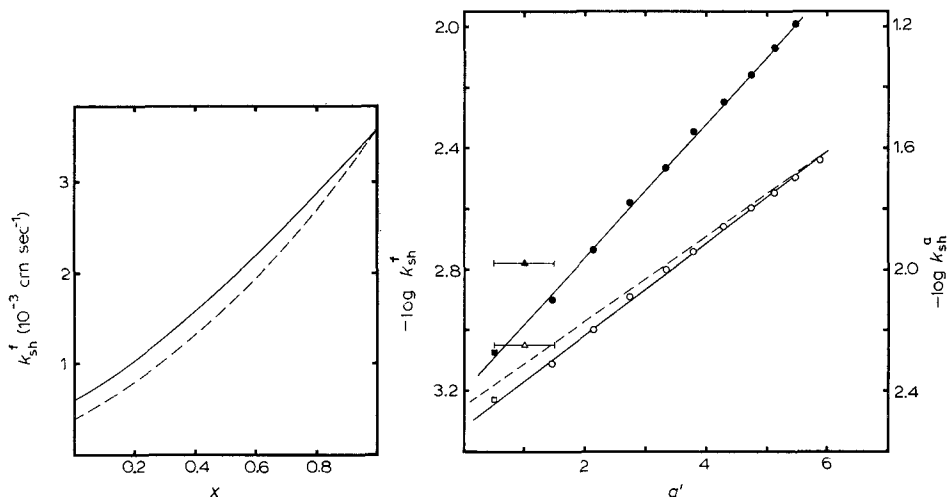


Fig. 7. Formal "true" rate constants of $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$ electrode reaction in $(1-x) M \text{ KCl} + x M \text{ KI}$ solns. (---), k_{sh}^a (from curve in Fig. 1) corrected only for the Frumkin effect; (—), *idem*, corrected also for existing complexes (see text).

Fig. 8. Relation between the rate constant of $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$ electrode reaction and amount of specifically adsorbed anions. White symbols, $\log k_{\text{sh}}^t$, black symbols, $\log k_{\text{sh}}^a$, both *vs.* q^1 from curve 3 in Fig. 5. Dashed line: $\log k_{\text{sh}}^t$ *vs.* q^1 from curve 1 in Fig. 5. (○, ●), $(1-x) M \text{ KCl} + x M \text{ KI}$; (□, ■), $1 M \text{ KCl}$; (△, ▲), $1 M \text{ KBr}$.

of this correction and of the Frumkin correction are demonstrated separately. The latter has been calculated with the aid of the ϕ_2 -potentials given above, together with $\alpha = 0.70$.

The "true" rate constant obtained still appears to depend strongly on x . It should be realized, however, that with the definition of k_{sh}^f in eqn. (2), it is implicitly assumed that the exchange reaction proceeds *via* the Zn^{2+} ion. That this assumption is not *a-priori* correct, follows, for example, from the work of GERISCHER¹⁸, in which it was shown that in a number of cases a certain zinc complex is the reacting species, although its concentration can be quite low compared to the dominant zinc species.

Relation between k_{sh}^f and x on the assumption of complex reactants

A model may be adopted, in which, in principle, all zinc species, $ZnX_{\nu}^{2-\nu}$, take part in the electrode reaction, each with its own exchange current density, which according to GERISCHER is given by

$$i_{0,x,\nu} = nF k_{x,\nu} [Zn]^{\beta} [ZnX_{\nu}^{2-\nu}]^{\alpha} [X^{-}]^{\nu\beta} \exp[(\nu - \alpha n)(F/RT)\phi_2] \quad (5)$$

where according to the absolute rate theory, $k_{x,\nu}$ is the formal exchange rate under hypothetical standard conditions ($[Zn][X^{-}]^{\nu} = [ZnX_{\nu}^{2-\nu}]$ and $\phi_2 = 0$). Let $K_{x,\nu}$ be the formal stability constant of the ν th complex, defined as

$$[ZnX_{\nu}^{2-\nu}]/[Zn^{2+}]_t [X^{-}]^{\nu} = K_{x,\nu} \quad (6)$$

Then

$$i_{0,x,\nu} = nF k_{x,\nu} [Zn]^{\beta} [Zn^{2+}]_t^{\alpha} [X^{-}]^{\nu} K_{x,\nu}^{\alpha} \exp[(\nu - \alpha n)(F/RT)\phi_2] \quad (7)$$

In the case of KCl + KI mixtures, this equation pertains to all possible chloride and iodide complexes of zinc and to the aquo-zinc ion ($\nu = 0$). The measured exchange current density will be the sum of all individual $i_{0,x,\nu}$ values, so

$$i_0 = nF [Zn]^{\beta} [Zn^{2+}]_t^{\alpha} \exp\left(-\frac{\alpha n F}{RT} \phi_2\right) \times \left\{ k_{aq} + \sum_{\nu=1,2,\dots} k_{I,\nu} K_{I,\nu}^{\alpha} [I^{-}]^{\nu} \exp\left(\frac{\nu F}{RT} \phi_2\right) + \sum_{\nu=1,2} k_{Cl,\nu} K_{Cl,\nu}^{\alpha} [Cl^{-}]^{\nu} \exp\left(\frac{\nu F}{RT} \phi_2\right) \right\} \quad (8)$$

This expression is, in fact, a simplification, as α is assumed to be the same for all partial exchange processes. Since, experimentally, α appears to be independent of composition, this seems at least a good approximation.

With eqns. (2) and (3) and $[I^{-}] = x$ and $[Cl^{-}] = 1 - x$, it follows that

$$k_{sh}^f = k_{aq} + \sum_{\nu=1,2,\dots} \{k_{I,\nu} K_{I,\nu}^{\alpha} x^{\nu} + k_{Cl,\nu} K_{Cl,\nu}^{\alpha} (1-x)^{\nu}\} \exp\left(\frac{\nu F}{RT} \phi_2\right) \\ = A + Bx + Cx^2 + \dots \quad (9)$$

The curves drawn in Fig. 7 can be fitted to eqn. (9) with the following coefficients for KCl + KI mixtures:

$$A = 0.58 \times 10^{-3}, \quad B = 2.1 \times 10^{-3}, \quad C = 0.9 \times 10^{-3},$$

the higher-order terms being negligibly small. The same reasoning can, of course, be applied to $KNO_3 + KI$ mixtures if Cl is replaced by NO_3 . Assuming that for the

calculation of k_{sh}^f in these mixtures the ϕ_2 vs. x plot of Fig. 6 can be used, we calculate for $KNO_3 + KI$ mixtures:

$$A = 0.33 \times 10^{-3}, \quad B = 2.2 \times 10^{-3}, \quad C = 1.1 \times 10^{-3}.$$

In the simplest interpretation, these results imply that the dominant reactants are $Zn^{2+}(aq)$, $ZnCl^+$, ZnI^+ and ZnI_2 .

A similar theory is supported by BLACKLEDGE AND HUSH⁴ for explaining the relation between i_0 and I^- or Cl^- in solutions of $2 M NaClO_4 + y M NaI$ or $NaCl$. The interpretation of their results leads to the same conclusion as regards the reacting species. Note that the parameter, k_c , determined by these authors, is equivalent to $k_{X,r}K_{X,r}^\alpha$ in our notation.

Although the model described seems to be confirmed by the experimental facts, it still leaves the most interesting question unanswered, *i.e.*, what makes the rate constants of the iodide complexes so large, despite the instability of the latter? As their concentration in the solution is extremely small, the complex formation, preceding charge transfer, must take place at the reaction site in the double layer. In eqns. (5)–(9) this is accounted for by the Frumkin correction terms, which imply that the reaction site is identified with the outer Helmholtz plane and that the reaction rate is influenced only by the structure of the diffuse double layer. However, it seems to be equally—or even more—realistic to take into account the iodide ions present in the *non-diffuse part* of the double layer.

Relation between k_{sh}^f and the amount of specific adsorption

TAMAMUSHI *et al.*³ postulate that the electrode surface can be divided into a “naked” part $(1 - \vartheta)$ at which the electrode reaction proceeds with a rate constant k_1 , and a part, ϑ , covered with halide ions, at which the reaction proceeds with a higher rate constant, k_2 . The overall rate constant is given by

$$k_{sh}^f = (1 - \vartheta)k_1 + \vartheta k_2 \quad (10)$$

From this model we infer that k_{sh}^f should be a linear function of the specifically adsorbed charge. A comparison of Fig. 7 and Fig. 5 shows, however, that this is not the case. Instead, the data suggest that k_{sh}^f increases exponentially with q^1 .

We therefore plotted the logarithm of the k_{sh}^f -values of $KCl + KI$ mixtures against q^1 and obtained, in fact, a surprisingly straight line, see Fig. 8. The plot of $\log k_{sh}^a$ in the same figure demonstrates that the corrections for existing complexes and ϕ_2 -potentials have only a minor effect on the slope of the line. Furthermore, it makes little difference, whether q^1 is taken from curve 1 or curve 3 in Fig. 5. Note that the points for $1 M KCl$ and $1 M KBr$ fit reasonably well on the lines. Also the k_{sh} -data for $KBr + KI$ and $KCl + KBr$ mixtures (Figs. 1 and 2) qualitatively indicate that the increase of k_{sh} with the amount of specific adsorption is—at least to a first approximation—not dependent on the nature of the anion.

This result can be interpreted in a very simple way with the aid of the definition of k_{sh} in the absolute rate theory¹

$$k_{sh} = \frac{kT}{h} \exp \left[\frac{-\overrightarrow{\Delta G_{\ddagger}^0} + \alpha n F \phi_M^0}{RT} \right] = \frac{kT}{h} \exp \left[\frac{-\overleftarrow{\Delta G_{\ddagger}^0} - \beta n F \phi_M^0}{RT} \right] \quad (11)$$

where ϕ_M^0 is the inner potential of the electrode at the standard potential of the redox couple and ΔG_{\ddagger}^0 is the chemical standard free energy of activation ($\overrightarrow{\quad}$ and $\overleftarrow{\quad}$

pertain to oxidation and reduction, respectively). As all the other symbols in eqn. (11) represent constants, Fig. 8 can be explained on the basis of a single exchange mechanism with an activation energy that decreases linearly with the specifically adsorbed charge ($\mu\text{C cm}^{-2}$), according to

$$\Delta G_{\pm}^0 = (\Delta G_{\pm}^0)_{q^1=0} - 205 q^1 \text{ cal mole}^{-1} \quad (12)$$

Although the experimental facts described in this paper, do not lead to a definite decision between the "complex reactant model" and the "specific adsorption model", we believe that the latter is fairly plausible. SCHMIDT AND MARK¹⁹ presented a quantum chemical theory on the mechanism of charge transfer at an electrode, in which the solvation sheath adjacent to the electrode plays an important part. In this connection, it seems logical that the presence of polarizable anions like halides may change the energy level of the activated state. In any case, there is some evidence in the literature to support the idea that specific adsorption of anions is essential for their accelerating effect on electrode reactions. For example, the anomalous polarograms of In(III) in SCN^- and halide solutions^{20,21} indicate that the rate constants of these systems depend on the potential qualitatively in the same way as the inner-layer charge. Moreover, the experiments of GERISCHER¹⁹, which convincingly support the "complex reactant" model, do not conflict with our views, although they were mostly performed at rather negative potentials where no significant specific adsorption of anions exists. In most cases it is observed that the reacting species is an uncharged particle, *e.g.*, Zn(OH)_2 or Zn(COO)_2 , so that the low activation energy apparently pertaining to these complexes may be due also to adsorption in the double layer.

It may be noticed that, if our model holds, one should be very cautious in the determination of parameters of electrode reactions requiring variations in the experimental conditions that may be accompanied by a change in the amount of specific adsorption (*e.g.*, potential or temperature variation for the determination of the transfer coefficient and the heat of activation, respectively). On the other hand, anomalous results observed in such experiments, may supply more evidence in favour of the model, and may eventually be used for its refinement. This will be further investigated.

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SUMMARY

The $\text{Zn}^{2+}/\text{Zn(Hg)}$ electrode in binary 1 M potassium halide solutions has been studied using the oscilloscopic method for the determination of the kinetic parameters. The apparent standard heterogeneous rate constant, k_{sh} , is found to be a non-linear function of the mole fraction, x , of the components of the base electrolyte.

Taking into account the Frumkin correction and the occurrence of complex formation, the measured k_{sh} -values in $(1-x) M \text{ KCl} + x M \text{ KI}$ are compared with the amount of specific adsorbed anions, q^1 . A linear relation is found between $\log k_{sh}$ and q^1 (Fig. 8), from which it is inferred that the energy of activation decreases linearly with q^1 . This model is preferred to the assumption of complex reactants.

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