

ELECTRODE KINETICS AND DOUBLE LAYER STRUCTURE

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Several electrochemical methods have been developed in recent years for the study of the kinetic parameters of electrode reactions. These methods have been used for obtaining an abundance of experimental data for the standard heterogeneous rate constant, k_{sh} , of electrode reactions, mostly limited to reactions at a mercury electrode.

As early as 1933, Frumkin recognized the essential correlation between the double layer structure at the electrode interface and electrode kinetics. As enough data for the kinetic parameters are yet available, interest is growing in this correlation, because it may result in a better understanding of heterogeneous reaction rates. According to Frumkin the potential difference existing in the double layer, influences the kinetic parameters for two reasons: (a) It influences the effective potential difference which favours or hinders the reaction. (b) The effective concentration of reacting species is different from the "bulk" concentration. The Frumkin effect with its limitations is discussed.

Adsorption of electroinactive species, e.g. organic adsorbates, may have two effects: variation of the potential difference in the double layer and hence of the Frumkin correction and secondly a blocking effect. Some examples, illustrating these effects, are presented. If the anions of the supporting electrolyte were specifically adsorbed at the interface, it appeared that the Frumkin correction did not suffice. For some reactions, e.g. the zinc system in mixed halide solutions, we found a linear relation between $\log k_{sh}$ and the amount of specifically adsorbed anions q^{-1} , from which it is inferred that the energy of activation for the electrode reaction decreases linearly with q^{-1} .

Quite frequently, the electroactive species themselves are adsorbed at the interface. In that case the adsorption complicates matters considerably, e.g. the mass transport equations change, so that the electrochemical methods, as normally used, are inapplicable. Recently Delahay has presented expressions based on the concept of the coupling between faradaic and double layer charging processes. These expressions can be used successfully for systems with adsorption of the electroactive species. Such systems have been investigated with sine wave methods and some results are presented. Almost all systems with adsorption of the reacting species were found to be mass transfer controlled, so that no influence of the double layer structure on the kinetic parameters could be investigated for these cases.

1. Introduction

Electrode processes are heterogeneous reactions at a metal-solution interface with kinetics depending on the variables, e.g. potential differences, characterizing the conditions at the interface. Several methods have been developed, especially in recent years, for the study of the kinetics of such electrode reactions. These methods have been used for obtaining an abundance of experimental data, mostly limited to reactions at a mercury electrode.

For a simple electrode reaction, $R \rightleftharpoons O + ne$, involving the exchange of n electrons in one charge transfer step, the faradaic current, i_F , can be represented as (cf. ref. 1, chapter 7)

$$i_F = i_0^a \left[\frac{C_R}{C_R^*} \exp \left\{ \frac{\alpha n F}{RT} \eta \right\} - \frac{C_O}{C_O^*} \exp \left\{ - \frac{\beta n F}{RT} \eta \right\} \right], \quad (1)$$

where C_O and C_R denote the concentrations at the electrode surface, C_O^* and C_R^* the bulk concentrations, α the transfer coefficient with $\beta = 1 - \alpha$ and the overvoltage $\eta = E - E_{eq}$.

At the equilibrium potential ($\eta = 0$), the net current is zero. Then the forward (oxidation) and the backward (reduction) current balance each other and are equal to the so-called apparent exchange current density i_0^a . A high exchange current density indicates a low activation energy involved in the charge transfer step.

The apparent exchange current density i_0^a is given by¹⁾

$$i_0^a = n F k_{sh}^a (C_O^*)^\alpha (C_R^*)^\beta, \quad (2)$$

with k_{sh}^a the apparent heterogeneous rate constant. In eqs. (1) and (2) activities rather than concentrations should be used. However, it is common practice not to consider the influence of the activity coefficients. Therefore, the rate constant k_{sh}^a should be considered as an operational parameter. The transfer coefficient α must be considered as a parameter, which characterizes the state of the activated complex in one way or another. The essential meaning of it, however, is not yet fully understood.

The rate constant k_{sh} is of the form

$$k_{sh}^a = (kT/h) \exp(-\Delta G_0^\ddagger/kT) / \gamma_\ddagger, \quad (3)$$

where kT/h is the universal frequency factor, ΔG_0^\ddagger is the standard free energy of activation of the charge transfer step at the standard potential of the electrode reaction and γ_\ddagger is the activity coefficient of the activated complex, which is usually assumed to be independent of the potential and solution composition.

Experiments have shown that rate constants can differ much, even if one electrode reaction is studied in different electrolyte solutions. The reasons for the changes in the rate of the electrode reaction can be manifold and are up to now not fully understood. An important factor appears to be the structure of the electrical double layer. A good survey of the correlation between double layer and electrode kinetics has been given by Delahay¹⁾. Some of the effects and our ideas about the problem will be presented here.

2. Frumkin effect

As early as 1933, Frumkin²⁾ recognized the existence of the correlation between double layer structure and electrode kinetics.

First a short review of the models for the double layer is given. (For extensive reviews, see refs. 1, 4 and 13.)

Following the double layer concept of Stern³⁾ and Grahame⁴⁾, ions cannot approach the electrode surface within a certain distance. If no specific

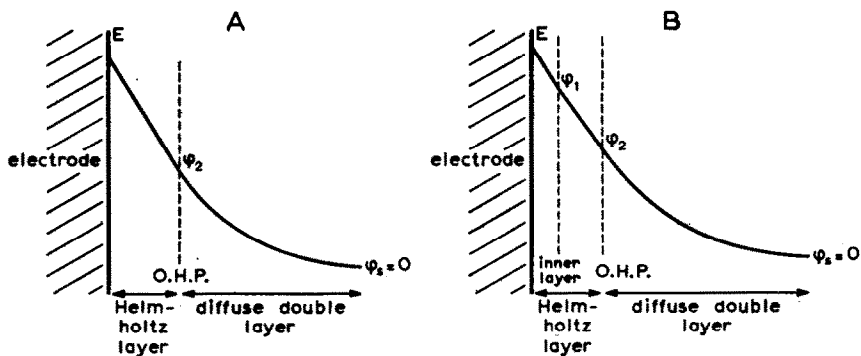


Fig. 1. Models for the electrode-solution interface, in the case of non-specific adsorption (A) and specific adsorption (B).

adsorption is present, the plane of closest approach (the so-called outer Helmholtz plane, O.H.P.) is assumed to be situated at a distance, equal to the radius of the hydrated ions. The potential, ϕ_2 , in the O.H.P. is not equal to the potential in the bulk of the solution, ϕ_s , see fig. 1A. Ions are attracted or repelled in the region between O.H.P. and bulk (diffuse double layer).

The potential differences in the double layer influence the kinetics of the electrode reaction in two ways^{1, 2)}:

(a) Instead of the concentrations at the electrode surface, C_O and C_R , the concentrations at the O.H.P. must be taken.

(b) The effective potential difference which favours or hinders the electrode reaction is $E - \phi_2$ instead of E .

The two effects, called the Frumkin effect, result in

$$i_0^a = i_0^t \exp \left\{ (\beta n - z) \frac{F \phi_2}{RT} \right\}, \quad (4a)$$

or

$$k_{sh}^a = k_{sh}^t \exp \left\{ (\beta n - z) \frac{F \phi_2}{RT} \right\}, \quad (4b)$$

where z is the ionic valence of O. The "true" value of i_0 or k_{sh} can be calculated from the measured "apparent" quantities,* when ϕ_2 values are known from double layer studies.

In order to verify eq. (4), it is necessary to have a fairly accurate understanding of the double layer, which limits most work to mercury electrodes. Especially the Frumkin school⁵⁾, Gierst⁶⁾ and Delahay and coworkers^{7, 8)}

TABLE I
Variations of apparent exchange current with ϕ_2 for the reduction of Zn^{++} on Zn(Hg) at 25°C*

Electrolyte (mole/litre)	ϕ_2 (mV)	i_0^a (mA/cm ²)	i_0^t (mA/cm ²)
0.025 M Mg(ClO ₄) ₂	-63.0	12.0	0.40
0.05	-56.8	9.0	0.43
0.125	-46.3	4.7	0.37
0.25	-41.1	2.7	0.38
0.025 M Ba(ClO ₄) ₂	-60.8	9.1	0.33
0.05	-52.7	5.7	0.39
0.125	-42.8	3.2	0.31
0.250	-36.0	2.1	0.39

* For $C_{Zn(II)} = 2$ mM/litre, $C_{Zn(Hg)} = 0.048$ M/litre; i_0^t computed for $\alpha = 0.30$ (after Aramata and Delahay⁸⁾).

have investigated the Frumkin effect. In many cases a good agreement is found, see table I. More often the agreement is only of a qualitative character. This may result from many reasons.

(i) Specific adsorption. If ions are specifically adsorbed at the interface, they can approach the electrode more closely, to the inner layer, fig. 1B, the inner Helmholtz plane, where the potential is ϕ_1 . The amount of specifically adsorbed ions is usually given in terms of their corresponding charge in the inner layer, e.g. q_-^1 for specifically adsorbed anions. When species are adsorbed, ϕ_2 will change. If i_0^a is corrected for the new ϕ_2 values, no agreement is often found. Some examples hereabout are presented in the next parts. Further, the choice of the potential ϕ_2 in the Frumkin correction is far from settled, when there is specific adsorption of the supporting electrolyte. E.g., it appears for the reduction of nitromethane in iodide medium⁷⁾ that the potential ϕ_1 at the inner layer is a better choice than ϕ_2 .

(ii) Discreteness of charge. An important difficulty remains because in the definition of ϕ_1 and ϕ_2 it was tacitly assumed that there are equipotential planes parallel to the plane of the interface. This assumption neglects the

* Superscript "t" means true values, superscript "a" means apparent values.

“discreteness of charge” effect. Local variations of the potential due to the discrete nature of the ionic charges must be considered, especially when electrolytes with different ionic valences are used⁹).

(iii) Ion pair formation. Ion pair formation in the double layer¹⁰ may be another reason for discrepancies.

In the next parts some other double layer effects are presented.

3. Adsorption of electroinactive species

Adsorption at the interface of electroinactive species like organic molecules may have a profound influence on the rate of an electrode reaction. At least two effects must be considered. The adsorption changes the potential differences in the double layer considerably and hence the Frumkin correction has become quite different. Also a “blocking” effect occurs. Usually, the rate of the electrode reaction at the covered parts of the electrode is

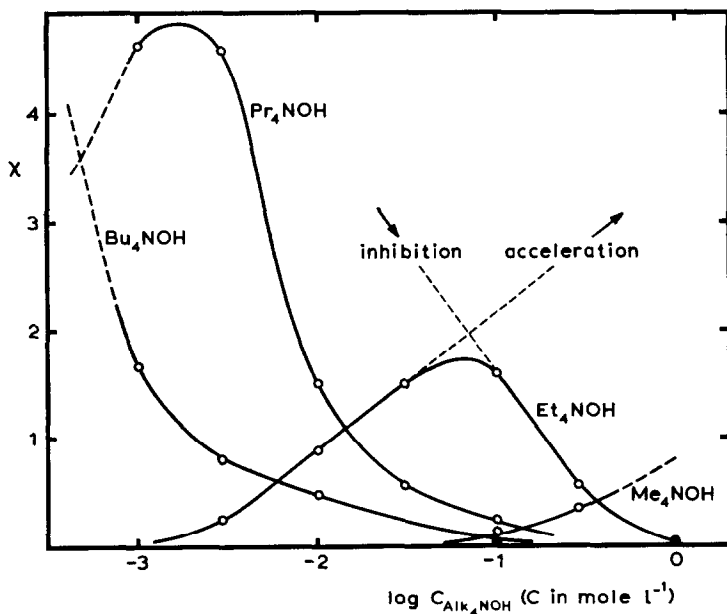


Fig. 2. Variations of the rate of polarographic reduction of 2×10^{-4} M chromate in different tetra-alkylammonium hydroxides of varying concentration (in moles per litre) at 25°C. Rates were corrected for mass transfer and were measured at -0.75 V versus S.C.E. on main wave of chromate. The parameter χ is proportional to the rate of discharge and is given by $(12t/7D)^{\frac{1}{2}} k$ where t is the drop time, D is the diffusion coefficient of chromate and the rate of the chromate reduction is equal to the product of k by the chromate concentration, corrected for mass transfer. Abbreviations: Me (methyl), Et (ethyl), Pr (propyl), Bu (butyl) (after Gierst et al.¹¹).

smaller than at the uncovered parts. A simple model for the blocking effect leads to the following expression

$$i_0^a = (1 - \theta) i_0^{\theta=0} + \theta i_0^{\theta=1}, \quad (5)$$

where θ is the surface coverage of the adsorbed species and $i_0^{\theta=0}$ and $i_0^{\theta=1}$ are the exchange current densities at the uncovered and covered parts of the electrode ($i_0^{\theta=0} > i_0^{\theta=1}$).

A good example of the mentioned effects is the reduction of chromate in tetra-alkyl ammonium hydroxides¹¹), fig. 2. The tetra-alkyl ammonium ions are strongly adsorbed. Therefore, ϕ_2 becomes less negative and the repulsion of the anions CrO_4^{2-} becomes less important. At low concentrations of the hydroxides, especially for the small tetra-methyl and ethyl ammonium ions the Frumkin effect is predominant, resulting in an increase of the reaction rate. At higher concentrations, the blocking effect becomes so important that a decrease of the reaction rate results. Especially for the larger alkyl hydroxides the blocking effect is so predominant, that no competition between the two effects can be observed in these cases.

The zinc discharge in magnesium perchlorate in the presence of organic adsorbates has been studied by Delahay and coworkers^{8,12}). It can be seen from fig. 3 that the reaction rate decreases strongly with increasing coverage. Only for n-amyl alcohol, eq. (5) is obeyed to some extent, for the other curves there is no agreement. The authors pointed out that the calculation

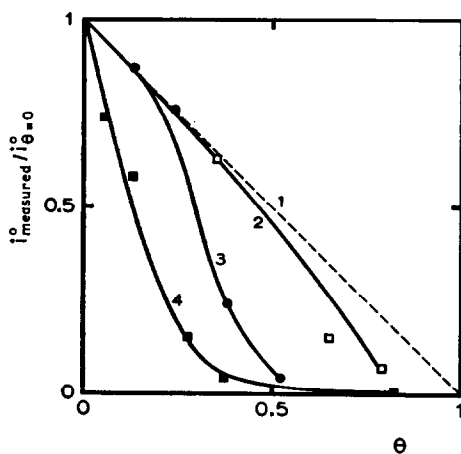


Fig. 3. Influence of coverage on the apparent exchange current for the discharge of 2 mM zinc ion in 0.125 M magnesium perchlorate on 0.046 M zinc-amalgam at 25°C. The ratio $i_{\text{measured}}^0 / i_{\theta=0}^0$ was computed for the potential ϕ_2 that prevailed for i_{measured}^0 ; $i_{\theta=0}^0$ was corrected accordingly. Linear ideal correction (line 1); n-amyl alcohol (curve 2); thymol (3); cyclohexanol (4) (after Aramata and Delahay⁸), Torsi¹²)).

of ϕ_2 and thus the Frumkin correction is quite tentative. Also, the coverage θ may have large experimental errors. The large decrease of i_0 at high coverages may result from the fact that penetration of zinc through the adsorbed layer becomes determinative.

4. Specific adsorption of the supporting electrolyte

The rate of charge transfer appears to be strongly dependent on the nature of the anion of the supporting electrolyte, especially in the series of the halides and thiocyanate. Most of these studies are qualitative: the rate constant k_{sh}^a is found to increase in a way parallel to the specific adsorbability

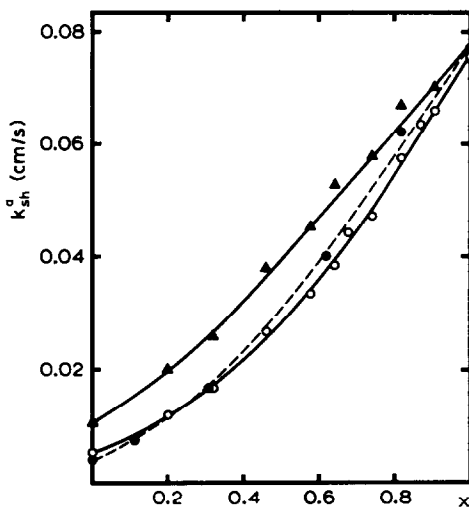


Fig. 4. Apparent rate constants, k_{sh}^a , of $Zn^{2+}/Zn(Hg)$ electrode reaction as a function of x in mixed solutions; (O) $(1-x)$ M KCl + x M KI; (●) $(1-x)$ M KNO_3 + x M KI (dashed curve); (▲) $(1-x)$ M KBr + x M KI (ref. 16).

of the anions (so, $Cl < Br < CNS < I$) and the explanation is sought in the Frumkin effect. In connection with their work on the $Zn^{2+}/Zn(Hg)$ reaction in halide solutions¹⁴) and the $In^{3+}/In(Hg)$ reaction in thiocyanate solutions¹⁵), Tanaka and coworkers postulated the idea that charge transfer proceeds faster at a place where an anion is adsorbed ("ligand" or "bridging" effect). This would imply that a relation similar to eq. (5) must be found, with θ denoting the coverage by specifically adsorbed anions and $i_0^{\theta=1} > i_0^{\theta=0}$.

In our laboratory, we have made a detailed study of the zinc reaction in halide solutions¹⁶). Apparent rate constants were determined from experiments performed at equilibrium potentials (with $C_{Zn^{2+}} = C_{Zn}$) in mixed

potassium halide solutions at a total concentration of 1 M. Typical results are shown in fig. 4. The considerable effect of I^- , which is much stronger adsorbed than Br^- or Cl^- , is evident. In order to consider the relation between the k_{sh} and the amount of specifically adsorbed anions, q_-^1 values for the mixed solutions of KCl and KI were calculated on the basis of some reasonable assumptions (fig. 5). It was assumed¹⁶) that the specific adsorption of iodide at the potential of interest, -1.04 V versus N.C.E., is much

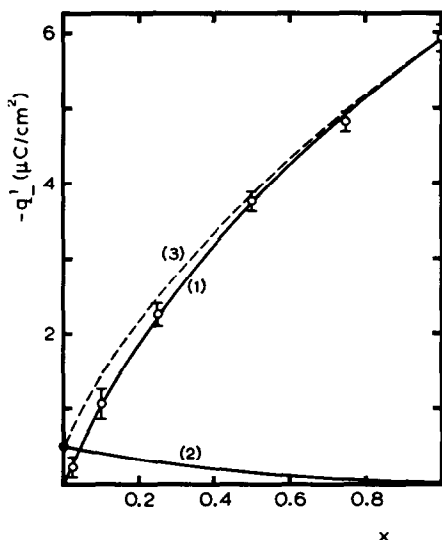


Fig. 5. (Curve 1) charge due to specific adsorption of anions at the equilibrium potential of $Zn^{2+}/Zn(Hg)$ electrode ($C_{Zn} = C_{Zn^{2+}} = 5$ mM) in solutions of $(1-x)$ M KF + x M KI; (curve 2) analogous plot, estimated for $(1-x)$ M KCl + x M KF; (curve 3) sum of 1 and 2 (ref. 16).

stronger than the adsorption of, e.g., chloride. Hence, the structure of the double layer in $(1-x)$ M KCl + x M KI may be assumed to be identical to that of $(1-x)$ M KF + x M KI. For the latter mixtures, an elegant method for obtaining q_-^1 values was proposed by Dutkiewicz and Parsons³⁰). From q_-^1 and the values of q (charge on the electrode), obtained from double layer capacity measurements, also the values of ϕ_2 as a function of x could be calculated according to the procedures of Grahame (ref. 1, chapter 4). Application of the Frumkin correction – i.e. calculation of the true k_{sh}^t values according to eq. (4b) – alters the curves in fig. 4 somewhat, but the shape remains the same. So, it can be concluded that the Frumkin effect cannot account for the very large changes. Comparison of fig. 4 with fig. 5 shows that a linear relation between k_{sh} and q_-^1 , as could be expected if eq. (5)

were valid, is not obtained. In fact, k_{sh} appears to be an exponential function of q_-^1 , as is shown in fig. 6. This result suggests that the free energy of activation of the charge transfer step, ΔG_0^\ddagger in eq. (3), is a linear function of the specifically adsorbed amount of iodide ions (cf. ref. 20).

Though the described experiments seem fairly convincing for this conclusion, they do not exclude a quite different interpretation in which complex

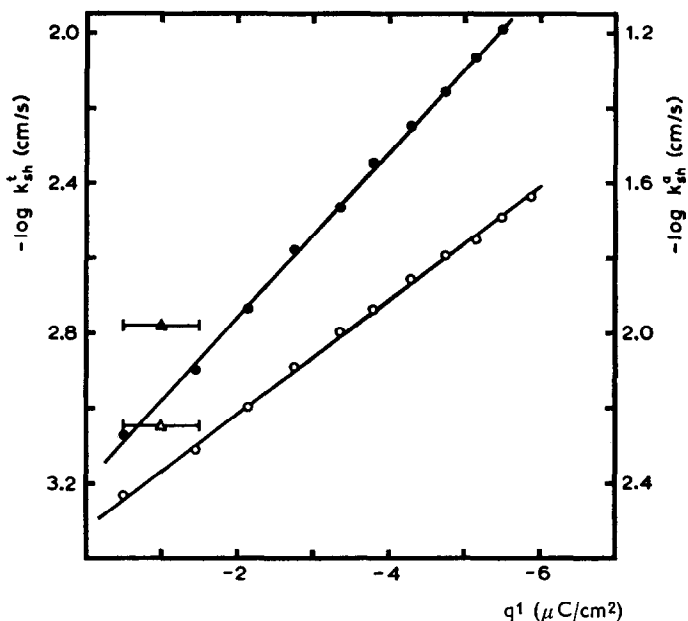


Fig. 6. Relation between the rate constant of $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$ electrode reaction, and amount of specifically adsorbed anions. Open symbols, $\log k_{sh}^\ddagger$; black symbols, $\log k_{sh}^0$, both versus q_-^1 from curve 3 in fig. 5. (○, ●) $(1-x)\text{ M KCl} + x\text{ M KI}$; (Δ, ▲) 1 M KBr (ref. 16).

formation in the solution plays a role¹⁷). Although the ability of Zn^{2+} ions to form complexes with I^- is much less than with Cl^- ions¹⁸), it could be possible that a zinc-iodide complex is reduced much faster than other complex zinc species and, of course, the amount of such a complex increases with increasing iodide concentration. Therefore in another series of experiments, performed in 1 M solutions of each of the halides (i.e., 1 M KI, KBr or KCl) apparent exchange current densities of the zinc reaction were measured as a function of the $C_{\text{O}}^*/C_{\text{R}}^*$ ratio¹⁹). Varying the O/R ratio means varying the mean electrode potential and, as the specifically adsorbed amount of the anions of the supporting electrolyte is a function of potential, it can be expected that the apparent rate constant is potential dependent too, if indeed the rate of charge transfer is correlated with

specific anion adsorption. As will be discussed below, the calculation of the rate constant is not unambiguous if $C_0^* \neq C_R^*$, but by careful analysis it could be shown that in a large potential range $\log k_{sh}$ varies with potential in the same way as q_-^1 . A plot of experimental $\log k_{sh}$ values vs. q_-^1 (fig. 7)

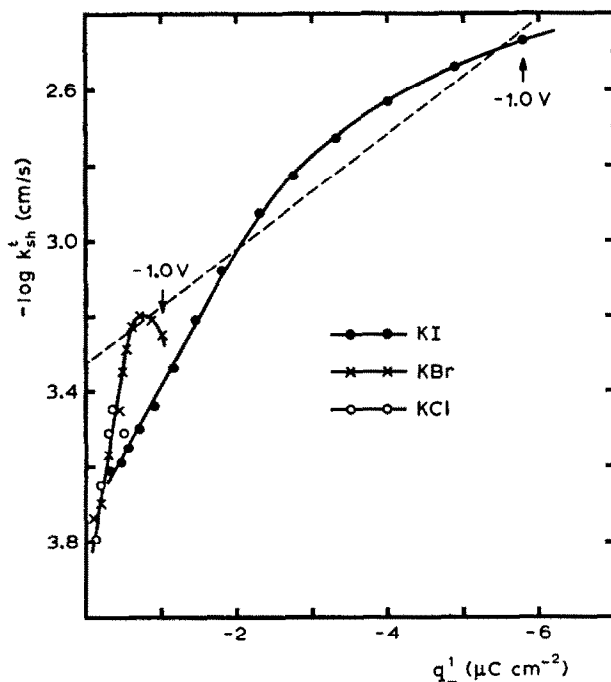


Fig. 7. True rate constants, plotted against the amount of specifically adsorbed anions. Solid curve: with potential as varied parameter; (●) KI; (×) KBr; (○) KCl (ref. 19); dashed curve: from fig. 6 at constant potential (-1.0 V versus S.C.E.) in $(1-x)$ M KCl + x M KI solution.

is linear, at least for the lower q_-^1 values, with different slopes for I^- , Br^- and Cl^- . The change in slope at large q_-^1 values may be interpreted as a decrease in effectiveness when q_-^1 is large (a kind of saturation effect), but it is more probable that the anomalous behaviour of the zinc electrode reaction at anodic potentials¹⁹) is already incipiently present at moderately cathodic potentials.

Very recently, Parsons²⁰) has proposed a simple and elegant model, which fits excellently to these experimental results. Briefly, the effect of the presence of the anions in the inner layer is reflected in the activity coefficient of the activated complex in eq. (3). Considerations based on double layer theory

indicate that this activity coefficient is given by

$$\gamma_{\neq} = \exp 2B_{\neq,1}\Gamma_{-}^{-1}, \quad (6)$$

where $\Gamma_{-}^{-1} = q_{-}^{-1}/F$ and $B_{\neq,1}$ is the second virial coefficient, accounting in the adsorption isotherm for the interaction between the adsorbed ions and the activated complex, which is supposed to be localized in the inner layer. This equation, which controls the slopes of the lines of fig. 7, appears to be obeyed at least qualitatively by our results on the zinc reaction and also by experiments on the hydrogen reaction^{20, 21}).

A quantitative treatment of the experimental data according to eq. (6) is impossible, because $B_{\neq,1}$ is not known. Parsons²⁰) expresses $B_{\neq,1}$ as $B_{\neq,1} = (z_{\neq}/z_1)B_{1,1}$, where $z_{\neq}e$ is the effective charge on the activated complex and z_1e the charge on the specifically adsorbed ions. $B_{1,1}$ is the virial coefficient expressing the first order interaction between the specifically adsorbed ions themselves. Values of $B_{1,1}$ may be calculated from double layer data and then from the experimental slopes of $\log k_{sh}$ versus q_{-}^{-1} , z_{\neq} can be computed. E.g., from the iodide curve in fig. 7, it follows that $B_{\neq,1} = -440 \text{ A}^2 \text{ ion}^{-1}$, hence²⁰) $z_{\neq} = +1.3$ since $B_{1,1} = 350 \text{ A}^2 \text{ ion}^{-1}$.

5. Consequences of potential-dependence of the rate constant for the study of electrode processes

If $C_O^* \neq C_R^*$, the value of i_0^a is governed by the two parameters k_{sh}^a and α (cf. eq. (2)), which are both important for a better understanding of the properties of electrode processes. The evaluation of both parameters is in principle obtained from a plot of $\log i_0^a$ against $\log C_O^*$ or $\log C_R^*$, as can easily be seen from eq. (2). However, if k_{sh}^a is potential-dependent, one has for example

$$\left(\frac{\partial \log i_0^a}{\partial \log C_O^*} \right)_{C_R^*} = \alpha + \left(\frac{\partial \log k_{sh}^a}{\partial \log C_O^*} \right)_{C_R^*} = \alpha + \frac{RT}{nF} \frac{d \log k_{sh}^a}{dE}. \quad (7)$$

The consequence is that the experimentally determined transfer coefficients principally contain a term due to the potential dependency of the rate constant. Due to the evidently strong influence of the double layer structure in many cases, as discussed in previous sections, it must be concluded that analysis of electrode kinetics should be performed with great care, especially if the real transfer coefficient itself is the point of interest.

We have studied this problem more in particular as regards its consequences for the faradaic impedance method²²). In the impedance of a galvanic cell, the charge transfer process is represented by a resistance $\vartheta = RT/nFi_0^a$ (charge transfer resistance). The most spectacular conclusion was that, under

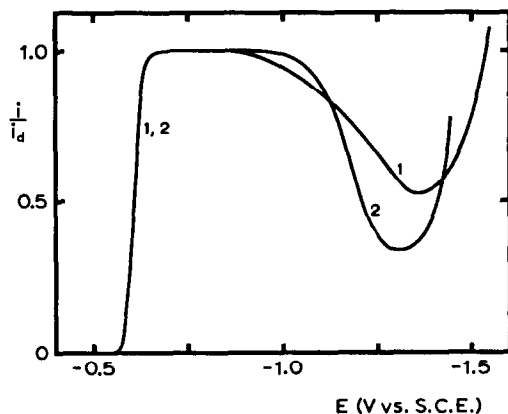


Fig. 8. Direct current polarograms for 2 mM In^{3+} in 1 M KCl (curve 1) and 1 M KSCN (curve 2). The current is given as a fraction of the limiting current, i_d (ref. 23).

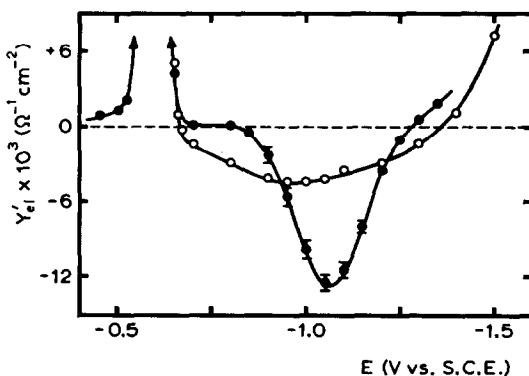


Fig. 9. The real component of the electrode admittance as a function of potential (in-phase ac polarogram) for 2 mM In^{3+} in: (○) 1 M KCl; (●) 1 M KSCN (ref. 23).

certain circumstances, ϑ can attain a negative value, due to the potential-dependency of k_{sh}^a . This means that a 180° phase shift exists between ac current and voltage. The existence of negative ϑ values has been proved experimentally in a number of cases^{15, 19, 22, 23}). Fig. 8 shows the dc polarograms for In^{3+} in 1 M KCl and 1 M KSCN. A minimum appears in the curves, indicating a strong potential-dependence of the charge transfer reaction²³). The real part of the electrode admittance Y'_{e1} at the potentials of the minimum, where $Y'_{e1} = 1/\vartheta$ is indeed negative (fig. 9).

6. Adsorption of the electroactive species

Specific adsorption of the electroactive species themselves is a very common occurrence, e.g. several metal ions are adsorbed from halide

solutions²⁴). The investigations on this subject have proved to be fruitful, especially as regards the theoretical basis of electrochemical methods.

Several authors have dealt with the problem of specific adsorption of the electroactive species on the basis of more or less different models. In our opinion, the best approach to the problem has been the idea of Delahay²⁵), that a coupling exists between faradaic and double layer charging processes. Only a rather brief discussion can be presented here. For a more detailed treatment the original literature and two reviews^{26, 27}) may be consulted.

In general, charge transport through an electrode surface can occur by two processes. One is the occurrence of a faradaic reaction, see eq. (1); the other is the charging current of the electrical double layer at the interface. Usually, the faradaic process is treated first in the development of a theory and only afterwards a correction is made for the double layer charging process. Delahay²⁵) has shown that this is wrong, especially when the reactants are adsorbed at the interface. He has given three general basic equations which should be used in all electrochemical derivations to describe the

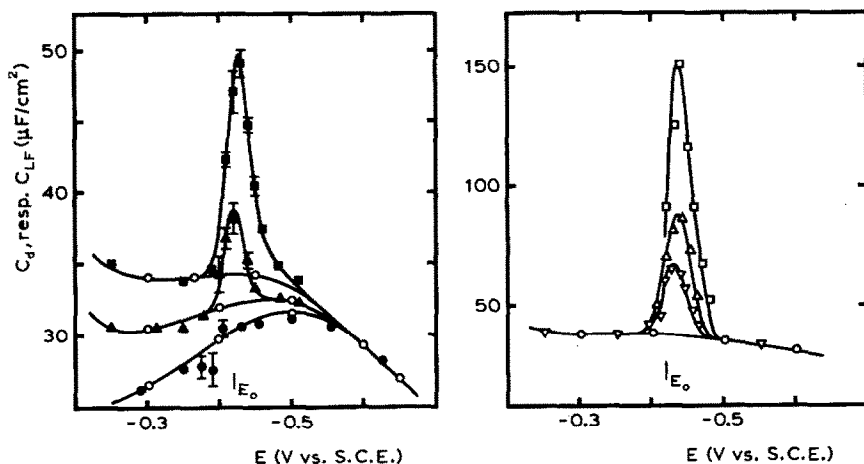


Fig. 10. The double-layer capacitance as a function of potential for $(1-x)$ M $\text{KNO}_3 + x$ M KCl mixtures with and without 0.5 mM Pb^{2+} . (\circ) C_d values for supporting electrolyte; C_{LF} values for solutions $+ 0.5 \text{ mM Pb}^{2+}$ for x values: (\bullet) 0; (\blacktriangle) 0.2; (\blacksquare) 0.4; (∇) 0.6; (\triangle) 0.8; (\square) 1.0 (ref. 28).

relation between faradaic current, charging current and the fluxes of O and R to and from the electrode surface.

Starting with those three equations expressions were developed for the overall electrode impedance, which are very suitable for systems with adsorption of reactants²⁸). It was assumed that the electrode reaction

proceeds reversibly (i_0^a large), because in that case the analysis of experimental impedances is feasible.

We have studied several systems with adsorption of the reactants, using the impedance method. It appears that the electrode impedance is quite different from the classical Randles' equations³¹). However, with the new expressions for the electrode impedance, based on Delahay's equations, a good fit with the experimental data was obtained. The lead system in M KNO_3 -KCl mixtures may serve as a good example²⁸), because the specific adsorption of lead at the interface is found to increase with increasing chloride concentrations. The charge distribution in the double layer and hence the double layer capacitance, C_d , are altered by the adsorption of lead. As can be seen from fig. 10, which shows capacitance curves for the supporting electrolyte with and without 0.5 mM Pb^{2+} , no adsorption of lead occurs from 1 M KNO_3 solutions (no changes in C_d). With increasing chloride concentrations the lead adsorption increases, as indicated by the increasing enhancement of the capacitance in the presence of lead, especially at potentials near the standard potential, E_0 , of the lead couple. At the same time, the measured impedances differ more and more from the classical theory, but they are in good agreement with the new equations. The increase of the capacitances near E_0 , as a function of electrode potential, can be interpreted by assuming a Henry isotherm for the lead adsorption, $\Gamma = \beta C_O$, with a negligible potential dependence of the coefficient β . Due to the slight adsorption of lead, the second virial coefficient B can be ignored. Moreover, it could be concluded from a comparison of Γ with the predominant lead complexes occurring at various chloride concentrations, that the neutral PbCl_2 species is adsorbed, in accordance with the findings of Barker and Bolzan²⁹).

Up to now, all systems with specific adsorption of reactants were found to proceed reversibly (i_0^a large), perhaps because the reactants interact strongly with the electrode in the adsorption process and approach the surface closely, so that the activation energy for the charge transfer process is lowered to such a degree, that it is no longer rate determining.

Further experiments may lead to a better understanding, why certain reactants are adsorbed at the interface and what the exact influence of specific adsorption is on electrode reaction rates. Ultimately, a better insight in the electrode processes proper may result.

Investigations of the kind described here, may seem to be academic in their relation to more practical topics in electrochemistry, as for example electrocatalysis. Yet we feel that it is inevitable first to obtain sufficient knowledge of the behaviour of the interface at an electrode as well defined as possible. For this purpose the mercury electrode is the proper choice. Once

the complications involved in a simple electrode process at a simple electrode surface, for example the potential-dependency of the rate constant, are understood completely, other complicating factors, such as surface roughness, dislocations, heterogeneity of the electrode surface, surface films, porosity, may be better understood.

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Discussion

J. A. A. KETELAAR (University, Amsterdam)

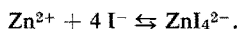
You want to distinguish between the case where there would be a difference in the rate constant for the complex zinc ion and for the uncomplexed ion. Because the coverage on the electrode will be different, you did experiments at a constant iodide concentration but at different potentials. However, I would remark that, though in those cases the equilibrium in the bulk is the same, this is not the case at the electrode surface because the electrochemical potential is different from that in the bulk and changes with potential will effect the percentage of complexing.

B. TIMMER

The chemical potential will change but this change is accounted for by the Frumkin correction. All the different zinc complexes are supposed to be in equilibrium.

J. A. A. KETELAAR

Yes, the equilibrium is shifted and this is not included in the Frumkin correction. Let us say ΔG^* (the total standard free energy of reaction) is the chemical free energy for



It will be affected by twice ϕ_2 . Of course some of the chemical activities are not proportional to kinetic activities. You can only guess how much.

R. PARSONS (University, Bristol)

I think so long as one works in terms of diffuse layer theory, the equilibrium constant for this reaction is constant right through the diffuse double layer. The change of the diffuse layer potential will not make any difference to the fraction of zinc which is in the same complex at different places near the electrode. This is true so long as you have diffuse layer theory but if there is a change in dielectric constant near the surface, then it will make a difference. However, I think the equilibrium constant is independent of the diffuse layer potential because the same number of charges are involved in both sides of the reaction.

B. TIMMER

From the dependence of the standard potential of the zinc electrode reaction on the iodide concentration, one can obtain an indication of the complex formation of zinc with iodide. However, it is difficult to distinguish between the change in diffusion potential and the change caused by complex formation. It is certain that complex formation in iodide solutions is very small or not present and there may be some complex formation with chloride ions¹⁸).

G. J. HOYTINK (University, Sheffield)

Do you have any idea why the zinc reduction is slow?

B. TIMMER

That is a difficult problem. No general theories exist why certain electrode reactions are slow or fast. Heyrovsky³²⁾ supposed that if two electrons are involved in the reaction, as is the case for the zinc reaction, it is likely that first one electron is transferred. The second electron is transferred more difficultly. So, a two-electron reaction should be a slow reaction. However, the cadmium reaction in KCl is a fast two electron reaction. Therefore it is a complex problem that is not yet solved. Some of the more obvious factors, like the influence of the diffuse layer near the electrode, must be better known before the question of why some reactions are slow or fast, can be answered.

J. G. HOOGLAND (Technical University, Eindhoven)

Mostly all reactions are written as if there is an interaction between the metal and the metal ion, but that is not right. You have to do, let us say with at least water adsorbed and the interaction is with that surface and not with a clean metal surface. So, possibly there is a slow charge transfer through that layer.

B. TIMMER

That is the case, but the influence of the adsorbed water layer is not clarified yet.

J. N. BUTLER (Tyco Laboratories, Waltham, Mass.)

Some light, or may be some confusion, will be shed on the matter of solvent interaction by our studies of the lithium amalgam electrode kinetics in LiCl-dimethylsulfoxide solutions³³⁾. Here is a one-electron reaction with a rate of the electron transfer reaction about a hundred times slower than it is in water. Other than that everything behaves exactly according to what you would expect from the diffuse double layer theory. The transfer coefficients are constant over a wide range of amalgam and electrolyte concentrations, the same holds for the stoichiometric number. The rate is slow enough (2×10^{-5} cm/sec) so that diffusion (even in this viscous solvent) is not rate determining. Perhaps the alkali metal reactions in aprotic solvents are the model systems you are looking for to study the effects of adsorption of electroactive species on electron transfer reactions.

W. J. PLIETH (Freie Universität, Berlin)

In your paper you formulated the discharge of a two-valent zinc ion as a single step. I think that at least the possibility exists that a single-valent zinc ion is involved representing an intermediate product within the complete electrode process, and several authors have found indications for the occurrence of such an intermediate. Have you found in your own investigations any sign that the electrode process consists of two such steps?

B. TIMMER

The role of intermediates in the mechanism of electrode reactions has been studied only superficially. According to Heyrovsky³²⁾ Zn^+ is an intermediate species, but in our opinion no experimental evidence has been presented up to now that irrefutably shows that Zn^+ is an intermediate³⁴⁾. Hush and Blackledge³⁵⁾ found that the transfer coefficient α is potential-dependent in the anodic region of the zinc reduction. We¹⁹⁾ found this also. We got a value of $\alpha = 0.81$ in the cathodic region, but in the anodic region $\alpha = 0.40$. Hush and Blackledge concluded that this could indicate that Zn^+ is involved. The steps $Zn^{2+} \rightarrow Zn^+$ and $Zn^+ \rightarrow Zn$ amalgam can of course have different transfer coefficients. So, there may be some indications that indeed Zn^+ as an intermediate can be detected, but I think it is still tentative.

W. J. PLIETH

For the rate determining steps this is unimportant because you get the velocity as a whole.

B. TIMMER

That is true but if the step $\text{Zn}^{2+} \rightarrow \text{Zn}^+$ is fast and $\text{Zn}^+ \rightarrow \text{Zn}$ is slow, the transfer coefficient of the second step is obtained. Visco has studied the reaction $\text{In}^{3+} \rightarrow \text{In}$ amalgam where three electrons are involved in the electrode reaction. He concluded that in some electrolyte solutions In^+ is an intermediate³⁶).

A. S. PORTER (Albright and Wilson, Warley)

A possible way of interpreting the change in rate constant with coverage of the surface is to treat the adsorbate as a layer of dipoles³⁷). These will produce an additional overpotential $\Delta\eta$, which equals when depolarization is taken into account

$$\Delta\eta = 4K\sigma\mu_0\theta/e(1 + 9\alpha\sigma^{2/3}\theta^{2/3}).$$

The symbols have the usual meaning and are defined in ref. 37. At low coverage, $\Delta\eta$ increases linearly with θ but varies less rapidly with θ as $\theta \rightarrow 1$. This expression fits the variation of deposition potential of nickel on mercury, as the coverage with coumarin increases and is qualitatively similar to Dr. Timmer's relationship between $\log k_{sh}$ and the amount of negative ions adsorbed when the variation in adsorption is brought about by varying the potential.

B. TIMMER

It is of course possible to make more complex models for explaining the change in rate constant. We think that it may be better not to accept such a model, but to consider a model as simple as possible.

A. S. PORTER

Perhaps I should say we were fortunate with this system in that we know the orientation of the molecule and its dipole moment.

B. TIMMER

It might have been better in your case first to correct the rate constant for the potential difference in the double layer (Frumkin correction). Perhaps only a blocking effect would have remained.