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ELECTRODE KINETICS AND DOUBLE-LAYER STRUCTURE

II. THE POTENTIAL-DEPENDENCE OF THE KINETIC PARAMETERS OF THE $Zn^{2+}/Zn(Hg)$ ELECTRODE REACTION

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INTRODUCTION

Recently[1], we presented a study concerning the relation between the standard heterogeneous rate constant, k_{sh}, of the $Zn^{2+}/Zn(Hg)$ electrode reaction and the composition of the base solution, consisting of 1 M mixed halides.

In the case of $[(1-x)\ M\ KCl + x\ M\ KI]$ base electrolyte the increase of k_{sh} with increasing x was especially marked; this could be plausibly interpreted by the hypothesis that the specific adsorption of iodide (or iodide + chloride) anions in the inner part of the double layer reduces the activation energy of the charge transfer reaction. In fact, a linear correlation was found between log k_{sh} (*i.e.*, activation energy) and the specifically adsorbed charge, q^1. However, following a theory of BLACKLEDGE AND HUSH[2] in a more generalized form, another explanation was possible, based on the assumption that the electrode reaction proceeds *via* two or more zinc–iodide complexes at a much greater rate than *via* the zinc–chloride or zinc–aquo complexes (complex reactants model). Although we preferred the first explanation (specific anion adsorption model) no definite decision between the two could be made on the basis of the reported experiments, which were performed at constant potential, q^1, the eventual concentration of ZnI_n complexes in the solution being varied simultaneously by changing the iodide concentration.

If, for any base electrolyte, the electrode potential is varied, the amount of specifically adsorbed anions changes independently and, consequently, a decision between the two models is possible in this way: if the specific anion adsorption model holds, the rate constant will depend on the electrode potential. We therefore investigated the kinetics of the $Zn^{2+}/Zn(Hg)$ electrode reaction as a function of the electrode potential by means of the faradaic impedance method. In our opinion this method is pre-eminently suitable for this purpose because of the easy introduction of a d.c. polarizing circuit[3]. Moreover, a theory of the potential-dependence of the faradaic impedance in the case of a potential-dependent k_{sh} is available[4]. In this paper, the results obtained in 1 M KI, KBr, KCl and $NaClO_4$ solutions are described and discussed.

EXPERIMENTAL

Cell impedances were measured in the usual way, using a cell with a dropping mercury electrode (drop time, 3 sec) and a mercury pool electrode connected to the leads of the a.c. bridge described earlier[3]. The potential of the DME was measured against a SCE by means of a vacuum tube voltmeter. The cell was kept at 25° and the solution was de-aerated with tank nitrogen, purified by passage through a vanadous sulfate solution. The cell solution was usually made up of 1 M base electrolyte, 10^{-3} M HCl or $HClO_4$, and $ZnSO_4$ in concentrations varying from 10^{-3} M for measurements in 1 M KI near to the half-wave potential, to $2 \cdot 10^{-2}$ M for measurements at far cathodic and far anodic potentials. In the other base electrolytes, the Zn^{2+} concentrations were $1 \cdot 10^{-2}$ and $2 \cdot 10^{-2}$ M throughout. For all systems, the double-layer capacitance of the DME in the supporting electrolyte was also measured.

In order to correct the d.c. potential scale in the a.c. measurements for the iR drop occurring in the cell at these high concentrations, d.c. polarograms were recorded with a Metrohm three-electrode polarograph. The iR drop never exceeded 10 mV.

RESULTS

As we intended to calculate the faradaic impedance by means of the complex plane analysis of Randles equivalent circuit[3,5,6], it was necessary to check whether the chosen electrode system is in accordance with this circuit. Therefore, the components, Z' and Z'', of the cell impedance were measured at fixed potentials (−0.92, −1.00 and −1.25 V *vs.* SCE) as a function of frequency, together with the value of the ohmic resistance, R_Ω, at a potential outside the faradaic region. From these data we calculated the components, Y_{el}' and Y_{el}'', of the electrode admittance as described earlier[5,7]. The frequency-dependence of Y_{el}' and Y_{el}'' appeared to be consistent with the expressions:

$$Y_{el}' = \frac{\theta + \sigma\omega^{-\frac{1}{2}}}{(\theta + \sigma\omega^{-\frac{1}{2}})^2 + \sigma^2\omega^{-1}} = \frac{1}{\sigma\omega^{-\frac{1}{2}}} \frac{p+1}{p^2+2p+2} \tag{1a}$$

$$Y_{el}'' = \frac{\sigma\omega^{-\frac{1}{2}}}{(\theta + \sigma\omega^{-\frac{1}{2}})^2 + \sigma^2\omega^{-1}} + \omega C_d = \frac{1}{\sigma\omega^{-\frac{1}{2}}} \frac{1}{p^2+2p+2} + \omega C_d \tag{1b}$$

In other words, application of the so-called frequency variation method[3,5,7] yielded frequency-independent and reasonable values for the charge transfer resistance, θ, the Warburg coefficient, σ, and the double-layer capacitance, C_d. Moreover, the latter was equal to the value obtained in the supporting electrolyte, and it is concluded therefore that the electrode system can be described by the Randles circuit with no significant adsorption of Zn^{2+} or Zn at the electrode–solution interface.

This result led us to conclude that the more sensitive concentration variation method could be used for the definite experiments. Therefore, Z' and Z'' were measured as a function of potential for various Zn^{2+} concentrations at a fixed frequency. At each potential, Y_{el}'' was plotted against Y_{el}' with the Zn^{2+} concentration as varying parameter, and from the slope, equal to $1/(p+1)$, the so-called "irreversibility quotient", $p = \theta/\sigma\omega^{-\frac{1}{2}}$, was obtained. This was done for 0.42, 1, 2 and 4 KHz in the case of KI and KCl but only for 1 KHz in the cases of KBr and $NaClO_4$. The

values of $p/\omega^{\frac{1}{2}} = p' = \theta/\sigma$ calculated at the various frequencies were found to be consistent within experimental error. The mean values are plotted against the d.c. potential in Fig. 1. From p and Y_{el}', the values of θ and σ were calculated according to eqn. (1a). The results for a Zn^{2+} concentration of $2 \cdot 10^{-2}$ M are given in Figs. 2 and 3. In the case of the 1 M KI base electrolyte, the values close to the half-wave potential are calculated from measurements at 10^{-3} or $5 \cdot 10^{-3}$ M Zn^{2+} concentrations but multiplied by 1/20 or 5/20, respectively.

For $NaClO_4$, the values of p' and σ near the peak potential are very inaccurate because of the high irreversibility and only the plots at far anodic and cathodic potentials are given. For the sake of clarity, accuracy limits are indicated only at some relevant points.

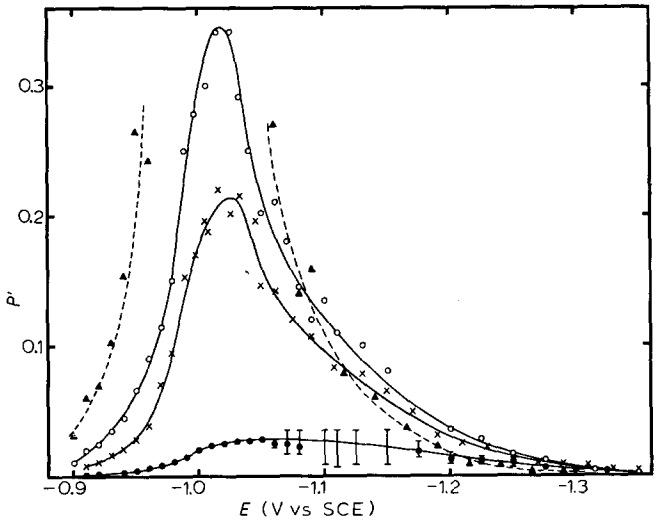

Fig. 1. Potential-dependence of $p' = \theta/\sigma$ for the Zn^{2+}/Zn(Hg) reaction in different 1 M base electrolytes. (●) KI, (×) KBr, (○) KCl, (▲) $NaClO_4$.

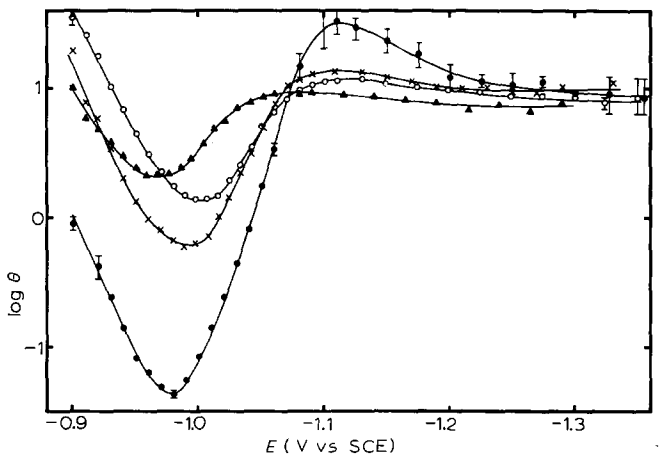

Fig. 2. The transfer resistance as a function of potential for $2 \cdot 10^{-2}$ M Zn^{2+}. (●) KI, (×) KBr, (○) KCl, (▲) $NaClO_4$.

In all cases the measurements were possible over a wide potential range, -0.9 to -1.35 V *vs.* SCE. This is not surprising for KCl and $NaClO_4$ solutions, because k_{sh}-values of approximately $3 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$ cm sec^{-1} (as usually reported for the $Zn^{2+}/Zn(Hg)$ reaction in these solutions[1,2,8]) are sufficiently low to give rise to irreversible behaviour, *i.e.*, the values of σ at far negative potentials are relatively low so that the faradaic admittance is substantially different from zero[9] (*cf.* eqn. (1)).

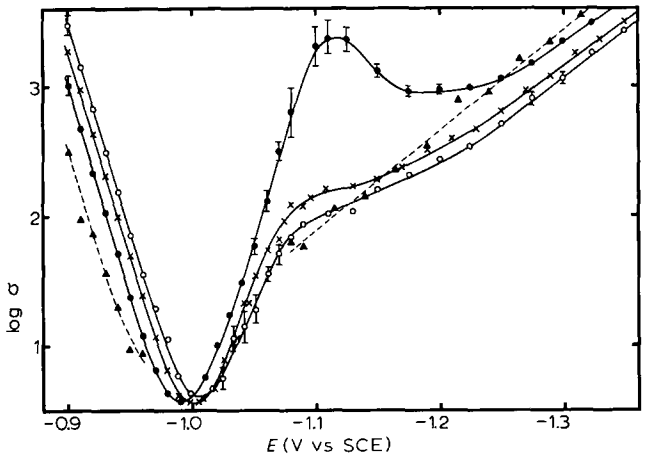

Fig. 3. The Warburg coefficient as a function of potential for $2 \cdot 10^{-2}$ M Zn^{2+}. (●) KI, (×) KBr, (○) KCl, (▲) $NaClO_4$.

Irreversible behaviour is not to be expected if $k_{sh} = ca.$ 10^{-1} cm sec^{-1}, as is relevant to the $Zn^{2+}/Zn(Hg)$ reaction in 1 M KI[1,8]. For example, at -1.25 V, log σ would be equal to about 5, whereas we measured log $\sigma = 3$. The similarity of the values in the far cathodic region for all solutions is a first indication that, at these potentials, k_{sh} is of the same order of magnitude irrespective of the base electrolyte. As the values of θ and p at more positive potentials, near -1.0 V, are markedly dependent on the base electrolyte, this must mean that k_{sh} decreases significantly with decreasing potential in the case of 1 M KI and probably also for 1 M KBr.

ANALYSIS OF FARADAIC IMPEDANCE PARAMETERS

Theoretical expressions for θ, σ and p' in the present case of an irreversible electrode reaction at the DME with potential-dependent apparent rate constant and the Red-component initially absent, can be derived from the general equations, published earlier[4,9], by introduction of $a_O/a_R = (D_O/D_R)^{\frac{1}{2}}$ and $C_R^* = 0$:

$$\theta = \frac{RT}{n^2F^2C_O^*k_{sh}^a} \frac{a_O(D_R/D_O)^{\frac{1}{2}\beta}\exp(\beta j) + \exp(j) + 1}{a_O(\beta - g) + (D_O/D_R)^{\frac{1}{2}\beta}\exp(\alpha j)} \tag{2}$$

$$\sigma = \frac{RT}{n^2F^2\sqrt{2}\,C_O^*D_O^{\frac{1}{2}\alpha}D_R^{\frac{1}{2}\beta}} \frac{a_O(D_R/D_O)^{\frac{1}{2}\beta}\exp(\beta j) + \exp(j) + 1}{a_O(\beta - g) + (D_O/D_R)^{\frac{1}{2}\beta}\exp(\alpha j)} \{\exp(\alpha j) + \exp(-\beta j)\} \tag{3}$$

$$p' = \theta/\sigma = (D_O^{\frac{1}{2}\alpha}D_R^{\frac{1}{2}\beta}\sqrt{2}/k_{sh}^a)\ 1/\{\exp(\alpha j) + \exp(-\beta j)\} \tag{4}$$

with

$$g=(RT/nFk_{sh}{}^{a})(dk_{sh}{}^{a}/dE)=(RT/nF)(d\ln k_{sh}{}^{a}/dE) \quad (5)$$

$$j=(nF/RT)(E-E_{\frac{1}{2}}{}^{r})=(nF/RT)(E-E_0)-\ln(D_R/D_O)^{\frac{1}{2}} \quad (6)$$

$$a_O=D_O{}^{\frac{1}{2}}/(^3/_7\pi t)^{\frac{1}{2}}k_{sh}{}^{a} \quad (7)$$

The introduction of the reversible half-wave potential instead of the standard potential has been made for convenience.

The subject of interest, the apparent rate constant, $k_{sh}{}^{a}$, as a function of E, will most easily be calculated from p' if j and α (or β) are known. The values of the diffusion coefficients may be taken from d.c. polarographic experiments; we will accept the literature values[9], $D_O=\frac{1}{2}D_R=8\cdot10^{-6}$ cm^{2}sec^{-1}. Evidently, an error in these values will cause only a systematic error in $k_{sh}{}^{a}$ without influencing the relative potential-dependence.

i. Determination of $E_{\frac{1}{2}}{}^{r}$

If $k_{sh}{}^{a}$ is sufficiently large, the terms in a_O can be dropped in eqns. (2) and (3), so that the so-called "d.c. reversible equations" for θ and σ result[3,9]:

$$\theta_{rev}=(RT/n^2F^2C_O{}^*k_{sh}{}^{a})(D_R/D_O)^{\frac{1}{2}\beta}\{\exp(\beta j)+\exp(-\alpha j)\} \quad (8)$$

$$\sigma_{rev}=(RT/n^2F^2\sqrt{2}C_O{}^*D_O{}^{\frac{1}{2}})\{\exp(j)+2+\exp(-j)\}=\tfrac{1}{4}\sigma_m\{\exp(j)+2+\exp(-j)\} \quad (9)$$

If, in addition $|j|$ is sufficiently large, *i.e.*, $E-E_{\frac{1}{2}}{}^{r}>(0.08/n)$V, the plot of log σ *vs.* E becomes a straight line with slope, $n/0.059$ V^{-1}.

According to Fig. 3, this case occurs for the KI system in the potential regions, $-0.9<E<-0.95$ and, $-1.04<E<-1.09$. The intersection ordinate of these two linear sections appears to be equal to log $\sigma_m-\log 4$, as eqn. (9) prescribes. Therefore, the abscissa of the intersection point may be set equal to the reversible half-wave potential, yielding $E_{\frac{1}{2}}^{r}=-0.995$ V *vs.* SCE.

For the KCl system, the theoretical $1/0.03$ V^{-1} slope in the log σ-plot is found only in the anodic region, but with the literature value $k_{sh}{}^{a}=ca.\ 5\cdot10^{-3}$ cm sec^{-1} and $t=3$ sec it can be calculated that the difference between eqns. (3) and (9) is negligible down to $E\approx E_{\frac{1}{2}}^{r}$. Consequently, $E_{\frac{1}{2}}^{r}$ will be equal to the potential where the extrapolated ordinate of the anodic straight section is equal to log $\sigma_m-\log 4$. The resulting value is $E_{\frac{1}{2}}^{r}=-1.005$ V *vs.* SCE. The same procedure can be applied to the plot for the KBr system ($k_{sh}=ca.\ 10^{-3}$ cm sec^{-1}) giving $E_{\frac{1}{2}}^{r}=-1.00$ V.

In the case of $NaClO_4$ base electrolyte, no use could be made of σ_m because of its high inaccuracy and the non-validity of eqn. (9). Only between -0.90 and -0.94 V is a straight line in the log σ-plot (Fig. 3) found, parallel to the other plots, about 13 mV positive to the plot for KI. As there is no reason to suppose that the diffusion coefficients of Zn^{2+} in 1 *M* $NaClO_4$ and 1 *M* KI solution differ significantly, it can be deduced that the reversible half-wave potential in $NaClO_4$ is *ca.* 0.98 V *vs.* SCE.

ii. Determination of $(\alpha+g)$

A separate determination of the transfer coefficient, which necessarily involves the examination of θ or p' as a function of potential, is theoretically impossible when k_{sh} is expected to be potential-dependent. Only the "apparent" transfer coefficients, $\alpha^{a}=\alpha+g$ or $\beta^{a}=\beta-g$, can be obtained, in which g itself may also depend

on the potential. A careful estimation at as many potentials as possible is thus required.

A plot of log p' *vs.* E will be most generally applicable, for which can be derived from eqn. (4):

$$\text{at } E-E_{\frac{1}{2}}{}^{r} > \frac{0.08}{n}\,\text{V}: \quad \frac{\mathrm{d}\log p'}{\mathrm{d}E} = -\frac{n}{0.059}(\alpha+g) \tag{10a}$$

$$\text{at } E-E_{\frac{1}{2}}{}^{r} < -\frac{0.08}{n}\,\text{V}: \quad \frac{\mathrm{d}\log p'}{\mathrm{d}E} = \frac{n}{0.059}(\beta-g) \tag{10b}$$

$$\text{Otherwise} \quad \frac{\mathrm{d}\log[p'\{\exp(j)+1\}]}{\mathrm{d}E} = \frac{n}{0.059}(\beta-g) \tag{10c}$$

In the case of d.c. reversible behaviour, as shown by a straight line with slope, $n/0.059\ \text{V}^{-1}$ in the log σ *vs.* E plot (see above), the information may be obtained directly from θ, as

$$\text{at } E-E_{\frac{1}{2}}{}^{r} > \frac{0.08}{n}\,\text{V}: \quad \frac{\mathrm{d}\log\theta_{\text{rev}}}{\mathrm{d}E} = \frac{n}{0.059}(\beta-g) \tag{11a}$$

$$\text{at } E-E_{\frac{1}{2}}{}^{r} < -\frac{0.08}{n}\,\text{V}: \quad \frac{\mathrm{d}\log\theta_{\text{rev}}}{\mathrm{d}E} = -\frac{n}{0.059}(\alpha+g) \tag{11b}$$

$$\text{otherwise,} \quad \frac{\mathrm{d}\log[\theta_{\text{rev}}/\{\exp(j)+1\}]}{\mathrm{d}E} = -\frac{n}{0.059}(\alpha+g) \tag{11c}$$

This procedure is essentially identical with the first one, but it is to be preferred when k_{sh} is rather low (as for the KCl medium) because then the accuracy in θ is much better than in p'. Note that, although in the anodic region the d.c. dependence obeys reversible behaviour, the faradaic impedance itself is still almost completely charge transfer-controlled.

In the far cathodic potential region, eqn. (2) can be simplified, as in the case of constant k_{sh}[9], to

$$\theta_- = \frac{RT}{n^2F^2}\,\frac{(3/7\pi t)^{\frac{1}{2}}}{Co^*Do^{\frac{1}{2}}}\,\frac{1}{\beta-g} = \frac{RT}{nFi_{\text{d}}}\,\frac{1}{\beta-g} \tag{12}$$

where i_{d} is the limiting current density in the d.c. polarogram. Thus, θ is independent of k_{sh} and potential (see Fig. 2), and $(\beta-g)$ can be obtained directly from the combination of the a.c. and d.c. polarographic experiment. In the same potential region we have from eqn. (3)

$$\sigma_- = (RT/n^2F^2\sqrt{2}\,Co^*Do^{\frac{1}{2}\alpha}D_{\text{R}}{}^{\frac{1}{2}\beta})\{k_{\text{sh}}{}^{\text{a}}(3/7\pi t)^{\frac{1}{2}}\exp(-\beta j)/Do^{\frac{1}{2}}(\beta-g)\} \tag{13}$$

and if g is not strongly potential-dependent,

$$\mathrm{d}\log\sigma_-/\mathrm{d}E = -(n/0.059)(\beta-g) \tag{14}$$

The results of the application of these procedures to the experimental data, summarized in Table 1, appear to be satisfactorily consistent in each of the reported potential regions. The inaccuracy is *ca.* 0.03, except at potentials more negative than -1.2 V, where it is *ca.* 0.01. The potential divisions in Table 1 have been chosen so that the change of the transfer coefficient with potential is clearly evident.

TABLE 1

APPARENT TRANSFER COEFFICIENTS AS A FUNCTION OF POTENTIAL

E	$NaClO_4$		KCl		KBr		KI		*Obtained from*
	$\alpha+g$	$\beta-g$	$\alpha+g$	$\beta-g$	$\alpha+g$	$\beta-g$	$\alpha+g$	$\beta-g$	
	0.48		0.42		0.40		0.37		p'
0.90–0.95				0.57		0.65		0.63	θ_{rev}
		0.42		0.45		0.38		0.43	p' (exp j + 1)
0.95–0.98			0.57		0.66		0.60		θ_{rev} (exp j + 1)$^{-1}$
				0.45		0.28		0.12	p' (exp j + 1)
0.99–1.01			0.57		0.66		0.90		θ_{rev} (exp j + 1)$^{-1}$
				0.21		0.22		0.02	p' (exp j + 1)
1.02–1.04					0.82		0.95		θ_{rev} (exp j + 1)$^{-1}$
		0.23		0.23		0.11		0.05	p'
1.05–1.08							0.98		θ_{rev}
1.08–1.15		0.23		0.19		0.12			p'
1.2–1.3		0.23		0.20		0.21		0.13	p'
		0.22		0.22		0.22		0.22	θ_-/i_g
1.3–1.4		0.22		0.22		0.21		0.19	σ_-

The marked potential-dependence of $\alpha+g$ and $\beta-g$ needs further consideration, which will be based on the specific anion adsorption model postulated in our previous paper[1]. In principle, the origin of a substantial value for g may be twofold:

$$g = \frac{RT}{nF}\frac{\mathrm{d}\ln k_{sh}{}^{a}}{\mathrm{d}E} = \frac{RT}{nF}\frac{\mathrm{d}\ln k_{sh}{}^{f}}{\mathrm{d}E} - \alpha\frac{\mathrm{d}\phi_2}{\mathrm{d}E} \tag{15}$$

where $k_{sh}{}^{f}$ is the true formal rate constant[1] and ϕ_2 is the potential of the outer Helmholtz plane. If ln $k_{sh}{}^{f}$ is a linear function of the amount of specifically adsorbed anions, q^1, the first term on the right-hand side of eqn. (15) will be proportional to $\mathrm{d}q^1/\mathrm{d}E$. Consequently, it will be positive and its value will in general decrease in the order KI > KBr > KCl > $NaClO_4$.

In the far cathodic region, the observed values of $\beta-g$ are the same in all base electrolytes. As the specific adsorption of even iodide ions at these potentials is extremely weak[10], this result indicates that here, $g=-\alpha\mathrm{d}\phi_2/\mathrm{d}E$, which can be calculated to be -0.03 from double-layer data for 1 M KI [10], 1 M KBr [11] and 1 M KCl [12] and will most probably be the same for 1 M $NaClO_4$. The most probable value for β is therefore $0.22-0.03=0.19\pm0.01$. For $NaClO_4$ and KCl base electrolytes, $\beta-g=0.22\pm0.02$ is maintained up to *ca.* -1.02 V, fully in accordance with the fact that specific adsorption from these solutions is only minor in that potential region. In the case of KI, and to a lesser extent for KBr, lower values for $\beta-g$ and higher values for $\alpha+g$ are found on going to more positive potentials; this can be interpreted as due to the contribution of $\mathrm{d}(\ln k_{sh}{}^{f})/\mathrm{d}E$ to g, parallel to the increase of $\mathrm{d}q^1/\mathrm{d}E$ [10].

Near the reversible half-wave potential, however, a sudden increase in $\beta-g$ (decrease in $\alpha+g$) is observed in all supporting electrolytes, which continues until a constant value, $\beta-g=0.60\pm0.03$, is reached in the anodic region. Along the lines of our interpretation this would mean that g becomes largely negative, which is improbable and cannot, of course, be explained with our model. Since the same value for $\beta-g$ is found at -0.9 to -0.95 *vs.* SCE in all solutions, the effect of $\mathrm{d}q^1/\mathrm{d}E$ seems to have vanished, though the differences in θ and p' still indicate a marked

dependence of the charge transfer rate on the nature of the base electrolyte. Our results are in agreement with those of HUSH AND BLACKLEDGE[13] who interpreted the anomalous low value of α(their β) at anodic potentials as being indicative of a two-step electrode reaction mechanism with the Zn^{+}-ion as an intermediate.

iii. Rate constant as a function of potential

Concluding that in the cathodic potential region the experimental data seem to come up to our expectations, we calculated $k_{sh}{}^{a}$-values from p' for all base electrolytes at potentials between -1.0 and -1.35 V (see Fig. 1) using eqn. (4) with $\beta=0.19$, $\alpha=1-\beta$, and $E_{\frac{1}{2}}{}^{r}=-0.98$, -1.005, -1.002 and -0.995 V *vs.* SCE, respectively for $NaClO_4$, KCl, KBr and KI solutions. The results (see Fig. 4) show a marked

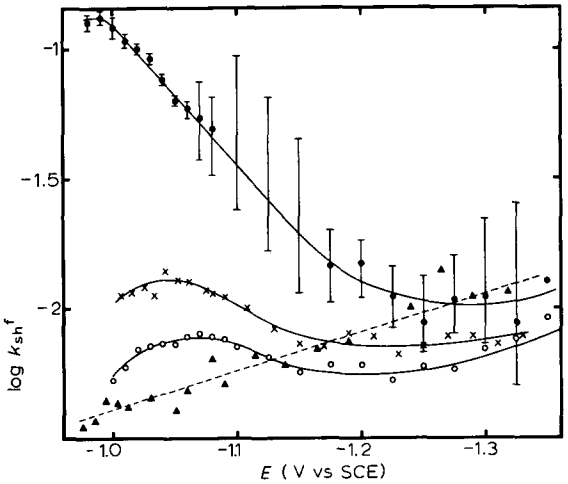

Fig. 4. Apparent standard heterogeneous rate constants as a function of potential, calcd. with $\beta = 0.19$. (●) KI, (×) KBr, (o) KCl, (▲) $NaClO_4$.

TABLE 2

APPARENT RATE CONSTANTS AT THE REVERSIBLE HALF-WAVE POTENTIAL AND IN THE ANODIC AND CATHODIC REGIONS

Base electrolyte	$k_{sh}{}^{a}\cdot 10^{3}$		
	$E > -0.95$ (*V vs. SCE*)	$E = E_{\frac{1}{2}}{}^{r}$	$E = -1.3$ (*V vs. SCE*)
1 *M* $NaClO_4$	5.3	3.6	11
1 *M* KCl	9.6	6.3	6.5
1 *M* KBr	34	11	7.5
1 *M* KI	350	125	10

potential-dependence of the apparent rate constant, and for KI and KBr, the expected significant increase of $k_{sh}{}^{a}$ with E. The $k_{sh}{}^{a}$-values at the reversible half-wave potential, listed in Table 2, are in good agreement with literature data[8]. Table 2 also contains the $k_{sh}{}^{a}$-values calculated from θ or p' at the anodic potentials, taking $\beta=0.6$ (see discussion) and at the far cathodic side, taking $\beta=0.19$.

DISCUSSION

Adequacy of the theory

Our theory of the potential-dependence of the faradaic impedance is based on the diffusion layer theory, which is known not to be exactly representative for the mass transport at a DME. A more rigorous treatment based on the semi-infinite linear diffusion theory, but only for constant k_{sh}, has been given by DELMASTRO AND SMITH[14], especially for the theory of a.c. polarography. The final expression in this work is given in terms of i/i_{rev}, which represents the deviation from reversible behaviour. It is easily derived that the potential-dependence of our σ and θ can be expressed with the aid of the function, $F(\lambda t^{\frac{1}{2}})$:

$$\frac{\sigma_{rev}}{\sigma} = \frac{\theta_{rev}}{\theta} = F(\lambda t^{\frac{1}{2}}) = 1 + \left(\frac{7}{3\pi}\right)^{\frac{1}{2}} \frac{(1.61 + \lambda t^{\frac{1}{2}})}{(1.13 + \lambda t^{\frac{1}{2}})^2} [\beta \exp(-j) - \alpha] \tag{16}$$

where θ_{rev} and σ_{rev} are given by eqns. (8) and (9) and

$$\lambda = (k_{sh}{}^a / D_O{}^{\frac{1}{2}\alpha} D_R{}^{\frac{1}{2}\beta})[\exp(\alpha j) + \exp(-\beta j)] = \sqrt{2}/p' \tag{17}$$

Note that the anodic transfer coefficient is represented by α in our notation, and by β in SMITH's notation. Different expressions are given in ref. 14 for $F(\lambda t^{\frac{1}{2}})$, depending on the type of electrode model. The most rigorous theory leads to a very complicated expression but a good approximation for a DME seems to be the "expanding plane model" which leads to eqn. (16). This can be compared with our treatment after combination of eqn. (2) with (8), or (3) with (9), together with (7) and (17):

$$\sigma_{rev}/\sigma = \theta_{rev}/\theta = 1 + \{(\beta - g)\exp(-j) - (\alpha + g)\}/\{1 + \lambda(3/7\pi t)^{\frac{1}{2}}\} \tag{18}$$

This suggests that β and α appearing in eqn. (16) must be considered as apparent transfer coefficients, in which the potential-dependence of the rate constant is incorporated.

It can be calculated that the difference between eqns. (18) and (16) is always less than 15% and as a rule does not exceed a few percent if $\lambda t^{\frac{1}{2}} > 7$. In our case, with $t = 3$ sec, this means $\lambda > 4$, or $p' < 0.35$. Except for $NaClO_4$, this condition is met for the Zn^{2+}/Zn(Hg) reaction (Fig. 1). Moreover, the potential-dependence of p' is independent of the nature of $F(\lambda t^{\frac{1}{2}})$, so there are no serious objections to the use of the diffusion-layer theory, which has the advantage that the idea of a potential-dependent rate constant is easily introduced into the equations. The only condition for this is negligibility of the effect of higher-order derivatives of k_{sh} to E by the use of low amplitudes[4].

Significancy of the potential-dependency of $k_{sh}{}^a$

The error in log $k_{sh}{}^a$, caused by the inaccuracy in p', is indicated for the KI case in Fig. 4 by the vertical bars. For the other systems, similar limits are relevant in the far cathodic region but as a rule the error is less than in the KI case at the other potentials. For $NaClO_4$ and KCl, p' is very inaccurate at potentials near $E_{\frac{1}{2}}{}^r$ and more reliable values for $k_{sh}{}^a$ were obtained from θ using eqn. (2) in which a_O, being of only minor influence, is estimated according to eqn. (7). In principle, a successive approximation procedure is possible, but this appeared to be superfluous.

Other sources of uncertainty are the choices of $E_{\frac{1}{2}}{}^r$ and α. An error of 10 mV

in $E_{\frac{1}{2}}{}^{r}$—which is certainly not exceeded in our study—would cause a negligible error if $E \approx E_{\frac{1}{2}}$, and a systematical error increasing to 0.06 in $\log k_{sh}{}^{a}$ for $E - E_{\frac{1}{2}}{}^{r} < -40$ mV with $\alpha \approx 0.8$. The inaccuracy of 0.02 in α (see Table 1) causes an error in $\log k_{sh}{}^{a}$, increasing from zero at $E - E_{\frac{1}{2}}{}^{r} = 0$ to 0.14 at $E - E_{\frac{1}{2}} = 350$ mV.

Thus, it can be concluded that the apparent rate constant of the $Zn^{2+}/Zn(Hg)$ reaction, calculated from our experiments as indicated above, is significantly potential-dependent in the cases of 1 *M* KI, 1 *M* KBr and 1 *M* $NaClO_4$ as supporting electrolytes. In the case of 1 *M* KCl it is just on the border of significance, probably as a result of the compensating effect of the attributions of specific adsorption ($k_{sh}{}^{f}$ increases with E) and the Frumkin correction ($d\phi_2/dE$ is positive, see eqn. (15).

Nevertheless, it may be noted that this conclusion is based on an unproved —and improvable—assumption, namely a constant, $\beta = 0.19 \pm 0.02$, in the whole cathodic region. The observations in the anodic region suggest that another interpretation of our experimental facts, namely a constant, $k_{sh}{}^{a}$, and a potential-dependent β, should not be excluded *a priori*. In other words, β could be calculated as a function of E with eqn. (4) in which the measured values of p' are introduced, together with the $k_{sh}{}^{a}$-value (determined at $E = E_{\frac{1}{2}}$) where α and β disappear from the exponentials. However, in the cases of KI and KBr this would lead to improbably low β-values of 0.1, and even 0.0, and it is difficult to explain why this does not occur in the other base electrolytes, where $\beta = 0.22$ would suffice. Moreover, in the very far cathodic region ($E < -1.3$ V *vs.* SCE) one would have $\beta = 0.17$ for KBr and $\beta = 0.10$ for KI, which is definitely inconsistent with the potential-dependence of θ and σ (see Figs. 2 and 3 and Table 1). Also, the maximum in the σ *vs.* E plot for KI can be explained only by a decrease of $k_{sh}{}^{a}$ with decreasing E and so even if β is potential-dependent, a potential-dependent rate constant is very likely for KI and KBr.

Relation between k_{sh} and double-layer structure

The qualitative correlation between $\log k_{sh}{}^{a}$ and the amount of specific adsorption of halide ions is evident after inspection of Fig. 4 in connection with q^1-data[10-12]. For a quantitative comparison it seems most realistic first to apply the Frumkin correction using ϕ_2-data from refs. 10-12 and $\alpha = 0.81$. The resulting "true formal" $\log k_{sh}{}^{f}$-values (see ref. 1) appear to be nearly independent of potential for $NaClO_4$ solution: only a slight gradual increase in $\log k_{sh}{}^{f}$ is observed from -3.66 at $E = E_{\frac{1}{2}}$ to -3.55 at $E = -1.35$ V *vs.* SCE. This is easily ascribed to a small systematic error in the chosen value of β. Thus, in 1 *M* $NaClO_4$ solution anion adsorption is either absent, or has no influence on the rate constant of the zinc reaction. For the three other solutions, $k_{sh}{}^{f}$ is found to be a function of potential. The values obtained, pertaining to various potentials, are plotted against the corresponding q^1-values, in Fig. 5*. It should be noted that the plots for KCl and KBr may have to be shifted upwards somewhat if a correction for complex formation is required[1]. The shift will not exceed 0.2 in $\log k_{sh}{}^{f}$.

The following conclusions may be drawn: (a) if $q^1 = 0$, the rate constant is the same for all base electrolytes within experimental error; (b) the accelerating

* In the original data, the q^1-values for Br^- are positive at far cathodic potentials[11]. On consultation with one of the authors, we shifted the q^1 *vs.* E curve upwards until it coincided with those of Cl^- and I^- at potentials between -1.3 and -1.4 V *vs.* SCE, in order to have a better comparison.

effect of specifically adsorbed chloride and bromide ions seems to be larger than that of iodide ions; (c) the accelerating effects of adsorbed iodide ions at negative potentials (up to *ca.* −1.1 V) is larger than at more positive potentials (−1.1 to −1.0 V *vs.* SCE). This may be interpreted as a decrease in effectiveness when q^1 is large (a kind of saturation effect) but, in our opinion, it is more probable that the anomalous behaviour at anodic potentials (*vide infra*) is already incipiently present at moderately cathodic potentials. In KCl, KBr and KI this seems to cause $k_{sh}{}^a$ to attain a limiting value near $E=E_{\frac{1}{2}}$. Note that the decrease in $k_{sh}{}^a$ at $E>E_{\frac{1}{2}}$, indicated in Fig. 4,

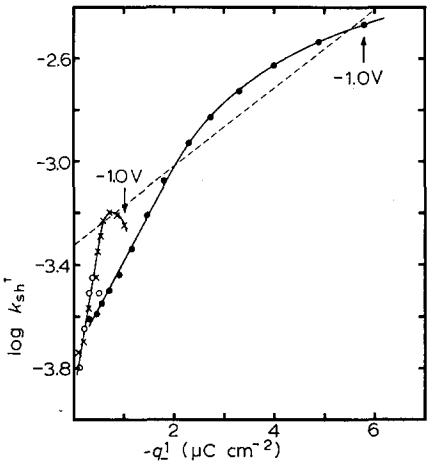

Fig. 5. ,,True" rate constants, plotted against the amount of specially adsorbed anions. (—) From the present work, with potential as varied parameter; (---), from ref. 1, at constant potential (−1.0 V *vs.* SCE) in (1 − *x*) *M* KCl + *x* *M* KI soln. (●) KI, (×) KBr, (○) KCl.

will be eliminated by choosing a higher value for β, which would be in accordance with the experimental facts. It is of interest in this connection that the smaller slope in the KI-curve in Fig. 5 closely resembles that of the straight line we obtained in our previous work[1] for log $k_{sh}{}^f$ *vs.* q^1 measured at the standard potential (*ca.* −1.0 V *vs.* SCE) in mixtures of (1 − *x*) MKCl + *x* MKI (dashed line in Fig. 5).

The kinetic parameters of the Zn^{2+}/Zn(Hg) reaction

The kinetic aspects of the zinc reaction although frequently considered as a classical subject have not to our knowledge been studied before in such a wide potential range as presented in this work. As in most relaxation methods, no d.c. polarisation is applied, the potential range covered by variation of the Ox/Red ratio is very small and close to E_0. Also, analysis of the d.c. current–voltage curve yields, as a rule, kinetic parameters pertaining to the half-wave potential. It may be clear that the physical meaning of such results should be considered preferably within the scope of a larger potential range if there is reason to suspect complications in the reaction mechanism. For example, the frequently reported value, $\beta^a=0.3$, pertains to a potential region where the gradual increase from 0.2 (for KI, even from 0.0) at the cathodic side, to 0.6 at the anodic side starts.

An apparent rate constant of 0.0 for the zinc reaction in 1 *M* KI at moderately cathodic potentials was also observed by BLACKLEDGE AND HUSH[2]. They interpreted

this as being indicative of a chemical reaction in the double layer, preceding charge transfer. However, our interpretation based on the idea of a potential-dependent rate constant seems more reasonable, since there is little doubt that β is different from zero at more cathodic potentials. It was mentioned earlier[1] that more of these authors' results could be interpreted with the specific anion adsorption model.

Our experiments in the anodic range confirm the anomalous transfer coefficient found already though less convincingly, by HUSH AND BLACKLEDGE[13]. In principle an "apparent" transfer coefficient is also concerned here, but in view of the common value found in all base solutions, we believe that we determined a "true" transfer coefficient (only the Frumkin correction might introduce $g \approx -0.03$) and that the mechanism of the electrode reaction is indeed different at anodic and cathodic potentials. As HUSH AND BLACKLEDGE suggest, there may be a two-step reaction mechanism. Another possibility is the interference of a chemical reaction preceding the oxidation and following the reduction, *i.e.*, coupled to the Red component. This reaction could be the formation and dissociation of Zn_2 molecules in the amalgam, the occurrence of which has recently been reported[15]. In both cases, however, the question remains, why does the effect of the base electrolyte on the rate constant still exist (see Table 2), whereas the potential-dependence of this effect is absent ($g=0$), or at least equal in all base electrolytes. If $g=0$, the apparent rate constants in the anodic region can be calculated from θ with eqn. (8) or from p' with eqn. (4). The results, listed in Table 2, are substantially higher than the $k_{sh}{}^{a}$-values obtained at the half-wave potential.

In conclusion, the impedance of the $Zn^{2+}/Zn(Hg)$ reaction in different media is consistent with the assumption that specific adsorption of anions accelerates the electrode reaction. However, the experiments in the anodic potential region reveal a complication in the reaction mechanism which cannot be clarified at present. It will be of interest to investigate this further and also to study the effect of specific adsorption on a system that is not complicated by a potential-dependent transfer coefficient.

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SUMMARY

The impedance of the $Zn^{2+}/Zn(Hg)$ electrode in 1 *M* KI, KBr, KCl and $NaClO_4$ solutions has been measured as a function of potential, using an externally polarised dropping mercury electrode. The potential-dependence of the faradaic impedance has been carefully analysed. It is shown that, in general, both the apparent rate constant and the apparent transfer coefficient are potential-dependent. In the cathodic potential region (-1.05 to -1.35 V *vs.* SCE) the results are in accordance

with a constant value, $\beta = 0.19 \pm 0.02$ for the "true" cathodic transfer coefficient and a potential-dependent rate constant which increases if the amount of specifically adsorbed anions increases. In the anodic potential region (-0.90 to -0.95 V *vs.* SCE) a significantly different transfer coefficient is found, $\beta = 0.60 \pm 0.03$, which indicates that the mechanism of the electrode reaction depends on the d.c. potential. It is suggested that the interpretation of kinetic parameters and the testing of simple theories with such systems should be approached with caution.

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