

## ON THE IMPEDANCE OF GALVANIC CELLS

### XIX. THE POTENTIAL DEPENDENCE OF THE FARADAIC IMPEDANCE IN THE CASE OF AN IRREVERSIBLE ELECTRODE REACTION; EXPERIMENTAL VERIFICATION FOR THE REDOX COUPLE $\text{Eu}^{3+}/\text{Eu}^{2+}$ IN 1 *M* $\text{NaClO}_4$ AND THE MECHANISM OF THE $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$ REACTION IN KCl

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#### INTRODUCTION

In a previous paper<sup>1</sup>, a theoretical treatment for the potential dependence of the faradaic impedance in the case that the electrode reaction behaves irreversibly with respect to d.c. current (irreversible electrode reaction) was presented. The system,  $\text{Eu}^{3+}/\text{Eu}^{2+}$  in 1 *M*  $\text{NaClO}_4$ , has been chosen to verify this theory. The rate constant of this redox couple is known to be  $k_{\text{sh}} \approx 10^{-4}$  cm sec<sup>-1</sup>, so that it is suitable as an example of an irreversible system. Moreover, since both  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  exist in the solution, there is no need of amalgams. From the theoretical expressions<sup>1</sup> it is predicted that two peaks occur in an a.c. polarogram if  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  are present at sufficiently large concentrations; this will be verified in this paper. Only one electron is involved in the reaction and therefore it is unlikely that an intermediate exists that could also give rise to more peaks<sup>3</sup> (see, however, ref. 4 and comments on this reference by GIERST AND CORNELISSEN<sup>2</sup>).

For the  $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$  reaction in 1 *M* KCl also, more peaks were observed in the a.c. polarogram<sup>5,6</sup>. This was explained by assuming that the reaction proceeds *via* univalent zinc. This assumption will be reconsidered in the light of the new theoretical expressions<sup>1</sup> and of additional experimental data described in this paper.

#### EXPERIMENTAL

##### *Europium*

Solutions of 20 mM  $\text{Eu}^{3+}$  in 1 *M*  $\text{NaClO}_4$  (pH 3) were prepared by dissolving  $\text{Eu}_2\text{O}_3$  (Fluka, "puriss") in a small excess of  $\text{HClO}_4$  and adding the appropriate amount of  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (Fluka, p.a.).  $\text{Eu}^{2+}$  was generated in the measuring cell by electrolysis, using a mercury pool at the bottom of the cell as a cathode, and another mercury pool in 1 *M* KCl (connected to the cell *via* a  $\text{NaNO}_3$ -agar salt bridge) as anode. The concentrations of  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  were determined polarographically.

The experiments were performed at 25°, using a dropping mercury electrode

(D.M.E.); the drop was knocked off mechanically every 4.6 sec. The solutions were de-aerated with tank nitrogen.

The a.c. polarograms were obtained by the complex plane method<sup>7</sup>; which means that the real and imaginary components,  $Z'$  and  $Z''$ , of the cell impedance are measured as a function of d.c. potential. The impedance measurements were performed with the a.c. bridge described previously<sup>7</sup>. The potential of the D.M.E. was measured against a S.C.E. by means of a potentiometer with high input resistance. The ohmic resistance,  $R_{\Omega}$ , of the cell was found either by extrapolation of  $Z'$  to infinite frequency or from the value of  $Z'$  at d.c. potentials where the faradaic impedance is infinite.

### Zinc

The  $Zn^{2+}/Zn(Hg)$  couple was studied at a Heyrovsky-type streaming mercury or zinc amalgam electrode (S.M.E.) in a solution of  $Zn^{2+}$  in 1 *M* KCl (pH 3). In this case, cell admittances were measured as a function of d.c. potential (as described previously<sup>8</sup>) instead of cell impedances, because in an impedance circuit the charging current causes a d.c. potential shift<sup>8,9</sup> which disturbs the measurements. The ohmic resistance was found by extrapolation of the cell admittance to infinite frequency.

## RESULTS AND DISCUSSION

### Europium

D.c. polarograms were recorded for different ratios  $Eu^{3+}/Eu^{2+}$  with a total concentration of 20 mM in 1 *M* NaClO<sub>4</sub> (pH 3). By plotting the diffusion limiting currents,  $i_{1a}$ , against  $i_{1c}$  for different ratios, a straight line is obtained (Fig. 1), from which the diffusion constants for  $Eu^{3+}$  and  $Eu^{2+}$  can be calculated using the Ilkovic

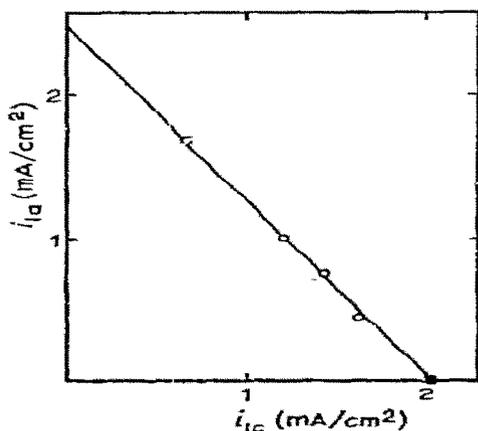


Fig. 1. Plot of the anodic limiting current,  $i_{1a}$ , vs. the cathodic limiting current,  $i_{1c}$ , for different ratios  $Eu^{3+}/Eu^{2+}$  at a total concn. of 20 mM. Drop time, 4.6 sec.

equation, *i.e.*,  $D_{Eu^{3+}} = 7.0 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$  and  $D_{Eu^{2+}} = 10.0 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ . A plot of  $\log i / [(1 - i/i_{1c}) - (1 + i/i_{1a}) \exp(F\eta/RT)]$  against  $\eta = E - E_{eq}$  (ref. 10; p. 171) calculated from a d.c. polarogram, yields  $\log i_0$  and  $\beta = 1 - \alpha$  ( $i$  is the current at the end of drop-life,  $i_0$  the exchange current density and  $\alpha$  the transfer coefficient).

The results are summarized in Table I.

The average value of  $\beta$  is  $0.57 \pm 0.04$ . It is possible to calculate the rate constant,  $k_{sh}$ , from the log  $i_0$ -values. However, this is not very accurate, due to the uncertainty in  $\beta$ . Better results are obtained by plotting  $\log i_0/C_{Eu^{3+}}$  against  $\log C_{Eu^{2+}}/C_{Eu^{3+}}$  (ref. 10; p. 167) yielding  $\beta = 0.60 \pm 0.05$  and  $k_{sh} = (2.5 \pm 0.5) \cdot 10^{-4}$  cm sec<sup>-1</sup>. It is also possible to make such a plot from  $i_0$ -values calculated from the measured impedances at the equilibrium potential<sup>7,11</sup> for different ratios of  $Eu^{3+}$  and  $Eu^{2+}$ . This plot yields

TABLE 1

VALUES OF  $\beta$  AND LOG  $i_0$ , OBTAINED FROM D.C. POLAROGRAMS

Concn. $Eu^{2+}$ (mM)	Concn. $Eu^{3+}$ (mM)	$\beta$	$\log i_0$
5.1	14.9	0.53	-3.70
10.1	9.9	0.60	-3.65
11.2	8.8	0.56	-3.62
13.5	6.5	0.61	-3.56

$\beta = 0.59$  and  $k_{sh} = (2.9 \pm 0.2) \cdot 10^{-4}$  cm sec<sup>-1</sup>, in good agreement with the result from the d.c. polarograms. These  $\beta$ - and  $k_{sh}$ -values are apparent values, as no double-layer correction has been made. The standard potential,  $E_0 = -605 \pm 5$  mV (SCE), was determined from the equilibrium potentials at different ratios  $Eu^{3+}/Eu^{2+}$ .

GIERST AND CORNELISSEN<sup>2</sup> have studied the  $Eu^{3+}/Eu^{2+}$  reaction in various concentrations of  $NaClO_4$  and reported  $D_{Eu^{3+}} = 7.1 \times 10^{-6}$  cm<sup>2</sup> sec<sup>-1</sup>,  $D_{Eu^{2+}} = 8.3 \times 10^{-6}$  cm<sup>2</sup> sec<sup>-1</sup> and  $E_0 = -600$  mV (SCE). From their Tafel plot for 1 M  $NaClO_4$ , it can be calculated that  $\alpha = 0.49$ ,  $\beta = 0.56$  and  $k_{sh} = 1.5 \times 10^{-4}$  cm sec<sup>-1</sup>. All these values are in reasonable or good agreement with the values reported in this paper.

The impedance measurements were analysed according to the complex plane method by calculating the quantity  $1/q = Y_{F'}$  (real component of the faradaic admittance) as a function of the electrode potential,  $q$  being defined by<sup>1,7</sup>

$$q = \theta + \sigma\omega^{-\frac{1}{2}} + \frac{\sigma^2\omega^{-1}}{\theta + \sigma\omega^{-\frac{1}{2}}} \quad (1)$$

in which  $\theta$  is the activation polarization resistance and  $\sigma$  the Warburg coefficient. It has been pointed out that a plot of  $1/q$  against  $E$  is essentially an ideal *real component a.c. polarogram*<sup>1</sup>.

These plots are given in Fig. 2 for different concentrations of  $Eu^{3+}$  and  $Eu^{2+}$ . It can be seen that even an irreversible electrode reaction as that for europium yields substantial peaks in such a polarogram, as was predicted theoretically<sup>1</sup>. From Fig. 3 it follows that the anodic peak height depends linearly on the  $Eu^{2+}$  concentration and the cathodic peak height on the  $Eu^{3+}$  concentration, as both  $\theta$  and  $\sigma$  should be inversely proportional to concentration<sup>7</sup>.

For 20 mM  $Eu^{3+}$ ,  $\theta$  and  $\sigma$  were evaluated from the frequency-dependence of  $1/q$ <sup>1,7</sup> determined at frequencies between 320 and 2000 Hz. The results are represented in Fig. 4a.

Another method of obtaining  $\theta$  and  $\sigma$  is by the *method of concentration variation*<sup>1,7</sup>, which is carried out in the following way. After subtraction of  $R_{\Omega}$  from  $Z'$ , the remainder is combined with  $Z''$  to calculate  $Y_{el'}$ , and  $Y_{el''}$ , the real and imaginary compo-

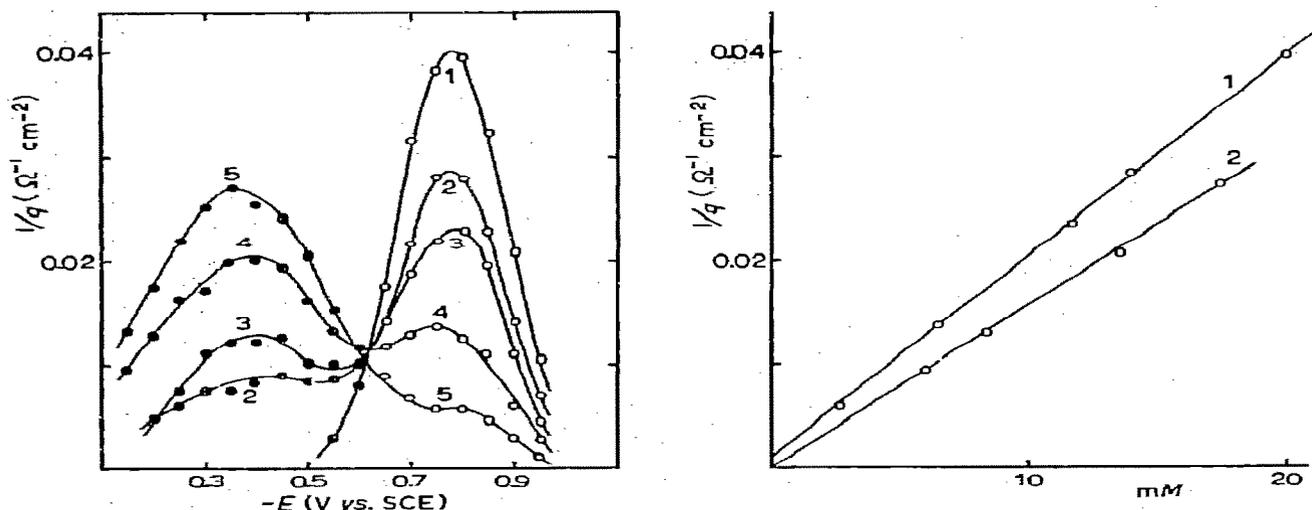


Fig. 2. The real component of the faradaic admittance ( $1/q$ ) as a function of potential at 480 Hz (D.M.E.). (●), potentials anodic to  $E_0$ ; (○), cathodic potentials. Concs.: (1), 20 mM  $\text{Eu}^{3+}$ ; (2), 14 mM  $\text{Eu}^{3+}$  + 6 mM  $\text{Eu}^{2+}$ ; (3), 11.7 mM  $\text{Eu}^{3+}$  + 8.3 mM  $\text{Eu}^{2+}$ ; (4), 6.5 mM  $\text{Eu}^{3+}$  + 13.5 mM  $\text{Eu}^{2+}$ ; (5), 2.6 mM  $\text{Eu}^{3+}$  + 17.4 mM  $\text{Eu}^{2+}$ .

Fig. 3. Calibration lines: (1),  $\text{Eu}^{3+}$ ; (2),  $\text{Eu}^{2+}$ .

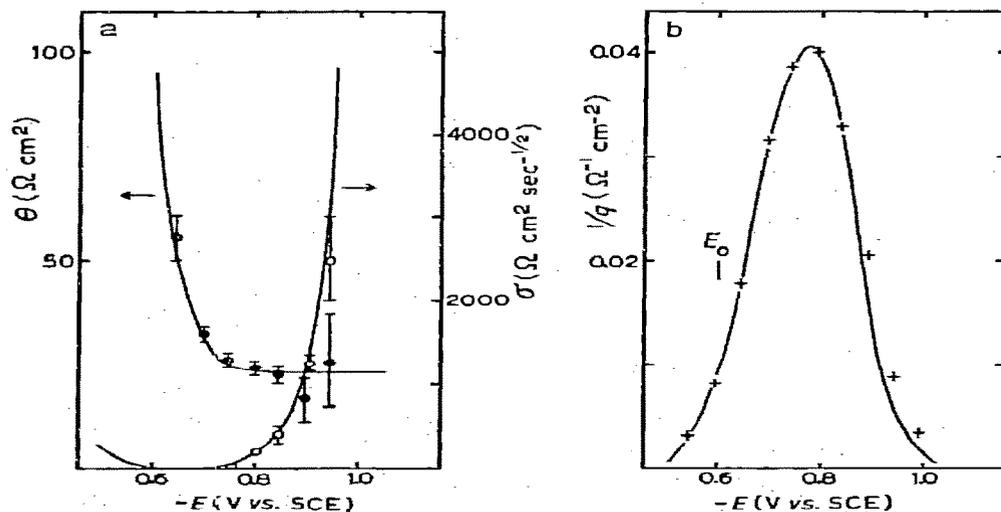


Fig. 4. (a). The activation polarization resistance  $\theta$  (●) and the Warburg coefficient  $\sigma$  (○) as a function of potential for 20 mM  $\text{Eu}^{3+}$  obtained with the frequency variation method (D.M.E.). Theoretical curves (full lines) are calcd. from eqn. 4.

(b) Plot of  $1/q$  vs. potential (+) for 20 mM  $\text{Eu}^{3+}$  at 480 Hz. Theoretical curve (full line) is calcd. from (1) and (4).

nents of the admittance of the electrode-solution interface (electrode admittance):

$$Y_{el}' = \frac{Z' - R_\Omega}{(Z' - R_\Omega)^2 + (Z'')^2} \quad (2)$$

$$Y_{el}'' = \frac{Z''}{(Z' - R_\Omega)^2 + (Z'')^2} \quad (3)$$

(note that  $Y_{ei}' = 1/q$ ). If  $p = \theta/\sigma\omega^{-1/2}$  and  $C_d$  is the double-layer capacity,  $Y_{ei}'' = \omega C_d + Y_{ei}'/(p + 1)$  holds; if at a certain potential, therefore,  $Y_{ei}'$  and  $Y_{ei}''$  are varied, a plot of  $Y_{ei}''$  against  $Y_{ei}'$  will be a straight line if  $C_d$  remains constant. Normally, the variation of  $Y_{ei}'$  and  $Y_{ei}''$  is effected by varying the total concentration of the electroactive species. In the case of an irreversible reaction, the procedure is also possible for sufficiently anodic or cathodic potentials, by varying the Ox/Red ratio, keeping the total concentration constant. The latter procedure has been followed in our case and indeed straight lines were obtained at different potentials. The  $p$ -values obtained in this way were in accordance with those of the frequency variation and were used to calculate  $\theta$  and  $\sigma$  from the  $1/q$ -curve in Fig. 1 for 6.5 mM  $\text{Eu}^{3+}$  and 13.5 mM  $\text{Eu}^{2+}$  (Fig. 5a).

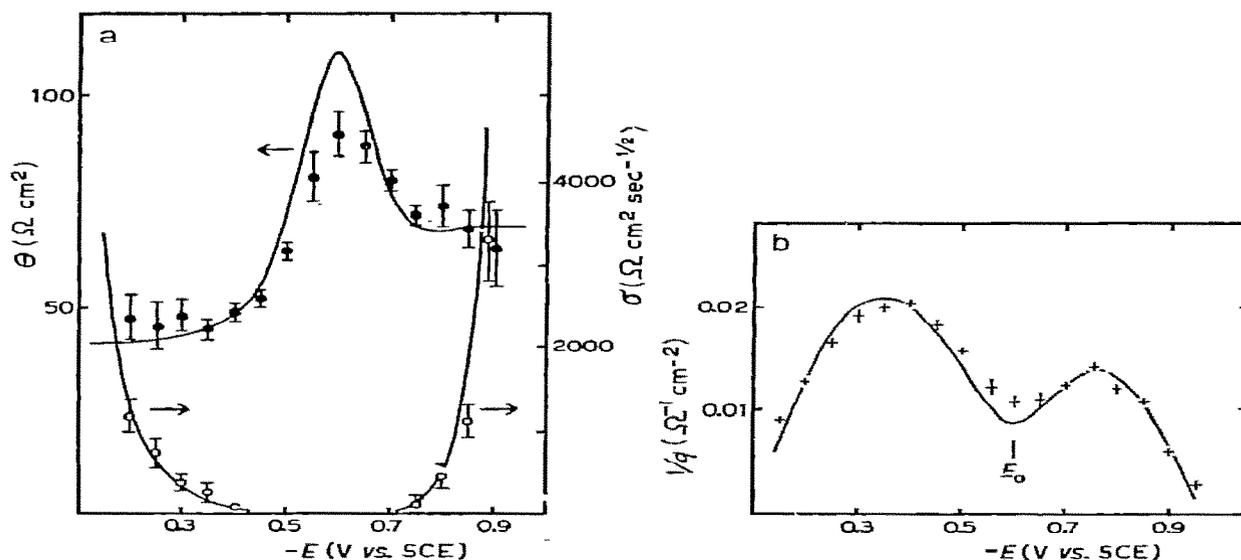


Fig. 5 (a). The activation polarization resistance  $\theta$  (●) and the Warburg coefficient  $\sigma$  (○) as a function of potential for 6.5 mM  $\text{Eu}^{3+}$  + 13.5 mM  $\text{Eu}^{2+}$  obtained with the concn. variation method (D.M.E.). Theoretical curves (full lines) are calcd. from eqn. 4.

(b) Plot of  $1/q$  vs. potential (+) for 6.5 mM  $\text{Eu}^{3+}$  + 13.5 mM  $\text{Eu}^{2+}$  at 480 Hz. Theoretical curve (full line) is calcd. from (1) and (4).

In Figs. 4 and 5, theoretical curves also have been drawn for comparison with the experimental results. The curves were calculated from the theoretical expressions<sup>1</sup> for  $\theta$  and  $\sigma$ :

$$\theta = \frac{RT}{n^2 F^2 k_{sh}} \cdot \frac{a_o + (a_o/a_R) \exp(\alpha\varphi) + \exp(-\beta\varphi)}{a_o \exp(-\beta\varphi) [\beta + (1/a_R) \exp(\alpha\varphi)] C_o^* + \exp(\alpha\varphi) [\alpha a_o + \exp(-\beta\varphi)] C_R^*} \quad (4a)$$

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \{ D_R^{-1/2} \exp(\alpha\varphi) + D_O^{-1/2} \exp(-\beta\varphi) \} \cdot \frac{a_o + (a_o/a_R) \exp(\alpha\varphi) + \exp(-\beta\varphi)}{a_o \exp(-\beta\varphi) [\beta + (1/a_R) \exp(\alpha\varphi)] C_o^* + \exp(\alpha\varphi) [\alpha a_o + \exp(-\beta\varphi)] C_R^*} \quad (4b)$$

in which  $\alpha = D/\delta k_{sh}$  where  $\delta$  is the thickness of the diffusion layer ( $\delta = \sqrt{3/7\pi D t}$  for a D.M.E.) and  $\varphi = nF/RT (E - E_0)$ . The necessary data for the calculation of the a.c.

curves were obtained from the d.c. measurements. The following values have been used:  $E_0 = -605$  mV (S.C.E.),  $\alpha = 0.4$ ,  $k_{sh} = 2.5 \times 10^{-4}$  cm sec $^{-1}$ ,  $D_0 = 7.0 \times 10^{-6}$  cm $^2$  sec $^{-1}$ ,  $D_R = 10.0 \times 10^{-6}$  cm $^2$  sec $^{-1}$ ,  $\nu/\omega = 54.9$  sec $^{-1}$  (480 Hz),  $a_0 = 3.9$  and  $a_R = 4.7$ .

The agreement between the experimental and theoretical results is very good for 20 mM Eu $^{3+}$  (Fig. 4). This is somewhat beyond expectation, in view of the fact that some data (especially  $\alpha$ ) used in the calculations are not accurately known. The curves in Fig. 5 for 6.5 mM Eu $^{3+}$  and 13.5 mM Eu $^{2+}$  do not agree well for potentials in the vicinity of  $E_0$ , but the agreement is still reasonable. At these potentials the theoretical curves are sensitive for errors in the  $k_{sh}$ -value inserted. If  $k_{sh} = 2.9 \times 10^{-4}$  cm sec $^{-1}$  is inserted, as was calculated from the a.c. measurements, a better fit of the theoretical and experimental curves is obtained. At potentials more remote from  $E_0$ ,  $\theta$  and  $\sigma$  are not very sensitive to the  $k_{sh}$ -value (cf. eqn. (20) and (22) of ref. 1) so that the calculated curves of Fig. 4 do not change at all, or only slightly, if the  $k_{sh}$ -value is varied.

Figure 3 shows that the  $i/q(\text{peak})$  against concentration plot passes through the origin for Eu $^{2+}$ , whereas the plot for Eu $^{3+}$  has a (small) positive intercept. This is explained by the fact that at the cathodic peak potential ( $-775$  mV) the contribution of  $C_R^*$  ( $=20$  mM if  $C_0^* = 0$ ) in the denominator of the expressions for  $\theta$  and  $\sigma$  (4) is not negligible, as can be calculated theoretically using the data given above. The experimental intercept is of the same magnitude as the theoretical one. At the anodic peak potential ( $-350$  mV), the contribution of the term in  $C_0^*$  is too small to be detected.

Summarizing, it can be concluded that the experimental results for the faradaic impedance of the Eu $^{3+}$ /Eu $^{2+}$  system are in good accordance with the theory for the potential dependence of the faradaic impedance in the case of irreversible electrode reactions $^1$ .

### Zinc

Recently $^6$  we communicated on the mechanism of the Zn $^{2+}$ /Zn(Hg) reaction. The occurrence of more than one peak in the  $i/q$ -plot was thought to prove that the reaction proceeds *via* univalent zinc. Theoretical calculations were made to show that for a one-step electrode reaction only one peak could occur. However, the theoretical expressions used were incorrect and a better treatment $^1$  shows that two peaks can occur.

The theoretical a.c. polarograms ( $i/q$ -plots) in ref. 1 (Figs. 1 and 2) have been calculated with parameters that are known to pertain to the Zn $^{2+}$ /Zn(Hg) reaction ( $\alpha$ ,  $D_0$ ,  $D_R$ ) at a D.M.E. ( $\delta_0$  and  $\delta_R$ ). The experimental  $i/q$ -plots for a D.M.E. with varying concentration of surfactant BRY 35 (Figs. 8 and 9 of ref. 6) agree qualitatively with the theoretical curves calculated for different  $k_{sh}$ -values. The experimental cathodic (Zn $^{2+}$ ) wave has the same height and shape as the corresponding theoretical one. The experimental anodic (zinc amalgam) wave is considerably lower than theory predicts. This could be caused by the fact that  $\delta_R \sim 2 \cdot 10^{-2}$  cm is too large with respect to the radius of the droplet,  $r \sim 5 \cdot 10^{-2}$  cm, so that the assumption of linear diffusion no longer holds. The *shoulder* in the anodic range at  $-0.45$  V (S.C.E.) (peak Ia in Fig. 8 of ref. 6) is not in accordance with the theory $^1$  presented. Probably, the potential dependence of the adsorption of the surfactant and therefore of the rate constant  $k_{sh}$ , has to be taken into account $^{12}$ .

Since this complication does not occur if the reaction is made more *irreversible* by using a S.M.E., a comparison of experiment and theory in this case seems worthwhile. For this purpose we measured the admittances of a streaming 3-mM zinc amalgam electrode in a 1 M KCl (pH 3) solution of 3 mM  $Zn^{2+}$  at different potentials for frequencies between 320 and 2500 Hz. From these measurements,  $\theta$  and  $\sigma$  were calculated as for europium (Fig. 6). The solution was adjusted to pH 3 because the small peak at -1330 mV (S.C.E.)<sup>5</sup>, earlier ascribed to the  $Zn(OH)_2/Zn$  reaction<sup>13</sup>, does not then appear.

For the calculation of the theoretical  $\theta$ - and  $\sigma$ -curves in Fig. 6, we inserted in (4) the following data<sup>7,14</sup> which are relevant to the zinc couple at a S.M.E.:

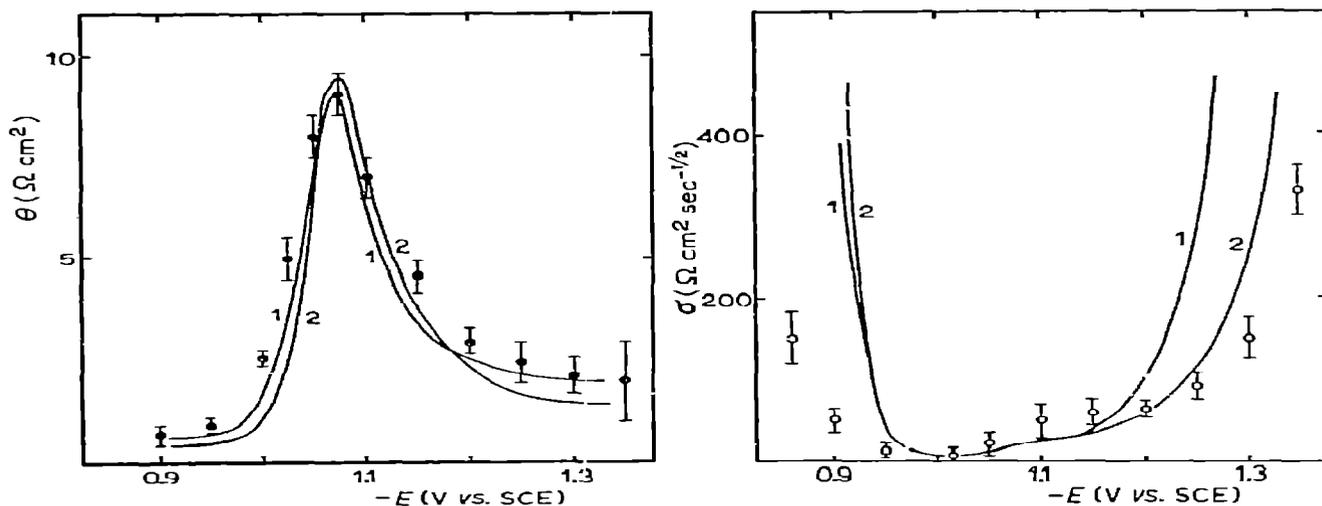


Fig. 6. The activation polarization resistance  $\theta$  (●) and the Warburg coefficient  $\sigma$  (○) as a function of potential for 3 mM  $Zn(Hg)$  + 3 mM  $Zn^{2+}$  in 1 M KCl (pH 3) obtained with the frequency variation method (S.M.E.). Theoretical curves (full lines) are calcd. from eqn. 4; (1),  $\alpha = 0.70$ ; (2),  $\alpha = 0.75$ . For other data see text.

$D_{Zn} = 2 D_{Zn^{2+}} = 1.6 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ ,  $n=2$ ,  $E_0 = -1025 \text{ mV (S.C.E.)}$  and for curve 1  $\alpha = 0.7$ ,  $a_0/a_R = 0.8$ ,  $a_0 = 10$ ,  $k_{sh} = 3.8 \times 10^{-3} \text{ cm sec}^{-1}$  and for curve 2,  $\alpha = 0.75$ ,  $a_0 = a_R = 15$ ,  $k_{sh} = 4.2 \times 10^{-3} \text{ cm sec}^{-1}$ †. The main difference between the two curves is caused by  $\alpha$ ; the other data are chosen to obtain the best fit with the experimental results. It should be noted that, strictly speaking, (4) may not be used for a S.M.E.<sup>5</sup>, but in this case the more rigorous expression<sup>5</sup> reduces to (4) since the frequencies used are sufficiently high<sup>8</sup>. The agreement between experimental and theoretical results is reasonable, considering that the d.c. potential is not corrected for the ohmic drop in the solution ( $R \sim 30 \Omega$  and the direct current of the order of milliamperes).

The same data have been used to calculate theoretical  $1/q$ -plots for the S.M.E.; these can be compared with the experimental plots already published<sup>6</sup>. Again, the agreement is good and even the *shoulder* in the  $1/q$ -plot for  $C_{Zn^*} = 0$  appears in the theoretical curve; this shoulder does not prove, therefore, that two electrode reactions are taking place.

We also measured admittances of a S.M.E. in 0.1 M and 1 M KCl solutions

† Theoretically  $\delta = \frac{1}{2} \sqrt{\pi D t}$  for a S.M.E., if  $t$  is the contact time, as can be derived from the limiting current expression for a S.M.E.

(pH 3) with varying concentration of BRY 35 up to 1 g/l. The  $i/q$ -plots obtained from these measurements have, qualitatively, the same form as the curves for a D.M.E. in the presence of BRY 35<sup>6</sup>. They are not represented here, as it is difficult to interpret them quantitatively. The unknown potential dependence of  $k_{sh}$  has to be taken into account<sup>12</sup>; moreover, the concentration profiles of the electroactive species and BRY 35 at a S.M.E. are not known exactly<sup>5</sup> and it would be difficult to obtain for this case even simplified expressions for the faradaic impedance.

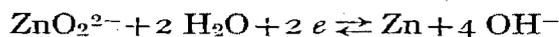
It may be concluded that the a.c. measurements at the D.M.E. and the S.M.E. for the zinc redox couple in 1 M KCl give no definite evidence of an intermediate  $Zn^+$  as was thought in a previous paper<sup>6</sup>.

Some investigators<sup>7,13</sup> have reported the occurrence of a small second peak in the a.c. polarograms of zinc in 1 M KCl at a D.M.E. In *normal a.c. polarograms* this peak was found to disappear on lowering the pH or de-aerating the solution<sup>13</sup> and therefore it was ascribed to the formation of  $Zn(OH)_2$  on the electrode surface due to  $OH^-$  arising from the reduction of  $O_2$ . According to our experience the second peak becomes smaller in acidic solutions, but does not disappear (*cf.* dashed curve in Fig. 9 of ref. 6). This is fully in accordance with the theoretical polarogram, given in ref. 1 (curve 1 in Fig. 1) and it must therefore be concluded that the second peak found for acid solutions is due to the  $Zn^{2+}/Zn(Hg)$  reaction as is the first peak. The enhancement in neutral solution may be explained in two ways: either by the assumption that  $Zn(OH)_2$  is formed, or by the assumption that  $k_{sh}$  decreases slightly resulting in a lowering of the first peak and an increase in the second.

#### *Existence of univalent zinc*

The mechanism of the  $Zn^{2+}/Zn(Hg)$  reaction has been the subject of many investigations and the existence of the  $Zn^+$  ion as an intermediate is postulated in a number of publications. We comment below on these papers in the light of our own findings.

DIRKSE<sup>15</sup> concluded that the electrode reaction of zinc in KOH solutions proceeds *via*  $Zn^+$ , erroneously supposing that the reaction is reversible, as he noticed in a later paper<sup>16</sup>. His experimental data can be explained fully by the assumption that the irreversible electrode reaction



proceeds with  $\alpha = 0.48$ .

HUSH AND BLACKLEDGE<sup>14</sup> measured  $k_{sh}$  and  $\alpha$  of the zinc couple in  $NaClO_4$  solutions of different ionic strength. They concluded from the concentration dependence of  $k_{sh}$  and  $\alpha$  that there is some evidence for the consecutive-step mechanism. However, it should be noted that the corrections for the double-layer structure (*Frumkin theory*, ref. 10, chap. 7) in the case of a single charge-transfer step should be made in the calculation of  $k_{sh}$  and  $\alpha$  before drawing conclusions from a concentration dependence.

The Frumkin correction for  $k_{sh}$  can be made according to<sup>10</sup>

$$(k_{sh})_{app} = (k_{sh})_t \exp(\beta n - Z_O) F\varphi_2/RT \quad (5)$$

in which  $(k_{sh})_{app}$  and  $(k_{sh})_t$  are the rate constants without and with the double-layer correction,  $Z_O$  is the ionic valence with sign of the oxidized form of the electroactive

nspecies and  $\varphi_2$  is the potential in the outer plane of closest approach. Unfortunately, we have no data for  $\varphi_2$  for NaClO<sub>4</sub> solutions, but at potentials close to  $E_0$  of the zinc couple, specific adsorption of ClO<sub>4</sub><sup>-</sup> is small<sup>17</sup> and data for NaF<sup>18</sup> or KCl<sup>19</sup> may be used as an approximation. With these data it can be calculated from (5) that in the concentration range 0.1–1 *M*,  $(k_{sh})_{app}$  for a simultaneous two-electron transfer behaves similarly to that observed by HUSH AND BLACKLEDGE. Moreover, a correction should be made for the change in activity coefficients. If the reasonable assumption is made that the activity coefficients increase for decreasing concentration, the apparent  $k_{sh}$ -values will increase, in accordance with experiment.

From the current-voltage relation with double-layer correction<sup>10</sup>, it can be derived in our notation that

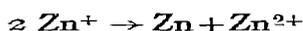
$$1 - \alpha_{app} = (\beta_{app}) = 1 - \alpha_t + (\alpha_t - 1 + Z_0/n) (\varphi_2 - \varphi_2^{eq}) / (E - E_{eq}) \quad (6)$$

If  $\alpha_t = 0.70$  and  $Z_0 = n = 2$  are inserted, this expression yields, with the  $\varphi_2$ -data of NaF, that  $\beta_{app}$  changes from 0.32 to 0.35 for 1 to 0.1 *M* solutions. For the  $\varphi_2$ -values of KCl,  $\beta_{app}$  ranges from 0.33 to 0.36. It can be seen that an increase in  $\beta_{app}$  can be explained in this way. The increase in  $\beta$  observed by HUSH AND BLACKLEDGE is, however, larger than was calculated from (6) with approximate data for  $\varphi_2$ , and should be otherwise explained. On the other hand, KORYTA<sup>20</sup> has made an analogous investigation of the zinc reaction in NaNO<sub>3</sub> solutions which shows that  $k_{sh}$  and  $\alpha$  are independent of the NaNO<sub>3</sub> concentration if the proper double-layer corrections are made. Thus from the concentration dependence of  $k_{sh}$  and  $\alpha$  found by HUSH AND BLACKLEDGE<sup>14</sup> little evidence remains for the existence of the Zn<sup>+</sup> ion.

The high value of  $\beta$  at anodic overpotentials, calculated by these authors from the amalgam dissolution currents, could indicate the existence of Zn<sup>+</sup>. However, it should be noted that, frequently, a maximum occurs in the anodic Zn(Hg) current (*cf.* dashed curve in Fig. 6 of ref. 6), which possibly could lead to an erroneous value of  $\beta$ . This is supported by the rather large inaccuracy in  $\beta$  found by HUSH AND BLACKLEDGE.

To explain the irreversibility of the zinc electrode reaction apparent from the oscillograms, HEYROVSKÝ<sup>21,22</sup> assumed that the Zn<sup>+</sup> intermediate exists. This is said to be indicated by the dependence of the oscillograms on temperature, frequency and the presence of gelatine. In our opinion, HEYROVSKÝ has presented a possible theoretical explanation for the irreversibility of the zinc reaction but has given no conclusive experimental proof for the existence of Zn<sup>+</sup>. The different positions of the anodic and cathodic incisions only prove the irreversible character of a reaction, (*cf.* in the voltage sweep method<sup>23</sup>, even for reversible reactions, the anodic and cathodic peak are 2.2 *RT/nF* apart) but do not necessarily imply the existence of an intermediate. The dependence on temperature, frequency and gelatine cannot be interpreted in terms of any mechanism until theoretical expressions are available for the oscillograms of irreversible electrode reactions.

Finally, if the Zn<sup>+</sup> ion is an intermediate in the zinc reaction, the most acceptable fate of Zn<sup>+</sup> is the dismutation<sup>5,6</sup>



We have made a chronopotentiometric study to obtain, if possible, the value of the dismutation rate constant,  $k$ . Transition times,  $\tau$ , of 20 sec–10 msec were measured

at a hanging mercury drop in 5 mM and 10 mM  $Zn^{2+}$  solutions in 1 M KCl (pH 3) with 20 and 50 mg/l of the surfactant, BRV 35. For  $\tau > 1$  sec, a correction was made for the sphericity of the drop<sup>24</sup>. From a plot of  $i/\tau$  against  $i^3$ , the rate constant,  $k$ , can be calculated<sup>25</sup>. These plots showed that the dismutation, if present, is very fast ( $k > 10^9$  l/mole sec). It is, therefore, unlikely that  $Zn^+$  could be detected experimentally.

In our opinion, no definite proof for the existence of the  $Zn^+$  ion as an intermediate in the zinc electrode reaction has so far been presented in literature. The experimental data can be explained by the one-step electrode reaction



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#### SUMMARY

An experimental verification of the theory for the potential dependence of the faradaic impedance in the case of irreversible electrode reactions, described in part XVIII, is presented for the  $Eu^{3+}/Eu^{2+}$  couple in 1 M  $NaClO_4$  at a D.M.E. It is shown that two peaks occur in an a.c. polarogram, if both  $Eu^{3+}$  and  $Eu^{2+}$  are present. A good quantitative agreement exists between the experimentally found- and theoretically calculated-faradaic impedance as a function of electrode potential.

The consequences of the theoretical treatment in part XVIII are discussed for the zinc couple in the presence of surfactants. The a.c. measurements do not prove that the reaction proceeds *via* univalent zinc, as was concluded earlier. The evidence for the existence of the  $Zn^+$  ion, published by a number of authors, is discussed and it is concluded that no definite proof for the existence of  $Zn^+$  has so far been presented.

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