

## ON THE IMPEDANCE OF GALVANIC CELLS—XVII. THE MECHANISM OF THE $Zn^{2+}/Zn(Hg)$ ELECTRODE REACTION\*

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**Abstract**—A theory is presented of the complex behaviour of the streaming zinc amalgam electrode in a  $Zn^{2+}$  solution. It is assumed that the  $Zn^{2+}/Zn^+$  and the  $Zn^+/Zn(Hg)$  electrode reactions occur at potentials where at the *dropping* amalgam electrode the  $Zn^{2+}$ -resp.  $Zn$ -concentration at the electrode surface is virtually zero as a consequence of the  $Zn^{2+}/Zn(Hg)$  electrode reaction. At the *streaming* amalgam electrode the  $Zn^{2+}/Zn(Hg)$  reaction behaves more irreversibly owing to the increased mass transfer. Consequently the surface concentration of  $Zn^{2+}$  resp.  $Zn$  is finite in the neighbourhood of the standard potential of the redox couple  $Zn^{2+}/Zn^+$  resp.  $Zn^+/Zn(Hg)$ , this giving rise to additional peaks in the ac polarogram.

With a view to the fact that the one-electron-transfer reactions appear to be more reversible than the two-electron-transfer reaction, it can be expected that similar ac polarograms will be obtained for the dropping electrode, if the electrode processes are forced to behave more irreversibly *eg* by the addition of a surface-active substance. Experiments confirming this idea are described.

**Résumé**—On présente une théorie à fin d'expliquer le comportement complexe de l'électrode à veine d'amalgame de zinc en solution d'ions  $Zn^{2+}$ . On suppose que les réactions électrochimiques  $Zn^{2+}/Zn^+$  et  $Zn^+/Zn(Hg)$  ont lieu à des tensions auxquelles la teneur des ions  $Zn^{2+}$  à la surface d'une électrode à gouttes d'amalgame égale pratiquement zéro par suite de la réaction  $Zn^{2+}/Zn(Hg)$ . A l'électrode à veine d'amalgame la réaction  $Zn^{2+}/Zn(Hg)$  se comporte plus irréversiblement grâce à l'accroissement du transport convectif. Conséquemment la teneur superficielle des ions  $Zn^{2+}$  sur  $Zn(Hg)$  vaut plus que zéro et la tension est voisine du potentiel standard du couple  $Zn^{2+}/Zn^+$  par rapport à  $Zn^+/Zn(Hg)$ , si bien qu'on observe des ondes additionnelles dans le polarogramme du courant alternatif.

Vu que les transferts d'un électron paraissent être plus réversibles que le transfert de deux électrons, on peut s'attendre à des polarogrammes du courant alternatif similaires pour l'électrode à gouttes, si on rend le comportement des réactions électrochimiques plus irréversible par addition d'une substance qui est absorbée à la surface de l'électrode. On décrit quelques expériences pour confirmer cette théorie.

**Zusammenfassung**—Es wird eine Theorie zur Erklärung des komplizierten Verhaltens der strömenden Zinkamalgamelektrode in einer  $Zn^{2+}$ -Lösung entwickelt. Dabei wird angenommen, dass die Elektrodenreaktionen  $Zn^{2+}/Zn^+$  und  $Zn^+/Zn(Hg)$  verlaufen bei Potentialen wobei an der *tropfenden* Amalgamelektrode die  $Zn^{2+}$ -bzw.  $Zn(Hg)$ -Konzentration auf Null reduziert ist infolge der  $Zn^{2+}/Zn(Hg)$ -Reaktion. An der *strömenden* Amalgamelektrode verhält sich die  $Zn^{2+}/Zn(Hg)$ -Reaktion irreversibler wegen des erhöhten Massentransports, was zur Folge hat, dass die Oberflächenkonzentration von  $Zn^{2+}$  bzw.  $Zn(Hg)$  endlich ist beim Normalpotential des Redoxpaares  $Zn^{2+}/Zn^+$  bzw.  $Zn^+/Zn(Hg)$ . Dadurch entstehen zusätzliche Wellen im Wechselstrompolarogramm.

Da die Ein-Elektron-Übergangsreaktionen reversibler erscheinen als die Zwei-Elektronen-Übergangsreaktion, kann man erwarten ähnliche Wechselstrompolarogramme an der tropfenden Elektrode zu erzielen, wenn man die Elektrodenprozesse irreversibler macht mittels Zusatz einer oberflächenaktiven Substanz. Einige Experimente zur Bestätigung dieser Idee werden beschrieben.

### INTRODUCTION

THE  $Zn^{2+}/Zn(Hg)$  electrode reaction has been the subject of many electrochemical investigations. It is common to test a new method or apparatus for the study of electrode kinetics by comparing the results obtained for the  $Zn^{2+}/Zn(Hg)$  couple

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with those of other methods.<sup>1-8</sup> A number of publications, however, reports some abnormal features, which were tentatively explained by means of speculations about the mechanism of the electron-transfer reaction. Hush and Blackledge<sup>9</sup> concluded from their experiments that the two electrons are transferred in separate steps, the reaction  $\text{Zn}^{2+}/\text{Zn}^+$  being the slowest step. On the other hand Heyrovsky<sup>10</sup> proposed a mechanism in which the reduction of  $\text{Zn}^{2+}$  proceeds by a one-electron transfer leading to  $\text{Zn}^+$ , followed by a dismutation reaction, whereas the Zn in the amalgam is directly oxidized to  $\text{Zn}^{2+}$ . This theory was based on the oscillopolarographic behaviour of solutions containing  $\text{Zn}^{2+}$  at the *dropping* and the *streaming mercury electrode*.

Recently, we reported<sup>11</sup> the anomalous behaviour of a cell consisting of a *streaming zinc-amalgam electrode* in solutions containing  $\text{Zn}^{2+}$  and 1 M KCl or  $\text{KNO}_3$ . The ac polarogram of such a cell exhibits three peaks, respectively at  $-0.95$ ,  $-1.17$  and  $-1.33$  V (sce). The first, which corresponds to an anodic wave in the dc polarogram, is proportional to the concentration of Zn in the amalgam and independent of the concentration of  $\text{Zn}^{2+}$  ion. The second peak corresponds to the cathodic dc wave, is proportional to the  $\text{Zn}^{2+}$  concentration and independent of the Zn concentration. The third peak is probably due to the reduction of a small amount of  $\text{Zn}(\text{OH})_2$  formed at the electrode surface.<sup>7,12,13</sup> We concluded that the first and the second peak could be ascribed to the reactions



and



respectively, the most acceptable fate of the product  $\text{Zn}^+$  being the dismutation



At the *dropping zinc-amalgam electrode*, the ac polarogram exhibits—apart from the small  $\text{Zn}(\text{OH})_2$  peak—only one peak at the standard potential ( $-1.0$  V (sce)) of the  $\text{Zn}^{2+}/\text{Zn}$  couple, its height being a function of both concentrations. If it is assumed that the overall reaction  $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$  proceeds according to the mechanism described above, this peak would be the sum of the individual  $\text{Zn}/\text{Zn}^+$  and  $\text{Zn}^{2+}/\text{Zn}^+$  peaks. The appearance of two peaks at the streaming electrode could then be explained by the fact that the suppression of diffusion polarization at this electrode causes a shift of the half-wave and peak-potential of the  $\text{Zn}/\text{Zn}^+$  reaction to a more positive and of the  $\text{Zn}^{2+}/\text{Zn}^+$  reaction to a more negative value. This theory, however, cannot be valid, since the single peak observed at the dropping electrode is much smaller than the two peaks obtained at the streaming electrode, instead of being the sum. Consequently it must be concluded that at the dropping and the streaming  $\text{Zn}(\text{Hg})/\text{Zn}^{2+}$  electrode different reaction mechanisms occur.

In this communication we present a possible explanation for the described phenomena, based upon the classical theory of electrode-reaction kinetics. In addition some experiments will be described, which confirm our theory.

#### THEORY

The occurrence of peaks in the ac polarogram can be predicted by studying the potential dependence of the faradaic impedance  $Z_f$ , given by the well-known

expressions

$$Z_t = \theta + \sigma\omega^{-1/2} - j\sigma\omega^{-1/2} \quad (4)$$

$$\theta = \frac{RT}{n^2 F^2 K_{sh} C_{ox}^\alpha C_{red}^{(1-\alpha)}} \quad (5)$$

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2D_{ox}D_{red}}} \frac{C_{ox} \sqrt{D_{ox}} + C_{red} \sqrt{D_{red}}}{C_{ox}C_{red}} \approx \frac{RT}{n^2 F^2 \sqrt{2D}} \frac{C_{ox} + C_{red}}{C_{ox}C_{red}}, \quad (6)$$

where  $C_{ox}$  and  $C_{red}$  pertain to the concentrations at the electrode surface<sup>7,15</sup> and consequently are functions of the electrode potential  $E$  and the bulk concentrations  $C_{ox}^*$  and  $C_{red}^*$ .

Evidently  $\theta$  attains a minimum value  $\theta_m$  at that potential where  $C_{ox}^\alpha C_{red}^{(1-\alpha)}$  is maximal, while  $\sigma$  has a minimum value  $\sigma_m$  if  $C_{ox}C_{red}$  is maximal ( $C_{ox} + C_{red} = C_{ox}^* + C_{red}^*$  is independent of  $E$ ). It can be shown<sup>7,15</sup> that, if the contribution of activation polarization to the *direct* current/voltage relation is negligible (*reversible* electrode reaction), these potentials are close to the standard potential  $E^\circ$  of the redox couple. Consequently  $Z_t$  will attain a minimum value at a potential near to  $E^\circ$ , this minimum giving rise to a peak in the ac polarogram. Far from the standard potential either  $C_{ox}$  or  $C_{red}$  is virtually zero, so that  $\theta$  and  $\sigma$  are infinite—and the faradaic alternating current is zero—at potentials where a limiting current is observed in the dc polarogram.

If the electrode reaction is not purely reversible, the influence of activation polarization on the relation between surface concentration and electrode potential has to be accounted for. For the dropping mercury electrode this has been accomplished by Matsuda<sup>16</sup> in a quantitative treatment, based on the theory of semi-infinite linear diffusion.<sup>14</sup> For the streaming mercury electrode we prefer a treatment based on the concept of Nernst's diffusion layer (steady state theory<sup>14</sup>). Since we wish to compare the dropping with the streaming electrode, we assume that the mathematics of the steady state theory, which is much less involved, is qualitatively valid for both electrodes. According to this mathematics, the surface concentrations can be calculated as a function of  $E$  from the expressions

$$C_{ox} = C_{ox}^* + \frac{\delta}{nFD_{ox}} \bar{i} \quad \text{and} \quad C_{red} = C_{red}^* - \frac{\delta}{nFD_{red}} \bar{i} \quad (7)$$

$$\bar{i} = \frac{nF[C_{red}^* e^{\alpha\varphi} - C_{ox}^* e^{-(1-\alpha)\varphi}]}{\frac{1}{k_{sh}} + \frac{\delta}{D_{red}} e^{\alpha\varphi} + \frac{\delta}{D_{ox}} e^{-(1-\alpha)\varphi}} \quad (8)$$

in which  $\bar{i}$  is the direct current,  $\delta$  the thickness of the diffusion layer and  $\varphi = nF(E - E_0)/RT$ . The results are

$$C_{ox} = \frac{C_{ox}^* \left\{ \frac{D_{ox}}{\delta k_{sh}} + \frac{D_{ox}}{D_{red}} e^{\alpha\varphi} \right\} + C_{red}^* e^{\alpha\varphi}}{\frac{D_{ox}}{\delta k_{sh}} + \frac{D_{ox}}{D_{red}} e^{\alpha\varphi} + e^{-(1-\alpha)\varphi}} \quad (9a)$$

$$C_{red} = \frac{C_{ox}^* e^{-(1-\alpha)\varphi} + C_{red}^* \left\{ \frac{D_{red}}{\delta k_{sh}} + \frac{D_{red}}{D_{ox}} e^{-(1-\alpha)\varphi} \right\}}{\frac{D_{red}}{\delta k_{sh}} + e^{\alpha\varphi} + \frac{D_{red}}{D_{ox}} e^{-(1-\alpha)\varphi}} \quad (9b)$$

Evidently the term  $D/\delta k_{\text{sh}}$  accounts for the influence of activation polarization on the surface concentrations. In Fig. 1  $C_{\text{ox}}$  and  $C_{\text{red}}$ , calculated from (9) by inserting  $C_{\text{ox}}^* = C_{\text{red}}^* = C^*$ ,  $D_{\text{ox}} = D_{\text{red}} = D$ ,  $n = 2$  and  $\alpha = 0.7$  (which is usually found for the  $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$  reaction), are plotted against  $E - E_0$  for  $D/\delta k_{\text{sh}} = 1, 30$  and  $1000$ . In Fig. 2 the corresponding values of  $C_{\text{ox}}^\alpha$   $C_{\text{red}}^{(1-\alpha)}$  are represented. Since the activation polarization predominates in the faradaic impedance of the  $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$  couple,<sup>6,7</sup> this plot predicts approximately the shape of the ac polarogram of this couple for different values of  $D/\delta k_{\text{sh}}$ , in the case that  $C_{\text{ox}}^* = C_{\text{red}}^*$ . In Figs. 3 and 4 analogous plots are given for the case where  $C_{\text{red}}^* = 0$ .

For the  $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$  electrode reaction in 1 M KCl  $k_{\text{sh}} \approx 10^{-3}$  cm/s and  $D \approx 10^{-5}$  cm<sup>2</sup>/s.<sup>1,7</sup> At the *dropping electrode*  $\delta$  is of the order of  $10^{-2}$ , so  $D/\delta k_{\text{sh}} = ca 1$ . This means that the dc wave is almost reversible and that the ac polarogram has the shape of curve 1 in Fig. 2 or 4. This is in good agreement with well-known experimental facts (see also Fig. 9), which suggests that the electrode reaction really proceeds by a simple two-electron transfer.

If this is true, the same two-electron transfer should also occur at the *streaming electrode*. This is confirmed by the fact that from impedance measurements at equilibrium potential for this electrode values of  $k_{\text{sh}}$  have been obtained, which agree well with values obtained at the dropping or hanging drop electrode.<sup>8</sup> Since for the streaming electrode  $\delta$  is 10 or 100 times smaller, an ac polarogram of the shape of curve 2 in Fig. 2 or 4 would be expected. Evidently this curve still shows only one peak. Consequently the two peaks, which are observed by experiment, must be ascribed to a different mechanism. This mechanism can be represented by the reactions (1) and (2) only if it is assumed that these reactions can proceed *beside* the two-electron transfer, both at the streaming and the dropping electrode.

Since the univalent state of zinc is unstable, the standard potential  $E_{2,1}^\circ$  of the  $\text{Zn}^{2+}/\text{Zn}^+$  couple will be more negative than the standard potential  $E_{2,0}^\circ$  of the  $\text{Zn}^{2+}/\text{Zn}$  couple, whereas the standard potential  $E_{1,0}^\circ$  of the  $\text{Zn}^+/\text{Zn}$  couple will be positive with respect to  $E_{2,0}^\circ$ .<sup>17</sup> So, a peak due to reaction (1) must be expected at a potential anodic to  $E_{2,0}^\circ$  and a peak due to reaction (2) at a potential cathodic to  $E_{2,0}^\circ$ .

If, however,  $E_{2,0}^\circ - E_{2,1}^\circ$  is too large, the reduction of  $\text{Zn}^{2+}$  to  $\text{Zn}^+$  occurs in a potential region where the *surface concentration*  $C_{\text{Zn}^{2+}}$  is zero, owing to the reduction of  $\text{Zn}^{2+}$  to  $\text{Zn}$ . In that case the faradaic impedance of *both* reactions is infinite in that potential region, so that the one-electron transfer cannot give rise to a peak in the ac polarogram. Evidently this is the case for the *dropping electrode*, where  $C_{\text{Zn}^{2+}}$  is virtually zero at potentials 100 mV below  $E_{2,0}^\circ$  (curve 1, Fig. 1 or 3). At the *streaming electrode* (curve 2)  $C_{\text{Zn}^{2+}}$  becomes zero at a potential 250 mV below  $E_{2,0}^\circ$ . Obviously the one-electron transfer begins to proceed with a marked velocity just between those potentials, so that at the streaming electrode a peak is observed. The same reasoning can hold for the oxidation of  $\text{Zn}$  to  $\text{Zn}^+$ : if this reaction starts at a potential between 50 mV and 125 mV positive to  $E_{2,0}^\circ$ , it can give rise to an ac peak only at the streaming electrode.

Summarizing, we can explain the ac polarographic behaviour of the dropping and the streaming zinc amalgam electrode in  $\text{Zn}^{2+}$  solutions with the assumption that the faradaic alternating current can be carried by three parallel mechanisms:

- (i) the electrode reaction  $\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn}$  predominating at  $-1.0$  V (sce).
- (ii) the electrode reaction  $\text{Zn} \rightleftharpoons \text{Zn}^+ + e$  predominating at potentials  $> -1.0$  V

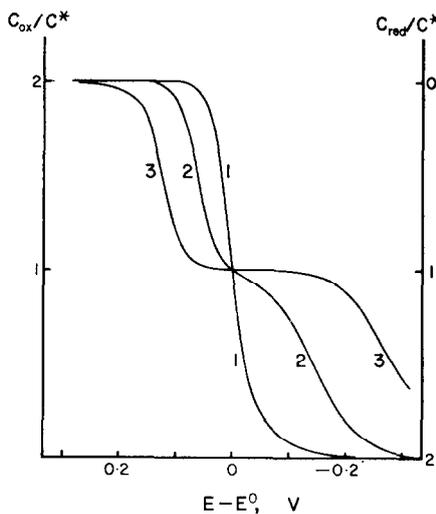


FIG. 1. Surface concentrations as a function of potential for the two-electron transfer reaction  $Zn^{2+}/Zn(Hg)$ .  $C_{Zn}^* = C_{Zn^{2+}}^* = C^*$ ,  $\alpha = 0.7$ ,  $D_{Zn} \approx D_{Zn^{2+}} = D$ . Values of  $D/\delta k_{sh}$ : 1 (curve 1), 30 (curve 2) and 1000 (curve 3).

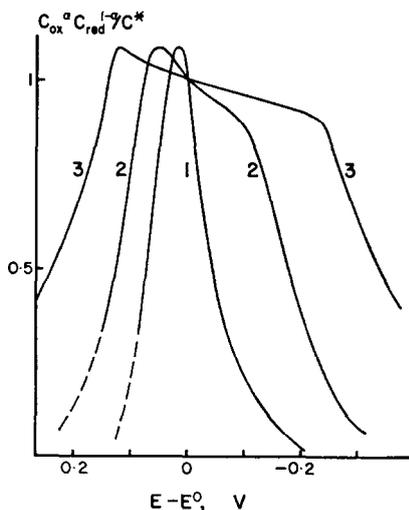


FIG. 2. Shape of ac polarograms corresponding to Fig. 1. Control by activation polarization is supposed ( $\theta \gg \sigma\omega^{-1/2}$ ).

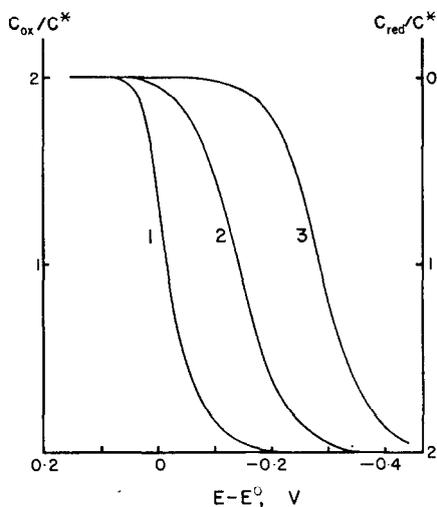


FIG. 3. Surface concentrations as a function of potential for the two-electron transfer reaction  $Zn^{2+}/Zn(Hg)$ .  $C_{Zn}^* = 0$ ,  $C_{Zn^{2+}}^* = 2C^*$ ,  $\alpha = 0.7$ ,  $D_{Zn} \approx D_{Zn^{2+}} = D$ . Values of  $D/\delta k_{sh}$ : 1 (curve 1), 30 (curve 2) and 1000 (curve 3).

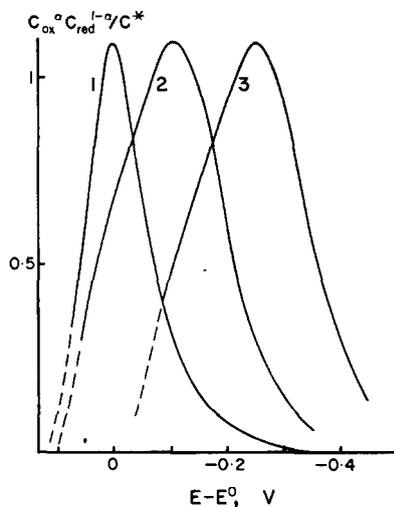


FIG. 4. Shape of ac polarograms corresponding to Fig. 1 for the case where  $\theta \gg \sigma\omega^{-1/2}$ .

(iii) the electrode reaction  $\text{Zn}^{2+} + e \rightleftharpoons \text{Zn}^+$  predominating at potentials  $< -1.0$  V. Mechanisms (ii) and (iii) are considerable only if the surface concentration of the stable component exceeds zero. Experimentally this is the case if the term  $D/\delta k_{\text{sh}}$  for the two-electron transfer is sufficiently large, which is realized at the streaming electrode.

It is a well-known fact that addition of a surface-active substance causes a lowering of the reaction rate constant  $k_{\text{sh}}$ . In that case the peaks due to the one-electron transfer reactions should be observed also in the ac polarogram of the *dropping electrode*, because they appear to be more reversible than the two-electron transfer reaction. In the following sections we will describe a number of such experiments, which were performed in order to verify the theory presented above.

#### EXPERIMENTAL

All measurements were performed at 25°C. The cell solution, which contained 1 M KCl as a supporting electrolyte, was freed from dissolved oxygen by means of tank nitrogen. Sometimes  $10^{-3}$  M HCl was added in order to avoid formation of  $\text{Zn}(\text{OH})_2$ .

The ac polarograms were obtained by the complex plane method,<sup>6,7</sup> which means that the real and imaginary components  $Z'$  and  $Z''$  of the cell impedance are measured as a function of dc potential  $E$ .

*Dropping electrode.* The impedance measurements were performed by means of the ac bridge described previously.<sup>7</sup> The zinc amalgam was prepared in a common mercury reservoir by 24 h electrolysis under nitrogen atmosphere. The capillary was connected to the reservoir by a short silicon tube.

Because of the low height of the mercury level the drop surface had to be determined as a function of potential, in order to correct the measurements for the right electrode surface.

An amalgam pool of the same composition as the dropping electrode served as a counter electrode for the ac measurements. The dc potential was measured against sce by means of a potentiometer with high input resistance.

For comparison dc polarograms were determined by measuring the dc current flowing between the dropping electrode and the amalgam pool as a function of potential.

All readings and adjustments were made at the end of drop-life.

The surface active substance was a polyoxyethylene lauryl ether, BRY 35 (Atlas-Goldschmidt GmbH, Essen, Germany). This detergent is known to be adsorbed at mercury over a wide potential range and to have a strongly inhibiting effect.<sup>23</sup>

*Streaming electrode.* The experiments with the streaming mercury or amalgam electrode were performed as described earlier.<sup>8</sup> In this case the complex admittance was measured instead of the impedance, but the latter can easily be calculated from the results (bilinear transformation).

All ac measurements were performed with a frequency of 1000 c/s.

#### RESULTS

In order to get information about the adsorption of the polyoxyethylene lauryl ether, we measured the double layer capacitance as a function of potential of the dme in 1 M KCl with BRY 35 added in various concentrations. The results are shown in Fig. 5.

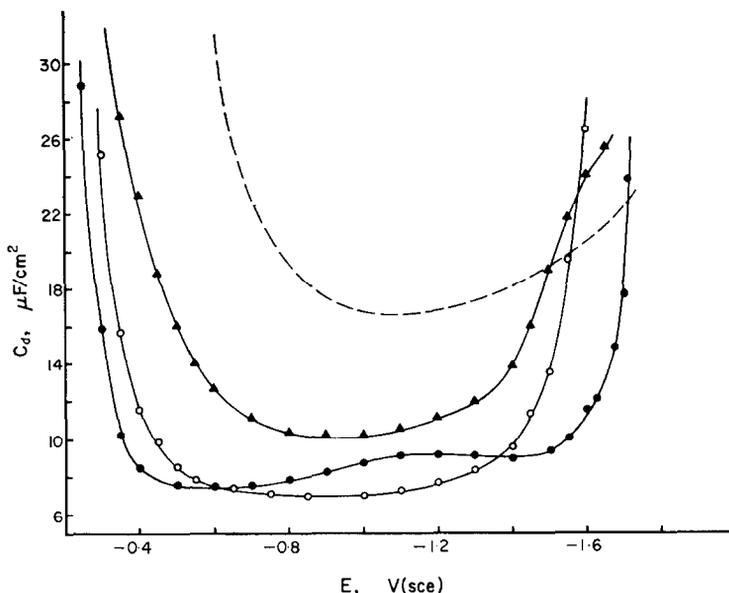


Fig. 5. Capacitance potential curves for the dropping mercury electrode in 1 M KCl. Concentrations of BRY 35: — — 0, ▲ 10, ○ 16, ● 64 mg/l.

It is seen that the standard potential of the  $Zn^{2+}/Zn(Hg)$  couple (*ca*  $-1.0$  V (sce)) lies well in the region of adsorption, so that one may expect that its electrode reaction will be inhibited on addition of BRY 35. In fact the dc polarograms, represented in Fig. 6, show more "irreversible" character with increasing BRY 35 concentration.

According to Catherino and Jordan<sup>18</sup> it should be possible to elucidate the mechanism of the electrode reaction by analysis of these polarograms. In our opinion, however, a definite conclusion can hardly be drawn, especially when the mechanism proposed in this paper (simultaneous occurrence of *two* reaction paths) is expected. More and better information can be obtained from ac polarograms.

In Fig. 7 typical complex-impedance-plane polarograms are represented for the streaming electrode and the dropping electrode with BRY 35 added. The qualitative similarity, which was expected in the theoretical section, is evident: both polarograms show two distinct peaks. The difference in shape can be explained<sup>7,15</sup> by the different values of the double layer capacitance, which depends on the concentration of BRY 35 (see Fig. 5).

A juster comparison can be made if the contribution of the double layer capacitance is eliminated. This is realized by calculation of the quantity  $q$  from the impedance co-ordinates  $Z'$  and  $Z''$  according to

$$q = \frac{(Z' - R_{\Omega})^2 + (Z'')^2}{Z' - R_{\Omega}} \quad (10)$$

in which,  $R_{\Omega}$  is the ohmic resistance of the cell solution. Its value is easily found from the "base-line" in the impedance-plane polarogram or by extrapolation of  $Z'$  to infinite frequency. It has been shown<sup>7</sup> that  $q$  is related to the activation polarization

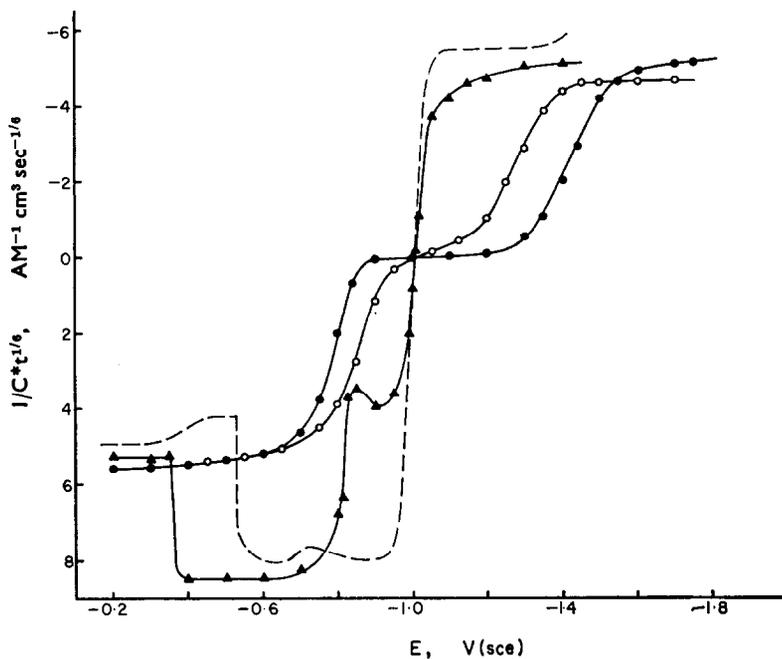


FIG. 6. Dc polarograms of the dropping zinc amalgam electrode in 1 M KCl solutions, containing  $Zn^{2+}$  ions. Currents are normalized for drop-time and concentration. Equal concentrations of Zn and  $Zn^{2+}$ : — 4,  $\blacktriangle$  10,  $\circ$  15,  $\bullet$  10 mMl. Concentrations of BRY 35: — 0,  $\blacktriangle$  10,  $\circ$  16,  $\bullet$  64 mg/l.

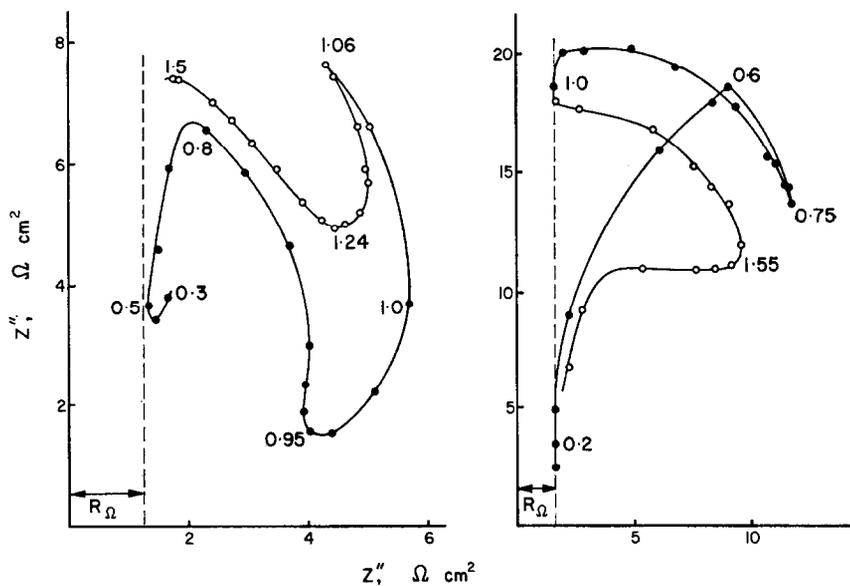


FIG. 7. Complex impedance plane polarograms. (a) streaming electrode, 1 M KCl,  $10^{-3}$  M HCl, 1 mM Zn and  $Zn^{2+}$ ; (b) dropping electrode, 1 M KCl, 10 mM Zn and  $Zn^{2+}$ , 64 mg/l BRY 35.  $\bullet$  potentials anodic to  $E_{Zn^{2+}/Zn}^0$ ,  $\circ$  cathodic potentials. Numbers denote potential in negative V (sce).

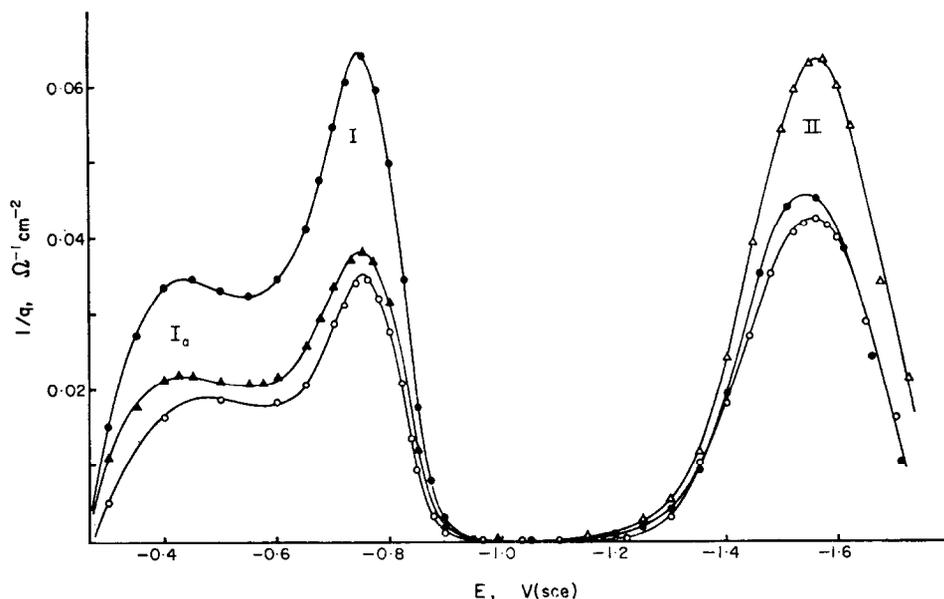


FIG. 8. Ac polarograms for the dropping electrode in 1 M KCl obtained by the method of complex plane analysis. Concentration of BRY 35, 64 mg/l.  $\circ$   $C_{\text{Zn}} = C_{\text{Zn}^{2+}} = 10$  mM,  $\bullet$   $C_{\text{Zn}} = 17$ ,  $C_{\text{Zn}^{2+}} = 10$  mM,  $\blacktriangle$   $C_{\text{Zn}} = 10$ ,  $C_{\text{Zn}^{2+}} = 15$  mM,  $\triangle$   $C_{\text{Zn}} = 0$ ,  $C_{\text{Zn}^{2+}} = 15$  mM.

resistance  $\theta$  (cf 5) and the Warburg coefficient  $\sigma$  (6) according to

$$q = \theta + \sigma\omega^{-1/2} + \frac{\sigma^2\omega^{-1}}{\theta + \sigma\omega^{-1/2}} \quad (11)$$

(For the streaming electrode this expression is slightly different<sup>8</sup>.)

It is easily verified that for both the streaming and the dropping electrode  $q$  is identical to the reciprocal value of  $A_r'$ , the real component of the faradaic admittance. Consequently a plot of  $1/q$  against dc potential is essentially an ideal "real component ac polarogram",<sup>19</sup> which would be obtained with a phase-selective ac polarograph, if the ohmic resistance were zero. In Figs. 8–10 such plots are represented.

#### DISCUSSION

The theory concerning the mechanism of the  $\text{Zn}^{2+}/\text{Zn}(\text{Hg})$  electrode reaction in 1 M KCl, presented in this paper, is affirmed by the following observations:

(i) The ac polarogram of a zinc amalgam electrode in  $\text{Zn}^{2+}$  solution shows at least two peaks if  $D/\delta k_{\text{sh}}$  is made large either by making  $\delta$  small (streaming electrode) or by lowering  $k_{\text{sh}}$  (dropping electrode with BRY 35 added).

(ii) The height of the anodic peak (I) is proportional to the concentration  $C_{\text{Zn}}^*$  of Zn in the amalgam and independent of the concentration  $C_{\text{Zn}^{2+}}^*$  in the solution, whereas for the cathodic peak (II) the opposite is true (Fig. 8).

(iii) For  $C_{\text{Zn}}^* = 0$ , the ac polarogram of the streaming electrode is clearly composed of two peaks (Fig. 10), which indicates that both the two-electron transfer and the one-electron transfer occur. Note that at the streaming *amalgam* electrode the  $\text{Zn}^{2+}/\text{Zn}$ -peak has disappeared, since it is overlapped by the large  $\text{Zn}/\text{Zn}^+$  peak (cf the

theoretical polarograms in Figs. 2 and 4). At the dropping electrode it has disappeared too, since the lowering of  $k_{sh}$  causes an increased  $\theta$  so that  $1/q$  decreases on addition of BRY 35.

This implies that the one-electron transfer reactions are more nearly "reversible" than the two-electron transfer: addition of 64 mg/l BRY 35 suppresses the latter completely, while the former show considerable peaks. From the peak heights in

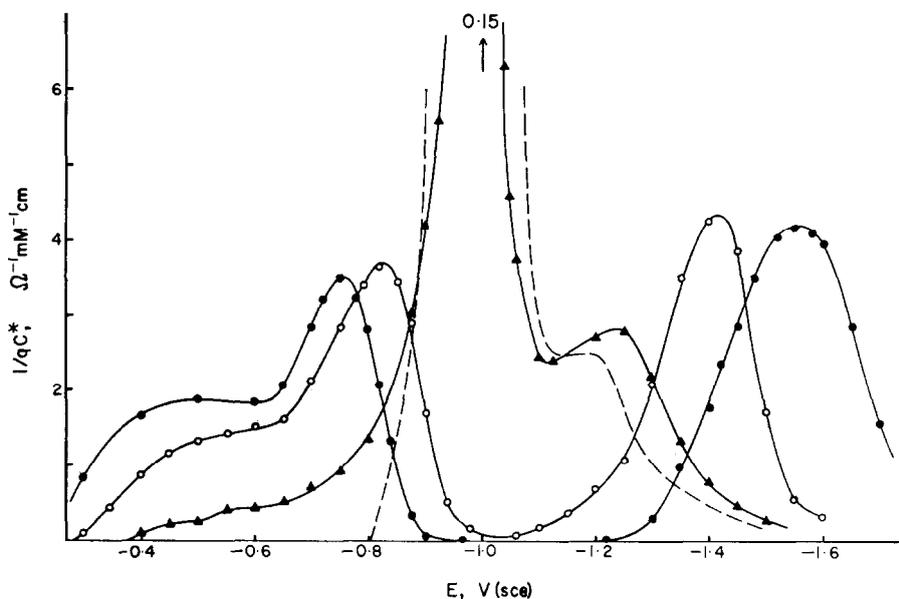


FIG. 9. AC polarograms for the dropping electrode in 1 M KCl obtained by the method of complex plane analysis. Ordinates are normalized for concentration. ●, 10 mM Zn and  $Zn^{2+}$ , 64 mg/l BRY 35, ○ 15 mM Zn and  $Zn^{2+}$ , 16 mg/l BRY 35, 1 mM HCl added, ▲, 10 mM Zn and  $Zn^{2+}$ , 10 mg/l BRY 35, 1 mM HCl added, — — 4 mM Zn and  $Zn^{2+}$ , no BRY 35 added, 1 mM HCl added.

Fig. 10 it can be calculated with (5) (assuming that  $\sigma\omega^{-1/2} \ll \theta$  and  $\alpha \approx 0.5$ ) that for reaction (1)  $k_{sh} > 2 \times 10^{-2}$  and for reaction (2)  $k_{sh} > 10^{-2}$  cm/s.

The influence of the BRY 35 concentration on the peak potentials (Fig. 9) can be explained easily by considering Fig. 1 and (5): the formation of  $Zn^+$  will proceed more rapidly from  $E_{2,0}^{\circ}$ , so the potentials where  $C_{Zn}^{(1-\alpha)}C_{Zn^+}^{\alpha}$  and  $C_{Zn^{2+}}^{\alpha}C_{Zn^+}^{(1-\alpha)}$  are maximal will differ more from  $E_{2,0}^{\circ} = -1.0$  V as  $D/\delta k_{sh}$  is larger. In addition the absolute values of these products will be larger, but evidently this effect is compensated by the inhibition, so that the peak heights are *apparently* independent of BRY 35 concentration.

In Fig. 9 it is observed that even if no BRY 35 is added, a small "shoulder" appears in the cathodic branch. This might be due to the  $Zn^{2+}/Zn^+$  reaction or to the reduction of some—still present— $Zn(OH)_2$ . A decision between these possibilities could be made if the influence of pH is studied more rigorously.

Hitherto we have assumed that the reaction product of the one-electron-transfer reactions,  $Zn^+$ , disproportionates into Zn and  $Zn^{2+}$ . For the cathodic reaction this seems to be justified, since the peak potential  $E_{p,II}$  of peak II is considerably more

negative than the half-wave potential  $E_{1/2,II}$  of the cathodic dc wave (*cf* Figs. 7 and 8 or 9): at the latter  $C_{Zn^{2+}} = \frac{1}{2}C_{Zn^{2+}}^*$ , but as a consequence of the disproportionation  $C_{Zn^+} < \frac{1}{2}C_{Zn^{2+}}$  so that  $C_{Zn^{2+}}^{\alpha} C_{Zn^+}^{(1-\alpha)}$  is maximal at a more negative potential.

For the anodic peak, however, the peak potential  $E_{p,I}$  differs only slightly from  $E_{1/2,I}$  and moreover a second anodic peak  $I_a$  is observed at ca  $-0.45$  V (sce). The height of this peak depends on the amalgam concentration  $C_{Zn}^*$ , but the relation is not linear. The peak  $I_a$  occurs in a potential region where a limiting current is

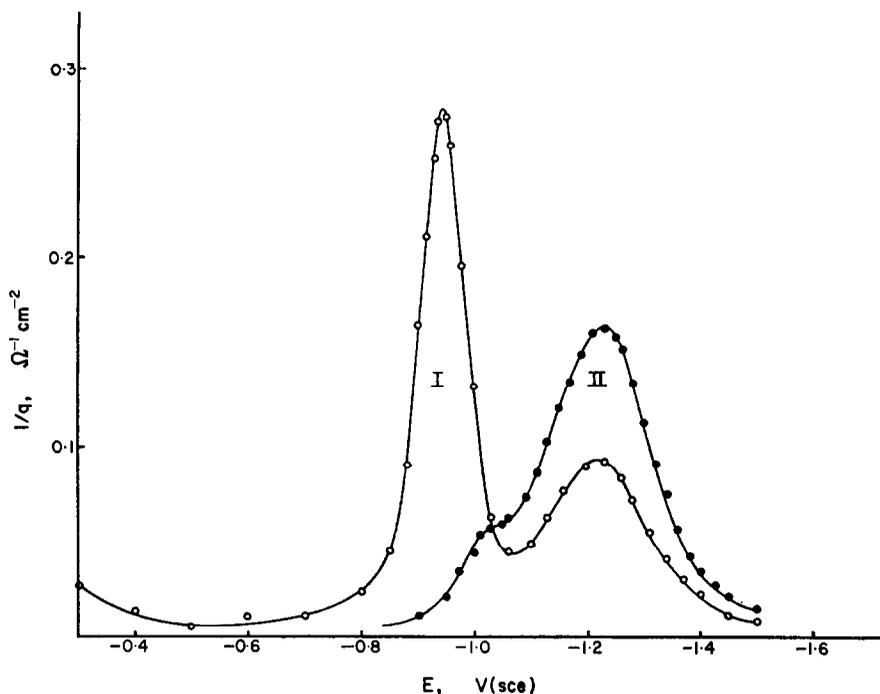


FIG. 10. Ac polarograms for the streaming electrode in 1 M KCl +  $10^{-3}$  M HCl, obtained by the method of complex plane analysis. ○,  $C_{Zn} = C_{Zn^{2+}} = 1$  mM, ●,  $C_{Zn} = 0$ ,  $C_{Zn^{2+}} = 2$  mM.

observed in the dc polarogram, with other words where the concentration of Zn at the electrode surface  $C_{Zn}$  is zero. It seems most probable that this peak can be ascribed to the oxidation of  $Zn^+$  to  $Zn^{2+}$  at the electrode surface, which occurs besides the disproportionation. This theory, however, is not proved definitely.

From the limiting currents, shown in Fig. 6, the number of electrons involved in the overall reaction, can be calculated by means of the Ilkovic equation. With  $D_{Zn} \approx 1.6 \times 10^{-5}$  and  $D_{Zn^{2+}} = 8 \times 10^{-6}$  it follows that in all cases  $n$  approximates 2, both for the anodic and the cathodic reaction (for zero BRY 35 concentration, the anodic limiting current is set equal to the current observed at  $-0.3$  V, according to Kolthoff<sup>19</sup>). This suggests that, whatever the mechanism, the  $Zn^+$  ions react further, rapidly, before they can diffuse into the solution.

The  $Zn^{2+}/Zn(Hg)$  electrode reaction has been studied frequently by analysis of direct current/potential curves.<sup>2,3,9,20-23</sup> With a view to the present investigation it will be clear that one should be very cautious in the interpretation of such studies, especially

if a surface-active substance is added: the nature of the predominant electron-transfer mechanism can change if the potential is varied. This might, for example, explain the anomalous value of  $\alpha$  found by Hush and Blackledge<sup>9</sup> from current/potential data at highly anodic potentials. As mentioned before, ac polarograms appear to be more informative, in particular if the influences of the ohmic resistance and the double layer capacitance are eliminated in the way shown in this paper.

It should be noted that the complex-plane analysis (calculation of  $q$  as a function of potential) is essential; in normal ac polarograms the peaks due to the  $Zn^{2+}/Zn^+$  reaction would have been swallowed by the tensammetric wave of the surfactant (compare Figs. 5 and 9).

Probably further information, *eg* about the kinetic parameters of the one-electron transfer reactions, can be gained from a more detailed study of the influence of frequency on the ac polarograms. We intend to extend our investigations in this direction.

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