

## ELECTRODE PROCESSES AT MERCURY IN THE FAR CATHODIC POTENTIAL REGION

### I. THE REDUCTION OF $K^+$ AND $Na^+$ IN NEUTRAL AQUEOUS MEDIA

R. M. REEVES, M. SLUYTERS-REHBACH AND J. H. SLUYTERS

*Laboratory of Analytical Chemistry, State University, Utrecht (The Netherlands)*

(Received 8th April 1971)

#### INTRODUCTION

Studies of the electrical double layer and electrode kinetics at  $E < -1.5$  V (SCE) at the dropping mercury electrode in aqueous solutions have been relatively limited. Double layer studies have been principally concerned with the adsorption of caesium<sup>1-3</sup>, and the tetraalkyl ammonium salts<sup>4</sup>. The most recent detailed kinetic studies have been directed towards an evaluation of the reduction of  $Ba^{2+}$  and  $K^+$ , at a mercury electrode<sup>5,6</sup>. Using small amplitude a.c. techniques, these studies indicated that these were simple electron transfers accompanied by amalgam formation. Imai and Delahay<sup>7</sup> also studied the alkali metal reductions using faradaic rectification but their analysis was suspect and has been criticised<sup>6</sup>. The lack of broader evidence for the mechanism of electrode processes in this potential region prompted a further study of alkali metal reductions.

The impedance technique developed by Sluyters<sup>8</sup> is entirely suitable for this type of study as it eliminates the need for a prior knowledge of the double layer capacity in the presence of the faradaic process. The analysis procedure for such a case has been described as the "frequency variation" method. As the alkali metals are among the most electropositive, it is difficult to find a supporting electrolyte which itself does not contribute to the faradaic impedance in the potential region of the alkali metal reductions. Only  $Li^+$  the alkaline earth metals,  $Ca^{2+}$  and  $Mg^{2+}$ , and the tetraalkyl ammonium salts might be considered.  $Li^+$  is unsuitable because of its unusual hydration properties which may modify the potential at the reduction site. The polyvalent ions may have a similar effect. Tetraalkyl ammonium ions are specifically adsorbed over a wide range of potentials and have been shown to modify the kinetic parameters of many electrode reactions. In order to avoid these complications, it seems more profitable to study the electrode reactions in pure solutions of the alkali metal salts, under conditions which allow the ions of the electrolyte to serve as the electroactive species and the supporting electrolyte simultaneously, *i.e.* at potentials far anodic of  $E_0$ .

In the cathodic region, cations may be specifically adsorbed. This is known to occur with caesium<sup>2</sup>, but the complete absence of specific adsorption of the other alkali metal cations is not proven. It is well known that the common anions are desorbed by  $-1.6$  V. On the basis of the simplest double layer model it would seem likely that variation of the anion should have no influence on the reduction process. This hypothesis will be further investigated through detailed impedance measurements

in solutions of KI, KBr, KCl, KF and NaI and polarographic measurements on a wider range of salts.

A further study of the cathodic rise in capacity in the presence of the potassium wave<sup>6</sup>, was thought desirable.

#### THEORY

The principles of the complex plane analysis are fully discussed elsewhere<sup>8</sup>. In order to interpret the results of these impedance measurements, it is necessary to review the principal methods of analysis and the conclusions which may be drawn for the various limiting cases. For all systems, in the absence of complications such as reactant adsorption or coupled chemical reactions, to which a simple equivalent circuit may be applied, the following analysis may be used.

From the measured resistance ( $R_s$ ) and capacity ( $C_s$ ), the impedance components,  $Z'_{el}$  and  $Z''_{el}$  of the electrode interface may be calculated using,

$$Z'_{el} = R_s - R_{\Omega} \quad (1a)$$

$$Z''_{el} = 1/\omega C_s \quad (1b)$$

where  $R_{\Omega}$  is the ohmic resistance of the system determined either at potentials outside the faradaic region or from determinations of  $R_s$  at frequencies sufficiently high as to observe frequency independent values of  $R_s$  (ca. 10 kHz). It is usual to treat the impedance in terms of admittance components  $Y'_{el}$  and  $Y''_{el}$  through,

$$Y'_{el} = \frac{Z'_{el}}{Z'^2_{el} + Z''^2_{el}} \quad (2a)$$

$$Y''_{el} = \frac{Z''_{el}}{Z'^2_{el} + Z''^2_{el}} \quad (2b)$$

In the case of a simple electrode reaction,  $Y'_{el}$  and  $Y''_{el}$  are combinations of three parameters:  $\theta$  the charge transfer resistance,  $\sigma$  the Warburg coefficient and  $C_d$  the double-layer capacity:

$$Y'_{el} = \frac{\omega^{\frac{1}{2}}}{\sigma} \frac{p+1}{p^2+2p+2} \quad (3a)$$

$$Y''_{el} = \frac{\omega^{\frac{1}{2}}}{\sigma} \frac{1}{p^2+2p+2} + \omega C_d \quad (3b)$$

$$p = \frac{\theta}{\sigma\omega^{-\frac{1}{2}}} = p'\sqrt{\omega} \quad (4)$$

Using values of  $\omega^{\frac{1}{2}}/Y'_{el}$  at constant  $E$  as a function of frequency and an iterative procedure, it is possible to find unique values of  $p'$  and  $\sigma$  through eqn. (3a). These results may then be substituted into eqn. (3b) and  $C_d$  may be calculated. The  $C_d$  value so derived must be independent of frequency, thus providing an alternative internal check on the procedure. At low values of  $p'$ , experimental errors tend to be magnified<sup>6</sup> and care must be taken in deriving the error limits of  $p'$  and  $C_d$ .

The parameter  $p'$  is a function of potential and contains information on the

kinetic parameters  $k_{sh}$ , the standard heterogeneous rate constant and the transfer coefficient,  $\alpha$ , according to,

$$p' = \frac{2^{\frac{1}{2}}}{k_{sh} D_O^{-\frac{1}{2}} \exp(-\beta\varphi) + D_R^{-\frac{1}{2}} \exp(\alpha\varphi)} \quad (5)$$

where  $\varphi = nF(E - E_0)/RT$ .

The degree of reversibility of the reaction may be readily inferred from the values of  $p'$ . If  $p' < 3 \times 10^{-3}$  the term containing  $p$  in eqn. (3a) is no longer frequency dependent and equals 0.5. The system is considered reversible in this case. If  $p' > 3 \times 10^{-1}$ , eqn. (3a) reduces to

$$Y'_{el} = \frac{\omega^{\frac{1}{2}}}{\sigma p} = \frac{1}{\theta}$$

so instead of  $p'$  and  $\sigma$  only  $\theta$  can be determined.

If  $E_0$  and the diffusion coefficients are known,  $\alpha$  and  $k_{sh}$  may be determined from  $p'$ . If  $E \ll E_0$  or  $E \gg E_0$ , the latter case being established in our experiments, a plot of  $\log p'$  vs.  $E$  should be linear and from its slope  $\alpha$  can be determined without knowledge of  $D_R$ ,  $D_O$  and  $E_0$ .

The potential dependence of  $\sigma$  and  $\theta$  is in general rather complicated, but there are a number of simplifications which may be applied depending on the reduction characteristics of the system studied<sup>8</sup>. The following cases are relevant to the present study;

(a) If  $E \gg E_0$ , and  $k_{sh}$  is large enough to give a d.c. reversible wave,  $\sigma$  may be expressed by,

$$\sigma = \frac{RT}{n^2 F^2 c_O^* 2^{\frac{1}{2}}} \frac{\exp(\varphi)}{D_R^{\frac{1}{2}}} \quad (6a)$$

and  $\theta$  by,

$$\theta = \frac{RT}{n^2 F^2 k_{sh} c_O^*} \exp(\beta\varphi) \quad (6b)$$

(b) If the system is very irreversible so that the faradaic reaction occurs at potentials  $E \ll E_0$ , the following equation for  $\theta$  may be applied,

$$\theta = \frac{RT}{n^2 F^2 c_O^* k_{sh}} \frac{1 + a_O \exp(\beta\varphi)}{\beta a_O} \quad (7)$$

where  $a_O = (7D_O)^{\frac{1}{2}}/k_{sh}(3\pi t)^{\frac{1}{2}}$  for a DME. If  $k_{sh}$  is sufficiently small,  $a_O \exp(\beta\varphi) \gg 1$  in eqn. (7), and a linear plot of  $\log \theta$  vs.  $E$  from which values of  $\beta$  or  $\beta n$  if  $n$  is unknown, may be derived.

During the course of this study, it was necessary to consider the case in which two electrode reactions are proceeding simultaneously (mixed current case). In such a case, partial or complete separation is possible depending on the degree of reversibility of each reduction. The simplest case is that of a completely irreversible reduction (2) in the presence of an almost reversible reduction (1). The electrode admittance may then be expressed as follows<sup>9</sup>:

$$Y'_{el} = \frac{\omega^{\frac{1}{2}}}{\sigma_1} \frac{p'_1 \omega^{\frac{1}{2}} + 1}{(p'_1 \omega^{\frac{1}{2}} + 1)^2 + 1} + \frac{1}{\theta_2} \quad (8a)$$

$$Y_{el}'' = \frac{\omega^{\frac{1}{2}}}{\sigma_1} \frac{1}{(p_1' \omega^{\frac{1}{2}} + 1)^2 + 1} + \omega C_d \quad (8b)$$

Using plots of  $Y_{el}'$  vs.  $\omega^{\frac{1}{2}}$ ,  $\sigma_1$  may be derived from the limiting slope of the plot at  $\omega \rightarrow 0$  and  $\theta_2$  from the ordinate intercept. These parameters may then be treated as separate entities as described in the earlier section. The success of this separation depends on the magnitude of  $p_1'$ . Small deviations from reversibility in (1) are manifested by a reduction in slope of the plots at higher frequencies, ( $3 \times 10^{-3} < p_1' < 3 \times 10^{-1}$ ). With larger values of  $p_1'$  this analysis becomes progressively more imprecise as the deviations from linearity occur over a large fraction of the experimentally accessible frequency range.

This type of analysis always depends on the form of the equivalent circuit used and the degree of experimental precision during comparison with the model. It will become clear during the subsequent discussion that the systems studied may be adequately treated using the methods described.

#### EXPERIMENTAL

The impedance of a dropping mercury electrode was determined using a series RC bridge with Wagner earth as used in previous studies<sup>8</sup>. The amplitude of the sinusoidal wave applied to the bridge was 5–8 mV. The bridge was modified with an extra 50 Hz filter and was triggered by the drop relay a fraction of a second before the drop was knocked off.

Measurements of equivalent capacity  $C_s$  and resistance  $R_s$  were recorded as a function of frequency, 225–10,000 Hz, and electrode potential against SCE. The capillaries for the dropping mercury electrode were specially constructed and siliconed as described elsewhere<sup>10</sup>. A hanging mercury electrode was not employed due to the possibility of the occurrence of the hydrogen evolution reaction at any platinum faults exposed to the solution at the very negative potentials used in this study. Alternative extrusion designs were rejected due to problems with solution creepage. Glassware was cleaned and steamed<sup>10</sup> and water was purified by distillation from concentrated alkaline potassium permanganate. Mercury was redistilled prior to use in a freshly cleaned still<sup>10</sup>. Salts were of p.a. (Merk) or A.R. (B.D.H.) grade and were recrystallised when necessary. No evidence of impurities was noted during the measurements. The cell was immersed in a water thermostat at 25.0°C. For the polarographic measurements a Metrohm polarograph with resistance compensation was used.

#### RESULTS AND DISCUSSION

The problems encountered in earlier work<sup>6</sup>, namely the determination of the ohmic resistance of the system in the absence of the faradaic process and the performance of the capillaries in the negative potential region employed, were further investigated. If standard polarographic capillaries were employed with or without siliconing, the drops were never entirely reproducible and as a consequence of the low head of mercury that had to be employed in order to obtain useful drop times, the ohmic resistance of the solution was found to vary with potential. In this case the

solution resistance was obtained from plots of  $1/r$  vs.  $R_\Omega$ , where  $r$  is the drop radius. The slopes of these lines agreed closely with the theoretical formula derived by Kolthoff *et al*<sup>11</sup>,  $1.1 \Omega \text{ cm}$ . The frequency dispersion of  $C_s$  and  $R_\Omega$  was usually significant when these capillaries were used. The use of drawn capillaries, siliconed in the vapour phase, reduced the frequency dispersion of the capacity and the ohmic resistance to within experimental error. Moreover, measurements could be made at drop times  $> 3 \text{ s}$  under a head of  $70 \text{ cm Hg}$  at  $-2.0 \text{ V}$ .

The analysis of the electrode reaction in  $1 \text{ M KCl}$  will be presented first. The electrode admittance was obtained in the form  $\omega^{3/2}/Y_{e1}'$  over a wide range of frequencies in accordance with eqn. (3a). This admittance function increased significantly in value at each potential studied and could be used to calculate values of  $\sigma$  and  $p'$ . The graphical fitting procedure used in an earlier publication<sup>6</sup> was found to be less satisfactory than a calculation procedure based on eqns. (3a) and (4). The errors in  $p'$  and  $\sigma$  were derived from the spread of results. At most potentials an error of  $\pm 1 \times 10^{-3}$  was found for  $p'$ . The potential range studied in these systems was wider than formerly used, it being possible to record significant values of electrode impedance over the range  $-1.8$  to  $-2.0 \text{ V}$ .

In Fig. 1 the plot of  $\log \sigma$  vs.  $E$  is shown for  $KCl$ . The plot is sensibly linear and has a slope of  $-16.6 \text{ V}^{-1}$  in agreement with the theoretical slope which may be derived from eqn. (6a). According to eqn. (5), when  $E \gg E_0$ , plots of  $\log p'$  vs.  $E$  must be linear. This behaviour is shown in Fig. 2. Usually,  $p'$  is observed to increase with potential as  $E \rightarrow E_0$ , but such simple behaviour seems evidently not to be obeyed by this system, the decrease in the value of  $p'$  with potential being significant. This implies that  $\alpha$  must be negative ( $-0.26 \pm 0.06$ ). This unusual observation prompted us

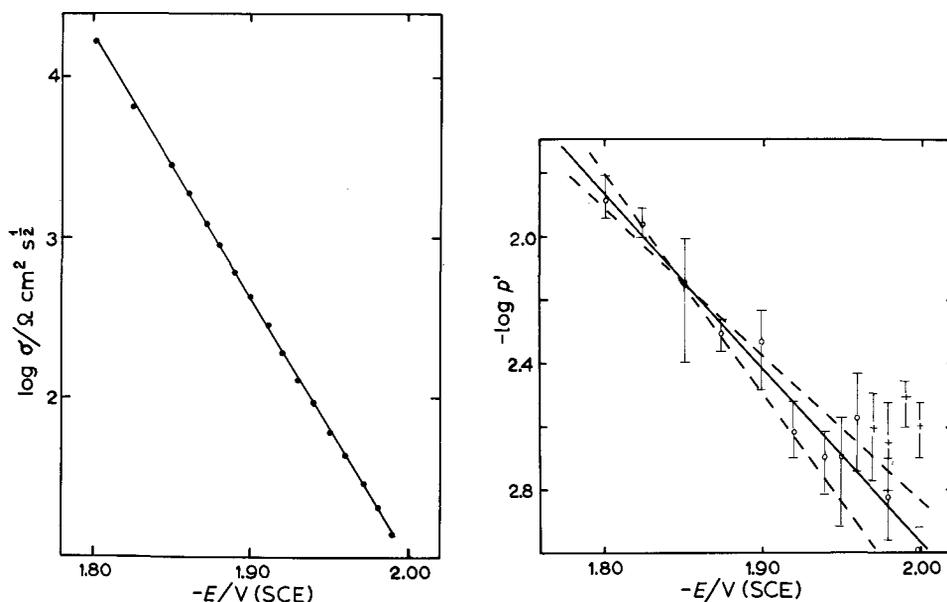


Fig. 1. The Warburg coefficient as a function of potential for  $1 \text{ M KCl}$ , ignoring the mixed current case.

Fig. 2. Plot of  $\log p'$  vs. potential according to eqn. (5) for  $1 \text{ M KCl}$ . (+) Data from ref. 6.

to a critical examination of the applied analysis procedure.

As the potential region in which the  $K^+$  reduction occurs is not remote from the potential of decomposition of pure water, it might be possible that water reduction occurs simultaneously. Such a phenomenon would result in a mixed current being observed and a mixed current analysis has to be applied.

The data were analysed using plots of  $Y'_{e1}$  vs.  $\omega^{\frac{1}{2}}$  at each potential, according to eqn. (8). At lower frequencies these plots appeared linear. Values of the slopes and intercepts of these lines were derived using a combination of graphical and least squares procedures. The slopes yielded values of  $\sigma_1$  which were systematically slightly higher than the value derived from the previous analysis. Extrapolation of the lines to  $\omega^{\frac{1}{2}}=0$  always resulted in significantly positive values of the intercept on the ordinate at  $E > -1.91$  V. At  $E < -1.91$  V, positive intercepts could still be derived, but the possible errors reduced the significance of the values. On the basis of eqn. (8), one can conclude that parallel to an almost reversible electrode reaction, corresponding to  $\sigma_1$  (the  $K^+$  reduction), a completely irreversible electrode reaction occurs, represented by the charge transfer resistance  $\theta_2$ .

The admittance of the  $K^+$  reduction was now reanalysed using the methods already described for the former analysis. The new values of  $\sigma_1$  and  $p'$  were derived after subtraction of the term  $1/\theta_2$  from the real part of the admittance. These  $\sigma_1$  values were in agreement with the results of the graphical treatment. No detectable frequency dispersion was observed in  $\omega^{\frac{1}{2}}/Y'_{e1}$  at  $E < -1.85$  V. From this it may be inferred that  $p'$  is  $< 3 \times 10^{-3}$  and that the reduction is reversible over the entire potential range studied. Some increase in  $\omega^{\frac{1}{2}}/Y'_{e1}$  at higher frequencies were still detected at  $E > -1.85$  V, but these have been ignored in the general analysis. The small admittance values observed in this potential region displayed considerable experimental scatter which was magnified by the subtraction of the experimentally determined  $1/\theta_2$ .

The analysis, as presented in this paper, serves to emphasise the caution that must be taken during the analysis of results of perturbation techniques, even of the seemingly simpler systems. The data in Table 1 serve to illustrate this point. The data at  $-1.900$  V in  $1 M$  KCl are presented as a function of frequency. The values of  $\sqrt{\omega}/Y'_{e1}$  calculated ignoring the mixed current are presented in column 2, while the data in column 3 are calculated after subtraction of  $\theta_2 = 85 \Omega \text{ cm}^2$  from  $Y'_{e1}$  according to eqn.

TABLE 1

THE INFLUENCE OF THE IRREVERSIBLE REDUCTION ON THE FUNCTION  $\sqrt{\omega}/Y'_{e1}$ 

Frequency/Hz	$\sqrt{\omega(Y'_{e1})^{-1}}/\Omega \text{ cm}^2 \text{ s}^{\frac{1}{2}}$	$\sqrt{\omega(Y'_{e1})^{-1}}/\Omega \text{ cm}^2 \text{ s}^{\frac{1}{2}}$
225	770	970
275	790	970
325	790	990
400	790	970
800	830	970
1000	840	960
1500	850	950
3000	920	970

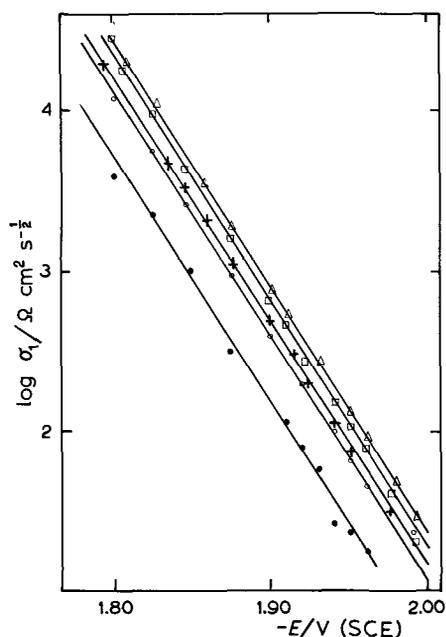


Fig. 3. The Warburg coefficient as a function of potential, plotted according to eqn. (6a), for 1 *M* aqueous solns. of: (●) NaI, (○) KF, (+) KCl, (□) KBr (Δ) KI, as derived from the mixed current analysis. Plots for the potassium salts have been successively displaced to more cathodic potentials by steps of 4 mV, for clarity of presentation.

(8a). The decrease in the frequency dispersion of the values is immediately obvious.

The lack of influence of the anion on the reduction process is shown in Fig. 3. The values of  $\sigma_1$ , derived using the mixed current analysis, agree closely for all the potassium halides. The slopes of the lines have the theoretical value  $-16.6 \text{ V}^{-1}$ . The influence of other anions was investigated more qualitatively by measuring the d.c. polarograms of 1 *M* solutions of KCl, KBr, KI, KF, KOH, KCNS,  $K_2CO_3$ , K oxalate and K acetate. The cathodic currents at the negative end of the potential range were superimposable within limits which could be correlated with the differences in bulk activities.

Solutions of potassium nitrate and nitrite were the only exceptions to this rule. Studies concerning salts including these anions will be published separately.

The behaviour of sodium ions was found to be similar to that of potassium. This evidence was obtained using a 1 *M* solution of NaI. The first analysis, ignoring the irreversible contribution to the impedance, yielded values of  $p'$  and  $\sigma$ . The principal features of the plot of  $\log p'$  vs.  $E$  were similar to those shown in Fig. 2 for potassium.  $Y'_{e1}$  was then reanalysed using eqn. (8a). This analysis again realised values of  $\theta_2$  which when subtracted from  $Y'_{e1}$  according to eqn. (8a) yielded values of  $\omega^{\frac{1}{2}}/Y'_{e1}$  which were independent of frequency. The new values of  $\sigma_1$ , plotted according to eqn. (5), when  $E \gg E_0$ , are shown in Fig. 3. This plot again has the theoretical slope. The displacement in the potential scales of these plots when  $Na^+$  is substituted for  $K^+$  (24 mV), agrees closely with the difference in the half-wave potentials (25 mV) of these ions<sup>12</sup>.

At this stage in the analysis it is necessary to consider the imaginary component of the admittance,  $Y_{e1}'$ , which is related to  $\sigma_1$ ,  $p'$  and  $C_d$  through eqn. (8b). Of these parameters,  $\sigma_1$  is known from the analysis of  $Y_{e1}$ ; furthermore it has been shown that  $p' < 3 \times 10^{-3}$ . It was shown in an earlier publication<sup>6</sup> that when eqn. (8b) is used to calculate  $C_d$ , the result might contain a considerable error when even a slightly incorrect value of  $p'$  is inserted. This is a consequence of the differing degrees of sensitivity of the first terms in eqns. (8a) and (8b) to changes in  $p'$ . It may be shown that the first term in eqn. (8a) deviates significantly from  $\omega^{\frac{1}{2}}/2\sigma$  when  $p' > 3 \times 10^{-3}$ , while the first term in eqn. (8b) is more sensitive to the value of  $p'$ , showing significant deviations from  $\omega^{\frac{1}{2}}/2\sigma$  when  $p' > 5 \times 10^{-4}$ . An alternative method for the determination of  $p'$  is suggested by these observations.  $C_d$  may be calculated as a function of frequency using a series of values of  $p'$ . The value of  $p'$  which results in a minimal frequency dispersion in  $C_d$  is then chosen. This method, however, requires the *a priori* assumption that the capacity is independent of frequency<sup>13</sup>. This assumption is not valid if the electroactive species is significantly adsorbed in the double layer. This analytical procedure was applied to our data and it was found that  $p' = 0$  gave the minimal frequency dispersion (less than  $\pm 0.2 \mu\text{F cm}^{-2}$  between 320 and 3000 Hz), so that we conclude that  $p' < 5 \times 10^{-4}$ . The resulting capacity data are shown in Table 2 for 1 M KCl and 1 M NaI. The rise in  $C_d$  observed previously (although obtained, as it now appears, by an incorrect analysis) does indeed seem to be a real phenomenon. It seems, moreover, to be correlated with the occurrence of the electrode reaction, as the rise in capacity in NaI solution is observed at more anodic potentials in agreement with the shift in the  $\log \sigma_1$  vs.  $E$  plot when  $\text{Na}^+$  is substituted for  $\text{K}^+$ . The possible errors in the capacity values make an evaluation of the precise magnitude of the rise impossible.

The irreversible reaction corresponding to the  $\theta_2$  values observed, remains to be discussed further. As the electrolyte solution contains only pure water and the salt, it is quite conceivable that this reaction concerns the evolution of hydrogen as

TABLE 2  
DOUBLE LAYER CAPACITY

$-E/V(\text{SCE})$	KCl		NaI	
	$C^a/\mu\text{F cm}^{-2}$	$C^b/\mu\text{F cm}^{-2}$	Error in $C/\mu\text{F cm}^{-2}$	$C/\mu\text{F cm}^{-2}$
1.900	24.9	24.7	0.5	25.3
1.910	25.5	24.9	0.8	26.4
1.920	26.2	25.1	1.2	27.6
1.930	25.7	25.8	1.7	28.8
1.940	25.7	26.3	2.7	33.6
1.950	27.4	27.5	4	34.1
1.960	26.6	28.5	6	56
1.970	33	36	12	—
1.980	40	56	20	—

<sup>a</sup> From ref. 6.

<sup>b</sup> This work.

a result of decomposition of the solvent. This is in agreement with several studies of the decomposition of alkali amalgams recently reconsidered by Frumkin *et al.*<sup>14</sup>. The conclusions from Frumkin's study were that at  $pH < 10$  hydrogen evolution is due to the "electrochemical" reduction of the hydrogen ion, in the same way as hydrogen is reduced in more acidic media, whereas at  $pH > 10$  the amalgam reacts "chemically" with water. These two processes are considered to be distinguishable.

Anticipating results to be published<sup>15</sup>, it should be noted that a contribution of a second, irreversible, reaction to the electrode admittance has also been observed during studies of the reduction of lithium from 1 M LiCl solutions (at  $pH$  7.2 as in the present study). In this case, however, there is no detectable reduction process at  $E > -2.05$  V, the irreversible reaction only being observed with the onset of the  $Li^+$  reduction ( $E < -2.05$  V). This means that the presence of the alkali metal at the interface is essential for the irreversible reaction to occur, irrespective of the question whether it concerns hydrogen ion or water reduction. In other words, the alkali metal, present as an amalgam, acts as a catalyst for the evolution of hydrogen from water. Such a conclusion has not to our knowledge been previously mentioned, and in particular the role of the amalgam phase has not been so clearly identified.

A more detailed examination of, for example, the potential dependence of  $\theta_2$ , is not possible due to the large errors these values contain when they are derived from the mixed current analysis by extrapolation to  $\omega^{\frac{1}{2}} = 0$ . However, it can be shown that more information can be obtained by considering the d.c. current in the same potential region. This current,  $i_T$ , will be the sum of a contribution  $i_{\text{alkali}}$  due to the alkali metal reduction, and a contribution  $i_H$  of the hydrogen evolution current:

$$i_T = i_{\text{alkali}} + i_H \quad (9)$$

$i_{\text{alkali}}$  may be calculated precisely from  $\sigma_1$ . The alkali metal ion reduction is d.c. reversible and since the ion concentration in the bulk is large,  $c_O$  at the electrode surface will be equal to the bulk concentration  $c_O^*$ . Under these conditions eqn. (6a) may be written as<sup>8</sup>:

$$\sigma_1 = \frac{RT}{n^2 F^2 2^{\frac{1}{2}} D_R^{\frac{1}{2}}} \frac{1}{c_R} \quad (10)$$

The corresponding d.c. current will be described by:

$$i_{\text{alkali}} = -nF \left( \frac{7D_R}{3\pi t} \right)^{\frac{1}{2}} (c_R - c_R^*) \quad (11)$$

$$= nF c_R^* \left( \frac{7D_R}{3\pi t} \right)^{\frac{1}{2}} - \frac{RT}{nF} \left( \frac{7}{6\pi t} \right)^{\frac{1}{2}} \frac{1}{\sigma_1} \quad (12)$$

where  $t$  is the drop time of the DME,  $c_R$  the surface concentration of the alkali metal and  $c_R^*$  its eventual bulk concentration ( $c_R^* = 0$  in our case).

Similarly  $i_H$  is related to  $\theta_2$ . For a very irreversible reaction  $i_H$  may be described by:

$$i_H = -nF k_{\text{sh}} c_O^* \exp(-\beta\varphi) \quad (13)$$

which combined with

$$\theta_2 = \frac{RT}{n^2 F^2 k_{\text{sh}} c_O^*} \frac{\exp(\beta\varphi)}{\beta} \quad (14)$$

gives

$$\theta_2 = - \frac{RT}{nF\beta} \frac{1}{i_H} \quad (15)$$

In eqns. (13) and (14)  $c_O^*$  denotes the concentration of water or protons.

Using  $i_T$  determined from a d.c. polarogram, values of  $i_{\text{alkali}}$  calculated according to eqn. (12) when  $c_R^* = 0$ ,  $i_H$  may be calculated from eqn. (9). The d.c. currents  $i_T$ ,  $i_{\text{alkali}}$  and  $i_H$  are shown in Fig. 4 for 1 M KCl. A similar plot was obtained at more anodic potentials for NaI. Note that  $i_H$  and  $i_{\text{alkali}}$  are of the same order of magnitude, contrary to the respective contributions to the electrode admittance.

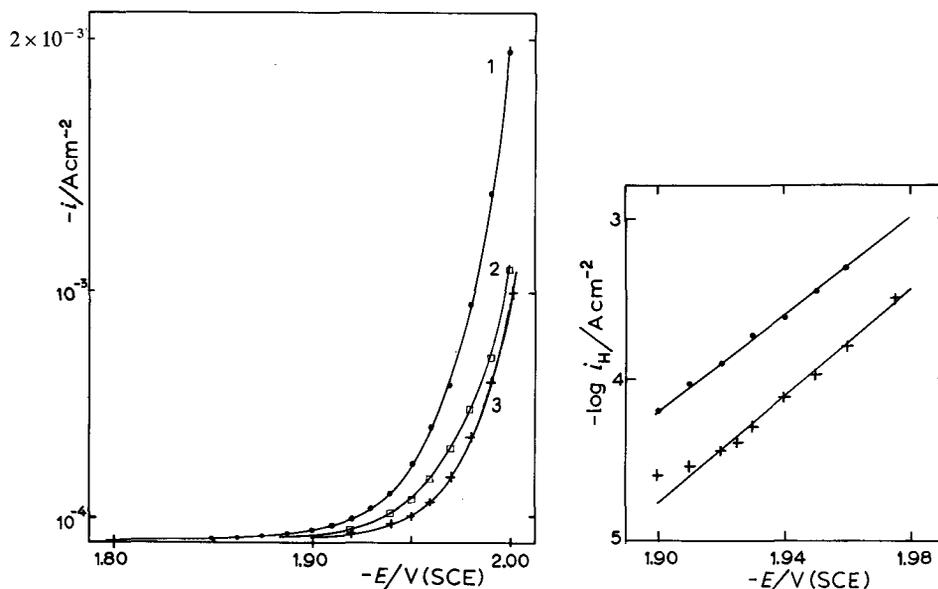


Fig. 4. D.c. current vs. potential plots for 1 M KCl at the dropping mercury electrode; (1) Total d.c. current passed by the electrode in the potential region studied, (2) current due to the potassium reaction calcd. according to eqn. (12) with  $c_R^* = 0$ , (3) current due to the irreversible reduction occurring during the reduction of potassium.

Fig. 5. Tafel plots of the current due to the irreversible reduction for: (●) 1 M NaI, (+) 1 M KCl.

The values of  $\log i_H$  plotted against potential in Fig. 5 show a linear relationship according to eqn. (13). The slopes of these plots were found to be  $1/0.061$  and  $1/0.067$   $V^{-1}$ . This gives a value of  $\beta n$  0.98 for  $K^+$  and 0.89 for  $Na^+$ . Assuming  $n=1$ , these values of  $\beta$  are anomalous when it is considered in the context of the hydrogen evolution reaction in acidic media for which a value of  $\beta \sim 0.5$  is usually found.

As a distinct cation dependence is observed, the possibility of the amalgam reacting directly with water or with protons must be considered. Using potassium as an example, the following reactions might be considered:



or



The potassium ion formed in this reaction, participates in the alkali ion reduction process. Since this process has been found to be d.c. reversible, the concentrations  $c_K$  and  $c_{K^+}$  at the electrode surface obey the Nernst equation. As the reduction involves a negligible amount of the cations present in the solution,  $c_{K^+} = c_{K^+}^*$  will hold and therefore  $c_R$  in eqn. (10) is not influenced by the occurrence of the decomposition reaction. In other words, the potential dependence of  $\sigma_1$  is not coupled to the accompanying hydrogen evolution reaction.

On the basis of the reaction scheme (16) the hydrogen evolution current might tentatively be described by a relationship of the form:

$$i_H = nF k c_{H_2O} c_K \quad (17)$$

or with  $c_{H^+}$  instead of  $c_{H_2O}$  (concentrations in the inner layer).

From the Nernst equation for the reversible amalgam electrode

$$c_K = c_{K^+}^* \exp(-\phi) \quad (18)$$

Substituting eqn. (18) into eqn. (17) yields

$$i_H = nF k c_{H_2O} c_{K^+}^* \exp(-\phi) \quad (19)$$

which is in accordance with the slopes found in Fig. 5.

Considering a faradaic current density  $\Delta i$  to be superimposed on the d.c. current density  $i_H$ , eqn. (19) may be rewritten as

$$i_H + \Delta i = nF k c_{H_2O} c_{K^+}^* \exp(-\phi) \exp\left(\frac{nF}{RT} \Delta E\right) \quad (20)$$

Expanding the term  $\Delta E$  as a Fourier series and retaining only first order terms, leads to

$$i_H + \Delta i = nF k c_{H_2O} c_{K^+}^* \left(1 + \frac{nF}{RT} \Delta E\right) \exp(-\phi) \quad (21)$$

Subtracting eqn. (20) from eqn. (21) yields

$$\Delta i = nF k c_{H_2O} c_{K^+}^* \exp(-\phi) \frac{nF}{RT} \Delta E \quad (22)$$

hence

$$\frac{\Delta E}{\Delta i} = \frac{RT}{n^2 F^2 k c_{H_2O} c_{K^+}^* \exp(-\phi)} = \frac{RT}{nF i_H} \quad (23)$$

after substituting with eqn. (19). As  $\theta$  is defined as a resistive term, eqn. (23) represents the expression for  $\theta$  corresponding to the suggested reactions in eqns. (16a) and (16b).

The values of  $\theta_2$  may now be calculated for potassium and sodium using eqn. (23). These values may be compared with the values derived from the intercepts of the  $Y_{e1}'$  vs.  $\omega^{\frac{1}{2}}$  plots. The relevant data are given as a function of potential for both potassium and sodium in Table 3. Evidently the values derived from the intercepts of the  $Y_{e1}'/\omega^{\frac{1}{2}}$  plots are minimum values, the results obtained from  $i_H$  being more precise.

It is interesting to compare  $k$ , as defined in the above reaction sequence, in the presence of potassium with  $k$  in the presence of sodium. This comparison is readily achieved in the following way. With an estimated diffusion coefficient  $D_R = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , eqn. (10) enables  $c_K$  and  $c_{Na}$  to be calculated. Thus for both metals  $kc_{H_2O}$  can be

TABLE 3

A COMPARISON OF THE VALUES OF  $\theta_2$  DERIVED FROM d.c. AND a.c. MEASUREMENTS

1 M KCl solution			1 M NaCl solution	
$E/V$ (SCE)	$\theta_2/\Omega \text{ cm}^2$ (d.c. data)	$\theta_2/\Omega \text{ cm}^2$ (a.c. data)	$\theta_2/\Omega \text{ cm}^2$ (d.c. data)	$\theta_2/\Omega \text{ cm}^2$ (a.c. data)
1.800	3700	3500	15500	560
1.825	3200	2400	6200	488
1.850	2300	1130	3040	210
1.875	1850	525	1120	125
1.900	1030	250	433	87
1.925	640	71	180	34
1.950	250	55	66	9
1.975	88	27	—	—

calculated from eqn. (17). In this way a ratio  $k_{\text{Na}}/k_{\text{K}} = 1.3$  is found.

A direct consequence of the present observations is the effect exerted by the water reduction on the determination of standard potentials of the alkali metals. These are usually investigated by measurement of the rest potential of a dropping alkali-amalgam electrode in contact with the corresponding alkali salt solution. From Fig. 6 it is clear that this potential is a so-called mixed potential  $E^m$ , which is more anodic than the Nernst potential  $E^n$  pertaining to the bulk concentration of  $\text{K}^+$  and  $\text{K}(\text{Hg})$ . This implies that from a simple potentiometric measurement, it is impossible to determine correctly the standard potential of the alkali metals.

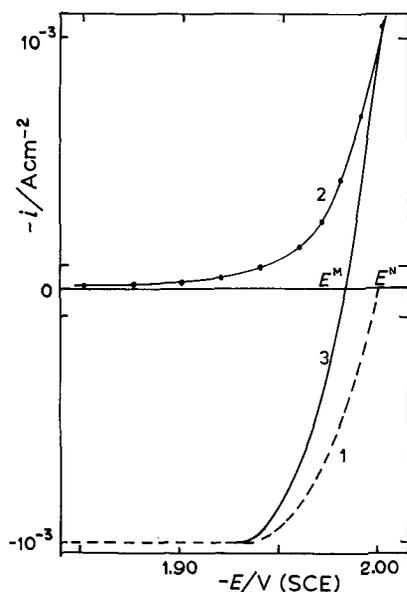


Fig. 6. The influence of a mixed current on the measurement of the Nernst potential ( $E^N$ ). Current vs. potential curves; (1) 5 mM  $\text{K}(\text{Hg})$  in contact with 1 M KCl calcd. from eqn. (12), (2) irreversible reaction due to water or  $\text{H}^+$  reduction, (3) composite current vs. potential curve.

The magnitude of the error in such a determination may be estimated as follows. From the value of  $\sigma_1$  at  $-2.00$  V the surface concentration of the alkali metal may be calculated. This is *ca.* 5.6 mM. If a homogeneous amalgam with this as the bulk concentration were brought into contact with a 1 M alkali salt solution in water, the current-voltage characteristic would approximate to the dotted curve in Fig. 6 (all calculations were made with an estimated diffusion coefficient  $D_R = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ). The shift in rest potential, as determined graphically, is 13 mV.

On the basis of the interpretation of our results an expression for the error may also be derived. If the alkali ion concentration  $c_O^*$  is large as compared to the alkali amalgam concentration  $c_R$ , the surface concentration  $c_O$  at  $E^m$  will be equal to  $c_O^*$ , but the surface concentration  $c_R$  at  $E^m$  will differ from  $c_R^*$ . Thus

$$E^m = E_0 + \frac{RT}{nF} \ln \frac{c_O^*}{c_R} \quad (24)$$

Since at the rest potential  $i_H = -i_{\text{alkali}}$ , a combination of eqns. (11) and (17), leads to

$$\frac{c_R^*}{c_R} = 1 + k c_{\text{H}_2\text{O}} \left( \frac{3\pi t}{7D_R} \right)^{\frac{1}{2}} \quad (25)$$

Consequently

$$\begin{aligned} E^m &= E_0 + \frac{RT}{nF} \ln \frac{c_O^*}{c_R^*} + \frac{RT}{nF} \ln \left\{ 1 + k c_{\text{H}_2\text{O}} \left( \frac{3\pi t}{7D_R} \right)^{\frac{1}{2}} \right\} \\ &= E^n + \frac{RT}{nF} \ln \left\{ 1 + k c_{\text{H}_2\text{O}} \left( \frac{3\pi t}{7D_R} \right)^{\frac{1}{2}} \right\} \end{aligned} \quad (26)$$

The value of the correction term is easily calculated by a proper combination of the value of  $i_H$  and  $\sigma_1$  (compare eqns. (10) and (17)). In our case it amounts  $17 \pm 2$  mV for sodium and  $13 \pm 2$  mV for potassium. Note that the term representing the error contains only constants, so that no improvement can be expected from the use of very dilute amalgams, opposite to what intuitively could be supposed.

The reasoning in the last two paragraphs provides several means of correcting for the error in potentiometric measurements introduced by the mixed current effect. First, eqn. (26) shows that  $E^n$  can be found by extrapolation to  $t=0$  of a  $E^m$  vs.  $\sqrt{t}$  plot, which should become linear at small drop times. Second, if impedance measurements are made at the rest potential, the actual surface concentration  $c_R$  can be calculated from eqn. (10) if  $D_R$  is known. After introduction of  $c_R$  into eqn. (24),  $E_0$  is readily calculated. Note that, if the alkali ions are not present in excess,  $c_O^*$  in eqn. (24) should be replaced by  $c_O$ . This is easily calculated from the relationship:

$$c_O D_O^{\frac{1}{2}} + c_R D_R^{\frac{1}{2}} = c_O^* D_O^{\frac{1}{2}} + c_R^* D_R^{\frac{1}{2}} \quad (27)$$

Finally, as a general conclusion it can be stated that carefully performed impedance studies are of great help and even essential in investigations of the technologically important processes involving the reduction of alkali ions in water and eventually other protic solvents.

#### ACKNOWLEDGEMENTS

The award of a European postdoctoral fellowship to one of us (R.M.R.) by the

Royal Society is gratefully acknowledged. This investigation was also supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO).

#### SUMMARY

The reduction of  $K^+$  and  $Na^+$  ions at the dropping mercury electrode in 1 M aqueous solutions of halide salts has been studied using d.c. polarography and electrode impedance measurements as a function of frequency and electrode potential. The results confirm that the reductions are reversible but that the primary reduction process is accompanied by an irreversible secondary process which seems likely to be reduction of water. The influence of this process on the analysis of the  $K^+$  wave is discussed. The implications of the observation of a coupled process are more generally discussed. In particular, it is concluded that potentiometric measurements of the standard potentials of alkali-amalgam/alkali ion redox couples are always in error because a mixed potential is observed instead of the Nernst potential. Two principally different correction procedures are suggested.

#### REFERENCES

- 1 D. C. GRAHAME, *J. Electrochem. Soc.*, 98 (1951) 34.
- 2 R. PARSONS AND A. STOCKTON, *J. Electroanal. Chem.*, 25 (1970) App. 10.
- 3 A. N. FRUMKIN, B. B. DAMASKIN AND N. V. NIKOLAEVA-FEDOROVICH, *Dokl. Akad. Nauk SSSR*, 115 (1951) 751.
- 4 A. N. FRUMKIN in J. O'M. BOCKRIS (Ed.), *Modern Aspects of Electrochemistry*, Vol. 3, Butterworths, London, 1965, chap. 2.
- 5 B. TIMMER, M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *J. Electroanal. Chem.*, 24 (1970) 287.
- 6 M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *Electrochim. Acta*, 11 (1966) 73.
- 7 H. IMAI AND P. DELAHAY, *J. Phys. Chem.*, 66 (1962) 1683.
- 8 M. SLUYTERS-REHBACH AND J. H. SLUYTERS in A. J. BARD (Ed.), *Electroanalytical Chemistry*, Vol. 7, Dekker, 1970.
- 9 B. G. DEKKER, M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *J. Electroanal. Chem.*, 23 (1969) 9.
- 10 R. M. REEVES, *Thesis*, University of Southampton, 1969.
- 11 I. M. KOLTHOFF, J. C. MARSHALL AND S. L. GUPTA, *J. Electroanal. Chem.*, 3 (1962) 209.
- 12 J. HEYROVSKÝ, *Principles of Polarography*, Academic Press, New York, 1966, p. 387.
- 13 P. DELAHAY, *J. Phys. Chem.*, 70 (1966) 2373.
- 14 A. N. FRUMKIN, V. KORSHANOV AND I. BAGOZKAYA, *Electrochim. Acta*, 15 (1970) 289.
- 15 R. M. REEVES, M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *J. Electroanal. Chem.*, 34 (1972) 69.
- 16 GMELIN, *Handbuch der Anorganischen Chemie*, No. 34, (1964).

*J. Electroanal. Chem.*, 34 (1972)