ELECTRODE PROCESSES AT MERCURY IN THE FAR CATHODIC POTENTIAL REGION

IV. INHIBITION OF THE K$^+$ REDUCTION BY ELECTROGENERATED HYDROGEN IN THE CASE OF MIXED KCl+HCl SOLUTIONS

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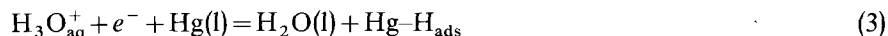
INTRODUCTION

The electrode process occurring at mercury in aqueous solutions of alkali metal salts, at the limit of cathodic polarization, has been described in previous parts of this series[1]. Under a variety of solution conditions, cation reduction was found to be accompanied by an irreversible parallel chemical reaction. This was due to the dissolution of the alkali metal amalgam formed during primary alkali metal reduction, *e.g.*
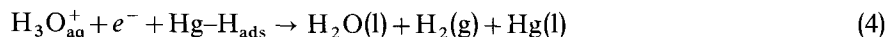
$$K^+ + Hg + e^- \rightarrow K(Hg) \tag{1}$$

$$K(Hg) + H_2O \rightarrow H + K^+ + OH^- \tag{2a}$$

$$2H \rightarrow H_2 \tag{2b}$$

The primary process tended to be reversible for K$^+$ and Na$^+$ while the Li$^+$ reduction was significantly less reversible. The influence of pH ($7.0 \leqslant$ pH $\leqslant 14$) on the K$^+$ reduction was investigated but no significant change in the reaction mechanism was observed. The reaction was found to be generally independent of the anion employed.

The primary aim of the present work is to study the cation reduction process in KCl solutions in the pH range $7.0 \geqslant$ pH $\geqslant 2.31$, the acidity being maintained by use of HCl. *A priori*, this study must involve the reactions described by eqns. (1) and (2) and the hydrogen evolution reaction (HER) on mercury. A large number of reviews have been devoted to the controversial HER since the first quantitative studies were made by Tafel[2].

Although there is no general agreement as to the reduction mechanism on mercury, most workers seem to favour[3,4]

$$H_3O^+_{aq} + e^- + Hg(l) = H_2O(l) + Hg\text{--}H_{ads} \tag{3}$$

as being the slowest stage in the HER in acid solution. The argument for this mechanism is based on a lack of measurable hydrogen coverage. In this case the desorption of H_{ads} occurs at least as rapidly as the process in eqn. (3), through the following:

$$H_3O^+_{aq} + e^- + Hg\text{--}H_{ads} \rightarrow H_2O(l) + H_2(g) + Hg(l) \tag{4}$$

or

$$2Hg\text{--}H_{ads} \rightarrow 2Hg(l) + H_2(g) \tag{5}$$

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In at least one recent study[5] it has been shown that desorption does not seem to keep pace with eqn. (3), the imbalance resulting in diffusion of hydrogen atoms into the mercury possibly to form an amalgam as suggested by Heyrovsky[6]. Irrespective of the mechanism involved, the HER on mercury is an irreversible process and may be treated simply in admittance calculations[7].

In order that comparison could be made with previous studies, the K^+ concentration was maintained at $1\ M$.

EXPERIMENTAL

The experimental methods employed have been described elsewhere[1]. The real and imaginary components of the admittance, Y'_{el} and Y''_{el}, were calculated from the measured values of equivalent capacitance and resistance. Where necessary, the shielding effect of the dropping mercury electrode (DME) was corrected for by using the value of the solution resistance as measured at each frequency outside the faradaic region[8]. Capillaries with significant frequency dispersion of the capacitance were not employed. The potential of the DME was measured against a saturated calomel electrode. The solution was deoxygenated using presaturated purified nitrogen. AnalaR KCl and HCl were employed. Water was freshly distilled from alkaline permanganate. The acid solutions were made by dilution of a stock solution of HCl in $1\ M$ KCl. The acid concentration was varied in this way between 10^{-7} and $4.87 \times 10^{-3}\ M$ in nine steps as shown in the results. The maximum acid concentration was controlled by the necessity of obtaining precise results at $E < -1.900\ V$. The stock solution was standardised by acid base titration. During measurement of the a.c. and d.c. data, the acid concentration was continuously monitored using a Metrohm pH electrode repeatedly standardised with freshly prepared (pH = 6.50) buffer.

The theoretical background to this study has been discussed in previous publications[1]. The relevant features will be introduced when necessary in subsequent discussion.

RESULTS

Significant impedance data were recorded at $E > -2.000$ V. The accessible potential range depended upon the acid concentration and on the capillary. Data at $E < -1.975$ V were only accessible to precise measurement at $[H^+] < 7.3 \times 10^{-4}\ M$. In all cases, the admittance was determined at five or more potentials in the potential region $E < -1.900$ V. D.c. polarograms were recorded for the potential region, $-1.500 > E > -2.000$ V, for all solutions studied. The potential of the working electrode, when not controlled potentiostatically, was corrected for the IR drop using the d.c. data and the a.c. solution resistance. This correction was made prior to the admittance analysis. The subsequent discussion will be concerned with the data derived at $E \leqslant -1.900$ V.

The impedance data were transformed into the admittance components and were inspected, in the first instance, as plots of the real component, Y'_{el}, vs. the square root of the angular frequency, $\sqrt{\omega}$, at each potential studied. These plots were linear within experimental error. Extrapolation of these plots to $\sqrt{\omega} = 0$ yielded positive intercepts on the ordinate at all potentials studies.
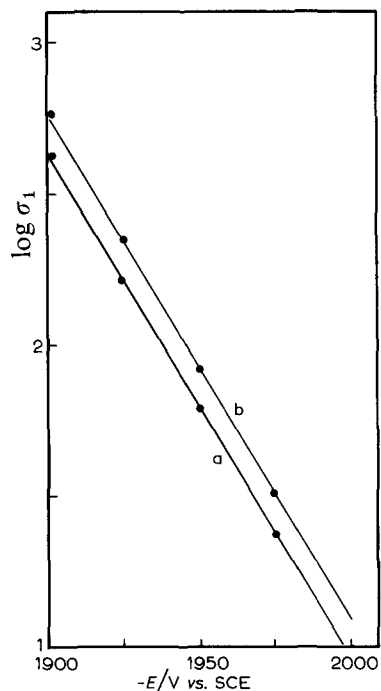
Fig. 1. Plot of log σ_1 vs. electrode potential at hydrogen ion concn. [H$^+$] (a) 10^{-7}, (b) 4.87×10^{-3} M.

The real part of the admittance in this system is given by:

$$Y'_{el} = \frac{\sqrt{\omega}}{\sigma_1} \frac{p+1}{p^2+2p+2} + \frac{1}{\theta_2} \tag{6}$$

where $p = \theta_1/\sigma_1 \omega^{-\frac{1}{2}}$, with p the irreversibility coefficient, θ_1 the charge transfer resistance and σ_1 the Warburg coefficient of the potassium reaction, and θ_2 the charge transfer resistance of the parallel irreversible reaction which, as has been shown in previous studies, is associated with the potassium reaction. The admittance due to the HER was under all conditions negligible with respect to that of the K$^+$ reduction. At high acid concentrations, the K$^+$ reduction occurred in the limiting current region of the HER. As the acid concentration is lowered, the peak admittance of the HER moves into the K$^+$ reduction region, but at the same time its value decreases so that it remains negligible.

The linearity of the plots of Y'_{el} vs. $\sqrt{\omega}$ suggests that the value of p in eqn. (6) is small. The slopes of these lines yield directly σ_1. The resultant values of σ_1 are plotted in the form log σ_1 vs. E in Fig. 1. The data are shown only for the extremes of acid concentration, [H$^+$] = 10^{-7} and [H$^+$] = 4.87×10^{-3} M. The lines are parallel with a slope of -16.6 V^{-1}. This slope agrees with the theoretical potential dependence of the Warburg coefficient which, at $E \gg E_0$ when only the oxidised species is present, is given by[9]:

$$\sigma_1 = \frac{RT}{n^2 F^2 c_O^* (2D_O)^{\frac{1}{2}}} \exp\left[\frac{nF}{RT}(E - E_{\frac{1}{2}}^r)\right] \tag{7}$$

where $E_{\frac{1}{2}}^{r}$ is the reversible half wave potential. This corresponds to a theoretical slope of -16.6 V^{-1}, for the slope of the log σ_1 vs. E plot. When the σ_1 values obtained at other acid concentrations were plotted in the form of Fig. 1, but on a large scale, a series of parallel lines was obtained all of which displayed the same slope, -16.6 V^{-1}. These lay in between the extreme lines shown in Fig. 1. This phenomenon will be discussed below.

According to eqn. (6), the intercept of the plot, Y_{el}' vs. $\sqrt{\omega}$ on the ordinate at $\sqrt{\omega}=0$ is equivalent to $1/\theta_2$. As observed previously, the precise magnitudes of these intercepts are subject to error, especially at more negative potentials. More precise values of θ_2 can be obtained in the following way:

For the potassium wave, the d.c. current, i_K, due to the potassium reaction, can be calculated from σ_1 using[1]:

$$i_K = -(7/6\pi t)^{\frac{1}{2}}(RT/nF\sigma_1) \tag{8}$$

where t is the drop time of the DME. In previous studies, the existence of θ_2 was proved[1]. This corresponds to a d.c. current, i_H, due to the irreversible reaction, cf. eqn. (2), given by:

$$\theta_2 = -RT/\beta nF \, i_H \tag{9}$$

where β is the cathodic transfer coefficient.
The total d.c. current, i_t, of the potassium wave will be the sum of i_K and i_H,

$$i_t = i_H + i_K \tag{10}$$

This total wave is superimposed on the wave due to the HER itself. At all except the lowest acid concentration, the hydrogen ion concentration was such as to provide a limiting current on the hydrogen wave in the d.c. polarograms. This occurred before
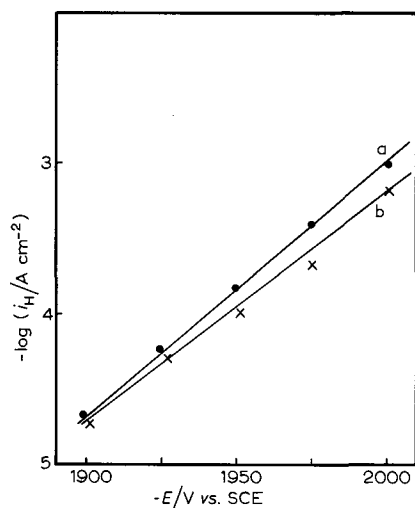

Fig. 2. Plots of log i_H vs. potential for hydrogen ion concn. (a) 10^{-7}, (b) 4.87×10^{-3} M.
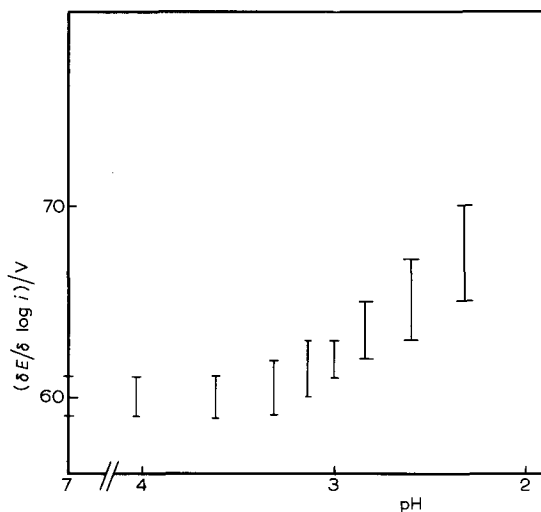
Fig. 3. Plots of slopes in Fig. 2 vs. pH.

the onset of the potassium wave. By extrapolating this limiting current into the potassium wave region, a baseline was obtained for the potassium wave.

As i_t is now known and i_K may be calculated from eqn. (8), i_H may now be derived from eqn. (10) and hence θ_2 may be calculated from eqn. (9). The logarithmic plots of the current component i_H are shown as a function of E for the extremes of acid concentration, $[H^+] = 10^{-7}$ and 4.87×10^{-3} M, in Fig. 2. The plots are linear at both concentrations. The lines are not parallel but evidently the hydrogen current decreases as the bulk hydrogen ion concentration increases. As a direct relationship between the potassium current and the hydrogen current has been established[1], the shift in the lines in Fig. 2 can obviously be correlated with the shift in the log σ_1 vs. E plots in Fig. 1.

Plotting the data for θ_2 on a large scale for the various pH values in the form of log i_H vs. E, results in a series of lines which lie within the lines at $[H^+] = 10^{-7}$ and 4.87×10^{-3} M and show a systematic deviation from the line at pH 7. The slopes of the lines are shown in the form $\partial E/\partial \log i_H$ as a function of pH in Fig. 3. The slope of the plot, log i_H vs. E, at pH 7 agrees with the data previously obtained for KCl solutions[1]. The value of the slope in acidic solutions agrees closely with the value obtained for KOH media. The slopes, however, still deviate from the value usually found for the HER in acidic solutions 0.120 V. From these observations, it can be concluded that in 1 M KCl under acidic conditions, as in all systems previously studied[1], a significant contribution is due to the irreversible parallel amalgam dissolution reaction.

The small values of p in eqn. (6), as inferred from the linearity of the Y'_{el} vs. $\sqrt{\omega}$ plots, suggests that no further information regarding the potassium charge transfer resistance can be derived from the real part of the admittance. It was shown earlier[1], that the imaginary part of the admittance, Y''_{el}, is more sensitive to the value of p. This imaginary component is given by:

$$Y''_{el} = \frac{\sqrt{\omega}}{\sigma_1} \frac{p+1}{p^2+2p+2} + \omega C \tag{11}$$

where C is the double layer capacity. In order to utilise this equation, it is necessary to assume that the double layer capacity is frequency independent in the faradaic region and that there is no coupling of the double layer and faradaic parameters. During earlier studies of these systems, no peculiarities were found in the values of the double layer capacity calculated using eqn. (11).

The influence of the frequency dispersion of the capillary on this calculation is important. In this case, the frequency dispersion of the solution resistance has been subtracted, and capillaries displaying frequency dispersion of the capacitive component were rejected. The choice of the best value of p' and the associated values of the double layer capacity, was recently discussed[1]. The capacity was calculated directly from eqn. (11) using graphical values of σ_1 and a range of values for $p' = p\omega^{-\frac{1}{2}}$. The procedure adopted previously has been extended to this study[1]. The largest values of p' which yielded frequency independent values of capacity were chosen. The value of both p' and C are shown in Table 1 as a function of pH and potential. The capacities agreed, at constant potential at all values of pH, within experimental error. The observed values of p' are generally in the range $10^{-3} < p' < 3 \times 10^{-3}$ but do not display systematic potential dependence. This implies that it is not possible to use these values of p' to calculate α, the anodic transfer coefficient, and hence k_{sh}, the rate

TABLE 1

VALUES OF THE DOUBLE LAYER CAPACITY AND p'

$-E/V$ (vs. SCE) pH	a	1.800	1.825	1.850	1.875	1.900	1.925	1.950	1.975
7.0	1	23.9	24.5	25.2	26.3	26.3	28.5	30.1	33
	2	1.5	2.0	1.0	1.5	2.0	1.5	2.0	1.0
4.01	1	23.3	24.3	25.2	25.8	26.5	27.5	31.1	34
	2	1.0	1.5	1.0	1.0	0.5	1.5	2.0	2.0
3.61	1	23.8	24.6	25.3	26.4	26.8	27.8	29.1	35
	2	1.5	1.0	0.5	1.0	1.5	1.5	1.5	1.0
3.31	1	23.7	24.2	25.1	26.3	27.5	27.9	29.8	38
	2	2.0	1.5	1.0	1.0	1.0	1.0	2.0	1.0
3.14	1	23.6	24.4	25.3	26.2	27.2	28.3	30.2	37
	2	2.0	1.5	1.0	1.0	1.0	1.0	2.5	2.0
3.01	1	23.3	24.2	24.0	26.0	27.5	28.0	31.2	35
	2	1.5	2.0	1.5	1.0	1.0	1.0	1.5	1.5
2.83	1	23.3	24.1	24.1	26.0	26.8	27.3	28.9	32
	2	1·5	1.0	1.0	1.5	0.5	1.5	1.0	2.0
2.61	1	23.2	24.1	25.1	26.2	27.1	28.9	30.4	33
	2	2.0	1.0	0.5	1.5	1.0	1.0	1.0	1.5
2.31	1	23.4	24.2	24.9	25.9	27.9	28.7	30.2	37
	2	1.5	1.5	2.0	1.5	2.5	1.0	1.5	2.0
Errors[b]		0.3	0.3	0.6	0.8	1.5	3.5	7.4	19

[a] (1) value of the double layer capacity in $\mu F\ cm^{-2}$. (2) Maximum value of p' ($\times 10^{-3}$) which yielded a frequency independent double layer capacity.
[b] Error in the double layer capacity at 800 Hz calcd. assuming a 1 Ω error in the measured soln. resistance and a 1 % error in the measured capacity. Values in $\mu F\ cm^{-2}$.

constant for the potassium reduction reaction in this system. This observation agrees closely with observations in KOH media.

DISCUSSION

The first of the conclusions to this study deals with the potassium reaction and the second with the total system including the HER. The potassium reaction in acidic media appears to be accompanied by a second irreversible reduction process. This agrees with observations in earlier studies where it was interpreted as being due to the chemical reaction of the amalgam, formed during the potassium reduction, with water. While the magnitude of the values changes with pH, both the d.c. currents i_K and i_H are related. In KCl in neutral aqueous solutions, their ratio was somewhat potential independent (0.75) but in KOH solutions a value of βn less than unity was found. This resulted in a significant potential dependence of the ratio i_H/i_K, 0.48–1.00. For this study, the value for neutral KCl was 0.76 and potential independent. The values for the more acidic solutions were lower and showed significant potential dependence, cf. Table 2. This behaviour is to be expected in view of the pH dependence of the slope of the lines in Fig. 2. The pH dependence of these slopes must, however, be considered in terms of possible errors involved in the determination of i_K and i_H. According to eqns. (8) and (10) these errors depend on the degree of precision in

TABLE 2

VALUES OF THE RATIO i_H/i_K

pH \ $-E/V$ (vs. SCE)	1.900	1.925	1.950	1.975
7.0	0.73	0.77	0.77	0.78
4.01	0.73	0.77	0.77	0.81
3.61	0.74	0.78	0.78	0.78
3.31	0.71	0.77	0.79	0.74
3.14	0.72	0.78	0.76	0.70
3.01	0.72	0.78	0.76	0.66
2.83	0.75	0.82	0.72	0.63
2.61	0.78	0.86	0.74	0.36
2.31	0.93	0.86	0.60	0.31

measuring i_t and σ_1. The errors in the Warburg coefficients were estimated by assuming a 1 Ω error in solution resistance and a 1% error in the measured capacity, cf. Table 1. At 800 Hz, in the potential range $-1.900 \geqslant E \geqslant -1.975$ V, the probable error was less than 3%. This error could not possibly account for the changes observed. The current component, i_K, was derived from the d.c. polarographic wave by subtracting from the total d.c. current the limiting current of the HER. It was necessary to extrapolate this latter current into the potential region of the potassium wave. The possible error in this limiting current extrapolation will decrease at lower pH values as the separation of the potassium and hydrogen waves increases. The change in βn, and consequently in the ratio i_K/i_H, seems to be a real feature of the system.

One of the most surprising results of this study is the shift in the log σ_1 vs. E plots and, correspondingly, in the log i_H vs. E plots with decreasing pH. The simplest probable explanation of this might be found in terms of the liquid potential between the solutions: KCl 1 M/KCl 1 $M + x$ mM HCl.

A cathodic potential displacement in Figs. 1 and 2 might account for the shifts. Such a horizontal displacement would amount to 8 mV and could arise from the differing cation mobilities in the system. The significance of this contribution was further investigated by studying the pH dependence of the half wave potential of 2 mM Cd^{2+} in 1 M KCl using a 1 M KCl bridge to a saturated calomel electrode. The d.c. polarographic waves were entirely superimposable up to a hydrogen ion concentration of 13 mM which indicates that the presence of a liquid junction cannot be inferred to explain the observation.

The other possibility must therefore be considered, viz. to interpret the shift as a vertical displacement; in other words, at any given potential σ_1 and θ_2 increase as the pH decreases. This is visualised in Figs. 4 and 5 where, for selected potentials, σ_1 and θ_2 are plotted as a function of pH. Generally, it may be inferred that, due to the presence of HCl in the system, the degree of K$^+$ diffusion is reduced and that, as a consequence, the coupled amalgam decomposition reaction is similarly changed.

The change in σ_1 could be interpreted as being due to a change in the diffusion coefficients. However, the observed change in σ_1, 25%, would require an unreasonable change, 50%, in the diffusion coefficient. This, in turn, would require a similar change in the viscosity of the solution or in the solvation of the cation. The alternative and more reasonable explanation is that a change in the available surface area of the elec-
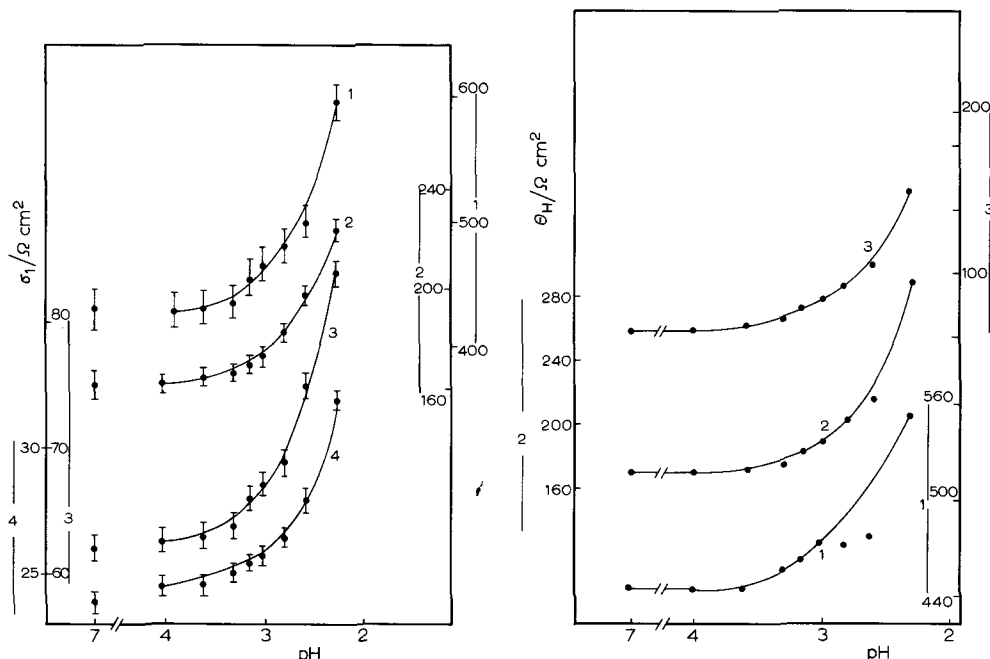
Fig. 4. Plots of σ_1 vs. pH at E: (1) –1.900, (2) –1.925, (3) –1.950, (4) –1.975 V.

Fig. 5. Plots of θ_H calcd. from eqn. (9) vs. pH at E: (1) – 1.925, (2) – 1.950, (3) – 1.975 V.

trode and not a solvent property is responsible for the effect. It is thus necessary to introduce the concept of blocking of the electrode surface available to the potassium reaction by the hydrogen evolution reaction.

The change in σ_1 with hydrogen ion concentration, may be related to a surface coverage factor, S_H. This term would represent the fraction of the electrode blocked by the HER and could be defined by:

$$S_H = \left(\sigma_1^{pH=x} - \sigma_1^{pH=7.0}\right)/\sigma_1^{pH=x} \tag{12}$$

This can be calculated directly from the data in Fig. 2, and S_H is shown as a function of acid concentration in Fig. 6. A linear dependence on acid concentration seems to result. In an earlier publication, a relationship between i_K and θ_2, (i_H), was derived. The decrease in the potassium reduction reaction is parallelled by a similar decrease in amalgam dissolution reaction as may be seen from Fig. 5. It is therefore possible to reformulate the surface coverage in terms of θ_2,

$$S_H = \left(\theta_2^{pH=x} - \theta_2^{pH=7.0}\right)/\theta_2^{pH=x} \tag{13}$$

These values are also shown in Fig. 6. They lie somewhat higher in general than the values derived from eqn. (12). This is a result of the non- parallelism of the plots in Fig. 3. The general nature of these results is complementary and shows significant electrode blockage by the HER.

This result seems to be in direct contradiction with the data reviewed by Frumkin[4] in 1961. He concluded that no experimental evidence had been found for

the presence of adsorbed hydrogen ions on the surface of cathodically polarised mercury. No pseudo-capacity or deviation from expected behaviour was observed in 1 M H_2SO_4 up to an overvoltage of 1.3 V. Although most studies in intervening years have tended to confirm this conclusion, in a small number of cases deviations from the expected behaviour have been found. These data have not been derived, as was most of the earlier data, from overpotential determinations. In the most precise work to date,
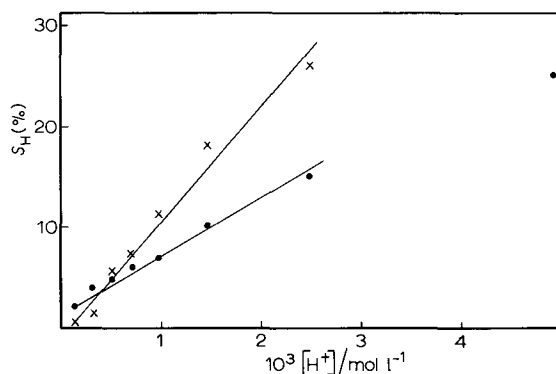

Fig. 6. Degree of surface coverage $vs.$ bulk hydrogen ion concn. Data derived from ($\bullet$) σ_1, ($\times$) θ_2.

Smith and Heintze[5] found that the electrolytic yield, by measurement of volume changes during electrolysis of HCl, was considerably less than 100 %. The experimental yield was 40–83 %, seemingly dependent on the current density employed. The authors suggested that the desorption rate, eqns. (4) and (5), was slower than the reaction rate, eqn. (3), under their conditions. They suggested a parallel reaction to these three, the diffusion of hydrogen atoms into the mercury:

$$Hg\text{–}H_{ads} \rightarrow H_{abs}(\text{in mercury}) + Hg \tag{14}$$

This would be dependent on the hydrogen current. If this step had a rapid equilibrium, S_H could be potential independent as we have observed, and the coverage could be maintained by constant out-diffusion from the metal. Such a process would not produce a pseudo-capacity and would agree with our observations of a pH and frequency independent double layer capacity.

    In conclusion, the precise mechanism that causes the electrode blocking is not at this stage clear. These new data support the proposals of Smith and Heintze without fully confirming them. The simplest way to explain the effect is coverage of the electrode by hydrogen gas. Further d.c. studies of this effect are at present in progress in this laboratory.

ACKNOWLEDGEMENTS

SUMMARY

    The reduction of K^+ from 1 M KCl solution was studied in the presence of HCl at concentrations $0-5 \times 10^{-3}$ M. The primary K^+ reduction process is reversible at all values of pH within the limitations of the measuring technique. The primary process is accompanied by a parallel irreversible reaction due to an amalgam dissolution reaction. The characteristics of this process were similar at all values of pH to systems previously studied. An increase in the Warburg coefficients of the potassium ion reduction with decreasing pH was observed. The only plausible explanation was considered to be the blocking of the electrode by a product of the hydrogen ion reduction. The parallel amalgam decomposition reaction was similarly impeded. These results are compared briefly with previous studies of hydrogen ion reduction.

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