

## ON THE IMPEDANCE OF GALVANIC CELLS

XXV. THE DOUBLE-LAYER CAPACITANCE OF THE DROPPING MERCURY ELECTRODE IN 1 M HCl, 7.5 M HCl AND 5.2 M HClO<sub>4</sub> AND THE KINETIC PARAMETERS OF THE HYDROGEN ELECTRODE REACTION AS A FUNCTION OF TEMPERATURE IN THESE SOLUTIONS

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### INTRODUCTION

One of the interesting problems in electrochemistry is the theoretical interpretation of the kinetic parameters of electrode reactions. The most studied subject in this respect is probably the hydrogen evolution reaction on mercury. For example, the relation between overvoltage and double-layer structure has been investigated by Frumkin<sup>1</sup>, and various attempts have been made to assess a scheme for the reaction mechanism (for a review, see Vetter<sup>2</sup>). Parsons and Bockris<sup>3</sup> have given a calculation of the theoretical energy of activation based on the model of the so-called discharge reaction<sup>2</sup>, the result of which compares favourably with experimental values. From this and also from other work<sup>4-10</sup> it appears worthwhile to study the temperature-dependence of the exchange current density,  $i_0$ , and the transfer coefficient,  $\beta$ .

Unfortunately, the inconsistencies of the abundance of experimental data<sup>11</sup> available for the hydrogen electrode make it difficult to draw decisive conclusions. Also, anomalous results are often reported, and need further investigation. Most of this work has been concerned with the determination of the Tafel<sup>12</sup> parameters by direct current methods.

As part of a general programme for the study of the effect of temperature on the parameters of electrode reactions, and the properties of the electrode-solution interface, we investigated the impedance of the dropping mercury electrode in concentrated acid solutions at different temperatures. The advantage of the impedance method is that it contains information both on the electrode reaction and the double-layer capacitance, even in the potential region where the faradaic process occurs<sup>13,14</sup>. As the rate of an electrode reaction is closely related to the structure of the double layer, this may be a valuable parameter.

Moreover, the H<sup>+</sup>/H<sub>2</sub>(Hg) reaction appears to be a suitable system for the demonstration of the applicability of the impedance method to the study of irreversible systems, as postulated recently<sup>15</sup>.

In this paper, we report the results of measurements in aqueous 1 M HCl, in the eutectic mixtures of composition, 7.5 M HCl, and 5.2 M HClO<sub>4</sub>. The eutectic compositions were chosen because they have very low freezing points.

A critical discussion will be given in the light of the existing literature, especially as regards the temperature-dependence of the transfer coefficient, which for 7.5 M HCl was observed by Bockris and Matthews<sup>10</sup> to be anomalous.

## EXPERIMENTAL

The cell consisted of two sections, one for the dropping mercury electrode (cathode) and a mercury pool counter electrode (anode), and the other for a reversible hydrogen reference electrode. The latter consisted of a short piece of coiled platinum wire coated with platinum black. The two compartments were connected by a short capillary, the top of which was near the DME. The whole system was saturated with hydrogen gas, which was deoxygenated (by passing it through a column filled with reduced copper oxide in a very active form, BTS-Katalysator, BASF at a temperature of 50°) and then equilibrated with a solution of the same composition and temperature as in the measuring cell.

Care was taken to eliminate impurities from the solutions: reagent-grade HCl and HClO<sub>4</sub> were used, and water was distilled twice, successively from acid and alkaline permanganate solution. The mercury was doubly-distilled.

All glassware was cleaned with dichromic acid and steamed out for a few hours. Immediately before use it was rinsed with doubly-distilled water.

For some experiments, the solution was pre-electrolyzed overnight at 5 mA/cm<sup>2</sup> using an auxiliary Pt cathode which was removed shortly before the measurements. However, as we found no difference in the results for the same experiment with and without pre-electrolysis, this was omitted.

The impedance measurements were carried out at potentials as far cathodic as possible, *i.e.*, until the rapid evolution of hydrogen bubbles disturbed the regular dropping of the mercury, which was mechanically controlled. The impedance and d.c. potential measurements were made with the a.c. bridge and additional set-up as described elsewhere<sup>13</sup>.

A special provision was made for temperature control. The cell was surrounded by two jackets; the outer jacket was evacuated, and through the inner one methanol or water was circulated from a cryostat or thermostat, depending on the temperature range desired. In this way the accuracy was better than 0.1°.

## RESULTS

*Interpretation of impedance measurements*

Since the H<sup>+</sup>/H<sub>2</sub>(Hg) electrode reaction is extremely irreversible, polarization to fairly negative potentials is required to obtain a substantial faradaic current, both for d.c. and a.c. At more positive potentials, the measured impedance yielded directly the values of the ohmic resistance,  $R_{\Omega}$ , and the double-layer capacity,  $C_d$ . In the faradaic region itself, the components  $Z'$  and  $Z''$  of the cell impedance were determined as a function of frequency (420–3000 Hz) and analyzed according to the complex plane method<sup>13,14</sup>. As in our present investigations the double-layer capacitance is not *a priori* known (no indifferent electrolyte added), the so-called frequency variation method had to be applied, *i.e.*, we considered the frequency-dependence of the components  $Y'_{el}$  and  $Y''_{el}$ , of the electrode admittance, calculated from

$$Y'_{el} = \frac{Z' - R_{\Omega}}{(Z' - R_{\Omega})^2 + Z''^2} \quad (1a)$$

$$Y''_{el} = \frac{Z''}{(Z' - R_{\Omega})^2 + Z''^2} \quad (1b)$$

In all cases,  $Y'_{el}$  and  $Y''_{el}/\omega$  were independent of frequency, indicating that diffusion polarization is negligible, as would be expected for the  $H^+/H_2(Hg)$  electrode at the foot of the reduction wave. Thus, the impedance data enable the calculation<sup>16</sup> of the transfer resistance,  $\theta = 1/Y'_{el}$ , and the double-layer capacitance,  $C_d = Y''_{el}/\omega$ .

*Potential-dependence of the transfer resistance*

A general equation for the potential-dependence of  $\theta$  has been given by Timmer *et al.*<sup>16</sup>. Since in the present case  $E \ll E_O$ , the simplified equation may be considered:

$$\theta = \frac{RT}{n^2 F^2 k_{sh}^a} \cdot \frac{a_O + \exp [ - (\beta n F / RT)(E - E_O) ]}{\beta a_O C_O^* \exp [ - (\beta n F / RT)(E - E_O) ]} \quad (2)$$

in which  $C_O^*$  is the  $H^+$  concentration,  $k_{sh}^a$  the apparent standard heterogeneous rate constant,  $\beta$  the cathodic transfer coefficient and  $a_O = (7D_O/3\pi t)^{1/2} k_{sh}^{-1}$  for a DME. If  $k_{sh}$  is sufficiently small,  $a_O \gg \exp [ - (\beta n F / RT)(E - E_O) ]$ , leading to

$$\theta = \frac{RT}{n^2 F^2 k_{sh}^a \beta C_O^*} \exp \left[ \frac{\beta n F}{RT} (E - E_O) \right] \quad (3)$$

For a comparison with literature data it is more convenient to count the potential,  $E$ , from the reversible equilibrium potential,  $E_{eq}$ , and to consider values of  $i_O$ , the exchange current density, at  $E_{eq}$ :

$$i_O = n F k_{sh}^a C_O^{*\alpha} C_R^{*\beta} \quad (4)$$

With eqn. (4) and  $E - E_{eq} = \eta$ , eqn. (3) can be transformed into

$$\theta = \frac{RT}{n F \beta i_O} \exp \frac{\beta n F}{RT} \eta \quad (5)$$

or

$$\ln \theta = \ln \frac{RT}{n F \beta i_O} + \frac{\beta n F}{RT} \eta \quad (6)$$

As in all cases of the present study  $\log \theta$  *vs.*  $\eta$  plots were linear, it can be concluded that the conditions for eqn. (3) are fulfilled. The values of  $\beta$  and  $i_O$  can be calculated from the slope and the intercept of such a plot. The slope is, in fact, the reciprocal of the Tafel<sup>12</sup> parameter,  $b$ .

*Temperature-dependence of  $i_O$  and  $\beta$*

*i.* 1 M HCl. The measurements with this solution were carried out at 0°, 15°, 25° and 45°. At each temperature,  $\theta$  was determined at about 10 potentials in a range of about 200 mV. The value of  $\theta$  never exceeded 1000  $\Omega$  cm<sup>2</sup> (higher values cannot be determined accurately<sup>13</sup>). The reproducibility was good. The equations of the  $\log \theta$  *vs.*  $\eta$  plots were assessed by the method of least squares. The results are presented in Table 1, together with the values for  $\beta$  and  $\log i_O$ . The averaged errors are,  $\pm 0.02$  in  $\beta$  and  $\pm 0.30$  in  $\log i_O$ .

In order to make a direct comparison with d.c. measurements, a Tafel line was also recorded at 25°. The result was in excellent agreement with that of the impedance method, confirming the applicability of the latter. Our results are in reasonable agree-

ment with those of Jofa and Stepanova<sup>5</sup> ( $\log i_0 = -11.7$  and  $\beta = 0.49$  at  $20^\circ$ ) and of De B ethune<sup>17</sup> ( $\log i_0 = -11.53 \pm 0.05$  and  $\beta = 0.50$  at  $25^\circ$ ).

An important conclusion from Table 1 is that the transfer coefficient does not vary significantly with temperature in the range investigated. This is in agreement with the experience of Jofa and Stepanova<sup>5</sup> and also of Post and Hiskey<sup>8</sup> for  $0.1 M$  HCl, although the latter authors observed above  $35^\circ$  an increase in  $\beta$  from 0.50 to

TABLE 1  
DATA FOR  $1.0 M$  HCl

Temp. (°C)	Eqns. of $\log \theta$ vs. overpotential, $\eta$ ( $\theta$ in $\Omega \text{ cm}^2$ , $\eta$ in volts)	$\beta$	$\log i_0$ ( $i_0$ in $A \text{ cm}^{-2}$ )
0	$\log \theta = 12.30 + 9.59 \eta$	0.52	-13.65
+15	$\log \theta = 11.74 + 9.36 \eta$	0.53	-13.08
+25	$\log \theta = 10.68 + 8.64 \eta$	0.51	-11.98
+45	$\log \theta = 9.99 + 8.43 \eta$	0.53	-11.28

0.55 at  $91.3^\circ$ . However, Bockris and Parsons<sup>7</sup> reported a significant temperature-dependency of  $\beta$ , for  $0.1 M$  HCl solution. As these authors found identical Tafel lines for HCl solutions on changing the acid concentration from  $0.01 M$  to  $1 M$ , a comparison with our results seems to be justified and the disagreement has to be considered.

The apparent heat of activation at the reversible potential,  $\Delta H$ , can be obtained from a plot of  $\log i_0$  vs.  $1/T$ . Figure 1 shows that our plot for  $1 M$  HCl (curve 1)

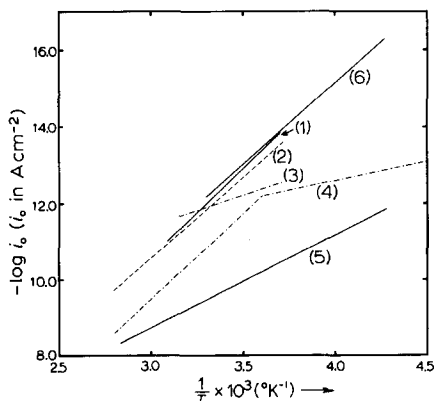


Fig. 1. Dependence of  $i_0$  on temp.: (1),  $1.0 M$  HCl (this work); (2),  $0.1 M$  HCl (Post and Hiskey<sup>8</sup>); (3),  $0.1 M$  HCl (Bockris and Parsons<sup>7</sup>); (4),  $7.5 M$  HCl (Bockris and Matthews<sup>10</sup>); (5),  $7.5 M$  HCl (this work); (6),  $5.2 M$  HClO<sub>4</sub> (this work).

agrees satisfactorily with that derived from the data of Post and Hiskey<sup>8</sup> for  $0.1 M$  HCl (curve 2). The  $\Delta H$ -values are  $21.1 \pm 2.0 \text{ kcal mole}^{-1}$  for curve 1 and  $19.3 \text{ kcal mole}^{-1}$  for curve 2. A similar treatment of the data of Bockris and Parsons<sup>7</sup>, however, produces a deviating plot (curve 3) with a  $\Delta H$ -value of  $7.2 \text{ kcal mole}^{-1}$ . On the other hand, the authors report an apparent heat of activation of  $21.1 \text{ kcal mole}^{-1}$ , calculated from  $(\partial \eta / \partial T)_i$  in a way which theoretically should give the same result as the calcula-

tion from Fig. 1. The discrepancy is caused by the temperature-dependency of  $\beta$ , found by Bockris and Parsons and which, in our opinion, is incorrect.

ii. *7.5 M HCl*. The measurements in *7.5 M HCl* have been made in a temperature range,  $-35^\circ$  to  $+72^\circ$ . The equations for the  $\log \theta$  vs.  $\eta$  lines, the values of  $\beta$ , and of  $\log i_0$  are given in Table 2. The averaged errors are,  $\pm 0.01$  in  $\beta$  and  $\pm 0.20$  in  $\log i_0$ . Again, an excellent agreement was found with a d.c. Tafel line recorded at  $25^\circ$ .

TABLE 2

DATA FOR 7.5 M HCl

Temp. (°C)	Eqns. of $\log \theta$ vs. overpotential, $\eta$ ( $\theta$ in $\Omega \text{ cm}^2$ , $\eta$ in volts)	$\beta$	$\log i_0$ ( $i_0$ in $A \text{ cm}^{-2}$ )
-35	$\log \theta = 10.39 + 8.24 \eta$	0.389	-11.66
-25	$\log \theta = 9.96 + 8.14 \eta$	0.400	-11.23
-15	$\log \theta = 9.30 + 7.78 \eta$	0.398	-10.55
-5	$\log \theta = 9.42 + 8.21 \eta$	0.436	-10.70
+5	$\log \theta = 9.10 + 8.19 \eta$	0.452	-10.38
+10	$\log \theta = 8.74 + 7.97 \eta$	0.447	-10.00
+15	$\log \theta = 8.61 + 7.97 \eta$	0.455	-9.88
+20	$\log \theta = 8.50 + 7.99 \eta$	0.464	-9.77
+25	$\log \theta = 8.53 + 8.17 \eta$	0.483	-9.80
+35	$\log \theta = 8.06 + 8.03 \eta$	0.491	-9.33
+45	$\log \theta = 7.89 + 8.14 \eta$	0.514	-9.16
+50	$\log \theta = 7.58 + 7.91 \eta$	0.507	-8.85
+55	$\log \theta = 7.61 + 8.14 \eta$	0.530	-8.88
+65	$\log \theta = 7.25 + 7.99 \eta$	0.536	-8.52
+72	$\log \theta = 7.13 + 8.04 \eta$	0.550	-8.40

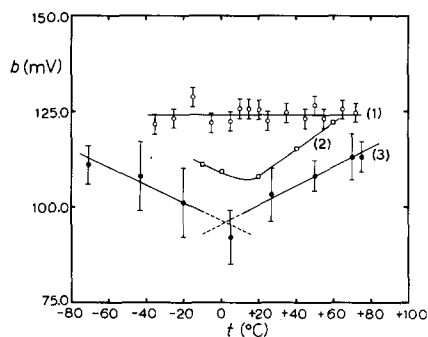


Fig. 2. Dependence of Tafel parameter,  $b$ , on temp.: (1), *7.5 M HCl* (this work); (2), *7.0 M HCl* (Jofa and Stepanova<sup>5</sup>); (3), *7.5 M HCl* (Bockris and Matthews<sup>10</sup>).

The most remarkable result of these measurements is the very marked temperature-dependence of  $\beta$  in Table 2. To our knowledge, such a significant trend of the transfer coefficient with temperature has not previously been published. Bockris and Matthews<sup>10</sup> also studied the  $H^+/H_2(Hg)$  reaction in *7.5 M HCl* and observed an anomalous temperature-dependence of the Tafel slope  $b$ , with a minimum at  $+5^\circ$ . For comparison, we calculated  $b$  from our measurements and plotted it against temperature in Fig. 2, together with the results of Bockris and Matthews<sup>10</sup>, and of Jofa and Stepanova<sup>5</sup> for *7 M HCl*, which cover a smaller temperature range.

It can be seen that the minimum found by Bockris and Matthews is not very significant, whereas our results indicate quite significantly that the Tafel slope is independent of temperature. In other words, we find  $\beta$  to be proportional to the absolute temperature, with a temperature coefficient,  $1.56 \cdot 10^{-3}$  degree $^{-1}$ .

Our values for the exchange current density are also in disagreement with those of Bockris and Matthews<sup>10</sup> (see Fig. 1) who report two values for the apparent heat of activation,  $\Delta H_0$ , at the reversible potential:  $\Delta H_0 = 21.0$  kcal mole $^{-1}$  for  $t = +5^\circ$  to  $+60^\circ$  and  $\Delta H_0 = 5$  kcal mole $^{-1}$  for  $t = +5^\circ$  to  $-71^\circ$ , with a sharp discontinuity at  $+5^\circ$ . We find  $\Delta H_0 = 11.1 \pm 0.5$  kcal mole $^{-1}$  for the whole temperature range ( $-35^\circ$  to  $+72^\circ$ ).

iii.  $5.2 M HClO_4$ . The measurements in this medium were carried out to compare the behaviour of the  $H^+/H_2(Hg)$  electrode in  $7.5 M HCl$  (where specific adsorption of chloride may play a role) with that in a concentrated acid solution with no (or anyway less) specific anion adsorption.

The results, obtained as before, are presented in Table 3. The averaged errors are,  $\pm 0.02$  in  $\beta$  and  $\pm 0.50$  in  $\log i_0$ .

TABLE 3

DATA FOR  $5.2 M HClO_4$ 

Temp. (°C)	Egns. of $\log \theta$ vs. overpotential, $\eta$ ( $\theta$ in $\Omega cm^2$ , $\eta$ in volts)	$\beta$	$\log i_0$ ( $i_0$ in $A cm^{-2}$ )
-39	$\log \theta = 15.11 + 11.20 \eta$	0.52	-16.52
-35	$\log \theta = 14.17 + 10.50 \eta$	0.50	-15.56
-25	$\log \theta = 14.25 + 10.80 \eta$	0.53	-15.64
-5	$\log \theta = 12.90 + 10.10 \eta$	0.54	-14.26
0	$\log \theta = 11.74 + 9.19 \eta$	0.50	-13.07
+5	$\log \theta = 11.71 + 9.26 \eta$	0.50	-13.03
+10	$\log \theta = 12.23 + 9.80 \eta$	0.55	-13.58
+15	$\log \theta = 11.93 + 9.62 \eta$	0.55	-13.28
+25	$\log \theta = 10.86 + 8.82 \eta$	0.52	-12.17

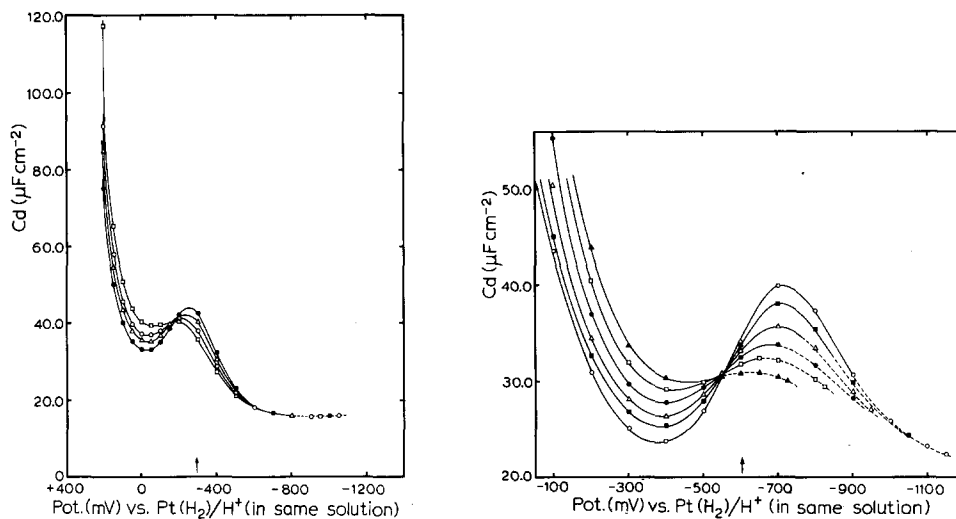
The transfer coefficient is clearly not significantly temperature-dependent within the range investigated. The apparent heat of activation at the reversible potential, calculated from the Arrhenius plot (Fig. 1) is  $19.5 \pm 2.2$  kcal mole $^{-1}$ .

To our knowledge, the effect of temperature on this system has not previously been investigated.

#### Temperature-dependence of the double-layer capacity in $1 M HCl$ , $7.5 M HCl$ and $5.2 M HClO_4$

The data on  $C_d$ , obtained in the region of  $H^+$  reduction from  $Y_{cl}''/\omega$  (eqn. 1b), were extended to more positive potentials by direct measurements of the electrode capacitance. The results for  $1 M HCl$ ,  $7.5 M HCl$  and  $5.2 M HClO_4$  are shown in Figs. 3, 4 and 5.

The dashed portions of the curves indicate the region where the hydrogen evolution reaction occurs and form a quite logical prolongation of the more positive parts, which might suggest that effects of coupling between the faradaic admittance



Figs. 3-4. Capacity-potential curves for mercury. (3) in 1.0 M HCl at: ( $\square$ ), +45°; ( $\circ$ ), +25°; ( $\triangle$ ), +15°; ( $\bullet$ ), 0°. (4) in 7.5 M HCl at: ( $\blacktriangle$ ), +65°; ( $\square$ ), +45°; ( $\bullet$ ), +25°; ( $\triangle$ ), +5°; ( $\blacksquare$ ), -15°; ( $\circ$ ), -35°. The dashed part in the curves indicates the region of the hydrogen evolution reaction. The vertical arrow indicates the position of the p.z.c. at 25°.

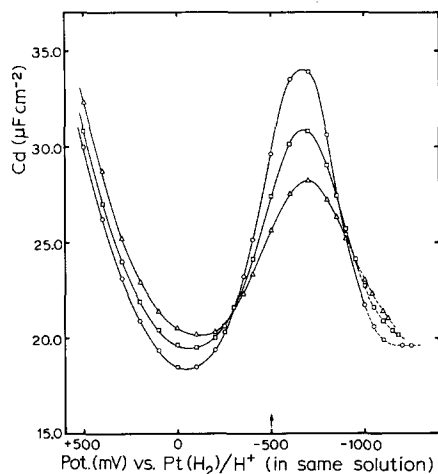


Fig. 5. Capacity-potential curves for mercury in 5.2 M HClO<sub>4</sub> at several temps.: ( $\triangle$ ), +25°; ( $\square$ ), -5°; ( $\circ$ ), -35°. The dashed part in the curves indicates the region of the hydrogen evolution reaction. The vertical arrow indicates the position of the p.z.c. at 25°.

and (specific) adsorption of electroactive species are negligible<sup>18</sup>. For 1 M HCl the capacity minimum in the negative potential region is 16  $\mu\text{F}/\text{cm}^2$ .

In all cases, the capacity-potential curves pass through a common point, situated on the left-hand side of the so-called "hump". This behaviour is similar to that of plots of the inner-layer capacity *vs.* electrode charge, published by Grahame<sup>19</sup> for 0.8 M NaF. Because of the high electrolyte concentrations, our capacities may also be considered as approximately equal to the inner layer capacities. A comparison

with Grahame's data suggests that specific adsorption of chloride has little effect on the general shape of the curves, except that the hump seems to be somewhat more pronounced.

In contrast with the case of hydrochloric acid, where the curves tend to coincide in the negative potential region, the capacity-potential curves for 5.2 M HClO<sub>4</sub> have a second common intersection point which is situated in the potential region where the hydrogen evolution reaction begins. (Fig. 5).

In Figs. 3, 4 and 5 the potentials of zero charge, p.z.c., at 25° are also indicated. The p.z.c. was determined by means of drop-time measurements and was found to be in agreement with literature values<sup>20</sup>. Only a slight temperature-dependence of the p.z.c. was found, in accordance with the measurements of Paik *et al.*<sup>21</sup> in 1 M KCl solution. In Fig. 3 it can be seen that the maximum of the hump in 1 M HCl is observed at a potential positive to the p.z.c., similar to the fluoride case. This was ascribed by Mott and Watts-Tobin<sup>22</sup> to specific anion adsorption, although this is rather unlikely for fluoride<sup>23</sup>. The position of the hump appears to be an important feature in the development of theories for explaining its occurrence<sup>24</sup>. Satisfactory explanations for all phenomena have not yet been given, especially for the fact that in some solvents (water, dimethylsulfoxide<sup>24</sup>, sulfolane<sup>25</sup>) the hump is found anodic to the p.z.c., and in other solvents (formamide, N-methylformamide) on the cathodic side. Our experiments in concentrated acids have revealed a new phenomenon, which, as far as we know, has not been previously observed: in 7.5 M aqueous HCl and 5.2 M aqueous HClO<sub>4</sub> the humps are situated at potentials negative to the p.z.c. This suggests that the effect of increasing the electrolyte concentration has also to be considered.

#### DISCUSSION

It has been stated that the temperature-dependence of the transfer coefficient of the hydrogen electrode reaction might be of diagnostic value, especially with respect to the so-called proton-tunnelling mechanism<sup>26</sup>. However, Conway and Salomon<sup>9</sup> showed that the occurrence of tunnelling at a mercury electrode is improbable. Instead, they support the view of Bockris and Parsons<sup>7</sup>, that "a satisfactory account of the variation of  $\beta$  with temperature could be given on the basis of the variation of the thickness of the double layer with temperature, deduced from the temperature dependence of the double-layer capacitance." As, according to Parsons and Bockris<sup>3</sup>,  $\beta$  is an inverse function of the double-layer thickness, the observed decrease of  $\beta$  with decreasing temperature should correspond to a decrease in capacity. However, our capacity measurements in 7.5 M HCl show an increase in capacity with decreasing temperature in the potential region of the hydrogen reduction. As this region coincides with the hump region, where dielectric saturation may be incomplete, it is quite reasonable to ascribe this trend to the variation of the dielectric constant with temperature<sup>22</sup>. In the far negative potential region, the capacity-potential curves clearly tend to coincide, so that no evidence for the temperature-dependence of the double-layer thickness can be deduced from our experiments. On the other hand, the capacity in 5.2 M HClO<sub>4</sub> shows a decrease with decreasing temperature in the "hydrogen region", but in this case  $\beta$  is found to be independent of temperature.

In our opinion, the explanation must be sought, anyway in the first instance,



in considering that the experimentally-determined value of  $\beta$  is not necessarily a "real" transfer coefficient. It has been shown recently<sup>27</sup>, that the rate constant,  $k_{sh}$ , and thus  $i_o$ , can be a function of potential. In that case the slope of the  $\log \theta$  vs.  $\eta$  plot (see eqn. 6) becomes

$$\left(\frac{\partial \ln \theta}{\partial \eta}\right)_T = \frac{\beta nF}{RT} - \left(\frac{\partial \ln i_o}{\partial \eta}\right)_T \quad (7)$$

A similar expression may be derived for the slope of the d.c. current-voltage curve:

$$\ln i = \ln i_o - \frac{\beta nF}{RT} \eta \quad (8)$$

giving

$$\left(\frac{\partial \ln i}{\partial \eta}\right)_T = -\frac{\beta nF}{RT} + \left(\frac{\partial \ln i_o}{\partial \eta}\right)_T \quad (9)$$

The "apparent transfer coefficient"  $\beta_{app}$ , calculated with (7) or (9) is equal to

$$\beta_{app} = \frac{RT}{nF} \left(\frac{\partial \ln \theta}{\partial \eta}\right)_T = -\frac{RT}{nF} \left(\frac{\partial \ln i}{\partial \eta}\right)_T = \beta - \frac{RT}{nF} \left(\frac{\partial \ln i_o}{\partial \eta}\right)_T = \beta - g \quad (10)$$

If  $\beta$  is considered as a fundamental constant (independent of  $\eta$  and  $T$ ) the following conclusions can be drawn from the results reported in this paper: (a) For 1 M HCl and 5.2 M HClO<sub>4</sub> solutions,  $g$  in eqn. (10) is probably negligible, because  $\beta_{app}$  is independent of temperature. (b) For the 7.5 M HCl solution,  $g$  has a substantial value: as  $\beta_{app}$  is found to be independent of potential and a linear function of temperature,  $\partial \ln i_o / \partial \eta$  is not significantly dependent on  $\eta$  and  $T$  in the range investigated.

Bockris and Matthews<sup>10</sup> developed a similar idea, ascribing their anomalous Tafel slopes for 7.5 M and 3 M HCl to the fact that  $k_{sh}^a$  in eqn. (4) contains the Frumkin correction term, in which the outer Helmholtz plane potential,  $\phi_2$ , is potential-dependent. However, this effect is not, as the authors suggest, characteristic for a solution from which anions (*i.e.*, chloride ions) are specifically adsorbed. Moreover, it is too small for a quantitative explanation of the anomalous  $\beta$ -values. Recently<sup>28,29</sup>, we showed that the presence of specifically adsorbed anions, itself can have a considerable influence on the rate constant of the Zn<sup>2+</sup>/Zn(Hg) electrode reaction, in decreasing the activation energy of the charge transfer. It seems reasonable to apply this view also to the H<sup>+</sup>/H<sub>2</sub>(Hg) reaction. This means that, if specific adsorption is significant, the change of the specifically adsorbed amount with potential causes the activation energy, and thus  $i_o$ , to be potential-dependent. As specific adsorption increases with decreasing temperature, it can be expected that the heat of activation is temperature-dependent also, and consequently the  $\Delta H$ -value, calculated for 7.5 M HCl, will be the mean value of the  $\Delta H$ -values pertaining to the temperatures in the range investigated. It may be noted that the temperature and potential range of the measurements is obviously very important to the results obtained and this may explain the discrepancies between the results of different investigators, *e.g.* between the work of Bockris and Matthews and ours.

The present results are unsuitable for more quantitative considerations, but we hope to make further investigations in that direction.

## ACKNOWLEDGEMENT

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## SUMMARY

The impedance of the dropping mercury electrode in aqueous solutions in 1 M HCl, 7.5 M HCl and 5.2 M HClO<sub>4</sub>, saturated with hydrogen at one atmosphere was measured at temperatures between -39° and +72° both in and outside the potential region where the electrode reaction,  $e + H^+ \rightleftharpoons \frac{1}{2} H_2$ , proceeds.

Analysis of the impedance data gave information about both the kinetics of the electrode reaction and the double-layer capacity. Exchange current densities and transfer coefficients are reported. The apparent heat of activation is 21.1 kcal mole<sup>-1</sup> for 1 M HCl, 19.5 kcal mole<sup>-1</sup> for 5.2 M HClO<sub>4</sub>, and 11.1 kcal mole<sup>-1</sup> for 7.5 M HCl. In the latter solution the transfer coefficient is found to be a linear function of temperature. In 1 M HCl and 5.2 M HClO<sub>4</sub> the transfer coefficient is virtually independent of temperature.

In 1 M HCl the hump in the capacity curve is situated anodically to the potential of zero charge but in 7.5 M HCl and 5.2 M HClO<sub>4</sub> this is reversed.

In both 1 M HCl and 7.5 M HCl the capacity-potential curves show one potential where the double-layer capacitance is independent of temperature. In the case of 5.2 M HClO<sub>4</sub>, this occurs at two potentials, situated at either side of the potential of zero charge.

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