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ON THE IMPEDANCE OF GALVANIC CELLS

XXVII. THE TEMPERATURE-DEPENDENCE OF THE KINETIC PARAMETERS OF THE HYDROGEN ELECTRODE REACTION ON MERCURY IN CONCENTRATED HI

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INTRODUCTION

In a previous paper[1] we presented a study concerning the temperature-dependence of the kinetic parameters of the hydrogen evolution reaction on Hg in 1 *M* HCl, 7.5 *M* HCl and 5.2 *M* $HClO_4$. In the case of 1 *M* HCl and 5.2 *M* $HClO_4$, the transfer coefficient β was found to be independent of temperature; in the case of 7.5 *M* HCl β was found to increase linearly with temperature. From the temperature-dependences of the exchange current densities i_0 the values of the apparent heats of activation ΔH were calculated: for 1 *M* HCl and 5.2 *M* $HClO_4$, $\Delta H \approx 20$ kcal mol^{-1} and for 7.5 *M* HCl, $\Delta H = 11.1$ kcal mol^{-1}. An explanation for these results was sought by considering that the experimentally determined β and i_0 values are influenced by specific adsorption of anions, which is potential-dependent. This would cause i_0 to be potential-dependent also and consequently β would contain a contribution from $\partial \ln i_0/\partial E$[1,2].

From this it appeared worthwhile to study the temperature-dependence of β and i_0 for a solution with strong specific anion adsorption such as iodide solutions[3]. In this paper, the results obtained in 57% HI solution (≈ 7.6 *M*) are described and discussed.

EXPERIMENTAL

The impedance of a dropping mercury electrode placed in the azeotropic mixture of hydriodic acid and water (the solution contains 57% HI) was measured.

The measuring cell was similar to that described previously[1]: in the hope of improving the purity of the solution the main compartment of the cell was made of quartz. Three electrodes were placed in the cell: a mechanically controlled dropping mercury electrode, a mercury pool counter electrode and a platinized hydrogen reference electrode. The whole system was saturated with hydrogen gas, which was purified by passage through a column filled with BTS-Katalysator (BASF) at a temperature of 50°C, and then equilibrated with a solution of the same composition and temperature as in the measuring cell. The mercury used for the electrodes was doubly-distilled.

The azeotropic hydriodic acid solution was obtained by distillation of a concentrated HI solution in a purified nitrogen atmosphere. The receiver flask was

made of quartz. A small amount of hypophosphorous acid was added to the solution in the distillation vessel in order to keep this solution and the distillate free from iodine[4]. The distillation and all other manipulations with hydriodic acid were performed with exclusion of light.

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

The impedance measurements were performed with the a.c. bridge as described elsewhere[5]. The potential range investigated was taken as wide as possible: on the cathodic side it is limited by the rapid evolution of hydrogen bubbles which disturbs regular dropping of the mercury, and on the anodic side by the very high capacity values which cannot be determined accurately with the a.c. bridge.

The temperature was controlled to within $\pm 0.1°C$.

RESULTS

The components Z' and Z'' of the cell impedance were measured at fixed potentials as a function of frequency (420–2000 Hz). The ohmic resistance R_Ω of the cell was found by extrapolation of Z' to infinite frequency. From these data the components Y'_{el} and Y''_{el} of the electrode admittance were calculated as described earlier[1].

The measurements were performed at temperatures $+25°$, $+15°$, $+5°$, $-5°$, $-15°$, $-25°$ and $-35°C$. In a previous paper[6] it has been shown that in 57% HI at $+15°C$, the potential region where the hydrogen reaction is measurable, partly coincides with the potential region where mercury dissolves to HgI_4^{2-}. This appeared to be the case also at $+25°$ and $+5°C$. In this potential region (-540 to -590 mV) Y'_{el} is a linear function of the square root of the frequency $\omega^{\frac{1}{2}}$, from which it can be deduced[6] that one of the reactions, Hg/HgI_4^{2-}, is reversible and the other $H^+/H_2(Hg)$ irreversible. The Warburg coefficient σ_1 of the former reaction, the transfer resistance θ_2 of the latter, and the double-layer capacity C_d have been obtained according to the equations:

$$Y'_{el} = \frac{\omega^{\frac{1}{2}}}{2\sigma_1} + \frac{1}{\theta_2} \quad (1a) \qquad\qquad Y''_{el} = \frac{\omega^{\frac{1}{2}}}{2\sigma_1} + \omega C_d \quad (1b)$$

At potentials more negative than -590 mV, the θ_2 values were obtained directly as $\theta_2 = 1/Y'_{el}$ since the contribution of the Hg/HgI_4^{2-} reaction is here negligible. The results are presented in Figs. 1 and 2.

At potentials more negative than -590 mV, the log θ_2 *vs.* E plots are linear, which is in accordance with the theory for a completely charge transfer controlled electrode reaction[7].

From the slopes and the intercepts, the values of the cathodic transfer coefficients β and the exchange current densities i_0 of the hydrogen evolution reaction were calculated. The results are given in Figs. 3 and 4.

An important conclusion from Fig. 3 is that the transfer coefficient decreases with temperature. The temperature coefficient of β was calculated from the slope of the line $\partial\beta/\partial T = -1.4 \times 10^{-3}$ degree^{-1}.

The apparent heat of activation at the reversible potential, ΔH, was calculated from the slope of the log i_0 *vs.* $1/T$ plot (Fig. 4): $\Delta H = 21.6 \pm 1.8$ kcal mol^{-1}. This

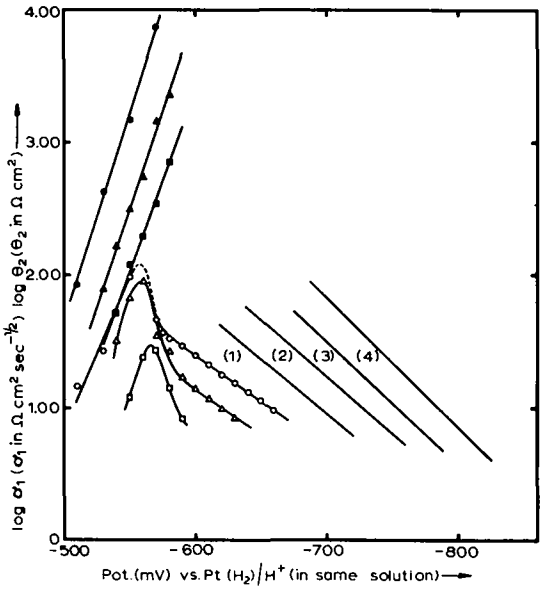


Fig. 1. Plots of the logarithmic values of the Warburg coefficients σ_1 (dark spots) and the activation polarization resistances θ_2 (light spots) as a function of potential for a mercury electrode in 57% HI at several temps.: (■, □) +25°; (▲, △) +15°; (●, ○) +5°C; and exptl. log θ_2 lines for: (1) −5°; (2) −15°; (3) −25°; (4) −35°C.

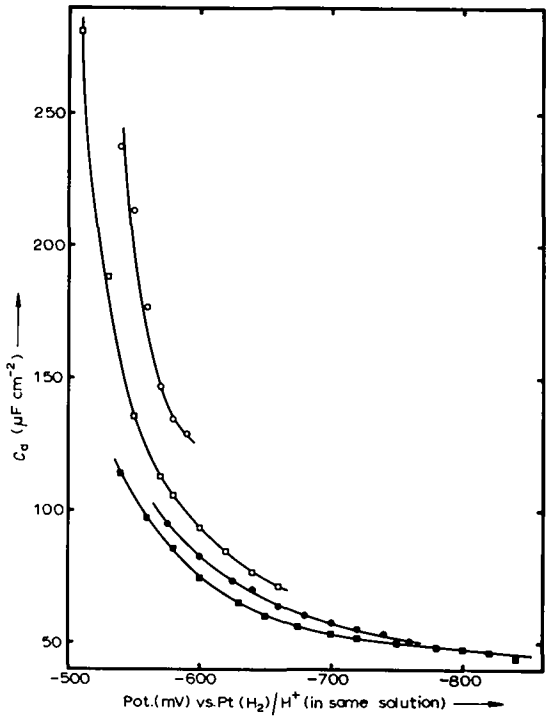
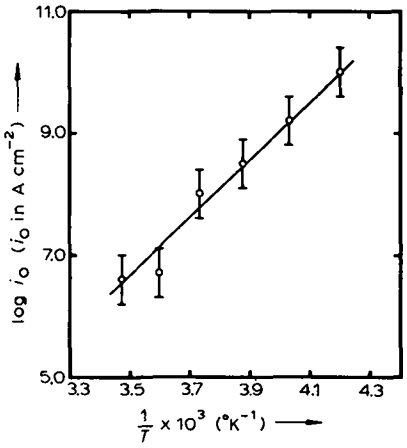


Fig. 2. Capacity–potential curves for mercury in 57% HI at several temps.: (○) +25°; (□) +5°; (●) −15°; (■) −35°C.



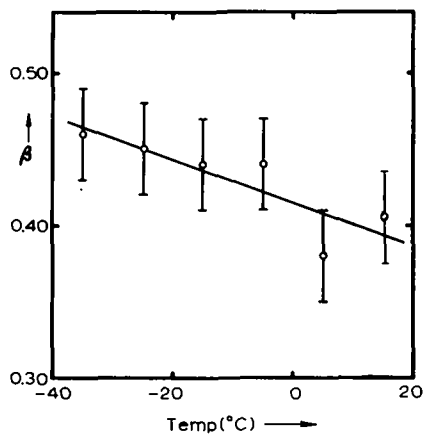


Fig. 3. Dependence of β on temp. for Hg in 57% HI.

Fig. 4. Dependence of i_0 on temp. for Hg in 57% HI.

value is in agreement with the values of about 20 kcal mol^{-1} which are normally found for the hydrogen evolution reaction on mercury[8].

DISCUSSION

(A) The most notable result of the measurements is that the transfer coefficient, β, decreases with temperature (Fig. 3) in the temperature and potential range investigated. To the authors' knowledge such a phenomenon has not been reported before. Previously[1] we reported on the results of measurements on the $H^+/H_2(Hg)$ reaction in 7.5 *M* HCl, in which case an increase of β with temperature was found. The explanation was sought by considering that the experimentally determined value of β is not a "real" transfer coefficient but contains a contribution from the potential-dependence of i_0. In that case the observed "apparent transfer coefficient" β_{app} is equal to:

$$\beta_{app} = \beta - \frac{RT}{nF}\left(\frac{\partial \ln i_0}{\partial E}\right)_T = \beta - g \qquad (2)$$

where β is considered as a fundamental constant (independent of E and T).

The potential-dependence of i_0 can be caused by the Frumkin effect, but it is also very probable that the accelerating effect of the specifically adsorbed iodide ions q'_- is responsible. That this effect (which has been demonstrated for other electrode reactions on mercury[9]) exists also for the hydrogen electrode, may be inferred from the variation of log i_0 with the nature and concentration of the anion, *e.g.* at 15°C we have found for log i_0 −13.3 in 5.2 *M* $HClO_4$, −13.1 in 1 *M* HCl, −9.9 in 7.5 *M* HCl, and in the present paper, −6.6 in 7.6 *M* HI. The amount of specific adsorption from the concentrated solutions is not known, but, in view of what is known from double-layer measurements at lower concentrations[10,11], it is reasonable to expect that it increases in the same direction.

Continuing the argument in this way, the temperature-dependence of β_{app} could be due to that of g, represented by

$$g = \frac{RT}{nF}\left(\frac{\partial \ln i_0}{\partial q'_-}\right)_{E,T}\left(\frac{\partial q'_-}{\partial E}\right)_T \tag{3}$$

From our experiments it would appear that, with increasing temperature, g decreases for 7.5 M HCl and increases for 7.6 M HI. Recently, Minc and Andrzejczak[12] investigated the adsorption of NCS^- on mercury for concentrations up to 6 M and at two temperatures. From their experiments it can be seen that the temperature coefficient of $(\partial q'_-/\partial E)_T$ can be either positive or negative, depending on the concentration and the temperature. In this connection it will be interesting to determine q'_- as a function of potential and temperature for concentrated Cl^- and I^- solutions. With such data the influence of the first derivative in (3) could also be investigated, using the model recently introduced by Parsons[13], which relates $(\partial \ln i_0/\partial q'_-)_{E,T}$ to the second virial coefficient $B_{1,1}$ in the adsorption isotherm.

If, on the other hand, the temperature-dependence of β_{app} must be traced to that of the "real" β in eqn. (2), it is worthwhile to note that in 7.6 M HI a decrease of β with temperature is found together with an increase in the double-layer capacity, whereas in 7.5 M HCl the increase in β with temperature coincides with a decrease in the double-layer capacitance. If changes in the capacitance in these concentrated solutions may be interpreted as changes in the double-layer thickness, this would mean that both in HCl and HI there is a simultaneous increase in β and the double-layer thickness. This is in contradiction with what could be expected from a theory proposed by Parsons and Bockris[14].

(B) In Fig. 1 a kind of hump appears in the log θ_2 *vs.* E curves in the potential region where the hydrogen evolution reaction coincides with the mercury dissolution reaction. There is no doubt that the equivalent circuit of the impedance used for the evaluation of the impedance parameters σ_1, θ_2 and C_d is correct. Two arguments for the correctness of the analysis can be given.

(i) The log σ_1 *vs.* E plots are straight lines, which is in accordance with the theory for a completely diffusion-controlled electrode reaction[7]. From the slopes of the lines, the number of electrons involved in the electrode reactions can be calculated. For all temperatures (*i.e.* +5°, +15° and +25°C) $n = 1.7$, which is in reasonable agreement with the theoretical value $n = 2$.

(ii) No frequency dispersion in the calculated C_d-values was observed. Moreover, the general shape of the C_d *vs.* E curves is similar to those obtained for I^- solutions by other workers[3,15].

Going from −590 mV to less negative potentials, the initial increase in the slope of the log θ_2 *vs.* E curves could be interpreted as a change in the apparent transfer coefficient. The inaccuracy of the log θ_2 values and the small potential range of the measurements prevented any significant temperature-dependence being observed: for all temperatures investigated, the slopes of the right-hand side of the humps correspond to $\beta_{app} = 1.3 \pm 0.3$.

Recently, Krishtalik[16] presented a study of the hydrogen reduction on mercury in various supporting electrolytes, especially with a view to the so-called "barrierless discharge" theory. In the case of barrierless discharge, the transfer coefficient is theoretically equal to unity. According to Krishtalik, the phenomenon was observed at very low current densities in a potential region somewhat more positive than the potential region of our measurements. It is likely, therefore, that our result $\beta = 1.3 \pm 0.3$

indicates the occurrence of barrierless discharge. It is not possible to calculate the heat of activation ΔH from our experiments owing to the inaccuracy of the log θ_2 *vs.* E lines.

The phenomenon that log θ_2 decreases on the anodic side of the hump is of special interest. This could mean that some irreversible oxidation reaction takes over the role of the irreversible hydrogen evolution reaction. In such a case, the θ_2 value obtained must be considered as a substitution value: $\theta_2 = \theta_H\theta_3/\theta_H + \theta_3$, θ_H being the transfer resistance of the $H^+/H_2(Hg)$ reaction, and θ_3 that of the other reaction. However, this explanation is unlikely since it is not clear which reaction can take over the role of the hydrogen reduction reaction. Another explanation can be sought in considering that the presence of HgI_4^{2-} species diminishes the heat of activation of the hydrogen evolution reaction. The model for such a catalysing effect is not yet understood and this will have to be investigated further.

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SUMMARY

The impedance of a dropping mercury electrode in 57% HI ($\approx$7.6 M) was measured at temperatures between $-35°$ and $+25°C$. In a certain potential and temperature region, two reactions were found to be proceeding simultaneously: the reversible Hg/HgI_4^{2-} reaction and the irreversible $H^+/H_2(Hg)$ reaction. Analysis of the impedance data gave information about the impedance parameters of both electrode reactions, and about the double-layer capacity. The temperature-dependences of the transfer coefficient and the exchange current density of the $H^+/H_2(Hg)$ reaction are reported. The transfer coefficient decreases with temperature. The apparent heat of activation is 21.6 kcal mol^{-1}.

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