ON THE IMPEDANCE OF GALVANIC CELLS

XXI. ANALYSIS OF THE ELECTRODE IMPEDANCE IN THE CASE OF A NON-REVERSIBLE ELECTRODE REACTION WITH SPECIFIC ADSORPTION OF THE ELECTROACTIVE SPECIES; APPLICATION TO THE Pb^{2+}/Pb(Hg) ELECTRODE IN 1 M KCl

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INTRODUCTION

It is generally known that the impedance of a galvanic cell cannot be analysed with RANDLES' classical vector construction method[1] when the electrode reaction involves a species which is adsorbed at the electrode–solution interface. In this case, the phase angle of the faradaic impedance, calculated from the electrode admittance after subtraction of the double-layer admittance, pertaining to the supporting electrolyte, apparently exceeds 45°, contrary to the theory.

For the electrode reactions Tl^+/Tl(Hg) and Hg_2^{2+}/Hg, we have demonstrated[2,3] by means of the complex plane analysis method, that the electrode impedance, Z_{el} (*i.e.*, the cell impedance less the ohmic resistance) behaves as a Warburg impedance in parallel with a frequency-independent capacitance, the latter being larger than the double-layer capacitance, measured in the absence of the electrode reaction. Thus, in both cases the electrode reaction appears to be reversible within the limits of the complex plane method.

Since lead ions seem to be specifically adsorbed at mercury in chloride solutions[4] and the electrode reaction Pb^{2+}/Pb(Hg) is probably not ideally reversible[5], it was of interest to study the impedance of this system and determine if in this case also, specific adsorption results only in an enhanced capacitance in RANDLES' equivalent circuit. It will be shown in this paper, that this is not the case and that the measured impedances should be interpreted with the aid of a more complex model for the electrode impedance.

A number of such models have been reviewed by BATICLE AND PERDU[6]. The most general theory seems to be that of SENDA AND DELAHAY[7], who rationalise the assumption that the charge transfer occurs between adsorbed species. BATICLE AND PERDU outlined a procedure for analyzing measured impedances according to the equivalent circuit of this theory. In our opinion, there are two serious objections to their treatment. First, the parameters of the circuit are obtained by extrapolation to zero or infinite frequency, where the impedance is predicted to obey simplified equations. In view of the large number of parameters, it is difficult to check the correctness and accuracy of the results. Usually, more combinations of parameters are possible. Secondly, the analysis involves subtraction of the double-layer admittance,

which is not known and must be supposed to be equal to that measured in the supporting electrolyte.

Recently DELAHAY[8] has stated that "*a priori* separation of faradaic and double layer charging currents is not justified theoretically", since the reactants participating in an electrode reaction, are partly concerned in charging the electrical double layer. This theory of "charge separation or recombination" is in principle relevant to all non-steady state techniques applied to any electrode process with specific or non-specific adsorption (*i.e.*, adsorption in the diffuse double layer). From our experience with earlier impedance studies it seems to us, however, that DELAHAY over-estimated the effect in the latter case, *e.g.*, for the Zn reaction in various solutions[11,12] (1 M KCl, 0.1 M KCl, 1 M KI) no departure from Randles behaviour, or increase of capacitance has been found, in spite of the large effect for 0.1 M and small, but significant, effect predicted for 1 M solutions. In the case of specific adsorption the effect may be quite significant and important in the interpretation of non-steady state measurements.

Starting from this important new insight into electrochemistry, DELAHAY derived new expressions for the cell impedance[9]. These expressions are in accordance with our interpretation of our experiments on the Tl+/Tl(Hg) and the Hg_2^{2+}/Hg electrode reaction and consequently they give a physical meaning to the enhanced double-layer capacitance, which, according to DELAHAY, is equal to the second derivative of the interfacial tension with respect to potential. This is confirmed by our recently published[10] experiments for the Hg_2^{2+}/Hg electrode, which we now feel were interpreted incorrectly.

In this paper we investigate the question of whether the impedance of the Pb^{2+}/Pb(Hg) electrode in 1 M KCl can be interpreted in terms of the equivalent circuits of SENDA[7] or DELAHAY.

EXPERIMENTS AND RESULTS

The cell consisted of a D.M.E. and a mercury pool electrode placed in a solution of 0.5 mM $Pb(NO_3)_2$, 0.01 M HCl and 1 M KCl. The D.M.E. was kept at the peak potential of the a.c. polarogram (−0.437 V *vs.* SCE). The impedance components, Z' and Z'', corresponding to this potential, were measured at various frequencies with the aid of the a.c. bridge described earlier[11].

The ohmic resistance, R_Ω, evaluated by extrapolation to infinite frequency, was subtracted from Z' in order to obtain the electrode impedance in its real and imaginary components, $Z_{el}' = Z' − R_\Omega$ and $Z_{el}'' = Z''$, or the components $Y_{el}' = Z_{el}'/[(Z_{el}')^2 + (Z_{el}'')^2]$ and $Y_{el}'' = Z_{el}''/[(Z_{el}')^2 + (Z_{el}'')^2]$ of the electrode admittance. The results are given in Table 1. The accuracy in Z_{el}' is ± 0.03 and in Z_{el}'' *ca.* $\pm 1\%$.

ANALYSIS

(i) Randles' circuit

If the electrode impedance is in accordance with the RANDLES circuit, the parameters of the faradaic impedance can be obtained, without *a priori* knowledge of the double-layer capacitance, from the frequency dispersion of Y_{el}'.

We have[11],

$$\frac{\sqrt{\omega}}{Y_{el}'} = \left\{\theta + \sigma\omega^{-\frac{1}{2}} + \frac{\sigma^2\omega^{-1}}{\theta + \sigma\omega^{-\frac{1}{2}}}\right\}\omega^{\frac{1}{2}} = \sigma\left\{p'\omega^{\frac{1}{2}} + 1 + \frac{1}{p'\omega^{\frac{1}{2}}+1}\right\} \tag{1}$$

Extrapolation to zero frequency of a plot of $\sqrt{\omega}/Y_{el}'$ against $\sqrt{\omega}$ should yield the value of σ. The value of p' can be evaluated from the increase with frequency, preferably by a curve-fitting procedure.

From Fig. 1 it appears, however, that in the present case $\sqrt{\omega}/Y_{el}'$ *decreases with increasing frequency*. This means that eqn. (1) — and thus the RANDLES circuit— are not applicable to the $Pb^{2+}/Pb(Hg)$ electrode in $1\ M$ KCl.

TABLE 1

COMPONENTS OF THE ELECTRODE IMPEDANCE AND ADMITTANCE OF THE $Pb^{2+}/Pb(Hg)$ ELECTRODE AT THE PEAK POTENTIAL $R_\Omega = 1.91 \pm 0.02\ \Omega\ cm^2$

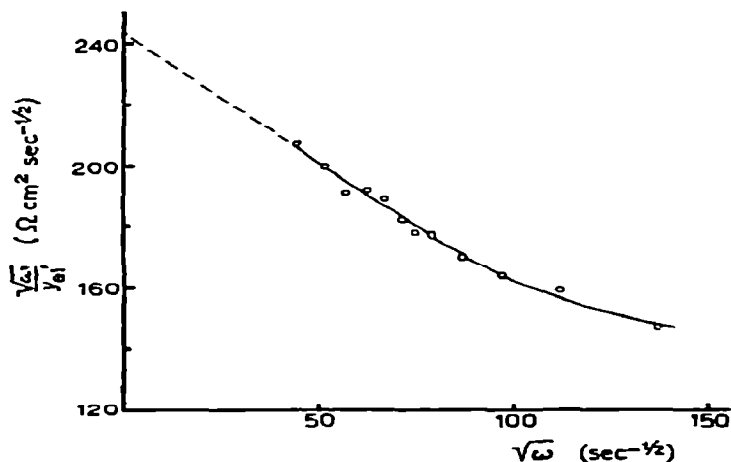| Frequency (Hz)	Z_{el}' ($\Omega\ cm^2$)	Z_{el}'' ($\Omega\ cm^2$)	Y_{el}' ($\Omega^{-1}\ cm^{-2}$)	Y_{el}'' ($\Omega^{-1}\ cm^{-2}$)	$Y_{el}'/(Y_{el}'' - \omega C_d)$	
					($C_d = 40\ \mu F$)	($C_d = 50\ \mu F$)
320	1.07	1.95	0.215	0.395	0.69	0.73
420	0.85	1.61	0.255	0.485	0.67	0.72
520	0.73	1.38	0.30	0.565	0.69	0.74
620	0.63	1.24	0.325	0.64	0.67	0.73
720	0.55	1.12	0.355	0.72	0.65	0.72
820	0.51	1.02	0.395	0.79	0.67	0.74
900	0.47	0.94	0.425	0.85	0.68	0.74
1000	0.43	0.88	0.45	0.92	0.68	0.75
1200	0.38	0.78	0.51	1.04	0.69	0.77
1500	0.31	0.66	0.59	1.25	0.68	0.76
2000	0.25	0.54	0.70	1.52	0.68	0.78
3000	0.18	0.40	0.94	2.08	0.70	0.82
4000	0.14	0.33	1.08	2.54	0.70	0.83

Fig. 1. The frequency-dependence of $\sqrt{\omega}/Y_{el}'$.
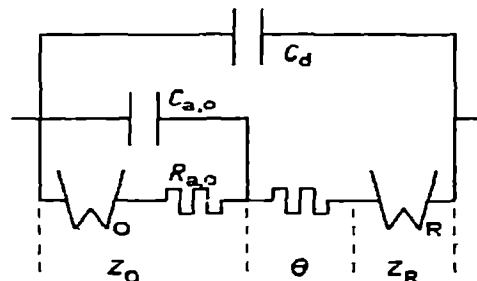
Fig. 2. Equiv. circuit according to SENDA AND DELAHAY, for adsorption of the Ox-component only.

(ii) Senda and Delahay's circuit

The complex expressions for the faradaic impedance resulting from the theory of SENDA AND DELAHAY[7], can be reduced in several cases where one or more of the parameters are negligible. According to BATICLE AND PERDU[6] one can decide which case predominates, from the frequency-dependence of the phase angle, ϕ_a, of the apparent faradaic admittance. As mentioned before, the difficulty arises that the components, Y_f' and Y_f'', of the faradaic admittance must be calculated from the electrode admittance by subtraction of the double-layer admittance. Although BATICLE AND PERDU did not state it explicitly, we suppose that they assume that the adsorption of the electroactive species has no influence on the latter, so that

$$Y_f' = Y_{el}' \quad \text{and} \quad Y_f'' = Y_{el}'' - \omega C_d \tag{2}$$

in which C_d is the double-layer capacitance measured in the supporting electrolyte at the same potential.

If we apply this to our experimental data in Table 1, taking $C_d = 40\,\mu\text{F cm}^{-2}$ in 1 M KCl at -0.44 V vs. S.C.E., the result is that $\cot\phi_a = Y_f'/Y_f''$ is almost a constant in the reported frequency range, with a mean value of 0.68 (see Table 1). This is suggestive of case (d) in BATICLE's treatment, which implies infinitely fast electron transfer ($\theta \approx 0$) and adsorption of one of the reactants (see Fig. 2); it is reasonable to assume that this is the Pb^{2+} ion. In the following we will suppose that these simplifications are allowed.

The evaluation of σ following the indications of BATICLE AND PERDU fails, because plots of R_f and $1/\omega C_f$ (their notation) against $\omega^{-\frac{1}{2}}$ are not parallel. We therefore propose a different analysis.

From Fig. 2 it follows that the faradaic impedance, Z_f, can be split up into three parts, regarding the mass transport of the Ox component (Z_O), the transfer reaction (θ), and the mass transport of the Red component (Z_R). Then,

$$Z_f' = \frac{Y_f'}{Y_f'^2 + Y_f''^2} \quad \text{and} \quad Z_f'' = \frac{Y_f''}{Y_f'^2 + Y_f''^2} \tag{3}$$

$$Z_O' = Z_f' - \theta - Z_R' \approx Z_f' - \sigma_R \omega^{-\frac{1}{2}} \tag{4}$$

$$Z_O'' = Z_f'' - Z_R'' = Z_f'' - \sigma_R \omega^{-\frac{1}{2}} \tag{5}$$

in which σ_R is the Warburg coefficient pertaining to the Red component.

The equivalent circuit representing Z_O is exactly similar to the RANDLES circuit. This means that the validity of the model can be checked by calculating

$$\frac{1}{Y_O'} = \frac{Z_O'^2 + Z_O''^2}{Z_O'} = R_{a,O} + \sigma_O \omega^{-\frac{1}{2}} + \frac{\sigma_O^2 \omega^{-1}}{R_{a,O} + \sigma_O \omega^{-\frac{1}{2}}} \tag{6}$$

at various frequencies, so that $R_{a,O}$ and σ_O can be obtained (cf. eqn. (1)).

The values of σ_R and σ_O can be calculated according to the theory of the potential-dependence of the faradaic impedance[11,12].

As the electrode reaction is reversible to d.c. current,

$$\sigma_O = \frac{RT}{n^2 F^2 \sqrt{2}} \frac{1}{C_O \sqrt{D_O}} = \frac{RT}{n^2 F^2 \sqrt{2}} \frac{1 + \exp[-(nF/RT)(E - E_{\frac{1}{2}})]}{C_O^* \sqrt{D_O}} \tag{7a}$$

$$\sigma_R = \frac{RT}{n^2 F^2 \sqrt{2}} \frac{1}{C_R \sqrt{D_R}} = \frac{RT}{n^2 F^2 \sqrt{2}} \frac{1 + \exp[(nF/RT)(E-E_{\frac{1}{2}})]}{C_o^* \sqrt{D_o}} \tag{7b}$$

$$\sigma = \sigma_O + \sigma_R \tag{7c}$$

in which C_O^* is the bulk concentration of the Pb^{2+} ion (0.5×10^{-6} mole cm^{-3}) and D_O its diffusion coefficient ($10 \cdot 10^{-6}$ cm^2 sec^{-1}, from d.c. polarography). Normally, the peak potential of the a.c. polarogram, i.e., the potential where σ is minimal, equals the half-wave potential, which would lead to $\sigma_O = \sigma_R = 60$ Ω cm^2 $sec^{-\frac{1}{2}}$. In our case, however, this should not necessarily hold, since W_O in Fig. 2 is shunted by the capacitance $C_{a,o}$. We found experimentally that the peak potential coincided with $E_{\frac{1}{2}}$ with a precision of ca. 5 mV. This means that σ_O and σ_R lie between 50 and 75 Ω cm^2 $sec^{-\frac{1}{2}}$, their sum being 120–125 Ω cm^2 $sec^{-\frac{1}{2}}$.

Applying eqns. (2) and (3) with $C_d = 40$ μF cm^{-2} to the data in Table 1 we calculated values for Z_f' and Z_f''. The results show that, especially at the higher frequencies, $Z_f'\sqrt{\omega}$ is nearly constant and approximately equal to 50 Ω $cm^2 sec^{-\frac{1}{2}}$. This can only mean that the pseudocapacitance, $C_{a,o}$, largely shunts the impedance, $W_O + R_{a,o}$, so that at the higher frequencies

$$Z_O' \approx 0 \quad \text{and} \quad Z_f' \approx \sigma_R \omega^{-\frac{1}{2}} \tag{8}$$

$$Z_O'' \approx \frac{1}{\omega C_{a,o}} \quad \text{and} \quad Z_f'' \approx \sigma_R \omega^{-\frac{1}{2}} + \frac{1}{\omega C_{a,o}} \tag{9}$$

Obviously, plots of $Z_f'\sqrt{\omega}$ and $Z_f''\sqrt{\omega}$ against $\omega^{-\frac{1}{2}}$ should yield straight lines, the former with approximately zero slope, the latter with a slope $1/C_{a,o}$. Both plots should have the same intercept, σ_R. From Fig. 3 it appears that an equal intercept is not found, if $C_d = 40$ μF cm^{-2} is inserted. The desired result is obtained, if it is assumed that the double-layer capacitance is increased by the specific adsorption of Pb^{2+} to 50–55 μF
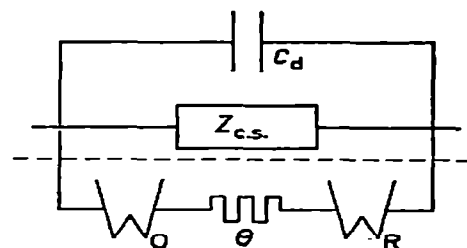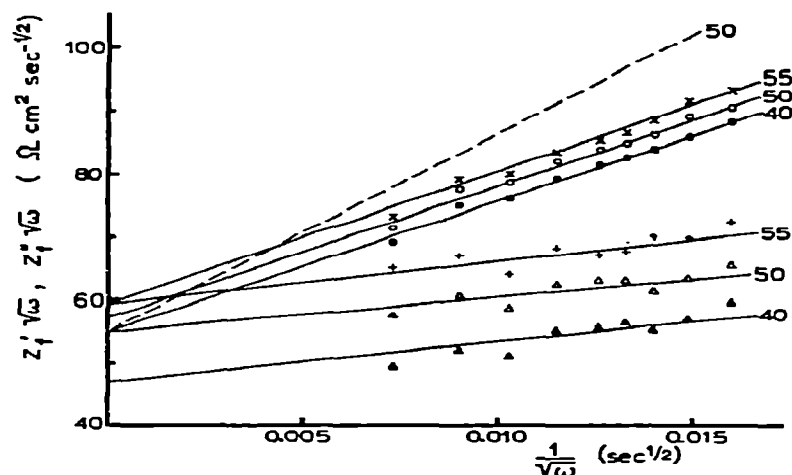

Fig. 3. Plot of $Z_f'\sqrt{\omega}$ (▲, △ and +) and $Z_f''\sqrt{\omega}$ (●, ○ and ×) against $1/\sqrt{\omega}$. Numbers indicate selected values of C_d in μF cm^{-2}, for which Z_f' and Z_f'' are calculated. Dashed line: final plot of the successive approximation procedure, with slope $1/C_{a,o}$, for $R_{a,o} = 0$ (see text).

Fig. 4. Equiv. circuit according to DELAHAY's theory of charge separation or recombination. The part above the dashed line is equivalent to the double-layer impedance as defined by DELAHAY[5].

cm^{-2}, leading to $\sigma_R = 55$–$60\ \Omega\ cm^2\ sec^{-\frac{1}{2}}$ and $C_{a,o} = 500\ \mu F\ cm^{-2}$, and consequently $\sigma_o = 60$–$65\ \Omega\ cm^2\ sec^{-\frac{1}{2}}$.

It should be noted that with these data, eqn. (9) does not hold if $R_{a,o}$ is negligibly small. For, if $R_{a,o} = 0$,

$$Z_t'' \sqrt{\omega} = \frac{1}{C_{a,o}\omega^{\frac{1}{2}}} \left\{ \frac{2\sigma_o^2 \omega C_{a,o}^2 + \sigma_o \omega^{\frac{1}{2}} C_{a,o}}{2\sigma_o^2 \omega C_{a,o} + 2\sigma_o \omega^{\frac{1}{2}} C_{a,o} + 1} \right\} + \sigma_R \qquad (10)$$

e.g., at 2000 Hz the term in the brackets is ca. 0.8. Since this correction factor, A, changes only slightly with frequency, a virtually straight line is still obtained in Fig. 3, but its slope is smaller than $1/C_{a,o}$. The true value of $C_{a,o}$ (with $R_{a,o} = 0$) can be found by a successive approximation procedure, calculating A with the above-mentioned values for σ_o and $C_{a,o}$ and plotting $[Z_t'' \sqrt{\omega} - \sigma_R]\ (1/A) + \sigma_R$ against $\omega^{-\frac{1}{2}}$. The slope of this plot gives a new value for $C_{a,o}$, yielding a new correction factor, etc., until consistency is reached. In Fig. 3, the final plot is drawn for $C_d = 50\ \mu F$ cm^{-2}. It appears that the intercept is only slightly lowered, whereas $C_{a,o}$ is reduced to $300\ \mu F\ cm^{-2}$.

On the other hand, it is easily calculated that eqn. (9) holds down to 620 Hz if $R_{a,o} = 1\ \Omega\ cm^2$ or larger. Consequently, it can be concluded that the impedance of the $Pb^{2+}/Pb(Hg)$ electrode, measured at the peak potential, can be represented by the circuit of Fig. 2 with the following data: $R_{a,o} \geqslant 0$, $300 \leqslant C_{a,o} \leqslant 500$, $53 < \sigma_R < 58$, $62 < \sigma_o < 67$, $\theta \approx 0$ and $45 \leqslant C_d \leqslant 55$ (dimensions as in the text).

(iii) Delahay's circuit, including charge separation or recombination

The expressions for the electrode impedance in the case where charge separation or recombination has to be accounted for, are given by DELAHAY[9] in a rather complicated form, so that the frequency-dependence is not surveyable. For our considerations it is useful to rewrite them in more tractable expressions, by substituting

$$\lambda_T = -nF\bar{C}_O \frac{\omega^{\frac{1}{2}} D_O^{\frac{1}{2}}}{\sqrt{2}} = -\frac{RT}{nF} \frac{\omega^{\frac{1}{2}}}{2\sigma_o}$$

$$\lambda_M = -nF\bar{C}_R \frac{\omega^{\frac{1}{2}} D_R^{\frac{1}{2}}}{\sqrt{2}} = -\frac{RT}{nF} \frac{\omega^{\frac{1}{2}}}{2\sigma_R}$$

$$\sigma_o + \sigma_R = \sigma$$

$$\mu_M = \omega K_R, \quad \mu_T = \omega K_O$$

$$\frac{\sigma_o}{\sigma} K_O - \frac{\sigma_R}{\sigma} K_R = K$$

$$(C_{dl})_{\omega \to \infty} = \frac{dq}{dE} = C_d$$

$$p = p'\omega^{\frac{1}{2}} = \frac{\theta}{\sigma\omega^{-\frac{1}{2}}}$$

$$i_o = \frac{RT}{nF\theta}$$

into eqns. (8) and (9) of ref. 9 and calculating the real and imaginary components

of the electrode admittance. The result is

$$Y_{el}' = \frac{1}{R_p} = \frac{\omega^{\frac{1}{2}}}{\sigma} \frac{p+1}{p^2+2p+2} + \omega K \frac{p}{p^2+2p+2} \tag{11}$$

$$Y_{el}'' = \omega C_p = \frac{\omega^{\frac{1}{2}}}{\sigma} \frac{1}{p^2+2p+2} + \omega K \frac{p+2}{p^2+2p+2} + \omega C_d \tag{12}$$

Evidently, the charge separation or recombination formally introduces a "pseudo double-layer impedance" parallel to the "normal" double-layer capacitance and to the "normal faradaic impedance" (Fig. 4), which can be represented by a "Warburg-like" impedance and a capacitance in series:

$$Z_{c.s.} = \frac{\theta \omega^{-\frac{1}{2}}}{2\sigma K}(1-j) - j\frac{1}{\omega K} = \frac{p}{2\omega K} - j\frac{p+2}{2\omega K} \tag{13}$$

As pointed out by DELAHAY, the equivalent circuit in Fig. 4 reduces in theory to the RANDLES circuit in the extreme cases where $p \to \infty$ (irreversible reaction) or $p \to 0$ (reversible reaction). Then the original complex plane analysis may be applied, yielding the values of θ and C_d in the former case, and of σ and C_d+K in the latter. However, the criterion for these cases to occur in practice should not be the frequency-dependence of the double-layer impedance, as defined by DELAHAY (see Fig. 4), because its components are not *a priori* known. Only the frequency-dependences of Y_{el}' and Y_{el}'', which can be measured, are possible criteria.

The irreversible case may be said to occur if Y_{el}' is independent of frequency within the range covered by the measurements, normally between $\omega_1 = 10^3$ and $\omega_2 = 2 \cdot 10^4$ sec^{-1}. If $p' > 0.5$, eqns. (11) and (12) reduce in this range within 5% to

$$Y_{el}' = \frac{1}{\theta} + \frac{\omega K}{p} = \frac{1}{\theta} + \frac{\sigma K \omega^{\frac{1}{2}}}{\theta} \tag{14}$$

$$Y_{el}'' = \frac{\omega K}{p} + \omega C_d = \frac{\sigma K \omega^{\frac{1}{2}}}{\theta} + \omega C_d \tag{15}$$

Y_{el}' is virtually independent of frequency if $\sigma K(\omega_2^{\frac{1}{2}} - \omega_1^{\frac{1}{2}}) < 0.05$, which, for $\sigma = 100$ (*ca.* 1 mM solutions) means $K < 6 \mu F$ cm^{-2}. As we will see below, this value is unusually small for a case of specific adsorption. On the other hand, if K is larger, the values of θ, σK and C_d may be easily obtained from plots of Y_{el}' and $Y_{el}'\omega^{-\frac{1}{2}}$ against $\omega^{\frac{1}{2}}$. Therefore, all the parameters of the equivalent circuit can be calculated if σ is estimated in accordance with the theory of the faradaic impedance[13]. The results should be checked for consistency with $p' > 0.5$.

The frequency-independence of $Y_{el}'\omega^{-\frac{1}{2}}$, is in the complex plane analysis, the criterion for reversibility. In the frequency range mentioned this is the case if $p' < 5 \cdot 10^{-3}$ and $\sigma \omega_2 K p' < 0.05$ or $K < 2.5/\sigma p' \mu F$ cm^{-2}. Then $Y_{el}' \approx \sqrt{\omega}/2\sigma$ and $Y_{el}'' - Y_{el}' \approx \omega(C_d+K)$. Obviously, we met these conditions with the Tl$^+$/Tl(Hg) and the Hg$_2^{2+}$/Hg electrode[2,3].

It should be noted, that in the particular case where $p' = 2\sigma K$, or close to this value, eqns. (11) and (12) become

$$Y' = 1/2\sigma\omega^{-\frac{1}{2}} \tag{16}$$

$$Y'' = 1/2\sigma\omega^{-\frac{1}{2}} + \omega C_d \tag{17}$$

Then a "normal" and "ideal reversible" behaviour of the electrode admittance would be observed, whereas in reality the reaction can be moderately irreversible, being accompanied by charge separation or recombination.

Finally, it is easily deduced that $\sqrt{\omega}/Y_{el}'$ increases with ω if $p' > 2\sigma K$, and decreases with ω if $p' < 2\sigma K$. The latter should be the case for the $Pb^{2+}/Pb(Hg)$ electrode.

The general analysis of the electrode admittance is in principle possible, if Y_{el}' and Y_{el}'' are measured at three different frequencies, for then eqn. (11) yields three equations from which the unknown quantities σ, p' and K can be obtained. Insertion of the results into eqn. (12) gives C_d. In practice, the calculation is rather involved and more reliable results may be expected if a whole series of experimental data at different frequencies is fitted into a calculated curve. Moreover, the value of σ may be estimated either by calculation from the diffusion coefficients, or from a plot of $\omega^{\frac{1}{2}}/Y_{el}'$ against $\omega^{\frac{1}{2}}$, which on extrapolation to $\omega = 0$ should give 2σ.

In our case, the latter procedure leads to $\sigma \approx 125$ (Fig. 1), but this result might be doubtful, because the extrapolation has to be performed from rather high frequencies. Actually, it is in good accordance with $\sigma = 120$–125 Ω cm^2 sec$^{-\frac{1}{2}}$, calculated with eqn. (7 a–c). Since a diffusion coefficient obtained from σ, usually differs less than 10% from that obtained from the limiting d.c. current[5], it is reasonable to assume that $115 < \sigma < 130$ cm^2 sec$^{-\frac{1}{2}}$.

Once σ is known, p' and K can be calculated from the values of Y_{el}' at two selected frequencies, for which we chose 420 and 2000 Hz. The results for five selected values of σ are listed in Table 2. The consistency of these numbers with the data at the other frequencies in Table 1 can be checked by plotting $\{Y_{el}'(p^2+2p+2)/p\}-\{\omega^{\frac{1}{2}}/\sigma\}$ against ω, which, according to eqn. (11), should be a straight line with slope

TABLE 2

PARAMETERS OF DELAHAY'S CIRCUIT

σ (Ω cm^2 sec$^{-\frac{1}{2}}$)	$p' \cdot 10^2$	θ (Ω cm^2)		K (μF cm^{-2})		C_d (μF cm^{-2})	
		plot A	plot B	plot A	plot B	plot B	plot C
110	0.5			125	125	0	6
115	0.8	0.9	0.9	125	122	26	28
120	1.3	1.5⁵	1.5⁵	145	140	40	42
125	1.7	2.1	2.1	165	160	44	46
130	2.0	2.7	2.6	190	170	45	51

K and intercept $1/\theta$ (Fig. 5, plot A). Evidently, all combinations in Table 2 satisfy a straight line and the resulting value of θ equals $p'\sigma$ in each case.

Another straight line is obtained, if $Y_{el}'(p+2)/p - Y_{el}''$ is plotted against ω (Fig. 5, plot B). The slope of this line is $-C_d$ and the intercept again, $1/\theta$. In this way, these quantities are derived from the experimental data, while only an estimated value for p' is introduced. Again, all the values of p' in Table 2 lead to straight lines, but the plot with $p' = 0.5 \times 10^{-2}$ gives the improbable result $C_d = 0$.

The value of K can also be obtained, only dependent on p', following the correlation

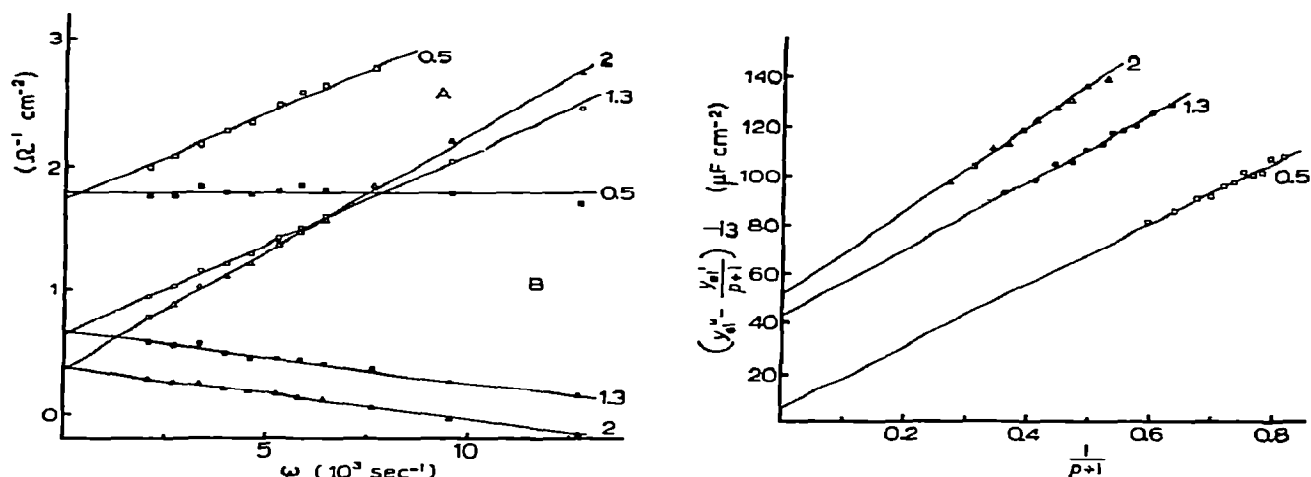$$\frac{1}{\omega}\left(Y_{el}'' - \frac{Y_{el}'}{p+1}\right) = C_d + \frac{K}{p+1}$$

Fig. 5. Plot A ($\bigcirc$, $\square$, $\triangle$): $\{Y_{el}'(p^2 + 2p + 2)/p\} - \{\sqrt{\omega/\sigma}\}$ against ω, yielding $1/\theta$ as intercept and K as slope. Plot B ($\bullet$, $\blacksquare$, $\blacktriangle$): $Y_{el}'(p + 2)/p - Y_{el}''$ against ω, yielding $1/\theta$ as intercept and $-C_d$ as slope. Numbers indicate values of $p' \cdot 10^2$.

Fig. 6. Plot C: Evaluation of C_d (intercept) and K (slope) from a plot of $\{Y_{el}'' - Y_{el}'/(p + 1)\} \times 1/\omega$ against $1/(p + 1)$. Numbers indicate values of $p' \cdot 10^2$.

Plots of the left-hand member against $1/(p+1)$ yield straight lines (Fig. 6, plot C) with different values for C_d (the intercept) and K (the slope) corresponding to different values of p'.

The results of the various plots are summarized in Table 2. With $p' = 2 \cdot 10^{-2}$ a discrepancy arises between the results of plot C and those of A and B. This seems to indicate an upper limit for the possible values for σ and p'. A lower limit does not manifest itself by discrepancies, but it is evident that values of $\sigma < 0.5 \times 10^{-2}$ in any case are not possible, since this would imply that C_d is negative. It must be stressed that C_d is not necessarily equal to the double-layer capacitance in the pure supporting electrolyte, as the adsorption of the electroactive ions may influence dq/dE. On the other hand, it is remarkable that for $\sigma = 120–125$ (still the most probable value) we find $C_d \approx 41–45$ μF cm^{-2}, close to $C_d = 40$ μF cm^{-2} in the absence of Pb^{2+}.

It can be concluded that the impedance of the Pb^{2+}/Pb(Hg) electrode in 1 M KCl can be represented by the equivalent circuit in Fig. 4 with the most probable parameters $115 < \sigma < 125$, $1 < \theta < 2$, $27 < C_d < 45$ and $125 < K < 165$ (dimensions as in Table 2).

DISCUSSION

The fact that, as DELAHAY stated, faradaic and double-layer charging processes cannot be separated, makes the theory of electrode impedance much more complicated. The foregoing analysis shows, however, that the parameters describing a model for the *whole electrode impedance* can be determined within certain limits. From the results one may deduce whether the electroactive species is more, or less, strongly adsorbed. In our example, the Pb^{2+}/Pb(Hg) electrode in 1 M KCl, it is evident that specific adsorption of Pb^{2+} certainly plays a role.

It is intriguing that both the models we studied, *formally* apply to the measured

impedances, with only one contradictory result, namely $\theta = 0$ in SENDA's circuit and $\theta \approx 1.5\ \Omega$ cm^2 in DELAHAY's circuit. We believe that it is not impossible that the former will still give consistent results if a priori $\theta \approx 1.5\ \Omega$ cm^2 is postulated; probably the value for C_d will increase further, whereas the other parameters will retain the reported values.

In DELAHAY's theory, the surface excesses of the electroactive species are accounted for in a relatively simple way, which, as it seems to us, implies that the surface concentrations of Ox and Red are related by the Nernst equation. It is questionable whether this is real for a non-ideal reversible electrode or even for a reversible electrode with specific adsorption of the reactants, in the non-steady state. It is noticeable that, if the Nernst equation holds, the adsorption capacitances, $C_{a,o}$ and K_o, as defined in the respective theories, are closely related. For

$$K_O = nF \left\{ \left(\frac{d\Gamma_o}{dE}\right)_{c_R} + \left(\frac{d\Gamma_o}{dE}\right)_{c_O} \right\}_{\eta-o}$$

As in the theory of SENDA AND DELAHAY, it may be assumed that the second term in the right-hand member is negligible; thus,

$$K_O = nF\ \frac{d\Gamma_o}{dC_O} \left(\frac{dC_o}{dE}\right)_{c_R} = \frac{n^2 F^2}{RT}\ \frac{d\Gamma_o}{dC_O}\ C_o = C_{a,o}$$

This seems to be supported by our experiments, since we found, with $R_{a,o} = 0$, that $C_{a,o} \approx 300\ \mu F$ cm^{-2} and $K = K_o \sigma_o/\sigma = K_o/2 \approx 150\ \mu F$ cm^{-2}. On the other hand, there is a striking difference between the models as regards the frequency-dependence of Y_{el}' in the ideal-reversible case: SENDA's circuit still requires decrease of $\omega^{\frac{1}{2}}/Y_{el}'$ with frequency, whereas DELAHAY's circuit predicts it to be constant. Note that with the latter, C_d and K cannot be separated in the ideal-reversible case.

Probably more decisive conclusions may be drawn if more detailed investigations, both theoretical and experimental (e.g., regarding concentration- and potential-dependence of the evaluated parameters) are available. Further work in this field is in progress in this laboratory and the results will be published later.

SUMMARY

The impedance of the Pb^{2+}/Pb(Hg) electrode has been measured in order to demonstrate the effect of specific adsorption of the electroactive species. The simple RANDLES' circuit is not in accordance with the experimental facts and therefore an attempt has been made to interpret them in terms of the theory of SENDA AND DELAHAY, or DELAHAY's new charge separation model. The procedure for evaluating the parameters is fully outlined. It is found that the experimental data fit both models.

REFERENCES

1 J. E. B. RANDLES, *Discussions Faraday Soc.*, 1 (1947) 11.
2 M. SLUYTERS-REHBACH, B. TIMMER AND J. H. SLUYTERS, *Rec. Trav. Chim.*, 82 (1963) 553.
3 M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *Rec. Trav. Chim.*, 83 (1964) 217, 967.
4 G. C. BARKER, *Electrode Processes 1959*, edited by E. YAEGER, Wiley, New York, 1961, p. 325.
5 T. BIEGLER AND H. A. LAITINEN, *Anal. Chem.*, 37 (1965) 572.
6 A. M. BATICLE AND F. PERDU, *J. Electroanal. Chem.*, 12 (1966) 15.
7 M. SENDA AND P. DELAHAY, *J. Phys. Chem.*, 65 (1961) 1580.
8 P. DELAHAY, *J. Phys. Chem.*, 70 (1966) 2373.
9 P. DELAHAY AND G. G. SUSBIELLES, *J. Phys Chem.*, 70 (1966) 3150.
10 M. SLUYTERS-REHBACH, W. J. A. WOITTIEZ AND J. H. SLUYTERS, *J. Electroanal. Chem.*, 13 (1967) 31.
11 M. SLUYTERS-REHBACH AND J. H SLUYTERS, *Rec. Trav. Chim*, 82 (1963) 525, 535.
12 B. TIMMER, M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *J. Electroanal. Chem*, 14 (1967) 169, 181.