

SHORT COMMUNICATIONS**Comment on the paper "Adsorption et impedance faradique" by A. M. Baticle and F. Perdu**

The study of electrode processes with specific adsorption of reactants is at present of special interest, especially with regard to the interpretation of impedances of galvanic cells. Recently, DELAHAY¹ has given a theory for the most general case, taking into account charge transfer, diffusion and adsorption of the reactants; this unfortunately, turns out to be very complicated, so that interpretation of cell impedances in terms of an equivalent circuit seems hardly feasible. Until some way round this has been found, it is certainly worthwhile to fit experimental data to a less rigorous circuit derived on the basis of some approximations. For example we showed that at frequencies between 0.2 and 8 kHz, the Tl⁺/Tl(Hg) electrode in 1 M KNO₃ and 1 M KNO₃ + 0.1 M KCl appears to behave like a normal Randles' circuit with only an additional capacitance, ΔC , parallel to the double-layer capacitance². On the other hand, BATICLE AND PERDU³ communicated in this journal that the same electrode in 0.5 M H₂SO₄ does not meet the Randles' circuit and that the more elaborate circuit proposed by SENDA AND DELAHAY⁴ is to be preferred. However, we have some comments on BATICLES' paper, which in our opinion are of sufficient interest to justify this Note.

I. Calculation of the impedance $R_r - j/\omega C_r$

For their analysis, BATICLE AND PERDU have to correct the measured impedance, $R_s - j/\omega C_s$, for the attributions of the ohmic resistance, R_E , and the double-layer capacitance, C_E (see their Fig. 1). The evaluation of R_E by extrapolation of R_s to infinite frequency is known to be without objections, except that subtraction of the "high frequency", R_E , leaves, at the lower frequencies, a minor frequency-dependent attribution of the solution resistance introduced by cell geometry (capillary response⁵). Therefore, $R_s - R_{s,\omega=0}$ should not be too small, say not below 10% of R_E .

However, from Fig. 1 (ref. 3) it follows immediately that, when $R_t = 0$, C_s at $\omega \rightarrow \infty$ does not reduce to C_E , but to

$$C_s \xrightarrow{\omega \rightarrow \infty} C_E + C_{aO} C_{aR} / (C_{aO} + C_{aR}) \quad (1)$$

Therefore, theoretically C_E can be found by extrapolation of C_s to infinite frequency only if $R_t > 0$. In practice the value obtained must be definitely wrong when the extrapolation is made from a frequency range where R_t is negligibly small. This may be illustrated by the following example. We infer that, after subtraction of $C_{s(\omega \rightarrow \infty)}$ and $R_{s(\omega \rightarrow \infty)}$, there remains an impedance, $R_r - j/\omega C_r$, that has no capacitive component at $\omega = \infty$. In other words, C_r must become zero on extrapolation to infinite frequency. Unfortunately, values of C_r were not reported in ref. 3 but we may use the values recalculated from the reported parameters which, according to the authors, are in good agreement with the experimental values (see also point 5). We recalculated, therefore, C_s for case II³ at various frequencies and found that a plot of

C_r vs. ω^{-1} approximates a straight line with a slight bending at the highest frequencies (40 kHz). A plot of C_r vs. $\omega^{-\frac{1}{2}}$ yields a perfect straight line (Fig. 1) with, however, an intercept of *ca.* 40 $\mu\text{F cm}^{-2}$. To check, we also calculated the capacity, C_s , of the total electrode impedance, arbitrarily taking $C_E = 100 \mu\text{F cm}^{-2}$. A plot of this C_s vs. $\omega^{-\frac{1}{2}}$ gives a similar straight line with intercept 140 $\mu\text{F cm}^{-2}$.

That BATICLE AND PERDU also did not find this extra capacitance of 40 $\mu\text{F cm}^{-2}$, is somewhat puzzling.

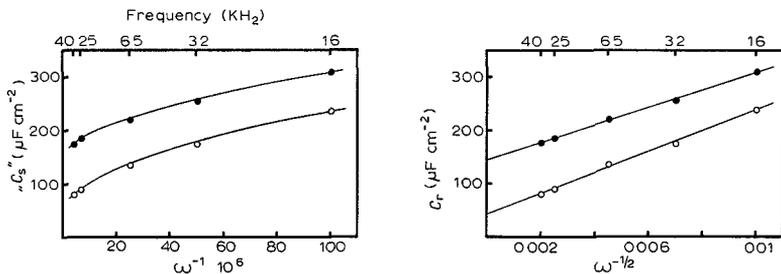


Fig. 1 Apparent electrode capacity, C_r (○) and measured capacity, " C_s " (●), as a function of frequency, calcd. from the data reported for case II in ref. 3, taking $C_E = 100 \mu\text{F cm}^{-2}$. See also text.

This example clearly demonstrates the *practical* invalidity of obtaining C_E by extrapolation to infinite frequency in the case of the $\text{Tl}^+/\text{Tl}(\text{Hg})$ electrode. The limit for R_t that should be exceeded depends on the other variables and is not easily calculated. Since, however, BATICLE AND PERDU report in their Table 2 that R_t is either zero or very small, we believe that their evaluation of C_E is incorrect also in the other cases (see also point 5). Clearly, such a doubtful start to the analysis must have considerable influence on the parameters calculated later.

2. Frequency-dependence of $\cot\theta$, R_r and $1/\omega C_r$

The plot of $\cot\theta$ vs. $\omega^{\frac{1}{2}}$, proposed in an earlier paper by BATICLE AND PERDU⁶, as a basis for a qualitative decision about the equivalent circuit, appears to be of less value in the present case. In our paper² on the Tl reaction we stated that for the Randles' circuit with additional capacitance and negligible R_t

$$\cot\theta = \omega C_r R_r = 1/(1 + 2\sigma \omega^{\frac{1}{2}} \Delta C) \quad (2)$$

Plots of $1/\cot\theta$ (taken from Fig. 2, ref. 3) vs. $\omega^{\frac{1}{2}}$ appear to be straight lines, in accordance with (2), up to 25 kHz, in some cases even up to 40 kHz. Deviations at higher frequencies, attributed by BATICLE AND PERDU to the existence of a finite adsorption resistance, R_{a0} (see also their reply), might well fall within the experimental error due to subtraction of the ohmic resistance. This error is reported (ref. 3, p. 370) to exceed 10%. The frequency-dependence of $\cot\theta$ is therefore suggestive of a Randles' circuit, as with the plots of R_r and $1/\omega C_r$ vs. $\omega^{-\frac{1}{2}}$. In this connection it should be noted that it is useless to confirm the parallelism of these plots at low frequencies by a plot of $1/\omega C_r$ vs. R_r as in Fig. 8. The intercept in the latter is naturally identical with the distance obtained in the first.

3. Determination of the charge transfer resistance R_t

The exact equation for R_r in the circuit of SENDA AND DELAHAY⁴ (see Fig. 1,

ref. 3) may be written in the form:

$$R_r = R_t + \omega^{-2} \Sigma \frac{I}{R_{ai} C_{ai}^2} \frac{I}{1 + I/p_i + [1 + I/\sigma_i \omega^{\frac{1}{2}} C_{ai}]^2 / p_i (p_i + 1)} \quad (3)$$

in which $p_i = R_{ai}/\sigma_i \omega^{-\frac{1}{2}}$. This equation reduces to eqn. (3) given by BATICLE AND PERDU at such high frequencies that the denominator of the second fraction reduces to $1 + (I/p_i)$ while, in addition, $I/p_i < 0.3$. From the values reported in their Tables 2 and 3 it can be calculated that in none of cases I – IV are these conditions fulfilled. For example, for case IV we calculated (at $\omega = 25 \cdot 10^4$ (40 kHz)) the summation term to be $2.3 \cdot 10^{-9}$ with the exact equation, and $-4 \cdot 10^{-9}$ with BATICLE'S eqn. (3). Clearly, the approximation is by no means valid and consequently the values for R_t in Table 2 (ref. 3) have no meaning. Moreover, even if R_t had been determined without an approximation, the results would have been in error because of the doubtful evaluation of C_E . The accordance with literature values is in this case a rather doubtful argument, since in the quoted works of RANGLES⁷ and BARKER⁸, the adsorption of reactants could not be accounted for.

To get some idea of the feasibility of the extrapolation of R_r vs. ω^{-2} , we made such a plot (Fig. 2) for case II (reported $R_t \sim 0$) and case IV (reported $R_t = 0.060$), again with the values recalculated from the reported parameters. We cannot see how such a precise result ($R_t = 0.060$ in case IV) can be obtained, even from the highest frequencies, when the error due to the ohmic resistance must be extremely large.

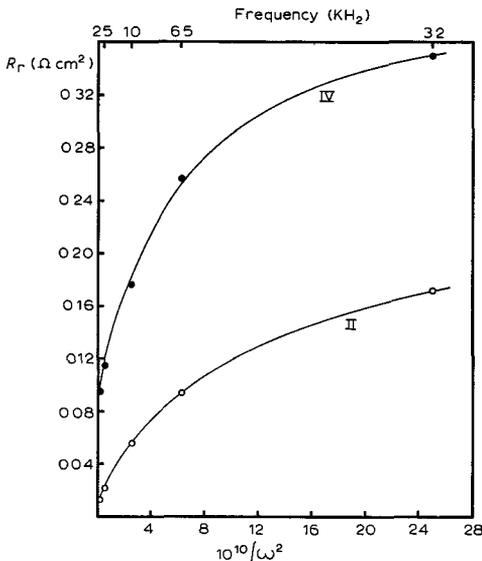


Fig. 2 Apparent resistive component as a function of frequency, calcd from the data reported for cases II and IV in ref. 3

4. Calculation of the adsorption capacitance and resistance

The error in the evaluation of C_E and R_t throws suspicion on the values of C_{ai} and R_{ai} reported by BATICLE AND PERDU in their Table 3, because the quantities A and B needed for the calculations are obtained from C_E and R_t . Serious errors are

possible; e.g., in case VI, R_t amounts to ca. 25% of $R_r - \sigma\omega^{-\frac{1}{2}}$ at 1.6 kHz and even 80% of $R_r - \sigma\omega^{-\frac{1}{2}}$ at 40 kHz.

Too much importance should not be attached to the coincidence of the measured impedance components and those recalculated from the evaluated parameters. This only shows that it is possible for the equivalent circuit considered to describe the experimental facts within the applied frequency range, but it does not prove that other equivalent circuits, or even the same circuit with another set of parameters, would not fit (*cf.* our analysis of the $\text{Pb}^{2+}/\text{Pb}(\text{Hg})$ electrode⁹). In this connection it would have been useful to report the precision of the results.

5. The possibility of the Randles' circuit with additional capacitance

In the discussion of their paper, BATICLE AND PERDU comment upon our interpretation of the impedance of the $\text{Tl}^+/\text{Tl}(\text{Hg})$ electrode. They state, incorrectly, that we supposed the transfer resistance to be negligible and that we applied a graphical analysis. Actually, we considered just the same overall impedance as represented in eqn. (19) of BATICLE AND PERDU, therefore the latter is by no means original. Furthermore, we feel that our method of evaluating the parameters is much simpler than their method: eqns. (20) and (21) contain in principle three unknowns and have to be solved with at least two different frequencies. However, we understand (see also their reply) that BATICLE AND PERDU consider σ as a known quantity obtained from R_r and $1/\omega C_r$ (after subtraction of C_E , which is a rather doubtful quantity, see point 1) at low frequencies. In our opinion, it is illogical to solve the unknown $C = C_E + \Delta C_E$ from eqn. (20) in ref. 3 after such a procedure. As BATICLE AND PERDU have said that insertion of their experimental data into those equations did not lead to consistent results, we tried to check this with our own method.

As the data on the total cell impedance were not reported, we recalculated the components, R_r and $1/\omega C_r$, from the tabulated values of R_t , D_o , D_r , C_{aO} , C_{aR} , R_{aO} and R_{aR} using the expressions pertaining to SENDA's circuit. The calculations were performed for cases I-VI at some frequencies in order to check whether the results could fit the equation for the Randles' circuit:

$$1/(R_r - j/\omega C_r) = j\omega \Delta C_E + 1/\{R_t + \sigma\omega^{-\frac{1}{2}}(1 - j)\} \quad (4)$$

Obviously, if this is the case, the components, R_s and $1/\omega C_s$, of the total impedance must fit the analogous eqn. (19) of ref. 3, since C_E is a capacitance parallel to ΔC_E .

The first step in our method is the calculation of:

$$\{R_r^2 + (1/\omega C_r)^2\}/R_r = q = R_t + \sigma\omega^{-\frac{1}{2}} + \sigma^2\omega^{-1}/(R_t + \sigma\omega^{-\frac{1}{2}}) \quad (5)$$

From the frequency dispersion of q , the values of R_t and σ may be obtained, but for all cases I-VI we found q/ω to be virtually constant up to 25 kHz, and we conclude therefore that R_t is negligibly small, as we found for the Tl reaction in KNO_3 solutions. Again, the existence of a finite R_t or R_a is assumed by BATICLE AND PERDU on the basis of measurements at very high frequencies where the error due to the ohmic resistance is large.

The values of $\frac{1}{2}q/\omega = \sigma$ agree with those obtained by BATICLE AND PERDU from the low-frequency data (see their eqn. (4) and Table 2). Introduction of these values, together with $R_t = 0$, into eqn. (4) leads to ΔC_E -values constant, within experimental error, up to 25 kHz. As measurements at higher frequencies, are valueless

in our opinion, because of their inaccuracy, it can be concluded that the impedance of the $Tl^+/Tl(Hg)$ electrode in $0.5 M H_2SO_4$ fits the Randles' circuit, in contrast with the statements of BATICLE AND PERDU. Actually, in cases I, II and VI (high amalgam concentrations) the attribution of the Red-component to the impedance appears to be negligible up to 40 kHz, and R_t is reported to be zero or negligibly small, so that in these cases SENDA's circuit automatically becomes identical with Randles' circuit, with $C_{aO} = \Delta C_E$

Of course, C_s is still frequency-dependent (*cf.* Fig. 1) but this does not mean that the Randles' circuit is invalid as stated by BATICLE AND PERDU¹ in their introduction. We think that they misunderstand the method for checking the validity of Randles' circuit, because their argument on this point, and also in section 5, is confused.

The question arises, how can real values for ΔC_E be found, when, in fact, ΔC_E should have been incorporated into the apparent C_E obtained at $\omega \rightarrow \infty$. This may be due to experimental deviations which are likely to occur at frequencies as high as 50 kHz. This is supported by the negative ΔC_E calculated by us in case VI.

In conclusion, we wish to stress that care should be taken in fitting experimental data to an equivalent circuit that rationalizes specific adsorption of reactants. Consistency of the calculated parameters with the approximations used should be checked, taking into account the accuracy of the measurements.

Finally, since all redox systems with adsorption of reactants so far studied^{2,3,9-12} appear to proceed with an immeasurable rate of charge transfer, a causal connection between reversibility and presence of specific adsorption might exist. If so, simultaneous control by adsorption and charge transfer would not occur in practice. This would be of great value to electrochemistry as relatively simple expressions for the electrode impedance could then be used¹⁰, these, in the case of weak adsorption, become identical with those of the Randles' circuit with an additional concentration-dependent capacitance.

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Received May 4th, 1967; in revised form, October 27th, 1967