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ANALYSIS AND INTERPRETATION
OF
IMPEDENCE MEASUREMENTS
ON
FERROCYANIDE - FERRICYANIDE ELECTROLYTIC CELLS

Technical Report No. 2
to the
OFFICE OF NAVAL RESEARCH
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Research Contract
Nonr-604(00)

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By
A. Edward Remick
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INTRODUCTION

The first Technical Report (1) prepared in connection with this research project was issued in April 1953. Although at that time we had not completed the mathematical and theoretical analysis of our data, we felt that it would be unwise to delay the report longer. Accordingly we presented at that time all of our experimental data together with such interpretation as we were able to give without further extensive study and computations. We now wish to present a more complete analysis of our data. No new experimental data will be given in this report. References to tables and equations in our first report will be made by prefixing the letter A to the number of the table or equation as given in the first report.

THEORETICAL INTERPRETATION

Our ultimate objective is three-fold. (1) We wish to analyse the behavior of an electrode into its components. This analysis can be graphically represented by an equivalent circuit consisting of both conventional and unconventional circuit elements. Tentatively we accept Grahame's equivalent circuit modified by the introduction of an

"electrode layer resistance," R_L , as shown in Fig. A-I.

(2) We wish to establish the fundamental nature of the unconventional circuit elements. (3) We wish to apply this fundamental knowledge to the elucidation of the mechanism of electrochemical redox reactions.

An excellent start toward our goal has been made by Rozental and Ershler (2), Randles (3,7), Grahame (4) and Gerischer (5) all of whom have made contributions to the mathematical theory of what Grahame calls the "Warburg impedance." There are many points of similarity in the theories of these five men but Grahame's theory seems to be the most complete and we have therefore concentrated our efforts on determining to what extent his theory is capable of quantitatively, or at least qualitatively, interpreting our data. As described in our first report, we made impedance bridge measurements on alternating current electrolytic cells fitted with platinum electrodes and containing aqueous solutions of potassium ferrocyanide and ferricyanide in equimolar concentrations together with either potassium sulfate or sodium benzene sulfonate as supporting electrolyte. The variables studied were frequency, ionic strength and depolarizer concentration.

In order to compute the equivalent series capacitance (C_g^*) and resistance (R_g^*) of the faradaic branch of the circuit, it is necessary to know the double layer capacity (C_d). There are two common methods of determining C_d in

cells containing depolarizers. The one involving an extrapolation of C_s (the series equivalent capacitance of the entire cell) to a zero value of $1/\sqrt{\omega}$ is not to be recommended for Q-dispersion data when alternating current alone is used because the double layer capacity is a function of E_{AB} (the potential drop from A to B of Fig. A-1) and E_{AB} changes with the frequency because the Warburg impedance is frequency-dependent.

The second method is the one commonly used by polarographers. It consists of making capacitance measurements on the supporting electrolyte alone. The results of such measurements were given in Table A-II. The ionic strengths there listed are not the actual values; they are the values which would obtain if to each potassium sulfate solution one added enough depolarizer to make the solution 0.005M in both ferrocyanide and ferricyanide. Thus each value of C_s in Table A-II may be taken to be the C_d value corresponding to the same ionic strength and the same frequency in Table A-I.

The double layer capacities determined in this manner show some dispersion. At first this fact caused us some concern because Grahame (6) had found no dispersion of C_d occurs with ideal polarized electrodes and we therefore rejected this method of measuring C_d (1). However, his method of measurement was very different from ours since he used a D.C. bias voltage together with a very small alternating current. He showed that C_d is a function of the

voltage and hence we would expect our measurements of C_d to vary somewhat with the frequency at constant half-wave area because under these conditions E_{AB} would vary with the frequency. These considerations suggested that perhaps the capacitances given in our Table A-II really were double layer capacitances despite their dispersion. Nevertheless, the fact that these values decrease with an increase in frequency certainly suggests that a small faradaic current is flowing. Be that as it may, the fact remains that these C_d values are very small compared to C_s and hence the small dispersion, even though spurious, will not be of much practical importance. We therefore used these C_d values to calculate R_s^* and C_s^* by means of our Eq's. (A-8) and (A-9).

Effect of Frequency. Grahame's theory (4) leads to his Eq's (38) and (39) which, for reversible systems in which $\theta = 0$, reduce to the following equations:

$$R_s^* = \eta \omega^{-1/2} \quad (1)$$

$$C_s^* = \eta^{-1} \omega^{-1/2} \quad (2)$$

These two equations give us a simple method of comparing experiment and theory. They require that plots of both R_s^* and C_s^* against $1/\sqrt{\omega}$ be linear and that the same value of η be obtained from the slope of either curve. Both curves should pass through the origin.

The necessary data for making these tests have been computed from the figures given in Tables A-I and A-II and

assembled in Table I. The equations used were Eq's. (A-8), (A-9) and the following:

$$\begin{aligned}R_{\Delta} &= R_S - R_T - R_L \\M &= \frac{2 R_{\Delta}}{R_{\Delta}^2 + X_S^2} \\N &= \frac{2 X_S}{R_{\Delta}^2 + X_S^2} - \frac{1}{X_d}\end{aligned}$$

in which the symbols have the meanings previously associated with them. In Table I C_S^* is Grahame's pseudocapacitance and R_S^* may reasonably be called the "pseudoresistance when θ is zero. Plots of C_S^* and R_S^* against $1/\sqrt{\omega}$ were found to be linear (Figs. 1 and 2). Moreover, they passed through the origin in those cases where a sufficient excess of supporting electrolyte was present (i.e., ionic strength = 0.5300 or 0.6805 with the concentration (w) of the depolarizer equal to 0.005, 0.010 or 0.015 molar.) In the experiment where this excess was greatest, the mean deviation of C_S^* values from linearity was 1.4 μ F; for R_S^* , it was 0.39 ohm. The larger percentage error in R_S^* is to be expected since R_S^* values are more sensitive than those of C_S^* to the rather considerable errors in R_{Δ} .

The next phase of the test is the comparison of the values of η calculated respectively from the slopes of the C_S^* and R_S^* curves. This comparison is not impressive, as might be expected from the poor precision of the R_S^* values. The results of the comparison are given in Table II, from which it is evident that to a first rough approximation the

values of η calculated from C_S^* are the same as those calculated from the corresponding values of R_S^* .

The identity of the values of η calculated from Eq's. (1) and (2) may be tested in another way not involving the uncertainty inherent in the graphical determination of slopes. Grahame pointed out that eliminating η by the simultaneous solution of Eq's. (1) and (2) yields the equation $R_S^* C_S^* \omega = 1$ when θ is zero. Values of this product are readily calculated from the data in Table I and are presented in Table III. It will be noticed that agreement with theory is better at low frequencies. This conceivably could mean that the reaction is not rapid enough to be reversible at the higher frequencies. In any event, we can state that in the experiment in which the supporting electrolyte was present in greatest excess, the agreement between theory and experiment is satisfactory up to 1000 c.p.s.

The above tests furnish reasonably good verification for the equations developed by Grahame insofar as they are concerned with the frequency-dependance of C_S^* and R_S^* . It should be remarked that the predicted linear dependence of C_S^* and R_S^* on $1/\sqrt{\omega}$ was found by Rozental and Ershler (2) to hold true for measurements made with a mercury electrode in a solution of mercurous nitrate containing a large excess of perchloric acid and by Randles (7) using both mercury and platinum electrodes with various oxidation-reduction systems including the ferrocyanide-ferricyanide system.

Effect of concentration of depolarizer. Let us next examine the concordance between theory and experiment achieved with relation to variations of the concentration of the depolarizer in the bulk of the solution. Experimentally we find that plots of the bulk concentration of oxidant (or reductant) against the values of C_S^* at ionic strength 0.6805 (Table I) are accurately linear. The corresponding plots of $1/R_S^*$ also show a definite tendency to be linear but the precision is poor, as would be expected from our previous remarks. It might be mentioned incidentally that the corresponding plots of $1/R_\Delta$ show no tendency to be linear except at 200 c.p.s.

If now we seek evidence that these linear relationships are in accord with theory, we find that they are demanded by Randles' (3) Eq's. (16) and (17). However, if these equations are to be used for the ferrocyanide-ferricyanide solutions, it must be remembered that they would involve the assumption that the diffusion coefficients of ferrocyanide and ferricyanide are the same. This assumption is not completely justified since Kolthoff and Lingane (8) give 0.74×10^{-5} and $0.89 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ respectively for the diffusion coefficients at infinite dilution.

Grahame's equations express concentrations in terms of w_1 (the concentration at the electrode surface), not in terms of concentrations in the bulk of the solution, and are therefore difficult to apply rigorously to our experimental data. An approximate solution of the problem may be achieved,

however, on the basis of two reasonable assumptions:

(1) equilibrium in the electron transfer reaction is continuously established between the electrode and the adjacent layer of electrolyte, and (2) using time-average values, $w_{ox} = C_{ox}$ and $w_{Red} = C_{Red}$, where C symbolizes molar concentrations in the bulk of the solution. The first assumption is surely justified at sufficiently low frequencies, the determination of the maximum valid frequency being an experimental matter. In regard to the second assumption, it must be recognized that bridge measurements give only average values of R_s and C_s and these are related to average values of w_{ox} and w_{Red} . In the steady state (or, better, in the cyclic state) which is presumably achieved in the electrolytic cell when alternating current alone is used, it would seem that w_{ox} would vary cyclically above and below C_{ox} so that on the average the two would be equal for small currents. A similar statement applies to w_{Red} and C_{Red} .

If we express the Nernst equation in terms of concentrations rather than activities, we may write:

$$E = E_0 - (RT/nF) \ln (w_{ox}/w_{Red}) \quad (3)$$

Partial differentiation of this equation with respect to concentration and combination with Grahame's definition of β , viz.,

$$\beta_i = \partial E / \partial w_i \quad (4)$$

gives the two equations:

$$\beta_{\text{ox}} = \partial E / \partial w_{\text{ox}} = - RT/nF w_{\text{ox}} \quad (5)$$

$$\beta_{\text{Red}} = \partial E / \partial w_{\text{Red}} = RT/nF w_{\text{Red}} \quad (6)$$

Combination of Grahame's definition for η , viz.,

$$\eta = \sum_1 \beta_1 \nu_1 / \sqrt{\epsilon_1} \quad (7)$$

with Eq's. (5) and (6), introduction of numerical values for ν and recognition that in our poised solutions $C_{\text{ox}} = C_{\text{Red}} = w_{\text{ox}} = w_{\text{Red}} = C$, yields the equation:

$$\eta = \frac{RT}{nFC} \left(\frac{\sqrt{2\epsilon_{\text{Red}}} + \sqrt{2\epsilon_{\text{ox}}}}{2\sqrt{\epsilon_{\text{ox}} \epsilon_{\text{Red}}}} \right) \quad (8)$$

Combining this equation with Eq (2) gives:

$$C_s^* = \frac{2 nFC}{RT \sqrt{\omega}} \left(\frac{\sqrt{\epsilon_{\text{ox}} + \epsilon_{\text{Red}}}}{\sqrt{2\epsilon_{\text{Red}} + \sqrt{2\epsilon_{\text{ox}}}}} \right) \quad (9)$$

If the temperature and frequency are held constant and if we assume, as a first approximation, that in the presence of an appreciable excess of supporting electrolyte and at constant ionic strength the diffusion coefficients are independent of C , Eq. (9) becomes:

$$C_s^* = kC \quad (10)$$

where k is a constant. Similarly, Eq's. (2) and (8) lead to the equation

$$R_s^* = \frac{k'}{C} \quad (11)$$

Obviously Eq's. (10) and (11) are the desired equations showing that C is a linear function of C_S^* and $1/R_S^*$ and that both curves pass through the origin, as observed experimentally in the presence of a fairly large excess of supporting electrolyte.

This same dependence of C_S^* and $1/R_S^*$ on the concentration is demanded by Eq's (4) of Rozental and Ershler (2) although their constants are not the same as ours--indeed their equations were developed for a metal-metallic ion type of electrode.

The relationship between the constants in Eq's. (10) and (11) is:

$$k = 1/k'\omega \quad (12)$$

This equation can be tested by determining the two constants respectively from the slopes of the plots of C_S^* against C and of $1/R_S^*$ against C . Table IV gives the calculated values of k and $1/k'$. The comparison is very satisfactory. It is incidentally apparent that the assumptions which went into Eq. (12) are good approximations to the truth.

The Electrode Layer Resistance. In our preceding Technical Report (1) we showed that there is a frequency-independent component of the cell resistance in addition to the electrolytic resistance (R_T). We tentatively called it the "electrode layer resistance" and symbolized it as R_L . We consider, especially since the concordance between

experiment and theory demonstrated in the preceding section of the present report was achieved only by taking R_L into account, that the existence of such a resistance has been demonstrated. It does not follow, of course, that R_L is the resistance of a poorly conducting electrode layer. It might have quite a different origin.

One other possible origin is a slow electron discharge step. It will be remembered that we assumed Grahame's θ (which is a frequency-independent resistance associated with a slow discharge step) to be zero. It is natural to inquire whether the alternative assumption of a zero value for R_L and a finite value for θ would not lead to equally satisfactory agreement with experiment. If it did, it would demonstrate only that R_L and θ are not both equal to zero and the problem then would shift to seeking independent evidence as to which one, if either, is zero.

One might guess from the galvanic behavior of ferrocyanide-ferricyanide half-cells that this redox system is highly reversible and therefore that θ is zero. The contrary conclusion was reached, however, by Randles (7). Using platinum electrodes and either potassium chloride or potassium sulfate as supporting electrolyte, his impedance measurements led him to the conclusion that the electron transfer step is measurably slow. From the value of θ (which he symbolized as $R_v - \frac{1}{\omega C_r}$) he calculated a value of about 0.1 cm sec^{-1} for the specific reaction rate at 20° .

It is significant that he used an equivalent circuit like Grahame's and gave no consideration to the possibility of an electrode layer resistance despite the fact that he made the following observations: (1) Immediately after immersing the electrodes, θ changed rapidly for a few minutes although C_S^* changed very little; (2) Addition of gelatin increased θ but did not affect C_S^* . He concluded that the latter effect is almost certainly due to gelatin adsorbed on the electrode surface.

Clearly, there is some justification for suspecting that Randles' θ should have been considered as an electrode layer resistance and therefore that the electron exchange is much more rapid than he indicated. It would be highly desirable to find some independent source of information relating to the speed of electron transfer. The "reversibility" of the ferrocyanide-ferricyanide system observed in measuring equilibrium potentials is no criterion for reaction speeds which would appear very rapid in an alternating potential field of, say, 200 c.p.s. The same objection could be raised with respect to studies on the rate of electron exchange as judged by radioactive tracer techniques, which show the exchange between ferrocyanide and ferricyanide ions to be complete in four minutes or less (9). There is, however, one piece of evidence which seems to be pertinent. Silverman and Remick (10), working with platinum electrodes in a solution containing equimolar concentrations of

ferrocyanide and ferricyanide, found that the oscillograms relating cell potential to current were straight lines at 100 c.p.s. using current densities up to 88.8 ma cm^{-2} . No doubt the "straight lines" would have appeared as very thin ellipses had higher amplification been possible but under the same conditions solutions containing no components of a "reversible" redox system appeared as very fat ellipses. The conclusion is inescapable that the depolarizing action of the ferrocyanide-ferricyanide is so rapid, compared to the alternating current period of 0.01 sec., that no detectable polarization of the electrode occurred in this poised solution where the concentration polarization is characteristically negligible. Similar results were obtained at 300 c.p.s. at a somewhat lower current density.

In view of this evidence, we are compelled to conclude that it is θ , not R_L , which is zero in our experiments. Further evidence leading to the conclusion that R_L is not zero is furnished by the fact that R_L is determined by extrapolation of R_s to infinite frequency. In terms of Grahame's theory, the impedance of the faradaic branch of the circuit, including θ , is infinite when the frequency is infinite; therefore R_L cannot be in the faradaic branch.

Effect of Ionic Strength. Table I shows clearly that an increase in ionic strength at constant concentration of depolarizer and constant frequency results in an increase of C_s^* while R_s^* usually rises slightly to a maximum and then falls comparatively rapidly.

There are apparent three ways in which the ionic strength might affect the values of C_S^* and R_S^* : (1) Up to a point, an increase in ionic strength would diminish the effect of electrical migration. Let us call this the migration effect. (2) The coulombic interactions between the electrode and the depolarizer ions would be diminished by an increase in ionic strength in a manner reminiscent of the Bronsted-Christiansen-Scatchard equation used in chemical kinetics (11). Let us call this the kinetic effect. (3) The activity coefficients of the depolarizer ions would be affected by interionic attractive forces and this effect would be reflected in Eq's. (5) and (6) where, strictly speaking, the concentration terms should be replaced by activities. Let us call this the thermodynamic effect.

These three effects will now be considered in turn as possible explanations of the observed influence of ionic strength on the values of C_S^* and R_S^* .

Judging from the general experience of polarographers, it would not be expected that electrical migration would be effectively eliminated in any of the solutions used in studying ionic strength variations except the most concentrated one. The migration effect would, therefore, be expected to be a factor of importance. It could be formulated mathematically by using Grahame's theory of the faradaic admittance (4) and developing the equations which would follow from that theory if electrical migration were

not assumed to be absent. This would be difficult but if it could be done, it would give us a means of determining the charge type of the participating species in electroreduction. Such information would be very valuable to those engaged in the study of redox mechanisms.

We must reject the kinetic effect as a probable explanation of our results because we have already concluded that the electrochemical reactions involved are essentially instantaneous. It should be remarked, however, that Randles (7), studying the alternating current electrolysis of the chromocyanide-chromicyanide system, concluded that an increase in ionic strength increased the reaction rate because it cut down the repulsion of the negatively charged depolarizer ions by the electrode. This explanation seems to be incomplete, however, because impedance bridge measurements give average values of capacitance and resistance for both the anodic and cathodic half-cycles and the ions in question are repelled by the electrode during one half cycle and attracted during the other.

Finally, we must consider the thermodynamic effect. An obvious approach to the relation between ionic strength and activity coefficients is the use of the Debye-Hückel limiting law. This law is not apt to give a quantitatively accurate description of the behavior of solutions as concentrated as ours but it should at least give a reliable prediction of the direction of the effect. The mathematical

procedure is as follows. Start with Eq (7), which defines γ , using activities, f_w , in place of concentrations, w , and remembering that $w_{\text{ox}} = w_{\text{red}} = w$. Substitute this value of γ into Eq (2) and differentiate C_s^* with respect to the ionic strength, μ , taking ω , T , w and ϵ as constants. This procedure yields the equation:

$$\frac{dC_s^*}{d\mu} = \frac{2nFw \sqrt{\epsilon_{\text{ox}} \epsilon_{\text{red}}}}{RT\sqrt{\omega} (f_{\text{ox}} \sqrt{2\epsilon_{\text{ox}}} + f_{\text{red}} \sqrt{2\epsilon_{\text{red}}})^2} \left[f_{\text{ox}}^2 \sqrt{2\epsilon_{\text{ox}}} \frac{df_{\text{red}}}{d\mu} + f_{\text{red}}^2 \sqrt{2\epsilon_{\text{red}}} \frac{df_{\text{ox}}}{d\mu} \right] \quad (13)$$

Next, introduce the Debye-Hückel limiting law

$$\ln f_1 = -2.303 A z^2 \sqrt{\mu}$$

which may be written

$$f_1 = \exp(-K_1 \sqrt{\mu}) \quad (14)$$

where

$$K_1 = 2.303 A z^2 \quad (15)$$

Differentiation gives

$$\frac{df_1}{d\mu} = \frac{-K_1}{2\sqrt{\mu}} \exp(-K_1 \sqrt{\mu}) \quad (16)$$

Eq (16) may now be used for the evaluation of the terms $df_{\text{ox}}/d\mu$ and $df_{\text{red}}/d\mu$ in Eq (13). Appropriate substitution and simplification finally yields the equation:

$$\frac{dc_s^*}{d\mu} = \frac{-nFw \sqrt{\epsilon_{ox}\epsilon_{red}}}{RT \sqrt{\omega\mu} (f_{ox}\sqrt{2\epsilon_{ox}} + f_{red}\sqrt{2\epsilon_{red}})^2} \left[f_{ox}^2 \sqrt{2\epsilon_{ox}} K_{red} \exp(-K_{red}\sqrt{\mu}) \right. \\ \left. + f_{red}^2 \sqrt{2\epsilon_{red}} K_{ox} \exp(-K_{ox}\sqrt{\mu}) \right] \quad (17)$$

where K_{ox} and K_{red} are specific values of K_1 in Eq (15).

Eq (15) shows that K_{ox} and K_{red} are both positive. Since all of the other quantities in Eq (17) are obviously positive, it is clear that $dc_s^*/d\mu$ has a negative value. Since this is contrary to our experimental observations, it seems fairly safe to conclude that the observed effect of ionic strength on C_s^* is not to be ascribed primarily to the influence of interionic attraction on the activity coefficients of the depolarizer ions.

One may reasonably doubt the reality of the maxima observed in the curves relating R_s^* and ionic strength. These maxima are slight and occur at low ionic strengths where Grahame's equations would not be expected to hold accurately. In general we rather expect all variables except frequency to effect C_s^* and R_s^* in opposite directions and such is probably true of the ionic strength.

Having now considered all three effects we can only conclude that if any one of them is the major cause of the observed influence of the ionic strength on the values of C_s^* and R_s^* , it must be the migration effect. The truth of

this suspicion, however, can be demonstrated only by carrying out a suitable mathematical analysis of the problem, as suggested above. Finally, it must be admitted that the evidence on the basis of which the kinetic effect was ruled out is not very strong. Clearly the theory of the ionic strength effect is an unsolved problem.

TABLE II

COMPARISON OF THE VALUES OF
OBTAINED FROM THE SLOPES OF THE PLOTS OF $1/\sqrt{\omega}$
AGAINST R_S^* AND C_S^* .

<u>Ionic Strength</u>	<u>Conc. of oxidant & reductant</u>	<u>from R_S^*</u>	<u>from C_S^*</u>
0.6805	0.005M	140	137
0.6805	.010	79.0	74.6
0.6805	.015	49.0	49.7
0.5300	.005	179	150
0.3821	.005	171	174
0.2314	.005	166	157

TABLE III

VALUES OF $R_s^* C_s^* \omega$

<u>Ionic</u>						
<u>Strength</u>	0.6805	0.6805	0.6805	0.5300	0.3821	0.2314
<u>Conc. (w)</u>	0.005	0.010	0.015	0.005	0.005	0.005
<u>Frequency</u>						
200 c.p.s.	0.98	1.03	1.01	1.01	1.03	1.03
400	0.99	.93	.93	1.13	1.03	1.02
600	0.95	1.04	.99	1.11	1.13	1.00
800	0.99	1.09	1.03	1.14	1.19	1.03
1000	0.98	1.13	.99	1.16	1.27	0.91
1500	0.88	1.11	1.04	1.17	1.28	1.00
2000	0.88	1.09	0.91	1.12	1.16	0.96
2500	0.91	1.14	0.96	1.15	1.25	1.01
3000	0.91	1.17	1.01	1.25	1.36	0.92
3500	0.86	1.14	0.91	1.12	1.25	0.91
4000	0.81	1.10	0.80	1.10	1.21	0.89
5000	0.79	0.96	0.75	1.15	1.09	0.75

TABLE IV

TEST OF EQUATION (12)

<u>f</u>	<u>k</u>	<u>1/k'ω</u>	<u>f</u>	<u>k</u>	<u>1/k'ω</u>
200	0.0378	0.0382	2000	0.0119	0.0130
400	.0273	.0286	2500	.0105	.0109
600	.0216	.0215	3000	.0098	.0098
800	.0194	.0183	3500	.0089	.0097
1000	.0175	.0175	4000	.0081	.0097
1500	.0133	.0141	5000	.0073	.0087

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