ELECTRIC IMPEDANCE AND RECTIFICATION OF FUSED ANION-CATION MEMBRANES IN SOLUTION

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ABSTRACT At relatively high currents, fused anion-cation membranes give rise to rectifying and reactive effects. The rectification becomes less pronounced with increasing frequency. This effect results from changes in the concentration profiles of the ions during the positive and negative phases of the AC cycle. With reduction of the current, the voltage-current response becomes linear. The reactive effect can then be separated from the rectifying effect. The former effect can be attributed essentially to two factors: (*a*) the presence of transition regions of fixed charge and (*b*) the diffusion mechanism of the ions in an AC field. The first factor is largely frequency-independent and the second, frequency-dependent. A first approximation equivalent circuit is described. This circuit involves frequency-dependent elements.

INTRODUCTION

The physical and chemical mechanisms underlying many dielectric and impedance effects of complex membranes, both living and non-living, are as yet incompletely understood. By chemical means, artificial membranes of relatively simple structure can be produced. The investigation of these membranes in electrolytic solution can serve to shed light on the processes responsible for the anomalous electrical behavior of organic membranes.

Lovrecek, Despic, and Bockris (1) obtained rectification across a membrane in which highly mobile protons were present on one side of the membrane and highly mobile hydroxyl ions on the other side of the membrane. They attributed the rectifying properties as resulting from the H^+ and OH^- ions being impelled toward each other during one phase of the alternating current cycle through the system and away from each other during the other phase, the first phase representing the case of easier current flow. Maslov and Ovodova (2) produced systems operating in the same mode, namely $2d \gg L_D$ as defined in the next paragraph. At low currents these systems behaved like a pure resistance.

Mauro (3) showed that reactive effects could arise from the close juxtaposition of anion-cation membranes. The theory corresponded to Shockley's theory of the *p-n* junction (4). One condition for a capacitative effect with a relatively large shunt resistance was given as $2d \ll L_D$, where $2d$ is the distance of separation between the positive and negative fixed charge membranes and L_D is the "Debye length" of the solution. Mauro gave some experimental evidence of the existence of reactive effects in such systems. He showed voltage-time plots of the transient response upon closing and opening the circuit containing the membrane centrally located in a two-compartment solution of KCl. While such plots indicated a capacitative effect, they did not reveal the nature of the capacitance and of the resistance.

The present paper deals with a series of experiments performed with fused cation-anion membranes with the purpose of studying the reactive effects. Relatively large currents of the order of a milliampere or of a fraction of a milliampere and small currents of the order of a microampere or of a fraction of a microampere were used. Oscillograph records were obtained of the *I-V* characteristics in both cases and by means of the dual trace of the oscilloscope, the current and voltage variations as a function of time were also photographically recorded. Moreover, at low currents the frequency dependence of resistance, reactance, and impedance in the microampere range was studied in detail for frequencies extending from 0.1 to 10,000 cps. An approximate equivalent circuit of the system was obtained for these frequencies.

METHODS

As indicated in Fig. 1, a cylindrical lucite cell was used in these experiments. The part filled with electrolytic solution had a length of 10.0 cm and a cross-sectional area of 0.72 cm^2. The voltage electrodes were separated by a distance of 1.4 cm. The membrane, centrally located, divided the cell into two compartments and each compartment was filled with the same KCl solution, either 0.1 or 0.2 M.

Preliminary tests of the cell containing the KCl solution but without the membranes were made with a variety of four-electrode systems. These tests revealed that, unless considerable care was exercised in the design of an electrode system and unless one of the current electrodes of the cell was grounded, capacitative effects sufficient to mask the membrane effects resulted. The four-electrode system which was finally adopted as shown in Fig. 1 and which was typical of systems used in biological work (5) gave rise to a linear and purely resistive response in the absence of membranes for frequencies up to 5000 cps. For frequencies from 5000 to 10,000 cps a slight capacitative effect resulted from the electronic apparatus, as shown by replacing the solution with standard resistors and obtaining the same calibration curve as was obtained with the solution. All measurements were taken in a Faraday cage to eliminate stray fields.

In this work as shown in Fig. 1, each current electrode consisted of a lead circular plate and three layers in series of Pb-agar, KNO_3-agar, and test solution–agar. The voltage electrodes were made of the same materials as the current electrodes.

A cationite membrane 0.2 mm in thickness (AMFion *C*-103)[1] and an anionite membrane 0.15 mm in thickness (AMFion *A*-104)[1] were dried in an oven at 100°C for 30

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[1] Purchased from American Machine and Foundry Company, Springdale, Connecticut.

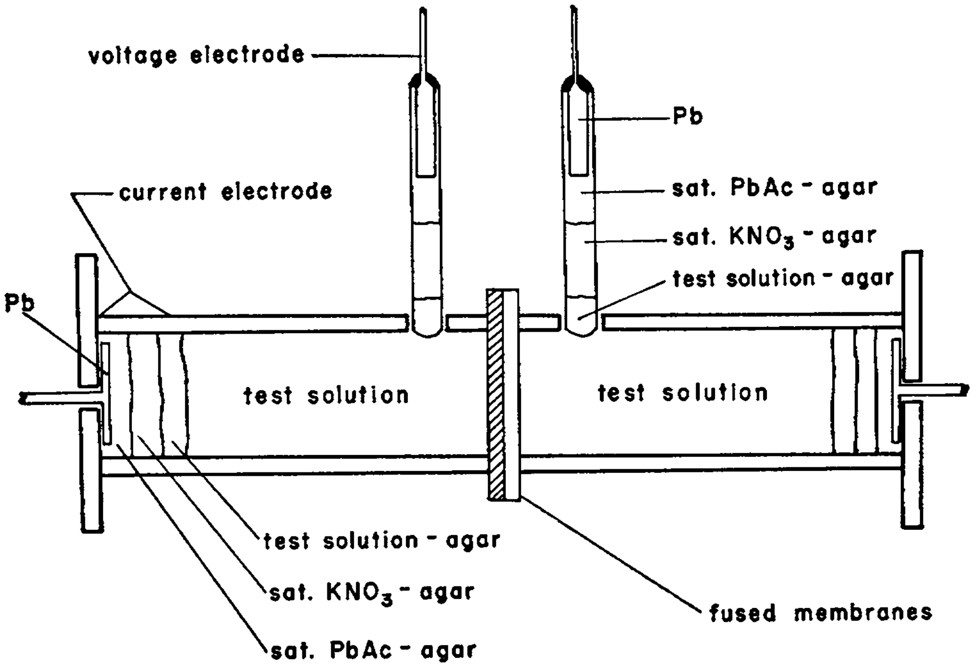

FIGURE 1 Experimental cell.

minutes. These were then fused according to a technique outlined by Friedlander (6). The dry samples were placed one on top of the other between sheets of aluminum foil and compressed in a Carver press at a temperature of 150°C and a pressure of approximately 200 to 500 psi. The samples were compressed for 2 to 3 minutes. These membranes exhibited stable resistive and reactive effects after they attained equilibrium in solution.

Previously AMF membranes, *C*-60 and *A*-60, were fused under a variety of conditions. These membranes did not maintain contact in solution over a period longer than several minutes. In this case, the reactive and resistive effects resulting from the fused membranes decayed in the course of time. This decay could be attributed to the separation of the membranes upon swelling. For these membranes, the effective lifetime could be extended in some measure by placing a cation membrane on the anion side of the centrally fused membranes and an anion membrane on the cation side. In this manner the lifetime could be prolonged as a rule for at least an hour and on occasion for several hours. The reactive effects were due to the fused membranes and in no way resulted from the cation and anion membranes flanking the fused membranes. These effects were tested by leaving all conditions the same except for the replacement of the centrally fused membranes, with an anion and a cation membrane which were not fused. In the latter case, the response was linear and the impedance had a low, resistive value with no reactive component. Since reactive effects occurred only for fused membranes, they served to confirm aspects of Mauro's space charge theory.

It is to be noted that for the stable membranes, the maximum open-circuit voltage across the membrane was 5 mv and as a rule this voltage was much less than 5 mv. For these membranes in the course of measurement of impedance as described below, the ellipse did not shift on the oscilloscope screen. For the unstable membranes the open-circuit voltage was as high as 120 mv. Since this voltage for the stable membranes was never more than 5 mv, any decoupling effects could be regarded as minimal.

For the rectification experiments, it was found that the higher the impedance, the smaller the current that was needed to produce rectification. Thus fused membranes with impedances in the low frequency range of the order of 50,000 ohms or higher required only a fraction of a microampere. On the other hand, the reactive effects were best studied with membranes having impedance of the order of 5000 ohms. In these cases, at least several microamperes could be used instead of fractions of a microampere. These currents raised the voltage drop significantly above the noise level. Moreover, membranes of moderate impedance gave ellipses on the oscilloscope with no detectable distortion over the widest range of frequencies and hence the reactive effects could be best separated from the rectifying effects.

The current-voltage characteristics as mentioned earlier will be described in the next section. At this point, the method of obtaining the impedance as a function of frequency will be briefly outlined.

For this purpose, a standard resistor of 10,000 to 50,000 ohms was placed in series with the membrane of unknown impedance. The voltage-detecting electrodes were connected to the vertical plates of the oscilloscope while the two leads across the standard resistor were connected to the horizontal plates of the oscilloscope. The passage of alternating current through both elements in series produced an ellipse on the oscilloscope. From the ellipse shown in Fig. 2, the reactance and impedance of the unknown element could be determined. For the same current, the following ratios hold (7), namely,

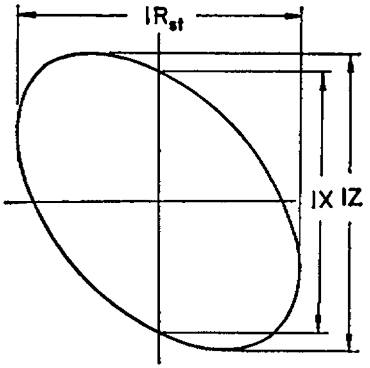

FIGURE 2 Ellipse on oscilloscope showing voltage drops.

$$\frac{X}{IX} = \frac{Z}{IZ} = \frac{R_{st}}{IR_{st}}.$$

The denominators denote voltage drops. In these equations,

R_{st} = resistance of the standard resistor,
X = reactance of unknown element,
Z = impedance of the unknown element.

A camera was attached to the screen of the oscilloscope. A clock was located in the interior of the camera so that the photograph gave both Lissajou figure and the time at which the picture was taken. A series of seventeen frequencies from 0.1 cps to 10 kcps could be photographed in an interval of approximately 2 to 3 minutes. For the *C*-60 and *A*-60 membranes the impedance varied with time. In this case, the photographic measurements were repeated at several later times, each set taking approximately 2 to 3 minutes.

RESULTS AND DISCUSSION

Fig. 3, which is an *I*-*V* characteristic for relatively large currents taken at a frequency of 6 cps, shows the rectifying effects resulting from these currents passing through the test chamber. The shape of the curve corresponds to that found by Lovrecek *et. al.* Thus the rectification can be attributed to changes in concentration properties of the ions (K+ and Cl−) in the vicinity of the membrane as the current alternates.

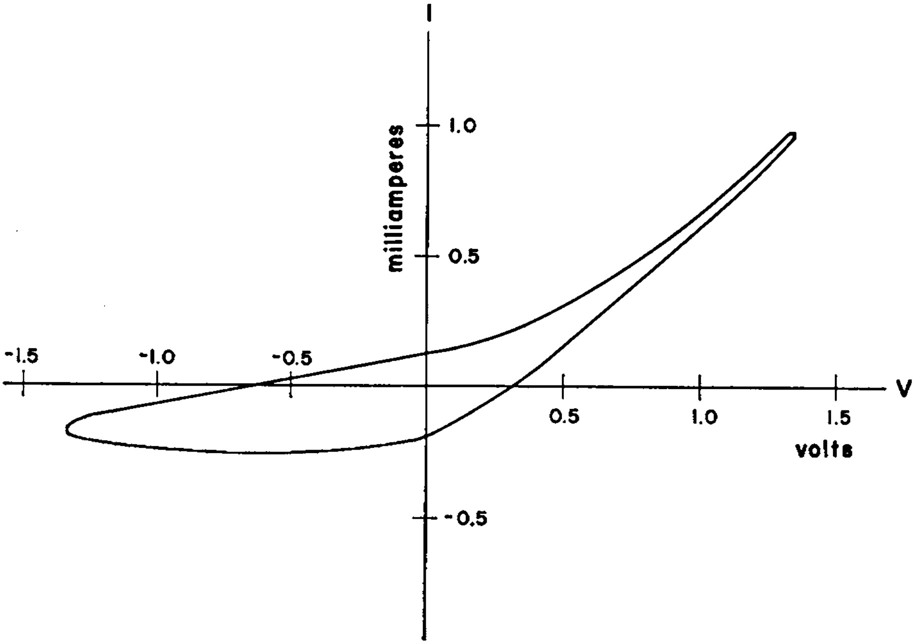

FIGURE 3 Rectification of fused cation-anion membranes in electrolytic solution.

In Fig. 4, the voltage and current at a frequency of 0.5 cps (obtained from the dual trace of the oscilloscope) are each plotted as a function of time. Similar curves were obtained for different frequencies. However, for increasing frequency, the rectifying effect decreased. The curves show a relative shift in phase, and the current curve is distorted. The phase shift implies the existence of reactance and the

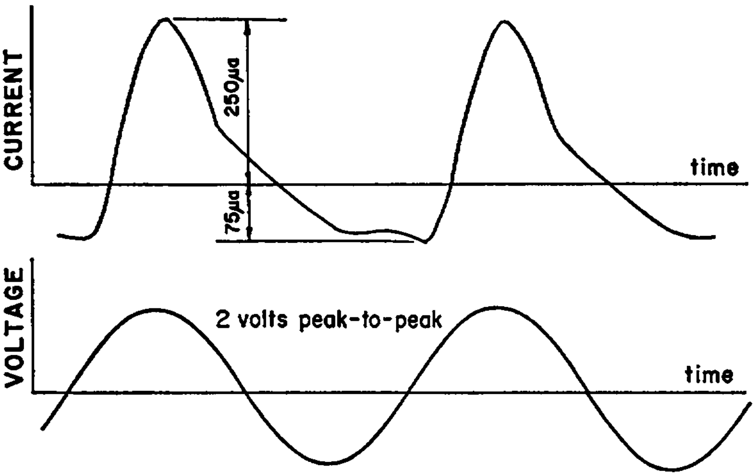

FIGURE 4 Dual trace of voltage and current as a function of time for relatively high currents.

distorted wave, rectification. As the current is reduced, the distortion becomes less but a phase shift remains.

Thus, in Fig. 5, the current and voltage waves for low currents are sinusoidal in character but out of phase with respect to each other. At low currents, the system shows little or negligible rectification and the system approaches linearity.

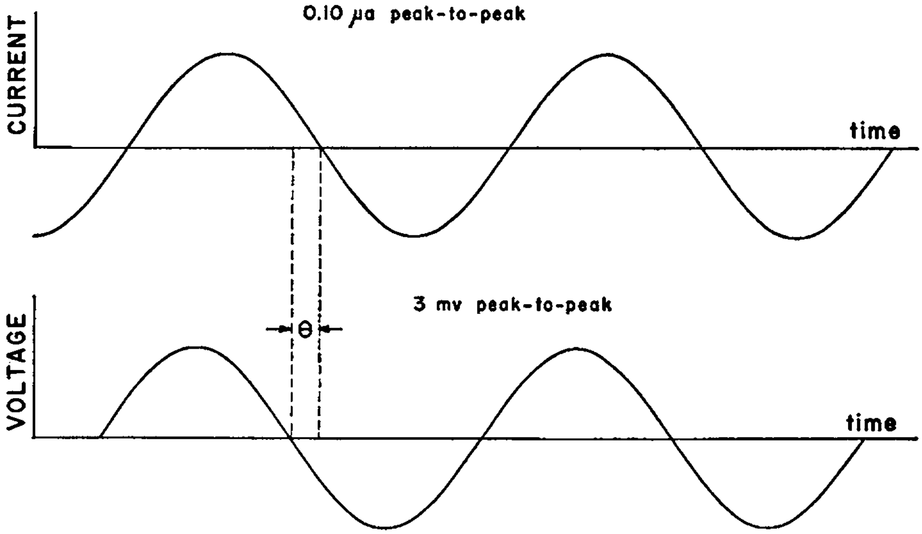

FIGURE 5 Dual trace of voltage and current as a function of time for relatively low currents.

The decrease in rectifying effects with increasing frequency results from the fact that the ions cannot readily follow the variations of the alternating field at the higher frequencies. Hence the same conditions tend to prevail in the system during the positive and negative phases of the alternating current cycle. The reactive component results from the existence of at least two properties of the system. First, the existence of a transition region between fixed charges of opposite sign produces a relatively frequency-independent component in accordance with Mauro's theory (3). Secondly, for strong electrolytes, perturbed by applied alternating current, ionic diffusion so induced can be frequency-dependent. Since such a process requires time, the alternating voltage-current response is frequency-dependent (8). Present data (reported below) will be interpreted in terms of frequency-dependent components.

As stated previously, the voltage-current response of the system is linear for low applied current. In this region, the nature of the capacitance and resistance was investigated. Area impedances of the order of 5000 ohm-cm^2 and frequencies of 0.1 to 1.0 cps gave only slight distortion of the ellipse. For higher frequencies no distortion is evident. Hence the data suffice to obtain an approximate equivalent circuit for the range of frequencies extending from 0.1 to 10,000 cps.

In Fig. 6, a typical reactance *versus* resistance plot is made. In this figure and the one to follow, the actual impedance is given. The area impedance can be obtained by multiplying the impedance values by the cross-sectional area of the membrane (0.72 cm^2). The experimental points appear to fall on two intersecting circles whose centers lie below the horizontal axis. Such results occur often in the study of dielectrics and in impedance measurements in biology. A circle with a center below the x axis has been interpreted as being due to a phenomenon called polarization capacity (9, 10), or alternatively as finite relaxation time of the dielectric (10, 11).

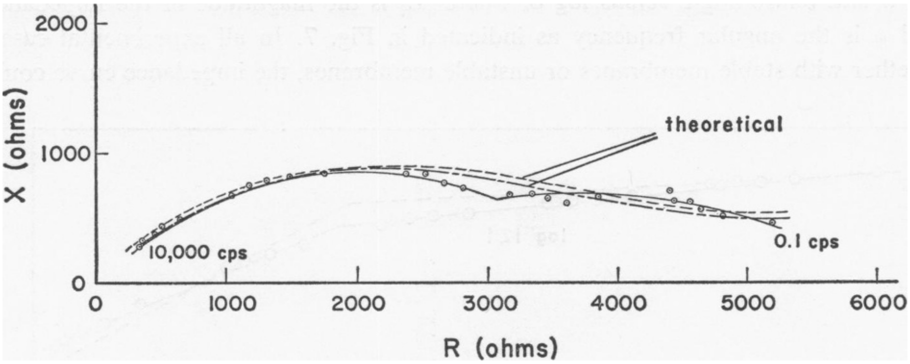

FIGURE 6 Impedance locus of stable anion-cation membranes for frequencies ranging from 0.1 to 10,000 cps.

It was first thought that for the double-arc locus an equivalent circuit might be obtained by two impedance branches in parallel (or in series), each branch consisting of an impedance of the Cole type (9), namely,

$$Z = r_\infty + \frac{(r_0 - r_\infty)}{1 + (j\omega T)^\alpha}$$

where

r_0 = resistance at zero frequency,
r_∞ = resistance at infinite frequency,
ω = angular frequency,
T = time constant of the system.

Some difficulty existed in the exact location of the centers of the circles. However, the main difficulty in this approach was that an analysis based on this equivalent circuit presented in the general case a formidable, if not impossible, task in fitting the parameters for each branch. It was, therefore, decided to abandon this approach and to attempt, as a first approximation, a partial solution of the problem by the adaptation of a method of modern network synthesis. Then, by the addition of a series resistance and a shunt resistance, the model would correspond rather closely to the Cole-type model above.

To apply network synthesis, the experimental points are plotted as log $|Z|$ *versus* log ω and phase angle *versus* log ω, where $|Z|$ is the magnitude of the impedance and ω is the angular frequency as indicated in Fig. 7. In all experimental cases, whether with stable membranes or unstable membranes, the impedance curve could

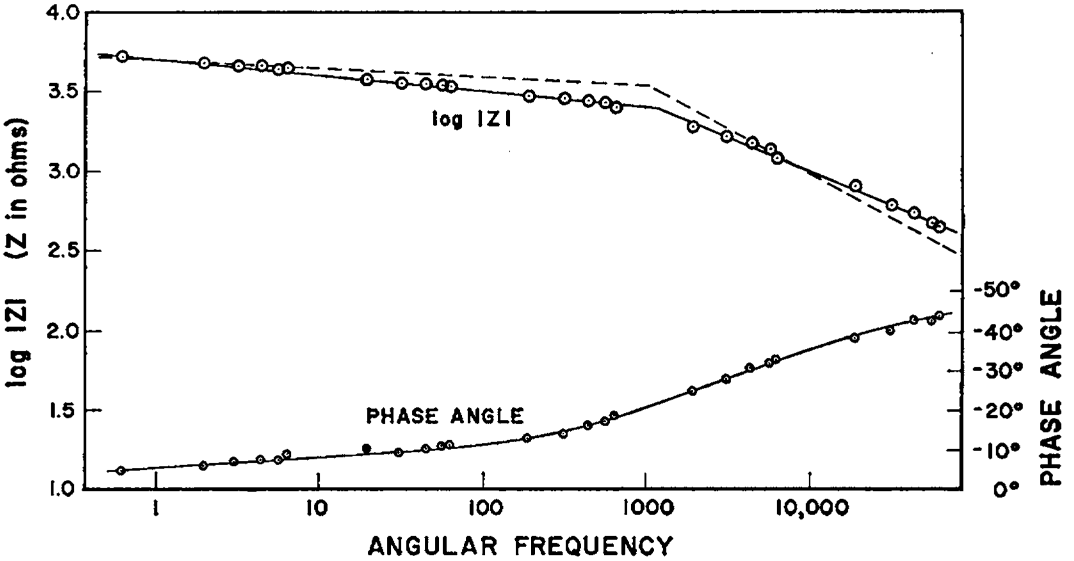

FIGURE 7 $\text{Log}_{10}|Z|$ and phase angle as functions of $\log_{10}\omega$ of stable anion-cation membranes.

be plotted as two straight-line segments. The slopes for the unstable membranes of series 60 (not shown herein) differed from those of the slopes for the stable membranes of series 100 (shown in Fig. 7) but the curves could always be represented as two straight segments. Such plots are called Bode plots, and in general are smooth curves rather than straight segments.

For ordinary resistance and reactance elements, the different parts of the smooth curve normally obtained can be approximated by straight-line segments having slopes of zero or integral value. In these cases, the equivalent circuit can be systematically obtained by methods of network synthesis (12). In the present case, the slopes have non-integral values so that these methods are either not applicable or can be applied only as a guide. As shown below, slopes with non-integral values can give rise to frequency-dependent components.

An approximate equivalent circuit for the frequency range 0.1 cps to 10 kcps can be estimated as follows. Based on network synthesis for slopes of zero or integral value, the equivalent impedance was assumed to be of the form

$$Z(\omega) = \frac{K}{(j\omega)^{\alpha}[1 + (j\omega T)^{\beta}]},$$

where K, α, and β are constants, $j = \sqrt{-1}$, and $T = 1/\omega_b$ with ω_b the angular frequency at the break point or intersection point of the two lines. This form is applicable to all the fused anion-cation membranes studied herein. For regular network synthesis without dielectric losses α and β would be zero or unity.

On a logarithmic plot, we have

$$\log |Z| = \log K - \alpha \log \omega - \log |1 + (j\omega T)^{\beta}|.$$

For low values of ω, $\alpha \log \omega$ is a dominant term. Hence α is obtained from the slope of the first line. At very high frequencies,

$$\log |Z| \approx \log K - \beta \log T - (\alpha + \beta) \log \omega.$$

Therefore, the slope of the second line gives $\alpha + \beta$, and hence β. The values of α and β thus obtained must satisfy the phase angles at the extreme ends of the curve of phase angle, namely $-\pi/2\ \alpha$ at the low frequency end and $-\pi/2\ (\alpha + \beta)$ at the high frequency end. Hence by trial and error methods, α and β must be adjusted until values are found that reasonably satisfy the data. The upper broken curve of Fig. 7 indicates the adjustment made in α and β to fit the data within the limitations of the model. The value of $\log K$ can be obtained from the x intercept of the first line, that is, from $\log |Z| = \log K - \alpha \log \omega$. Proceeding in this manner, we get

$$Z(\omega) = \frac{5200}{(j\omega)^{0.055}\left[1 + \left(\frac{j\omega}{1020}\right)^{0.495}\right]}.$$

The upper broken curve of Fig. 6 (which is equivalent to Fig. 7) was drawn from computations of this function.

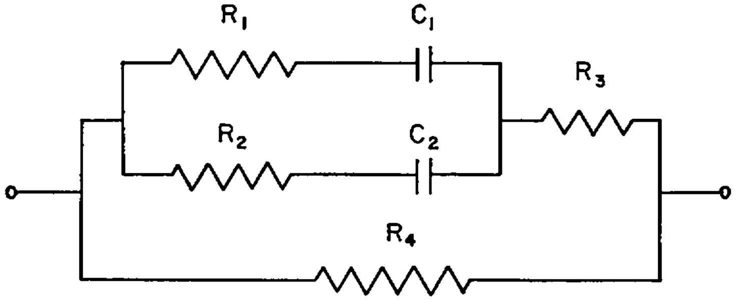

FIGURE 8 Equivalent circuit of stable anion-cation membranes.

The next step was to obtain an equivalent circuit. It was found that the frequency-dependent components of Fig. 8 corresponded to the expression for $Z(\omega)$ in the foregoing provided that

$$\begin{aligned} R_1(\omega) &= R_{01}\omega^{-\alpha}, \\ X_1(\omega) &= X_{01}\omega^{-\alpha}, \\ R_2(\omega) &= R_{02}\omega^{-(\alpha+\beta)} \\ X_2(\omega) &= X_{02}\omega^{-(\alpha+\beta)}, \end{aligned}$$

where R_{01}, X_{01}, R_{02}, X_{02}, α, and β are constants. It will now be shown that these circuit elements give the required function $Z(\omega)$ and that the circuit is equivalent to a polarization capacity function of Cole in each branch of the parallel network.

For the top branch of the parallel circuit we have

$$Z_1 = R_{01}\omega^{-\alpha} - jX_{01}\omega^{-\alpha}$$

or

$$Z_1 = \sqrt{R_{01}^2 + X_{01}^2}\left[\frac{R_{01}}{\sqrt{R_{01}^2 + X_{01}^2}} - \frac{jX_{01}}{\sqrt{R_{01}^2 + X_{01}^2}}\right]\omega^{-\alpha}.$$

If now we make the substitutions

$$\begin{aligned} \cos\phi_1 &= \frac{R_{01}}{\sqrt{R_{01}^2 + X_{01}^2}}, \\ \sin\phi_1 &= \frac{X_{01}}{\sqrt{R_{01}^2 + X_{01}^2}}, \end{aligned}$$

and in turn define α and K_1 by the relations

$$\begin{aligned} \phi_1 &= \frac{\pi}{2}\alpha, \\ K_1 &= \sqrt{R_{01}^2 + X_{01}^2}, \end{aligned}$$

we obtain

$$Z_1 = \frac{K_1}{(j\omega)^{\alpha}}.$$

In a similar manner it follows that

$$Z_2 = \frac{K_2}{(j\omega)^{\alpha+\beta}},$$

where

$$\phi_2 = \frac{\pi}{2}(\alpha + \beta),$$

$$K_2 = \sqrt{R_{02}^2 + X_{02}^2}.$$

The functions Z_1 and Z_2 correspond to the polarization elements of Cole (13). Impedances represented by the general form $Z = K(j\omega)^{-\alpha}$, where K and α are constants, give in parallel combination the desired form for $Z(\omega)$ as shown below.

The total network impedance function is given by

$$Z = \frac{Z_1 Z_2}{Z_1 + Z_2}$$

which, upon substitution and rearrangement, yields

$$Z = \frac{K_1}{(j\omega)^{\alpha} + \frac{K_1}{K_2}(j\omega)^{\alpha+\beta}}.$$

If we now let $K_1/K_2 = T_1{}^{\beta}$, the desired form

$$Z(\omega) = \frac{K_1}{(j\omega)^{\alpha}[1 + (j\omega T_1)^{\beta}]}$$

is obtained.

The analysis of the data gave circuit components with values

$$C_1 = 2220\omega^{\alpha-1} = 2220\omega^{-0.945},$$

$$C_2 = 7.88\omega^{\alpha+\beta-1} = 7.88\,\omega^{-0.45},$$

$$R_1 = 5190\,\omega^{-\alpha} = 5190\,\omega^{-0.055},$$

$$R_2 = 108{,}000\,\omega^{-\alpha-\beta} = 108{,}000\,\omega^{-0.55},$$

where the capacitance C is expressed in microfarads and the resistance R in ohms.

These four elements are illustrated in Fig. 8. The addition of a small series resistance $R_3 = 100$ ohms improves the fit at the high frequency end. The addition of a shunt resistance across the network of five elements makes the equivalent circuit resemble closely the Cole-type circuit which was extremely difficult to solve. A shunt resistance $R_4 = 143{,}000$ ohms was chosen.

The upper broken curve of Fig. 6 shows the fit for the four frequency-dependent elements alone. The lower broken curve of Fig. 6 shows the fit for the entire equivalent circuit. Part of the error can be attributed to the experimental difficulties in determining the phase angle accurately and some error in determining the magnitude of the impedance. More significantly a less restrictive form of the function $Z(\omega)$ might yield the double-arc character of the impedance, but because of the existence of fractional exponents such as α and β, an analytic expression in closed form yielding the equivalent circuit cannot be derived. In any case, since fractional exponents are needed, this fact brings out the likely existence of frequency-dependent components.

Mauro's theory shows that the transition regions of fixed charge give rise to capacitance. Such capacitative effects are found experimentally. The order of the capacitance at 100 cps is 2.6 μf per cm^2 and at 1000 cps is 0.33 μf per cm^2. These values correspond within orders of magnitude with values occurring in biological systems. The experimental data indicate, moreover, that the capacitance and the resistance are not of an ordinary type but include frequency-dependent elements. These elements appear to represent polarization capacity. Since all the experimental data, whether with stable or unstable elements, gave rise to two straight segments with non-integral slopes as in Fig. 7, it might be inferred that membranes for which $2d \ll L_D$ in electrolyte solution constitute one source of the property of polarization capacity.

CONCLUSIONS

At relatively high currents, rectifying and reactive effects occur. As the current is reduced rectification becomes less pronounced and eventually the reactive effects predominate. The latter effects are the most significant when the system approaches linearity. Also as the frequency increases, the rectifying effects decrease.

Rectification appears to result primarily from changes in the concentration profiles of the ions during the positive and negative phases of the AC cycle. During one phase resistance increases because of ion depletion somewhere in the membrane and during the other phase resistance decreases because of ion accumulation.

At low currents, the predominant reactive effect occurs for membranes for which $2d \ll L_D$. Part of the reactance is due to the presence of transition regions of fixed charge in the membranes. Another part of the reactance is due to concentration profiles of ions displaced by applied current. The latter is made evident from the frequency-dependent elements within the restrictive assumptions inherent in the present model.

It has been shown analytically that the model used in the present report is closely similar to that employed previously by Cole. Thus fixed charge membranes in electrolytic solution might be one source of the polarization capacity found in biological systems.

This work has been supported by a National Institute of Health grant, GM 10523-01.
Received for publication, May 25, 1963.

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