

THE ELECTRICAL PROPERTIES OF SYNTHETIC MEMBRANES

BY WILHELM S. ALBRINK* AND RAYMOND M. FUOSS

(From the Sterling Chemistry Laboratory, Yale University, New Haven)

(Received for publication October 5, 1948)

INTRODUCTION

The purpose of this paper is to present the results of a preliminary investigation of the electrical properties of synthetic membranes which are strong electrolytes. Cole (1) has studied a variety of biological membranes and found that their impedance locus (2) is, in general, a circular arc. Michaelis (3) and his coworkers have made extensive studies of collodion membranes; likewise, Sollner (4) has worked with a number of synthetic membranes, especially those derived from cellulose. But most of this work was primarily concerned with concentration potentials and osmotic behavior. Goldman (5), however, studied the a. c. electrical properties of collodion membranes containing phospholipids, and found impedance plots similar to those found by Cole for the biological membranes.

Working with naturally occurring substances involves several inherent difficulties: the structure is not always known; the structure is determined by the source of the material and not by the experimenter; and many of the materials (especially proteins and living membranes) change chemically and physically on standing. In connection with Project NR 054-002 of the Office of Naval Research, we have recently synthesized some polyelectrolytic materials which can be cast in the form of thin films. Some of these are insoluble in water. In contrast to most natural substances, which are either weak carboxylic acids or nitrogen bases, our compounds are strong electrolytes, similar electrically to potassium bromide. It therefore seemed of interest to investigate their electrical properties; although this work was interrupted at an early stage, some results were obtained which may be useful.

EXPERIMENTAL

A mixture of 5 parts 4-vinylpyridine and 95 parts styrene were copolymerized (6) in 20 per cent solution in toluene, using 1 per cent benzoyl peroxide on the monomer mixture as a catalyst. The resulting product is a linear polymer which has on an average a pyridyl group attached to every fortieth carbon atom of the chain. By addition of *n*-butyl bromide in nitromethane solution to the copolymer, the heterocyclic nitrogens are converted to butyl-pyridonium ions

* Present address: Department of Pathology, School of Medicine, Yale University.

and the resulting structure is now a polyelectrolyte, with large cations and small, mobile counter ions. Solutions of the polyelectrolyte in methyl ethyl ketone gave by our usual casting technique (7) films which were much too brittle to handle. On plasticizing with 30 per cent by weight of dutrex 25 (Shell Oil Company; suggested by Mr. Robert L. Speer), films were obtained which were pliable when warm.

These films were clamped between the halves of a split conductance cell (internal diameter, 22 mm.) with platinized disc electrodes about 40 mm. to each side of the membrane. The cell was then filled with electrolyte and the composite series circuit

Electrolyte / Membrane / Electrolyte (I)

was measured at various frequencies in the audio-range, using a General Radio type 716 C bridge. The cell was placed in a metal box for electrical shielding; shield and one electrode were connected to the grounded point of the bridge and the other electrode to the "unknown" terminal. For more precise work, a guarded circuit should, of course, be used. Correction was made for lead and stray capacity. Measurements were made at room temperature (*ca.* 26°); our cell design was not suitable for thermostating.

Bridge balance drifted very rapidly immediately after filling the cell with electrolyte or after changing electrolyte, but gradually settled down to reasonable constancy after about 24 hours. These drifts were largely due to the diffusion involved in setting up equilibrium between the ions in the solution and those in the membrane. As a matter of fact, the membrane acts much like an exchange resin; the polycations are immobilized in the membrane while the anions are free to diffuse into and through it.

RESULTS

Results for a typical membrane in 0.1 N potassium bromide are shown in Table I, where frequency, (observed) equivalent parallel capacitance, and (observed) tangent of loss angle are given in the first three columns. The average thickness of the membrane, computed from weight (0.173 gm.) and area (3.8 cm.²) was 0.0140 cm.; the equivalent geometrical capacitance C_0 of the membrane was 24.4 $\mu\mu\text{f}$. The resistance of the cell, filled with 0.1 N potassium bromide and without the membrane barrier, was 177 ohms; since the resistance of the aggregate (I) was of the order of many megohms, we may neglect the resistance of the electrolyte used to make contact with the membrane and assume the capacity and tangent of Table I to refer to the membrane alone.

If we consider the membrane and the electrolyte it contains as a parallel circuit, the resistance element R_x is given from the observed data by the familiar relationship

$$\tan\delta = 1/\omega C_x R_x .$$

Cole and his coworkers usually convert their data to the equivalent *series* circuit by means of the equations

$$R_s = \frac{R_x}{1 + (R_x C_x \omega)^2} = \frac{1}{\omega C_x} \frac{\tan \delta}{1 + \tan^2 \delta}$$

$$-X_s = \frac{R_x^2 C_x \omega}{1 + (R_x C_x \omega)^2} = \frac{1}{\omega C_x} \frac{1}{1 + \tan^2 \delta}$$

A plot of $(-X_s)$ against R_s gives a circular arc. We have computed the observed values of C_x and $\tan \delta$ of Table I to the corresponding equivalent series quantities; these data are shown in Fig. 1. It will be seen that the points lie on a curve, which over its somewhat limited range can be fitted by a circular arc

TABLE I
Electrical Properties of Membrane of Copolymer 4-Vinyl-N-n-Butyl Pyridonium Bromide-Styrene

f	C_x	$\tan \delta$	ϵ''	ϵ'
100 c.	342.0 μmf	0.427	0.94	(14.02)
150 "	308.8	0.334	0.84	(12.58)
200 "	292.0	0.280	0.81	(11.97)
400 "	266.4	0.196	0.86	(10.92)
500 "	260.5	0.175	0.85	(10.58)
1 kc.	242.0	0.126	0.74	9.91
2 "	232.6	0.099	0.69	9.55
5 "	223.6	0.075	0.59	9.15
10 "	216.0	0.064	0.52	8.85
20 "	211.0	0.058	0.48	8.65

whose center lies just below the horizontal axis. The extrapolated limit corresponding to zero frequency is 13.0 megohms, which agrees with the value found by another extrapolation method which will be described shortly. Our lowest frequency, 100 cycles, carries us only about one-third the way around the arc; it is obvious that very low frequencies would be needed to reach the descending limb of the curve for our membranes. The similarity to the curves for natural membranes is, however, unmistakable.

It seems reasonable to assume that part of the in-phase current through the membrane is purely electrolytic, and part of it is an A. C. loss associated with a relaxation process. This suggests another analysis of the data. Suppose we calculate the electrolytic loss, subtract this from the total in-phase component, and then examine the resulting admittance which will be the response due to the membrane itself. A specific conductance κ_0 is equivalent (8) to an ionic loss factor ϵ''_i ; at frequency f given by

$$\epsilon''_i = 9\kappa_0 \times 10^{12}/5f. \quad (1)$$

The total loss factor observed, ϵ''_t , is then

$$\epsilon''_t = \epsilon'' + \epsilon''_i \quad (2)$$

where ϵ'' is the power absorption per cycle due to A. C. mechanisms such as dipole rotation. If we recall that

$$\tan \delta = \epsilon''_i / \epsilon' = \epsilon''_i C_0 / C_x \quad (3)$$

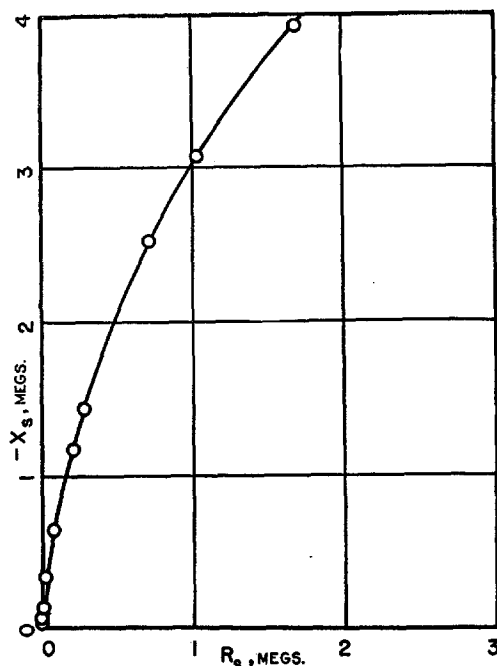


FIG. 1. Cole plot for synthetic membrane.

where C_x is the measured unknown capacity and ϵ' is dielectric constant, we have, on substitution of (1) and (3) into (2)

$$f C_x \tan \delta = 1.8 \times 10^{12} C_0 \kappa_0 + \epsilon'' C_0 f \quad (4)$$

Equation (4) furnishes a convenient means of analyzing the data to separate A. C. and D. C. components, because ϵ'' does not, as a rule, change rapidly with frequency at low frequencies for polymeric systems (9). As shown in Fig. 2, a plot of $f C_x \tan \delta$ against frequency is linear and extrapolation to zero frequency determines the ionic conductance κ_0 :

$$\kappa_0 = (f C_x \tan \delta)_{f=0} / 1.8 \times 10^{12} C_0 \quad (5)$$

where $(f C_x \tan \delta)_{f=0}$ is the intercept I at zero frequency. For the example of Table I and Fig. 2, we find $\kappa_0 = 2.8 \times 10^{-10}$ mho. Membranes were

measured in other electrolytes, including hydrobromic acid and potassium hydroxide solutions; very briefly summarized, the D. C. conductance of the membrane changed with the electrolytic environment, *but the A. C. properties were substantially unaffected.*

The difference between $C_x \tan \delta$ and the ratio of intercept to frequency then gives the A. C. loss factor after division by the geometrical capacitance C_0 :

$$e'' = (C_x \tan \delta - I/f)/C_0 \quad (6)$$

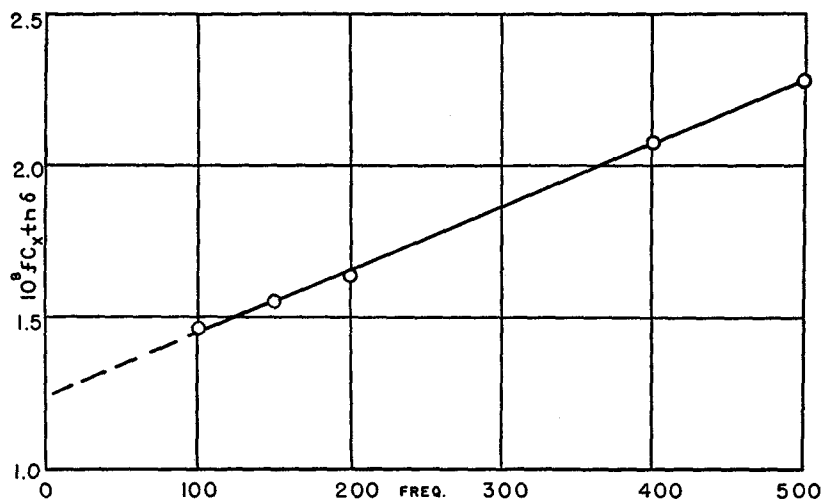


FIG. 2. Determination of D. C. conductance.

These values are given in the fourth column of Table I; the dielectric constants,

$$e' = C_x/C_0 \quad (7)$$

are given in the fifth.

A plot of the loss factors *versus* logarithm of frequency is given as the middle curve of Fig. 3 (ordinates right); the data at low frequencies scatter somewhat, because they represent a small difference between large quantities (*cf.* Fig. 2) but a maximum in the decade between 10 and 100 cycles is indicated. The very slow decrement in the audio-frequency range suggests the presence of a wide distribution (10) of relaxation times in the membrane. When dielectric constant is plotted against $\log f$, an approximately linear curve is obtained in the audio-frequency range, which is again characteristic of a broad distribution. A sharp rise in apparent dielectric constant is noted below 1 kilocycle; we are inclined to ascribe this to electrode polarization and to assume that the dielectric constant of the membrane follows the solid curve in Fig. 3. (Similar fictitious sharp rises in dielectric constant have been observed for other systems (11) at low frequencies.)

In order to compare the data with those for other systems, we used the method of Fuoss and Kirkwood (10): a plot of hyperbolic anticosine of the ratio (ϵ''_m/ϵ'') against logarithm of frequency is shown as the lower curve of Fig. 3. For ϵ''_m , the maximum value of the a. c. loss factor, we used 0.90. The audio-frequency points lie on a straight line with slope 0.475; multiplica-

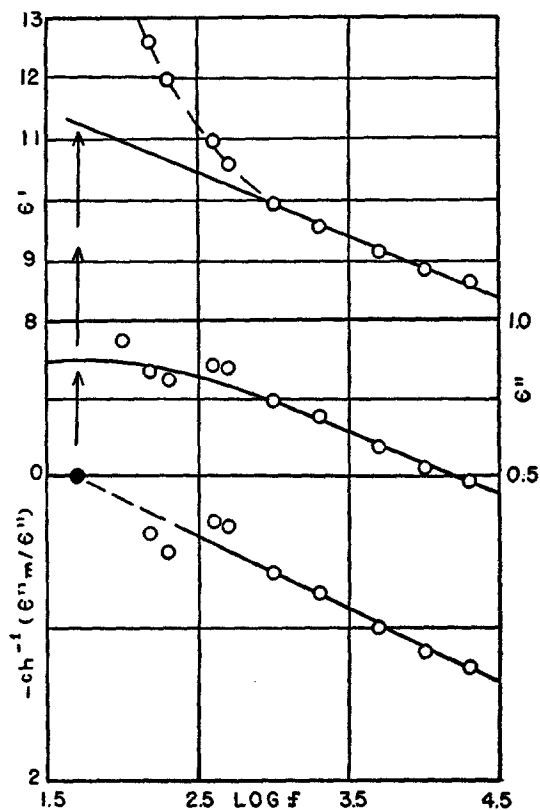


FIG. 3. Membrane characteristics.

tion by 0.4343 gives 0.206 as the value of α , the distribution parameter (10). Extrapolation of the audio-frequency (12) data to $ch^{-1}(\epsilon''_m/\epsilon'') = 0$ determines $\log f_m = 1.70$; *i. e.*, the peak loss is at 50 cycles. Using Table VII of reference 12, we find that $\alpha = 0.206$ corresponds to $\beta = 0.284$. By extrapolating the solid curve at the top of Fig. 2 to $\log f = 1.70$, we find $\epsilon'_m = 11.5$ as the dielectric constant of the membrane at the frequency corresponding to maximum loss. Using equations (19) and (20) of reference 12, we find $\epsilon_0 = 15.5$ as the static dielectric constant and $\epsilon_\infty = 7.5$ as the limiting dielectric constant of the membrane. The latter value is much higher than the probable index of re-

fraction; it seems pointless to discuss this item until further data are available, because our value of C_0 for example, may, be incorrect.

From the values of β , ϵ'_m , and ϵ''_m , we may, however, compute the constants of a circular arc which is shown as the solid curve in Fig. 4. With the exception of the 100 cycle point, the data conform very well to this arc.

The results show that the synthetic membrane gives an impedance locus which is similar to that found for biological membranes; furthermore, we can separate the total electrical response into an in-phase electrolytic conductance superimposed on a purely A. C. mechanism. This suggests that a similar interpretation might be applied to the data on the natural membranes. If we had a pure capacity parallel with an electrolytic resistance, the $X_c - R_c$ plots would

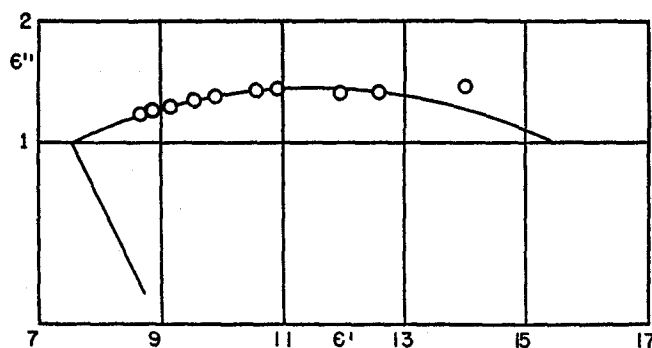


FIG. 4. A. C. components of synthetic membrane.

be true semicircles; as A. C. loss develops in the capacitive component, the center of the arc drops below the horizontal axis. But regardless of the properties of the capacitor, the center will always be near the axis when the parallel resistance is low; in other words, a high electrolytic conductance can mask the properties inherent in the structure of the membrane itself. In our membranes, for example, the broad distribution of relaxation times characteristic of the polymer structure is revealed only after correction is made for the electrolytic conductance.

In any case, the data clearly show that synthetic membranes which contain polar groups, and which permit ion exchange, give A. C. electrical properties which are similar in a general way to those exhibited by biological membranes. As suggested in the introduction, it does seem that the synthetic membranes offer another tool in biological research, because, within reasonable limits, their structure and environment may be varied at will. Analogies in electrical properties between natural and synthetic membranes may then permit some conclusions about the structure of the former.

SUMMARY

By the addition of *n*-butyl bromide to a 1:19 copolymer of 4-vinylpyridine and styrene, water-insoluble, strong polyelectrolytes can be prepared. The addition of a hydrocarbon plasticizer permits the casting of flexible films in which large polycations are immobilized but in which bromide ions (or other small anions) are free to move. Electrical measurements on these membranes showed that they could be represented by a complex admittance: an electrolytic conductance in parallel with a pure a. c. impedance. The latter gives a circular arc when real component is plotted against imaginary. These synthetic membranes thus resemble in their electrical behavior that found by Cole for a variety of biological membranes.

REFERENCES

1. Cole, K. S., *J. Gen. Physiol.*, 1932, **15**, 641; Cole and coworkers, *J. Gen. Physiol.*, 1935, **18**, 877; 1936, **19**, 609, 624; 1937, **21**, 189; 1938, **21**, 583, 591, 757; 1938, **22**, 37; 1939, **22**, 649; 1941, **24**, 535; 1942, **25**, 765, and other papers.
2. Cole, K. S., and Cole, R. H., *J. Chem. Phys.*, 1941, **9**, 341.
3. Michaelis, L., and coworkers, *J. Gen. Physiol.*, 1926, **10**, 575, 671, 685; *Bull. Nat. Research Council No. 69*, 1929, 119; *Kolloid-Z.*, 1933, **62**, 2, and other papers.
4. Sollner, K., and coworkers, *J. Gen. Physiol.*, 1940, **24**, 1; 1941, **24**, 467; 1942, **25**, 411; 1942, **26**, 17; 1943, **26**, 309, 369, and other papers.
5. Goldman, D. E., *J. Gen. Physiol.*, 1943, **27**, 37.
6. Cathers, George I., Thesis, Yale University, 1948; Fuoss, R. M., and Cathers, G. I., *J. Polymer Sc.*, 1947, **2**, 12. Fuoss, R. M., and Strauss, U. P., *J. Polymer Sc.*, 1948, **3**, 246.
7. Fuoss, R. M., and Mead, D. J., *J. Physic. Chem.*, 1943, **47**, 59.
8. Mead, D. J., and Fuoss, R. M., *J. Am. Chem. Soc.*, 1945, **67**, 1566.
9. Fuoss, R. M., *J. Am. Chem. Soc.*, 1938, **60**, 451.
10. Fuoss, R. M., and Kirkwood, J. G., *J. Am. Chem. Soc.*, 1941, **63**, 385. Kirkwood, J. G., and Fuoss, R. M., *J. Chem. Phys.*, 1941, **9**, 329.
11. Fuoss, R. M., *J. Am. Chem. Soc.*, 1939, **61**, 2329, Fig. 10.
12. Fuoss, R. M., *J. Am. Chem. Soc.*, 1941, **63**, 2401.