STUDIES WITH COMPOSITE MEMBRANES

I. PREPARATION AND MEASUREMENT

OF IMPEDANCES

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ABSTRACT   Simple and composite membranes have been prepared from 2% collodion solutions containing different amounts of polystyrenesulfonic acid (PSSA). Various membrane parameters such as water content, electrolyte uptake, exchange capacity, and permselectivity of these membranes have been determined. The resistance and capacitance of simple membranes have been measured as functions of both external electrolyte concentration and internal fixed charge density. The impedance characteristics of composite membranes also have been determined and discussed in terms of the resistance and capacitance characteristics of simple membranes from which the composite structures have been formed.

INTRODUCTION

Biological membranes show asymmetric behavior when the same drug or reagent is applied in different ways (Adelman and Senft, 1968; Lakshminarayanaiah, 1969 a). For example, it is observed in the case of the giant axon of the squid that tetrodotoxin blocks the initial inward sodium current through the nerve membrane when the toxin is applied externally (Narahashi et al., 1964; Nakamura et al., 1965). Internal application of the same drug at the same concentration has no effect on the sodium current, although at higher internal concentrations, it becomes effective (Narahashi et al., 1966). On the other hand, tetraethylammonium ion blocks the late outward potassium current through the nerve membrane when applied internally (Tasaki and Hagiwara, 1957; Armstrong and Binstock, 1965; Armstrong, 1966). Similarly, cesium ion is able to block the outward potassium current when applied internally (Chandler and Meves, 1965; Adelman and Senft, 1966), but is without effect on this current when applied externally (Pickard et al., 1964). These asymmetries in behavior indicate the existence of dissimilar membrane surfaces. This dissimilarity may arise from a number of factors, some of which are differences in fixed charge density, porosity, selectivity, etc., of the two membrane faces. Other biological membranes, for example, frog skin (Ussing,

1966), gastric mucosa (Rehm, 1966), toad bladder (DiBona et al., 1969), etc., are considered to possess composite structures. In order to understand the behavior of these complex biological systems, simple polymeric membranes for quite some time (Lakshminarayanaiah, 1965) and lipid bilayer membranes in recent years (Mueller et al., 1962 a, b) have been used as models by a number of investigators whose work has been reviewed by Lakshminarayanaiah (1969 b).

In a series of theoretical papers, Kedem and Katchalsky (1963 a, b, c) have discussed the behavior of complex membranes. Recently such complex membranes have been prepared (Liquori and Botre, 1964, 1967; Liquori et al., 1966; Hays, 1968; de Korosy, 1968) and used in a few studies as models (Botre et al., 1967; Hays, 1968) to understand the behavior of living membranes. We have been engaged in similar studies to develop complex artificial systems. Composite membranes of two types, layer type and sandwich type, have been prepared from 2% collodion solutions containing different amounts of polystyrenesulfonic acid (PSSA). The impedance characteristics of these, and also of the simple membranes from which the composite membranes have been formed, are described in this paper.

EXPERIMENTAL

Simple membranes of collodion containing various amounts of PSSA were prepared by following the steps given by Neihof (1954) for the dissolution method. Styrene polymer (The Borden Chemical Co., Philadelphia, Pa.) used for the preparation of PSSA had a molecular weight of 35,000. PSSA, after purification, had an acid value of 4.0 meq/g as opposed to 5.4 meq/g, the theoretical value which could be derived on the assumption that every benzene ring had one sulfonic acid group. Membranes were cast on clean and dry glass plates from a 2% solution of Parlodion (pyroxylin, purified nitrocellulose, Mallinckrodt Chemical Works, St. Louis, Mo.) in alcohol-ether (3:1 ratio) containing a definite amount of PSSA. A Gardner film-casting knife (Gardner Laboratory, Inc., Bethesda, Md.), preset to produce a membrane of definite thickness, was used to spread the membrane-forming solution which, on spreading, was allowed to dry for 1 hr at room temperature and for another $\frac{1}{2}$ hr at 60–70°C in an oven. The simple membranes were designated A, B, C, D, E, F, G, and H, and contained 8.3, 4.2, 2.1, 1.0, 0.8, 0.2, 0.02, and 0.002 mg PSSA per ml of the membrane-forming solution, respectively. Some membranes were also cast from a solution of nitrocellulose (concentration ~2%) which was formed from the commercial collodion (USP, Fisher Scientific Company, Pittsburgh, Pa.). The final alcohol:ether ratio was 1:2.5.
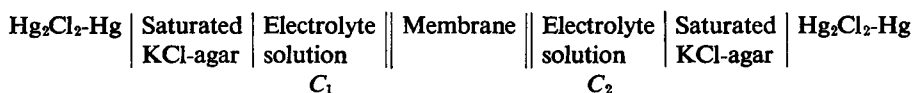
The composite membranes, otherwise called asymmetric membranes, of two types described by Liquori and Botre (1964, 1967), were prepared by following their steps although the compositions of the membrane-forming solutions were different. Type one, called the layer-type membranes, designated AD, AF, AG, AH, and ADFGH, were formed by casting different layers of 2% Parlodion solutions containing varying amounts of PSSA (8.3–0.002 mg/ml), one on top of the other (layer of lowest PSSA content first), in the way described by Liquori and Botre (1964). For example, the composite membrane AD was formed by first forming the simple membrane D as described above. Then on top of it, membrane A was formed by spreading and drying the membrane-forming solution A, i.e., 2% Parlodion solution containing 8.3 mg PSSA per ml of membrane-forming solution. All these membranes

were formed from Parlodion solutions in which the alcohol:ether ratio was 3:1. Type two, called sandwich-type membranes, were formed as outlined by Liquori and Botre (1967) by trapping a layer of PSSA (4 mg/ml) between high charge density membrane ($\sim$2% collodion, USP, Fisher Scientific Company, containing 10 mg PSSA per ml) and low charge density membrane ($\sim$2% collodion, USP, Fisher Scientific Company, containing 1 mg PSSA per ml). In this case, the alcohol:ether proportion was 1:2.5.

The membranes, simple and composite, were converted into the sodium form by treating them with about 200 ml of a strong solution (2–3 N) of NaCl. They were usually left in this solution for future use. When they were required, they were taken out of this solution and washed thoroughly with deionized water and equilibrated for about 2 hr with gentle stirring in about 100 ml of the solution to be used in the experiment.

The water content, electrolyte uptake, and exchange capacity of the different membranes were estimated by following the procedures described in our earlier publications (Lakshminarayanaiah and Subrahmanyan, 1964; Lakshminarayanaiah and Brennen, 1966; Lakshminarayanaiah and Siddiqi, 1970). These membrane parameters, which were determined accurate to $\pm$5% using at least three membranes, are given in Table I.

The electrochemical cells of the type

$$\text{Hg}_2\text{Cl}_2\text{-Hg} \left| \begin{array}{c} \text{Saturated} \\ \text{KCl-agar} \end{array} \right| \begin{array}{c} \text{Electrolyte} \\ \text{solution} \\ C_1 \end{array} \left|\left| \text{Membrane} \right|\right| \begin{array}{c} \text{Electrolyte} \\ \text{solution} \\ C_2 \end{array} \left| \begin{array}{c} \text{Saturated} \\ \text{KCl-agar} \end{array} \right| \text{Hg}_2\text{Cl}_2\text{-Hg}$$

were used for measuring electrical potentials arising across different types of membranes. The potentials were measured using a Keithley microvoltmeter (Keithley Instruments, Inc., Cleveland, Ohio) at room temperature (air-conditioned).

The concentration potentials arising across the simple membranes were measured by maintaining a tenfold difference in concentration (i.e., (C_2/C_1) = 10) in the range 0.001–1.0 N. At least four membranes were used in each concentration step. The mean and the standard error of the mean of these measurements were computed. The potentials measured

TABLE I

EQUILIBRIUM PROPERTIES OF SIMPLE AND COMPOSITE (LAYER-TYPE) MEMBRANES FORMED FROM 2% SOLUTION OF PARLODION IN ALCOHOL-ETHER (3:1 RATIO) CONTAINING DIFFERENT AMOUNTS OF POLYSTYRENESULFONIC ACID

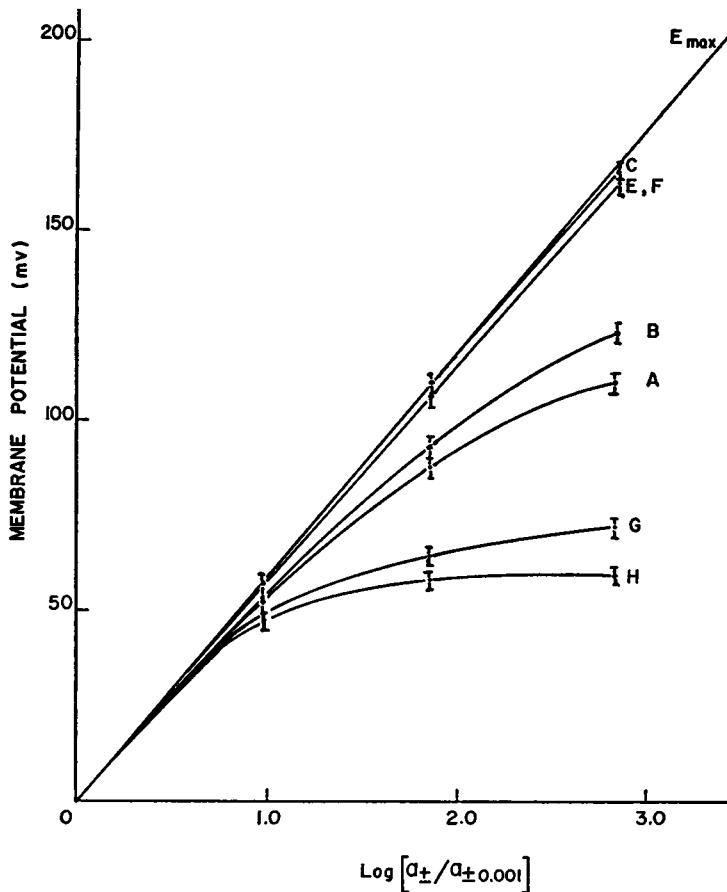| Membrane	Amt of PSSA	Water content	Exchange capacity (Acid given into 2 N NaCl)	Chloride uptake in 0.1 N NaCl
	mg/ml	*g H$_2$O/100 g wet membrane in H-form*	*meq/g wet membrane*	*meq/g wet membrane*
A	8.3	39.0	0.57	7.0 $\times$ 10^{-3}
B	4.2	30.3	0.40	6.6 $\times$ 10^{-3}
C	2.1	12.2	0.35	4.6 $\times$ 10^{-3}
D	1.0	—	0.17	4.0 $\times$ 10^{-3}
E	0.8	10.7	0.08	4.0 $\times$ 10^{-3}
F	0.2	8.5	0.02	3.0 $\times$ 10^{-3}
G	0.02	7.0	0.01	—
H	0.002	7.0	0.01	3.0 $\times$ 10^{-3}
ADFGH	—	15.0	0.16	8.0 $\times$ 10^{-3}

FIGURE 1 Electrical potentials (mv) arising across simple membranes plotted as a function of log $(a_{\pm}/a_{\pm 0.001})$. E_{max} represents the maximum theoretical Nernst potential. A, B, C, E, F, G, and H represent potentials arising across 2% Parlodion membranes (alcohol:ether ratio = 3:1) containing different amounts of PSSA (A = 8.3, B = 4.2, C = 2.1, E = 0.8, F = 0.2, G = 0.02, and H = 0.002 mg PSSA per ml of membrane-forming solution).

for the different concentration steps were added and the corresponding standard error for the added mean was calculated. The means with their standard errors (1 standard error) were plotted against log $(a_{\pm}/a_{\pm 0.001})$ where $a_{\pm}$ was the mean activity of the solution of higher concentration. This plot is shown in Fig. 1 along with the straight line E_{max} which represents the maximum theoretical value of the potential calculated according to the Nernst equation

$$E_{max} = \frac{RT}{F} \ln \frac{a_{\pm}}{a_{\pm 0.001}}. \tag{1}$$

Electrical potentials were not observed across simple membranes when the same electrolyte of the same concentration (i.e., $C_2 = C_1$) was placed on its two sides. Under similar conditions, composite membranes, both layer and sandwich types, generated considerable potentials, and these are described in Part II (Lakshminarayanaiah and Siddiqi, 1971).
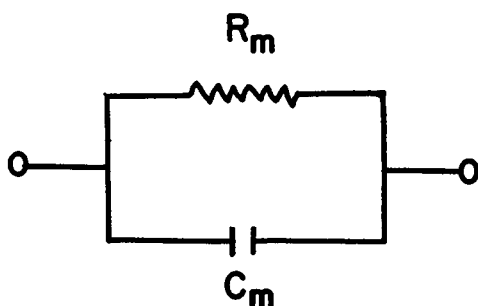
FIGURE 2 The equivalent electrical circuit for a simple membrane. R_m and C_m are membrane resistance and capacitance respectively.

The impedances of the membranes were measured on a General Radio Z-Y bridge (General Radio Co., Concord, Mass.) using the membrane cell described elsewhere (Lakshminarayanaiah and Subrahmanyan, 1968). The cell was kept in a water thermostat maintained at 25 ±0.01°C. In this method, purified mercury equilibrated with the solution in which the membrane had to be used was placed on either side of the membrane. Extensive use of this method has indicated that the following additional precautions should be taken to realize reproducible values:

(a) There should be no trapped air particularly at the corners of the cell near the membrane faces.

(b) Mercury is likely to be oxidized to form mercuric oxide which would form films on membrane faces and cause irreproducibility. This seems to be the major factor affecting the reproducibility of the results. Using only purified mercury has eliminated this problem in our studies and has given reproducible results.

The resistance R_x and the reactance X_x of the simple membranes, considered equivalent to the electrical circuit shown in Fig. 2, were measured on the General Radio Z-Y bridge. By the usual analysis (Lakshminarayanaiah and Shanes, 1965) the membrane resistance R_m and capacitance C_m were evaluated from the equations

$$R_m = R_x \left[1 + \left(\frac{X_x}{R_x} \right)^2 \right], \tag{2}$$

$$\omega C_m R_m = \frac{X_x}{R_x}, \tag{3}$$

where $\omega = 2\pi f$ and f is the frequency (10^3 cycles/sec) used to measure R_x and X_x. R_m and C_m are expressed in ohms·cm² and μF/cm² respectively and are given in Table II as functions of both external electrolyte concentration and quantity of fixed charge present in the membrane. The impedance Z of a membrane is given by

$$Z = \sqrt{R_x^2 + X_x^2} \tag{4}$$

and the values derived for simple and layer-type composite membranes in equilibrium with 0.01 N NaCl solution are given in Table III. Similar values derived for the other simple and sandwich-type membranes are given in Table IV. All these impedance measurements had an error of ±10%.

MEMBRANE RESISTANCE R_m AND CAPACITANCE C_m OF SIMPLE MEMBRANES AS A FUNCTION OF EXTERNAL ELECTROLYTE CONCENTRATION*

Mem- brane‡	Amt PSSA	NaCl concentration (eq/liter)							
		10^{-4}		10^{-3}		10^{-2}		10^{-1}	
		R_m	C_m	R_m	C_m	R_m	C_m	R_m	C_m
	mg/ml	ohms·cm²	μF/cm²	ohms·cm²	μF/cm²	ohms·cm²	μF/cm²	ohms·cm²	μF/cm²
A	8.3	29.2	8.2	21.8	12.6	9.5	21.6	5.1	46.0
B	4.2	45.7	5.4	30.4	9.6	20.0	18.6	6.5	40.4
C	2.1	43.0	4.5	29.4	8.0	25.0	15.0	7.3	36.6
D	1.0	107.7	0.7	77.8	0.5	64.9	0.4	12.1	3.7
F	0.2	1.4×10^4	0.006	0.8×10^4	0.012	0.4×10^4	0.022	0.2×10^4	0.030
G	0.02	8.9×10^4	0.0018	6.6×10^4	0.0014	3.5×10^4	0.010	0.7×10^4	0.006
H	0.002	19.5×10^4	0.0006	11.0×10^4	0.0006	4.1×10^4	0.004	1.8×10^4	0.002

* Membrane thickness ~ 0.02 mm.
‡ 2% Parlodion; alcohol: ether (3:1).

IMPEDANCES OF SIMPLE AND COMPOSITE MEMBRANES IN EQUILIBRIUM WITH 0.01 N NaCl SOLUTION

Membrane*	Thick- ness	X_x	R_x	Z (equation 4)
	mm	ohms	ohms	ohms
Simple				
A	0.025	13‡	10‡	16.4
D	0.030	30‡	180‡	182
F	0.020	0.4×10^4	0.8×10^4	0.9×10^4
G	0.018	0.6×10^4	1.6×10^4	1.7×10^4
H	0.017	3.2×10^4	5.4×10^4	6.3×10^4
Composite layer type				
AD	0.040	10	10	14.2
AF	0.045	8.5	22.0	23.5
AG	0.040	13.5	30.0	32.9
AH	0.040	35.0	80.0	87.3
ADFGH	0.095	1.7×10^4	4.3×10^4	4.6×10^4

* 2% Parlodion; alcohol:ether (3:1).
‡ Values for R_m and C_m calculated from equations 2 and 3 for membranes A and D are 9.1 ohms·cm², 22.8 μF/cm² and 63.0 ohms·cm², 0.42 μF/cm². These values for a membrane thickness of 0.02 mm (i.e., ½ thickness of composite membrane AD) become 7.3 and 42.0 ohms·cm² for R_m of A and D, and 28.5 and 0.63 μF/cm² for C_m of A and D respectively.

Membrane*	Amt of PSSA	Thickness	X_x	R_x	Z (equation 4)
	mg/ml	mm	ohms	ohms	ohms
High charge	10.0	0.200	9.0‡	21.0‡	22.8
Low charge	1.0	0.200	22.0‡	115.0‡	117.1
Sandwich	—	0.180	14.0	42.0	44.2

* 2% collodion; alcohol:ether (1:2.5).
‡ Values for R_m and C_m calculated from equations 2 and 3 for high and low charge density membranes are 8.5 ohms·cm², 8.0 μF/cm² and 40.6 ohms·cm², 0.8 μF/cm². Corrected for membrane area (0.34 cm²) and thickness (0.06 mm) these become 7.5 ohms (R_H) and 9.1 μF (C_H) for high charge density membrane and 36 ohms (R_L) and 0.91 μF (C_L) for low charge density membrane.

RESULTS AND DISCUSSION

The results of Table I show that the water content of the simple membranes with large quantities of PSSA in them is high. Consequently the quantity of PSSA present in the membrane determines both its porosity and the fixed charge density. How these two parameters interact to control the over-all permselectivity of the membrane is shown in Fig. 1. Although membranes A and B have high quantities of PSSA, they generate potentials which are lower than those generated by membranes C, E, and F containing low quantities of PSSA. Despite their high exchange capacities, membranes A and B because of their high water contents (i.e., high porosities) are not able to exclude coions such as chloride from the membrane phase (see last column of Table I). Thus these two factors, viz. the ability to prevent coion uptake brought about by the tightness of the membrane (i.e., less water present) and the presence of fixed negative charge (0.02 meq/g) on the membrane, are responsible for the high electrical potentials generated by membranes E and F. Membranes G and H have the tightness required for excluding coions as effectively as E and F. However, they do not have the capacity for generating the diffusion potentials because of the lack of fixed groups. These two factors are effectively combined in a suitable proportion in membrane C. It has an exchange capacity of 0.35 meq/g and 12.2% water and has the highest permselectivity in that the potentials are very close to the theoretically predicted E_{max} values given by equation 1.

In agreement with what has been described above, it is found that the resistance R_m of simple membranes which contain high PSSA is low, whereas the R_m of those which contain low PSSA is high (see Table II). This can be attributed to the presence of more charge carriers (counterions and coions) in the case of membranes

ELECTROLYTE CONTENT OF MEMBRANE E
AS A FUNCTION OF EXTERNAL
NaCl SOLUTION

Solution concentration	Na+	Cl−
eq/liter	meq/g wet membrane	meq/g wet membrane
0.0001	0.411	1.3×10^{-3}
0.001	0.411	1.5×10^{-3}
0.01	0.422	2.1×10^{-3}
0.1	0.442	4.0×10^{-3}
0.5	0.468	12.7×10^{-3}

of high PSSA content. On this basis, the increase in R_m with decrease in external electrolyte concentration observed in all cases given in Table II may be explained. As the external concentration is decreased, the electrolyte uptake of the membrane also is decreased. This can be seen in the electrolyte uptake data given in Table V for the membrane E. Similar behavior was noted in the case of composite membranes whose impedances also increased with decrease in the external electrolyte concentration (values not given).

The data obtained with simple membranes formed from collodion solutions (alcohol:ether ratio = 1:2.5) and given in Table IV show that the values for the membrane resistances for both high charge and low charge density membranes (thickness ∼0.2 mm) are low compared to simple membranes (thickness ∼0.02 mm) formed from Parlodion solutions (alcohol:ether ratio = 3:1). Obviously the increased proportion of ether in the membrane-forming solution made these membranes more porous. Membrane D (see Table II) corresponds to the low charge density membrane (see Table IV) in respect to its PSSA content. But the values for R_m of these two membranes are different. Increase of alcohol:ether proportion by about 7.5 times reduced the value of R_m of the low charge density membrane by nearly 0.06 times when proper correction for differences in the thickness of the two membranes was made.

The other interesting property of simple membranes is the change in the value of their capacitance when their PSSA and electrolyte contents are increased. Data given in Table II show that increase of both PSSA content and the concentration of the external electrolyte solution gave higher values for C_m. According to the parallel plate capacitor equation,

$$9 \times 10^{11} \, C_m = (\epsilon/4\pi \, d), \tag{5}$$

(where C_m is in farads per square centimeter, ϵ is the dielectric constant, and d is

the thickness in centimeters), this increase in the value of C_m can arise from a decrease in the thickness of the membrane or an increase in the dielectric constant of the membrane material or both. Increase of PSSA content of the membrane increased the membrane water content (see Table I) but for any given PSSA content, the membrane thickness remained practically constant when the concentration of the external electrolyte was changed. Since the species present in the membrane causing this change in C_m (i.e., PSSA, ions, and water) are all polar in nature, increase in C_m with increase in PSSA and electrolyte content of the membrane can be attributed to an increase in the value of ϵ. A similar effect of electrolyte concentration on C_m was noted also in our earlier studies with thin Parlodion membranes (Lakshminarayanaiah and Shanes, 1965).

Although values for R_m and C_m can be computed easily for simple membranes from bridge readings of R_x and X_x, such a calculation cannot be done for composite membranes primarily because they cannot be described by any definite equivalent circuit. Nevertheless, their impedances can be obtained from equation 4. These values given in Tables III and IV indicate some interesting points. The composite membrane AD formed from simple membranes A and D has a value for its impedance Z which is less than the value realized for either membrane A or D. In the case of other composite membranes (AF, AG, and AH) the Z values lie between the values obtained for the two simple membranes but are closer to the value of membrane A. In the case of the highly composite membrane ADFGH, the Z value is higher and closer to that of the membrane H.

It is very difficult to represent any of the composite membranes by equivalent circuits of the type shown in Fig. 2 for the simple membranes. However an ideal case, where the simple membranes (A, D, F, G, and H), retaining their identity, combine to form the composite membrane ADFGH, may be considered. This structure can be represented by the equivalent circuit shown in Fig. 3. Such an ideal system, in practice, is very difficult to construct. The interactions involved in its
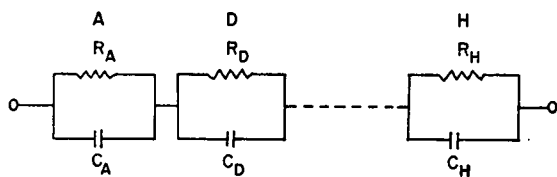

FIGURE 3

FIGURE 4

FIGURE 3 The equivalent electrical circuit for an ideal composite membrane built from simple membranes A, D, $\cdots$, H. R's and C's are simple membrane resistances and capacitances respectively.
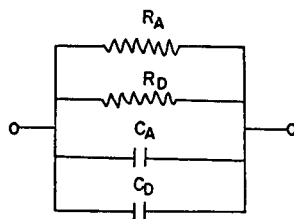
FIGURE 4 A probable equivalent electrical circuit for the layer-type composite membrane AD. R's and C's are simple membrane resistances and capacitances respectively.

formation are unknown and cannot be controlled. Many possibilities of composite membrane formation even from two simple membranes exist and some of these are examined below.

If we assume that the composite membrane AD conforms to the circuit given in Fig. 3, the impedance of the circuit for the two units A and D is given by

$$\frac{R_A}{1 + i\omega C_A R_A} + \frac{R_D}{1 + i\omega C_D R_D},$$ (6)

where R_j and C_j are the resistance and capacitance of simple membrane j and $i = \sqrt{-1}$. Separating the real and imaginary parts of equation 6 yields

$$R_x = \frac{R_A}{1 + \omega^2 C_A^2 R_A^2} + \frac{R_D}{1 + \omega^2 C_D^2 R_D^2},$$ (7)

$$X_x = \frac{\omega C_A R_A^2}{1 + \omega^2 C_A^2 R_A^2} + \frac{\omega C_D R_D^2}{1 + \omega^2 C_D^2 R_D^2}.$$ (8)

From equations 7 and 8, values for R_x and X_x can be computed, as the values of R_A, R_D, C_A, and C_D are known from independent measurements using simple membranes with 0.01 N NaCl solution (see Table VI). Substituting the values after correction for thickness (i.e., $\frac{1}{2}$ thickness of membrane AD: $R_A = 21.4$ ohms, $C_A = 9.7$ μF, $R_D = 123$ ohms, and $C_D = 0.214$ μF) in the above equations, and solving them, give values of 128 and 32 (ohms) for R_x and X_x respectively. These do not agree with the observed values of 10.0 and 10.0 (see Table III). Similar disagreement was noted also in the case of the other membranes AF, AG, and AH. To compromise this discrepancy, one must add a series negative impedance to the membrane elements A and D. As no such negative impedance is known to exist in these artificial systems, the ideal circuit must be either rejected or modified. Rejection in favor of the other possibility, viz. formation of an entirely different membrane out of A and D possessing its own characteristics, gives some interesting results. Values of R_x and X_x for the membrane AD (i.e., 10.0 and 10.0 ohms) by the usual analysis using equations 2 and 3 give values of 6.8 ohms·cm² and 23.2

TABLE VI

VALUES OF R_m AND C_m FOR SIMPLE MEMBRANES (AREA = 0.34 cm²)
IN EQUILIBRIUM WITH 0.01 N NaCl SOLUTION*

Membrane	A	D	F	G	H
Thickness, *mm*	0.025	0.030	0.020	0.018	0.017
R_j, *ohms*	26.7	185	1×10^4	1.8×10^4	7.3×10^4
C_j, *μF*	7.75	0.143	0.008	0.0033	0.0013

* Calculated according to equations 2 and 3 from the data given in Table III.

μF/cm² for R_m and C_m respectively. If the elements R_A, R_D, C_A, and C_D are coupled to form the circuit shown in Fig. 4, then the use of the values given above for R_A, R_D, C_A, and C_D yield the values 6.2 ohms·cm² and 29.1 μF/cm² for R_m and C_m. These values are close to those derived above from the simple circuit (Fig. 2); however, this agreement is considered fortuitous in view of the fact that such a scheme (Fig. 4) is found inapplicable to the other membranes AF, AG, and AH. Consequently, modifying the ideal scheme (Fig. 3) seems to be realistic. This modification is to assume that membrane A retains its characteristics and that the properties of membrane D in series with A are altered. Even this scheme fails because equations 7 and 8 lead to negative values for C_D. A better scheme is to assume that the membrane AD is composed oe three units, the two units A and D holding between them a third unit formed from A and D. This would conform in principle to the circuit shown in Fig. 3. As the middle unit is formed at the expense of A and D, the thicknesses of A and D will be affected. We assume (because equal volumes of A and D are used to form AD), for the sake of simplicity, that the thicknesses of A and D are reduced to the same extent, while their unit resistance (R_m) and capacitance (C_m) characteristics remain unaltered. Provided the thicknesses of the end units A and D are known, the unknown parameters of the middle unit can be quantitatively estimated. There is no straightforward way to derive these. The only way this can be done reasonably is to use the data of Table III with equations 7 and 8. These equations upon expansion to include the characteristics (R_k and C_k) of the middle unit, become

$$R_x = \frac{R_A'}{1 + \omega^2(R_A')^2(C_A')^2} + \frac{R_k}{1 + \omega^2 R_k^2 C_k^2} + \frac{R_D'}{1 + \omega^2(R_D')^2(C_D')^2}, \quad (9)$$

$$X_x = \frac{\omega C_A'(R_A')^2}{1 + \omega^2(R_A')^2(C_A')^2} + \frac{\omega C_k R_k^2}{1 + \omega^2 R_k^2 C_k^2} + \frac{\omega C_D'(R_D')^2}{1 + \omega^2(R_D')^2(C_D')^2}, \quad (10)$$

where R_x and X_x are the measured values for the composite membrane AD (see Table III) and R_A', R_D', C_A', C_D' are the resistance and capacitance values for the simple membranes A and D corresponding to their reduced thicknesses (i.e., as they prevail in composite membrane AD). For any arbitrarily chosen thickness, for example 0.01, 0.001, 0.0001 mm, etc., values for R_A', R_D', C_A', C_D' can be calculated from the values given in Table VI. Using these values in equations 9 and 10, sample calculations can be made to derive values for R_k and C_k. Such calculations gave negative values for the factor $[R_k/(1 + \omega^2 R_k^2 C_k^2)]$. However, when values of R_A', R_D', C_A', C_D' corresponding to a membrane thickness of 0.0015 mm were used, a small positive value (0.3) was obtained for the same factor. Similar calculations using equation 10 gave a higher value (7.94) for the factor $[(\omega R_k^2 C_k)/(1 + \omega^2 R_k^2 C_k^2)]$. Solving these gave values of 210 ohms and 20 μF for R_k and C_k respectively. The results of similar calculations pertaining to the other composite membranes are collected in Table VII. The values of R_k (except membrane AD) de-

CHARACTERISTICS OF THE MIDDLE UNIT PRESENT IN THE
COMPOSITE MEMBRANE*

Composite membrane	AD	AF	AG	AH
Composite membrane thickness, *mm*	0.040	0.045	0.040	0.040
Assumed thickness of end units, *mm*	0.0015	0.00004	0.000034	0.000018
Middle unit thickness, *mm*	0.037	0.0449	0.0399	0.03996
Characteristics of simple membrane corresponding to the thickness assumed	(A) (D)	(A) (F)	(A) (G)	(A) (H)
R_j , *ohms*	1.6:9.3	0.043:20	0.036:34	0.019:72
C_j , *µF*	129:2.4	4850:4	5700:1.76	10780:1.67
$\dfrac{R_k}{1 + \omega^2 R_k^2 C_k^2}$	0.3	6.084	0.1864	34.3
$\dfrac{\omega R_k^2 C_k}{1 + \omega^2 R_k^2 C_k^2}$	7.94	0.4593	2.38	0.6
R_k , *ohms*	210	6.1	30.6	34.3
C_k , *µF*	20	1.97	65.7	0.08

* Computed from equations 9 and 10 using the known characteristics of simple membranes.

rived for the middle units, whose thicknesses are nearly the same as the thicknesses of the composite membranes themselves, appear reasonable. The exception noted (membrane AD) here confirms the fact, already mentioned above, that the various units are united according to Fig. 4 and not according to Fig. 3. The values of C_k also appear reasonable although the value for membrane AG is high. This is difficult to explain, but it could arise as a rare event where PSSA got localized without being uniformly dispersed during spreading. The other important point of this circuit analysis is the fact that the thicknesses of the end units are of microscopic dimensions (see Table VII). Whether these dimensions and the values derived for the characteristics of the middle units (i.e., R_k and C_k values) are real or not is difficult to prove. In any case, all the layer-type membranes including the highly complex membrane ADFGH can be described qualitatively by the series equivalent circuit of Fig. 3.

The situation with respect to the sandwich-type membrane is less complex than that with respect to the layer type. This is because during the formation of the sandwich type, the two simple membranes retain their individual characteristics to a large extent when they become part of the composite structure. The sandwich type therefore can be depicted with some degree of certainty by the circuit of Fig. 3. Using the same assumptions and approximations given above, values for R_k and C_k of the middle unit formed from high and low charge density membranes can be derived from the data given at the bottom of Table IV. When values of R_H , R_L , C_H , and C_L (H = high and L = low charge density membrane) corresponding to membrane thickness of 0.06 mm are used in equations 9 and 10, positive values of 1.2 and 4.2 are obtained for the factors $[R_k/(1 + \omega^2 R_k^2 C_k^2)]$ and $[(\omega R_k^2 C_k)/$
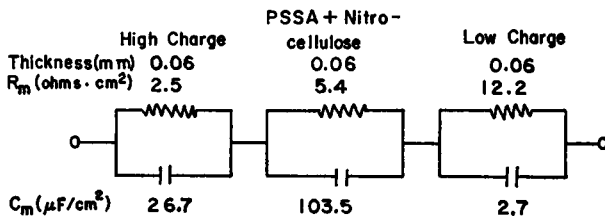
FIGURE 5   The equivalent electrical circuit for a sandwich-type composite membrane.

$(1 + \omega^2 R_k^2 C_k^2)$]. Solving these gives 15.8 ohms and 35.2 μF for R_k and C_k respectively. The value of R_k is intermediate between the values of R_H (7.5 ohms) and R_L (36 ohms), whereas the value of C_k is very high compared to the values of C_H (9.1 μF) and C_L (0.91 μF). This high value as discussed already is because of the presence of a high proportion of PSSA. Consequently the sandwich-type membrane can be represented quantitatively by the circuit of Fig. 5.

In essence then, when sandwich-type membranes are formed from simple membranes of high and low charge density, an extra unit is formed in the middle at the expense of the end units. These end units have their thicknesses reduced but retain their essential resistance and capacitance characteristics. In the case of the layer-type membranes also, a similar phenomenon happens, but the end units have their thicknesses reduced to microscopic dimensions. In either case the impedance is intermediate between the impedances of the high and low charge density simple membranes existing at the two ends of the composite structure; however, in this study, an exception is found in the case of the membrane AD.

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