Electrochemical Properties of Thin Parlodion Membranes

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Synopsis

Thin membranes (50–800 A. thick) formed by spreading a solution of Parlodion in isoamyl acetate on the air–water interface have been characterized. The electrical resistance and capacitance of these membranes prepared from each of the three Parlodion concentrations viz., 5, 10, and 20 mg./ml. solution, have been measured as functions of both membrane thickness and external electrolyte (KCl) concentration. Capacitance values corroborate the thickness inferred from the weight of material transferred to cover a fixed area. Membrane resistance drops with increase in thickness. Resistivity of a membrane 100 A. thick rises with decrease in external electrolyte concentration. Acid and alkaline solutions of KCl lower membrane resistance due to increased porosity of the membrane brought about possibly by the hydrolysis of the membrane material. Membrane potentials arising across these membranes also have been measured as functions of both membrane thickness and external electrolyte concentration. The bi-ionic potentials confirmed the usual order of penetrability of alkali metal ions observed in artificial membranes. A study of the effect of pH on membrane potentials indicates that the electrochemical activity of the membrane may be attributed to the presence of odd and terminal carboxyl groups in the nitrocellulose matrix of the membrane.

I. INTRODUCTION

Extensive literature describing the electrochemical properties of thick collodion membranes exists. They have been considered as model systems simulating the behavior of cell membranes[1] which are believed to be about 100 A. thick.[2,3] Membranes of this order of thickness, even though formed successfully from various materials,[4,5] have not been characterized so far by subjecting them to suitable electrochemical study. Probably the fragile nature of these membranes prevented such an investigation. Although handling of these membranes is difficult, techniques have been devised for the first time to make reproducible measurements of electrical resistance, capacitance and isothermal diffusion potentials across them possible. These measurements in themselves are not novel, but the results which are described in this paper are new for a system which is experimentally very difficult to work with and which probably because of the order of thickness dealt with represents a better model to develop to assume the likeness of natural membranes forming the boundaries of living cells.

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II. EXPERIMENTAL

Materials and Methods

The preparation on the air–solution interface of membranes, 50–1000 A. thick, from solutions of Parlodion (purified pyroxylin, Mallinckrodt) in isoamyl acetate is described elsewhere.[5] The type of cell described therein was used for casting membranes and for making all electrical measurements. Three different concentrations of Parlodion, 5, 10, and 20 mg /ml. solution, were used to form membranes.

Isoamyl acetate solvent (Fisher certified reagent) was purified either by sending it down a column of Florisil (Floridin Co.) or by distillation when "gross" impurities were suspected.

The solutions were made up from Fisher certified substances and distilled water redistilled in a two-stage quartz still with either acid or alkaline permanganate.   The potassium pyroglutamate (KPg) solutions were made up by neutralizing known weights of L-pyroglutamic acid (Mann Research Lab. Inc.) with KOH to pH 6.2, the pH of equilibrium water.

The pH of electrolyte solutions was adjusted by adding small amounts of HCl or KOH.

Resistance and Capacitance

A platinized platinum foil (circle, diameter = 2.5 cm.) fused to a glass tube by way of a piece of platinum wire was introduced through a hole bored through the rubber stopper of the membrane-forming cell[6] and formed one of the electrodes.   The other electrode was also a piece of circular (diameter = 0.3 cm.) platinized platinum foil held in a glass tube in the manner shown in Figure 1.   With the help of the rubber tubing and pinch cock the glass tube was filled with the electrolyte solution.   The area of the end of the tube contacting the membrane surface was estimated at 0.283 cm.^{2}.

The clean cell containing the bigger electrode was filled to the brim with the solution (for example 0.1N KCl) and the Parlodion membrane of the required thickness was formed on its surface.   The smaller electrode, also containing the same electrolyte and held in a sturdy three-dimensional micromanipulator (W. R. Prior & Co.), was gently brought to the surface of the membrane.   A General Radio impedance-admittance bridge served to measure the equivalent series resistance and reactance of the electrical circuit of the electrolyte–membrane system (Fig. 2) at a frequency of 10^3 cycles/sec. and at the laboratory temperature of 22 ± 1°C.

Membranes were cast also on other aqueous phases containing different electrolytes (LiCl, NaCl, or CaCl$_2$) and nonelectrolyte (sucrose).   In the case of sucrose, the membrane was formed on another identical cell not containing the platinum electrode but inside it a bent tube through which water may be introduced to lift the membrane and to float it off on to the surface of water contained in a liter beaker.   By using the cell containing the electrode and the required electrolyte solution in it, the membrane was
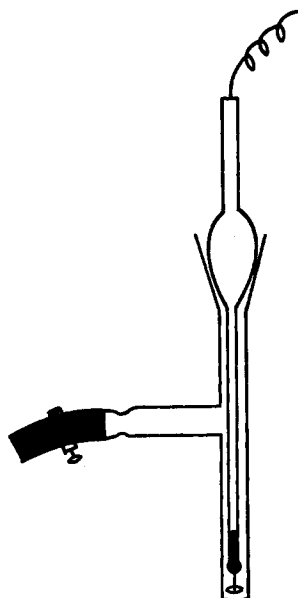
Fig. 1. Top fluid electrode containing the small circular platinized platinum electrode with rubber tubing and pinch cock.
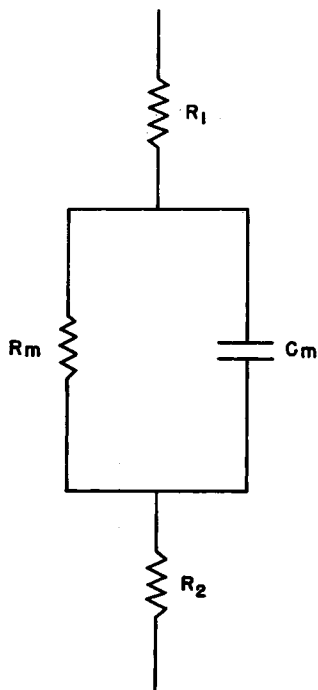

Fig. 2. The equivalent electrical circuit. Membrane resistance R_m and capacitance C_m with electrolyte resistances R_1 and R_2.

removed for measurements.   The solution was always replaced by a fresh sample before any measurement.

In the study of electrolyte diffusion through the membrane, $0.01N$ KCl was used in the top fluid electrode and $0.1N$ KCl solution in the cell or vice versa.   The bridge was balanced as soon as the top electrode contacted the membrane surface, and at regular intervals of time the bridge readings were taken either at the same point (for time studies) or at different points (to determine reproducibility).

Membrane Potentials

Through a second hole bored through the rubber stopper of the membrane-forming cell,[6] one end of a salt bridge was introduced.   The other end was connected to a saturated calomel half cell by way of saturated KCl solution.   In the place of the small platinum electrode (Fig. 1), one end of another salt bridge was introduced and its other end was connected to a second calomel half cell by way of saturated KCl solution to form the membrane system, Hg, Hg_2Cl_2|saturated KCl|KCl (C_1)||membrane||KCl (C_2)|saturated KCl|Hg_2Cl_2, Hg.   This probe element, filled with the appropriate electrolyte solution, was held in the micromanipulator for contacting the membrane surface successively at a number of points.   Usually the more dilute solution was kept in this probe.   The potentials were measured on a Keithley 610A electrometer allowing 0.2 mv. precision.

In experiments where stirring of the solution was tried, a fluid electrode of the type shown in Figure 3 was used to contact the membrane.   The glass
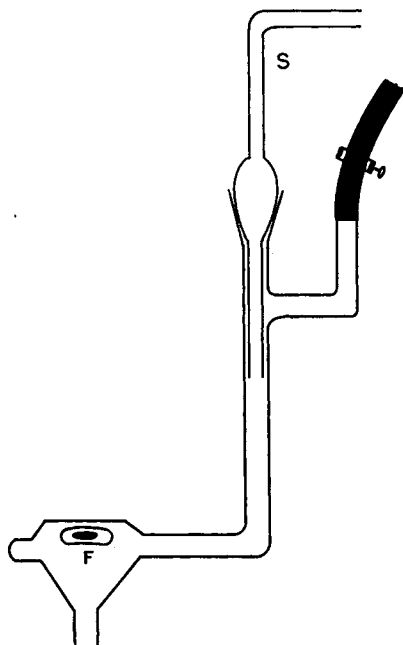

Fig. 3. Top bigger fluid electrode with iron cored glass float F and one end of salt bridge S.

float containing an iron core was rotated using a magnetic stirrer. Stirring of the liquid in the bottom cell was unsuccessful, as the swirling liquid mangled the membrane.

III. RESULTS

The electrolyte–membrane system was considered equivalent to an electrical circuit (Fig. 2) which by the usual analysis[7] gave

$$R_x = R_1 + R_2 + [R_m/(1 + w^2C_m^2R_m^2)]$$ (1)

$$X_x = -[wC_mR_m^2/(1 + w^2C_m^2R_m^2)]$$ (2)

where R_x and $-X_x$ are the equivalent series values of resistance and capacitative reactance, respectively, recorded by the bridge. R_1 and R_2 are the resistances of the electrolyte on either side of the membrane. Their combined value $R = R_1 + R_2$ was obtained in the absence of the membrane. R_m and C_m are the respective membrane resistance and capacitance. w has its usual significance and is given by $w = 2\pi f'$, where f' is the frequency $(10^3$ cycles/sec.).
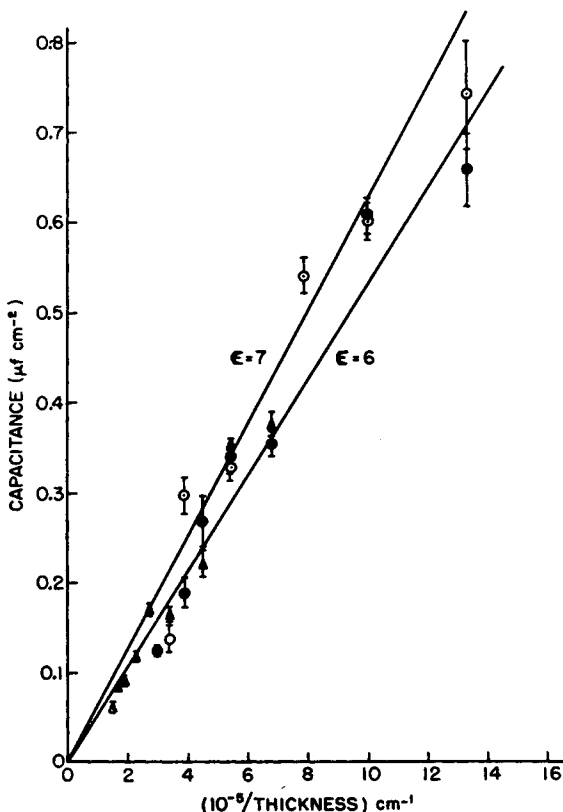

Fig. 4. Membrane capacitance related to reciprocal of thickness of membrane prepared from (⊙) 5 mg./ml., (●) 10 mg./ml., and (△) 20 mg./ml. Parlodion solution. The straight lines are the theoretical capacitance values for $\epsilon = 6$ and $\epsilon = 7$.
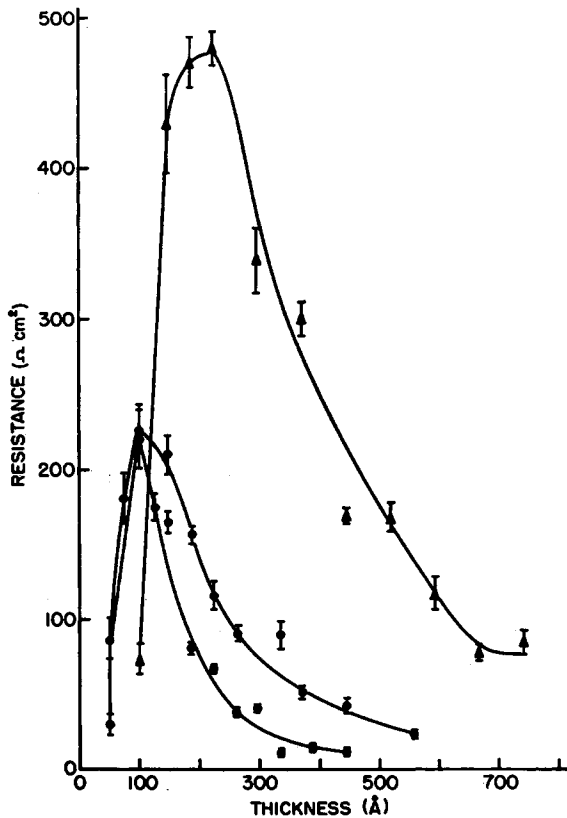
Fig. 5. Resistance of membrane prepared from (⊙) 5 mg./ml., (●) 10 mg./ml., and (△) 20 mg./ml. Parlodion solutions related to membrane thickness.

Dividing eq. (2) by eq. (1) yields

$$X_x/(R_x - R) = wC_mR_m \tag{3}$$

On substituting for $w^2C_m^2R_m^2$ in eq. (1), the resistance of the membrane R_m is evaluated by

$$R_m = (R_x - R)\{1 + [X_x/(R_x - R)]^2\} \tag{4}$$

and hence C_m can be calculated from eq. (3).

The values of R_m and C_m are expressed as ohm-cm.^{2} and μF./cm.^{2}, respectively.

The measurements of electrical resistance and capacitance have been made on a number of membranes of the same thickness at least five resistance–reactance readings being taken on the same membrane. A similar procedure was followed for membrane potential determinations. The data plotted in Figures 4, 5, and 8 represent the means and standard errors (1 S.E.) of at least 30 measurements.

Capacity and Thickness of Membrane

In Figure 4 are given the capacitance values of membranes formed from the three concentrations of Parlodion solution plotted against the reciprocal of the inferred membrane thickness. Alongside are given lines representing the same plots of capacitance values calculated for various thicknesses using values of 6 and 7 for the dielectric constant of Parlodion in the equation

$$9 \times 10^{11}C = \epsilon A/4\pi t \tag{5}$$

where C is the capacitance in farads, ϵ is the dielectric constant, A is the area in square centimeters, and t is the thickness in centimeters. The line with the steeper slope is for $\epsilon = 7$. Parlodion (purified pyroxylin) has $\epsilon = 6.4$ at 10^6 cycles.[8]

The experimental points lie within or near the limits set by these two lines. Points representing greater thicknesses were obtained by using membranes formed from 20 mg./ml. Parlodion solution. It was found difficult to form thick and uniform membranes from the 5 or 10 mg./ml. solutions. Visual examination of these membranes revealed a number of imperfections which are reflected in the exhibition of interference colors only at isolated points on the membrane, whereas membranes of corresponding thickness formed from 20 mg./ml. solution showed colors uniformly over the whole membrane surface. No such interference colors were seen on membranes of lower thicknesses.

Resistance and Thickness of Membrane

The results of the resistance of membrane obtained as a function of its thickness for the three Parlodion concentrations are presented in Figure 5. The resistance versus thickness curves have an unusual but identical form. Dilute solutions give low resistance membranes and denser solution produces high resistance membranes.

Very thin membranes (<75 A.) have low resistances and indicate a high degree of porosity. How porous they are can be tested by depositing tiny drops of aqueous solution on the membrane surface by use of a 1 μl. Hamilton syringe. Membranes of high resistance support these drops indefinitely. Neither their size nor shape changes significantly over a period of time; if the membranes are grossly porous, however, the drops sink in a few seconds and in some places they stay on. This phenomenon was noticed with 50 A. membranes formed from 5 and 10 mg./ml. solutions. In view of this, it is inferred that the structure is perforated, and as more material is transferred the perforations are filled up, giving peaks representing fewer number of pores and higher resistance.

Effect of the Nature of Subphase

Membranes, 100 A. thick were cast from 10 mg./ml. Parlodion solution on other aqueous phases containing different substances. The values of membrane resistance and capacitance are collected in Table I. Contrary to the action of acid or alkaline solution in producing low resistance mem-

TABLE I

Resistance and Capacitance of 100 A. Thick Membrane
Cast on Various Aqueous Subphases

Subphase	Resistance, ohm-cm.^{2}	Capacitance, μF./cm.^{2}
0.1N KCl	227 ± 16[a]	0.61 ± 0.02[a]
35% Sucrose[b]	197 ± 10	0.56 ± 0.03
0.1N LiCl	220 ± 12	0.66 ± 0.04
0.1N NaCl	191 ± 8	0.59 ± 0.03
0.1N CaCl₂	305 ± 64	0.62 ± 0.04
0.1N KCl (with 0.001N acid)	81 ± 3	0.71 ± 0.04
0.1N KCl (with 0.001N alkali)	9 ± 1	1.26 ± 0.16

[a] One standard error of the mean.
[b] Measurement made with 0.1N KCl solution.

branes, the resistances of membranes formed on solutions of sucrose, LiCl, and NaCl are high and close to the value obtained with KCl.

Membranes formed on 0.01N HCl or KOH subphase alone never supported drops of water indefinitely. The drops sank in a few seconds. When the concentration of acid or alkali was increased, the membranes disintegrated so completely on a molecular level that drops of water could not be supported. Both acid and alkali are known to degrade nitrocellulose[9] and hydrolyze isoamyl acetate,[10] and the action of alkali is more potent than that of the acid.[11] However, the membranes formed on 0.001N acid or alkali solution are not affected to such an extent as to make measurements impossible. They supported drops of water and enabled electrical measurements to be made. The values given in Table I refer to 0.1N KCl solution containing 0.001N HCl or KOH. Low membrane resistance therefore indicates a high degree of porosity resulting from chemical damage to the membrane material.

CaCl₂ solutions produced membranes with relatively high resistance, which may be attributed to the cationic ability, by virtue of its divalence, to tie up (less dissociated)[12] the few carboxyl groups known to be present in nitrocellulose.[13]

The capacitance values vary slightly from electrolyte to electrolyte, but alkaline solutions produce relatively high values for C_m.

Effect of External Electrolyte Concentration and pH

The membrane resistance (Fig. 6) and capacitance (Table II) measured as functions of both external electrolyte concentration and pH refer again to 100 A. thick membranes formed from 10 mg./ml. Parlodion solution.

Whatever the pH, it is seen that in general the membrane resistance increased with decrease in the concentration of the external electrolyte. The quantity of electrolyte outside controls the amount of electrolyte inside the membrane. The fixed ion concentration of the Parlodion being small (10^{-3} meq./g.),[13] little Donnan effect comes into play.
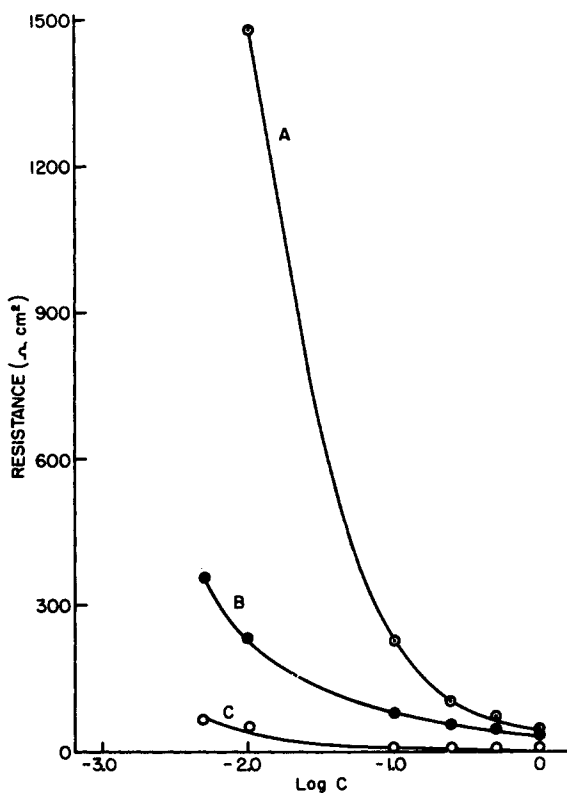
Fig. 6. The variation of resistance of 100 A. thick membrane with the concentration and pH of the external electrolyte solution: (*A*) KCl solution, pH 6.2; (*B*) acid KCl solution, pH 3.0; (*C*) alkaline KCl solution, pH 10.0.

At pH $= 6.2$, membrane resistance is the highest for any given external concentration. At $0.01N$, the membrane resistance is 1.5×10^3 ohm-cm.^{2}, whereas the bulk material 100 A. thick would have a value of 10^5 ohm-cm.^{2}.[8]

When the pH is decreased to 3, the resistance decreased, and further decrease is observed at pH $= 10$.

TABLE II

Capacitance of 100 A. Thick Membrane as a Function
of External Electrolyte Concentration and pH

pH	Electrolyte	C_m at various external electrolyte concentrations, $\mu F./cm.^2$					
		1.000 eq./l.	0.500 eq./l.	0.250 eq./l.	0.100 eq./l.	0.010 eq./l.	0.005 eq./l.
6.2	KCl	0.813	0.883	0.934	0.607	0.683	—
3.0	KCl + 0.001N HCl	0.887	0.890	0.861	0.707	0.781	0.547
10.0	KCl + 0.001N KOH	2.200	1.600	1.320	1.260	1.950	1.200

Membrane Potentials

Electrical potentials arising across thin membranes separating two solutions of the same electrolyte but of different concentration (Fig. 7) and of
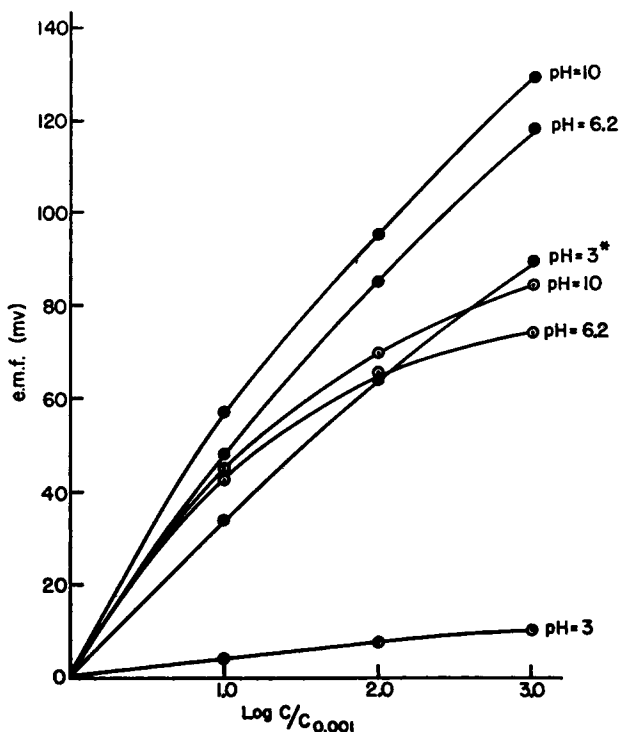

Fig. 7. Membrane potentials plotted as a function of logarithm of concentration of the external solution: (⊙) KCl solutions; (●) KPg solutions. pH 3 curve corresponds almost to the liquid junction potentials between the two solutions.

different electrolytes (uni-univalent) of the same concentration (Table III) refer to 75 A. membranes formed from 20 mg./ml. Parlodion solution. The same solution was used to form membranes to collect the data presented in Figure 8 and Table IV.

The potentials increase as the external concentration is decreased, but their variation is not found to be linear with the logarithm of the external

TABLE III

Emf of the Membrane Cell (Bi-ionic Potentials), Hg, Hg$_2$Cl$_2$| Saturated KCl| Soln. 1; 0.01N|| Membrane 75 A.|| Soln. 2; 0.01N |Saturated KCl| Hg$_2$Cl$_2$, Hg at 22°C.

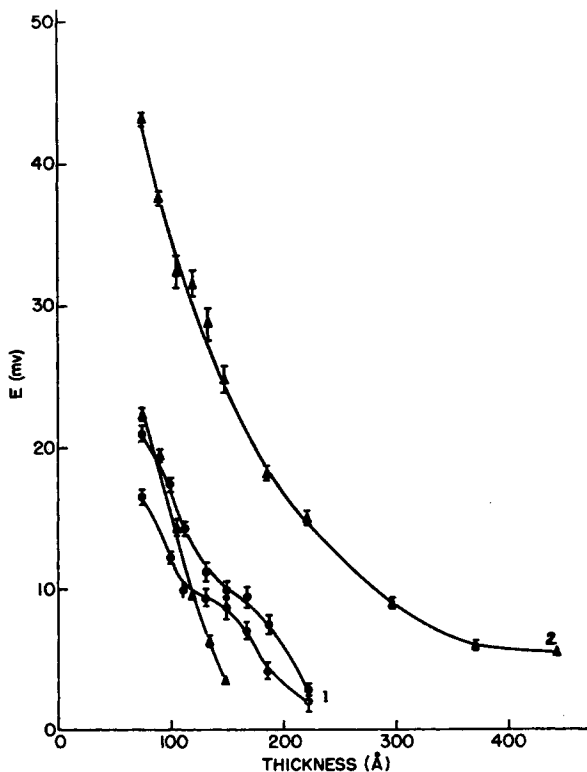| Solution 1	Solution 2	emf, mV.
KCl	LiCl	+25.6 ± 0.6
KCl	NaCl	+18.2 ± 0.4
KCl	KCl	+0.2 ± 0.0
KCl	CsCl	−4.3 ± 0.6

Fig. 8. Typical curves relating membrane potentials to thickness of membrane formed from (⊙) 5 mg./ml., (●) 10 mg./ml., and (△) 20 mg./ml. Parlodion solutions. Curves 1 refer to 0.1 and 0.01N KCl solutions; curve 2 refers to 0.01 and 0.001N KCl solutions.

concentration. This behavior is in agreement with what has been described in the literature for thick collodion membranes.

No asymmetry of membrane faces was noticed when the direction of electrolyte concentration gradient was reversed by keeping 0.01N KCl solution in the subphase and 0.1N KCl on top. The emf observed (16.9 mv.) was close to 16.6 mv. realized with 0.1N solution in the subphase. Using the same solution (0.1 or 0.01N KCl) or a mixture of two salt solutions (0.005N

TABLE IV

Emf of the Membrane Cell, Hg, Hg$_2$Cl$_2$| Saturated KCl| 0.01N KCl|| Membrane 75 A.|| 0.001N KCl| Saturated KCl| Hg$_2$Cl$_2$, Hg, as a Function of pH at 22°C.

pH	emf mv.
6.2	+43.5 ± 0.5
10.0	+44.3 ± 0.6
3.0[a]	+2.7 ± 1.0[a]

[a] The emf between solutions only was 2.0 mv. Change of pH produced the above potentials reversibly.

KCl + 0.005N NaCl) on either side of the membrane never gave potentials greater than ±0.5 mv.

The potentials recorded in Figures 7 and 8 and Tables III and IV were obtained by bringing the mobile top electrode usually containing the more dilute solution (which was positive) gently into contact with the membrane surface. Immediately the reading on the electrometer was noted. Depending on the surrounding electrolyte solution and the thickness of the membrane, the potentials decay slowly or rapidly. Dilute solutions (0.01 and 0.001N KCl) and thin membranes (75 A.) give slowly decaying potentials, whereas thick membranes and strong solutions (0.1 and 1.0N KCl) give rapidly decaying potentials. In the present experimental setup no means exist to arrest the decay of potentials by stirring both the solutions. However, the solution in the top electrode was stirred to stabilize the potentials (see discussion).

IV. DISCUSSION

The possibility of confirmation of the thickness of membrane inferred from the weight of Parlodion covering a fixed area of the aqueous surface is provided by the capacitance measurements.

The slopes of the three straight lines representing sets of points (Fig. 4) obtained for membranes formed from each of the three Parlodion concentration were computed by the method of least squares; and from eq. (5) the corresponding values for ϵ were derived. These values were found to be 6.6, 5.9, and 6.9, for 5, 10, and 20 mg./ml. concentrations of Parlodion, respectively. The average agrees with the literature value of 6.4. This demonstrates that capacitance measurements can be used to determine the thickness of thin membranes and that the inferred thickness is real.

It is further supported by the small scatter of the points and by the values of the intercepts which the three lines made with the ordinate. The theoretical value of the intercept should be zero, whereas the actual values realized are +0.0015, +0.0125, and −0.0218 for the three concentrations, giving an average of −0.0026.

The change of resistance with the thickness and area of the membrane is usually given by

$$R = \rho t / A \qquad (6)$$

where R is the resistance in ohms, t and A are thickness (centimeters) and area (square centimeters) of the membrane, respectively, and ρ is a constant (specific resistance or resistivity in ohm-cm.).

Examination of the curves (Fig. 5) in the light of the eq. (6) reveals that R instead of increasing linearly with t is found to decrease with t. Several possibilities to account for this may be suggested. Thus the physical structure may be different for membranes of different thickness. Studies of monolayers of various substances[14] have indicated that polar molecules form oriented monolayers at an air–water interface. So in the present case the possibility exists that nitro groups in the nitrocellulose chain, being
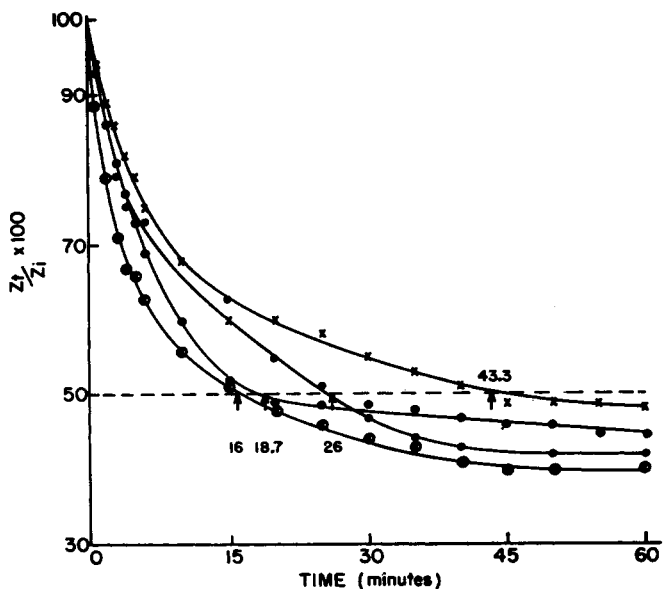
Fig. 9. Decay of impedance with time of membranes of different thickness: (●) 59 A.; (×) 100 A.; (○) 185 A.; ⊕ 296 A.   Arrows mark the half times.
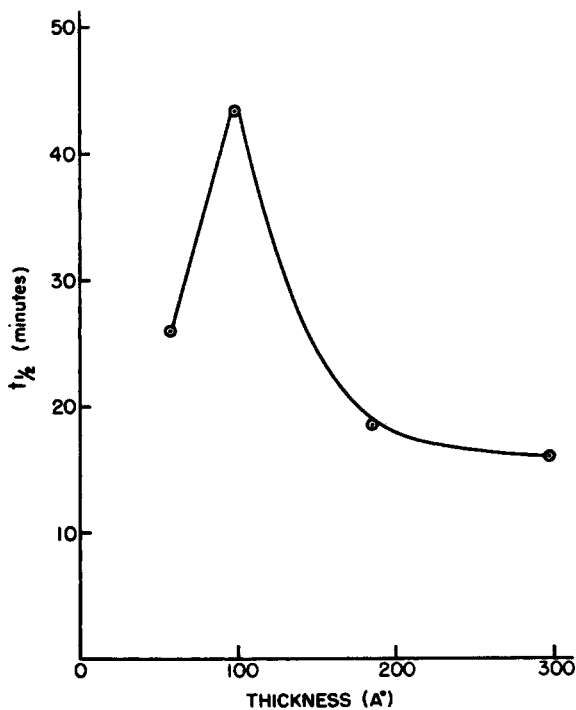

Fig. 10. Time taken by the membrane impedance to reach half its initial value ($t_{1/2}$) related to membrane thickness.

polar in nature, are highly oriented when Parlodion solution is spread to form a thin membrane.   When membranes are built up in thickness the degree of orientation may be reduced.

Membrane thickness is built up by adding more of the solution to cover the same area.   When the Parlodion solution is transferred to the aqueous phase, a little of the solvent dissolves (isoamyl acetate has a solubility of 0.16 g./100 ml. of water at 25°C.) and the rest evaporates by diffusing through the body of the membrane making the membrane porous.   The quantity of solvent evaporating this way could determine the difference in the physical structure of the membrane, i.e., with respect to size and number of pores.   Thicker membranes, being formed by the addition of more solution and hence more solvent, would be rendered more porous and as a consequence would have lower resistance.   The degree of orientation of the polar groups in these being probably small, may also contribute to reduce the resistance.   Very thin membranes, as already noted, have lower resistance and thereby point to the abundance of pores in them.

This argument receives support from the results of electrolyte diffusion experiments presented in Figures 9 and 10.   The decay of impedance of the system $0.1N$ KCl $\rightleftharpoons$ membrane $\rightleftharpoons$ $0.01N$ KCl due to solvent and solute transfer was followed with time, membranes of different thickness formed from 10 mg./ml. Parlodion solution being used (Fig. 9).   The time taken for the impedance of the system to reach half its initial value ($t^1/_2$) is plotted against thickness in Figure 10.   The relative porosity of the membranes is indicated by $t^1/_2$ values, shorter times being required for a more porous membrane to reach any specified impedance value.   The nature of the curve is similar to the resistance versus thickness curves.

In the case of the alkali metal chlorides, it is seen from Table I that the resistance of the membrane does not seem to depend on the mobility of the alkali metal ion.   In ordinary aqueous solutions, the mobilities are as Li $<$ Na $<$ K, whereas the resistance of the membrane is almost independent of the nature of the electrolyte solution.   This independence probably implies presence of little electrolyte in the membrane phase.   However the divalent Ca increased the membrane resistance, the reasons for which have already been noted.

Electrolyte content of the membrane phase is controlled by the concentration of the external solution; the higher the concentration, the higher the electrolyte content of the membrane, and so the membrane resistance decreased as the external electrolyte concentration increased (Fig. 6).   Acid or alkaline KCl solution produced low resistance membranes (Fig. 6, curves B and C).   As already described, the relative decrease in membrane resistance is due to increase in the porosity of the membrane brought about by the chemical action of acid or alkali on nitrocellulose.   As the alkali action is more effective than that of the acid, membranes at pH 10 are more porous and hence more conducting.

Certain specific trends exhibited by the capacitance values (Table II) require some comment. C_m values at high external electrolyte concentra-

tions are in general higher than corresponding values obtained with low external concentrations. Alkaline KCl solutions which produce membranes of high porosity also form membranes having high C_m values. This seems to suggest that the presence of large quantities of electrolyte in the interstices of the membrane may be responsible for the high values. This suggestion is difficult to accept unless there is some specific interaction of the electrolyte with the membrane material. Further, other porous membranes (acid KCl membranes) also give high C_m values. Greater porosity and hence presence of more electrolyte in the pores seems to favor entry and incorporation of foreign elements into the membrane matrix, making the whole more polar. The foreign elements could only be the polar molecules of water and K^+ and Cl^- ions.

The emfs of membrane cells presented in Figures 7 and 8 reflect the same physical and chemical characteristics of the membrane as the resistance and capacitance. Thin membranes (75 A.), even though as porous as some thick membranes and more porous than 100 A. membranes (Fig. 5), produce the highest potential for any given values of surrounding electrolyte. The factors causing this are (1) the number and the size of pores and (2) the number of chemical groups generating the observed emf. The former controls the resistance of the membrane and the latter controls the potential. The 75-A. membrane, by virtue of its thinness (orientation of its polar groups), possesses the full electromotive capacity of its ionogenic groups. The drop in emf, as the membrane thickness is built (see however Sollner and Carr[15]) can be interpreted to indicate masking of the groups without being exposed to the pore liquid. This indicates, then, an increase in the porosity of relatively low density fixed-charge regions as the thickness of the membrane is built up.

According to Sollner et al.,[16] the fixed-charge groups responsible for the electrochemical activity of untreated collodion (nitrocellulose precipitated from alcohol–ether solution) are the carboxyl groups formed during the bleaching of nitrocellulose. Wilbrandt,[17] however, attributed the electromotive capacity to the polar nitro groups present in the membrane material. In effect, both the nitro groups and the end and stray carboxyl groups are responsible for the anionic repulsion and cationic activity. It is unfortunate that no means exist to estimate them quantitatively by suitable exchange reactions. However a value of the order of 10^{-3} meq./g. of material has been estimated[13] as the exchange capacity of the untreated collodion.

Actual sites responsible for the electrochemical activity can be inferred from measurements of membrane potentials as a function of the pH of solutions. It is known from studies on ion exchange[13] that strong acid ionogenic groups, e.g., HSO_3, attached to the resin matrix of the ion exchanger are active over the whole pH range (pK < 1), whereas weak acid groups, e.g., COOH, are not active at low pH but active at moderate and high pH (pK 4–6), and very weak acid groups, e.g., phenolic OH, are active only at high pH (pK 9–10).

From Table IV, it is seen that at low pH, the membrane exhibits no activ-

ity and produces emfs equal to the values observed when the two liquids only are contacted. As the pH is increased, the values of the potential improve. This improvement can only be ascribed to the existence of carboxyl groups in the membrane phase and exertion of their full electrochemical activity at pH 10. If the polar nitro groups were responsible for the observed activity, the membrane potentials should have remained unaffected over the whole pH range, as the dipole character of the nitrocellulose would not be affected by the pH of the medium.

The decay of potentials referred to already, is due to diffusion (see Fig. 9). The factors controlling this are: (a) porosity of the membrane, (b) thickness of membrane, (c) concentration of external electrolyte solutions and their gradient across the membrane, (d) concentration of ionogenic groups fixed to the cellulose matrix, and (e) the small volume of the top probe in the present setup.

The volume of the solution in the top vessel being small, the concentration of the solution was greatly affected by transfer of both solvent and solute. When the size of the vessel was increased (Fig. 3) the decay was slow, and when the solution was stirred it was completely arrested in the case of dilute solutions (0.01 and 0.001N) and slowed down considerably with stronger solutions.

It is known from studies on ion exchange[13] that a high concentration of fixed charge confers great selectivity to the membrane, and as a result it completely excludes coions from its interstices when it is in equilibrium with dilute electrolyte solutions. Consequently, transfer of electrolyte across the membrane from the strong solution side to the other is prevented. Osmotic water transport in the opposite direction is negligible.[18]

In the present study with thin membranes, it is difficult to exclude coions from the membrane phase by increasing the concentration of fixed charge. Sollner[19] has shown that caustic action on collodion increased the concentration of fixed groups by the oxidation of the products of hydrolysis of nitrocellulose. Membranes cast on 0.001N KOH were hydrolyzed. It is possible that more COOH groups are produced. But their effect could not be seen due to increased membrane porosity.

Even thick membranes containing a number of ionized groups when they are in contact with electrolyte solutions (well stirred) whose concentrations are in considerable excess of the strength of the ionized groups fixed to the organic network give decaying potentials.[18]

The other approach to arrest the decay was to decrease membrane concentration of coions by using a large anion. Potassium pyroglutamate solutions were used. In dilute solutions very slowly decaying potentials were observed, but on stirring the decay was completely arrested. When the pH of these solutions was increased to 10, the theoretically predicted maximum value for the potential was realized with dilute solutions (0.01 and 0.001N), and this was stable. The emf data presented in Figure 7 are in keeping with the predictions of the fixed charge theory of membrane potentials proposed simultaneously by Teorell[20] and Meyer and Sievers.[21]

When the external concentrations are greater than the concentration of fixed charge of the membrane, the usual diffusion equation

$$E = RT/F(t_+ - t_-) \ln a_1/a_2$$

is obtained (t_+ and t_- are the transport number of cation and anion in the membrane phase and a_1 and a_2 are the activities of the two solutions).

When t_- is zero, i.e., exclusion of coion from the membrane phase, the Nernst equation

$$E = (RT/F) \ln a_1/a_2$$

gives the maximum limit of the potential which could be reached. This was realized when t_- was made nearly zero in the case of the large pyroglutamate ion in dilute alkaline solutions. Under these conditions, there is probably some increase of fixed charge concentration of the matrix also.

The selectivity that these thin membranes exert towards alkali metal ions is indicated by the bi-ionic potentials recorded in Table III. The origin of these potentials and their significance are discussed by Sollner et al.[22] The sequence of potentials observed by them for various cations is also observed in the present study, i.e., Li < Na < K < Cs; in other words, penetrability increases in this order.

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Résumé

Les membranes minces (50–800 A. d'épaisseur) formées en couvrant la surface de contact air-eau d'une solution de Parlodion dans l'acétate d'isoamyle, ont été caractérisées. La résistance électrique et la capacitance de ces membranes préparées à partir de trois concentrations de Parlodion, notamment 5, 10 et 20 mg par ml de solution, ont été mesurées en fonction de l'épaisseur de la membrane et en fonction de la concentration extérieure en électrolyte, en employant le KCl. Les valeurs des capacitances confirment les épaisseurs considérées, qui sont déduites du poids du matériel employé pour couvrir une surface constante. La résistance des membranes décroît avec un accroissement de l'épaisseur. La résistivité d'une membrane de 100 A. d'épaisseur augmente avec une diminution de la concentration extérieure en électrolyte. Des solutions acides el alcalines de KCl abaissent la résistance des membranes, abaissement qui est dû à un accroissement de la porosité de la membrane, due probablement à l'hydrolyse du matériel de la membrane. Les potentiels de membrane se formant entre ces membranes, ont également été mesurés en fonction de l'épaisseur de la membrane et de la concentration extérieure en électrolyte. Les potentiels bi-ioniques confirment l'ordre habituel de la pénétrabilité des ions des métaux alcalins, observée pour des membranes artificielles. Une étude de l'effet du pH sur les potentiels des membranes indiquent que l'activité électrochimique de la membrane peut être attribuée à la présence de fonctions carboxyliques terminales dans la matrice de nitrocellulose de la membrane.

Zusammenfassung

Dünne (50–800 A. dicke), durch Spreitung einer Parlodionlösung in Isoamylacetat an der Luft-Wassergrenzfläche gebildete Membranen wurden charakterisiert. Elektrischer Widerstand und Kapazität dieser mit drei verschiedenen Parlodionkonzentrationen, 5, 10 und 20 mg ml Lösung, hergestellten Membranen wurden als Funktionen der Membrandicke und der äusseren Elektrolytkonzentration unter Verwendung von KCl gemessen. Die Kapazitätswerte entsprechen der aus dem Gewicht des zur Bedeckung einer bestimmten Fläche übertragenen Materials gefolgerten Dicke. Der Membranwiderstand nimmt mit wachsender Dicke ab. Der spezifische Widerstand einer 100 A. dicken Membran nimmt mit zunehmender äusserer Elektrolytkonzentration zu. Saure und alkalische Lösungen von KCl setzen den Membranwiderstand wegen der, möglicherweise durch die Hydrolyse des Membranmaterials, erhöhten Porosität der Membran herab. Das an diesen Membranen ausgebildete Membranpotential wurde ebenfalls als Funktion der Membrandicke und der äusseren Elektrolytkonzentration gemessen. Die biionischen Potentiale bestätigen die in künstlich hergestellten Membranen beobachtete Penetrabilitätsreihenfolge der Alkalimetallionen. Eine Untersuchung des Einflusses des pH-Wertes auf das Membranpotential lässt vermuten, dass die elektrochemische Aktivität der Membranen der Anwesenheit einzelner und endständiger Carboxylgruppen in der Nitrozellulosematrix der Membran zugeschrieben werden kann.