Studies with Thin Membranes.   I. Characterization of Parlodion Membranes Formed by Multiple Dip Technique and by Incorporation of Lipoidal Substances

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Synopsis

Parlodion membranes formed by the dipping technique using solutions of Parlodion in isoamyl acetate of concentrations extending to 3% have been characterized.   The thickness of the membrane increased with increase in the viscosity of the membrane-forming solution.   Although the membrane resistance increased with increase in its thickness, the specific resistance ρ of the different membranes was not a constant but increased with increase in thickness and showed a tendency to attain a limiting value. The effects of different cations at the same concentration and of the same cation at different concentrations on membrane properties have been studied.   Membranes formed by multiple dips into the same solution and into different solutions of Parlodion have also been characterized in respect of their electrical resistance, capacitance, and specific resistance.   In general, all Parlodion solutions on a second dip gave membranes of increased thickness and resistance.   Subsequent dips always increased membrane thickness and resistance except in the case of 0.25% solution which produced a membrane of approximately the same thickness and resistivity.   The dipping and the spreading techniques of membrane formation have been used to introduce stearic acid, phosphatidyl L-serine, and cholesterol into the Parlodion matrix, and the lipoidal membranes so prepared have been characterized.

INTRODUCTION

In a previous communication,[1] a simple method was described for forming thin Parlodion membranes, 100 A. in thickness, on an air–water interface by depositing a solution of Parlodion in isoamyl acetate solvent under conditions of controlled evaporation.   A detailed account of the electrochemical properties of the membranes so prepared was given in a recent paper,[2] in which it was shown that the membrane thickness derived by the substitution of the capacitance value in the equation

$$9 \times 10^{11} C = (\epsilon a)/(4\pi t) \tag{1}$$

(where C is membrane capacitance in farads, ϵ is the dielectric constant equal to 6.4, a is the area in square centimeters, and t is the thickness in centimeters) agreed with the thickness estimated from the amount of

Parlodion deposited to cover a fixed area. Parlodion membranes thus behaved like dielectric films whose thickness may therefore be inferred from their measured capacitance. The method was used by Lakshminaray-anaiah[3] to estimate the thickness of Parlodion membranes prepared by the Carnell-Cassidy technique,[4] thereby eliminating the serious drawback of that technique, viz., the uncertainty about membrane thickness.

Extensive use in our laboratory of the Lakshminarayanaiah-Shanes technique[1] to prepare thin Parlodion membranes under a variety of conditions has indicated that unless the air–water interface and the solvent were free from traces of surfactants, porous (low electrical resistance) membranes would be produced. Further, it was found difficult to manipulate the impedance characteristics of the membrane, as the factors determining them were limited in number and not subject to control. On the contrary, the Carnell-Cassidy technique, extensively used recently by Carnell,[5] involves a number of variables, for example, rate of evaporation of solvent, concentration of Parlodion solution, the way the glass plate is dipped into parlodion solution and dried, and the number of times it is done this way. By altering these experimental variables one at a time, keeping the others constant, it is possible to obtain a membrane "tailor-made" to suit any specific purpose.

In the application of the Carnell-Cassidy technique to the preparation of Parlodion membranes[3] it was shown that by dipping the glass plate once into Parlodion solution and drying, the use of increasing concentrations always gave membranes of increasing resistivity without conforming to the equation

$$R = \rho(t/a) \tag{2}$$

where R is the resistance in ohms of the membrane of thickness t (centimeters) and area a (square centimeters) and ρ is the specific resistance. So, it was thought that by using the same solution to build membrane thickness by multiple dips of the glass plate and drying after each dip into the Parlodion solution, one would be able to form membranes whose resistance behavior would be according to eq. (2). The results of such a study are described in this paper, as well as the characteristics of membranes formed by using the two techniques referred to above and containing lipoidal molecules in their structure.

EXPERIMENTAL

Preparation of Membranes

The procedure described in the previous paper[3] was used to prepare membranes ranging in thickness from 95 to 4000 A. Multiple dips into the same Parlodion solution or dips into other solutions of different concentration were always carried out after the membrane formed on the glass plate was dry, as revealed by the absence of interference colors of the evaporating solvent, particularly at the base of the glass plate, which was

held upright in the enclosed metal frame. In addition to using Parlodion concentrations already employed,[3] 1.5, 1.75, 2.0, and 3.0% (w/v) solutions were used to form membranes.

Incorporation of Lipoidal Substances

The lipoidal substances used were stearic acid, phosphatidyl L-serine (C. P. Mann Research) and cholesterol (C. P. Mann Research). As stearic acid and cholesterol were soluble in isoamyl acetate, a known quantity of ether was dissolved with a known quantity of Parlodion in isoamyl acetate and made up to a known volume. A known weight of phosphatidyl L-serine (PLS) was dissolved in a minimum quantity of chloroform and mixed with Parlodion solution to form standard mixtures. These solutions were used to form membranes by employing either the spreading technique of Lakshminarayanaiah and Shanes[1] or the dipping technique of Carnell and Cassidy.[3,4]

Measurements of Resistance, Thickness, and Membrane Potential

The procedures described elsewhere[2,3] were used. Though the resistance and capacitance of all membranes derived were unambiguous, the thickness of pure Parlodion membranes only could be determined. The thickness of membranes containing lipoidal substances could not be evaluated, as the dielectric constant of the mixed membrane material was not known.

In the determination of membrane impedance, the glass tubing holding the platinized platinum electrode (Fig. 1 of the previous paper[2]) serving as the top electrode and contacting a membrane area of 0.283 cm.[2] was replaced by a wider tube which contacted the membrane surface to cover an area of 0.786 cm.[2]. This enabled the measurement of impedances of 2 and 3% membranes made by multiple dipping. The multiple dip experiments with 3% Parlodion solution were, however, limited, due to the limitations of the $Z-Y$ bridge or, rather, because a wider glass tube, of open end area greater than 0.786 cm.[2] could not be used to overcome the limitations of the bridge, as the electrolyte solution could not be held in the open end of the tube by suction and closure of the rubber tubing.

RESULTS AND DISCUSSION

Relationship between the Viscosity of Parlodion Solutions and the Thickness of Membranes Formed

The thickness of membranes formed by the Carnell-Cassidy technique are plotted in Figure 1 as a function of the concentration of the Parlodion solution. No linear relationship between the thickness of the membrane formed and the concentration of the solution exists. In the same figure are given the viscosity values of the different Parlodion solutions. The thickness and the viscosity curves run almost parallel, the thickness of the
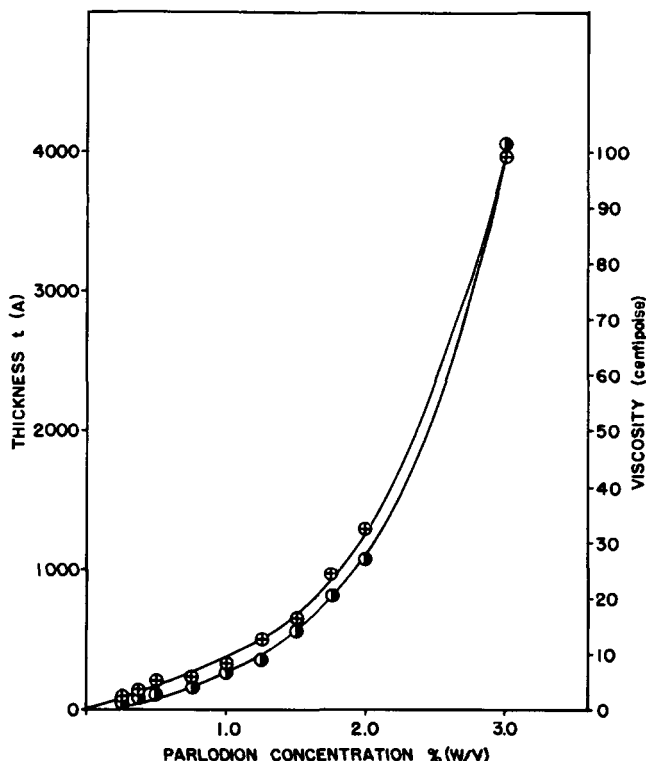
Fig. 1. Dependence of (◑) viscosity and of (⊕) membrane thickness on the concentration of Parlodion solution.

membrane increasing with increasing viscosity of the solution used to form it. As a result, a plot of solution viscosity against membrane thickness (Fig. 2) gives a straight line up to Parlodion concentrations of 2%; above that the linearity ceases, the rise in viscosity of the 3% solution being proportionately more than what it is for solutions in the range 0.25–2.0%. The 3% solution should produce a membrane of thickness 5000 A. if formation were to follow the linearity noticed for solutions up to 2%, but the thickness is only 3940 A. Whether this deviation is what it should be or indicates lack of rigid control over variables controlling membrane formation is difficult to say. Great care was observed to exercise good control over all the variables. Despite this, thickness formation being what it is, it seems futile to attempt correlations between the different factors controlling membrane formation.

In Figure 3, the variation of membrane resistance with thickness is given. Here again the resistance variation deviates from eq. (2), in that the product Ra does not increase linearly with t and so a constant value for ρ is not realized. However, as the thickness of the membrane is increased by using higher concentrations of Parlodion solution, ρ increases and seems to reach a limiting value. Parlodion concentrations higher than 3% could
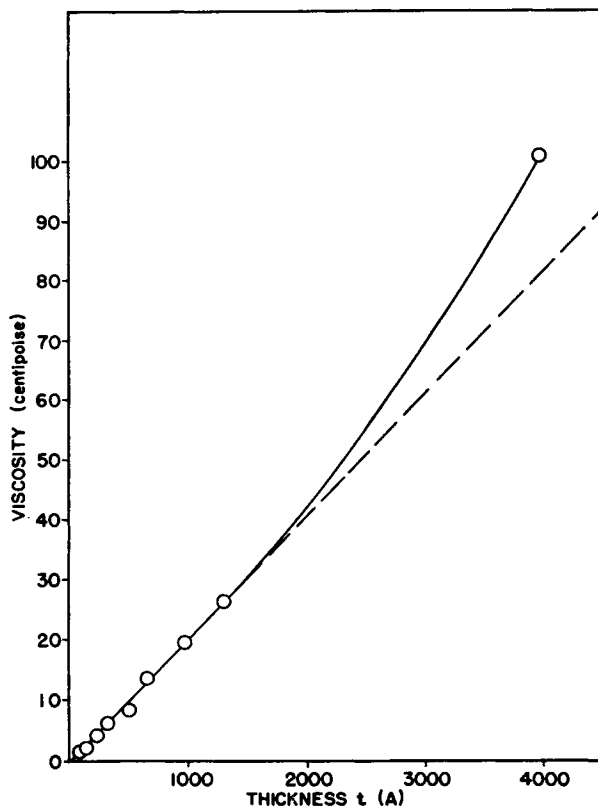
Fig. 2. Plot of membrane thickness against viscosity of the Parlodion solution.

not be used, as the membranes formed from such solutions could not be characterized under the conditions employed in the impedance measurements, due to limitations on the use of the bridge.

Effect of Different Cations on Membrane Characteristics

With different electrolytes, particularly the biologically important cations, viz., K^+, Na^+, and Ca^{++}, of concentration $0.1N$, the membrane resistance and thickness have been evaluated. It is seen from the results of Table I that the thickness of membranes is almost the same, regardless of the type of cation used to evaluate it. However the membrane resistance changed, and the change is in keeping with the order of specific conductances k observed in ordinary aqueous solutions, i.e., $Li^+ < Ca^{+2} < Na^+ < K^+$ except for Na and K forms of membranes for which the values of k are almost equal. This trend persists for all the membranes formed from 0.25, 1.0, and 3.0% solutions. However, for the membranes formed from different solutions, the absolute value of k decreases as the Parlodion concentration is increased. This is in accordance with the fact that the quantity of electrolyte present in the membrane phase decreases as the
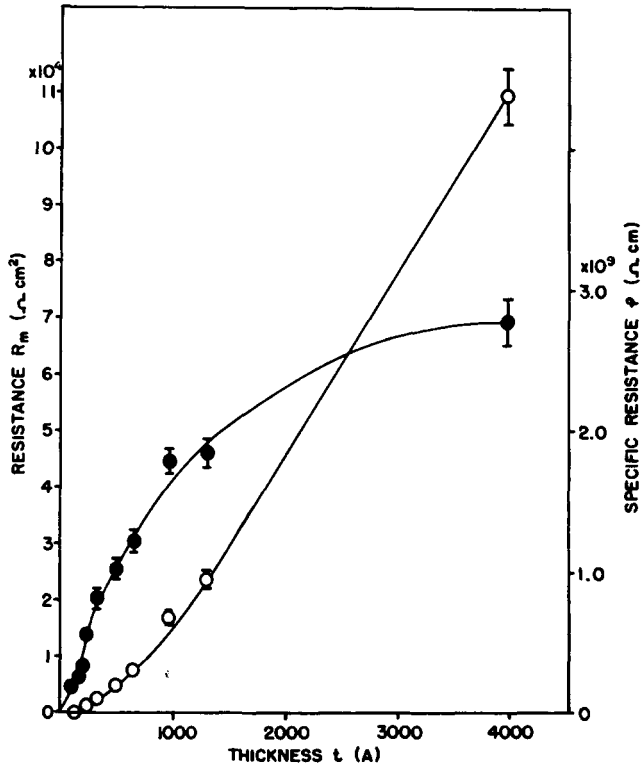
Fig. 3. Variation of (O) membrane resistance R_m and (●) specific resistance ρ with membrane thickness.

TABLE I

Effect of Different Cations on the Resistance and Thickness of Membranes
Formed from Different Concentrations of Parlodion Solution

Parlodion solution Concn., % (w/v)	Electrolyte (0.1N)	Resistance, ohm-cm.²	Thickness, A.	Specific conductance. $k \times 10^9$, ohm⁻¹ cm.⁻¹
0.25	LiCl	302 ± 15[a]	103 ± 6[a]	3.4
	NaCl	176 ± 14	92 ± 5	5.2
	KCl	185 ± 10	95 ± 3	5.1
	CaCl₂	233 ± 11	94 ± 4	4.0
1.0	LiCl	5049 ± 258	352 ± 8	0.70
	NaCl	2802 ± 218	320 ± 8	1.14
	KCl	2692 ± 231	325 ± 6	1.21
	CaCl₂	4827 ± 269	350 ± 5	0.72
3.0	LiCl	234,750 ± 68,433	3822 ± 96	0.16
	NaCl	109,620 ± 7,542	3997 ± 88	0.37
	KCl	109,933 ± 6,374	3940 ± 67	0.36
	CaCl₂	200,485 ± 52,735	4035 ± 61	0.20

[a] One standard error of the mean.

membranes become less porous with the increase in the concentration of the Parlodion solution forming it. The value of k of a 100-A. membrane in different ionic forms is nearly 3×10^6 times and that of a 4000-A. membrane is nearly 5×10^7 times smaller than the k values of $0.1N$ electrolyte solutions. These values indicate presence of little electrolyte in the membrane phase. Still, membrane discrimination exists against Li and Ca ion which, because of their greater hydrated ionic size, are probably excluded from the membrane phase to a relatively greater extent than are K and Na ions.

Effect of External Electrolyte Concentration on the Membrane Resistance and Capacitance

The results of previous study[2] showed that as the external electrolyte concentration (pH = 6.2) increased, membrane resistance decreased, whereas membrane capacitance increased. These effects were enhanced as the pH was either increased or decreased, the enhancement being more marked at higher pH. These changes were attributed to the presence of increasing quantities of electrolyte in the membrane phase. The change in membrane resistance is very well understood on this basis, whereas the change in capacitance is difficult to understand and therefore requires further study. In order to probe the effect of external electrolyte concentration on membrane capacitance, the resistance and capacitance of 100-A. membranes prepared by the Lakshminarayanaiah-Shanes technique and a series of membranes prepared by the Carnell-Cassidy technique from 0.25, 1.0, and 2.0% Parlodion solutions were determined, potassium pyroglutamate (relatively bigger anion) being used with the 100-A. membranes and KCl with the other membranes. These results are given in Tables II and III. The variation of membrane resistance and capacitance in the case of potassium pyroglutamate (Table II) is analogous to what was observed in the previous study.[2]

The results for the other series of membranes, with using KCl as the

TABLE II
Resistance and Capacitance of 100-A. Thick Membrane formed by the
Lakshminarayanaiah-Shanes Technique as a Function of External
Electrolyte (Potassium Pyroglutamate) Concentration

External solution concn., N	Resistance, ohm-cm.^{2}	Capacitance, μf./cm.^{2}
1.00	9.8 ± 0.4[a]	2.260 ± 0.210[a]
0.50	30.2 ± 4.7	0.595 ± 0.045
0.25	67.6 ± 2.3	0.582 ± 0.021
0.10	177 ± 6	0.578 ± 0.024
0.01	639 ± 31	0.491 ± 0.020
0.005	1373 ± 127	0.434 ± 0.019

[a] One standard error of the mean.

TABLE III

Resistance and Capacitance of Membranes Formed by the Carnell-Cassidy
Technique from Different Concentrations of Parlodion Solution as a Function of
External KCl Electrolyte Concentration

Parlodion solution concn., % (w/v)	Electrolyte concn., N	Resistance, ohm-cm.^{2}	Capacitance, μf./cm.^{2}
0.25	1.00	20 ± 2[a]	0.904 + 0.093[a]
	0.50	44 ± 7	0.587 ± 0.084
	0.10	185 ± 10	0.601 ± 0.017
	0.01	524 ± 65	0.394 ± 0.016
1.0	1.00	1199 ± 49	0.179 ± 0.008
	0.50	1059 ± 97	0.185 ± 0.008
	0.10	2692 ± 231	0.177 ± 0.003
	0.01	5134 ± 414	0.094 ± 0.005
3.0	1.00	60,157 ± 4,764	0.0143 ± 0.0004
	0.50	62,465 ± 7,363	0.0138 ± 0.0003
	0.10	109,933 ± 6,374	0.0144 ± 0.0003
	0.01	124,840 ± 11,477	0.0140 ± 0.0003

[a] One standard error of the mean.

external electrolyte, are presented in Table III, and they bring out a very interesting point. Although the resistance values vary in accordance with the results of Table II, the capacitance values undergo a change which seems to indicate why capacitance values of more porous membranes increase with increase in the external electrolyte concentration. Results of Table III in the case of 0.25% membranes, which are about 100 A. thick, show that the capacitance increases with increase in external concentration. The membranes from 1.0% solution, which are less porous than those from 0.25% solution, show an increase in capacitance as the solution concentration changed from 0.01 to 0.1N, whereas for the change in concentration from 0.1 to 1.0N there is no significant capacitance change. The membranes from 3.0% solution, which are less porous than those from 1.0% solution, show no variation in capacitance which is completely independent of the external electrolyte concentration. It is seen from membrane resistance values that for a 100-fold decrease in external concentration the increase in resistance is 26.2-fold for 0.25% membranes, 4.3-fold for 1.0% membranes, and only 2.1-fold for 3.0% membranes, indicating thereby the progressive exclusion of electrolyte from the membrane phase as tighter membranes are formed. Therefore, the presence of more electrolyte is responsible in the case of very porous membranes for the increase in capacitance observed with increase in the concentration of external electrolyte. Unless there is a specific interaction of the ions and/or of water with the membrane material to form dipolar molecules, capacitance would not be expected to increase. It is assumed, of course, that the membrane thickness remains constant. Measurement of dielectric constants of these thin membranes should

provide the required confirmatory evidence for the increase in the observed membrane capacitance. These investigations are being planned.

Characteristics of Membranes formed by Multiple Dips

The data obtained for membranes formed by multiple dips made on drying after each dip into the same solution employing 0.25, 0.5, 1.0, and 2.0% Parlodion solutions are shown in Figures 4, 5, 6, and 7, respectively. The following trends in membrane characteristics are noticed.

(*1*) The second dip always made the resistance of the first dip membrane higher in the case of all the solutions, whereas the thickness, although increased in the case of 1 and 2% membranes, did not change significantly in the case of membranes formed from the other two dilute solutions. As a result, a second dip always increased the resistivity of the first dip membrane.

(*2*) Subsequent dips in the case of 0.25% solution neither built the membrane thickness nor increased its resistance in any striking way, the values tending to fluctuate around a common value. This resulted in the production of a membrane of constant specific resistance.

(*3*) A similar trend is noticeable with membranes formed from 0.5, 1.0, and 2.0% solutions. In the case of 2% solution, however, the membrane
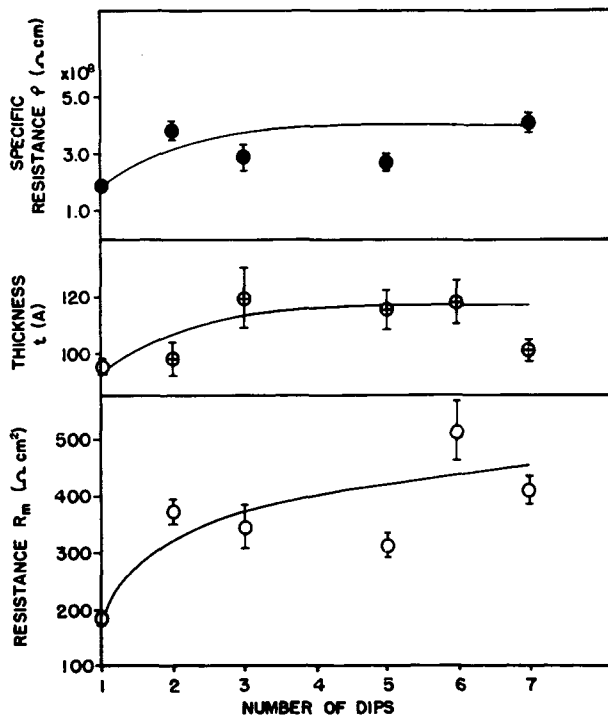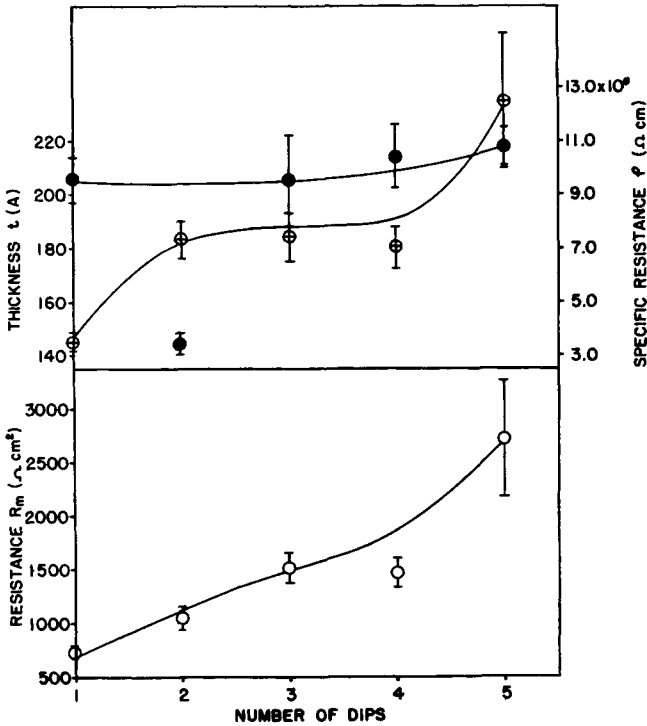

Fig. 4. Dependence of (O) membrane resistance R_m, ($\oplus$) thickness t, and ($\bullet$) specific resistance ρ on the number of dips of glass plate into 0.25% Parlodion solution.

Fig. 5. Dependence of (O) membrane resistance R_m, ($\oplus$) thickness t, and ($\bullet$) specific resistance ρ on the number of dips of glass plate into 0.5% Parlodion solution.

thickness rose steadily after each dip, although it did not conform to eq. (2), as the resistivity also rose steadily. From this variation it may be anticipated that, provided very strong Parlodion solutions are employed, membrane thickness may be built by multiple dips. The increase in resistance may not follow eq. (2) unless the Parlodion concentration used reaches the limit of 100% solution. In other words, by a suitable technique, as, for example, by molding under high pressures of solid Parlodion into different thickness, can one hope to realize constant values for ρ. With the dilute solution, even though a constant ρ was reached, the membrane thickness never changed. With stronger solutions, one can only hope to realize, by multiple dip technique, thicker membranes of increasing ρ indicating dissimilar physical structures for the membranes formed from the same material.

In Table IV are given the values for R_m, t, and ρ realized by first and second dips into a 3% solution. Membrane characteristics of the third and fourth dips could not be measured on the bridge under the conditions of the experiment. The results of the dips into different solutions, i.e., first dip in strong solution and second dip in dilute solution, are according to expectations, in that both resistance and thickness decreased. The
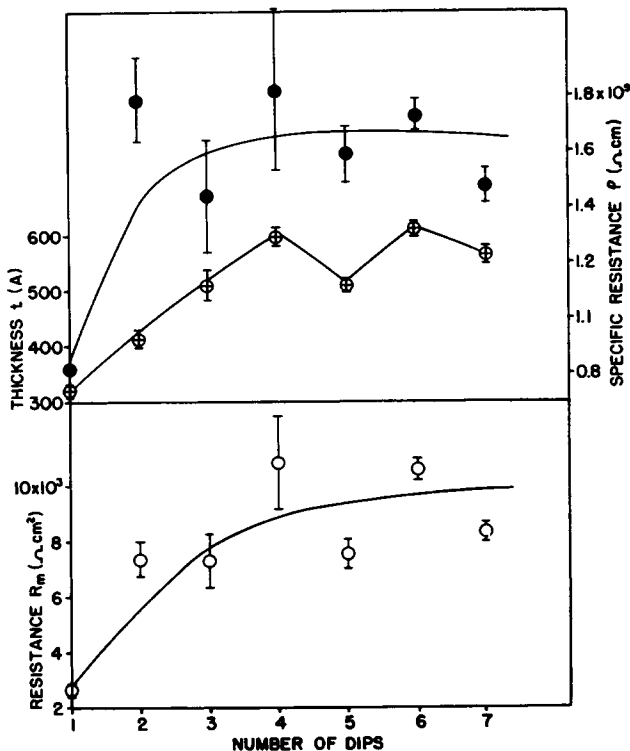
Fig. 6. Dependence of (O) membrane resistance R_m, ($\oplus$) thickness t, and ($\bullet$) specific resistance ρ on the number of dips of glass plate into 1.0% Parlodion solution.

reverse was obtained for first dip in dilute solution and second dip in strong solution.

Incorporation of Lipoidal Substances into the Membrane Structure

Both the spreading and the dipping techniques were used to introduce lipoidal molecules into the Parlodion membrane matrix. The spreading technique was found to be of limited applicability, as only small quantities of lipoidal substances could be incorporated into the membrane structure, whereas the dipping technique could be used to introduce large quantities of lipids, the limiting factor being the lipid solubility in the solvent or the Parlodion solution. The two techniques yielded two distinct types of lipoidal membranes.

Characteristics of Lipoidal Membranes Formed by the Spreading Technique. In the course of the development of the technique for membrane formation, it was noticed that the presence of surface-active agents in the aqueous subphase on which the membrane was formed always produced intact membranes whose resistances were very low. This phenomenon was not observed when alkali or acid $KMnO_4$-distilled water was
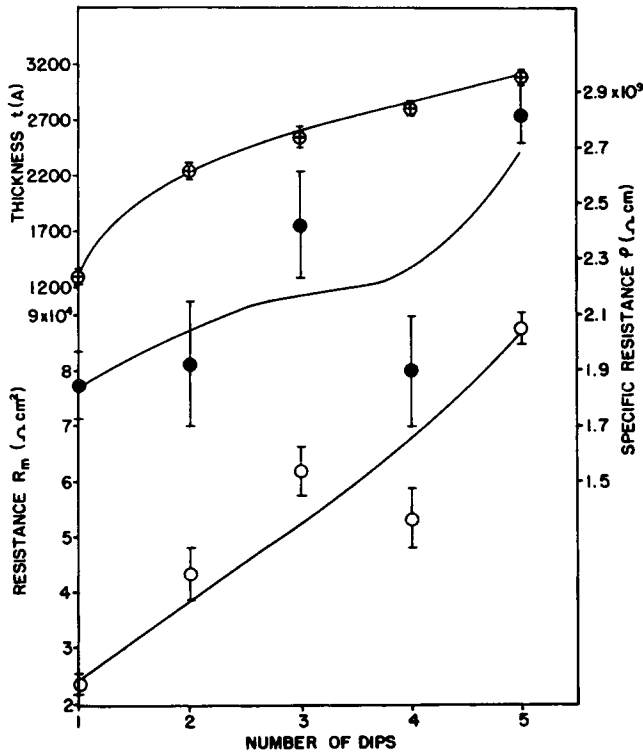
Fig. 7. Dependence of (O) membrane resistance R_m, (⊕) thickness t, and (●) specific resistance ρ on the number of dips of glass plate into 2.0% Parlodion solution.

TABLE IV

Resistance and Thickness of Membranes Formed by Multiple Dips by the Carnell-Cassidy Technique

Parlodion solution concn., % (w/v)	Dip	Resistance R_m, ohm-cm.^{2}	Thickness t, A.	Specific resistance $\rho \times 10^{-9}$, ohm-cm.
3.0	1st	109,933 ± 6374[a]	3940 ± 67[a]	2.79 ± 0.22[a]
	2nd	263,100 ± 18607	5810 ± 145	4.53 ± 0.48
2.0	1st	23,953 ± 1500	1297 ± 25	1.85 ± 0.16
0.25	2nd	6,350 ± 612	464 ± 8	1.37 ± 0.15
0.25	1st	185 ± 10	95 ± 3	0.19 ± 0.01
1.00	2nd	2,800 ± 250	350 ± 12	0.80 ± 0.07

[a] One standard error of the mean.

used.   Introduction of a trace of surfactant to this water again produced low resistance membranes.   As the lipoidal substances used in this study are surface-active, spreading of Parlodion solution containing these sub-
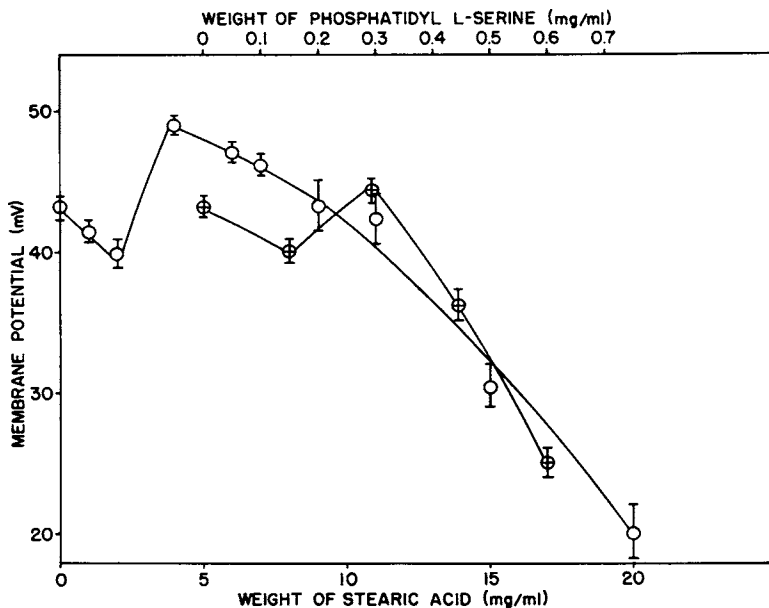
Fig. 8. Dependence of membrane potential on the weights of (O) stearic acid and
(⊕) phosphatidyl L-serine contained in membranes formed by the spreading technique
of Lakshminarayanaiah and Shanes; 1.36 μl. of 20 mg./ml. Parlodion solution con-
taining different weights of lipid was used to form the membrane.

stances produced low resistance membranes and so those results are not
presented in this paper. The membrane potentials they generated when
they separated 0.01 and 0.001N KCl solutions are given in Figure 8. It is
observed in the case of both stearic acid and phosphatidyl L-serine (PLS)
that the electrical potentials decrease to start with, increase, and then pro-
gressively decrease with the introduction of increasing quantities of
lipoidal molecules into the membrane phase. The initial decrease is trivial
and insignificant. The increase is attributable to the action of increased
fixed charges (more carboxyl groups) introduced into the membrane phase.
The continuous decrease in membrane potential following incorporation of
increasing quantities of lipoidal molecules into the membrane is brought
about by a slow breakdown of the physical structure of the membrane.
This was revealed by the inability of the membrane to hold drops of water
on its surface for significant lengths of time. Membranes holding large
quantities of lipids never supported drops of water. This criterion was
used to establish their integrity and usefulness.

In a similar type of study, Gershfeld[6] has reported that stearic acid mem-
branes distinguished between Na and K ions. It was found that $R_m^{Na^+}/R_m^{K^+}$
= 4 and $E_m^{Na^+}/E_m^{K^+}$ = $^1/_3$ (where R_m and E_m are resistance and membrane

potential, respectively) in contrast to pure Parlodion membranes, for which $R_m^{Na^+}/R_m^{K^+} = 2$ and $E_m^{Na^+}/E_m^{K^+} = 1$ Our studies indicate $R_m^{Na^+}/R_m^{K^+} = 0.8$ for Parlodion and 1.0 for Parlodion membranes containing stearic acid. The results presented in Table V give for the ratio $E_m^{Na^+}/E_m^{K^+}$ a value of 0.9 for Parlodion and 0.7 for stearic acid-containing membranes and thus indicate absence of any discrimination between Na and K ions by stearic acid membranes.   This is further confirmed by the identical bi-ionic potentials (see last column, Table V) generated by pure and stearic acid-containing Parlodion membranes.

TABLE V
Membrane Potential Generated across Parlodion and Lipoidal Membranes
Separating Dilute Electrolyte Solutions

Membrane type	Membrane potential, mv.		
	KCl (0.01–0.001N)	NaCl (0.01–0.001N)	Bi-ionic NaCl–KCl (0.01N)
Parlodion[a]	43.1 ± 0.8	39.5 ± 0.9	21.2 ± 0.3
Stearic acid[b]	39.9 ± 0.9	28.2 ± 0.3	21.2 ± 0.3

[a] Parlodion solution, 20 mg./ml., 1.36 μl. spread to form 100 A. thick membrane.

[b] Parlodion solution, 20 mg./ml., containing 2 mg./ml. stearic acid. 1.36 μl. of solution mixture spread.

Parlodion membranes containing stearic acid have been used as models to understand the action of drugs on biological membranes.[7] In fact, a startling claim that they act like living membranes has been reported.[8] The action of the so-called labilizers and stabilizers[7,9] has been studied by use of these membranes.   The relative decline of resistance of a 100-A. thick Parlodion membrane containing 5% stearic acid held between two solutions (each of concentration 0.1N) of NaCl, one of which contained $2 \times 10^{-5}M$ veratrine (labilizer) has been attributed to the action of veratrine in withdrawing fatty acid from the membrane phase.   This increased the permeability of the membrane to ions and thus resembled the action of veratrine on living membrane.   A careful repetition of this work with the use of 100-A. Parlodion membranes containing either stearic acid or PLS did not show any significant decrease in resistance on treatment of one of the aqueous phases with veratrine.   What has been reported may be one of those artifacts (either increase or decrease) normally observed in the course of impedance measurements when the system is taking time to reach an equilibrium state.

Characteristics of Lipoidal Membranes Formed by the Dipping Technique.   Unlike the membranes formed by the spreading technique, the membranes formed by this technique have good resistivity characteristics and generate stable membrane potentials.   The resistance and capacitance values of membranes formed by adding increasing quantities of stearic acid
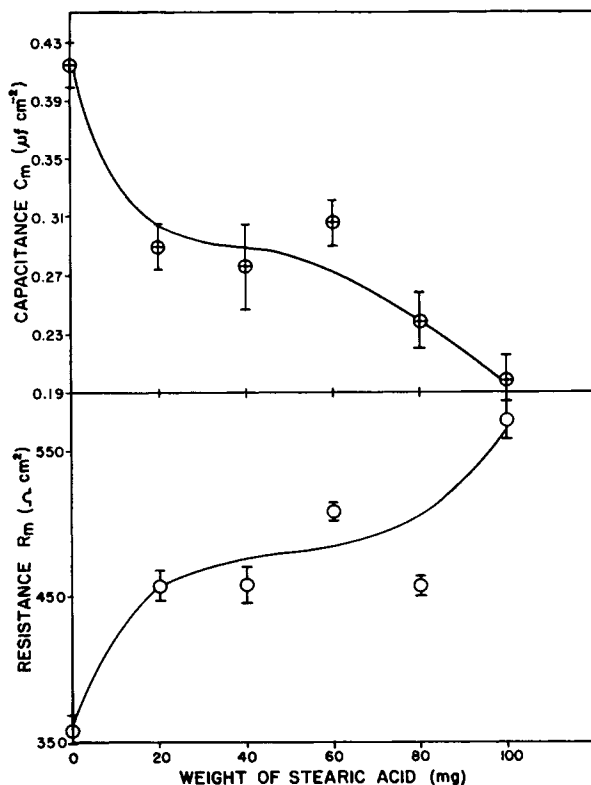
Fig. 9. Dependence of (O) membrane resistance R_m and ($\oplus$) capacitance C_m on the weight of stearic acid present in the membrane formed by the dipping technique of Carnell and Cassidy with 0.375% Parlodion solution containing different weights of stearic acid.

are given in Figure 9.   Incorporation of more stearic acid gave membranes of increasing R_m and decreasing C_m.   This seems to indicate formation of thicker membranes.   Unlike the spreading technique, this technique enables introduction of more lipid into the membrane structure.   All the lipoidal membranes whose resistance and capacitance values are given in Table VI, produced membrane potentials whose magnitude (for 0.01 and 0.001N KCl $\approx$ 46 mv.) was equal to that of pure Parlodion membranes. NaCl solutions gave potentials such that the ratio $E_m^{Na^+}/E_m^{K^+}$ was 0.8 for both Parlodion and lipoidal membranes.   The values of the ratio $R_m^{Na^+}/R_m^{K^+}$ (were 1.7, 1.1, 1.2, and 1.1 for Parlodion, stearic acid, PLS, and cholesterol+ PLS mixture membranes, respectively.   The resistance ratio $R_m^{Ca^{++}}/R_m^{M^+}$, (where M$^+$ is Na$^+$ or K$^+$) is 1.1–1.9 for Parlodion, 1.3–1.4 for stearic acid, 1.2–1.5 for PLS, and 1.4–1.5 for cholesterol + PLS mixture membranes. Thus for lipoidal membranes $R_m^{Ca^{++}}/R_m^{Na^+ \ or \ K^+}$ is between 1.2 and 1.5. This increase is due to the ability of divalent calcium to tie up carboxyl groups more effectively than monovalent sodium or potassium.

TABLE VI

Resistance and Capacitance of Lipoidal Membranes Formed by the Plate-Dipping Technique in Different Cationic Forms

Membrane	KCl (0.1N)		NaCl (0.1N)		CaCl$_2$ (0.1N)	
	R_m, ohm-cm.^{2}	C_m, μf/cm.^{2}	R_m, ohm-cm.^{2}	C_m, μf/cm.^{2}	R_m, ohm-cm.^{2}	C_m, μf/cm.^{2}
Parlodion (pure)[a]	345 ± 27	0.42 ± 0.02	577 ± 27	0.37 ± 0.05	650 ± 30	0.43 ± 0.04
Stearic acid[b]	444 ± 23	0.25 ± 0.01	486 ± 26	0.22 ± 0.01	648 ± 32	0.30 ± 0.01
Phosphatidyl L-serine[c]	385 ± 23	0.47 ± 0.02	471 ± 27	0.36 ± 0.02	581 ± 31	0.36 ± 0.03
Cholesterol[d]	380 ± 41	0.11 ± 0.01				
Cholesterol + PLS[e]	579 ± 31	0.16 ± 0.01	644 ± 28	0.18 ± 0.01	882 ± 54	0.14 ± 0.01

[a] 0.375% solution.
[b] 0.375% Parlodion solution containing 50 mg. stearic acid.
[c] 0.375% Parlodion solution containing 39 mg. PLS.
[d] 0.375% Parlodion solution containing 200 mg. cholesterol.
[e] 0.375% Parlodion solution containing 200 mg. cholesterol and 80 mg. PLS.

The resistance characteristics of membranes containing PLS, cholesterol, and their mixture present a trend which seems to indicate some molecular interaction between cholesterol and PLS in forming Parlodion membranes containing their mixtures. PLS and cholesterol individually form membranes having the same resistance value but in combination produce membranes whose R_m value is nearly 1.5 times higher than that of either cholesterol or PLS membrane. The reactive groups in PLS are a basic amino group, acidic carboxyl (of serine), and a hydroxyl (of phosphoric acid) group, whereas cholesterol has a weakly acidic secondary alcoholic OH group. Consequently the possibility exists for the alcoholic OH group to be attracted to the amino group. When the molecules are organized by these electrostatic interactions, however weak they may be, a relatively rigid structure is bound to be formed.

The capacitance values of PLS membranes are almost the same as those of pure Parlodion membranes. In the case of other lipoidal membranes the vaues are lower. This lowering is due to the formation of thicker membranes. Since the dielectric constants for these different mixtures of lipids and Parlodion forming the membrane material are unknown, a clear evaluation of capacitance changes must await availability of information about the dielectric constants of these materials.

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Résumé

On a caractérisé des membranes à base de parlodion préparé par trempage dans des solutions de parlodion dans l'acétate d'isoamyle à des concentrations atteignant jusqu'à 3%. L'épaisseur de la membrane croît avec un accroissement de la viscosité de la solution dont on forme la membrane. Bien que la résistance des membranes croît avec l'accroissement de son épaisseur, la résistance spécifique ρ de différentes membranes n'était pas constante mais croissait avec une augmentation d'épaisseur et montrait une tendance à atteindre une valeur limite. Les effets de différents cations à la même concentrations et pour un même cation à différentes concentrations sur les propriétés de la membrane ont été étudiés. Les membranes formées par trempages multiples dans la même solution et dans des solutions différentes de parlodion ont également été caractérisées, en ce qui concerne leur résistance électrique, leur capacitance et leur résistance spécifique. Toutes les solutions de parlodion en général, fournissaient des membranes,

au second trempage, d'épaisseur accrue et de résistance également augmentée. Les trempages subséquents augmentent toujours l'épaisseur des membranes et leur résistance, excepté dans le cas de solutions à 0.25% qui produit une membrane d'approximativement la même épaisseur et même résistivité. Les techniques de trempage et d'étalement en vue de former la membrane ont été utilisées en vue d'introduire dans la matrice de parlodion de l'acide stéarique, de lap hosphatidyl-L-sérine et du cholestérol, et les membranes lipoides ainsi préparées ont été également caractérisées.

Zusammenfassung

Durch das Eintauchverfahren mit Parlodionlösungen in Isoamylacatat mit Konzentrationen bis zu 3% gebildete Parlodionmembrane wurden charakterisiert. Die Dicke der Membrane nimmt mit zunehmender Viskosität der membranbildenden Lösung zu. Der Membranwiderstand nahm zwar mit steigender Dicke zu, der spezifische Widerstand ρ der verschiedenen Membranen war jedoch nicht konstant, sondern stieg mit zunehmender Dicke an und zeigte eine Tendenz zur Erreichung eines Grenzwerts. Der Einfluss verschiedener Kationen bei gleicher Konzentration und des gleichen Kations bei verschiedenen Konzentrationen auf die Membraneigenschaften wurde untersucht. Weiters wurden Membrane, die durch mehrfaches Eintauchen in die gleiche Lösung oder in verschiedene Parlodionlösungen gebildet wurden, in Bezug auf ihren elektrischen Widerstand, ihre Kapazität und den spezifischen Widerstand charakterisiert. Alle Parlodionlösungen lieferten allgemein bei einem zweiten Tauchen Membrane mit erhöhter Dicke und erhöhtem Widerstand. Aufeinanderfolgendes Tauchen erhöhte die Membrandicke und den Widerstand mit Ausnahme des Falles einer 0,25%igen Lösung, welche eine Memban mit angenähert der gleichen Dicke und dem gleichen Widerstand lieferte. Das Tauchen und die Spreitungsverfahren für die Membranbildung wurden zur Einführung von Stearinsäure, Phosphatidyl-L-serin und Cholesterol in die Parlodionmatrix benützt und die so erhaltenen Lipoiden Membrane wurden charakterisiert.