

## Preparation and Characterization of Thin Parlodion Membranes

N. LAKSHMINARAYANIAH, *Department of Pharmacology, School of  
Medicine, University of Pennsylvania, Philadelphia, Pennsylvania*

### Synopsis

Parlodion membranes 95 to 500 A. thick have been prepared on a glass surface by dipping a clean glass plate into the Parlodion solution and subsequently evaporating the solvent under controlled conditions by keeping the glass plate vertical in a metallic frame and covered with an inverted beaker. The membrane may be floated off on to an aqueous surface. Capacitance measurement established the thickness of the membrane. Electrical resistance and isothermal diffusion potentials arising across them when they separate different salt solutions have also been measured at room temperature.

In a previous study,<sup>1</sup> it was found that the electrical resistance of Parlodion membranes and isothermal diffusion potentials arising across them when they separated different salt solutions, decreased with increase in membrane thickness which was built by transferring more of the Parlodion solution to cover a fixed area of the aqueous surface. It was suggested that the increase in porosity of the membrane and masking of the effect of some of the ionogenic carboxyl groups present as the thicker membranes were formed, were probably responsible for the observed decrease in the membrane resistance and the emf.

In order to confirm these suggestions, thin membranes (95-500 A. thick) were prepared by a different technique. The thickness of the membrane was developed not by using larger volumes of the standard Parlodion solution but by increasing the concentration of the membrane-forming solution. This principle is inherent in the method of membrane formation developed by Carnell and Cassidy.<sup>2</sup> In our previous attempts,<sup>3</sup> difficulty was experienced in floating the membrane off the glass plate on to an aqueous surface. Further, there was the uncertainty about membrane thickness and hence required another independent method to infer the thickness. But recent work<sup>1</sup> has shown that this uncertainty can be eliminated by measuring the membrane capacitance. Use of the General Radio impedance-admittance ( $Z$ - $Y$ ) bridge to measure the resistance of the membrane gave also the required capacitance value from which the thickness of the membrane could be deduced.

## EXPERIMENTAL

### Preparation of Membranes

The Carnell-Cassidy technique<sup>2</sup> was used to prepare thin Parlodion membranes, 95–500 Å. in thickness. The difficulties encountered previously<sup>3</sup> were resolved by following the procedure detailed below.

A glass plate, 76 mm. long, 25 mm. wide, and about 1 mm. thick, was cleaned in hot chromic acid solution (solid  $\text{Na}_2\text{Cr}_2\text{O}_7$  + concentrated  $\text{H}_2\text{SO}_4$ ) containing excess dichromate. The plate was washed in running tap water and finally with distilled water a number of times. It was dried by rubbing with a piece of clean, absorbent, and lint-free cloth. It was held upright (lengthwise) in a clamp held in a micromanipulator by moving which the plate was slowly introduced into 80 ml. solution of Parlodion (purified pyroxylin, Mallinckrodt) in isoamyl acetate (Fisher certified) contained in a wide-mouthed bottle (150 ml.) until the end of the plate touched the bottom of the bottle. Immediately the plate was moved up slowly and out and placed upright in a metallic frame standing on a wire gauze below and upon which filter papers were placed. The whole assembly was covered with a 600 ml. beaker. The Parlodion solution flowed down the glass plate and was taken up by the filter paper. After about 5 min. (10–25 min. in case of strong Parlodion solutions) when the glass plate was dry, as was indicated by the absence of interference colors exhibited by the evaporating solvent, the three edges of the glass plate were scored with the sharp edge of a knife. The end of the plate was gradually lowered into water or preferably the electrolyte solution to be used in the subsequent electrical measurements contained in a 600 ml. beaker filled to its brim.

Membranes were prepared from 0.25, 0.38, 0.50, 0.75, 1.00, and 1.25% (w/v) Parlodion solutions.

### Measurement of Resistance and Thickness

A cell containing a bigger platinized platinum foil (circular, diameter 2.5 cm.) electrode used in previous work,<sup>1</sup> was slightly modified as shown in Figure 1. The side tube S was made slightly taller than the height of the 600 ml. beaker (about 15 cm.) which was filled with the electrolyte solution (usually 0.1N KCl) in which the cell was kept immersed before removing the membrane from the glass plate on to the surface of the solution. The membrane floating on the aqueous surface was lifted by using the cell which was thus filled to its brim not only with the electrolyte solution but also had the membrane supported on its surface. With the use of a smaller fluid electrode (platinized platinum with 0.1N KCl) described elsewhere,<sup>1</sup> the equivalent series resistance and reactance of the membrane-electrolyte system was measured with the aid of the *Z*-*Y* bridge at the room temperature ( $22 \pm 1^\circ\text{C}.$ ) employing a frequency of  $10^8$  cycles/sec.

The resistance  $R_m$  (in ohm-cm.<sup>2</sup>) and capacitance  $C_m$  (in  $\mu\text{f.}\cdot\text{cm.}^{-2}$ )

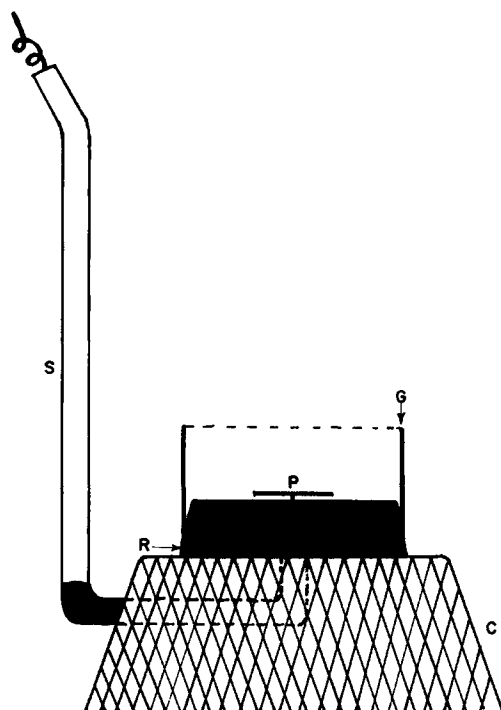


Fig. 1. Resistance cell with side tube *S*, sitting on a bark ring *C*. *R* is the rubber stopper for glass ring *G*, which held the electrolyte solution over whose surface the membrane rested. *P* is the circular platinized platinum electrode.

were calculated from the equations given in the previous paper.<sup>1</sup> The membrane thickness  $t$  (in Angstroms) was calculated from the equation  $t = 56.56/C_m$ , where a value of 6.4 was used for the dielectric constant of Parlodion.<sup>4</sup>

### Measurement of Membrane Potential

A cell (Fig. 2) containing a bent tube (salt bridge) and immersed in the aqueous electrolyte solution (0.01*N* KCl) before the membrane was removed from the glass plate was used to lift the membrane from the aqueous surface. A membrane cell Hg-Hg<sub>2</sub>Cl<sub>2</sub>|saturated KCl|0.01*N* KCl|Membrane|0.001*N* KCl|saturated KCl|Hg<sub>2</sub>Cl<sub>2</sub>-Hg described already<sup>1</sup> was formed, and its potential was measured on a Keithley 151 microvoltmeter at room temperature (22°C.).

### RESULTS AND DISCUSSION

The value of the resistance  $R_m$ , the thickness  $t$ , of the membranes formed from different concentrations of Parlodion solution and the emf arising

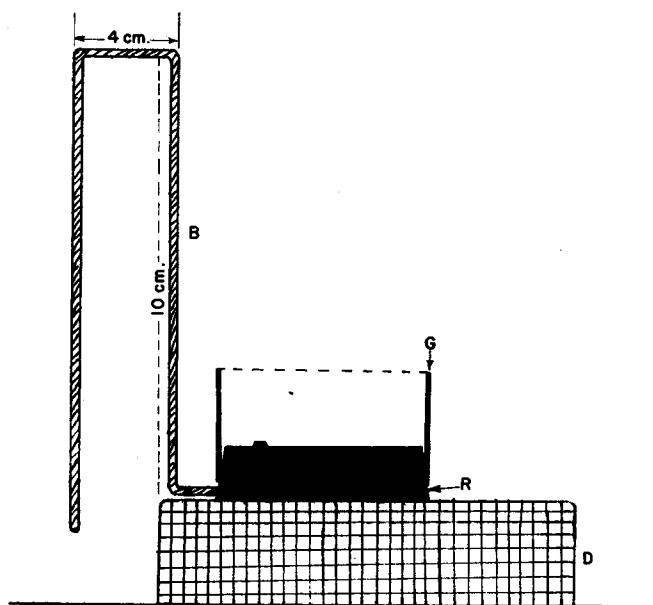


Fig. 2. Emf cell with salt bridge *B*, one end of which introduced through the rubber stopper seal *R*, for glass ring *G* sitting on an inverted petri dish *D*. Membrane supported on the surface of 0.01 *N* KCl solution contained in *G*.

across the membranes when they separated 0.01 and 0.001*N* KCl solutions are given in Table I.

The following conclusions may be drawn from the results: (1) the thickness of the membrane formed from different Parlodion solutions increased with increase in the Parlodion concentration; (2) the resistance of the membrane increased with increase in its thickness; (3) the emf was independent of the membrane thickness.

TABLE I  
Resistance, Thickness, and Emf of Membranes  
Formed from Different Parlodion Solutions

Concn. Parlodion solution, % (w/v)	Thickness <i>t</i> , A.	Resistance $R_m$ , ohm-cm. <sup>2</sup>	Emf, mv.	Specific resistance $\rho$ , ohm-cm.
0.25	95 ± 3 <sup>a</sup>	185 ± 10 <sup>a</sup>	48 ± 1.0 <sup>a</sup>	1.95 × 10 <sup>8</sup>
0.38	137 ± 5	358 ± 55	48 ± 1.0	2.61 × 10 <sup>8</sup>
0.50	205 ± 8	720 ± 49	48 ± 1.0	3.51 × 10 <sup>8</sup>
0.75	225 ± 6	1290 ± 73	49 ± 1.3	5.73 × 10 <sup>8</sup>
1.00	325 ± 6	2692 ± 231	48 ± 1.0	8.28 × 10 <sup>8</sup>
1.25	500 ± 12	5160 ± 321	48 ± 0.9	10.32 × 10 <sup>8</sup>

<sup>a</sup> One standard error of the mean. No asymmetry potential was observed across the membranes.

Conclusion (1) is to be expected as a consequence of the decrease in fluidity (reciprocal of viscosity) usually observed with polymer solutions as their concentration is increased. This decrease caused decrease in the rate of flow of Parlodion solution down the glass plate as the concentration of the solution was increased, and as a result the thickness of the material deposited with the evaporation of the solvent increased.

Conclusion (2) is at variance with what was observed in the previous study.<sup>1</sup> The porosity of the membrane obviously depended on the amount of solvent evaporating from the Parlodion solution during the period of formation of the membrane. Although the resistance increased with increase in the thickness of the membrane, the increase is not linear to thickness  $t$ , according to the equation  $R = \rho t/a$  (where  $a$  is area in square centimeters) as the values of  $\rho$ , specific resistance given in Table I are not constant but increase with increase in the concentration of the Parlodion solution. Denser solutions thus seem to favor tighter packing of material into the membrane. If the same Parlodion solution is used to build the thickness of the membrane by multiple dips and drying of the glass plate after each dip into Parlodion solution, one may expect to form membranes whose resistance behavior would conform to the above equation. This point is being investigated.

Conclusion (3) is different not only from our previous study but also from the study of Sollner and Carr,<sup>5</sup> who observed increase in emf with increase in membrane thickness. Consideration of the present results rules out the possibility of decrease in emf observed with increase in thickness as being due to masking of some of the ionogenic groups. The differences in the physical structure of the membranes, as for example, the number of pores and their relative size and distribution, seem to control the thickness dependence of the emf.

The factors controlling the electromotive ability and the resistance of the membrane are (1) density of ionogenic fixed groups and (2) pore size. The interplay of these two factors gives an overall electromotive capacity, however low, which seems to have a limiting value above which the emf is independent of membrane thickness as observed in the present study and below which the emf goes down as observed in the previous study. The overall resistance also depends on these two factors. At constant pore size which is very difficult to achieve on a practical level, the resistance would go down, assuming complete ionization of the active groups, with increase in the density of fixed charge and at constant fixed charge, the resistance would again go down with increase in pore size (as observed in the previous study) and would go up with decrease in pore size as observed in the present study.

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### Résumé

On a préparé sur une surface de verre des membranes de Parlodion de 95 à 500 A. d'épaisseur, en trempant une plaque de verre propre dans une solution de Parlodion et en évaporant ultérieurement le solvant en prenant garde de maintenir verticalement la plaque de verre dans un cadre métallique et de la couvrir d'un bécber renversé. Les membranes peuvent être isolées par immersion sous une surface aqueuse. On établit l'épaisseur des membranes par des mesures de capacité. La résistance électrique et les potentiels de diffusion isotherme existant au travers de ces membranes lorsqu'elles sont séparées par des solutions de différentes salines ont également été mesurés à température de chambre.

### Zusammenfassung

95 bis 500 A. dicke Parlodionmembranen wurden auf einer Glasoberfläche durch Eintauchen einer reinen Glasplatte in die Parlodionlösung und darauf folgende Verdampfung des Lösungsmittels unter kontrollierten Bedingungen durch Vertikalhalten der mit einem Becherglas bedeckten Glasplatte in einem Metallrahmen dargestellt. Die Membranen können auf eine wässrige Oberfläche übertragen werden. Die Membrandicke wurde durch Kapazitätssmessungen ermittelt. Weiters wurde der elektrische Widerstand und die isothermen Diffusionspotentiale durch die Membran bei Trennung verschiedener Salzlösungen bei Raumtemperatur gemessen.

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