

Membrane Potentials of Thin Nitrocellulose Membranes

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Synopsis

The membrane potentials of thin (300–1300 Å.) nitrocellulose (Parlodion) membranes have been investigated. Measurements were made in a Lucite cell by use of calomel electrodes with 0.05*N* KCl and 0.1*N* KCl. Variables having an influence on membrane structure, such as solvent polarity, temperature, and thickness, have been studied in relation to membrane potential. The range of potentials observed for Parlodion (2.1–9.2 mv.) is believed to be the result of differences in the orientation of the nitrocellulose molecules (and their accompanying electrochemically active carboxyl groups) in the membrane structure.

INTRODUCTION

The electrochemical activity (i.e., ion exchange activity) of a membrane depends on the quantity and activity of the potentially dissociable acidic or basic groups within the pores of the membrane.¹

The variable electrochemical activity of membranes prepared from nitrocellulose (Collodion) has been discussed by a number of investigators.^{2–7}

Sollner⁶ and his co-workers offer evidence to show that the variable electrochemical behavior of collodion membranes may be explained by the presence of different quantities of carboxyl groups on the nitrocellulose chain. These carboxyl groups apparently are formed by the oxidation of hydroxyl groups on cellulose during the manufacture of nitrocellulose. By subjecting commercial nitrocellulose samples to additional oxidation reactions, Sollner⁸ was able to produce membranes of high electrochemical activity. These membranes were quite thick (about 300,000 Å.), and they exhibited highly reproducible potentials approaching the theoretical maximum.

Wilbrandt³ has suggested that the variability of potentials exhibited by membranes prepared from various commercial nitrocellulose samples is the result of variability in the spatial orientation of the nitrocellulose molecules. Mathieu⁹ found that when a film is formed from a nitrocellulose solution by evaporation of the solvent, x-ray studies revealed both very sharp and very indistinct interference patterns.

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The investigation reported in this paper was undertaken to explore the variability of membrane potentials of very thin (300–1300 Å.) nitrocellulose membranes prepared from commercial nitrocellulose (Parlodion). In this study, thin nitrocellulose membranes of high uniformity are prepared by film-forming techniques previously described¹⁰ and recently refined.¹¹

Data are presented which show the effect of membrane preparation variables, such as the nature of the solvent, the temperature, and the film thickness, on membrane potential.

EXPERIMENTAL

Materials

The film-forming commercial nitrocellulose investigated in this study was Parlodion. When cellulose is nitrated to produce a nitrated cellulose containing 10.5–12.0% nitrogen (corresponding to approximately a dinitrate), the product is called pyroxylin.¹² Purified pyroxylin is called Parlodion by the manufacturer (Mallinckrodt Chemical Works).

The following solvents, which were employed to dissolve Parlodion, were all of reagent grade or better: acetone (Matheson, Coleman, Bell, AX 125), acetonitrile (M.C.B., AX 148), acrylonitrile (M.C.B., AX 350), 2-butanone (M.C.B., BX 1670), 4-butyrolactone (Eastman, 6922), cyclohexanone (M.C.B., CX 2355), diethyl ether (M.C.B., EX 190), *N,N*-dimethylformamide (Eastman, S5870), ethyl alcohol (Commercial Solvents, Gold Shield, absolute), isoamyl acetate (Eastman 298), mesityl oxide (M.C.B., MX 415), methyl alcohol (M.C.B., MX 475), nitromethane (M.C.B., NX 613), 2-pentanone (Eastman, P 1928), tetrahydrofuran (Eastman, 5308).

Methods

The Parlodion was dissolved in the appropriate solvent by overnight stirring (with magnetic stirrers) in closed, amber-colored bottles at room temperature. The membranes were cast on glass strips (5½ in. long, 1½ in. wide, and about 3/16 in. thick) by techniques previously described¹⁰ and recently refined.¹¹ The membranes, from both surfaces of the glass strip, were floated off on distilled water (at room temperature) contained in a large glass jar. Membrane thickness was determined by the method of Blodgett.^{10,13} Repeated experiments verified that the thickness range of the membranes on each side of the glass was identical. Thus, in a given experiment, the membrane from one side of the glass was floated onto a chrome strip for a thickness determination and the membrane from the other side of the glass was cut into sections (while still on the surface of the water), with ordinary scissors, for membrane potential studies. The membranes (about 1½ in. square) were picked up from the surface of the water on flat Lucite rings. These plastic rings were 64 mm. in diameter and 1.5 mm. thick with a 12.5-mm. hole in the center. To make certain that

the membranes adhered satisfactorily to the Lucite rings, it was customary to coat them with a uniformly thin layer of Grippit (Sanford Ink Company), a waterproof cement. The ring was then held with tweezers and lowered, in a horizontal position, until it touched the membrane floating on the water. The membrane (which now adhered to the Lucite ring) was now lifted carefully from the water surface, with the emerging edge of the plastic ring approaching a right angle with the water. The rings holding the membranes were hung with wire hooks in large glass beakers. The beakers were covered with aluminum foil and the membranes were allowed to dry, at least overnight, at room temperature. This drying period was found to be essential for the removal of the last traces of solvent from the membrane. The membrane potential of the dry membrane was determined in an especially designed Lucite cell. The cell was fabricated from Lucite rod and was composed of two half cells held together by four threaded, stainless steel rods (3 mm. \times 108 mm. long) running symmetrically through the entire cell. Each half cell was flat on the bottom and was approximately 59 mm. high at the highest point and 64 mm. in diameter. A hole 32 mm. in diameter and 38 mm. deep with a capacity of about 30 ml. was drilled in the center of each half cell. The half cells were provided with gaskets cut to the appropriate size from a sheet of Vellumoid (Vellumoid Company, Worcester, Massachusetts). The Lucite ring holding the membrane was mounted between the half cells and the nuts on the stainless steel rods were tightened to produce a leakproof system. The top of each half cell was provided with three symmetrically placed holes; two of these were 12 mm. in diameter and one was 15 mm. in diameter. These were used to introduce salt solution, stirrers, or electrodes, as desired. On the bottom of each half cell, a hole 7.5 mm. in diameter was drilled to provide an opening for the rapid draining of the cell solutions.

The procedure for the potential measurements involved the use of calomel electrodes in potassium chloride solutions. The specific method employed was a modification of that described by Graydon and Stewart.¹⁴ The half cells were filled with salt solution from 50-ml. automatic burets delivering at approximately the same rate to maintain equal pressure on both sides of the membrane. Initially, the left side of the cell is filled with 0.05*N* KCl and the right side with 0.1*N* KCl. With the solutions at rest, 60 sec. after filling, the potential of the cell measured. The cell was then drained and fresh KCl solutions were introduced in half-cell positions opposite to those used for the initial potential reading, (i.e., 0.05*N* KCl on the right side of the cell and 0.10*N* KCl on the left side). The cell potential was again measured 60 sec. after filling. The cell was then filled with "mean" salt solution (0.075*N* KCl) and was allowed to stand; 30 min. after the initial filling, the mean salt solution was drained from the cell and the entire procedure just described was repeated; it was again repeated at 60 min. and 90 min.

The two readings obtained at each thirty minute interval were added together and divided by two to get the actual potential of the membrane.

Thus, four potential values were obtained for each membrane in a 90 min. period.

Repeated measurements indicated that the membranes reached equilibrium with the KCl solutions almost immediately.

All potential readings were made with a Leeds and Northrup, K-3 universal potentiometer with a Leeds and Northrup D.C. null detector. The potentiometer was standardized before each reading. Some difficulty was experienced with various commercial electrodes that were employed. The results were obtained with Leeds and Northrup calomel electrodes.

The entire system was checked at frequent intervals by determining the membrane potential of commercially available anionic and cationic exchange membranes.

RESULTS

A series of potential readings for a given membrane were generally reproducible to 0.1 mv. However, some membranes exhibited variations as high as 1 mv. or more. This probably resulted from some change in membrane structure, such as the size of the membrane pores, produced by exposure to cell conditions. The potentials reported in Tables I-IV of this investigation are the average of three or four readings. (In some instances, the membrane broke before all of the readings could be completed.)

The theoretical maximum concentration (membrane) potential for a membrane separating 0.1 and 0.05*N* KCl solutions is 16.3 mv.¹⁵ If the membrane is anionic, the potential is -16.3 mv.; if cationic, +16.3 mv. All of the membranes of this study were prepared from Parlodion; all of the membranes were found to be cationic in character, presumably because of the presence of dissociable acid group^{6,8} in the membrane structure.

The potentials observed varied from a low of 1.2 to a high of 9.2 mv., depending on such factors as the thickness of the membrane, the solvent employed to dissolve the Parlodion, and the temperature of membrane preparation. The results are illustrated in Tables I-IV.

The data of Table I show that membrane potentials for Parlodion membranes from a given solvent show a wide variation, even though the membrane thickness is constant. This variation is best explained by the random orientation of the nitrocellulose molecules as the solvent departs from the polymer structure.^{3,9} Random orientation of nitrocellulose molecules would produce varying quantities of active carboxyl groups⁶ which would extend into the pores of the membrane. The decrease in the potential range for thicker membranes could be explained by less freedom for random orientation in the more viscous Parlodion solutions (and films).

The data show that Parlodion membranes prepared from cyclohexanone exhibit a decrease in potential as thickness increases from 586 to 1318 Å. This is explained by a decrease in the ease of orientation of nitrocellulose molecules as the polymer concentration in the membrane solution increases. In contrast to this observation, the increase in potential with

TABLE I
Effect of Thickness on the Membrane Potentials of Parlodion Membranes
Prepared from a Variety of Solvents

Solvent	Temperature of membrane preparation, °C.	Membrane thickness range, A.	Membrane potentials, mv. ^a	Maximum potential range, mv.
Acetonitrile	50.0	366-415	6.7, 7.4 7.5, 9.2	2.5
Acrylonitrile	50.0	415-439	4.6, 6.7, 7.2, 8.0	3.4
Methanol	30.0	639-659	4.3, 4.7, 6.8, 7.0	2.7
Acetone	30.0	732-781	3.6, 4.2, 4.5, 4.6, 5.3, 5.6, 6.2	2.6
Tetrahydrofuran	30.0	732-781	4.5, 4.6, 5.6, 5.8 6.0, 7.0	2.5
2-Pentanone	50.0	732-781	2.1, 2.5, 2.8, 3.2, 3.9, 4.5	2.4
Ethyl alcohol	50.0	976-1074	3.8, 3.9, 4.0, 4.2, 4.3	0.5
Nitromethane	30.0	1025-1122	2.1, 2.9, 3.0, 3.1	1.0
Mesityl oxide	30.0	1220-1318	2.6, 2.9, 3.0, 3.2 3.3	0.7

^a Each potential is for a different sample of the same membrane.

TABLE II
Effect of Thickness on the Potentials of Parlodion Membranes
Prepared from Cyclohexanone at 20.0°C.

Solute/solvent, g./ml.	Thickness range, A.	Membrane potential, mv.
6/800	586-781	3.5
8/800	976-1220	3.3
10/800	1220->1318	2.9
12/800	>1318	4.1
14/800	1600 ^a	6.6
14/800	5500 ^{a,b}	4.7

^a Calculated from the mass and density of the membrane.

^b This membrane was prepared by dipping the glass slide six times (up and down) in the membrane solution. The slide was inverted after each dip to produce membranes of more uniform thickness. A drying time of 10 min. (in air at room temperature) was employed after each of the first three dips; a drying time of 15 min. was employed after each of the last three dips.

TABLE III
Effect of Temperature on the Potential of Parlodion Membranes

Solvent ^a	Solvent b.p., °C.	Potential, for given membrane preparation, mv.		Potential range, mv.	Thickness range, A.	
		30°C.	50°C.		30°C.	50°C.
Acetone	56.5	5.2	3.4	1.8	488-781	463-585
Methyl alcohol	64.6	5.4	2.4	3.0	639-659	537-610
Tetrahydrofuran	64-66	5.6	3.6	2.0	732-781	561-568
Ethyl alcohol	78.5	4.2	4.1	0.1	1171-1318	976-1074
Acrylonitrile	78-9	3.7	6.1	2.4	537-610	415-610
2-Butanone	79.6	3.0	2.9	0.1	1074-1318	634-1074
Acetonitrile	82	6.5	7.7	1.2	341-512	366-415
Nitromethane	101	2.5	3.2	0.7	1025-1122	537-830
2-Pentanone	101.7	4.1	3.1	1.0	732-1171	732-1171
Mesityl oxide	128.7	2.4	3.0	0.6	1220->1318	1024-1264
Isoamylacetate	142.5	2.3	2.2	0.1	732-1318	878-1073
Dimethylformamide	153.0	6.5	5.2	1.3	512-610	390-488
Cyclohexanone	156.7	4.0	5.5	1.5	512-561	439->1318

^a In order of increasing boiling point.

^b Data from *Handbook of Chemistry and Physics*.¹⁶

TABLE IV
Effect of Solvent Polarity on the Membrane
Potential of Parlodion Membranes

Solvent	Solvent dipole moment, Debye units ^a	Membrane potentials, mv.	
		30°C.	50°C.
Methyl alcohol	1.66	5.4	2.4
Ethyl alcohol	1.68	4.2	4.1
Isoamyl acetate	1.8	2.3	2.2
Acetone	2.72	4.9	3.4
2-Butanone	2.75	3.0	2.9
Cyclohexanone	2.8	4.0	5.5
Nitromethane	3.17	2.5	3.2
Acetonitrile	3.37	6.5	7.7
Acrylonitrile	3.88 ^b	3.7	6.1

^a Data of Weissberger et al.¹⁷

^b Data of American Cyanamid Co.¹⁸

thickness from 1318 to 1600 Å. would result from the fact that with increased membrane¹ thickness the average pore length in the membrane structure would increase and the probability that each pore would have an active dissociable group would be increased.

The lower potential for the relatively thick (5500 Å.) membrane can be explained by the loss of effective pore structure resulting from the special method of film preparation that was employed. The thickness data for the last two membranes in Table II show that washing away of polymer by solvent in the dipping process has occurred (i.e., the membrane prepared by six dips in the 14 g./ml. solution is not six times as thick as the preceding membrane prepared by one dip in the same solution). This solvent action would destroy some of the pore structure of the membrane. Also, the drying period for the membrane, followed by additional immersion in the membrane solution would tend to seal off some of the membrane pores resulting in less continuity in the membrane pore structure (i.e., a relatively large number of "dead-ends" would be present).

It can be concluded from the data of Table III that membrane potentials of thin Parlodion membranes (i.e., below about 732 Å.) are affected by the temperature of membrane preparation. However, the direction and/or magnitude of the potential change with temperature is not yet predictable. The effect is less pronounced with membranes in the 1000 Å. thickness range. It is probable that such variables as solvent polarity (see Table IV), the viscosity of the membrane solution, and the specific solvent interaction with the Parlodion in the solution process are all contributing factors to the net orientation of the active carboxyl groups which are responsible for the membrane potential.

For the solvents shown in Table IV, those with the lower dipole moments (1.66–2.75) yield membranes that show essentially no change or a decrease in potential with temperature, whereas those with the higher dipole

moments (2.8–3.88) produce membranes that show an increase in potential with temperature. Thus, very polar molecules (at somewhat elevated temperatures) do have an influence on the orientation of the active carboxyl groups on the nitrocellulose chains. As the polar solvent departs through the pore channels it is able to attract carboxyl groups into the membrane pores.

CONCLUSIONS

Properties of membranes,¹⁰ such as membrane potential, which are exhibited as the result of random spatial orientation of dissociable groups into the pores of the membrane would exhibit a more constant average value in bulky (300,000 Å.)⁸ membranes than would be the case with the relatively thin (300–1000 Å.) membranes of this investigation. In very thin membranes, the properties of the membrane molecules that can be exhibited with favorable spacial orientation are much more sensitive to membrane preparation conditions.

The data of this study show that the membrane potentials of thin Parlodion membranes are changed by film thickness, temperature, and solvent polarity. Our results support the observations of Wilbrandt³ and the experimental findings of Mathieu⁹ which indicated that the variability of potentials in nitrocellulose membranes was the result of the variability in the spacial orientation of the nitrocellulose molecules (with their accompanying carboxyl groups⁶).

Further studies of such factors as the influence of the viscosity of the membrane solution¹⁹ and the specific solvent interaction of nitrocellulose in the solution process²⁰ could yield results which would permit the production of membranes of more specific characteristics for particular applications.

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References

1. K. Sollner, S. Dray, E. Grim, and R. Neihof, in *Ion Transport across Membranes*, H. T. Clarke, Ed., Academic Press, New York, 1954, p. 144.
2. L. Michaelis and W. A. Perlzweig, *J. Gen. Physiol.*, **10**, 575 (1927).
3. W. Wilbrandt, *J. Gen. Physiol.*, **18**, 933 (1934–35).
4. K. Sollner and C. W. Carr, *J. Gen. Physiol.*, **26**, 309 (1941–43).
5. K. Sollner and I. Abrams, *J. Gen. Physiol.*, **24**, 1 (1940–41).
6. K. Sollner, I. Abrams, and C. W. Carr, *J. Gen. Physiol.*, **24**, 467 (1940–41).
7. K. Sollner and C. W. Carr, *J. Gen. Physiol.*, **26**, 17 (1942–43).
8. K. Sollner, *J. Phys. Chem.*, **49**, 47 (1945).
9. M. Mathieu, *Trans. Faraday Soc.*, **29**, 122 (1933).
10. P. H. Carnell and H. G. Cassidy, *J. Polymer Sci.*, **55**, 233 (1961).
11. P. H. Carnell, *J. Appl. Polymer Sci.*, **9**, 1863 (1965).

12. L. F. Fieser and M. Fieser, *Organic Chemistry*, 3rd Ed., Heath, Boston, 1956, p. 858.
13. K. B. Blodgett, *J. Am. Chem. Soc.*, **57**, 1007 (1935); *ibid.*, **56**, 495 (1934); *J. Phys. Chem.*, **41**, 975 (1937).
14. W. F. Graydon and R. J. Stewart, *J. Phys. Chem.*, **59**, 86 (1955).
15. K. Sollner and H. P. Gregor, *J. Phys. Colloid Chem.*, **54**, 330 (1950).
16. *Handbook of Chemistry and Physics*, 3rd Ed., Chemical Rubber Publishing Co., Cleveland, Ohio.
17. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., Eds., *Organic Solvents*, 2nd Ed., Interscience, New York, 1955, p. 275.
18. *The Chemistry of Acrylonitrile*, 2nd Ed., American Cyanamid, New York, 1959, p. 2.
19. F. Baker, *J. Chem. Soc.*, **101**, 1409 (1912).
20. M. L. Byron, *J. Phys. Chem.*, **30**, 1116 (1926).

Résumé

Les potentiels de membrane de membranes de nitrocellulose fine de 300-1300 Å (Parlodion) ont été étudiés. Des mesures ont été faites avec une cellule Ludite utilisant des électrodes au calomel avec du 0.05*N* KCl et 0.1*N* KCl. Des variables exerçant une influence sur la structure des membranes telles que la polarité des solvants, la température et l'épaisseur ont été étudiées en rapport avec le potentiel de membrane. Le domaine de potentiel observé pour le Parlodion (de 2.1 à 9.2 mv) résulte de la différence dans l'orientation des molécules de nitrocellulose (et de leurs groupes carboxyliques qui les accompagnent et qui sont activés électrochimiquement) au sein de la structure de la membrane.

Zusammenfassung

Die Membranpotentiale dünner (300-1300 Å) Nitrocellulose-(Parlodion)-membrane wurden untersucht. Die Messungen wurden in einer Lucite-Zelle mit Kalomelelektrode in 0,05*N* KCl und 0,1*N* KCl ausgeführt. Variable, die Einfluss auf die Membranstruktur besitzen, wie Lösungsmittelpolarität, Temperatur und Dicke, wurden in Bezug auf das Membranpotential untersucht. Es wird angenommen, dass der bei Parlodion beobachtete Potentialbereich (2,1 bis 9,2 mV) durch Unterschiede in der Orientierung der Nitrocellulosemoleküle (und der sie begleitenden elektrochemisch aktiven Carboxylgruppen) in der Membranstruktur bedingt ist.

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