

THE STRUCTURE OF THE COLLODION MEMBRANE AND ITS  
ELECTRICAL BEHAVIOR

XI. THE PREPARATION AND PROPERTIES OF "MEGAPERMESELECTIVE"  
COLLODION MEMBRANES COMBINING EXTREME IONIC  
SELECTIVITY WITH HIGH PERMEABILITY

BY CHARLES W. CARR AND KARL SOLLNER

(From the Department of Physiology, University of Minnesota, Minneapolis)

(Received for publication, September 5, 1944)

I

The classical investigations of Michaelis and collaborators<sup>1</sup> on the dried collodion membrane as well as the work of other investigators have revealed the basic physicochemical properties of membranes of porous character which are selectively cation-permeable.

Dried collodion membranes prepared from suitable collodion<sup>2-4</sup> were found to allow the cations of uni-univalent strong inorganic electrolytes in solution to pass through, whereas these membranes are almost impermeable to anions. This ionic selectivity has been shown to be due to the negative electrical charge of the membranes arising from the presence of dissociable acidic groups on the pore walls.<sup>4-6</sup>

The further study of the basic physicochemical properties of these membranes is impeded by certain unfavorable features, and their use in model systems is still more restricted for the same reasons. The electromotive properties of many of these membranes except in very dilute solutions do not approach the theoretically possible maximum values as closely as would be desirable; moreover they deteriorate during prolonged experiments. Their absolute permeability for non-electrolytes is very small, their ohmic resistance is very

Michaelis, L., and Fujita, A., *Biochem. Z.*, Berlin, 1925, **158**, 28; 1925, **161**, 47; 1925, **164**, 23. Michaelis, L., and Dokan, S., *Biochem. Z.*, Berlin, 1925, **162**, 258. Michaelis, L., and Hayashi, K., *Biochem. Z.*, Berlin, 1926, **173**, 411. Michaelis, L., and Perlzweig, W. A., *J. Gen. Physiol.*, 1926-27, **10**, 575. Michaelis, L., McEllsworth, R., and Weech, A. A., *J. Gen. Physiol.*, 1926-27, **10**, 671. Michaelis, L., Weech, A. A., and Yamatori, A., *J. Gen. Physiol.*, 1926-27, **10**, 685. Michaelis, L., *Bull. Nat. Research Council*, No. 69, 1929, 119; *Kolloid-Z.*, 1933, **62**, 2, and other publications.

<sup>2</sup> Michaelis, L., and Perlzweig, W. A., *J. Gen. Physiol.*, 1927, **10**, 575.

<sup>3</sup> Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **24**, 467.

<sup>4</sup> Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **25**, 7.

<sup>5</sup> Sollner, K., and Carr, C. W., *J. Gen. Physiol.*, 1944, **28**, 1.

<sup>6</sup> Sollner, K., and Anderman, J., *J. Gen. Physiol.*, 1944, **27**, 433.

high, and correspondingly the rate of exchange of the permeable ions through such membranes is extremely low. The absolute permeability of these membranes is indeed so small that in many cases weeks must elapse before quantities have penetrated which can be analyzed by microchemical methods.<sup>2,7,8</sup>

Some of these difficulties have recently been overcome to a certain extent. The "activated" collodion membranes prepared recently<sup>4,5</sup> have satisfactory electromotive characteristics which are maintained for prolonged periods. Their absolute permeability, however, is still extremely low. We have therefore undertaken to prepare membranes more suitable for further extensive experimentation.

The desired properties of such membranes can be enumerated briefly, as follows: (a) the membranes should show extreme ionic selectivity, even in solutions of relatively high electrolyte concentration; (b) the absolute permeability of the membranes for the permeable, "non-restricted" ions should be high; *i.e.*, their ohmic resistance should be low; (c) the membranes should not deteriorate to a significant extent even on prolonged contact with electrolyte solutions; (d) the membranes should be mechanically satisfactory, *i.e.* they should be uniform and strong enough to stand considerable handling and also should have a well defined shape, free from kinks and wrinkles.

In addition, the preparation of these membranes should be easy and reproducible.

## II

As indicated above the main experimental problem was to increase the absolute permeability of "activated"<sup>4</sup> collodion membranes without impairing their ionic selectivity.

In the first attempt to do this, dried membranes were prepared from oxidized collodion<sup>4</sup> and then swelled in various concentrations of ethyl alcohol. The permeability of these membranes increased markedly, but even when the collodion was swelled only a few per cent the characteristic concentration potential which originally had been 53 to 54 mv. dropped below 50 mv. Swelling of dried "oxidized membranes"<sup>4</sup> in alcohol and in alcohol vapor as well as the oxidation of alcohol-swelled membranes were likewise unsatisfactory.

A satisfactory solution of this problem consists in drying porous membranes oxidized with NaOH over a mandrel.<sup>9</sup>

The preparation of the new type of membranes can be carried out with several variations. The nature and concentration of the collodion solution used,

<sup>7</sup> Weech, A. A., and Michaelis, L., *J. Gen. Physiol.*, 1928, **12**, 55; see also Green, A. A., Weech, A. A., and Michaelis, L., *J. Gen. Physiol.*, 1929, **12**, 473.

<sup>8</sup> Netter, H., *Arch. Ges. Physiol.*, 1928, **220**, 107.

<sup>9</sup> We should like to thank Mr. Harry P. Gregor for valuable help in the preliminary stages of this work.

the method of preparation of the porous membrane, the method and the time of oxidation are the main variables. By suitably changing the conditions one can arrive at various degrees of ionic selectivity and permeability.

On account of the high absolute permeability and very high ionic selectivity shown by these new type membranes we suggest for them the designation "megapermselective" or "permselective" collodion membranes.

In the following paragraphs a description is given of the procedure that has proved to be the most satisfactory in the preparation of such membranes.

The preparation of these membranes at present requires some skill and patience, particularly if membranes of very low resistance are required. There is little doubt that further experience will lead to the elimination of some of the remaining difficulties, most likely by a more rigorous control of the conditions under which the membranes are prepared.

In order to obtain uniform and reproducible megapermselective membranes the porous membranes were prepared by pouring collodion solution on the outside of test tubes rotating horizontally.<sup>10</sup>

A small variable speed motor was used to drive five pulleys in series. On the axle of each pulley a rubber stopper was attached; 25 × 100 mm. pyrex test tubes each having a small hole in the bottom were fitted in a well centered position on the stoppers. The holes of the tubes had been sealed smoothly by allowing a drop of a concentrated sugar solution to dry in the hole while the tubes stood in an oven. (The sugar dissolves when the tubes are later placed into water; this allows removal of the membranes without damage from the casting tubes.)

A 4 per cent solution of collodion cotton (Baker collodion cotton, U.S.P., Pyroxilin) in absolute ether-alcohol (50:50) was poured slowly from a narrow-mouth bottle over the tubes while they were rotated, the drippings being caught in a beaker. The optimum speed of rotation was 15 to 18 R.P.M. If the speed is too great, the drops of collodion that form on the under side of the tube do not drop off but form ridges on the membranes; if the rotation is too slow, uneven spreading of the solution results. The rotating tubes must be covered evenly with collodion, for if any spots are missed, they cannot be patched without causing bumps and ridges. After the tubes had been rotated for 3 minutes, another layer was added in the same manner, and 3 minutes later a third and final layer was put on. The tubes were rotated for 8 more minutes; they finally were taken off the stoppers and immersed in distilled water which was changed repeatedly. After 30 minutes the membranes were ready for oxidation.

The porous membranes thus prepared were oxidized by placing the membranes still on the test tubes in 1 M NaOH for measured lengths of time.<sup>4</sup> After superficial washing with water they were then immersed in repeatedly changed distilled water and allowed to stand for 2 to 3 hours. The membranes still on the tubes were then taken out of the water and dried in air for several hours while standing in an upright position. Under most conditions a drying time of 5 or 6 hours gives satisfactory re-

<sup>10</sup> See, e.g., Bigelow, S. L., and Gemberling, A., *J. Am. Chem. Soc.*, 1907, **29**, 1576. Bigelow, S. L., *J. Am. Chem. Soc.*, 1907, **29**, 1675.

sults; with low relative humidities of the air (< 30 per cent) the drying should be broken off as soon as some out of a batch of membranes begin to crack. While drying, the membranes are prevented by the glass tubes from shrinking in area as would occur without this rigid support. They thus undergo what amounts to a stretching in two dimensions, the whole volume loss on drying being compensated for by a decrease in thickness. To remove these dried membranes from the tubes, they were soaked in water for 1 to 2 hours. This soaking in water not only swells the membranes slightly<sup>11</sup> and makes them less brittle, but also provides a lubricant for their movement over the glass. For easy handling the glass-clear, perfectly smooth membranes were tied securely with linen thread to glass rings which just fitted inside the open end of the membrane bag. For further use they are kept in water to which a crystal of thymol has been added as preservative. The thickness of these membranes is about 30  $\mu$ .<sup>12</sup>

We may add that the use of NaOBr as oxidizing agent is not advisable for the preparation of megapermselective membranes; membranes thus prepared are not much different in their permeability properties from the previously described<sup>8</sup> types of "activated" membranes.

Two sets of measurements were made to characterize the membranes. Measurements of the "characteristic concentration potential" (0.1 M KCl/0.01 M KCl) were made as a criterion of the ionic selectivity of the membranes, as described by Michaelis and collaborators.<sup>1</sup> For a measure of the absolute permeability of the membranes, their ohmic resistances were determined in 0.1 N KCl solution, using the Kohlrausch bridge method with an alternating current of about 1000 cycles per second. The measurements were made after 30 minutes' contact of the membranes with the KCl solution, though the resistance of some of the membranes still drops on longer immersion in the electrolyte solution.

<sup>11</sup> Carr, C. W., and Sollner, K., *J. Gen. Physiol.*, 1943, **27**, 77.

<sup>12</sup> In preparing the membranes the concentration of collodion and drying times can be changed considerably without materially affecting the final results. The concentration of collodion should be such that it drains off the rotating tube without leaving any lumps. This will vary with the brand of collodion, as the viscosity of collodion solutions greatly varies with different preparations. The drying time between the casting of the three layers and the final drying time should be adjusted so that when the membrane is placed in water it remains clear and no white spots appear. The temperature has some effect, though not much, on the optimum drying times. It is, however, important that the temperature of the room in which the membranes are cast be below 22°C., for if it is higher, bubbles are formed in the membranes. The number of layers should be such that the thickness of the final dried membranes is 30 to 50  $\mu$ . If they are appreciably thinner, they become very weak after the oxidation, and many of the membranes break while drying on the tubes or while they are being removed from the tubes. Membranes thicker than 50  $\mu$  do not seem to offer any advantages; they have, however, a lower permeability.

To determine the resistance of the bag-shaped membranes it was necessary to use special electrodes constructed and placed so that the current would pass in about equal density through the whole area of the membrane. The outside electrode consisted of a hexagonal cage 45 mm. wide and 120 mm. high made from thin glass rod and wound with platinum wire. The inside electrode was a platinum wire spiral wound round a glass rod. Both electrodes were platinized by electrolysis in 2 per cent chloroplatinic acid. To make a measurement a membrane was filled with 0.1 N KCl and clamped in position inside the cage electrode, which was immersed in a beaker filled with the same solution. The other electrode was then lowered to a fixed position into the inside of the membrane. The total resistance between the two electrodes was then measured. Next, the resistance of the system without the membrane was determined. Neglecting the resistance of the layer of solution replaced by the membrane, the difference in these two measurements can be taken as the resistance of the membrane.<sup>13</sup> Since all of the membranes were of approximately the same effective area (50 sq. cm.), the results of the resistance measurements are given below in the tables in ohms per membrane, as obtained experimentally.

As was pointed out previously,<sup>4</sup> oxidation with NaOH not only activates but also weakens porous membranes and finally destroys them. Therefore the effect of the time of oxidation in NaOH was studied (Table I).

In Table II are shown the results obtained with a number of membranes prepared with a uniform time of oxidation (but without rigid temperature control during the latter). The first eight membranes listed in this table were taken from eight different series to show the variation in properties which under these conditions may occur from one experiment to the next. The last five membranes in the table were prepared at the same time; they show the uniformity of the characteristics of the individual membrane specimens in one series.

### III

Table I shows that the "characteristic concentration potential" in all cases, with short as well as with long oxidation times, approaches the theoretically possible maximum of 55.1 mv. within 1 mv.; the resistance of the membranes, however, decreases sharply with increasing time of oxidation. One is able to produce at will membranes having resistances of almost any desired magnitude. Excessively strong oxidation obviously not only increases the

<sup>13</sup> In a few instances the resistance was also measured by using a direct current method. A constant E.M.F. caused a small current (*ca.* 10  $\mu$  amps.) to flow through a membrane and the electrode system. Then the membrane was removed from the system, a decade resistance box was added in series, and its resistance adjusted until the same current flowed as before. The resistance that had to be added corresponds to the resistance of the membrane. On account of membrane and electrode polarization, this method was only accurate to about 20 per cent. The direct current measurements agreed within this limit with the alternating current determinations.

number of pathways through the membrane, as indicated by the low resistance of the membranes, but also brings about an increase in the size of some of the

TABLE I  
*The Effect of the Time of Oxidation on the Properties of "Megapermselective" Collodion Membranes*

Oxidation time in 1 N NaOH	Characteristic concentration potential 0.1 M KCl/0.01 M KCl	Resistance in 0.1 M KCl ( $\pm 0.5 \Omega$ )	Water content in volume per cent
<i>min.</i>	<i>mv.</i>	$\Omega/50 \text{ cm.}^2$	
4	54.8	80	—
6	54.6	22	—
8	54.8	17	16.4
10	54.5	8	16.3
12	54.5	3	15.9
14	54.6	2	—
16	54.0	1.5	18.0
18		Membrane destroyed	

TABLE II  
*Characteristic Concentration Potential and Resistance of "Megapermselective" Collodion Membranes*

Membrane No.	Characteristic concentration potential 0.1 M KCl/0.01 M KCl ( $\pm 0.1 \text{ mv.}$ )	Resistance in 0.1 M KCl ( $\pm 0.5 \Omega$ )
	<i>mv.</i>	$\Omega/50 \text{ cm.}^2$
a (3)	54.5	11.0
b (4)	54.5	10.5
c (1)	54.6	2.5
d (1)	54.2	3.0
e (5)	54.8	6.0
f (1)	55.1	$1.0 \pm 0.2$
g (1)	55.0	$0.5 \pm 0.2$
h (1)	54.9	$0.5 \pm 0.2$
i (1)	54.5	3.0
i (2)	54.8	3.0
i (3)	54.7	3.0
i (4)	55.1	3.0
i (5)	54.7	3.0

pores so that they permit the passage of some anions; the membranes become slightly leaky and the concentration potential is therefore slightly lowered.<sup>14</sup> It

<sup>14</sup> The "leak" of anions can be calculated from the potential measurements. If  $\bar{u}$  and  $\bar{v}$  are the relative contributions of the cations and anions to the transport of current

should also be mentioned that the strength of the membranes decreases with increase in oxidation time. Membranes with resistances above 50 ohms can stand considerable handling without breaking, while the membranes of less than 10 ohms are fairly weak and break rather easily if not treated with care. The water content of the membranes varies from 16 to 18 volume per cent. This compares with a water content of about 10.5 volume per cent of conventional dried membranes prepared from the same collodion, this value being the same both for the original commercial and oxidized ("activated") preparations.<sup>11</sup> The higher water content, the great porosity, of the mega-

TABLE III  
*The Influence of Shrinking on the Properties of "Megapermselective" Collodion Membranes*

Membrane No.	Megapermselective membranes		The same membranes in the shrunken state	
	Characteristic concentration potential 0.1 M KCl/0.01 M KCl	Resistance in 0.1 M KCl	Characteristic concentration potential 0.1 M KCl/0.01 M KCl	Resistance in 0.1 M KCl
	<i>mv.</i>	$\Omega/50 \text{ cm.}^2$	<i>mv.</i>	$\Omega/50 \text{ cm.}^2$
j (2)	55.0	90	55.2	700
k (4)	55.1	30	54.9	90
l (3)	54.6	13	54.0	200
m (4)	54.7	15	54.0	175
n (1)	54.2	3.0	54.5	77

permselective membranes must be assumed to be one of the most important causes of their great absolute permeability.

Table II shows the still prevailing variation between different series and the uniformity of the different membrane specimens in any given series. The membranes keep their properties for several weeks on contact with water without any significant deterioration. Their ionic selectivity slightly decreases on prolonged contact with electrolyte solutions.

in the membrane, we may use the Nernst equation for the diffusion potential in this form:

$$E = \frac{\bar{u} - \bar{v}}{\bar{u} + \bar{v}} RT \ln \frac{c_1}{c_2}$$

The numerical value of  $RT \ln \frac{c_1}{c_2}$  in the case of 0.1 N KCl/0.01 N KCl, correcting for known activity coefficients, is 55.1 mv. If, e.g.; a potential of  $E = 54$  mv. is found with a membrane under these conditions the "leak" of anions can be calculated from the above equation. Introducing the numerical values in this equation we obtain the ratio:

$$\frac{\bar{u}}{\bar{v}} = \frac{109.1}{1.1},$$

corresponding to an anion leak of about 1 per cent.

The conventional dried collodion membranes do not change on repeated drying and wetting; they can be stored for months in the dry state without any changes in properties. Since the megapermselective membranes are dried over a form and thus are in a forced, stretched state, it was necessary to investigate whether or not they shrink if dried without support in the air and thereby change their properties. Some shrinkage did occur when the membranes were dried in air after they were removed from the tubes. The shrinkage was just visible, the membranes became very slightly wavy. The effect of this shrinkage on the concentration potentials and resistances of several membranes is shown in Table III.

Table III shows that drying in air without support greatly increases the resistance of the megapermselective membranes. The electromotive properties, however, which before shrinking were already very near the maximum, do not change significantly. The use of "shrunken" membranes will be profitable only in those instances in which dry storage of the membranes is desirable.

#### IV

To demonstrate the great absolute permeability of the megapermselective membranes in the most direct manner we have performed a few preliminary experiments on cation exchange across them. In one such experiment a bag-shaped membrane ( $1\Omega$  resistance in  $0.1\text{ N KCl}$ ) with an active area of about  $50\text{ cm.}^2$  containing  $30\text{ ml.}$  of  $0.1\text{ N NH}_4\text{Cl}$  solution was placed in a tube containing  $30\text{ ml.}$  of  $0.1\text{ N KNO}_3$  solution. After 4 hours without stirring the  $\text{KNO}_3$  solution had become  $0.03\text{ N}$  in  $\text{NH}_4^+$  ion concentration. This represented an exchange of  $0.9\text{ m.eq.}$  of cations during this period, while less than  $0.02\text{ m.eq.}$  of chloride ion "leaked" out into the  $\text{KNO}_3$  solution, the anion leak in this experiment being about 2 per cent. The leak through membranes of somewhat lower absolute permeability (3 to  $5\Omega$  in  $0.1\text{ N KCl}$ ) under the same conditions is much smaller, ordinarily below 1 per cent. Stirring increases the absolute rate of ion exchange several fold. The relative leak in more dilute solutions is always less, the leak of bivalent anions in similar experiments being immeasurably low. Our results indicate, in agreement with expectation, that there is a fair parallelism between the conductance of these membranes and their absolute permeability as measured by exchange rates.

The rate of cation exchange through megapermselective membranes is about two to four orders of magnitude greater than the rate reported by previous investigators,<sup>2,8</sup> moreover, the leak of anion is smaller—the ionic selectivity of the new membranes being much greater.

We have also tested the water permeability of the megapermselective membranes. A solution of  $0.2\text{ M}$  sucrose was placed inside of a membrane of  $3\Omega$



resistance (in 0.1 N KCl). The membrane connected to a rubber stopper carrying a capillary manometer tubing was placed in a beaker of water and the meniscus in the manometer was observed. After 24 hours the rise of the meniscus amounted to 100 mm. For the capillary used, this corresponded to a volume transport of 100 mm<sup>3</sup>. water during this period. When this experiment was performed with a dried collodion membrane of the conventional type no water movement was observed even after several days. Similar results were obtained with electrolyte solutions,<sup>15</sup> no detectable amount of electrolyte appearing in the water.

## v

The megapermselective collodion membranes fulfill almost completely the requirements originally prescribed for the desired selectively (cat) ion-permeable membranes. The membranes are extremely impermeable to anions, as measured by the characteristic concentration potential and direct exchange studies. The resistance of the membranes can be made almost as small as desired, the only disadvantage being that membranes of very low resistance (<10 ohms in 0.1 M KCl solution) in most instances are fairly weak and will stand only careful handling. Membranes of higher resistance, though weaker than unoxidized membranes, are sufficiently strong for considerable handling. The membranes are of a well defined shape and perfectly smooth; they can be stored in water for a long time (several weeks) without significant change in their ionic selectivity. Furthermore the method of preparation is simple and reproducible.

To show the improvement that has been made in the electrical properties (ionic selectivity and absolute permeability) of the membranes of the "dried" type, a comparison of several kinds of frequently used "dried" collodion membranes is presented in Table IV. The potentials and resistances were determined as described before. The membranes were all of nearly the same size; their thickness was 5 to 10  $\mu$  except for the megapermselective membranes which were 30  $\mu$  thick.

Table IV brings out clearly the advantages of the megapermselective membranes over the more conventional types of dried collodion membranes. Membranes which combine extreme ionic selectivity with any desired resistance, from 0.5 $\Omega$  to several hundred ohms per 50 cm.<sup>2</sup>, may be prepared now at will as may be required for different purposes.

<sup>15</sup> That anomalous osmosis may in these cases have been a contributing factor is not entirely ruled out. Theoretical considerations strongly favor the assumption that anomalous osmosis has not contributed to a significant extent to the observed effect. Only extensive experimental work can decide this question in a definite manner.

## VI

The availability of the megapermselective collodion membranes opens up a wide field for further investigation.

The new type membranes have already been used with considerable success in the electrometric titration of the alkali ions and of  $Mg^{++}$ .<sup>16</sup>

TABLE IV  
A Comparison of Electromotive Behavior and Resistance of Several Kinds of Conventional "Dried" and of "Megapermselective" Collodion Membranes

Description of membrane	Characteristic concentration potential 0.1 M KCl/0.01 M KCl	Resistance in 0.1 M KCl	Remarks
	<i>mv.</i>	$\Omega/50\text{ cm.}^2$	
Mallinckrodt "Parlodion," commercial preparation	25-40	>10000	Resistance <i>cannot</i> be adjusted at will
Baker Collodion U.S.P., commercial preparation	40-45	>10000	
Schering-Kahlbaum "Celloidin"*	40-53	~1500	
Crude collodion†	45-50	~2000	
Oxidized Collodion, Baker collodion U.S.P., oxidized with NaOBr	50-55	>10000	
Oxidized collodion, Baker collodion U.S.P., oxidized with NaOH	50-55	>10000	
"Oxidized" membranes, dried membranes oxidized with NaOBr	51-53	~1000	Resistance <i>can</i> be adjusted at will
"Megapermselective" membranes	54-55.1	< 1 to > 100	

\* The concentration potential of membranes prepared from this collodion drops appreciably on prolonged contact with water or electrolyte solutions.

† Obtained through the courtesy of the Monsanto Chemical Company, St. Louis, Mo.

In the study of ionic permeabilities through negative membranes it will be possible to extend the investigation to membranes of graded selectivity and also to the bivalent ions, the behavior of which is little known at present.

The megapermselective membranes also will allow the solution under well defined conditions of one of the most urgent problems in the whole field of membrane permeability; namely, the systematic comparison of the permeabilities of ions with those of non-electrolytes. At present very little is known about this problem, since the absolute permeability of membranes of distinct ionic selectivity was heretofore much too small to allow extensive and conclusive experimentation.

<sup>16</sup> Sollner, K., *J. Am. Chem. Soc.*, 1943, **65**, 2260.

Whether or not the megapermselective membranes may be suitable for the measurement of the osmotic pressure of electrolytes and low molecular weight non-electrolytes, has not been tested. Preliminary experimental evidence indicates that they may be used for the separation by ultrafiltration of low molecular weight solutes from the solvent.

A further fruitful field of investigation can be seen in the study of membrane equilibria which involve only strong inorganic electrolytes. Membranes of this type frequently have been discussed in the physiological literature but never have been realized experimentally in a satisfactory manner.

These and related problems are at present under investigation and we hope to be able to report the results in the near future. To discuss the possible usefulness of the megapermselective membranes for practical purposes in the laboratory or their application to industrial processes is outside the scope of the present paper.

#### SUMMARY

1. The electronegative membranes described in the literature which show a high degree of ionic selectivity (permitting cations to pass and restricting the anions) have serious shortcomings: their absolute permeability is extremely low, much too small for convenient experimentation; their ionic selectivity in most cases is not as perfect as would be desirable, and is moreover adversely affected by prolonged contact with electrolyte solutions.

2. A method has been worked out to prepare membranes substantially free from these defects. Porous collodion membranes were cast on the outside of rotating tubes and then oxidized with 1 M NaOH. By allowing the oxidized porous membranes to dry in air on the tubes membranes of desirable properties are obtained. These membranes are smooth, have a well defined shape, and allow considerable handling without breaking.

3. This new type membrane when tested for ionic selectivity by the measurement of the "characteristic concentration potential," consistently gives potentials of 54 to 55 mv., the maximum thermodynamically possible value (at 25°C.) being 55.1 mv. This high degree of ionic selectivity is not lost on prolonged contact with water, and is only very slowly affected by electrolyte solutions.

4. The absolute permeability of the new type membranes can be varied over a very wide range by changing the time of oxidation. Under optimum conditions membranes can be obtained with a resistance in 0.1 N KCl solution of only 0.5 ohms per 50 cm.<sup>2</sup> membrane area. The absolute rate of cation exchange through these membranes between solutions of different uni-univalent electrolytes is very high, in one case, *e.g.* 0.9 m.eq. cations per 4 hours, the anion leak being 0.02 m.eq. Thus, the absolute permeability of the new

type membranes is two to four orders of magnitude greater than the permeability of the dried collodion membranes and the oxidized ("activated") dried collodion membranes used heretofore. Because of the characteristic properties of the new type membranes the term "*megapermselective*" (or "*permselective*") collodion membranes is proposed for them.