

THE STRUCTURE OF THE COLLODION MEMBRANE AND  
ITS ELECTRICAL BEHAVIOR

VII. WATER UPTAKE AND SWELLING OF COLLODION MEMBRANES IN WATER  
AND SOLUTIONS OF STRONG INORGANIC ELECTROLYTES

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I

In preceding papers in this series we have dealt on the one hand with the chemical factors which determine the behavior of collodion membranes in solutions of strong electrolytes,<sup>1-3</sup> and on the other hand<sup>4, 5</sup> we have shown that the collodion membrane does not behave as a homogeneous interphase but that it has a micellar structure.

To get a clearer picture of the structure of the collodion membrane it is necessary to know if it is permanent and rigid, or if it undergoes changes when it is immersed in different solutions. From our previous knowledge no general answer can be given to this question. Concentrated solutions of many organic compounds are known to swell collodion membranes appreciably. Water and aqueous solutions of inorganic compounds, however, are generally believed to exert no specific influence on collodion membranes, but this has never been proven definitely. The present investigation is concerned with the changes in collodion membranes produced by water and aqueous solutions of strong inorganic electrolytes; the more complex phenomena occurring in aqueous solutions of organic compounds will be taken up in a subsequent communication.

There are two general types of collodion membranes:

(a) "Porous" collodion membranes are obtained by casting collodion films from ether-alcoholic or similar solutions and immersing them in water before the solvent has evaporated completely. The porosity of these membranes depends on the content of organic solvent at the time of their immersion in water; to retain this porosity the membranes must be stored continuously in water.

(b) "Dried" collodion membranes are obtained if the solvent is allowed to evaporate completely from a film of collodion, or if "porous" membranes are

<sup>1</sup> Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **24**, 467.

<sup>2</sup> Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **25**, 7.

<sup>3</sup> Sollner, K., Carr, C. W., and Abrams, I., *J. Gen. Physiol.*, 1942, **25**, 411.

<sup>4</sup> Sollner, K., and Carr, C. W., *J. Gen. Physiol.*, 1942, **26**, 17.

<sup>5</sup> Sollner, K., and Carr, C. W., *J. Gen. Physiol.*, 1943, **26**, 309.

allowed to dry completely in air. When such membranes are placed in water, they take up a small percentage of water but do not swell to form a porous structure of the type of the "porous" membranes. Membranes in this state will be called "water-wetted dried" membranes. They have been shown to be of porous character;<sup>4</sup> <sup>5</sup> *i.e.*, they contain pores, but the porosity is at a minimum.

In the past there has been some question concerning the way in which the water enters a dried membrane. The problem arises as to whether the water dissolves in the collodion or whether it enters pores as in porous clay membranes. In either case the assumption has always been made that the membrane does not swell, but this has not been proven.

Northrop<sup>6</sup> has shown that the amount of water retained by dried collodion is directly proportional to the water vapor pressure at the time of drying. Thus in a completely dry atmosphere all of the water can be removed. From these experiments Northrop postulates that the water goes into solution in the collodion. If this were the case, one would expect the membrane to swell to a certain extent; however, Northrop has not followed up this point.

Michaelis in his studies on the dried collodion membrane comes to the conclusion that it behaves as a rigid, porous structure which shows no trace of swelling after wetting, and that water enters the membrane by filling preformed pores.<sup>7, 8</sup> These preformed pores would be the micellar interstices which are assumed to exist between the collodion micelles forming the membrane. It was not shown, however, that the membrane had exactly the same structure when completely dry as when wetted with water.

Another investigator of collodion membranes, Manegold,<sup>9</sup> states specifically that dried collodion is non-swelling in water, but he gives no experimental proof of this statement.

The only information in the literature on measurements of volume changes in membranes pertains to membranes other than collodion. Zsigmondy membrane filters,<sup>10</sup> which are acetyl cellulose membranes,<sup>11</sup> have been found by Brukner<sup>12</sup> to shrink slightly in high concentrations of electrolytes. In 1 M NaCl he found a shrinkage of about 0.4 per cent in length and width of these membranes, and in 4 M NaCl the shrinkage went up to 1 per cent. McBain and

<sup>6</sup> Northrop, J. H., *J. Gen. Physiol.*, 1928, **12**, 435.

<sup>7</sup> Weech, A. A., and Michaelis, L., *J. Gen. Physiol.*, 1928, **12**, 221.

<sup>8</sup> Michaelis, L., *Bull. Nat. Research Council*, No. 69, 1929.

<sup>9</sup> Manegold, E., *Kolloid-Z.*, 1932, **61**, 140.

<sup>10</sup> Zsigmondy, R., and Bachmann, W., *Z. anorgan. u. allg. Chem.*, 1918, **103**, 1.

<sup>11</sup> Bachmann, W., *Kolloidchemische Untersuchungsmethode*, in *Berl-Lunge, Chemische-technische Untersuchungsmethoden*, Berlin, Julius Springer, 8th edition, 1934, **1**, 1087.

<sup>12</sup> Brukner, *Z. Ver. deutsch. Zuckerind.*, 1926, **76**, 3. (Quoted by Manegold, E., and Hoffmann, R., *Kolloid-Z.*, 1930, **50**, 207.)

Stuewer<sup>13</sup> measured the swelling of dry cellophane sheets when placed in water. This was done by determining the changes in each of the three dimensions, and it was found that the cellophane increased more than 100 per cent in thickness, about 10 per cent in width, but did not change in length. In addition, these authors have shown that the swelling is even more pronounced in strong solutions of  $\text{ZnCl}_2$ . Membranes previously swelled in water were found to double their thickness again when placed in 65 per cent  $\text{ZnCl}_2$  solution.

The current opinion<sup>14</sup> concerning the swelling of cellulose in water is that the unsubstituted hydroxyl groups in cellulose (cellophane) are responsible for its swelling. One should remember here that collodion is not a completely nitrated cellulose, for cellulose hexanitrate contains 14.14 per cent nitrogen as compared with 10.0–11.5 per cent nitrogen for collodion. Thus collodion has some unsubstituted hydroxyl groups, and these might easily determine its behavior in water.

In the experimental parts of this paper the following questions will be answered: (1) How much water does a completely dried collodion membrane take up when placed in water? (2) Does this water uptake cause any detectable change in the volume of the membrane? (3) Do dried collodion membranes swell or shrink when transferred from water to solutions of strong electrolytes? (4) Do "porous" collodion membranes swell or shrink when transferred from water to solutions of strong electrolytes?

## II

For the determination of the water uptake and possible volume changes of dried membranes, flat membranes similar to those used by most investigators proved to be the most suitable. Such membranes were completely dehydrated and then their weights and volumes were measured. After being immersed in water for some time, the membranes were again measured for their weight and volume. The increase in weight is equal to the water uptake, and any change in volume indicates swelling or shrinking.

The dried membranes were prepared as follows: 150 to 200 ml. of a 5 per cent collodion solution in ether-alcohol was poured out onto six perfectly flat glass plates ( $3\frac{1}{4}'' \times 4''$  photographic plates) which floated on and nearly covered a mercury surface. In casting the membranes the formation of gas bubbles was carefully avoided. After the collodion had dried in air for 24 hours, it was covered with water and allowed to stand for 4 to 5 hours. Then the membrane can be loosened easily from the glass plates. A large sheet of dried collodion was thus obtained, on which six rectangles were outlined by the glass plates. These were then cut into  $3 \times 4$  cm. membranes which were kept for further use in a desiccator. The thickness of these membranes in different castings varied between 0.10 and 0.15 mm.

<sup>13</sup> McBain, J. W., and Stuewer, R. F., *J. Physic. Chem.*, 1936, **40**, 1157.

<sup>14</sup> Gortner, R. A., *Outlines of biochemistry*, New York, John Wiley and Sons, 2nd edition, 1938, 682.

The volume change of dried collodion when immersed in water was determined with a pycnometer filled with mercury. Mercury was used as the reference liquid for two reasons. In the first place it was necessary to use mercury because it does not wet collodion, *i.e.* it does not enter any preformed pores that might exist, and it does not make the collodion swell. Water or any other liquid that wet collodion would obviously not give the true volume of a dried membrane, for in such a liquid it would no longer be in the dry state. In addition the use of mercury was advantageous since because of the great difference in density of collodion and mercury, small changes in volume could easily be detected.

The pycnometer was a 10 ml. glass bottle with a ground glass stopper. There was a small hole in the center of the stopper, and this extended into a capillary tubing of 1 mm. bore and 200 mm. in length. The pycnometer was first filled with mercury, an extra drop being left at the top of the capillary, and then clamped in a constant temperature bath ( $\pm 0.05^\circ\text{C}$ ). After temperature equilibrium was reached (less than 5 minutes) the drop at the top of the capillary was cut off with a knife-edge. This procedure was necessary because a change of  $1^\circ$  in temperature changed the total weight by 10 mg. The pycnometer then was taken out of the bath, wiped dry with filter paper, and weighed to within 1 mg. By repeating this procedure it was possible to make a number of measurements that agreed within 3 mg., the total weight being approximately 190 gm.

To make the weight and volume determinations, a dried membrane was first weighed to within 0.3 mg. in a closed weighing bottle. Next, it was folded three times to form a rectangular parallelepiped ( $1 \times 1 \times 3$  cm.) open at two ends. In this shape the membrane just fitted into the pycnometer, and air bubbles were least likely to be entrapped by the mercury. After the membrane was put in the pycnometer, any bubbles that formed were removed by inserting a thin glass rod into the mercury and allowing the bubbles to creep out along the rod. When no bubbles appeared to be present, the pycnometer was placed in the water bath and allowed to equilibrate as before. It was then taken out, wiped dry, and weighed again to 1 mg. Due to uncertainties in removing every small bubble, the variation in a series of determinations with the same membrane was as much as 10 mg. From the weight of the pycnometer without and with the membrane and the weight of the latter, the volume of the membrane was calculated. The total error in any one measurement did not exceed  $\pm 0.5$  per cent of the volume being measured.

After the weight and volume of the dried membrane were determined, the membrane was placed in water for a definite time. After this it was removed and quickly blotted dry of surface water with filter paper according to Hitchcock<sup>15</sup> and Weech and Michaelis.<sup>7</sup> It was immediately placed in the pycnometer and its volume again determined. It was then taken out, put in a closed weighing bottle, and weighed to within 0.3 mg. In this way the changes in weight and volume with time were followed until no further change occurred.

### III

It immediately became apparent that the behavior of the collodion membrane in water is less simple than was generally supposed. The membranes in equi-

<sup>15</sup> Hitchcock, D. I., *J. Gen. Physiol.*, 1925, **9**, 755.

librium with water showed volume increases of 5 to 11 per cent, depending on the brand of collodion used.

Since at first sight it is not quite easy to see the true relationship of weight increases and volume increases, a sample calculation is given below.

(a) Weight increase		
Weight of membrane wet .....		0.2185 gm.
“ “ “ dry .....		0.2040 “
“ increase of membrane on wetting .....		0.0145 “ = 14.5 mg.

(b) Volume increase		
	<i>Dry</i>	<i>Wet</i>
Weight of membrane .....	0.2040 gm.	0.2185 gm.
“ “ pycnometer + Hg .....	189.852 “	189.852 “
“ “ “ + Hg + membrane ..	188.325 “	188.216 “
Difference in weight .....	1.527 “	1.636 “
	1.527 “	1.636 “
	0.204 “	0.219 “
Weight of Hg displaced .....	1.731 “	1.855 “
Volume “ “ “ .....	$\frac{1.731}{13.53} = 0.1280$ cc.	$\frac{1.855}{13.53} = 0.1371$ cc.
“ “ membrane .....	0.1280 cc.	0.1371 cc.
Volume of membrane wet .....		0.1371 cc.
“ “ “ dry .....		0.1280 “
“ increase of membrane on wetting .....		0.0091 “ = 9.1 c. mm.

In order to visualize the quantitative meaning of these figures they must be reduced to a standard, either 1 gm. or 1 cc. of dry membrane. It is better to choose the cubic centimeter of dry material as a unit, for in this way the specific gravity factor is eliminated. Therefore the data have been recalculated for a quantity of collodion having a volume of 1 cc. in the dry state, and the weight and volume increases are expressed as milligrams and cubic millimeters respectively per 1 cc. of dry collodion. A sample calculation with the figures given before, follows:

$$\text{Weight increase of 1 cc. dry membrane on wetting (in mg.)} = \frac{0.2185 - 0.2040}{0.1280} 1000 = 113 \text{ mg.}$$

$$\text{Volume increase of 1 cc. dry membrane on wetting (in c. mm.)} = \frac{0.1371 - 0.1280}{0.1280} 1000 = 71 \text{ c. mm.}$$

In Table I are given the weight and volume measurements obtained with three membranes prepared from different brands of collodion after they had been immersed in water for 12 hours. In Fig. 1 are plotted the weight and volume increases against the time of immersion; from these curves it is seen that the values of Table I represent the equilibrium state.

TABLE I  
*Weight and Volume Increase of Dried Collodion Membranes on Wetting with Water*

Brand of collodion	Dry weight	Wet weight	Dry volume	Wet volume	Weight increase per cc. dry membrane	Volume increase per cc. dry membrane
	mg.	mg.	c. mm.	c. mm.	mg.	c. mm.
Mallinckrodt "Parlodion"	232.5	245.0	149.2	156.7	84	50
Baker collodion U.S.P.	204.0	218.5	128.0	137.1	113	71
Schering-Kahlbaum "Celloidin"	212.2	233.0	133.3	148.0	156	110

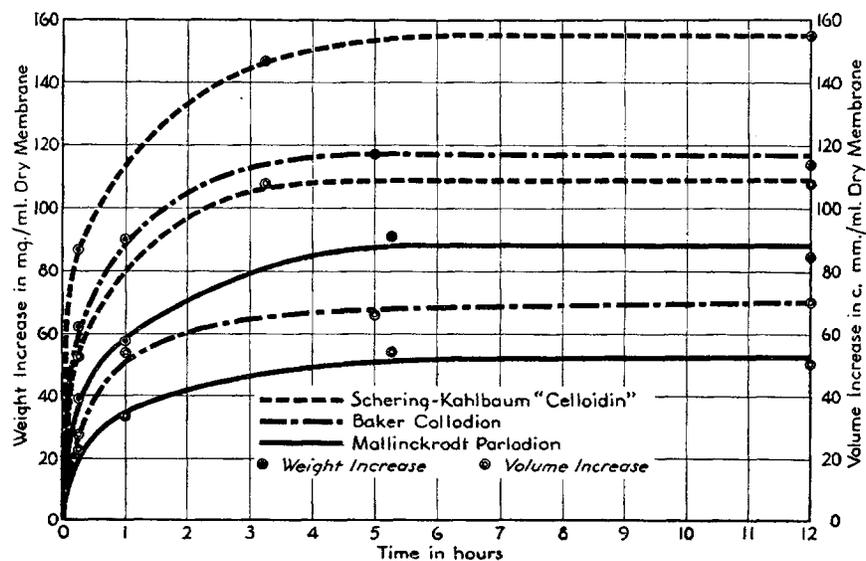


FIG. 1

Several additional experiments with Baker U.S.P. collodion indicate that membranes prepared under different conditions of drying may vary by as much as 20 c. mm. (mg.) per gm. dry collodion in their weight and volume increases. The difference of weight and volume increase, however, remains fairly constant. The differences between "Parlodion" and Baker U.S.P. collodion are still prob-

ably significant because the experiments were done at the same time under identical conditions.

It should also be mentioned here that the swelling curve for oxidized collodion was found to be identical with that of the original unoxidized preparation. Evidently the carboxyl groups that were introduced had no measurable effect on the swelling. This is in agreement with our former results<sup>9</sup> in which it was shown that the number of carboxyl groups introduced by oxidation was relatively small.

The weight and volume changes of dried collodion which occur in wetting seem to be completely reversible. Wetted membranes were allowed to dry and were then placed in water again for a few hours. This was repeated several times. On the fifth immersion the water uptake and the swelling were exactly the same as on the first within the experimental error.

The swelling of cellulose is known to decrease with increasing temperatures; for the case of cellophane membranes this point was recently stressed by McBain and Stuewer.<sup>13</sup> Since some knowledge of the temperature coefficient might possibly cast light on the mechanism of the swelling of collodion, this effect has been studied. The volumes and weights of six membranes were measured in the dry state. Then two of the membranes were put into water at 3°C., two in water at 25°C., and two in water at 50°C. After 12 hours the membranes were removed from the water and their weights and volumes again determined. From these experiments it was found that there is a very small negative temperature coefficient, the swelling at 50° being about 13 per cent less than it was at 3°.

#### IV

Before discussing the meaning and significance of the above results, it is best to state briefly the effects observed when a "water-wetted dried" collodion membrane is transferred from water to an electrolyte solution.

The first electrolyte solution tested was 1 M KCl, and the experimental procedure was the same as in the previous experiments. A water-wetted membrane was blotted dry, and then its volume was determined with the pycnometer. The membrane was placed in 1 M KCl for 24 hours and then removed and its volume again measured. Within the limit of experimental error there was no volume change.

Since the measurements with the pycnometer were laborious and time consuming, another method was worked out for the testing of the several electrolyte solutions to be studied. This involved the weighing of the membranes in the water-wetted state and after immersion in the solutions. Any increase or decrease in weight could be taken to indicate swelling or shrinking, provided that proper corrections are made for the specific gravity of the solutions which are taken up by the membranes.

There is considerable uncertainty as to the concentration of the solution which goes into the membrane. There is no doubt that not all of the water in a membrane is available even for KCl,<sup>16</sup> and polyvalent ions certainly do not penetrate dried collodion membranes with ease. In view of this fact that the problem of the mean electrolyte concentration of the water in a dried collodion membrane is still unsettled, the experimental data given below are evaluated on the basis of these two assumptions:

(a) The liquid taken up by the membrane is free from electrolyte; it is salt-free water, and (b) the liquid taken up by the membrane has the same composition and therefore the same specific gravity as the particular electrolyte solution in which the membranes were immersed.

TABLE II  
*Weight Changes of Dried Collodion Membranes on Transference from Water to Solutions of Strong Electrolytes*

1	2	3	4	5	6
Solution	Weight of membrane dry	Weight of membrane wetted with water	Weight of membrane wetted with solution	Change in weight (column 4 to column 3)	Change in weight (corrected for specific gravity)
	gm.	gm.	gm.	gm.	gm.
1 M KCl	0.528	0.563	0.563	0.000	-0.001
0.8 M K <sub>2</sub> SO <sub>4</sub>	0.382	0.407	0.407	0.000	-0.001
1 M K <sub>3</sub> Cit	0.397	0.421	0.421	0.000	-0.002
0.5 M K <sub>4</sub> Fe(CN) <sub>6</sub>	0.355	0.380	0.378	-0.002	-0.003
1 M CaCl <sub>2</sub>	0.525	0.554	0.553	-0.001	-0.002
1 M AlCl <sub>3</sub>	0.422	0.446	0.447	+0.001	0.000
1 M KNO <sub>3</sub>	0.457	0.485	0.484	-0.001	-0.002
1 M KCNS	0.479	0.507	0.509	+0.002	+0.001
1 M ZnCl <sub>2</sub>	0.443	0.471	0.469	-0.002	-0.003
1 M Ca(CNS) <sub>2</sub>	0.427	0.452	0.451	-0.001	-0.002
1 M HCl	0.428	0.456	0.454	-0.002	-0.002
1 M HNO <sub>3</sub>	0.465	0.496	0.496	0.000	0.000
H <sub>2</sub> O	0.348	0.372	0.371	-0.001	-0.001

Some situation intermediate between these two extremes is most probably the real one.

The procedure adopted for the weight method follows. The dry weights of the membranes were determined after they had been kept in a desiccator for at least 24 hours. Then they were placed in water for 24 hours; in this time equilibrium was reached. Next, they were blotted dry of surface water and transferred into a weighing

<sup>16</sup> Unpublished experiments of the authors show that the mean concentration of KCl inside a dried membrane is always much less than in the outside solution.

bottle and their weights determined. After this the membranes were put in the electrolyte solutions being tested and allowed to remain in them for 1 week. Then they were blotted dry, and their weights were determined as before.

The specific gravity of each electrolyte solution was determined in order to apply the proper correction as discussed above.

Table II gives a summary of the results obtained with a number of representative strong electrolytes. Column 1 gives the electrolytes and their approximate concentrations; column 2 the weight of the dry membranes, column 3 the weight in the water-wet state, and column 4 the weight of the membranes after reaching equilibrium with the electrolyte solutions. Column 5 is the change in weight on transference of the membranes to the electrolyte solutions under the assumption that the liquid taken up from the electrolytes is salt-free water. Column 6 is the change in weight if the water imbibed is assumed to have the specific gravity of the outside solution.

Since the changes that occurred are within the limits of the experimental error, we may conclude that "water-wetted dried" collodion membranes do not shrink or swell significantly when transferred from water to solutions of strong inorganic electrolytes.

#### V

There are several obvious conclusions which can be drawn from the data that have been obtained.

The dried collodion membrane, contrary to the general assumption, swells on wetting with water. The swelling varies with the different brands of collodion, being from 50 to 110 c. mm. per cc. of dry membrane at room temperature. Oxidized collodion swells exactly to the same extent as the unoxidized preparation.

Dehydrated dried collodion membranes on wetting with water undergo fundamental changes, and therefore the air-dry and "water-wetted dried" membranes are structurally different entities. It is not permissible, as it has been done occasionally in the past, to use experimental results (gas permeability) obtained with dry membranes to explain the structure of water-wetted membranes.

The "water-wetted dried" collodion membrane does not undergo significant structural changes when transferred from water to solutions of strong inorganic electrolytes. It can be considered a rigid structure which does not swell in aqueous solutions of the typical strong inorganic electrolytes.

Although "dried" collodion membranes do swell in water, our experiments furnish additional evidence that they contain preformed pores which can take up water. In all cases studied the water uptake was in excess of the volume increase amounting to 34 to 46 mg. (or c. mm.) per cc. dry collodion. It is most likely that at least a large fraction of this difference indicates preformed

pore space in the membrane. To analyze these data further, however, one must touch at least briefly the complicated problem of the swelling of micellar substances and also the problem of "bound" water.

According to Katz<sup>17</sup> intermicellar swelling occurs if the crystalline micelles of a colloidal material are pushed apart from each other by the swelling agent without a change of crystalline structure. Intramicellar swelling takes place if the swelling agent goes into the micelles loosening the contact of the macromolecules in the micelles and causing a change of the crystalline structure of the latter. "Bound" water in a colloidal system is defined as the water which is combined so strongly with the material that it is unavailable as solvent for other substances. As there is no sharp physical difference between "bound" and free water, different methods to determine "bound" water yield different results.<sup>18</sup> The formation of definite hydrates consists of a very strong binding of water, and this is supplemented by additional hydration with a gradual transition towards free water. Collodion is hygroscopic, taking up considerable amounts of water from the atmosphere, even if the latter is not saturated with water vapor. This water is bound very firmly to the collodion and is not available as solvent for other substances.

If water is taken up as "bound" water, it is compressed in a manner similar to the well known volume decrease observed on mixing water and alcohol. Therefore, the difference between water uptake (in milligrams) and the volume increase (in cubic millimeters) mentioned above is not necessarily a measure of the preformed pore space; it is entirely possible that compression may account for a substantial part of this difference. This side of the problem was not investigated further, however, because it becomes more of a problem in nitrocellulose chemistry than in membrane behavior.

On the basis of the foregoing discussion and the experimental results, the following picture is tentatively suggested for the water-wetted dried collodion membrane. Intermicellar and intramicellar swelling has taken place. The individual micelles have increased in volume over the dry state; there is less cohesion between the micelles; and the micelles which were pressed together by capillary forces on drying have assumed less forced positions. These processes in all probability tend to produce intermicellar pore space and thus to increase the porosity of the membrane over whatever porosity may have existed in the air-dry state.

<sup>17</sup> Katz, T. R., *Micellartheorie und Quellung der Zellulose*, in Hess, K., *Die Chemie der Zellulose und ihrer Begleiter*, Leipzig, Akademische Verlagsgesellschaft, 1928.

<sup>18</sup> For a review of the problem of "bound" water the reader may consult: Gortner, R. A., *Outlines of biochemistry*, New York, John Wiley and Sons, 2nd edition, 1938, 257; other investigators (see, e.g., Blanchard, K. C., *Cold Spring Harbor symposia on quantitative biology*, Cold Spring Harbor, Long Island Biological Association, 1940, 8, 1.) are still more sceptical about the idea of bound water than is indicated in the text.

From the picture presented in the last paragraph one very definite conclusion can be reached concerning the structure of the dried collodion membrane in relation to electrolyte permeability. The problem of the water uptake of these membranes must be restated. It is not important how much water is contained in the membrane, and how much of this water is "bound" and how much of it is "free" water. In addition it is not of fundamental interest what changes the collodion membrane undergoes on wetting. The important question now becomes, how much water in the water-wetted membranes is available for the typical membrane functions. Thus the abstract question of the water content of dried collodion membranes has changed to the more concrete and better defined problem of the availability of water in the membrane in useful pathways for different solutes.

An investigation of this problem has not been carried out as yet, for the conventional dried collodion membrane is not the best membrane for such studies. More useful information may be obtained by studying specially prepared membranes of very high ionic selectivity and of a permeability several orders of magnitude larger than that of the ordinary dried membranes. Such membranes have been prepared and will be described in a later paper.

## VI

Collodion membranes of high porosity, typical "porous" membranes, have also been investigated. Since the "porous" membranes do not exist in the dry state, there is only one possible change that can be measured; *i.e.*, the volume change on transfer from water to electrolyte solution. As in the case of the "water-wetted dried" membranes, it was sufficient to weigh the "porous" membranes water-wetted and after immersion in the various solutions. Changes in weight again indicate swelling or shrinkage, provided proper corrections are made for the specific gravity of the solution in the membrane.

The "porous" membranes were prepared in the same way as the "dried" ones with the exception of the drying time. In this case as soon as a tough skin had formed on the collodion (about  $1\frac{1}{2}$  hours<sup>19</sup>), the surface was covered with water. In this way membranes were obtained that contained 50 to 60 per cent by volume of water and were approximately 0.2 mm. in thickness. Pieces of membrane  $4 \times 10$  cm. were cut out, blotted dry, and weighed. They were then placed in the various solutions for 24 hours and, after being blotted, were weighed again. After this, the membranes were washed free of electrolyte, dried completely, and weighed once more. From this determination of the dry weight the water content was calculated, which was necessary in order to apply the correction for the specific gravity of the solution entering the mem-

<sup>19</sup>This time was considerably longer than for the "porous" membranes described in our previous papers because the films referred to above were much thicker than those used previously.

brane. The accuracy of the method was only  $\pm 0.6$  per cent, but this was sufficient for our purpose. Changes in porosity within these limits could hardly influence the behavior of "porous" membranes to a significant extent.

In Table III results are given for the same series of electrolytes that were used in the study on the dried membranes. In this case only the values that have been corrected for the specific gravity are reported since in the porous membranes, the electrolyte concentration in the membrane approaches that of the outside solution.

TABLE III  
*Weight Changes of Porous Collodion Membranes on Transference from Water to Solutions of Strong Electrolytes*

1	2	3	4
Solution	Weight of membrane wetted with water	Weight of membrane wetted with solution (corrected for specific gravity)	Change in weight (column 3 to column 2)
	gm.	gm.	gm.
1 M KCl	0.906	0.902	-0.004
0.8 M K <sub>2</sub> SO <sub>4</sub>	0.687	0.685	-0.002
1 M K <sub>3</sub> Cit	0.851	0.845	-0.006
0.5 M K <sub>4</sub> Fe(CN) <sub>6</sub>	0.921	0.908	-0.013
1 M CaCl <sub>2</sub>	0.691	0.689	-0.002
1 M AlCl <sub>3</sub>	0.659	0.654	-0.005
1 M KNO <sub>3</sub>	0.678	0.677	-0.001
1 M KCNS	0.646	0.649	+0.003
1 M ZnCl <sub>2</sub>	0.583	0.582	-0.001
1 M Ca(CNS) <sub>2</sub>	0.778	0.776	-0.002
1 M HCl	0.734	0.730	-0.004
1 M HNO <sub>3</sub>	0.865	0.865	0.000
H <sub>2</sub> O	0.761	0.760	-0.001

As with the dried membranes there is no detectable change in volume on the transference of "porous" membranes from water to strong electrolytes. Within these limits, at least, the structure of these "porous" membranes can be considered to be rigid and permanent.

As in the case of the dried membranes the problem next to be studied is not the total water content of these membranes, but how much of this water is available for electrolytes, and how large a fraction of this exists in useful pathways. It will not be as complex as in the former instance, because undoubtedly most of the water in the "porous" membranes exists in large pores accessible to almost all electrolytes. This problem can only be solved, however, by further studies on the permeability, electrolyte content, and resistance of collodion membranes of varying porosity.

## SUMMARY

1. The assumption has generally been made that collodion membranes are rigid and non-swelling in water and aqueous solutions of strong electrolytes, and considerable uncertainty exists as to the manner in which water is taken up by "dried" collodion membranes. In approaching these problems experimentally, the weight and volume changes of collodion membranes when placed in water and when transferred from water to solutions of strong electrolytes were determined.

2. Dried collodion membranes swell reversibly to an appreciable extent when placed in water, the swelling varying from 5 to 11 per cent depending on the brand of collodion. The water uptake and swelling of oxidized collodion is the same as the original unoxidized preparation.

3. The water uptake as determined by the weight increase is larger than could be accounted for by the volume increase, swelling accounting for only 60 to 70 per cent of the water taken up by the membranes.

4. When the "water-wetted dried" collodion membranes were transferred from water to solutions of various strong electrolytes, there was no detectable change in volume. Similarly, when the "porous" membranes were transferred from water to solutions of strong electrolytes, there was no significant volume change.

5. When dried collodion membranes swell in water, some of the water becomes "bound" water, and both intramicellar and intermicellar swelling seem to occur. Therefore, neither the weight increase nor the volume increase nor their difference can be taken as a measure of the true pore space of the membrane. It is concluded that the important problem is not the absolute water content, but how much water in the water-wet membranes is available in useful pathways for the different solutes.