THE STRUCTURE OF THE COLLODION MEMBRANE AND ITS ELECTRICAL BEHAVIOR

II, THE ACTIVATED COLLODION MEMBRANE

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In preceding communications1,2 we were led to the conclusion that the electrochemical activity of collodion membranes, as manifested by concentration potentials, etc., is due principally to acidic impurities. Accordingly, different brands of collodion differ widely as to their activity, the purer brands being less active. The impure (but active) foreign brands of collodion, heretofore generally used by workers in the field of electrochemical membrane investigation, are no longer obtainable. In order to continue our investigation, it became necessary to find methods to produce active collodion membranes at will.

The idea of inducing changes in the electrochemical characteristics of membranes is not entirely new. Many investigators have activated membranes by the adsorption of proteins, e.g. the proteinized membranes of Loeb.3 Other investigators use other organic compounds, usually dyestuffs. These may be adsorbed like proteins or they may be dissolved in the collodion solution4 previous to casting the membranes. Such membranes are interesting and useful in their own right, but are not altogether satisfactory substitutes for active collodion membranes. They very often show considerable asymmetry; moreover, the dyestuffs so far employed (according to the literature) are slowly released into the solution in contact with the membrane, whereby the character of the membrane is considerably changed. Meyer and Sievers5 used an oxidation method to activate a cellophane membrane. Oxidation obviously increases the number of dissociable groups (carboxyl groups) in the membrane. As far as we know, this particular point was not studied further by these inves-

1 Sollner, K., and Abrams, I., J. Gen. Physiol., 1940, 24, 1.
tigators. Recently, Sollner and Abrams\(^1\) have reported in a preliminary paper that the oxidation method can successfully be applied to collodion membranes.

At present we are interested primarily in having available collodion preparations which yield membranes capable of reproducing at least the effects (concentration potentials,\(^6\) anomalous osmosis,\(^7\) etc.) described by previous authors. Moreover, artificial activation of collodion membranes may provide a means of correlating certain empirical data with some more recent theoretical considerations concerning the problem of electrochemical membrane behavior (Meyer and Sievers,\(^8\) Teorell\(^9\)). According to these authors and our own experimental results, the factor determining the electrochemical activity of membranes is—ceteris paribus—the number of ionizable groups fixed immovably to the collodion per unit area; i.e., the potential charge density of the collodion-water interface. This charge density is obviously identical with the base exchange capacity of the interfaces. Since this particular phase of the membrane problem has not been adequately developed, we plan to discuss it in a separate paper. The present communication deals with the technique of preparing activated membranes by the oxidation method and with a description of the characteristics of such membranes.

**II**

The oxidation method can be used in several ways to obtain active collodion membranes. Three possibilities are easily seen: (1) the oxidation of membranes as such, (2) the oxidation of commercial collodion cotton, and (3) the oxidation of cellulose before its nitrification.

The first and second of these methods may be easily applied in the laboratory; they yield satisfactory results quite readily. We have not, therefore, attempted

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the third possibility—oxidation of cellulose with subsequent esterification to nitrocellulose, as such a procedure would be much less convenient.

Oxidation of cellulose is always accompanied by some degradation, i.e. a lowering of the mean molecular weight, mainly by splitting of the chain molecules. The same is undoubtedly true for cellulose derivatives (e.g., collodion). Too thorough oxidation may easily reduce the molecular weight to such an extent that the material involved does not yield membranes of sufficient strength for the intended investigations.

In oxidizing collodion membranes, one should be able to find experimental conditions under which the mass of the collodion making up the membrane is relatively little affected, whereas its surfaces, outer as well as inner, are rather highly oxidized. Since the activity of a membrane is obviously determined only by the degree of oxidation at the surfaces, one should be able to produce in this way highly active membranes of relatively great mechanical strength.

If membranes prepared from oxidized bulk collodion are to have an appreciable activity, the oxidation process must be carried much further. For this reason, if the oxidized collodion fibres are dissolved, the activated groups originally present mainly at (or near) the oxidized surfaces are distributed uniformly throughout the mass of the collodion. Therefore, if membranes are now cast, the number of activated groups per unit of area in the newly formed surfaces is much smaller than it was in the directly oxidized surfaces of the bulk material prior to dissolution. An appreciable concentration of activated groups in the surfaces of membranes prepared from solutions of bulk oxidized material can, therefore, be obtained only if the latter has undergone a most thorough oxidation.

The method of activating bulk collodion has the obvious advantage that relatively large quantities of material may be prepared in a single operation and that many active membranes can be prepared in the usual manner from the same solution.

For the oxidation of collodion, a number of different oxidizing agents were employed. Among the less effective ones were hydrogen peroxide, bromine water, and potassium permanganate. Sodium hypochlorite, calcium hypochlorite, and particularly sodium hypobromite were found to be effective. These oxidizing agents can, as a matter of course, be applied successfully to other cellulose derivatives and to cellulose, as shown by Meyer and Sievers for the case of cellophane.

In addition to these general oxidation methods, it was found that treatment with alkali was quite effective in producing activated membranes. This observation at first seemed strange; however, after consulting the literature, it was found that nitrocellulose in contact with alkaline solutions is not hydrolyzed in a straightforward manner to cellulose and nitric acid; rather, it undergoes a gradual decomposition of a complicated nature. Nitrite is formed in large
quantities and the nitrocellulose is gradually oxidized. Actually, prolonged
action of alkali destroys the material completely with the formation of low
molecular weight compounds, particularly acids. A detailed discussion of the
mechanism of the reaction of alkalis with nitrocellulose is obviously outside
the scope of our present investigation and the interested reader must be re-
ferred to the literature.\textsuperscript{10}

We have tested the above mentioned effective oxidizing agents over wide
ranges of concentration, pH, and reaction times.

The sodium hypochlorite solutions were prepared from commercial solutions
by diluting with distilled water. These weakly alkaline solutions were adjusted
to the desired pH by addition of hydrochloric acid. Here, as in the forthcoming
instances, pH was determined with a glass electrode.

Calcium hypochlorite solutions were prepared by adding 50 gm. of commercial
bleaching powder to 1 liter of water. The bleaching powder dissolves only
partially, yielding a milky solution. The pH of the originally alkaline solu-
tion was adjusted by the addition of hydrochloric acid as before. After the
insoluble material settled out, the more or less clear supernatant liquid was
used as the oxidizing solution.

The sodium hypobromite solutions were prepared by the addition of molecu-
lar bromine to sodium hydroxide solutions. By adding different amounts of
bromine, solutions of different pH are readily obtained. Solutions at pH 11
are slightly yellow; at pH 7, orange; at pH 6, deeply red. Saturation is reached
at about 5.8. For the best and most consistent results, the solutions should
be freshly prepared. In this paper, we characterize our solutions by referring
to the concentration of the sodium hydroxide solutions used and the pH rather
than by indicating the concentration of hypobromite, the latter being poorly
defined and dependent upon hydrogen ion concentration.

The alkaline treatment of our materials was in most cases effected with
sodium hydroxide solutions of different concentrations. Potassium hydroxide
seems to be about equally effective. Ammonia, on account of its smaller de-
gree of dissociation, is much less effective. The efficiency of other alkalis was
also ascertained, but none of them offers any particular advantage over sodium
hydroxide.

Our results show that the optimum conditions for the oxidation of bulk
collodion are vastly different from those for membranes. But even membranes
themselves require varying treatments according to their porosity. In the
following paragraphs, we give short descriptions of the best procedures of oxi-
dation which have been found to date. Other colloidions may require some
adjustment of time or concentration if membranes of the highest activity are
desired.

\textsuperscript{10} See particularly Schwalbe, C. G., Die Chemie der Cellulose, Berlin, Borntraeger,
London, 1906, \textbf{89}, 1759; and others.
The oxidation of membranes is carried out by immersing them for a certain time in the oxidizing solution. This treatment is followed by thorough washing. All operations were carried out at room temperature. To obtain optimum results with any given oxidizing agent, it is necessary to adjust properly the concentration, pH, and the reaction time. Immersion for excessively long periods in a really efficient solution may destroy the membranes. Higher concentrations require somewhat shorter reaction times.

With highly dried membranes, bleaching powder solutions were very ineffective, even when allowed to react for several days. Oxidation with sodium hypochlorite solution results in some activation, but in no case were potentials approaching the maximum observed. 0.1 M sodium hydroxide solution yields some increase in activity; stronger solutions have a great tendency to destroy the membranes. However, really satisfactory activation of highly dried membranes was never obtained with sodium hydroxide. Sodium hypobromite solutions in the slightly acid range (ca. pH 6) give consistently good results; alkaline solutions beyond a pH of 7 are too destructive to be useful. Though more dilute solutions are quite effective, the best results were obtained by saturating 0.5 M or 1.0 M sodium hydroxide solution with bromine. (The use of more concentrated solutions has no advantage.) These solutions, if freshly prepared, give consistently satisfactory results, the proper immersion time being about 3 hours. We recommend this last method for the activation of dried collodion membranes as the one most consistently satisfactory.

Porous membranes having a fair degree of activity may be obtained with solutions of sodium hypochlorite and calcium hypochlorite over a wide range of hydrogen ion concentration (pH 6-11.5). The activation is stronger when alkaline solutions are employed, but above a pH of about 10.5, there is much danger of the membranes being destroyed. Sodium hydroxide in concentrations above 0.02 M is suitable in activating porous membranes; the reaction time has to be chosen carefully to fit the concentration. For example, immersion for 45 minutes in 0.02 M sodium hydroxide yields membranes of about the same degree of activity as treatment for 5 to 10 minutes with 0.5 M solution. The activity obtained is only slightly better than that which results from oxidation with hypochlorites.

With porous (as well as with the dried) membranes, entirely satisfactory results were obtained consistently with sodium hypobromite solutions. The optimum pH range, however, was somewhat different, being between 7.0 and 9. Acid solutions are somewhat less effective; more alkaline solutions are too destructive. After some testing, we recommend the use of 0.5 M to 1.0 M sodium hydroxide solution with the addition of sufficient bromine to adjust the pH to a value between 7 and 9. The optimum oxidation time in such solutions was 3 to 4 hours for the membranes we usually used (the thickness of our porous
membranes being on the average 0.04–0.05 mm.). Thicker membranes may stand much longer oxidation without damage. Therefore, the likelihood of obtaining more highly activated membranes is greater with somewhat thicker films.

The changes in geometrical structure (porosity) which the membranes may undergo during oxidation will be discussed below after the presentation of the pertinent experimental data.

The physical properties of oxidized membranes are essentially the same as those which have not been treated. Moderately oxidized membranes are nearly as strong mechanically as those which are unoxidized. Increasing activation weakens them more and more; this is accompanied, particularly with porous membranes, by the appearance of an increasing degree of “plasticity,” a property which is practically absent in unoxidized membranes.

IV

Various methods of testing the electrochemical activity of membranes were used according to their porosity. In the case of highly dried membranes, the only practical method is the determination of the concentration potential (Michaelis) before and after oxidation. For highly porous membranes, the most sensitive method is to determine the extent of anomalous osmosis under standard conditions. In addition, we measured electroosmosis as well as concentration potentials before and after oxidation. We also determined the influence of oxidation on the rate of filtration and on the pore volume.

The effect of oxidation on three representative dried membranes is summarized in Table I.

The membranes were cast from 5 per cent Mallinckrodt “Parlodion” solution (75 per cent absolute ether, 25 per cent absolute alcohol) and dried for 24 hours. The concentration potentials for 0.1 M KCl/0.01 M KCl were then determined. After this, the membranes were oxidized for about 3 hours with sodium hypobromite solution, prepared by saturating molar sodium hydroxide with bromine. They were thoroughly washed with water to remove all traces of electrolyte and the concentration potentials again measured.

The values obtained after oxidation closely approach the thermodynamically possible maximum of about 56 mv. (at 25°C.), indicating an unusually high degree of ionic selectivity. The ohmic resistance of these membranes is very markedly decreased after oxidation.

In testing porous membranes, it was necessary to compare only membranes of the same general porosity characteristics. With some experience, it is not difficult to produce such membranes. One must use some good grade of colloidion dissolved in a standard solvent mixture; each time a membrane is cast, the same procedure has to be followed.
Commercial solutions of Baker or Merck "Collodion U.S.P." (5 per cent collodion in a mixture of 25 per cent alcohol and 75 per cent ether) were used for most of the following experiments; occasionally, we employed collodion cotton (Baker "Pyroxi- lin") or Mallinckrodt "Parlodion" (5 per cent dry material in 25 per cent absolute alcohol and 75 per cent absolute ether). The differences between these preparations are negligible for our present purposes.

The technique of preparing the membranes, as described previously, is briefly as follows: Collodion bags are cast in 30 X 110 mm. test tubes and allowed to dry several minutes. Next the bags are filled with water; they loosen from the glass spontaneously and are tied to glass rings with thread while still filled with water. Following this, they are kept in covered glass containers under water to which thymol has been added as a preservative. They are never allowed to dry. The membranes so prepared are fitted to rubber stoppers provided with a long capillary tube (inner diameter about 1.5 mm.). Those membranes were selected which, when filled with

### TABLE I

The Influence of Oxidation on the Concentration Potential across Dried Collodion Membranes

<table>
<thead>
<tr>
<th>Membrane No.</th>
<th>Concentration potential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before oxidation</td>
</tr>
<tr>
<td>1</td>
<td>16.8</td>
</tr>
<tr>
<td>2</td>
<td>25.3</td>
</tr>
<tr>
<td>3</td>
<td>11.0</td>
</tr>
</tbody>
</table>

0.25 molar sucrose solution and placed in water for 20 minutes, yield an osmotic rise ("sucrose value") of about 120 mm. of liquid in the capillary manometer. The adjustment of the zero reading is facilitated by a small glass syphon provided with a stopcock, allowing the rapid adjustment of the meniscus in the manometer to the proper level, corresponding to the capillary rise over the outside solution.

These membranes are very suitable for experiments concerning anomalous osmosis. Their water content varied only in rather narrow limits between 65 and 70 per cent by weight. They were rather thin, their average thickness being 0.04 to 0.05 mm., with appreciably thinner and thicker parts found on each individual membrane.

To test a membrane for anomalous osmosis, the collodion bag is filled with salt solution, our standard being $\frac{M}{512}$ potassium sulfate. The bag was then fitted with stopper and manometer tube and immersed in a beaker filled with pure water. The rise of the meniscus in the manometer tube after 20 minutes is taken as the measure of the extent of anomalous osmosis. This rate of rise is very characteristic for each membrane.
Table II shows the effect of alkaline treatment on porous membranes after different reaction times; the values in Table III were obtained with membranes oxidized in molar sodium hypobromite solution (pH 7.1).

**TABLE II**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Before oxidation</th>
<th>After oxidation</th>
<th>Membrane</th>
<th>Before oxidation</th>
<th>After oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Osmotic rise with sucrose 0.25 M</td>
<td>Anomalous osmosis with M K\textsubscript{2}SO\textsubscript{4}</td>
<td>Duration of treatment with sodium hydroxide</td>
<td>Osmotic rise with sucrose 0.25 M</td>
<td>Anomalous osmosis with M K\textsubscript{2}SO\textsubscript{4}</td>
</tr>
<tr>
<td>a</td>
<td>108 mm</td>
<td>34 mm</td>
<td>1 min</td>
<td>108 mm</td>
<td>100 mm</td>
</tr>
<tr>
<td>b</td>
<td>145 mm</td>
<td>53 mm</td>
<td>2 min</td>
<td>143 mm</td>
<td>178 mm</td>
</tr>
<tr>
<td>c</td>
<td>132 mm</td>
<td>42 mm</td>
<td>3 min</td>
<td>136 mm</td>
<td>155 mm</td>
</tr>
<tr>
<td>d</td>
<td>110 mm</td>
<td>40 mm</td>
<td>5 min</td>
<td>105 mm</td>
<td>223 mm</td>
</tr>
<tr>
<td>e</td>
<td>122 mm</td>
<td>54 mm</td>
<td>10 min</td>
<td>128 mm</td>
<td>290 mm</td>
</tr>
<tr>
<td>f</td>
<td>116 mm</td>
<td>38 mm</td>
<td>15 min</td>
<td>118 mm</td>
<td>284 mm</td>
</tr>
<tr>
<td>g</td>
<td>98 mm</td>
<td>32 mm</td>
<td>20 min</td>
<td>120 mm</td>
<td>295 mm</td>
</tr>
<tr>
<td>h</td>
<td>110 mm</td>
<td>44 mm</td>
<td>60 min</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**TABLE III**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Before oxidation</th>
<th>After oxidation</th>
<th>Membrane</th>
<th>Before oxidation</th>
<th>After oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Osmotic rise with sucrose 0.25 M</td>
<td>Anomalous osmosis with M K\textsubscript{2}SO\textsubscript{4}</td>
<td>Duration of oxidation</td>
<td>Osmotic rise with sucrose 0.25 M</td>
<td>Anomalous osmosis with M K\textsubscript{2}SO\textsubscript{4}</td>
</tr>
<tr>
<td>a</td>
<td>111 mm</td>
<td>43 mm</td>
<td>4 hrs</td>
<td>132 mm</td>
<td>312 mm</td>
</tr>
<tr>
<td>b</td>
<td>128 mm</td>
<td>46 mm</td>
<td>4 hrs</td>
<td>153 mm</td>
<td>346 mm</td>
</tr>
<tr>
<td>c</td>
<td>146 mm</td>
<td>58 mm</td>
<td>4 hrs</td>
<td>148 mm</td>
<td>356 mm</td>
</tr>
<tr>
<td>d</td>
<td>147 mm</td>
<td>55 mm</td>
<td>18 hrs</td>
<td>164 mm</td>
<td>352 mm</td>
</tr>
</tbody>
</table>

* The membranes used in this experiment were somewhat thicker than those we used ordinarily (see text).
† Prepared from 1 M sodium hydroxide solution, therefore actually about 0.5 M with respect to hypobromite ion.

The effect of alkaline treatment on the sucrose values is conspicuously small, though the activation as measured with anomalous osmosis is rather good. It seems that a limiting degree of activation is reached after a few minutes. The membranes which were immersed for less than 10 minutes showed great mechanical strength. The last three became progressively weaker. We have here an example of thorough activation of collodion membranes with a minimum change in spatial structure.
Such values as those given in Table III can be obtained quite regularly on oxidation with sodium hypobromite. This table also exemplifies the changes in behavior towards nonelectrolyte solutions which are generally observed. A graphic presentation of the effect of oxidation on anomalous osmosis has recently been published. Additional data are also contained in Table VII.

At this point, a brief discussion of the changes in the geometrical structure (porosity) which the membranes undergo on oxidation may be in order. Such changes may well be indicated by their behavior towards nonelectrolyte solutions. The observation of only very slight variations in the osmotic behavior of nonelectrolytes (see tables below and some previously published curves) has led us to conclude that the geometrical structure of our membranes is but little affected by oxidation. The experimental data indicate that these changes increase with longer oxidation times. Limited (minutes only) treatment with sodium hydroxide solutions and the oxidation with acid hypobromite, particularly the latter, seem to combine good activation with minimum changes in porosity. Filtration experiments also indicate that the changes in the geometrical structure of the membranes on oxidation are small. For example, filtration rates through three of our typical membranes previous to oxidation were 2.03, 2.38, and 2.05 ml. per hour under a hydrostatic head of 15 cm. water, the filtering area being roughly 100 cm². After oxidation, these values were 1.74, 2.14, and 1.98 ml. per hour. To minimize disturbances which could be caused by electrical forces, molar potassium chloride solution was used in these filtration experiments.

In order to further clarify the question of structural changes caused by oxidation, we performed some experiments with flat membranes having approximately the same porosity as our bag-shaped porous membranes. These membranes were measured as to length, width, and thickness, and their weight in the wet state (blotted with filter paper) was determined before and after oxidation. A loss of volume was detectable only by the weight measurements and this only in certain cases. Immersion of the membranes in 0.5 M sodium hydroxide solution for 10 minutes caused a loss in weight of about 3 per cent; 3 hours in molar sodium hypobromite at pH 9.0 and 7.1 resulted in a loss of about 2 per cent and 0.7 per cent respectively, the latter value being within the limits of 11 The anomalous osmosis values in these curves are appreciably higher than those in Table III for the following reason. The points of the curves were obtained by performing the experiments one after the other with decreasing electrolyte concentrations without any intermediate rinsing of the membranes with water. Therefore, at the beginning of each experiment, the pores of the membranes contained the electrolyte in even higher concentration than in the bulk of the solution. No time was thus required for its penetration into the membrane. For this reason, the anomalous osmotic liquid movement sets in immediately with full force without any initial latent period.
experimental error. The percentage of dry material of the membranes oxidized with hypobromite did not change significantly. Prolonged treatment, particularly with hydroxide, results in a considerable loss of material and change in porosity.

**TABLE IV**

*The Influence of Oxidation on the Concentration Potential across Porous Collodion Membranes*

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Before oxidation</th>
<th>After oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration potentials*</td>
<td>Concentration potentials*</td>
</tr>
<tr>
<td></td>
<td>Osmotic rise</td>
<td>KCl</td>
</tr>
<tr>
<td></td>
<td>with sucrose</td>
<td>0.1/0.01 M</td>
</tr>
<tr>
<td>a</td>
<td>mm.</td>
<td>mm.</td>
</tr>
<tr>
<td>122</td>
<td>2.8</td>
<td>0.1</td>
</tr>
<tr>
<td>125</td>
<td>2.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

* The dilute solution was positive in the external circuit.

**TABLE V**

*The Influence of Oxidation on the Electroosmosis through Porous Membranes*

(Current 10 m Amps.)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Concentration of KCl solution</th>
<th>Electroosmotic flow in 20 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>moles/liter</td>
<td>c.mm.</td>
</tr>
<tr>
<td>a</td>
<td>0.001</td>
<td>2420</td>
</tr>
<tr>
<td>0.005</td>
<td>730</td>
<td>2300</td>
</tr>
<tr>
<td>0.01</td>
<td>360</td>
<td>1210</td>
</tr>
<tr>
<td>0.05</td>
<td>0</td>
<td>490</td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
<td>360</td>
</tr>
<tr>
<td>b</td>
<td>0.001</td>
<td>1690</td>
</tr>
<tr>
<td>0.005</td>
<td>1090</td>
<td>3500</td>
</tr>
<tr>
<td>0.01</td>
<td>600</td>
<td>1930</td>
</tr>
<tr>
<td>0.05</td>
<td>0</td>
<td>120</td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

* Osmotic rises with sucrose solution as listed in Table IV.

The evidence presented indicates that careful oxidation does not cause major changes in the geometrical structure of collodion membranes, though minor alterations probably cannot be avoided entirely. These changes, however, are certainly much smaller than the differences found between different membrane specimens cast by hand under as constant conditions as possible.

The influence of oxidation on the dynamic membrane (concentration) potential of porous membranes is indicated by the data in Table IV. Various
concentrations of potassium chloride were used. Results obtained with sulfate and citrate solutions are similar. The membranes used for these experiments were cast from a 5 per cent solution of Mallinckrodt “Parlodion”; they were of the same porosity as those used for experiments on anomalous osmosis.

Table V summarizes the results of some electroosmosis experiments carried out with the same membranes as those in Table IV.

For the electroosmosis experiments, membranes secured to glass rings were fitted with a rubber stopper holding a 6 mm. wide glass tube. One electrode consisted of a platinum wire which protruded down through this tube. The other electrode was in the form of a platinum wire cage surrounding the membrane. The membrane was filled with an electrolyte solution and placed in a bath of the same solution. The current in all experiments was kept constant at 10 milliamperes by manual adjustment, the effective membrane area being about 100 cm², or slightly less. Before the actual measurements were made, the current was passed through the membranes for 10 minutes. After this, the zero position of the water meniscus in the glass tube was marked. A current of 10 milliamperes was now passed through the system for 20 minutes and the change in the position of the meniscus noted. From this change and the diameter of the tube, the electroosmotic transport is easily calculated. The quantities transported electroosmotically are directly proportional to the duration of the experiment and to the current applied, back filtration being negligible. Prolonged passage of the current through the membranes, particularly activated membranes, weakens them appreciably. They may be easily destroyed when strong currents are applied over a long period of time. The alkali developed at the membrane when the current passes is probably responsible for its destructive action.

The marked influence of oxidation is apparent. As one should expect from theoretical considerations, the relative effect of activation is more pronounced with the more concentrated electrolyte solutions.

V

The oxidation of collodion in bulk is performed by immersing dry fibrous collodion cotton in proper oxidizing solutions. After a suitable oxidation time,

13 This destruction (previously described for highly dried membranes by Michaelis, (Bull. Nat. Research Council, No. 69, 1929, 135), is accompanied by the dissolution of some of the destroyed material in the solution. Therefore, the use of collodion membranes for electrodialysis seems much less advisable than is generally assumed, particularly when very high degrees of purity are required. We are inclined to believe that the generation of soluble impurities may have seriously impaired some of the published work on highly purified inorganic colloids.
14 Though collodion is generally not explosive, great quantities of dry material should never be kept in the laboratory. The dry material should always be handled with due care.
the material is washed thoroughly with dilute hydrochloric acid and liberal quantities of distilled water. After this, it is dried in the open at moderately increased temperature. It is finally dissolved in ether-alcohol; 5 per cent solutions were used.

The material which may be most conveniently oxidized is collodion cotton (native nitrated cellulose fibres). It can be readily obtained from supply houses. It may also be reprecipitated collodion, obtained in the fibrous form by slowly dripping commercial collodion solutions into a great excess of violently stirred distilled water. For the subsequent oxidation, it makes little difference whether native or reprecipitated material is used.

Here, as with the membranes, we tried several oxidizing agents for varying reaction times at different pH. The oxidizing solutions used were the same as those described above. As before, the more alkaline solutions of hypochlorite and hypobromite are markedly more effective than those of lower pH. For reasons outlined above, the oxidation has to be much more thorough in the case of bulk collodion than with membranes.

Immersion of collodion cotton in sodium hypochlorite or hypobromite solutions at pH 6 to 10 for 2 days yielded only moderately active products; treatment for 16 hours at pH 11 to pH 11.5 was more effective. But the loss of material increases very markedly in the more alkaline solutions. Both sodium hypochlorite and hypobromite are less effective activating agents than bleaching powder (calcium hypochlorite) solutions. Treatment for 2 days with such solutions at pH 8 to pH 11.5 gives comparatively good activation. The yield is good, particularly if the reaction is carried out at a pH below 10.

The simplest method of oxidation is the treatment with sodium hydroxide. 0.02 M solution for 5 days is nearly as effective as 0.1 M for 2 days, 1 M for 30 minutes, or 2 M for 15 minutes. The loss of material under these conditions is moderate (less than 10 per cent). The activation of bulk collodion with hydroxide is at least as effective as any other method previously described. Membranes cast from such material are quite strong, though oxidation is always accompanied by some lowering in mean molecular weight, as evidenced by the somewhat lower viscosity of the solutions.

By carefully adjusting the conditions, one can obtain reasonably well activated collodion practically without any loss in mechanical strength (and of material). Too thorough oxidation, apart from the loss of material, results in a product of poor mechanical properties. Its solutions have a very low viscosity and membranes cast from them are somewhat plastic and weak, often too weak to be useful for experimental purposes. For this reason, the activation of collodion cannot be carried successfully beyond a certain point. The introduction of a maximum number of ionizable groups into the nitrocellulose

\(^{18}\) Collodion cotton (e.g., Baker “Pyroxilin”) comes moistened with alcohol. The alcohol must be allowed to evaporate before the above treatment is begun.
molecule is limited by the ability of the partially decomposed product to form mechanically adequate membranes.

With the oxidized collodion it is advisable, though not absolutely necessary, to use as solvent ether-alcohol mixtures of somewhat higher alcohol concentration than that used in commercial U.S.P. solutions (see above). We frequently used 35–40 per cent alcohol and 65–60 per cent ether. For the preparation and properties of dried membranes, the solvent composition, as it seems, is without significance; the preparation of porous membranes of any particular porosity may be greatly facilitated by use of the proper solvent mixture. However, for the time being, we would like merely to mention the solvent influence without discussing it further.

The activation of collodion in the dissolved state was also attempted. This reaction proceeds very rapidly and is difficult to control. Therefore, this method yielded rather indifferent results; very pronounced degradation was accompanied by only moderate activation.

For the activation of bulk collodion for general experimental purposes, we recommend a short (about 20 minutes) treatment with 1.0 M sodium hydroxide solutions. An alternative method involves the use of bleaching powder (50 gm./liter) solution in the slightly alkaline range (pH 8–10) using long (2 days) oxidation periods. It is advisable to use a sufficiently large excess of oxidizing solution (e.g., 1 liter molar sodium hydroxide solution for 50 gm. collodion). In this way, any desired quantity of activated collodion can easily be prepared and large numbers of membranes can thus be cast from the same material.

Dried membranes prepared from properly activated collodion regularly give concentration potentials (0.1 M KCl/0.01 M KCl) of 52 to 54 mv. These values are appreciably higher than those formerly obtained with even the most active commercial—now unobtainable—preparations. The concentration potentials of such membranes (using 0.01 M KCl/0.001 M KCl) vary between 56 and 58 mv. at room temperature. The ohmic resistance of such membranes is much lower than that of similar membranes prepared from untreated material. This effect seems to be particularly pronounced with membranes prepared from

Concerning additional methods of activating collodion membranes, we should like to mention that some casual attempts to produce sulfuric acid esters by treating collodion with sulfuric acid gave negative results. In some other experiments, we mixed some nitropectic acid with inactive collodion and obtained very active membranes. According to the literature (Henglein, F. A., and Schneider, G., Ber. chem. Ges., 1936, 69, 309), nitropectin (and nitropectic acid), when properly prepared, yields films similar to those of collodion. Such films of pure nitropectic acid should, as our experiments indicate, be electrochemically active.
collodion thoroughly activated with sodium hydroxide. We hope to be able
to investigate this and related points later.

In order to characterize the degree of activity of porous membranes prepared
from bulk oxidized collodion, some data concerning anomalous osmosis are
summarized in Table VI.

Variations between different batches are more sensitively detected by anomalous
osmosis measurements with porous membranes than by determinations of
concentration potentials on highly dried membranes.

Activity as good as that of samples a and b in Table VI are rather rare.
Collodion having an activity similar to that of samples c and d can be obtained
easily and regularly. It must be emphasized that the activity of our most

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Osmotic rise with sucrose 0.25 M</th>
<th>Anomalous osmotic rise with K$_2$SO$_4$, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial (unoxidized) collodion</td>
<td>110–140</td>
<td>35–55</td>
</tr>
<tr>
<td>Oxidized collodion sample a</td>
<td>140</td>
<td>260</td>
</tr>
<tr>
<td>Oxidized collodion sample b</td>
<td>132</td>
<td>250</td>
</tr>
<tr>
<td>Oxidized collodion sample c</td>
<td>130</td>
<td>211</td>
</tr>
<tr>
<td>Oxidized collodion sample d</td>
<td>136</td>
<td>180</td>
</tr>
</tbody>
</table>

active porous membranes prepared from bulk collodion does not approach
the degree of activation which may be regularly obtained by the oxidation of
membranes as such.

VII

Membranes prepared from crude collodion should (according to a preceding
paper) be active, since crude preparations are bound to contain acidic impuri-
ties. These acidic impurities are formed in the process of manufacture and are
removed by proper purification of the commercial preparations. According to
the technical literature, crude nitrocellulose is not sufficiently stable for safe
handling, at least in the dry state. Consequently, manufacturers are generally
reluctant to release any material in the crude state. Finally, however, we
procured a sample of crude collodion from the Monsanto Chemical Company.
When dissolved (in a mixture of 65 per cent ether and 35 per cent alcohol),
its solutions were turbid and yielded a sediment on centrifuging. (Only centri-
fuged solutions were used.) The activity of membranes prepared from these

17 For this sample we are greatly indebted to Mr. H. K. Nason, Assistant Director
of Research, Monsanto Chemical Company, Springfield, Massachusetts.
solutions, when tested by means of anomalous osmosis, was somewhat higher than the most active Schering-Kahlbaum preparation; on the other hand, they were definitely less active than most membranes prepared from collodion oxidized as discussed in the preceding paragraphs. Highly dried membranes gave values for the concentration potential (KCl 0.1 M/KCl 0.01 M) of 50 mv. and better. These values are similar, or possibly somewhat higher, than those reported by Michaelis and coworkers, who used membranes prepared from Schering-Kahlbaum "Celloidin."

Since crude collodion is not regularly available through supply houses or other regular trade channels, it seems superfluous to describe this product or its behavior in detail.

VIII

The results obtained with the oxidative activation of membranes lead one to infer that the differences observed in the membranes prepared from various brands of collodion (reported previously1) would disappear on oxidation. The verification of such an inference would be of importance in providing an insight into the structure of collodion membranes.

The best way to approach the above problem experimentally is to test the behavior of such membranes with anomalous osmosis. Table VII summarizes the behavior of membranes prepared from several brands of collodion before and after oxidation. The experimental technique was the same as that previously sketched.

In order to have reasonable uniformity in the membranes prepared from the different collodions,18 we selected those which gave as nearly as possible the same rate of pressure rise when tested with 0.25 M sucrose solution (Table VII a column 2). The pressure rise obtained during 20 minutes was taken as indicative of the porosity of the membrane. The rises of the liquid in the manometer tube after 20 minutes with different electrolytes are given beside the sucrose values (Table VII a columns 3, 4, and 5). The values given here were obtained in "repeat" experiments, carried out without washing the membranes after a preceding similar experiment with the same electrolyte concentration. These repeat values are always somewhat higher, as the electrolyte has already penetrated the membrane and the proper concentration gradient is established from the very beginning of the experiment. The electrolyte con-

18 To obtain such structural uniformity with the different brands of collodion, it was necessary to evaporate the original Schering-Kahlbaum collodion solutions to dryness and to redissolve the dry material in ether-alcohol prior to casting the membranes. For the experiments described in Table VII, we adhered to the standard solvent mixture (75 per cent ether and 25 per cent alcohol) and made the solutions uniformly 5 per cent. In parenthesis, we may add that in later experiments "Parlodion" membranes having a satisfactory porosity were obtained only by increasing the alcohol concentration to 40 per cent.
centrations used are approximately optimum concentrations for membranes of moderately good activity. After being thus tested, the membranes were oxidized for 3 hours in a solution prepared by saturating molar sodium hydroxide with bromine, the resulting solution having a pH of about 5.8. At this pH, the activation is good, but not necessarily optimal. After properly washing the membranes, the osmotic experiments with sucrose and electrolyte solutions were repeated.

The results are shown in Table VII. It may be noted that on account of the poor quality of Schering-Kahlbaum DAB 6, we were unable to obtain a membrane of this material which withstood oxidation without damage.

### TABLE VII

<table>
<thead>
<tr>
<th>Brand of collodion</th>
<th>Before oxidation</th>
<th>After oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anomalous osmosis</td>
<td>Anomalous osmosis</td>
</tr>
<tr>
<td>Mallinckrodt &quot;Parlodion&quot;</td>
<td>124 7 43 73</td>
<td>142 112 332 665</td>
</tr>
<tr>
<td>Merck collodion u.s.p.</td>
<td>128 14 54 112</td>
<td>140 124 290 650</td>
</tr>
<tr>
<td>Baker collodion u.s.p.</td>
<td>128 6 48 130</td>
<td>120 116 338 670</td>
</tr>
<tr>
<td>Schering-Kahlbaum Collo-</td>
<td>125 8 32 124</td>
<td>140 104 330 715</td>
</tr>
<tr>
<td>dium &quot;for analysis&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schering-Kahlbaum Collo-</td>
<td>115 16 83 190</td>
<td>145 75 173 620</td>
</tr>
<tr>
<td>dium &quot;zur Herstellung von Membranen&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schering-Kahlbaum &quot;Cel-</td>
<td>126 70 228 410</td>
<td>158 117 340 635</td>
</tr>
<tr>
<td>loidin&quot; &quot;for general use&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schering-Kahlbaum Collo-</td>
<td>124 26 195 390</td>
<td>Decomposes on oxidation</td>
</tr>
<tr>
<td>dium DAB 6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* This concentration was chosen because it gives maximum effects with membranes of medium activity.

A comparison of the pressure rises with sucrose solution (obtained with the same membranes) before and after oxidation shows that they are but little changed (Table VII, columns 2 and 6). This is particularly true for the better (less active) grades of collodion. The behavior of our membranes with electrolyte solutions, however, is most markedly changed after oxidation. They are all uniformly active, possessing far greater activity than even the most active commercial preparations. The differences between the various commercial preparations completely disappear on oxidation, a fact which indicates that membranes prepared from different collodions (if they behave fairly uniformly with nonelectrolytes) have a fairly similar geometrical structure. Thus the difference between membranes prepared from different brands of...
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collodion is to be found not in differences of their geometrical structure, but rather in their different electrochemical characteristics.

IX

DISCUSSION

Most of the points raised by the data which have been presented have been dealt with adequately in the foregoing sections. Certain other facts warrant further comment and correlation.

It should be said that the proposed methods of activation of collodion by oxidation are obviously not beyond possible improvement. They are simply methods found to be satisfactory with many different collodion preparations under varying conditions.

Concerning the origin of the oxidized groups in the active commercial preparations (as well as in the crude collodion), it may be appropriate to mention that the strength of the hypochlorite (and hypobromite) solutions we used was about the same as that used in technical bleaching solutions; the latter usually contains 2 to 5 gm., occasionally up to 25 gm. of “available chlorine” per liter—according to the material to be bleached. Cellulose swells in electrolyte solutions, and the native cellulose fibres are thus quite accessible to the action of bleaching agents. There is little wonder that considerable oxidation occurs during the manufacturing process, particularly if impure raw materials requiring thorough bleaching are used. The latter treatment in combination with the obviously rather superficial purification of the active collodions (as attested by their high ash and sulfate content), can readily account for the activity of certain commercial collodion preparations of poor quality which are no longer available.

The problem as to why one or the other of our oxidizing agents is more or less effective under different conditions probably cannot be solved at present; too many factors are involved. Among the strictly chemical factors are the change of oxidizing power in general with changing hydrogen ion concentration, the different possibilities of attacking the nitrocellulose in an oxidative and hydrolyzing manner, and the correlation of these two processes.

There are other problems in which chemical and structural factors are closely interwoven. For example, a given oxidizing agent may or may not penetrate into the smaller pores of the collodion, depending on its chemical characteristics, particularly its molecular (ionic) size. If the latter is large, it may be unable to reach the narrow pores of a dried membrane, unless it first causes considerable structural changes of a destructive nature.

This leads us to a very important point, namely the possible structural changes which occur on oxidation. We must expect such changes to be much more critical with dried than with porous membranes. The relative structural changes brought about by a certain oxidizing agent may be insignificant in
the wide pores of a porous membrane, whereas the same absolute change in the extremely minute pores of a dried membrane may easily result in proportionately enormous structural changes. Therefore, an oxidizing agent which gives optimum activation with porous membranes may be very unsuitable for dried membranes. For the latter, only such oxidizing agents which cause minimal structural changes (e.g., acid hypobromite solution) are suitable. Such activating agents, although they may not bring about maximum charge density, leave the pores sufficiently narrow to give rise to maximum concentration potentials.

Our own results lead to the conclusion that differences between active collodion membranes and membranes artificially impregnated with proteins, dyestuffs, etc., are not nearly so fundamental as formerly assumed. In all these cases, certain ionizable substances, foreign to the pure ideal nitrocellulose cause the activity.

The idea of increasing the base exchange capacity of cellulosic materials is certainly not new. Years ago, Schwalbe and Becker19 oxidized cellulose with the purpose of introducing acid groups and studied the base exchange properties of the oxidized products.

A brief explanation of the terms used to describe the activity of our membranes, particularly the porous ones, may be appropriate. Measurements of concentration potentials are basically the simplest way of characterizing dried membranes. In our opinion, simple potential values which are obtained experimentally are hardly less characteristic than any derived constants which may be calculated according to some newer theoretical concepts.8,9 In the case of porous membranes, the measurement of concentration potential (or anything derived from it) gives only an incomplete characterization. For a more detailed description of a membrane, potential measurements must be supplemented by some sort of electrokinetic experiments (e.g., electroosmosis measurements). A much more sensitive indicator of the electrochemical “activity” of actual membranes (having pores of different diameters20) is, as pointed out before, the extent of anomalous osmosis under standard conditions—as used in our experiments.

Most preceding studies (as well as our own) have neglected a matter of primary importance, namely, the conductivity of collodion membranes. Michaëlis and coworkers21 have investigated this problem to a limited extent. Conductivity measurements, performed with membranes of different activity,
would probably be rather helpful in elucidating their structure. From the experimental point of view, the problem of conductivity is particularly urgent with highly dried membranes. In the past, investigators have been concerned nearly exclusively with the electromotive properties (concentration potentials) of such membranes. By and large, as long as the resistance was not so high as to make measurements too difficult or inaccurate, a membrane was considered to approach perfection if the concentration potential approached the thermodynamically possible maximum. Ordinarily, dried membranes have such high electrical resistance (and low permeability for nonelectrolytes) as to make them more or less useless for many permeability studies. If highly selective membranes should be used for large scale permeability studies or for model experiments (e.g., straight permeability or Donnan equilibria with univalent strong electrolytes), they must combine both high ionic selectivity and low resistance. The oxidation method might conceivably offer a good means of preparing such membranes; however, this possibility requires further experimental investigation.

Finally, it seems worth while once more to stress the fact that the oxidation of membranes influences their behavior towards nonelectrolytes only slightly and that their geometrical structure is only little affected by such treatment. Membranes prepared from different brands of collodion completely lose their characteristic differences in behavior towards electrolyte solutions (Table VI) when oxidized (and remain, as implicitly said above, relatively unchanged in their behavior towards nonelectrolytes).

This indicates that the differences between membranes prepared from different brands of commercial collodion in their behavior towards electrolyte solutions have to be sought for primarily in their electrochemical structure, i.e. in the number (and nature) of dissociable groups in their surfaces. Particle size and particle size distribution are obviously, at least in the range of the investigated preparations, only a secondary factor.

With this statement, we do not infer that the differences of molecular weight between the different brands of collodion are not important for the spatial structure of the membranes. What we can say on the basis of our present experimental results is that the different commercial collodion preparations allow one to prepare membranes having obviously similar geometrical structures. There are great differences in the ease with which membranes of a given porosity (sucrose value) can be obtained from different collodion preparations, particularly if the same solvent mixture is used.

A deeper insight into the physical and chemical structure of the collodion membrane will be possible only after further experimental data are available. The most important problem seems to be the determination of the absolute charge density at collodion-water interfaces and the possible correlation of such data to the Meyer-Sievers-Teorell theory of electrochemical membrane
behavior. The water uptake and the swelling of collodion membranes in different electrolyte solutions also await investigation. We hope to deal with these problems in subsequent publications.

SUMMARY

1. The electrochemical behavior (concentration potential, anomalous osmosis, etc.) of collodion membranes is due to its acidic impurities. These impurities determine the possible charge density of the collodion—aqueous solution interfaces. This (possible) charge density is believed to be identical with the base exchange capacity of the interfaces under consideration.

2. The collodion preparations commercially available at present are too pure to yield membranes of sufficient activity for electrochemical membrane investigations. Crude collodion, a product which is only partially purified, shows considerable electrochemical activity because of its content of acidic impurities.

3. The inactive commercial collodion preparations can readily be activated by oxidation by virtue of the fact that oxidation increases the number of dissociable groups (carboxyl groups) on the collodion.

The oxidation method of activating collodion may be applied to membranes as such as well as to collodion in bulk.

4. The recommended oxidizing agents are sodium and calcium hypochlorite and sodium hypobromite. A further group of effective and recommended activating agents are solutions of strong alkalies. Alkalies cause a complicated decomposition of nitrocellulose with the formation of nitrites (and probably other nitrous compounds). These nitrites act upon the collodion as oxidizing agents, thus causing activation.

5. Detailed descriptions of tested oxidation procedures for highly dried membranes, porous membranes, and bulk collodion are given in the text, the optimum conditions being different in the three cases.

6. Collodion membranes oxidized as such show a much higher electrochemical activity than any previously described. Highly dried membranes after oxidation give concentration potentials which approach the thermodynamically possible maximum more closely than any given in the literature. Porous membranes after oxidation show greatly increased concentration potentials and yield much greater electroosmosis when a current is passed through. These effects are reflected in the enormous magnification of the extent of anomalous osmosis.

7. The behavior of the porous membranes toward nonelectrolytes changes but little on oxidation. The volume of such membranes, as well as their percent water content (pore space), remains constant within the limits of experimental error. From this observation and studies on the rate of filtration, it is concluded that the geometrical structure of membranes is but little changed on oxidation.
8. Collodion oxidized in bulk likewise yields very active membranes. Dried membranes prepared from activated bulk collodion consistently yield concentration potentials which approach the thermodynamically possible maximum very closely and are appreciably higher than any previously reported. Porous membranes prepared from bulk oxidized collodion show a degree of electrochemical activity surpassing anything described for the most active commercial collodion preparations. However, these membranes are less active than those oxidized as such.

9. Membranes prepared from different collodion preparations which behave fairly uniformly towards nonelectrolytes but very differently towards electrolyte solutions become similar in their behavior towards electrolytes after oxidation.

10. The geometrical structures of membranes prepared from different collodion preparations are essentially identical. The differences in their behavior towards electrolytes are due entirely to the electrochemical factor; i.e., the charge density at the water/collodion interface.

11. Certain general aspects of the foregoing experimental results are discussed briefly.