THE STRUCTURE OF THE COLLODION MEMBRANE AND ITS ELECTRICAL BEHAVIOR

III. THE BASE EXCHANGE PROPERTIES OF COLLODION

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In preceding papers it was shown that electrochemical behavior of collodion membranes (at least in solutions of strong, weakly adsorbable electrolytes) is due to the presence of acidic impurities in the collodion. Highly purified preparations exhibit only low electrochemical activity (as measured by concentration potentials, anomalous osmosis, etc.), and in our opinion, even this low activity is due to traces of acidic impurities; the ideal pure nitrocellulose should, in solutions of strong, weakly adsorbable electrolytes, be void of any distinct electrochemical activity. It was further pointed out that the charge density at the collodion-solution interface is the ultimate determining factor. This general concept was actually used some time ago in some very interesting attempts to put the theory of electrochemical membrane behavior on a quantitative basis (Teorell, Meyer and Sievers).

We came to the conclusion that a study of the base exchange capacity of the collodion-solution interfaces would be the best method of obtaining pertinent quantitative data to test these theories. The base exchange capacity of a given substance is defined as the maximum cation exchange which can take place between a base exchange body and an electrolyte solution. The base exchange capacity of a given interface should be the limiting value of the possible charge density. The actual effective charge density would be the product of the base exchange capacity and the degree of dissociation (or a similar function).

In the present paper we shall attempt to determine whether or not a quanti-

1 Sollner, K., and Abrams, I., J. Gen. Physiol., 1940, 24, 1.
tative correlation exists between base exchange capacity of collodion and its electrochemical “activity” as defined in previous papers. A quantitative evaluation of these and other data and an attempt to correlate them to the above mentioned quantitative theories will be the subject of a subsequent publication.

II

Little attention has previously been paid to this problem. Beutner, Caplan, and Loehr carried out experiments with “Celloidin” (Schering), a brand of collodion which exhibits unusually high electrochemical activity. They measured the titratable acidity of distilled water and 0.1 m potassium chloride solution into which equal numbers of cubes cut from commercial “Celloidin” gel had been placed and shaken for 48 hours. They found that both the water and potassium chloride solution became acid. The titratable acidity after this period of shaking with collodion in the case of the water was in most cases two thirds as great as with the potassium chloride solution. These workers also roughly estimated the pH of the same solutions by indicator methods and concluded that the electrolyte solution became more acid than did the distilled water; the former had a pH of about 3.8, and the latter, 4.8. Beutner, Caplan, and Loehr conclude that this differential effect determines the electrochemical activity of collodion.

Wilbrandt, repeating the experiments of Beutner, Caplan, and Loehr, could confirm the acidulation. He attributes it to the presence of nitric acid due to the hydrolysis of the collodion. However, Wilbrandt did not perform any quantitative measurements; moreover, his analytical method is open to criticism, the diphenylamine test used not being specific for nitric acid.

Meyer and Sievers, accepting the results of Beutner, Caplan, and Loehr, quote them in corroboration of their theory.

In addition, several studies on the base exchange properties of cellulose appear in the technical literature. A discussion of this material, however, is outside the scope of this paper, considering the restricted bearing upon our problem. The differences between cellulose and nitrocellulose are too great to allow a ready comparison.

III

Base exchange experiments are usually carried out in the following manner. First the material to be investigated for its base exchange properties is brought into as well defined a chemical state as possible by saturating it with cations

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5 Wilbrandt, W., J. Gen. Physiol., 1935, 18, 933.
of a single kind. This can be done in different ways. The sample may be treated with an electrolyte solution, e.g., sodium chloride, until all ions capable of exchange are replaced by sodium. Usually it is preferable to use a solution of acid (hydrochloric acid), as in this case the necessary subsequent washing does not cause any complications due to hydrolysis which occur if salts are used. Electrolysis also causes replacement of all other cations by hydrogen ions. We shall discuss solely hydrogen ion saturated material.

Known quantities of such material are brought into contact with a neutral salt solution. The hydrogen ions from the exchange body are replaced by the other cations in solution and the latter becomes acid. The quantity of titratable hydrogen ion in the supernatant solution represents the base exchange when no complicating reactions occur. It can be measured either by direct titration or by determining the hydrogen ion concentration with some physical method, e.g., the glass electrode. The two results should check within the limits of experimental error. If necessary one takes into account such correction factors as the carbon dioxide present and the activity (degree of dissociation) of the electrolyte solutions. Any sizable disagreement between the results of the two methods would indicate definitely that one is not dealing solely with true base exchange. The treatment with salt solution is, if necessary, repeated until (practically) complete exchange is achieved. Often a single treatment is sufficient since the salt is usually present in great excess so that the hydrogen ion is replaced nearly completely, even by weakly adsorbable cations.

If shaken with pure water, an ideal base exchange body saturated with hydrogen ions does not react at all. If it behaves differently, one is not dealing with a base exchange phenomenon but with something different, most likely solubility.

Base exchange is a very fast process provided the surfaces to be tested are easily accessible. If inner surfaces of the exchange body are accessible only with difficulty or if a diffusion through the solid substance of the base exchange body makes itself felt, the process may require a long time for completion. Attention should be called to the fact that collodion membranes show their characteristic electrochemical properties practically instantaneously on contact with salt solutions.

It is obvious from the data quoted earlier that the conditions of the experiments of Beutner, Caplan, and Loehr did not permit measurements of the true base exchange capacity of collodion. This is apparent from (1) the occurrence of large titration values for water which was in contact with their collodion and (2) the disagreement between the titration and pH values. The calculated pH values for the experiments quoted above are about 3.0 for the potassium chloride solution and 3.1 for the water. This compares with experimental values of 3.8 for the potassium chloride solution and 4.8 for water reported for a similar experiment by the same authors (see above).
In approaching our experimental problem, we first repeated the experiments of Beutner, Caplan, and Loehr using Schering-Kahlbaum "Celloidin" "for general use." We obtained experimental data very similar to theirs. (Our experimental figures are given below as cases 7 a and 7 b in Table II.)

For a more thorough investigation, it was necessary to study a great variety of collodion preparations of different origin and varying electrochemical activity. We have investigated several American and some foreign brands of collodion in the original state and after purification, and in addition, oxidized ("activated") collodion and crude nitrocellulose. The behavior of these materials was studied before and after special purification processes. In order to obtain data which can be compared intelligently, it was necessary to study the different collodion preparations in as nearly the same physical and chemical state as possible.

Uniformity of the physical state was achieved by allowing dilute collodion solutions to drip, under standardized experimental conditions, into a great excess of vigorously stirred distilled water in which it is precipitated immediately. The fibrous products so obtained were washed superficially and dried. The precipitated material, of course, shows certain differences as to fiber length, aggregation of fibers, etc., according to the different molecular weights of the different preparations. The material precipitated from solution gives a large surface for possible base exchange, certainly not smaller than the same weight of collodion in the form of membranes.

The ideal chemical state would require that all the acid groups in the collodion should be present in the free acid state, i.e., saturated with hydrogen ions. The extent to which this condition is fulfilled with our different collodion preparations is difficult to state exactly. In their manufacture they certainly have undergone a most thorough acid treatment. Nevertheless, they all contain some ash, though mostly in rather minute amounts. This ash is not composed of basic material only; it always contains some sulfate which was introduced in the manufacturing process. In the collodion, the sulfate is probably present partially in the semi-esterified form, partially in the free, uncombined state, the latter form being prevalent in crude (not thoroughly purified) collodion. If present as an acid ester, it contributes to the true acidity of the collodion; the uncombined fraction is present as mechanically admixed impurity, partially or entirely combined with some of the bases. A corresponding quantity of acid and base would thus be neutralized, neutralized also in their effect on the apparent base exchange properties of the collodion. It is very difficult to remove the last traces of these impurities, but, as shown previously, a large fraction can be extracted without seriously affecting the electrochemical activity of the collodion. One must also consider the fact that the impurities are distributed throughout the mass of the collodion; only a small fraction
could lie in the interfaces, where they might affect the electrochemical behavior. Moreover, water soluble, not strongly adsorbable impurities, e.g., inorganic ions can readily be washed off the collodion surfaces by treatment with water. The possible error in our base exchange experiments which could be due to the ash and sulfate content is insignificant, as will become apparent.

It is important to emphasize here that our exchange studies were carried out not with the native or purified fibers, but with freshly prepared fibrous material, obtained by dissolving our preparations in ether-alcohol and precipitating in distilled water. This was done with all samples unless otherwise indicated. This procedure assures one that only surfaces corresponding in their composition to the properties of mass of the collodion are studied. Without it, the experiments would be subject to the objection that surfaces were studied which had undergone a special treatment and thus are not representative of the collodion. With membranes, of course, one is always dealing with surfaces originating from dissolved material. The collodion surfaces used for the base exchange studies were, in this respect, analogous to those which occur in membranes cast from the same collodion solutions.

The exchange properties of the precipitated fibers were found to be the same, whether used with or without drying. For the sake of convenience, we used dried\textsuperscript{10} material in most cases.

The \textit{commercial collodion preparations} which we used in this work were precipitated from ether-alcohol solutions without any special purifying operations.

Most of the \textit{preparations which we purified} ourselves were treated with 60 per cent acetic acid or alcohol-water mixtures, as indicated in Table II, column 1. Great care was always taken to prevent the uptake of cations by using double distilled water.

The "oxidized" collodion was prepared from a pure commercial preparation by immersion for 24 hours in a sodium hypobromite solution, prepared by adding to molar sodium hydroxide solution enough bromine to adjust the pH to about 7 as described previously.\textsuperscript{3} The oxidized product was washed with water, dilute hydrochloric acid, and again, very thoroughly with double distilled water. The ash (and sulfate) content of properly purified oxidized collodion is very low, lower than that of the original material. Low molecular weight decomposition products originating from the oxidation process are also removed by the indicated treatment. For some of our experiments, this oxidized collodion was further purified by repeated washings with aqueous alcohol. We may add here that oxidized collodion prepared by immersion in sodium hydroxide\textsuperscript{3} behaves substantially the same as collodion oxidized with hypobromite. However, it is somewhat more difficult to free of low molecular

\textsuperscript{10} That dried collodion must be handled with due care was pointed out previously (Sollner, K., Abrams, I., and Carr, C. W., \textit{J. Gen. Physiol.}, 1941, 25, 7).
weight decomposition products on account of the stronger degradation associated with the alkaline treatment.

The samples of crude nitrocellulose listed in the tables, as well as several others which are not listed, were obtained through the courtesy of the Monsanto Chemical Company, Plastics Division. According to the information received, they were taken from the manufacturing process at the end of the washing to eliminate free acid, but before the purification steps intended to remove sulfuric esters and other impurities. The samples of crude material listed in Tables I and II are representative for crude collodion; several other lots which we have tested had very similar properties. Sample A was received wet with alcohol, having been washed several times with 95 per cent alcohol. Sample B was obtained in the water wet state. The combined effect of proper purification operations, such as boiling with water and boiling or repeated washing with alcohol of suitable concentration, allows one to prepare from sample B a product which is practically identical in its properties with sample A. In the same way, any desired degree of purity, base exchange capacity, and activity can be obtained with material from either batch at will. Several samples treated in the described manner are listed in Table II. Of course, each batch of crude collodion is slightly different as to ash and sulfate content, base exchange properties, and activity, according to the moment at which it was withdrawn from the regular manufacturing process.

Since the experiments of Beutner, Caplan, and Loehr indicate that at least some collodions do not show simple, true base exchange, each preparation was studied not only with an electrolyte solution but also with distilled water.

The electrolyte chosen was 0.5 M potassium chloride after we had established the fact that the electrolyte concentration is rather unimportant, provided it is not too low. All water used was double distilled and reasonably free from carbon dioxide (pH > 6.5). The salt solutions used in all our experiments showed pH values from 6.5 to 7 before the experiment, as measured with a Leeds and Northrup glass electrode.

All experiments were carried out in Pyrex Erlenmeyer flasks with glass stoppers which were properly steamed and aged before use. Water and potassium chloride

11 We are greatly indebted to the Monsanto Chemical Company for these samples, particularly to Mr. H. K. Nason, Assistant Director of Research, to whom we would also like to express our special thanks for very valuable information on crude nitrocellulose.

Since we have a large sample of crude water-wet nitrocellulose on hand, we shall be glad to place samples of this material at the disposal of other interested investigators as long as our supply remains.
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solutions kept in them for several days did not show any detectable change in pH (6.5 to 7 before and 6.5 to 7 after).

The titration values given in Tables I and II are milliliters of 0.01 N sodium hydroxide solution per gram of dry collodion. The titrations were carried out with a microburette, phenol red being used as indicator. The accuracy is about 0.03 ml. 0.01 N sodium hydroxide solution. The pH determinations may be assumed to be accurate to better than 0.1 unit.

VI

As indicated above, the influence of the time factor on the base exchange must be known. Table I gives titration and pH values obtained with two “active” collodion preparations at several reaction times.

Oxidized collodion was prepared by treating U.S.P. Baker Collodion Cotton with “molar” sodium hypobromite solution for 24 hours, as described above, followed by thorough washing. The “crude nitrocellulose” was prepared from sample “B” by removal of excess free sulfuric acid by boiling with water for several hours. Both samples were precipitated as described above.

9 gm. of dry collodion were added to 300 ml. of water and potassium chloride solution. These samples were shaken for several minutes by hand and allowed to react further under occasional shaking. 10 ml. samples of the clear supernatant fluid were removed after measured periods and their pH determined with the glass electrode. The samples were then titrated with sodium hydroxide solution.

Table I shows that base exchange with precipitated collodion is a rather slow process. Inaccessible inner surfaces or diffusion processes in and out of the solid material, or both, obviously play an important rôle. A material with an open structure, particularly if in a finely divided state, as is the case with our precipitated fibers, should reach base exchange equilibrium within very short periods.

An appreciable difference between the two preparations investigated is apparent. The precipitated crude collodion obviously has a more open structure than the precipitated oxidized collodion. The latter, though it eventually yields a greater base exchange, required about 6 hours to exchange to the same extent as the crude nitrocellulose in 15 minutes. The microscopic differences between the two preparations were too small to account for this difference. We are thus forced to conclude that the precipitated fibers have a somewhat different submicroscopic structure which obviously must result from molecular differences.

Table I also shows that the two tested collodion preparations fulfill, at least very closely, the first of the conditions necessary for true base exchange, namely, no reaction with water, which could be considered to be of real significance. The probable meaning of the slight shift of pH in the water will be discussed.
briefly below. There we will also see that the other necessary condition for true base exchange is also fulfilled, namely, agreement between the acidity values as found with our two independent methods, titration and electrometric pH determination.

Following the example of Beutner, Caplan, and Loehr, we arbitrarily chose 2 days as the standard reaction time for our further experiments, though much could be said in favor of a shorter time. However, the selection of the 2 day period is bound to bring out more clearly the differences between the active and inactive preparations. It has the further advantage of increasing the absolute effects, thus rendering them easier to determine.

The arbitrary choice of the reaction time, whatever its length may be, necessitates a brief discussion concerning the exact meaning of the experimental data. We measure the actual base exchange which takes place during the standard time. Table I indicates—and this is of importance—that our measurements listed in Table II give values much greater than those which in all probability correspond to the dissociable groups which cause the characteristic electrochemical behavior of membranes. The latter, as we may repeat here, appears

<table>
<thead>
<tr>
<th>Time of reaction</th>
<th>NaOH per gm. dry collodion on treatment with</th>
<th>pH values on treatment with</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05 M KCl</td>
<td>Water</td>
</tr>
<tr>
<td>15 min.</td>
<td>0.00</td>
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<tr>
<td>1 hr.</td>
<td>0.00</td>
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<td>6 hrs.</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>24 hrs.</td>
<td>0.13</td>
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<tr>
<td>2 days</td>
<td>0.29</td>
<td>0.00</td>
</tr>
<tr>
<td>1 wk.</td>
<td>0.54</td>
<td>0.00</td>
</tr>
<tr>
<td>2 wks.</td>
<td>0.57</td>
<td>0.00</td>
</tr>
<tr>
<td>5 wks.</td>
<td>0.56</td>
<td>0.00</td>
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<tr>
<td></td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>15 min.</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>1 hr.</td>
<td>0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>6 hrs.</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
<td>24 hrs.</td>
<td>0.27</td>
<td>0.00</td>
</tr>
<tr>
<td>2 days</td>
<td>0.30</td>
<td>0.00</td>
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<tr>
<td>1 wk.</td>
<td>0.35</td>
<td>0.00</td>
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<tr>
<td>2 wks.</td>
<td>0.39</td>
<td>0.00</td>
</tr>
<tr>
<td>5 wks.</td>
<td>0.39</td>
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</table>
nearly instantaneously on contact with electrolyte solutions. All the values, therefore, obtained with our standard method are decidedly higher than those which should be correlated to the electrochemical activity of collodion. We will have to consider the consequence of this fact later.

It may be noted that repeated renewal of the electrolyte solution does not alter the measured base exchange in a given period of time, as compared with that obtained when the collodion is in contact with the same solution over the whole period.

VII

In Table II are listed the base exchange and activity data obtained with some representative collodion preparations of different origin and different pretreatment. In all cases, unless indicated otherwise, precipitated fibers were used.

50 ml. of water or 0.5 M potassium chloride solution were added to 1.5 gm. of dry collodion in 125 ml. Pyrex Erlenmeyer flasks. In the case of the wet preparations, an amount of collodion corresponding to 1.5 gm. of dry material was taken. The samples were shaken for several minutes and allowed to react for 48 hours with occasional shaking. After this, 10 ml. samples of the supernatant, clear, fiber-free liquid were titrated; in another sample, the pH was determined with a glass electrode. Column 2 of Table II gives the brand and pretreatment—if any—of the studied collodion preparations. In the cases of "Celloidin Schering-Kahlbaum cut in cubes" (No. 7 a and 7 b)—following the procedure of Beutner, Caplan, and Loehr—the stiff (about 20 per cent) commercial Celloidin alco-gel was cut in small cubes (about 4 × 4 × 3 mm.) and treated exactly as the other (fibrous) preparations. Here too, the listed values are per gram of dry substance.

In columns 3 and 4 are listed the ash and sulfate content of our preparations, determined as described previously.

Columns 5 and 6 indicate the milliliters of 0.01 N NaOH solution used per gram of dry collodion after 48 hours contact with 0.5 M KCl solution and with water respectively.

Columns 7 and 8 show the pH values (as determined with a glass electrode) of the KCl solution and water after 48 hours contact with collodion. Whether or not any conclusions can be drawn from the experimentally measured pH values which lie between 5.3 and 7 will be discussed below.

Columns 9 and 10 give the pH values calculated from the titration values of columns 5 and 6 under the assumption that the NaOH used has neutralized HCl in an unbuffered system.

On account of the experimental limitations of our titrations, titration values of 0.00 ml. 0.01 M sodium hydroxide correspond in our table to calculated pH values which may lie anywhere between 5 and 7. Therefore, the calculated pH values in columns 9 and 10 are given in all these cases as >5 to indicate the limitations of our volumetric experiments.

Columns 11 and 12 indicate the electrochemical activity of the different collodion
preparations. Bag-shaped membranes were prepared as described previously. The same method of characterization was used as in preceding papers. The membranes tested were as far as possible of the same porosity, as indicated by their behavior when tested with sucrose solution. The figures in column 11 indicate the millimeter pressure rise observed 20 minutes after the membranes filled with 0.25 M sucrose solution were placed in distilled water. Column 12 gives the anomalous osmotic rise in millimeters of water obtained after 20 minutes with 5/1250 potassium sulfate solution. As shown previously, the rate of this rise is a rather sensitive indicator of the electrochemical activity of collodion.

Before discussing the main results of Table II, it is necessary to clarify some technical points. First, we may consider the question of the importance of the ash and sulfate content of our collodion preparations. As was pointed out above, there is no indication that the ash and sulfate content should appreciably influence the base exchange (and activity) of collodion. This view is substantiated by a close inspection and comparison of the data of columns 3 and 4, 5 and 6, 7 and 8, (and 12) of Table II; particular attention should be paid to the data referring to the genetically related samples 7, 7a, 8, and 9; 10 and 10b; 11 to 14. High ash and sulfate content is compatible with zero base exchange and high pH values (see particularly cases 6, 8, 9, 10, and 14). In the process of precipitation the surfaces of collodion have obviously been freed thoroughly from soluble impurities by their contact with water, though some of the sulfate may be present in an insoluble combined form. The bulk of the sulfate and ash found by analysis is obviously so thoroughly enclosed in the fibers that no significant amount is able to diffuse out within short periods. These impurities, therefore, can be disregarded completely for our further discussion.

The fact that drying does not seem to affect the base exchange properties of our precipitated fibers can be concluded from a comparison of cases 10 and 10a, 12 and 12a.

Case 10b, crude collodion in the state of native fibers (nitrat ed cotton) which was obtained in the alcohol wet state, is quoted to give an idea of the characteristics of such preparations.

Let us next consider the data obtained with the same material as that used by Beutner, Caplan, and Loehr—"Celloidin." Cases 7a and 7b are as accurate repetitions as possible of the experiments of these authors. The results listed in columns 5 to 8 are in complete agreement with theirs. We want to emphasize here again that some substance or substances which neutralize sodium hydroxide on titration obviously were dissolved in the water. Therefore, we are not dealing with a simple base exchange. This conclusion can also be derived from the fact that there is a large discrepancy between the experi-
mentally found pH values and those calculated from the titration data. For the "base exchange" with water, such a calculation is, of course, absolutely fictitious. The pH values indicate that the dissolved substances were either very weakly acid or contained some acidic component. In the case of the "base exchange" with potassium chloride solution the situation is substantially the same, though it may be that some (though very small) true base exchange occurred. A pH of 4.5 corresponds in our experiments to a titration value of only about 0.1 ml. 0.01 N sodium hydroxide. As we are dealing with acidic impurities, a buffering action upon the hydrochloric acid which may have been developed by true base exchange seems to be ruled out. Here again we are dealing mainly if not exclusively with some process of dissolution.

The nature of the soluble substances is without particular interest here, but this much must be said. It is known that inadequately purified nitrocellulose ("Celloidin" comes into this class1-2) not only contains water-soluble material which normally is removed by purification, but also decomposes spontaneously in course of time13 as shown on a large scale by Silberrad and Farmer.13 Nitrous compounds are formed in such preparations. They act upon the nitrocellulose forming many kinds of lower molecular weight substances mostly of an acidic nature. Moreover, they obviously render a fraction of the nitrocellulose water-soluble. These water-soluble compounds probably account for a very great part of the high titration values with sodium hydroxide solution.

It is known that alkalies do not react in a straightforward manner with many "nitro" compounds such as nitric acid esters, but destroy them in an oxidative manner with the formation of nitrites,14 etc. 1 gm. of nitrocellulose in contact with an excess of sodium hydroxide uses a quantity which corresponds to more than 1000 ml. of 0.01 N hydroxide solution. Thus a very small amount of dissolved nitro-compound may use up large quantities of hydroxide solution.

Here the question arises as to how far the behavior of the "Celloidin" gel cut in cubes is paralleled by the base exchange properties of material prepared from solutions of this preparation, as membranes would necessarily be. Case 7 of

12 Such spontaneous decomposition of "Celloidin" accounts also for the inability of Michaelis and collaborators (Green, A. A., Weech, A. A., and Michaelis, L., J. Gen. Physiol., 1929, 12, 473) to produce highly dried collodion membranes having a constant electrical conductivity, as suggested already by the above authors. One can expect that membranes prepared from better stabilized collodion would not present the same difficulties.


Table II shows the behavior of “Celloidin” after precipitation from ether-alcohol solution in water. There is no “base exchange” with water while with the potassium chloride solution, there is some appreciable reaction. Obviously, most of the soluble and reactive material is removed from the surfaces of the precipitated fibers in the very process of precipitation; no appreciable diffusion of such material from the interior of the fibers takes place, though the salt solution is obviously able to peptize some material (which reacts on titration with sodium hydroxide) as indicated by the discrepancy between the values in columns 7 and 9.

The large differences in the “base exchange” properties of “Celloidin” gel
TABLE II—Concluded

<table>
<thead>
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<th>1</th>
<th>2</th>
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<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
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<tbody>
<tr>
<td>10</td>
<td>Crude collodion cotton sample A (which was obtained washed with alcohol)</td>
<td>1.1</td>
<td>0.8</td>
<td>0.00</td>
<td>0.00</td>
<td>5.7</td>
<td>5.8</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>105</td>
<td>150</td>
<td>115</td>
</tr>
<tr>
<td>10a</td>
<td>Crude collodion cotton sample A, not dried after precipitation</td>
<td>0.00</td>
<td>0.00</td>
<td>5.6</td>
<td>5.9</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>115</td>
<td>160</td>
<td></td>
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<tr>
<td>10b</td>
<td>Crude collodion cotton sample A in the original fibrous state, (not precipitated)*</td>
<td>2.3</td>
<td>2.8</td>
<td>1.40</td>
<td>1.27</td>
<td>3.5</td>
<td>3.6</td>
<td>3.4</td>
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<td>122</td>
<td>166</td>
<td>136</td>
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<tr>
<td>11</td>
<td>Crude collodion cotton sample B*</td>
<td>1.0</td>
<td>3.4</td>
<td>0.67</td>
<td>0.00</td>
<td>3.9</td>
<td>5.0</td>
<td>3.7</td>
<td>&gt;5</td>
<td>122</td>
<td>166</td>
<td>136</td>
</tr>
<tr>
<td>12</td>
<td>Crude collodion cotton sample B, boiled 3 times 3 hrs. each with water</td>
<td>0.5</td>
<td>0.7</td>
<td>0.26</td>
<td>0.00</td>
<td>4.1</td>
<td>5.6</td>
<td>4.1</td>
<td>&gt;5</td>
<td>120</td>
<td>166</td>
<td>156</td>
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<tr>
<td>12a</td>
<td>Same as No. 12, but not dried after precipitation</td>
<td>0.23</td>
<td>0.00</td>
<td>4.1</td>
<td>5.8</td>
<td>4.1</td>
<td>&gt;5</td>
<td>135</td>
<td>187</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Crude collodion cotton sample B, washed 6 times with 95 per cent alcohol and boiled 3 times 30 min. each with water</td>
<td>1.0</td>
<td>1.4</td>
<td>0.06</td>
<td>0.00</td>
<td>4.7</td>
<td>6.1</td>
<td>4.7</td>
<td>&gt;5</td>
<td>120</td>
<td>166</td>
<td>136</td>
</tr>
<tr>
<td>14</td>
<td>Crude collodion cotton sample B, boiled 7 hrs. with 70 per cent alcohol (2 alcohol changes)</td>
<td>1.6</td>
<td>1.0</td>
<td>0.00</td>
<td>0.00</td>
<td>5.8</td>
<td>6.6</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>112</td>
<td>166</td>
<td>126</td>
</tr>
<tr>
<td>15</td>
<td>Oxidized collodion; (Baker collodion cotton, &quot;Pyroxilin&quot;) oxidized 24 hrs. with 1 M NaOBr</td>
<td>0.3</td>
<td>&lt;0.2</td>
<td>0.27</td>
<td>0.00</td>
<td>4.2</td>
<td>6.4</td>
<td>4.1</td>
<td>&gt;5</td>
<td>118</td>
<td>160</td>
<td>130</td>
</tr>
<tr>
<td>16</td>
<td>Oxidized collodion (No. 15), washed 8 times with 95 per cent alcohol</td>
<td>&lt;0.3</td>
<td>&lt;0.2</td>
<td>0.15</td>
<td>0.00</td>
<td>4.5</td>
<td>6.2</td>
<td>4.4</td>
<td>&gt;5</td>
<td>124</td>
<td>166</td>
<td>126</td>
</tr>
<tr>
<td>17</td>
<td>Oxidized collodion (No. 15), washed 16 times with 95 per cent alcohol</td>
<td>&lt;0.3</td>
<td>&lt;0.2</td>
<td>0.00</td>
<td>0.00</td>
<td>5.0</td>
<td>6.7</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>132</td>
<td>166</td>
<td>136</td>
</tr>
<tr>
<td>18</td>
<td>Oxidized collodion (No. 15), washed 25 times with 95 per cent alcohol</td>
<td>&lt;0.3</td>
<td>&lt;0.2</td>
<td>0.00</td>
<td>0.00</td>
<td>5.3</td>
<td>6.5</td>
<td>&gt;5</td>
<td>&gt;5</td>
<td>120</td>
<td>166</td>
<td>126</td>
</tr>
</tbody>
</table>

* This preparation contains much free sulfuric acid.

and fibers prepared from the same material make it improper to transfer data obtained with the former to the problem of the electrochemical behavior of membranes.

Precipitated Schering-Kahlbaum Collodion "zur Herstellung von Membranen" (case 5 in Table II) gives off small quantities of soluble material even into water, but is otherwise similar to the precipitated "Celloidin" (case 7). Like Schering-Kahlbaum "Celloidin", Schering-Kahlbaum Collodion "zur Herstellung von Membranen" was also classified in previous reports1, 2 as a poorly purified product.

IX

It is obvious that the collodion preparations mentioned in the preceding paragraphs are unsuitable for our purpose, namely, the study of the true base exchange properties. Only preparations which give zero titration values with water, and in addition, a reasonably good agreement between the experi-
mentally found pH values of column 7 and the calculated values of column 9 are suitable for this purpose. Approximate agreement between the two assures one that true base exchange occurs, though some other factor (solubility) may make itself felt to some extent. Fortunately, proper purification yields products of the desired properties.

Agreement ordinarily within the limits of our experimental (titration) error exists in cases of the precipitated preparations, 1, 2, 3, 4, 6, 8, 9, 10, 11, 12, 13, 14, and 15 to 18. None of these preparations, it may be noted, shows a reaction with water sufficiently large to be detected by titration. Cases 11, 12, 13, 15, and 16 precipitated crude collodion and precipitated oxidized collodion, show measurable base exchange values. In all the other cases, (1, 2, 3, 4, 6, 8, 9, 10, 14, 17, 18), the base exchange is too low to be measurable by titration (i.e., less than 0.03 ml.), and correspondingly, the pH values are greater than 5.

Focusing our attention now entirely on the cases mentioned in the preceding paragraph, we may finally turn toward our main objective, namely, the possible correlation of base exchange properties and electrochemical activity (as exemplified by the data on anomalous osmosis—column 12 of Table II) of the different samples of precipitated collodion.

If we take the titration values as the measure of the base exchange we find (1) cases which combine “zero” base exchange with low electrochemical activity, No. 1, 2, 3, and 4; (2) cases which combine measurable base exchange with great activity, No. 11, 12, 13, 15, and 16; (3) cases which combine “zero” base exchange with great activity, No. 6, 8, 9, 10, 14, 17, and 18.

As yet, we have not found a case combining chemically measurable base exchange with low activity.

It is particularly interesting to compare the genetically related samples: 5 with 6; 7 with 8 and 9; 11 and 12 with 13 and 14; 15 with 16 and 17 and 18. The relatively small, sometimes hardly significant changes in activity are somewhat in contrast with the large differences in base exchange.

The general result of Table II can thus be summarized by saying that no regular correlation exists between chemically measurable base exchange capacity and electrochemical activity.

Low as well as high activity can be associated with a base exchange capacity too low to be measurable by titration. High, i.e., measurable base exchange capacity always seems to be correlated with high electrochemical activity.

If we turn our attention now to the correlation between pH values and electrochemical activity, we arrive at exactly the same classification as before if we arbitrarily take pH 5 as a demarcation line. This, of course, is simply a necessary consequence of the fact that in all the cases which are considered here, a reasonable quantitative agreement exists between pH and base exchange data.

But now the question arises as to how far pH values greater than 5 may be
used as a basis for more far-reaching conclusions. It is not possible to answer this question without discussing some possible errors and the limitations of the method. Small pH changes near the neutral point, of course, mean very little if taken singly; but consistently analogous data when taken as a whole may have considerable weight and may be used for certain limited conclusions.

If our collodion preparations were perfectly inert substances, water in contact with them should not undergo a change in pH. However, this is not the case. The pH on treatment with water varied between 5.7 and 6.7 for the different samples tested. It is somewhat paradoxical that some of the "inactive" pure commercial preparations caused a greater shift in pH than most of the purified "active" samples. This is easily understood, however, on the basis of the fact that even very pure collodion is not absolutely stable. The "inactive" preparations had stood for some time before use and thus contained more soluble acidic impurities than the recently purified "active" preparations. This agrees also with the fact that some experiments, not listed in the tables, demonstrate that our specially purified products cause a greater shift in pH if not used in the freshly prepared state.

Since solubility effects may change the pH even in pure water from neutrality (pH 6.5 to 7) to a pH of 5.7, we are inclined to believe that such effects are appreciably stronger in salt solutions as the latter may have some peptizing effect. Without a special and thorough investigation of each individual case, it is impossible to say with accuracy how great a fraction of the pH change observed in potassium chloride solution must be attributed to true base exchange and how large a proportion to solubility. In some cases, e.g., in the not specially purified samples 1 and 4, the latter fraction is probably rather large. In cases 8, 17, and 18, on the other hand, true base exchange is most likely the prevailing factor, as can be concluded from a comparison with the respective genetically related samples.

No matter what limiting value we assume for the significance of the pH measurements in the potassium chloride solutions, i.e., whether 5.3 or 5.6, the main result of our investigation remains quite the same, though one or two cases (No. 1 and No. 4) would now be listed under a fourth heading, namely, cases which combine base exchange measurable by physical means with low electrochemical activity. With the present methods, no regular correlation can be found empirically between base exchange capacity as determined by physical methods and electrochemical activity.

16 Here we must disregard case 11 which is obviously influenced by its high content of free sulfuric acid, traces of which diffuse into the water during the long—48 hours—contact time.

18 We have gained the impression that extremely well purified collodion preparations also show a slight increase in activity when stored for prolonged periods; this is obviously likewise due to a slow decomposition and oxidation.
From the point of view of a membrane investigation, a more thorough study of the factors mentioned in the last few paragraphs would become a pertinent problem only after it has been shown that such a study could contribute materially to our fundamental knowledge of membrane structure. A more detailed discussion of any possible quantitative correlation of base exchange capacity and electrochemical activity would necessarily have to wait for much more accurate data. But for the reasons discussed above, it may be very difficult, perhaps impossible, to obtain such data with collodion. However, at this point, the following statement can be made with certainty: The base exchange capacity which is necessary to cause even great electrochemical activity of collodion is very small, just at the borderline of usefulness of the present experimental technique, more probably even beyond it.

We have arrived at this result without taking into account the time effect (Table I). Here we must remember that the electrochemical properties of collodion membranes are apparent nearly instantaneously on contact with electrolyte solutions. This means that the electrochemical behavior of membranes obviously is determined by those ionizable groups which lie exposed in the water-solution interface in the pores. It therefore would be preferable in a more thorough discussion of the correlation of electrochemical activity and base exchange to consider the base exchanges after short periods. Thus, the base exchanges which should be taken as the basis for any discussion are actually much smaller than the values of Table II, which refer to the exchange situation in fibrous collodion after 48 hours. Therefore, the italicized statement made above concerning the magnitude of the base exchange which is necessary to produce great electrochemical activity is true in an even more pointed manner.

The base exchange which corresponds to the true physical cause of the electrochemical activity of collodion is much too small to be determined with the available methods. Considering the instability of collodion, we doubt whether even a great improvement in technique could lead with this material to significant results.

In spite of this somewhat puzzling result reached in the last paragraph, there is no escape from the conclusion reached previously that dissociable groups built into the collodion cause its electrochemical activity. Preferential ion adsorption was shown to be ruled out as a major factor, at least in solutions of strong, weakly adsorbable ions. Such an assumption could never explain the differences in electrochemical activity which are observed with different collodion preparations.

A visualization of the true situation can obviously be found in the direction

17 On the basis of these considerations, one might expect that membranes prepared from the crude collodion (referred to in Table I b) would have at least not a lower electrochemical activity than those prepared from the oxidized collodion (Table I a). This is actually the case as can be seen from No. 12 and No. 15, columns 11 and 12 in Table II, which refer to the same preparations as Table I a and I b.
of the following reasoning: measurable base exchange disappears earlier on purification than the pronounced electrochemical activity. Our methods of determining the two are of different sensitivity. The electrochemical properties of the collodion, i.e., of the collodion-solution interfaces, are determined by a smaller number of ions than can be detected with certainty in the external solution. By proper and prolonged purification, one can reduce the number of dissociable groups contained in collodion to a very low level. Finally even the electrochemical activity disappears nearly entirely, as can be seen from the low “activity” of highly purified collodion. Cases 1, 3, and 4 refer to commercial collodion preparations. No. 1 (Mallinckrodt “Parlodion”), which is manufactured for greatest purity, is the purest and least active among all the many commercially available preparations we have tested. Case 2 is of particular interest since it shows that even this specially purified material loses activity when further purified. For this, fibrous Mallinckrodt “Parlodion” was boiled for 15 hours with 90 per cent alcohol (about 18 gm. of material per liter alcohol); the latter was changed twice to remove more thoroughly the soluble material. There is no reason to believe that even the very low residual activity of the purified “Parlodion” could not be reduced further by proper methods. Any activity above this level is therefore due to impurities foreign to the ideal nitrocellulose. In fact, we can be certain that the true reference point of activity, which is caused by the presence of dissociable impurities, lies considerably below the level obtained with the purified “Parlodion.” We may even venture to speculate that pure ideal nitrocellulose should be nearly completely void of any distinct electrochemical properties when immersed in pure water or aqueous solutions of strong inorganic electrolytes. Of course, at this low level of electrochemical activity, preferential ion adsorption could become an important factor even with weakly adsorbable electrolytes.

The bearing of the results of our base exchange studies upon the general problem of electrochemical membrane behavior is obvious, at least in a qualitative way.

It seems difficult to reconcile our results with the homogeneous phase theory on account of the extremely small concentration of active groups, which in some way or the other, obviously determine the electrochemical behavior of membranes. On the other hand, the pore theory too seems to run into great difficulties, at least when assuming more or less uniform, prismatic pores, as is tacitly assumed in the proposed mathematical theories. We should like to indicate briefly a line of reasoning which may overcome these difficulties, namely, the assumption of a geometrical-structural irregularity, such as must necessarily be assumed, a priori, for a microheterogeneous system such as the collodion membrane. If we think of pores not as uniform prismatic channels
but as random sequences of narrow constrictions and wide cavities, it is immedi-
ately evident that the narrowest constriction in each possible channel deter-
mines the permeability of the latter. A single charge at a point of constriction
could easily determine the electrochemical behavior of the whole pore. Thus
a very small number of dissociable groups in a membrane, less than that con-
tained in a monomolecular film of equal dimensions, could, if properly distrib-
uted, determine the electrochemical behavior even of voluminous structures.
It would be interesting to follow up some consequences of this general concept
and of its implications when applied to biological systems. It likewise would
be attractive to compare these ideas with certain theories of membrane struc-
ture and membrane behavior which are based on somewhat opposite assump-
tions.¹⁸

However, we prefer to postpone a more detailed discussion of these points
to a later date, until certain studies dealing with the uptake of liquid from
water and electrolyte solutions by dried collodion membranes and with their
swelling will, it is anticipated, contribute data which may allow us to discuss
profitably on an experimental basis the controversial problem of continuous
phase theory versus pore theory. The true situation seems to be less simple
than assumed by either theory. The above mentioned controversy obviously
must be settled at least to some extent before an attempt is made to deal with
a quantitative membrane theory. A quantitative test of certain aspects of
the outstanding examples of an electrochemical membrane theory based on a
correlation of concentration potential measurements and base exchange studies
on membranes is now being carried out. Using the methods (and prepara-
tions) described in this paper, it will show clearly the quantitative
significance of base exchange studies for the problem of electrochemical membrane behavior.

SUMMARY

1. Theoretical considerations lead to the conclusion that dissociable acidic
groups present to a varying extent in different collodion preparations determine
the electrochemical behavior of membranes cast from these preparations. It
is further reasoned that the base exchange capacity of the collodion surfaces is
the true quantitative measure of the abundance of the dissociable groups.

2. The concept of base exchange capacity and the base exchange method are
discussed. The conditions which allow a purposeful application of the latter
are stated.

3. The base exchange properties of a number of fibrous collodion prepara-
tions of different origins and after various types of treatment, having widely
varying electrochemical activities, are determined.

¹⁸ See, e.g., Manegold, E., Koloid-Z., 1932, 61, 140; and many other papers by
the same author in the Koloid-Zeitschrift.
4. With the chemical (titration) and physical (electrometric) methods employed, no regular correlation can be found between electrochemical activity and base exchange. The base exchange capacity which is necessary to cause even great electrochemical activity of collodion is extremely small.

5. Measurable to high base exchange capacity always seems to be associated with good or high electrochemical activity; but base exchange capacity too low to be definitely measurable with the available methods may be found with collodion preparations of high as well as with preparations of low electrochemical activity.

6. The bearing of these results upon the problem of the spatial and electrical structure of the collodion membrane is indicated briefly.