

THE STRUCTURE OF THE COLLODION MEMBRANE AND  
ITS ELECTRICAL BEHAVIOR

VIII. QUANTITATIVE STUDIES CONCERNING THE ACIDIC PROPERTIES OF  
COLLODION AND THEIR CORRELATION WITH MEMBRANE STRUCTURE  
AND ACTIVITY

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I

In preceding papers<sup>1-3</sup> it was shown that the electrochemical behavior of collodion membranes in solutions of strong, weakly adsorbable electrolytes is due to the presence of acidic impurities in the collodion. Pertinent quantitative data were obtained from base exchange studies.<sup>4</sup> No regular correlation was found between "electrochemical activity"<sup>1-4</sup> and base exchange capacity. A measurable base exchange capacity seems to be associated always with good or high electrochemical activity; but base exchange capacities too low to be definitely measurable with the methods used were found with collodion preparations of high as well as with low electrochemical activity.

The very low base exchange capacities even of very active preparations could be due to a very low content of acidic groups or to a lack of availability for base exchange of the majority of them. Thus, it became of interest to obtain quantitative information on the equivalent weight of collodion preparations of different electrochemical activity and to compare it with their base exchange capacity. In this way one could hope to obtain valuable information on the relative availability of the acid groups and on the submicroscopic, micellar structure of collodion fibers or collodion membranes from different preparations.

On certain aspects of this problem we already have some information. Work from this laboratory indicates that the base exchange capacity corresponds to but a fraction of all the acid groups present in collodion. Furthermore we already know what the rate at which base exchange occurs varies with different collodion preparations, faster base exchange being indicative of relatively open structure.<sup>4</sup>

<sup>1</sup> Sollner, K., and Abrams, I., *J. Gen. Physiol.*, 1940, **24**, 1.

<sup>2</sup> Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **24**, 467.

<sup>3</sup> Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **25**, 7.

<sup>4</sup> Sollner, K., Carr, C. W., and Abrams, I., *J. Gen. Physiol.*, 1942, **25**, 411.

## II

The experimental approach to our problem is quite obvious; a number of collodion preparations of different past history and varying electrochemical activity are brought into the state of free acids by the exchange of all other cations for hydrogen ions, and their acidity—their acid number—in the dissolved state as well as their base exchange capacity in the fibrous state are determined.

The preparations used in the present study were prepared in the same manner as described previously.<sup>4,5</sup> Electrodialysis for 72 hours did not change the free acidity of these preparations.

For the *base exchange* experiments, as in the prior work, fibrous collodion was employed. The reasons for the use of fibrous collodion were (1) that different preparations can readily be brought into approximately the same physical state, a condition which is necessary for any comparative investigation, (2) that the precipitated collodion fibers exhibit a maximum surface thus yielding the highest obtainable (and thus most easily determined) base exchange for each preparation, (3) that the collodion in this state is brought in a fairly reproducible manner into a condition similar to the state it assumes in highly porous membranes.

The base exchange experiments were carried out essentially as described previously,<sup>4</sup> in all cases the water blank was negligible.<sup>4</sup> The double distilled water used for all experiments had a pH of 6.5 to 7.2.

To measure the base exchange 50 ml. of water or 0.5 N potassium chloride solution was added to 1.5 gm. of dry fibrous collodion in 125 ml. Pyrex Erlenmeyer flasks. The samples were shaken for several minutes and allowed to react—unless otherwise stated—for 48 hours with occasional shaking. 10 ml. samples of the supernatant fiber-free liquid were used for the determination of the pH (with a glass electrode) and the same samples were also used for titration.

For the present work we used a somewhat more accurate titration procedure than previously. We made use of a micrometer microburette which allows readings to be made with an accuracy of about 0.001 ml.<sup>6</sup> Another change was that a glass electrode was used to determine the neutral point instead of phenol red, which was used in previous work. The reagent used for titration was 0.015 N sodium hydroxide. The accuracy of the experimental figures as given below in column 7 of Table I is about  $\pm 0.004$  ml. of 0.01 N solution. As previously the results given below in the tables are expressed in milliliters of 0.01 normal solution per gram of dry collodion.

The *acid number* was determined by potentiometric titration of the collodion which was dissolved in a suitable organic solvent as described by Clarke, Wooten, and Comp-

<sup>5</sup> In the present work the commercial preparations were treated more carefully than previously (Sollner, K., Carr, C. W., and Abrams, I., *J. Gen. Physiol.*, 1942, **25**, 411), for we had found that these preparations which were stored in the laboratory for some time gave off some acidic impurities arising from spontaneous decomposition. Repeated short boiling in the fibrous state with double distilled water satisfactorily removed these impurities.

<sup>6</sup> Dean, R. B., and Fetcher, E. S., Jr., *Science*, 1942, **96**, 237.

ton;<sup>7</sup> Wooten and Ruehle;<sup>8</sup> and Ruehle.<sup>9</sup> (See also below.<sup>10</sup>) The titration is performed with a solution of alkali hydroxide in an organic solvent. The electrode which responds to the change in acidity is a quinhydrone electrode; some quinhydrone is added to the collodion solution, with a bright platinum wire dipping into it. The reference electrode is a calomel half cell which is connected in the usual manner by means of a potassium chloride-agar bridge to the solution. To increase the conductance of the titrated solution some saturated solution of lithium chloride in alcohol is added. Nevertheless, the ohmic resistance of the system is rather high and an electron tube voltmeter must be used. For this purpose we have used the volt scale of a commercial (Leeds and Northrup) glass electrode.

We have tested a number of different solvents and solvent mixtures for their suitability for our special problem. Some of the solvents recommended in the literature are not obtainable in a sufficiently pure state and can be purified only with considerable difficulty. On account of their ready availability in great purity, we finally worked with acetone and absolute alcohol, mixtures of which show excellent solvent properties for collodion.

To obtain satisfactory results, it is necessary to take certain precautions. The quinhydrone should be carefully recrystallized and stored in a dark bottle. The platinum electrode must be heated in a flame prior to each experiment. The lithium chloride solution is prepared by refluxing 200 gm. of the best obtainable grade of the salt with 1 liter of absolute ethyl alcohol; it is stored in a dark bottle in the dark. The reagent used was 0.015 N potassium hydroxide dissolved in absolute ethyl alcohol. It is kept in a blackened Pyrex glass bottle in the dark. Advantageously, the bottle is kept rather full to minimize the influence of the oxygen of the air. Daily supplies are withdrawn from this bottle and kept ready for use in a small bottle. The titer of the potassium hydroxide solution was determined by titration of a known aqueous hydrochloric acid solution. The titer should be checked at frequent intervals, as any change in titer indicates a very disturbing change in the solution, probably due to spontaneous oxidation. The titrations were carried out with a micrometer microburette of the above mentioned type;<sup>6</sup> a stream of nitrogen bubbles was passed through the solution during the titration to stir the solution and to prevent the interference of carbon dioxide.

The experiments were carried out in 10 ml. of 2.5 per cent collodion solution in a mixture of 50 per cent acetone and 50 per cent absolute ethyl alcohol to which 0.5 ml. of the saturated solution of lithium chloride in alcohol was added. About 20 mg. of quinhydrone were added and nitrogen is bubbled through the solution. The electrodes are inserted into the solution and the potential difference is read on the millivolt scale of the electron tube voltmeter. The reagent is added step-wise and the

<sup>7</sup> Clarke, B. L., Wooten, L. A., and Compton, K. G., *Ind. and Eng. Chem., Analytical Edition*, 1931, **3**, 321.

<sup>8</sup> Wooten, L. A., and Ruehle, A. E., *Ind. and Eng. Chem., Analytical Edition*, 1934, **6**, 449.

<sup>9</sup> Ruehle, A. E., *Ind. and Eng. Chem., Analytical Edition*, 1938, **10**, 130.

<sup>10</sup> For valuable private information we are indebted to Dr. H. M. Spurlin, Hercules Experiment Station, Wilmington, Delaware.

corresponding potential values are determined. The true neutralization point is determined in the conventional graphic manner.

To test the titration method we have carried out some determinations of known concentrations of benzoic and salicylic acid; benzoic acid, undoubtedly, is a weaker acid than the "nitrocellulosic acid" in which we are interested.<sup>11</sup>

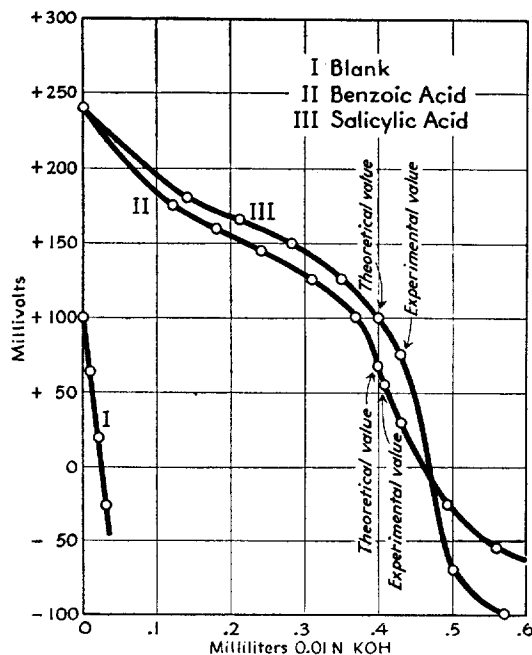


FIG. 1

Sample curves for benzoic and salicylic acid are given in Fig. 1, together with a blank. The latter, as can be seen easily, is negligible.

Sample curves for the titration of various collodion preparations are given in Fig. 2; the ordinate indicates millivolts, the abscissa, milliliters of 0.01 normal solution for 0.25 gm. collodion. The shape of the titration curves for collodion does not allow too accurate an evaluation. An error of  $\pm 5$  per cent may occur in many instances. This, however, is of no significance for our particular problem.

Any chemical reaction with the collodion aside from the straightforward

<sup>11</sup> The strength of "cellulosic acid," (oxycellulose) is of the same order of magnitude as salicylic acid. (See, *e.g.*, Neale, S. M., and Stringfellow, W. A., *Tr. Faraday Soc.*, 1937, **33**, 881.) One would expect that "nitrocellulosic acid," oxidized nitrocellulose, would be a stronger acid than non-nitrated oxycellulose.

neutralization of its free acid groups is bound to falsify the results. With a material so liable to be decomposed by alkali solutions as collodion it was therefore necessary to test whether or not the reagent added in the process of titration may not act upon the nitrocellulose. This was the more advisable as conceivably the quinhydrone too could be a disturbing factor.

To decide this question, a large sample of a relatively inactive collodion was dissolved in a mixture of 50 per cent acetone and 50 per cent absolute alcohol and titrated with 0.02 N alcoholic potassium hydroxide solution in the presence of the usual con-

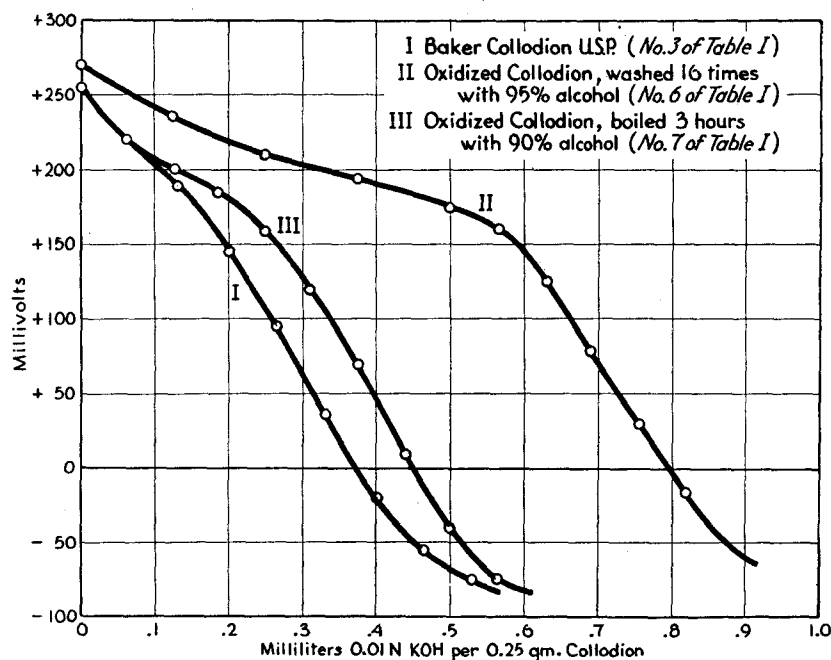


FIG. 2

centrations of lithium chloride and quinhydrone. Next the resulting solution was allowed to drip into a great excess of vigorously stirred water, our standard method of preparing fibrous collodion. The fibrous preparation thus obtained was washed and electrolyzed for 24 hours to return it to the state of free acidity. After this the material was dried.

A part of the dried product was again dissolved in the standard mixture of alcohol and acetone and titrated as before. The results of the first and this second titration agreed with each other well within limits of experimental error.

The other part of the collodion which had undergone titration, reprecipitation, electrolysis, and drying was dissolved in ether-alcohol. Membranes were prepared from this solution and their activity was compared by our usual anomalous osmosis

method<sup>1-4</sup> with the activity of membranes prepared from the original material. No difference between the two preparations could be detected.

From the two foregoing experiments it can be concluded that the collodion in the process of titration does not undergo any chemical changes which influence its acid number. Thus we are sure that the acid number as found by titration of collodion in the dissolved state can be considered to be the correct measure of the free acidity of the collodion.<sup>12</sup>

### III

In Table I are listed the acid values and base exchange data obtained with some representative preparations of different activity and varying acidity.

Column 2 of Table I gives a brief description of the nature of each preparation.

In columns 3 and 4 are listed the ash and SO<sub>4</sub> contents determined by previously described methods.<sup>2</sup>

Column 5 gives the acid values expressed in milliliters of 0.01 N hydroxide solution per gram of dry collodion, column 6 the acid values corrected for the base content of the ash.<sup>13</sup> Below we will see that for our purpose it is actually

<sup>12</sup> We have also tried the following method to determine the acid number of collodion; it was devised originally by Wilbrandt (Wilbrandt, W., *J. Gen. Physiol.*, 1935, **18**, 933) for a similar purpose, though on the basis of entirely different theoretical assumptions, which we have discussed and criticized in an earlier paper (Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **24**, 467). The method consists of determining the limiting number of equivalents per gram of collodion of basic material which renders the collodion electroneutral. Dried collodion membranes are prepared from a series of collodion solutions containing increasing concentrations of such basic substances as methylene blue or quinine. The concentration of basic materials is determined at which the concentration potential 0.1 M KCl/0.01 M KCl changes its sign. At this point the negative charges of the membrane are neutralized electrically by what is supposed to be an equivalent quantity of base. For a number of reasons such experiments give results which, though in rough agreement with the results of the titration method, are not better than semiquantitative in character. We therefore only mention this method without going into further details.

<sup>13</sup> The ash content is by no means all basic material; in most cases more than half of the weight of the ash is SO<sub>4</sub>. In one sample we found 26 per cent Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>, 7 per cent calcium oxide, and 11 per cent sodium oxide. The aluminum and iron oxides in all probability form but slightly dissociated or non-dissociable compounds. Thus, if we assume that 25 per cent of the weight of the ash behaves like sodium, we certainly have not underestimated the degree to which potentially active acid groups in the collodion are neutralized from the beginning. With an ash content of 0.1 mg. per gm. collodion this would correspond to 0.025 mg. sodium per gm. or about 1 milliequivalent of sodium per kilogram dry collodion. Expressed as are the acid num-

immaterial whether we base our considerations on the uncorrected or the corrected acid number values.

Column 7 indicates the milliliters of 0.01 *N* hydroxide solution per gram of dry collodion which were used to neutralize 0.5 *N* potassium chloride solution after 48 hours contact with the collodion.

Column 8 shows the pH values (as determined with a glass electrode) of the potassium chloride solution after 48 hours contact with collodion.

Column 9 gives the base exchange values calculated from the pH values of column 8 under the assumption that the acidity which is found experimentally is caused by hydrochloric acid in an unbuffered system. The difference between the base exchange values as obtained by direct titration (column 7) and those calculated from the pH values (column 9) is a measure of the dissolution of some material from the collodion which reacts with NaOH. The values of column 9 are therefore a more correct expression of the true base exchange than those of column 7. For a discussion of this point we refer to a prior paper.<sup>4</sup>

Columns 10 and 11 indicate the electrochemical activity of the different collodion preparations. The same method of characterization was used as in preceding papers.<sup>1-4</sup> The membranes tested were approximately of the same porosity, as indicated by their behavior when tested with sucrose solution, the figures in column 10 indicating the millimeter pressure rise observed 20 minutes after the membranes filled with 0.25 *M* sucrose solution were placed in distilled water. Column 11 gives the anomalous osmotic rise in millimeters of water obtained after 20 minutes with *m*/512 potassium sulfate solution. As shown previously,<sup>2, 3</sup> the rate of this rise is a rather sensitive indicator of the electrochemical activity of collodion.

Table II gives some representative data, demonstrating the influence of time upon the base exchange. The preparations 3*a*, 4*a*, and 6*a* used for these experiments were not the same but parallel samples of the corresponding preparations Nos. 3, 4, and 6 in Table I.

#### IV

We turn now to the discussion of the main problems of this paper: (*a*) the comparison of the acid number of preparations of different electrochemical activity; (*b*) the comparison of the base exchange capacity of the different preparations in the fibrous state; (*c*) the comparison between the base exchange capacity and the acid number of the individual collodion preparations; and (*d*)

\_\_\_\_\_ bers in Table I, this is 0.1 ml. of 0.01 *N* sodium hydroxide solution per gram dry collodion.

In calculating the values of column 6 the appropriate additions have been made to the values in column 5. Since the base content of the ash is probably lower rather than higher than the assumed 25 per cent sodium, some of the corrected values of column 6 are probably slightly too high.

TABLE I  
*Acid Number, Base Exchange, and Activity of Various Collodion Preparations*

1	2	3	4	5	6	7	8	9	10	11
	Brand of collodion and pretreatment (All preparations were precipitated from ether-alcohol solutions and dried)	Ash and SO <sub>4</sub> content		Acid No.		Base exchange data (48 hrs.)			Electrochemical activity	
		Ash per gm. dry collodion	SO <sub>4</sub> per gm. dry collodion	0.01 N KOH per gm. dry collodion		0.01 N NaOH per gm. dry collodion found experimentally on treatment with 0.5 M KCl	pH values found experimentally on treatment with 0.5 M KCl	0.01 N NaOH per gm. dry collodion, calculated from pH values of column 8	Osmotic rise with 0.25 M sucrose	Anomalous osmotic rise $\frac{m}{M}$ K <sub>2</sub> SO <sub>4</sub> with 512
				Experimental	Corrected for ash					
		mg.	mg.	ml.	ml.	ml.		ml.	mm.	mm.
1	Mallinckrodt "Parlodion," commercial preparation	<0.2	<0.1	1.0	1.2	0.011	6.3	0.0016	110 120 127	36 40 45
2	Mallinckrodt "Parlodion," boiled 8 hrs. in 90 per cent alcohol (2 alcohol changes)	Very low	Very low	0.85	1.0	0.008	6.4	0.0013	108 110 114	28 18 22
3	Baker Collodion u.s.p., commercial preparation	0.4	0.2	1.1	1.5	0.03	5.9	0.004	115 121 130	52 40 60
4	Oxidized collodion; (Baker Collodion Cotton, "Pyroxilin") oxidized 48 hrs. with 1 M NaOBr and boiled several times with water	0.3	<0.2	3.0	3.3	0.29	4.1	0.26	130 140 158	145 138 178
5	Oxidized collodion (No. 4), washed 8 times with 95 per cent alcohol	<0.3	<0.2	2.7	2.9	0.19	4.5	0.11	135 144 158	180 145 172
6	Oxidized collodion (No. 4), washed 16 times with 95 per cent alcohol	<0.3	<0.2	2.6	2.8	0.03	5.7	0.0066	122 138 148	137 145 155
7	Oxidized collodion (No. 4), boiled 3 hrs. with 90 per cent alcohol	<0.3	<0.2	1.4	1.6	0.03	5.7	0.0066	135 140 150	125 134 120



a comparison between the acid number and the base exchange capacity of the various preparations on the one hand and their electrochemical activity on the other.

The *acid numbers* of the different preparations (column 6, Table I) vary only from 1.0 ml. of 0.01 N hydroxide per gm. for the most highly purified preparation to 3.3 ml. for highly oxidized collodion. Only a small fraction of the total acidity can possibly be due to semiesterified sulfuric acid.<sup>14</sup> The ratio of the extremes of the observed acid numbers is only 1:3.3. The mean equivalent weights which correspond to these acid values are 100,000 and 30,000 respectively.<sup>15</sup>

<sup>14</sup> On the basis of more indirect evidence we came in an earlier publication (Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **24**, 467) to the conclusion that the sulfate content plays only a minor rôle if any in determining the electrochemical properties of collodion. This can now be shown definitely by comparing the sulfate contents (column 4 of Table I) with the corresponding acid numbers of column 6. If all the sulfate is present in the semiesterified form, a sulfate content of 0.1 mg. per gm. collodion corresponds fairly accurately to 0.1 ml. 0.01 N hydroxide solution. Thus, with the pure commercial preparations listed in Table I, the possible maximum contribution of sulfuric acid compounds to the overall acidity is only 8 to 13 per cent, with the oxidized collodion preparations less, corresponding to their higher titratable acidity.

<sup>15</sup> The acid numbers of the commercial collodion preparations vary from 1.2 to 1.5 ml. of 0.01 N hydroxide solution per gm. collodion; this corresponds to (mean) equivalent weights of 67,000 to 83,000. We may assume that our collodion corresponds fairly closely to cellulose tetranitrate which carries two O—NO<sub>2</sub> groups per glucose residue and has a "molecular weight" of 252. Then, the mean chain length per carboxyl group would be 260 to 330 glucose residues. Using the same technique as with collodion, we found a similar chain length also with several acetylcellulose preparations. Our results are in good agreement with the corresponding values given by different authors for purified cellulose; Heymann and Rabinov (Heymann, E., and Rabinov, G., *J. Physic. Chem.*, 1941, **45**, 1152), *e.g.*, find 300, Sookne and Harris (Sookne, A. M., and Harris, M., *J. Research Nat. Bureau Standards*, 1940, **25**, 47; (*Nat. Bureau Standards, Research Paper RP 1313*)) about 600 glucose residues per carboxyl group. The carboxyl groups are believed to be present as the one end group of the cellulose molecule. (See further, *e.g.*, Sookne, A. M., Fugitt, C. H., and Steinhart, J., *J. Research Nat. Bureau Standards*, 1940, **25**, 61; (*Nat. Bureau Standards, Research Paper RP 1314*); Neale, S. M., and Stringfellow, W. A., *Tr. Faraday Soc.*, 1937, **33**, 881.) We may add that it is customary to assume on the basis of viscosity, osmotic, and ultracentrifuge studies, that the degree of polymerization of native cellulose and nitrocellulose derived therefrom is about 2,000 to 3,000 glucose residues per molecule. (See, *e.g.*, Ott, E., *Ind. and Eng. Chem.*, 1940, **32**, 1641.)

From the foregoing figures it is clear that the dissociable acidic groups occupy only a very small fraction of the surface of cellulose and nitrocellulose molecules.

In considering the *base exchange capacity* it is necessary for the reasons outlined above to consider the figures calculated on the basis of pH measurements (column 9). In the following discussion we will assume that the very low base exchange values found with some preparations can be taken at their face value. However, we must recall that these values, as discussed previously at length,<sup>4</sup> are only maximum possible values; the figures given in the table for the cases 1, 2, and 3 are undoubtedly too high. The very great importance of the time factor will be discussed in the next section.

With the base exchange we find enormous differences between different preparations, less than 0.002 ml. of 0.01 N hydroxide solution per gm. for very inactive preparations (compare column 11), values as high as 0.26 ml. for oxidized collodion of high activity, and values down to 0.0066 ml. for oxidized collodion which was treated thoroughly with alcohol, but nevertheless has retained considerable electrochemical activity. The ratio of the lowest and the highest base exchange values reported in Table I is about 1:200, whereas the difference in the acid numbers of the same preparations is as noted above only 1:3.3.

We turn our attention next to the *correlation of acid number and base exchange capacity of the individual collodion preparations*. To do this, we compare the figures of columns 6 and 9 of Table I. This comparison shows that with the pure preparations 1, 2, and 3 not more than one in about 380 to 770 of all the acid groups is available for base exchange. With oxidized collodion, which was purified by repeated boiling with water, No. 4 of Table I, this ratio is about one in 13; with oxidized collodion, which was washed eight times with alcohol (No. 5), the ratio is increased to one in about 26; with more thoroughly purified oxidized collodion, the ratio increases to one in 240 for case 7 and one in 420 for case 6.

Thus we see that there are enormous differences in the availability for base exchange of the acidic groups of the various collodion preparations. The much higher base exchange capacity of oxidized collodion in the fibrous state is not so much due to its higher acid number as to its more open micellar structure. The variations between the several preparations are thus indicative of differences in micellar structure.

The more open structure of oxidized collodion is probably due to the presence of a small percentage of low molecular weight material which inhibits normal formation and arrangement of the micelles. That repelling forces between charged groups—the carboxyl groups—may play an important rôle in the formation of collodion micelles and their arrangement can on the basis of analogous cases be considered to be rather unlikely. The impurities which account for the open structure of oxidized collodion can be gradually removed by purification (cases 5 to 7 of Table I). But even very thorough purification yields a material of a somewhat more open structure (case 7) than the original unoxidized preparation, in spite of the fact that the acid number is reduced approximately to its original value.

We have so far not discussed the time factor with regard to the availability of the acidic groups for base exchange and the typical membrane functions. Our calculations so far have been made on the basis of the base exchange obtained after 48 hours. However, we must remember that membranes brought into a KCl solution assume (if they are not unduly thick) their final electrical

TABLE II  
*The Influence of the Time of Reaction on the Base Exchange of Various Collodion Preparations*

A. Baker collodion U.S.P. (sample 3a)		
Time of reaction	pH values on treatment with 0.5 M KCl	Ml. 0.01 N NaOH per gm. dry collodion calculated from pH values
5 min.	—	—
30 min.	6.8	0.0005
1 hr.	6.4	0.0013
6 hrs.	6.2	0.0021
12 hrs.	6.0	0.0033
24 hrs.	5.9	0.0042
48 hrs.	5.9	0.0042
B. Oxidized collodion (sample 4a)		
5 min.	6.0	0.0033
30 min.	5.5	0.011
1 hr.	5.0	0.033
6 hrs.	4.6	0.084
12 hrs.	4.2	0.21
24 hrs.	4.1	0.26
48 hrs.	4.1	0.26
C. Oxidized collodion washed 16 times with 95 per cent alcohol (sample 6a)		
5 min.	6.5	0.0011
30 min.	6.3	0.0017
1 hr.	6.1	0.0026
6 hrs.	5.9	0.0042
12 hrs.	5.8	0.0053
24 hrs.	5.7	0.0066
48 hrs.	5.7	0.0066

properties; *i.e.*, conductance and membrane potential, within several minutes, as soon as the electrolyte has penetrated. Therefore only those groups which are placed so as to exchange readily can contribute significantly to the characteristic properties of membranes. Though it is impossible to estimate accurately the quantity of these readily exchanging groups, experiments on the influence of time on the base exchange will give some useful hints. As before, we consider the base exchange values which are calculated from the experi-

mental pH values. Table II contains such data. The preparations used (3a, 4a, 6a) are, as said before, very similar to Nos. 3, 4, and 6 respectively in Table I.

If we look at the base exchange values obtained after 5 or 30 minutes we certainly obtain a more correct picture of the availability of the dissociable groups which determine the typical electrochemical properties of collodion. In addition we must consider the fact that collodion fibers exhibit a greater number of dissociable groups in readily available places than more coherent and compact structures like most collodion membranes, particularly fairly dense ones. On this basis we come to the conclusion that the ratio of available dissociable groups in collodion membranes to those present in the preparation is hardly less than fifty times and probably rather a thousand times smaller than given above. We may therefore estimate this ratio to be rather 1:500 to 1:1,000,000 than 1:13 to 1:770, according to the preparation used.<sup>16</sup>

Finally we turn to the *correlation of acid number and base exchange capacity of the various collodion preparations to their electrochemical activity.*

The acid numbers (column 6, Table I) on which we base this comparison do not need any critical remarks. For base exchange values we use the data obtained in 48 hour exchange experiments (column 9, Table I), keeping in mind the above discussed restrictions of their significance.

As a measure of the electrochemical activity we use the mean of the three values given in column 11 of Table I for each of the collodion preparations. It is necessary to recall briefly the basis and significance of these figures.<sup>1, 2, 3</sup> They represent the rate of anomalous osmosis observed under arbitrary but standardized conditions. Bag-shaped membranes (30 × 110 mm.) of approximately identical porosity (column 10 of Table I) filled with m/512 K<sub>2</sub>SO<sub>4</sub> solution are immersed in water and the pressure rise in a capillary manometer tube is measured after 20 minutes. This pressure rise according to experiments by Loeb is for a given membrane proportional to the electrokinetic ( $\zeta$ ) potential times the membrane ( $\epsilon$ ) potential.<sup>17</sup> Theoretical considerations of Sollner show that the relationship is more complicated.<sup>18</sup> The pressure rise, that is the extent of the anomalous osmosis, is proportional to the electrokinetic ( $\zeta$ ) potential times the difference of the  $\epsilon$ -potentials which arise between different parts or pores of the membrane; this difference is the driving force in the process of anomalous osmosis. The  $\zeta$ -potential increases with increasing charge density

<sup>16</sup> These ratios can be taken as a quantitative indication of the discrepancy between collodion membranes and membranes which behave as homogeneous "oil" phases. In the latter type of membranes all the functional groups (acid groups in our case) are available for the characteristic membrane function.

<sup>17</sup> Loeb, J., *J. Gen. Physiol.*, 1922, **4**, 463; and many other papers in the preceding volumes of the same Journal.

<sup>18</sup> Sollner, K., *Z. Elektrochem.*, 1930, **36**, 36; 1930, **36**, 234.

(number of exchanging groups per unit area) up to a certain limiting value which cannot be surpassed. Any further increase of the charge density does not lead to higher values of  $\zeta$ . The correlation of driving force and charge density is not simple; it is not necessarily proportional to the measurable membrane potential. Higher charge density need not necessarily lead to an increase of the difference between local membrane or pore potentials. A simple consideration shows that a positive correlation cannot be expected with high charge densities. Thus the anomalous osmotic pressure rise is by no means a simple and straightforward quantitative measure of the "electrochemical activity," particularly with highly active preparations.

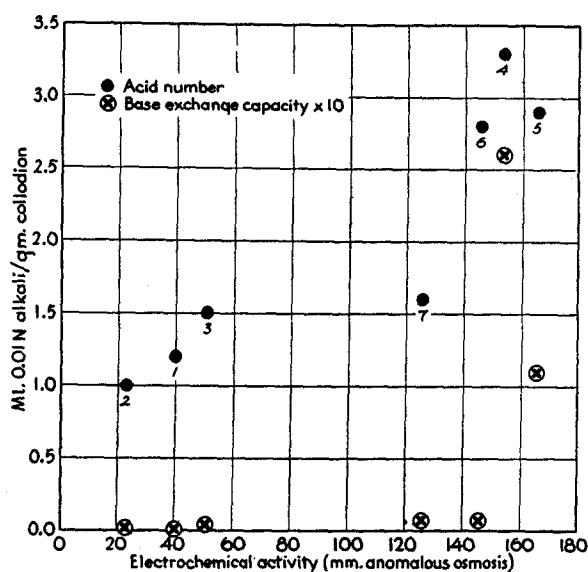


FIG. 3

With these reservations in mind we have plotted in Fig. 3 the electrochemical activity of the various preparations given in Table I against their acid numbers (dots) and base exchange capacities (crosses). In order to accommodate both sets of data in one graph the base exchange values are plotted enlarged ten times.

There is a reasonably good *correlation between acid number and electrochemical activity*. Low acid numbers are found with the preparations of lowest activity, the highest acid numbers are found with the most active preparations, though medium acid numbers are found with a fairly inactive (No. 3) as well as with a fairly active preparation (No. 7). An explanation of this latter discrepancy must be looked for in the above discussed difference in structure between the

commercial (No. 3) and the highly purified oxidized preparation (No. 7). The base exchange data indicate a somewhat more open structure of the latter material. One must assume that this results in a somewhat less smooth, more irregular, and rougher nature of the walls of the pores. This would lead to the exposure of a greater number of active groups in spots which can make an essential contribution towards the electrochemical activity.

The *correlation between base exchange capacity and activity* as pointed out in a previous paper is not as good. Low base exchange capacity is associated with low as well as with high electrochemical activity; high base exchange capacity is always associated with great electrochemical activity. Obviously the base exchange capacity which must be shown by a preparation to give rise to high electrochemical activity is very small, not more than barely measurable; any further increase in base exchange capacity does not cause a great positive increment in the electrochemical activity as measured by the anomalous osmosis method. This can be understood on the basis of two factors. First, as pointed out before, the electrochemical activity, as measured with the anomalous osmosis method, cannot be expected to increase steadily when the charge density increases over a certain level. The second factor must be looked for in this direction: the process of anomalous osmosis through the highly porous membranes used takes place essentially in the wider pores which traverse the membrane; it is inconsequential for this process if the functionally active pore walls have a microporous structure. If the pore walls have a structure of the latter type, parts of the membrane skeleton, which do not contribute to the process of anomalous osmosis, may easily be available for base exchange. Thus the more open microstructure, which as discussed above is found so pronouncedly with the less purified oxidized collodion preparations, easily may account for much of the apparent lack in parallelism between base exchange capacity and electrochemical activity as determined by the anomalous osmosis method. If the comparison between electrochemical activity and base exchange were based on short time base exchange values (Table II) a better agreement between the two sets of data would be found, since the differences in base exchange between the different preparations are less pronounced in short time experiments than after 48 hours. The inaccuracy of the very low short time base exchange values, however, makes it impractical to evaluate them quantitatively. In a forthcoming paper we intend to discuss certain aspects and consequences of the heteroporous character of collodion membranes.

One could attempt to use the acidity and base exchange capacity data, which were given above, for some comparison of collodion membranes with monomolecular films or for an estimation of the number of pores per unit area. However, we do not think that this at present would be a particularly fruitful beginning. The spread of the figures we could start out with is very wide; it also would be necessary to base the calculations on some additional estimates and some arbitrary assumptions. The problem of the number of pores per square

centimeter was treated in the past mostly on the basis of the assumption that pores of more or less uniform cross-section traverse the membrane in a fairly regular manner with little or no cross-connections. Such a situation, however, certainly does not prevail in dried collodion membranes or "porous" membranes of the type used in our previous work. We always must remember that the interstices in a collodion membrane are irregular, non-uniform, and inter-connected; furthermore many dead-end spaces exist undoubtedly.

The availability of the pore space for the most typical membrane function, the penetration of third substances, is moreover not only governed by the complex and unknown interplay of the above mentioned and similar factors, but also by the characteristics of the third substance. Pathways which are available for small molecules are unavailable for bigger ones.

In order to characterize structures like membranes with regard to their important functional properties, it is necessary to look for new approaches which are less formal than those ordinarily used in the past. A study of the functional properties of the membranes, their permeability, their ionic selectivity, *i.e.* their electromotive properties, and their conductance in solutions of various electrolytes and different concentration will furnish the data of most interest. Knowledge of the geometrical structure of membranes is of interest mainly in as far as it helps to coordinate, to explain, and to visualize the functional membrane properties.

This does not mean that the application of other physical methods in elucidating the structure of collodion membranes is of no interest. Quite to the contrary, we think that such methods should be exploited to the limit; such studies<sup>19</sup> are bound to give us a fuller understanding of the data which may be obtained with the above mentioned methods of functional membrane characterization.

Our next problems will be to prepare fairly uniform membranes with well

<sup>19</sup> Due to the wartime conditions we shall not be able to attack the purely physical aspects of our wider problem in the near future. The obvious approach would be the use of x-rays to obtain some information as to the size and arrangement of the micelles in collodion fibers, in porous and in dried membranes. We also think that the electron microscope could conceivably be of great help in the study of extremely thin membranes. If, *e.g.*, the molecules are arranged into micelles in such a manner that many end carboxyl groups come to lie next to each other, like the points of a bundle of pencils, then these groups, if neutralized with ions of a metal having a high atomic number (*e.g.*, Pb or Hg), may become visible with the electron microscope.

Another problem that requires fundamental investigation is the coordination of our findings with regard to the scarcity of dissociable groups in collodion with the conventional concepts of the electric double layer and of the electrokinetic potential. A combination of electroosmotic and cataphoretic studies with collodion should go far towards elucidation of this question. Some of the apparent difficulties will be resolved, at least partially, by the assumption of structural irregularities which we hope to discuss at greater length in a forthcoming paper.

defined electrochemical characteristics, and to investigate their electrochemical properties; *i.e.*, their conductance and electromotive behavior in solutions of different electrolytes.

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#### SUMMARY

1. The electrochemical behavior ("activity") of collodion membranes depends upon acidic, dissociable groups located in the interstices of the membranes. The active groups can be determined by base exchange measurements. High base exchange capacity is always found with preparations of great "electrochemical activity;" medium and low base exchange capacities occur with electrochemically active as well as with inactive preparations. The observed base exchange capacity is determined by two factors: the inherent acidity of the collodion (its mean equivalent weight) and the submicroscopic micellar structure of the collodion. A comparison of the base exchange capacity of various collodion preparations and their inherent acidities therefore allows certain conclusions to be drawn concerning the relative availability of the micellar surfaces in the different preparations.

2. The inherent acidity of various collodion preparations, their "acid number," was determined by electrometric titration. Collodion in the acidic state, *i.e.* after exchange of all other cations for  $H^+$  ions, was titrated in an organic solvent mixture with alcoholic KOH using a quinhydrone electrode. Details of the experimental procedure are given in the paper. The acid numbers, expressed in milliliters of 0.01 N KOH per gram dry collodion, vary from 1.0 for a highly purified collodion preparation of very low electrochemical activity to 3.3 for a highly oxidized sample of very high activity. Acid numbers of about 1.5 (corresponding to an equivalent weight of about 67,000) are found both with inactive commercial and with fairly active oxidized preparations. The base exchange capacity of the same preparations in the fibrous state as measured after 48 hours of exchange time varies from 0.0013 ml. 0.01 N NaOH per gm. dry collodion for the most inactive preparation up to 0.26 ml. 0.01 N NaOH per gm. for the most active preparation. Thus the acid numbers over the whole range investigated differ only in the ratio of 1:3.3, whereas the base exchange values differ in the range of 1:200.

3. In the inactive preparation only one in 770 acid groups is available for base exchange, in the most active collodion one group in 13; values between these extremes are found with commercial and alcohol purified oxidized preparations.

4. The high base exchange capacity of the electrochemically active preparations is not so much due to their higher acid number as to their more open structure. This difference in structure is ascribed to the presence of a small



fraction of low molecular weight material which inhibits normal formation and arrangement of the micelles.

5. Short time base exchange experiments with fibrous collodion indicate that the number of acid groups available for the typical electrochemical membrane functions may be estimated to be about 50 to 1000 times less numerous than those found in the 48 hour base exchange experiments. It is estimated that in membranes prepared even from the most active collodion not more than one in 500 acid groups may be available for the typical membrane functions; with the less active preparations this ratio is estimated to be as high as one in 1,000,000 or more.