

THE STRUCTURE OF THE COLLODION MEMBRANE AND ITS ELECTRICAL BEHAVIOR

I. THE BEHAVIOR AND PROPERTIES OF COMMERCIAL COLLODION

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In the past there have been very many investigations of the behavior of collodion membranes with special attention to the phenomena and problems associated with electrolyte diffusion, or more properly, ion penetration. However, the fundamental characteristics of such membranes are still inadequately understood. Highly dried membranes with low permeability and high selectivity were investigated thoroughly by Michaelis and his co-workers.¹ Their work and that of later students has not, however, satisfactorily elucidated the more intimate reasons for the behavior of such membranes. The characteristics and behavior of membranes of greater permeability, which have even more biological significance, have received less attention than they deserve.

The absolute necessity of further investigation of the properties of collodion membranes has recently been emphasized by our indifferently successful attempts² to reproduce the fundamental observations of Loeb³ on anomalous osmosis. Using a number of brands of collodion, only one (foreign) brand gave anomalous osmosis approaching the findings of Loeb.

This unexpected difference between different collodion preparations immediately suggested that even a partial clarification was bound to be of considerable importance. In order to be able to continue current investigations, we were forced to clarify this matter since, due to the war, it became

¹ Michaelis, L., and Fujita, A., *Biochem. Z.*, Berlin, 1925, **158**, 28; 1925, **161**, 47; 1925, **164**, 23; Michaelis, L., and Dokan, Sh., *Biochem. Z.*, Berlin, 1925, **162**, 258; Michaelis, L., and Hayashi, K., *Biochem. Z.*, Berlin, 1926, **173**, 411; Michaelis, L., and Perlzweig, W. A., *J. Gen. Physiol.*, 1927, **10**, 575; Michaelis, L., McEllsworth, R., and Weech, A. A., *J. Gen. Physiol.*, 1927, **10**, 671; Michaelis, L., Weech, A. A., and Yamatori, A., *J. Gen. Physiol.*, 1927, **10**, 685; Michaelis, L., *Bull. Nat. Research Council*, No. 69, 1929, 119; *Kolloid-Z.*, 1933, **62**, 2; and other publications.

² Sollner, K., and Abrams, I., *J. Gen. Physiol.*, 1940, **24**, 1.

³ Loeb, J., *J. Gen. Physiol.*, 1918-19, **1**, 717; 1919-20, **2**, 173, 225, 387, 563, 577, 659, 673; and many other papers in the succeeding volumes of the same *Journal*.

more and more difficult, finally impossible to procure the (imported) collodion which had the desired properties.

The resulting investigation has led to an increased knowledge of the factors responsible for the electrochemical behavior of collodion membranes. Furthermore, we are now able to prepare membranes of a very high degree of electrochemical activity at will in the laboratory (Part II, to be published later).

A review of the literature showed that other investigators have had similar experiences when studying the electrical, particularly electromotive properties of collodion membranes.

In 1927 Michaelis and Perlzweig⁴ tested at least ten different nitrocellulose preparations before finding one suitable for their studies of the electromotive behavior of highly dried collodion membranes. Only "Celloidin Schering" gave membranes which consistently showed maximum concentration potentials and reasonably measurable permeabilities (electric conductivity). The other preparations yielded membranes showing very poor electrical conductivity (permeability), low concentration potentials, or a combination of the two.

In 1935, Wilbrandt⁵ (in Michaelis' laboratory) observed the same fact again and remarks that "Kollodium Schering-Kahlbaum DAB 6" "yielded the membranes with the highest and the most consistent concentration potentials, while with other types of collodion lower and less consistent potentials were obtained" ". . . the membranes with low potentials often had a high resistance and vice versa." Table I shows the potentials of various types of membranes as found by Wilbrandt.

Some results concerning anomalous osmosis which have been obtained consistently by the present authors are summarized in Table II. It should be stated that anomalous osmosis is necessarily a very sensitive indicator of the electrical activity of a membrane.⁶ The values given are pressure rises in a manometer tubing after 20 minutes when a bag containing the solution indicated is placed into distilled water. For details of the technique the reader is referred to our previous paper. The membranes used

⁴ Michaelis, L., and Perlzweig, W. A., *J. Gen. Physiol.*, 1927, **10**, 575.

⁵ Wilbrandt, W., *J. Gen. Physiol.*, 1935, **18**, 933.

⁶ According to Loeb's experiments (see footnote 3) and the theory of one of us (Sollner, K., *Z. Elektrochem.*, 1930, **36**, 36, 234), the extent of anomalous osmosis is proportional to the product of electrokinetic (ζ) potential and membrane (ϵ) potential. As both of these magnitudes are directly dependent upon the electrochemical structure of a membrane, it is easily understood that any phenomenon which is proportional to the product of the two must necessarily be a very sensitive indicator of the "activity" of a membrane.

were, as far as possible, of the same porosity, as tested by their behavior towards sugar solution. No amount of effort and experimenting (*e.g.*, changing the porosity) obliterates these characteristic differences between

TABLE I
(After Wilbrandt)
Concentration Potentials of Collodion Membranes of Various Brands of Collodion, Measured between $\pi/100$ and $\pi/1000$ KCl (in mv.)

Brand of collodion	Concentration potential	
	Highest value	Lowest value
Collodion Mallinckrodt.....	25	16
Collodion Merck U.S.P. X.....	48	10
Kollodium Schering-Kahlbaum "zur Herstellung von Membranen".....	50	38
Kollodium Schering-Kahlbaum "zur Analyse".....	46	35
Kollodium Schering-Kahlbaum DAB 6.....	56	50

TABLE II
Anomalous Osmosis through Membranes Prepared from Several Brands of Collodion

Brand of collodion	Osmotic rise with sugar $\frac{M}{4}$	Anomalous osmosis		
		KCl $\frac{M^*}{256}$	K ₂ SO ₄ $\frac{M^*}{512}$	K ₂ -citrate $\frac{M^*}{128}$
		mm.	mm.	mm.
"Parlodion" Mallinckrodt.....	130	8	35	24
Collodion Merck U.S.P.....	128	14	54	112
Collodion Baker U.S.P.....	128	6	48	130
Collodium Schering-Kahlbaum "pro analysi".....	122	8	55	132
Collodium Schering-Kahlbaum "zur Herstellung von Membranen".....	125	19	100	262
"Celloidin" Schering-Kahlbaum "for general use".....	126	70	228	410
Collodium Schering-Kahlbaum DAB 6.....	124	26	195	390

* This concentration was chosen because it gives maximum effects with membranes of moderate activity.²

different brands of collodion. Several other brands⁷ of ether-alcohol soluble nitrocellulose not listed in the tables were also tested. Their behavior and their content of impurities are about the same as those found with the domestic brands of collodion obtainable from supply houses.

⁷ For providing such samples of nitrocellulose we should like to express our thanks to the Hercules Powder Company and the American Cyanamid and Chemical Corporation.

Incidentally, it may be mentioned that Preuner and Roder,⁸ investigating anomalous osmosis at about the same time as Loeb, used a Schering collodion, called "Kolloidin," for their experiments.

Though many casual remarks concerning our problems are contained in the membrane literature, only very few papers deal specifically with it. Most of the older work on collodion membranes assumes more or less tacitly that the electrical properties of such membranes are due to ion adsorption. This view, lately considered skeptically by many investigators, at least for strong electrolytes, could hardly furnish a basis for an explanation of our problem, namely, the differences between different brands of collodion.

Michaelis, in one of his latest papers on collodion membranes,⁹ makes the following statement pertaining to our problem:

"It must be left to a further study of the experts of collodion manufacture to investigate how this effect is influenced by the method of manufacturing. It certainly is not the degree of nitration. But after personal discussions with experts, I think it possible that the degree of degradation of the original cellulose molecule during the process of nitration is of importance. The specific effect seems to be greater the more intact the molecular size of the cellulose remains during nitration."

Wilbrandt, in considering this question, says "This difference is certainly not due to different sizes of pores, for the membranes with low potentials often had a high electric resistance and vice versa. Different degree of nitration does not seem, either, to be the cause." The NO₂-groups of the nitrocellulose—according to Wilbrandt—act as dipoles, with the negative charge directed towards the intermolecular spaces, *i.e.* towards the pores, thus causing in some way the charge of the membrane. "Now Mathieu," Wilbrandt continues, "has found that the rearrangement of the molecules in the films, especially in the highly nitrated ones, was very variable. Sometimes he obtained very sharp interferences, sometimes very indistinct patterns. It is highly probable that the variability of concentration potentials is due to this variability of the arrangement of the molecules."

Wilbrandt, in common with most earlier authors, bases his discussion of the collodion membrane and its behavior entirely on a consideration of the ideal nitrocellulose molecule. The ideal nitrocellulose molecule should be an inactive substance whatever its NO₂ content may be. However, it should be noted that collodion, *i.e.* ether-alcohol soluble nitrocellulose, is not cellulose hexanitrate but contains definitely less nitrogen. A detailed

⁸ Preuner, G., and Roder, O., *Z. Elektrochem.*, 1922, **28**, 54.

⁹ Michaelis, L., *Kolloid-Z.*, 1933, **62**, 2.

discussion of Wilbrandt's special views is beyond the scope of this paper. Suffice it to say that in our opinion it does not seem likely that dipoles should be able, in the manner indicated by Wilbrandt, to influence the charge of the membrane. The structure of an electrical double layer, particularly in the presence of considerable concentrations of electrolytes, can hardly be influenced to such an extent merely by oriented dipoles. The results of our investigations presented in this paper moreover make the hypothetical assumptions of Wilbrandt entirely unnecessary.

Meyer and Sievers,¹⁰ emphasizing a point mentioned by several earlier investigators, believe that the electrical properties of collodion membranes are due to acid groups: "These acid groups could be carboxyl groups which are always found in cellulose, or possibly semi-esterified sulfate groups." At another place they mention pectic substances as possible carriers of acid groups.

That cellulose and cellulose derivatives generally have a certain degree of acidity seems to be universally acknowledged. Cellulose chemists usually discuss these properties in a casual way under the heading "oxycellulose."¹¹ A recent paper of Beutner, Caplan, and Loehr¹² deals specifically with the acidic properties of collodion. In a subsequent paper we hope to discuss this problem from a broader angle and a quantitative point of view. Whatever the outcome of these investigations will be, the general idea that impurities of an acidic nature cause the electrochemical activity of collodion lends itself to an experimental test. According to this general view, activity and degree of impurity should go parallel, the most active brands being the most impure ones.

It seems to be not without significance that the most inactive of the brands of collodion ("Parlodion" Mallinckrodt) tested by Wilbrandt and ourselves is also the most expensive one and that Kollodium Schering-Kahlbaum DAB 6 and "Celloidin for general use" are the least expensive grades among the Schering-Kahlbaum preparations.

A product like ether-alcohol soluble nitrocellulose (collodion) is undoubtedly variable in different respects as to degree of nitration, particle

¹⁰ Meyer, K. H., and Sievers, J.-F., *Helv. Chim. Acta*, 1936, **19**, 649, 665.

¹¹ It is obviously outside the scope of this paper to discuss the very controversial matter of "oxycellulose." The interested reader is referred to the literature. Summaries may be found, e.g. in Schwalbe, C. G., *Die Chemie der Cellulose*, Berlin, Borntraeger, 1910/11 and 1918, particularly pp. 221 ff., and Hess, K., *Die Chemie der Zellulose und ihrer Begleiter*, Leipzig, Akademische Verlagsgesellschaft, 1928, particularly pp. 455 ff.

¹² Beutner, R., Caplan, M., and Loehr, W. M., *J. Biol. Chem.*, 1933, **101**, 391.

size distribution and mean molecular weight, impurities, etc. These factors may all be interrelated to some extent.

Nevertheless, a better knowledge of the factors basically determining the electrochemical behavior of collodion should carry us a step further toward the solution of a problem which has puzzled many investigators in the past.

It may be worthwhile at this point to recall the conventional process of nitrocellulose manufacture, which in essence is as follows: Cellulose is swelled in NaOH, bleached if necessary with chlorine to obtain a colorless product; it is then washed, dried, and treated with a mixture of nitric and sulfuric acids. This product is freed from acid by washing, followed by prolonged boiling with a very dilute acid solution or with water. For products of a high degree of purity, this boiling process may be carried on for 100 hours or longer. From the rather indefinite statements in the literature one gets the idea that this very prolonged washing is necessary to hydrolyze certain sulfuric acid compounds, probably esters.

One, therefore, has to expect that collodion prepared from poor, unclean raw material would always yield an "active" collodion, since thorough bleaching would be necessary. We may safely assume that such bleaching would yield many oxidized groups, the end groups of the cellulose chain molecule and possibly CH_2OH -groups being acted upon. Sufficient oxidation would result in the presence of carboxyl groups on the nitrocellulose chain. These acid groups could be the factor determining the electrochemical properties of membranes prepared from such material.

Since oxidation is known to cause a splitting of cellulose chains, one would expect that such a product would have a lowered mean molecular weight. Consequently it should show low tensile strength in the dry state, as in the form of a film, and low viscosity when dissolved.

Unclean raw material may also contain appreciable quantities of pectic substances; after treatment with alkali, they would actually be hydrolyzed to pectic acid. Such substances would not be destroyed by nitration; indeed, nitropectin has been described as having properties generally similar to those of nitrocellulose.¹⁸

Finally, any material which is not sufficiently purified (whatever the purity of the raw cellulose used may be) could contain sulfuric acid in some combined form. If present as acid cellulose esters, it would make the collodion "active."

A possible experimental approach to our problem was to determine whether parallelism between "activity" and ash content is indicated in a

¹⁸ Henglein, F. A., and Schneider, G., *Ber. chem. Ges.*, 1936, **69**, 309.

comparison of different brands of collodion. This method involves the rather reasonable assumption that the non-volatile bases originating from the materials and water used are present somewhat proportional to the number of acid groups.

Dried samples of the various collodions were therefore carefully ashed. In order to avoid too rapid combustion, it was found practical to thoroughly wet the samples with a

TABLE III
Some Chemical and Physical Characteristics of Several Brands of Collodion

1	2	3	4	5	6
Brand of collodion	Mg. ash per gm. dry collodion	Optical properties of commercial solutions	Tensile strength of membranes	Viscosity (relative values, water = 3.7)	Mg. SO ₄ per gm. dry collodion
"Parlodion" Mallinckrodt.....	0.16	Clear*	Very high	106	0.04
Collodion Merck U.S.P.....	0.23	Clear	Very high	93	0.2
Collodion Baker U.S.P.....	0.45	Clear	Very high	82	0.2
Collodium Schering-Kahlbaum "pro analysi".....	0.4	Very slightly turbid	High	88	0.3
Collodium Schering-Kahlbaum "zur Herstellung von Membranen".....	1.3	Turbid, small sediment	Poor	40	0.9
"Celloidin" Schering-Kahlbaum "for general use".....	3.6	Very turbid, sediment†	Poor	46	2.0
Collodium Schering-Kahlbaum DAB 6.....	3.5	Very turbid, heavy sediment	Very poor	28	3.1

* The solid commercial product yields a clear solution in ether-alcohol.

† The commercial product yields a very turbid, strongly yellowish solution in ether-alcohol; some sediment appears on standing.

mixture of equal amounts of alcohol and water and to burn slowly in a covered platinum crucible, adding only small quantities of the nitrocellulose at a time.

The results of these analyses are summarized in column 2 of Table III. A comparison with Table I and Table II reveals an obviously close parallelism between activity and ash content.

Columns 3, 4, and 5 of Table III give a comparison of other properties, namely, optical properties of the commercial solutions, tensile strength, and viscosity.

The domestic brands of collodion solutions are perfectly clear and

usually show no appreciable scattering of light. With the four grades of Schering-Kahlbaum collodion used there is a close parallelism between increasing turbidity and tendency toward sediment formation on the one hand and ash content on the other. Only Collodium Schering-Kahlbaum "pro analysi" was somewhat similar to the purer brands of collodion.

The tensile strength of membranes (of roughly the same thickness) was high for the three brands named first in Table III. It was somewhat less for Collodium Schering-Kahlbaum "pro analysi" and increasingly less for the next two preparations. Collodium Schering-Kahlbaum DAB 6 showed very poor strength.

The viscosity determinations were made with 5 per cent solutions of (previously dried) collodion in a mixture of equal parts of absolute ether and absolute alcohol. The time required for the meniscus to pass two marks on a 5 ml. pipette used as viscosimeter was measured. The experimental conditions were such as not to cause any complications due to evaporation. The water value of our pipette viscosimeter was 3.7 seconds. The time values found with the different collodions are given in column 5 of Table III.

Low tensile strength and low viscosity in solution are both strong indications of a lower molecular weight. The remarkably close parallelism between the several properties of these collodions cannot reasonably be considered to be fortuitous. However, it may be added that an exact quantitative correlation is impossible because we are dealing with too many variables.

The experimental results reported so far are in good agreement with the views outlined above. The more active grades of collodion are the poorer ones technically speaking, containing many impurities of an acid character; their mean molecular weight, moreover, is obviously considerably less, as can be readily concluded from the tensile strength and viscosity data.

Partial oxidation could readily account for the presence of acid groups and likewise for a lower molecular weight, as such an oxidative breakdown of cellulose is a well established fact.

This otherwise satisfactory explanation has not heretofore taken into account the possibility of the presence of acid sulfuric acid compounds in the collodion. Such compounds could cause all or part of the observed electrochemical activity, though their presence could not account for the lower molecular weight. The parallelism between activity and degradation of the nitrocellulose molecules would then be entirely accidental.

Our next step, therefore, was to determine whether or not the different brands of collodion contain sulfate, and if so, how much.

Collodion samples were ashed carefully as outlined above. The residues were analyzed and found to be substantially a mixture of aluminum, iron, and calcium sulfate, containing very little free base and no detectable quantities of silicic acid. The analytical results, however, indicated that a loss of sulfate may occur because of a lack of fixed alkali. To obtain correct sulfate values, therefore, the experiments were repeated with a changed technique. The collodion samples were thoroughly wetted with an alcoholic solution of sodium hydroxide and ashed after this treatment. The sulfate values found were accordingly higher than those obtained with the former technique. The results are listed in column 6 of Table III. These latter values represent in our opinion the true sulfate contents of the different collodions.¹⁴

These data show that the sulfate content also runs strictly parallel to the electrochemical activity of the different preparations. In order to cause activity the sulfate present must necessarily be in the form of an acid compound. Sulfuric acid esters of cellulose have been described repeatedly and their appearance in improperly purified nitrocellulose seems to be assumed quite generally.

However, it may be possible that the sulfate, as found by analysis, is present in a combined though inactive form, or merely as an admixture originating from the process of manufacture. How difficult it is to remove sulfuric acid from nitrocellulose can be gathered from the following experiment.

A sample of collodion (Merck U.S.P.) with a sulfate content of 0.2 mg. per gm. of dry material was dissolved in acetone. A solution of sulfuric acid in acetone was added until the mixture was about 0.1 molar with respect to sulfuric acid. After 2 hours the solution was allowed to drip slowly under stirring into a great excess of water. The fibrous product obtained was washed thoroughly and boiled for 35 hours with water. After washing and drying, an ether-alcohol solution was prepared and centrifuged to remove all insoluble particles and the sulfate content of this purified material was determined as before. Its sulfate content of 0.5 mg. per gm. dry collodion is more than twice that determined in the original material.

Membranes cast in the usual manner from ether-alcoholic solutions of this treated collodion showed no significant change in activity as compared with the original material. The possibility, therefore, is not entirely excluded that at least some of the sulfate content of collodion is present as inactive admixture, particularly in the more active, poorly purified products.

We are still confronted with the apparent correlation between sulfate

¹⁴ The conventional technical method of sulfate determination after Berl (*cf.* Berl-Lunge, *Chemisch-technische Untersuchungsmethoden*, Berlin, Julius Springer, 1934, 5, 735) does not seem readily applicable to the very small amounts of sulfate with which we had to deal.

content and activity in the commercial preparations; sulfate groups may be responsible for at least some of the activity of collodion, though the relative importance of this factor is still an open question.

There are two apparent ways to estimate the relative importance of sulfuric acid compounds for the activity of collodion. The most straightforward and theoretically simplest approach would be to compare the sulfate content with the total number of acid groups present in the collodion. Seemingly simple, it is beset with experimental difficulties. We, therefore, must postpone its discussion to a later paper, in the frame of which it will find a more proper place.

The other method would be to investigate the possibility of freeing active collodion of its sulfate content without total loss of activity.

Our plan, therefore, was to reduce in some way the sulfate content of active collodions down to the level of the more inactive brands and to see whether or not their activity is lost with the sulfate removal.

According to the literature, the desired purification could be tried in several ways.¹⁵ One could boil a sample for a long time in very dilute acid and water, as is done in the conventional commercial process. This procedure is supposed to hydrolyze sulfuric acid compounds. Furthermore, one could accelerate the hydrolysis of the assumed sulfuric acid esters by boiling with half concentrated acetic acid.

In judging the experiments described below, one has to consider that on boiling, not only sulfuric acid compounds may be hydrolyzed and thus rendered inactive, but also that any ionizable compound may be slowly dissolved. Once dissolved, such compounds would be largely lost in the boiling liquid. This is likewise true for oxidation products and acid esters which probably are not too different in their general properties.

We were able to obtain an adequate supply of only two of the more active brands of collodion, namely, "Celloidin, Schering-Kahlbaum, for general use," a very active preparation, and "Collodium, Schering-Kahlbaum, zur Herstellung von Membranen," a moderately active preparation.

To make them suitable for the intended purification, their rather dilute ether-alcoholic solutions were poured slowly into a great excess of water under continuous, vigorous stirring. The products so obtained are composed of fine fibres.

Boiling in water turned out to be a somewhat less suitable method for our purpose. Therefore, since we had to economize on our material, this method was applied only to one brand of collodion, "Celloidin, Schering-Kahlbaum, for general use." 30 gm. of Celloidin were treated in about 1.5 l. of liquid. The sample was heated every morning

¹⁵ See *e.g.*, Hess, K., *Die Chemie der Zellulose und ihrer Begleiter*, Leipzig, Akademische Verlagsgesellschaft, 1928, 367, 381, etc.

and allowed to boil for about 6–7 hours; on the next morning the liquid was renewed. The boiling liquid used for several days was very dilute hydrochloric acid, later on, distilled water. The water was replaced less frequently. After a boiling time of about 70 hours, the sulfate content was reduced to the desired level. The material was then thoroughly dried. The sulfate determination was carried out as described previously. An ash determination was also made.

The second method of purification was applied to both of our available active preparations. 12 gm. samples were boiled in about 700 ml. of 60 per cent acetic acid. After an appropriate time, the boiling was stopped and the material thoroughly freed of acetic acid by repeated boiling and thorough washing with water. It was finally dried. The boiling time necessary to reduce the sulfate content to the desired level was 10 hours for Collodion Schering-Kahlbaum "zur Herstellung von Membranen" and 16 hours for "Celloidin Schering-Kahlbaum for general use." The dry materials were analyzed for ash and sulfate content as in the preceding case.

In Table IV c the analytical data pertaining to our purified collodions are given. They are preceded by the corresponding data of active commercial collodions—Table IV a —and pure, inactive commercial collodions—Table IV b .

To compare the "activity" of the different preparations we used data concerning anomalous osmosis and concentration potentials obtained with the same membranes. Anomalous osmosis, as said above, is a very sensitive indicator as to the activity of such membranes.

Membranes of the original and purified collodions (dissolved in 75 per cent ether-25 per cent alcohol) were cast; the first three of each brand giving proper rises with sugar solution after 20 minutes (column 4 of Table IV) were used. They were all of about the same porosity. The anomalous osmosis experiments were carried out as indicated before. The corresponding manometric rises are listed in column 5 of Table IV. Column 6 gives the concentration potentials between 0.01 N and 0.02 N KCl solutions for the same membranes.

On examination of the facts summarized in Table IV, one sees that there is no necessary correlation between sulfate content and activity. Though the originally active brands of collodion lose some of their activity in the process of purification, they still are much more active than the better commercial preparations of the same sulfate content. We would prefer to attribute the decrease in activity on purification largely to a loss of active, but sulfate-free, substance. As said above, such compounds are, in our opinion, partially oxidized nitrocellulose molecules carrying carboxyl groups and having probably on the average a lower molecular weight and a much greater solubility than the more perfect, less oxidized nitrocellulose molecules. This view is substantiated by the fact that the filtered boiling liquids leave on evaporation a considerable residue of organic substance.

TABLE IV
Sulfate Content and Activity of Some Commercial and Purified Collodion Preparations

1	2	3	4	5	6
Brand of collodion	Mg. ash per gm. dry collodion	Mg. SO ₄ per gm. dry collodion	Osmotic rise with sugar $\frac{M}{4}$	Anomalous osmotic rise with K ₂ SO ₄ $\frac{M}{512}$	Concentration potential KCl 0.01 N / KCl 0.02 N
<i>Table IV a</i>					
			<i>mm.</i>	<i>mm.</i>	<i>mv.</i>
Collodion Schering-Kahlbaum "zur Herstellung von Membranen" (commercial preparation)	1.3	0.9	106	85	1.4
			118	98	1.4
			130	104	1.2
"Celloidin" Schering-Kahlbaum "for general use" (commercial preparation)	3.6	2.0	110	190	2.2
			126	228	3.6
			130	244	2.0
<i>Table IV b</i>					
			<i>mm.</i>	<i>mm.</i>	<i>mv.</i>
Collodion Merck U.S.P. (commercial preparation)	0.23	0.2	116	48	0.5
			125	46	0.8
			138	57	0.9
Collodion Baker U.S.P. (commercial preparation)	0.45	0.2	128	32	1.0
			130	47	1.1
			136	50	0.5
<i>Table IV c</i>					
			<i>mm.</i>	<i>mm.</i>	<i>mv.</i>
Collodion Schering-Kahlbaum "zur Herstellung von Membranen" (purified with acetic acid)	0.2	0.2	112	84	2.0
			126	98	1.1
			130	96	1.4
"Celloidin" Schering-Kahlbaum "for general use" (purified by boiling in water)	0.2	0.2	118	72	1.3
			136	93	2.1
			150	108	1.7
"Celloidin" Schering-Kahlbaum "for general use" (purified with acetic acid)	0.2	0.2	118	102	2.6
			130	126	2.3
			138	120	2.3

We are, therefore, very much inclined to think that the electrochemical activity of the more active collodion preparations is mainly due to sulfate-

free acidic compounds, sulfate-containing substances playing only a minor rôle.

GENERAL DISCUSSION

The evidence presented in the preceding pages integrates itself into a relatively simple picture.

The electrochemical "activity" of collodion is due to impurities of an acidic nature originating from the raw material and the manufacturing process. The purest brands of commercial collodion show very low activity. Therefore, the assumption that nitrocellulose as such is electrochemically very inactive¹⁶ seems justified.

The electrochemically active impurities are substantially not sulfuric acid compounds, as borne out by the fact that active commercial collodions can be largely freed from their sulfate content without parallel loss of activity.

This leads us to the conclusion that carboxyl groups must be responsible for the observed activity. Carboxyl groups are undoubtedly contained in all cellulose raw materials.¹⁷ Their number must be greatly increased by bleaching, particularly the excessive bleaching necessary with inferior raw material. Excessive bleaching yields products of lowered molecular weight; *i.e.*, low viscosity in solution and low tensile strength of films.

To obtain a true picture it is impossible to think of nitrocellulose in terms of ideal uniform molecules. Nitrocellulose is in reality composed of mole-

¹⁶ This undoubtedly applies to other cellulose derivatives, esters as well as ethers and also to straight cellulose and hydrocellulose.

The use of such membranes seems to offer some hope for successfully attacking the old experimental problem of measuring directly the osmotic pressure of electrolyte solutions. Investigators in this field have employed membranes which, it would seem, are particularly apt to give anomalous osmosis. We know; *e.g.*, that Cu-ferrocyanide is a very active membranè (Bernstein, *Elektrophysiologie*, Braunschweig, Friedrich Vieweg and Sohn, 1912, 164). The same is true for silicate membranes and probably many other membranes of salt character (Grollman, A., and Frazer, J. C. W., *J. Am. Chem. Soc.*, 1923, **43**, 1710; Grollman, A., Dissertation, Johns Hopkins University, 1923; Sollner, K., and Grollman, A., *Z. Elektrochem.*, 1932, **38**, 274; *Tr. Electrochem. Soc.*, 1932, **61**, 477, 487). The problem seems to be to find a membrane with so low a charge density that the electrical forces become negligible. It may be recalled here that Loeb was able to reduce practically to zero the activity of his proteinized collodion membranes simply by working at the isoelectric point of the particular protein used (Loeb, J., *J. Gen. Physiol.*, 1920, **4**, 463).

¹⁷ See *e.g.* Hess, K., *Die Chemie der Zellulose und ihrer Begleiter*, Leipzig, Akademische Verlagsgesellschaft, 1928, particularly pp. 54 *ff.*

cules of very different length and these molecules are by no means all perfect. Many of them carry—and this is the point important for us—carboxyl groups, some sulfate groups, and possibly some others. Thorough purification gradually removes these ionizable impurities.

The best grades of collodion, therefore, are composed of long fairly ideal nitrocellulose molecules, probably carrying only here and there a group (*e.g.*, carboxyl) not compatible with the ideal structure. Correspondingly, they are fairly inert.

Collodion purified to a lesser extent in any case contains many impurities, largely of lower molecular weight.

Collodion prepared from inferior raw material is composed of molecules of lower mean molecular weight.¹⁸ If not extremely well purified, such a material would be expected to contain many molecules carrying oxidized groups which originate from excessive bleaching.

This picture fits the three inferior grades of Schering-Kahlbaum¹⁹ collodion perfectly. The high sulfate content is obviously the result of a more superficial purification.

The correctness of our explanation of the electrochemical activity of collodion is further substantiated by the fact that collodion, as noted in a preceding paper,² can be activated by oxidation.

The results here obtained are somewhat unexpected and indeed ironical. The brands of collodion preferred by nearly all workers in the field of electrochemical membrane investigations are, technically speaking, the poorest ones.

If one tries to visualize the molecular mechanism of electrochemical membrane activity, one likewise arrives at a relatively clear picture. Without entering at this point into any discussion on the relative merits of different permeability theories (*i.e.*, pore *versus* homogeneous phase hypothesis) as applied to the collodion membrane, we shall employ the pore conception for the following discussion. It allows us to discuss without much distinction the highly dried (controversial) and the incompletely dried, undoubtedly porous collodion membranes.

As pointed out by several investigators, recently in a more quantitative form,^{10, 20} the electrochemical behavior of such a membrane depends upon the relative number and mobilities of all the ions present in the pores.

¹⁸ We are quite aware of the fact that low molecular weight does not necessarily have its origin in either poor raw material or oxidation. Such material is actually manufactured widely for special technical purposes from high grade raw material, special processes being used to reduce the molecular weight.

¹⁹ Unfortunately, several letters sent to the Schering-Kahlbaum Company requesting information on this problem remained unanswered.

²⁰ Teorell, T., *Proc. Soc. Exp. Biol. and Med.*, 1935, **33**, 282.

Some of the ions of one sign are fixed to the wall, their "gegen-ions" being freely movable in the aqueous phase. In very wide pores, or in pores of any size, if only a negligible number of ions is fixed to the pore walls, the specific membrane influence is negligible; high electrolyte concentrations in the aqueous phase likewise reduce the relative importance of the wall influence. In narrower pores and in more dilute electrolyte solutions, if by some means the relative number of ions fixed immovably to the pore walls is increased, the specific membrane influence increases. For our specific problem we are concerned only with the latter factor and the question is: what determines the number of ionizable points fixed immovably at a collodion/aqueous solution interface?

This situation with respect to the membrane (ϵ) potential applies *mutatis mutandis* quite as well to the electrokinetic (ζ) potential.

The older assumption of preferential ion adsorption has recently been questioned because of the extremely low adsorbability of strong inorganic electrolytes.

Our results also indicate that ion adsorption has only a very secondary, if any, influence on the electrochemical activity of collodion membranes in such solutions.

Lately, several investigators have assumed that the ionizable groups on collodion in strong electrolyte solution belong to the collodion itself. This view seems to be proven by our experiments. It seems much more familiar when one recalls the structure and behavior of proteinized membranes. In this case, everybody agrees that all the electrochemical properties of the membrane are due to the ionizable groups of the protein.

The great differences between different collodion preparations are now easily understood. The purest ones carry only a small number of dissociable groups and are, therefore, inactive. The less carefully prepared material contains many acidic groups and is electrochemically active. The number of ionizable groups per unit of area is an inherent property of the membrane material used. In any given solution, their dissociation, *i.e.* their actual effectiveness, depends on the nature and concentration of all the ions present, particularly the possible gegen-ions.

In our opinion the behavior of weakly adsorbable polyvalent ions, *e.g.* sulfate, has to be explained on the basis of a combination of mechanical and electrical sieving effects.

This conception, of course, does not apply without restriction to all situations. For example, if any of the ions present in solution is very strongly adsorbable, it must strongly influence the ionic build-up of the interfacial layer. In this case we can undoubtedly approach the situation formerly assumed also for strong electrolytes.

It is conceivable that with a membrane material which is completely or nearly completely void of any dissociable groups, even in solutions of strong electrolytes, preferential ion adsorption comes into play to a decisive extent. However, no case of this nature has so far been described for collodion membranes.

Previous mention was made of some of the factors which may possibly have a great influence on membranes cast from different collodions. They are degree of nitration, impurities, mean molecular weight, and particle size distribution. To this we may add the solvent used. The degree of nitration obviously (as pointed out by earlier investigators) is not a decisive factor, as attested by the fact that nitrocellulose of widely varying nitrogen content yields membranes having quite similar electrochemical properties. The paramount importance of impurities for the electrochemical behavior of collodion membranes is discussed in the preceding pages. Concerning the mean molecular weight and particle size distribution and the influence of the solvent, we are inclined to believe that these factors are quite intimately connected in a consideration of the spatial structure of membranes. Together, they probably determine the geometrical arrangement of the molecules in the films. We do not intend to discuss at this time this extremely complex problem since our present results have very little bearing upon it.

In subsequent papers we propose to discuss the preparation of artificially activated membranes and to investigate quantitatively the acidic properties of collodion, hoping that it may be possible to correlate such data with some of the newer theoretical considerations of electrochemical membrane behavior.

SUMMARY

1. The electrochemical behavior of membranes prepared from commercial collodion preparations varies widely, some preparations showing very high, other ones very low electrochemical efficiency ("activity").

2. The electrochemical activity of a collodion membrane depends entirely upon impurities of an acidic nature contained in the collodion used for casting the membrane.

3. The active acidic impurities are substantially due to partial oxidation which occurs in the manufacturing process. Sulfuric acid compounds; *e.g.*, acid sulfuric acid esters play only a minor rôle, if any.

4. The electrochemical behavior of collodion membranes in solutions of strong electrolytes is decisively dependent upon the acidic groups built permanently into the collodion surfaces. Preferential ion adsorption plays only a minor, if any, rôle.