

THE STRUCTURE OF THE COLLODION MEMBRANE AND ITS ELECTRICAL BEHAVIOR

V. THE INFLUENCE OF THE THICKNESS OF DRIED COLLODION MEMBRANES UPON THEIR ELECTROMOTIVE BEHAVIOR

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I

The electrochemical properties of collodion membranes are known to vary greatly with the nature of the collodion preparation used, more acid preparations yielding membranes of higher electrochemical activity.¹⁻⁵ The assumption has always been made, tacitly or expressly, that the thickness of the membrane is of no influence. Thus, it has been generally assumed that the characteristic concentration potential⁶ across dried collodion membranes must be independent of the thickness of the membranes.⁷

We became doubtful of the validity of this assumption. As was pointed out in a preceding communication,⁵ the concentration potentials across different membrane specimens frequently vary considerably, even if the membranes are prepared from the same collodion solution under conditions as nearly identical as possible. The following set of facts also needs to be considered. It has been demonstrated that the behavior of dried collodion membranes with solutions of strong electrolytes is due to (1) its micellar structural arrangement, that is, to the presence of interstices of larger than minimal (molecular) di-

¹ Michaelis, L., and Perlzweig, W. A., *J. Gen. Physiol.*, 1926-27, **10**, 575.

² Wilbrandt, W., *J. Gen. Physiol.*, 1935, **18**, 933.

³ Sollner, K., and Abrams, I., *J. Gen. Physiol.*, 1940, **24**, 1.

⁴ Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **24**, 467.

⁵ Sollner, K., and Carr, C. W., *J. Gen. Physiol.*, 1942, **26**, 17.

⁶ The characteristic concentration potential is defined by Michaelis and collaborators as the potential which arises when a membrane is interposed between 0.01 M and 0.1 M potassium chloride solution. Michaelis, L., and Fujita, A., *Biochem. Z.*, Berlin, 1925, **158**, 28; 1925, **161**, 47; 1925, **164**, 23; Michaelis, L., and Dokan, S., *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.*, 1926-27, **10**, 575; Michaelis, L., McEllsworth, R., and Weech, A. A., *J. Gen. Physiol.*, 1926-27, **10**, 671; Michaelis, L., Weech, A. A., and Yamatori, A., *J. Gen. Physiol.*, 1926-27, **10**, 685; Michaelis, L., *Bull. Nat. Research Council*, No. 69, 1929, 119; *Kolloid-Z.*, 1933, **62**, 2, and other publications.

⁷ Weech, A. A., and Michaelis, L., *J. Gen. Physiol.*, 1928, **12**, 221.

mensions,⁵ and (2) to the dissociable groups—carboxyl groups—present in some of the nitrocellulose molecules.^{4,8,9} It was further shown (3) that the surface concentration of these “active” groups—as determined by base exchange experiments—can be very small, even in highly active collodion preparations, smaller actually than can be determined with the conventional chemical and physical methods.⁹ Thus, there is some doubt as to whether there is a sufficient number of these active groups available to supply each of the interstices across a thin membrane with at least one active group.^{5,9} It is obvious that the chance of this occurrence diminishes with decreasing thickness of the membrane.

In the foregoing discussion we have assumed that a single active group in an interstice across the thickness of the membrane is sufficient to cause the maximal effect; *i.e.*, complete blocking of the passage of ions of the same sign. This assumption is supported by all the available experimental data, and is tacitly made in all theoretical work.

The measurable membrane potential with each individual membrane is, of course, a mean of the potentials of all the possible pathways across the membrane, each pathway contributing to the measurable effect according to its electrical characteristics, pore potential, and resistance. In other words, the pores which do not contain a dissociable group short circuit the electrical effect set up by the pores containing one or several such groups. For membranes containing somewhat larger pores this general concept has been used to explain the mechanism of anomalous osmosis.¹⁰ It is obvious that unduly large pores, and still more so, any cuts, holes, or cracks would influence the measurable effect very strongly by such short circuits.

In the experimental part we will discuss briefly the reasons why we feel certain that no larger mechanical defects are present even in thin collodion membranes and what evidence we have that unduly large pores (which could not be blocked by a single charge) do not seem to exist.

For reasons outlined above we decided to determine experimentally whether or not the concentration potential across dried collodion membranes is a function of their thickness. Any result is bound to cast considerable light on the interaction of geometrical and electrical factors in the constitution of the dried collodion membrane.

In addition a definitely positive decision is bound to contribute pertinent information concerning the relative merits of the continuous phase theory and

⁸ Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **25**, 7.

⁹ Sollner, K., Carr, C. W., and Abrams, I., *J. Gen. Physiol.*, 1942, **25**, 411.

¹⁰ Sollner, K., *Z. Electrochem.*, 1930, **36**, 36, 234; Sollner, K., and Grollman, A., *Z. Electrochem.*, 1932, **38**, 274; Grollman, A., and Sollner, K., *Tr. Electrochem. Soc.*, 1932, **61**, 477, 487; Sollner, K., *Kolloid-Z.*, 1933, **62**, 31.

the micellar structural theory, a problem which was dealt with from another point of view in the preceding communication.¹¹

The homogeneous phase theory would predict the concentration potential to be independent of thickness, unless special effects at the interfaces, for example orientation or film formation, came into play. In this case, which has not found adequate treatment in the literature, the interfacial layers would be different from the bulk phase; the whole interphase would be built up as: interfacial layer/bulk phase/interfacial layer. Such a "structural" arrangement of the "homogeneous" interphase could conceivably account for a dependence of the concentration potential upon the thickness of the membrane. However, if such conditions prevail, the homogeneous phase theory, as we are accustomed to think of it, would cease to be applicable.

A "micellar structural" theory would, at least for certain favorable cases, lead to the prediction that increasing thickness of the membrane would bring about increasing ionic selectivity, and consequently increasing concentration potentials, provided, as indicated above, that the thickness of the membranes be not great compared with the mean distance between two electrochemically active groups or spots within the membrane. In a highly schematic manner Figs. 1 and 2 give two possible ways to visualize the thickness effect. We assume, in agreement with the best information available, that the charged spots in a narrow pore prevent the passage of ions of the same sign but allow the passage of oppositely charged ions;¹² uncharged pores of proper dimensions allow the passage both of anions and cations. In the figures the membrane substance is indicated by striation; spots which prevent the passage of anions, due to a fixed negative charge (as is the case in collodion) are denoted by asterisks.

Figs. 1 *a*, 1 *b*, and 1 *c* show the simplest conceivable structure of a porous membrane. Fig. 1 *a*, representing a unit thickness of membrane, shows every other pore blocked for the passage of anions, the ratio of the free to the geometrically possible pathways thus being 0.5. If in a membrane twice as thick (Fig. 1 *b*) the charges are distributed at random, the number of pathways free for the permeation of anions would be $0.5 \times 0.5 = 0.25$ or 25 per cent; the ratio of

¹¹ For a brief statement of the problem, homogeneous phase theory *versus* micellar-structural theory and for some pertinent literature, the reader is referred to our preceding communication (Sollner, K., and Carr, C. W., *J. Gen. Physiol.*, 1942, **26**, 17.)

¹² The interstices in dried collodion membranes conform to this condition. This can readily be seen from the fact that dried collodion membranes on activation by oxidation become practically impermeable to anions, as evidenced by the nearly maximal concentration potentials across such membranes. (Sollner, K., Abrams, I., and Carr, C. W., *J. Gen. Physiol.*, 1941, **25**, 7; Sollner, K., and Carr, C. W., *J. Gen. Physiol.*, 1942, **26**, 17.)

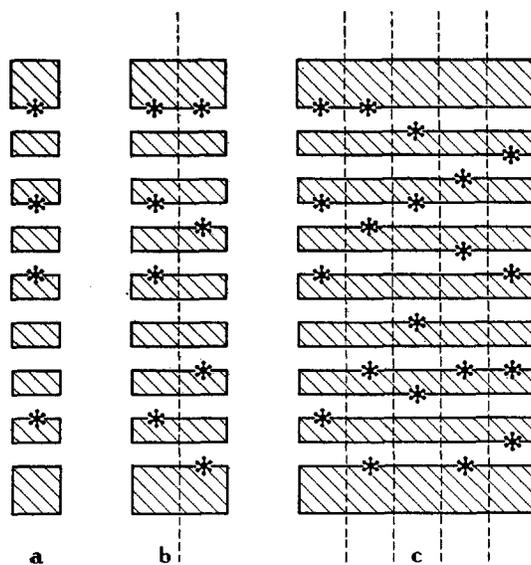


FIG. 1

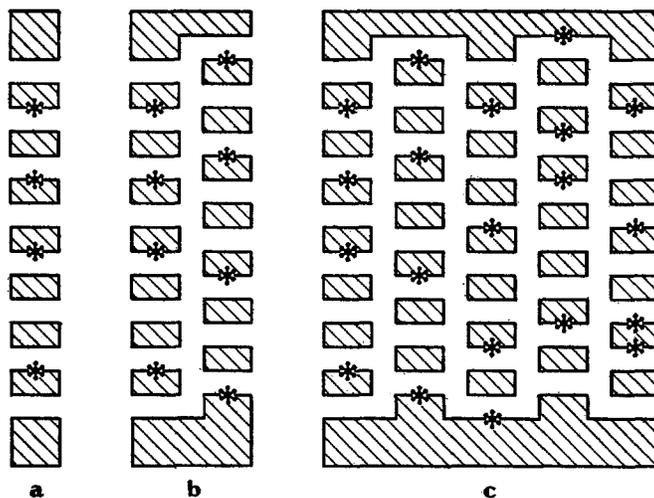


FIG. 2

possible pathways to pathways available for anions thus decreases in a geometrical series with increasing thickness of the membrane; Fig. 1 *c*, *e.g.* represents a five-layer membrane, which gives (statistically) a ratio of $1:(\frac{1}{2})^5 = 1:\frac{1}{32}$.

The potential across such membranes between the concentrations c_1 and c_2 in the case of a uni-univalent electrolyte can, according to Michaelis, be expressed as:

$$(1) \quad E = \frac{U - V}{U + V} RT \ln \frac{c_1}{c_2},$$

U and V being respectively the *mean* mobilities of all the cations and anions in the pores. However, this approach is too formal for our present purposes. Recently, it was shown experimentally that a certain number of anions are fixed permanently and immovably to the structure of the membrane, their mobility thus being zero.^{3,4,5,8,9,13,14,15}

It is outside the scope of this paper to discuss all the ramifications of this general concept. Our considerations are actually based on certain simplified assumptions. Nevertheless, they are sufficiently accurate to yield at least a semiquantitative picture of the true situation. Readers interested in the theoretical aspects of the matter must be referred to the papers of Teorell,¹³ and Meyer and Sievers^{14,15} which are based on a rigorous quantitative application of the above general concept.

If the fraction a of all possible pathways in the membrane is blocked for the movement of anions (but allows the passage of cations) and if u and v are the true mobilities of the movable cations and anions in the membrane, v_0 being the mobility of the fixed anions, the Nernst equation can be written as follows:

$$(2) \quad E = \frac{u - (1 - a)v - av_0}{u + (1 - a)v + av_0} RT \ln \frac{c_1}{c_2};$$

and since

$$(3) \quad \begin{aligned} v_0 &= 0 \\ E &= \frac{u - (1 - a)v}{u + (1 - a)v} RT \ln \frac{c_1}{c_2}. \end{aligned}$$

In the case of a membrane with n unit layers the equation for the case discussed above becomes

$$(4) \quad E_n = \frac{u - (1 - a)^n v}{u + (1 - a)^n v} RT \ln \frac{c_1}{c_2}$$

since only the fraction $(1 - a)^n$ of all possible pathways is available to anions.

Experiments of Meyer and Sievers¹⁵ indicate that the ratio of the mobilities of univalent anions and cations in a membrane of porous character does not

¹³ Teorell, R., *Proc. Soc. Exp. Biol. and Med.*, 1935, **33**, 282.

¹⁴ Meyer, K. H., and Sievers, J.-F., *Helv. Chim. Acta*, 1936, **19**, 649.

¹⁵ Meyer, K. H., and Sievers, J.-F., *Helv. Chim. Acta*, 1936, **19**, 665, 963.

differ appreciably from the ratio in free solution. If we assume this to be correct we may introduce the conventional figures for u and v in our equations. For the case of potassium chloride u is equal to v . If we consider this case, and a concentration ratio of 10:1 and further, a selectivity factor a per unit layer of $\frac{1}{2}$, as assumed in Fig. 1, then a monolayer membrane would yield 18.7 mv., a membrane composed of two layers 33.6 mv., a five-layer membrane 52.6 mv., etc., if the thermodynamically possible maximum is assumed to be to 56 mv.

However, the kind of very simple behavior which we just discussed is by no means necessarily inherent in membranes which have a structure. Another possibility is shown in Fig. 2. Fig. 2*a* represents a unit layer of membrane, 50 per cent of the pores being blocked for anions ($a = 0.5$). Fig. 2*b* shows a possible assembly of two such layers which allow a free cross connection of the pores between two adjacent membrane layers. If an electrolyte diffuses through such a membrane this space will soon be filled with electrolyte solution, the concentration of which, c_3 , is somewhere between the concentrations c_1 and c_2 on the two sides of the membrane. The potential across the whole of the membrane $E_{1,2}$ is the sum of the two single potentials across the two individual membrane layers:

$$(5) \quad E_{1,2} = E_{1,3} + E_{3,2}.$$

$$(6) \quad E_{1,3} = \frac{u - (1-a)v}{u + (1-a)v} RT \ln \frac{c_1}{c_3}$$

and

$$(7) \quad E_{3,2} = \frac{u - (1-a)v}{u + (1-a)v} RT \ln \frac{c_3}{c_2}$$

Therefore

$$(8) \quad E_{1,2} = \frac{u - (1-a)v}{u + (1-a)v} RT \left(\ln \frac{c_1}{c_3} + \ln \frac{c_3}{c_2} \right) =$$

$$(9) \quad E_{1,2} = \frac{u - (1-a)v}{u + (1-a)v} RT \ln \frac{c_1}{c_2}.$$

For a membrane of n layers thickness the equation becomes

$$(10) \quad \begin{aligned} E_{1,2} &= \frac{u - (1-a)v}{u + (1-a)v} RT \left(\ln \frac{c_1}{c_a} + \ln \frac{c_a}{c_b} + \dots + \ln \frac{c_{(n-2)}}{c_{(n-1)}} + \ln \frac{c_{(n-1)}}{c_2} \right) \\ &= \frac{u - (1-a)v}{u + (1-a)v} RT \ln \frac{c_1}{c_2} \end{aligned}$$

Thus the potential across a membrane as sketched in Figs. 2*b* and 2*c* is independent of the number of unit layers (plus connecting spaces) from which

the membrane is built. We also see that the concentration potential is independent of the distribution of the concentration drop from c_1 to c_2 among the several layers of the membrane.

Thus, we see that cross connections between different pores influence the behavior of membranes profoundly. According to the micellar structural theory therefore, the relative frequency of the blocking groups and branchings of the pores should be the paramount factor determining the electrochemical behavior of dried collodion membranes.

Many cases of a more complicated nature than those which were discussed are of course accessible to theoretical treatment. However, any further discussion seems superfluous at this point. The effects may lie anywhere between the two extremes represented by the two cases mentioned. No definite prediction as to the dependence of the concentration potential upon the membrane thickness can be made on the basis of the micellar structural theory; the latter is compatible with potentials which depend upon the membrane thickness as well as with potentials which are independent of it. However, one can expect the appearance of the thickness effect with some degree of certainty merely from a consideration of the chance distribution of charges. One would anticipate this effect particularly for very thin membranes prepared from not too active collodion preparations.

It is obvious that the absolute permeability per square centimeter of membrane decreases in all cases as the membrane thickness increases; with electrolyte solutions this means increased ohmic resistance with increasing thickness. However, for the present we are not concerned with this obvious effect, but will consider and investigate only the magnitude of the electromotive forces which may be caused by different membrane thicknesses.

II

The experiments which are necessary to test for the existence of the expected thickness effect are of an extremely simple nature; the electromotive properties, *e.g.* the characteristic concentration potential,⁶ of dried membranes are determined. Several collodion preparations of different activity were used, since this factor could easily be of great importance. One could expect that even very thin membranes prepared from a highly active preparation might yield nearly maximum concentration potential values; in this case, of course, no significant increase with increasing thickness could be expected.

Membranes cast from the same collodion solution under supposedly identical conditions may yield concentration potentials which vary widely.²⁻⁵ It therefore was necessary to cast a number of membranes from each solution in order to obtain significant mean values for the concentration potential.

Our experiments were carried out with bag-shaped membranes, since it is much easier to work with a large number of bag-shaped membranes than with

flat ones. Bag-shaped membranes have the additional advantage that rather thin membranes may be readily used.

Membranes of different thickness are most easily obtained by casting them from solutions of different concentration; the more concentrated solutions are more viscous and thus readily yield membranes of greater thickness, if one uses the conventional manual casting method.

This method is by no means perfect. Though the average thickness (see below) of different membrane specimens is remarkably constant in any given series, nevertheless, slightly thinner and thicker spots appear in each individual membrane. However, we want to stress the fact that a trained experimenter is able to produce membranes of great uniformity.¹⁶

Most of our membranes—many show bright interference colors when immersed in water—are too thin for accurate mechanical measurement of their thickness. We therefore determined their average thickness by area and weight determination in the dry state. The weight and area of several membranes of each kind were measured after carefully removing all unduly heavier parts which are frequently found near the open end of the membrane bags. The specific gravity of the dry membranes was taken as 1.6.

Here it may be asked what proof exists that the membranes, particularly the thinner ones, are intact. There is first, the method of Northrop,¹⁷ who tested membranes by filling them with 2 M sodium chloride solution and immersing them in 1 M silver nitrate; in this way holes may readily be detected by the formation of a precipitate. Further, there is the fact that considerable concentration potentials are consistently obtained. Occasionally, but rarely, a membrane is found which gives a zero concentration potential, or nearly so. Such membranes can nearly always be shown to leak and are discarded. That the membranes may be oxidized to yield nearly maximum concentration potentials (regardless of the potential they give in the original unoxidized state) seems to indicate strongly that they are without holes or cracks. That the membranes may be handled and stored for considerable time without any change in the characteristic concentration potential also indicates the absence of any cracks or cuts which would tend to grow in course of time.

The collodion preparations used were Baker Collodion, U.S.P. and Mallinckrodt "Parlodion," two of the best commercial preparations; a sample of oxidized collodion of very high electrochemical activity; and finally, purified "Parlodion," the least active preparation known to us. The methods of preparing the latter two preparations were described in previous papers.^{8,9} There one finds also data concerning their general properties and their electrochemical behavior. The batch of Mallinckrodt "Parlodion" used in the present work was significantly more active than batches used previously.

¹⁶ E.g. Nakagawa, J., *Jap. J. Med. Sc. III. Biophysics, Transactions and Abstracts*, 1937, **4**, 297.

¹⁷ Northrop, J. H., *J. Gen. Physiol.*, 1928, **11**, 233.

Solutions of 2, 4, 6, 8, and 10 per cent collodion in 75 per cent absolute ether and 25 per cent absolute alcohol were used. Appreciably more dilute solutions yield membranes which cannot be handled conveniently in the usual manner, whereas solutions containing more than 10 per cent collodion are—with the preparations used—too viscous to allow a satisfactory casting of membranes.

There is an additional method of preparing membranes of increasing thickness, namely, by superimposing several layers of collodion on top of each other, a new layer being added after the preceding one is dried completely. This method, however, suffers from the disadvantage that thin membranes (as prepared from dilute solutions) are largely dissolved on contact with the collodion solution added for the preparation of the next layer. With more concentrated solutions this effect is not so conspicuous, but there is a strong tendency for the membranes to loosen from the wall of the test tube in which they are cast; in this case irregular shrinkage sets in, thus causing the loss of many membranes.

The membranes were cast by hand in 22×85 mm. test tubes, dried for about 24 hours, and loosened in the usual way by the addition of distilled water. Next the membranes were fitted to glass rings for more secure and convenient handling. It was found to be immaterial whether the membranes were kept dry or immersed in distilled water prior to measuring the concentration potentials. The latter were measured in the usual manner, as described by Michaelis and collaborators.⁶ Since the ohmic resistance of many of the membranes (the thick ones prepared from high grade collodion) is rather high, the volt scale of a commercial electron-tube voltmeter (Leeds and Northrup glass electrode) was used as potentiometer in spite of its limited (± 1 mv.) accuracy. The potential values are easily and accurately reproducible with each membrane. On contact with the salt solution the final concentration potential is established nearly immediately within very few millivolts and reaches the final value in any case within a few minutes. All potential values given in the tables are final, reproducible values. Our membranes were, with very few exceptions, symmetrical within the limits of experimental error, the same potential being obtained whether the concentrated solution was in contact with the inside or outside of the membrane. The asymmetry of the few not completely symmetrical membranes was too small to influence our results to an appreciable extent.

Tables I and II present observations in representative series of our experiments. Each potential value represents one individual membrane. Fig. 3 summarizes the results graphically. All experimental values in Table I, Table II, and Fig. 3 are given as obtained at room temperature without correction. No membranes were left out of the tabulation except those which were manifestly damaged.

The mean of the concentration potential of each series of membranes, the magnitude which is of primary interest here, is given in bold face type at the bottom of the individual columns together with the standard deviation of the

TABLE I
The Influence of the Thickness upon the Concentration Potential 0.1 M KCl/0.01 M KCl across Dried Collodion Membranes. Membranes Prepared from Collodion Solutions of Different Concentration. Potentials in Millivolts
A. Mallinckrodt Parlodion

2 per cent (Average membrane thickness 2.7 μ)	4 per cent (Average membrane thickness 6.1 μ)	6 per cent (Average membrane thickness 8.9 μ)	8 per cent (Average membrane thickness 18 μ)	10 per cent (Average membrane thickness 27 μ)
<i>mv.</i>	<i>mv.</i>	<i>mv.</i>	<i>mv.</i>	<i>mv.</i>
33	24	36	42	46
33	43	42	44	42
10	44	41	43	43
20	40	40	44	40
32	22	40	44	43
20	40	40	44	41
30	37	23	43	42
29	38	40	38	42
33	40	42	45	43
28	42	41	42	41
27	40	40	44	45
10	39	41	42	43
25	32	40	43	42
26	36	42	41	42
27	23	40	41	45
26	15	32	42	40
26	34	33	42	42
18	32	35	40	45
31	33	41	41	42
33	35	39	40	45
Mean:	Mean:	Mean:	Mean:	Mean:
25.6 \pm 1.6	34.6 \pm 1.8	38.4 \pm 1.0	42.3 \pm 0.4	42.6 \pm 0.4

B. Purified Mallinckrodt Parlodion

2 per cent (Average membrane thickness 3.6 μ)	6 per cent (Average membrane thickness 12.0 μ)	10 per cent (Average membrane thickness 32.2 μ)
<i>mv.</i>	<i>mv.</i>	<i>mv.</i>
24	31	37
21	31	29
27	29	30
26	30	27
15	29	30
24	30	30
17	32	28
	32	35
	33	40
	31	
	32	
Mean	Mean:	Mean:
22.0 \pm 1.7	30.9 \pm 0.4	31.8 \pm 1.5

TABLE I—Concluded
C. Baker Collodion U.S.P.

2 per cent (Average mem- brane thickness 2.7 μ)	4 per cent (Average mem- brane thickness 4.4 μ)	6 per cent (Average mem- brane thickness 12.0 μ)	8 per cent (Average mem- brane thickness 24.5 μ)	10 per cent (Average mem- brane thickness 29.9 μ)
<i>mv.</i>	<i>mv.</i>	<i>mv.</i>	<i>mv.</i>	<i>mv.</i>
25	29	42	49	45
22	34	42	42	43
27	32	41	46	46
23	27	40	38	45
24	26	32	39	45
24	35	37	40	43
19	25	42	40	44
	25	41	40	41
Mean: 23.4 \pm 1.1	Mean: 29.1 \pm 1.4	Mean: 39.6 \pm 1.2	Mean: 41.7 \pm 1.3	Mean: 44.0 \pm 0.6

D. Oxidized Collodion

2 per cent (Average membrane thickness 2.7 μ)	4 per cent (Average membrane thickness 5.9 μ)	6 per cent (Average membrane thickness 18.2 μ)
<i>mv.</i>	<i>mv.</i>	<i>mv.</i>
44	52	54
49	51	54
47	49	53
50	53	55
44	44	56
47	53	55
44	47	55
	53	54
		54
Mean: 46.4 \pm 1.0	Mean: 50.2 \pm 1.2	Mean: 54.4 \pm 0.3

TABLE II

The Influence of the Thickness upon the Concentration Potential 0.1 M KCl/0.01 M KCl across Dried Collodion Membranes. Polylayer Membranes Prepared from 8 Per Cent Solutions. Concentration Potentials in Millivolts

A Purified Mallinckrodt Parlodion 4 layers (average membrane thickness 162 μ)	B Baker collodion u.s.p.	
	2 layers (average membrane thickness 79.7 μ)	4 layers (average membrane thickness 117 μ)
<i>mv.</i>	<i>mv.</i>	<i>mv.</i>
31	43	47
29	43	45
33	40	47
38	43	45
29		
30		
Mean: 31.7 \pm 1.4	Mean: 42.5 \pm 0.8	Mean: 46.0 \pm 0.6

mean. From the standard deviations of the means the high statistical significance of the differences in potential values of adjacent points on the ascending branches of the curves (Fig. 3) can readily be inferred. Thus, in the case of Mallinckrodt Parlodion the probability is 5000:1 that the difference between the values pertaining to the 2.7 and 6.1 μ membranes is not due to chance; it is only 15:1 for the 6.1 and 8.9 μ membranes, corresponding to the relatively small difference in the membrane thickness. The difference between the 8.9 and 18 μ membranes is not due to chance, with a probability of better than 3000:1. The difference between the 18 and 27 μ membranes, however, has a chance less than 1:1 to be significant. The significance of the thickness effect

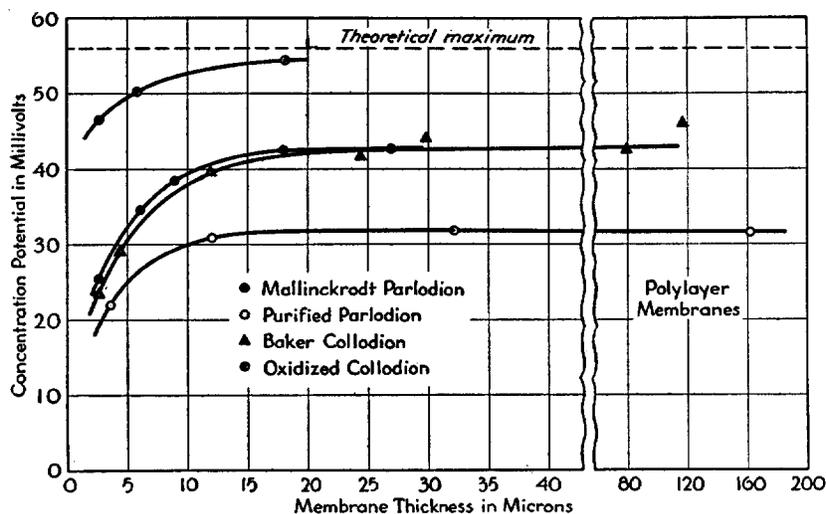


FIG. 3

with the other brands of collodion is similar to that given for Mallinckrodt Parlodion.

III

The general results of the experiments presented in Tables I and II can be read conveniently from Fig. 3 and may be summarized as follows:—

1. The concentration potential is a function of the membrane thickness with all the collodion preparations which were investigated.
2. With electrochemically *active* collodion nearly maximum values were obtained with membranes of less than 0.01 mm. thickness, the theoretically possible maximum being reached within 2 mv. with membranes of about 0.02 mm. thickness.
3. With rather *inactive* collodion preparations the potentials increase from low values in the case of the thinner membranes to medium values with thicker (0.02–0.03 mm.) membranes. Still thicker membranes do not yield appreci-

ably higher concentration potentials; actually, there is no indication that the theoretically possible maximum value could be obtained with membranes of any thickness.

The former assumption that the concentration potential is independent of membrane thickness must be abandoned. Parenthetically we may add that this conception had its origin in all probability in the preferential use of active collodion for membrane work and also in the nearly universal use of membranes of appreciably greater thickness than those used for the foregoing experiments.

If we recall the discussion in the first half of this paper we further come to the conclusion that the homogeneous phase theory cannot be applied to dried collodion membranes, as this theory predicts independence of concentration potential and membrane thickness. The experimental results are compatible in a general way with the micellar-structural theory. However, neither of the two simple cases discussed in the first half of this paper fits the experimental results adequately over the whole range of investigated membrane thicknesses.

The first of the suggested simple structural possibilities predicts an increase in the concentration potential and finally an approach to the maximum possible potential with increasing membrane thickness according to equation 4. The ascending branches of the curves agree in a qualitative way with this concept; however, we see that this maximum value is not reached as a rule. Rather, a constant potential value, different from the thermodynamically possible maximum is reached at a certain thickness of the membrane; this value does not seem to increase with still thicker membranes. Even if we consider only the ascending branches of the curves, it seems impossible to apply equation 4; whatever values for a (and the unit thickness of membrane) are tried, the experimental curves are too flat. The horizontal part of the curves, on the other hand, would be consistent with the second of the above possibilities as expressed in equation 10; however, this equation does not account at all for the ascending branches of our curves.

Obviously, the two possibilities which were discussed at the beginning of this paper are too simple; our problem therefore is to find a consistent and inherently probable way to explain the shape of our curves, not only for the experimentally accessible range, but also for the range of still thinner membranes; our experimental curves have to be extrapolated to or at least near to the point of intersection of the thickness and of the potential axes.

Any useful explanation obviously needs to assume greater structural complexity of the membranes than the two suggested possibilities. It is rather suggestive to assume that the orientation and aggregation of the collodion molecules in the surface layers and near them is different from the situation in the interior of the membrane. To simplify the argument we assume in the following discussion that the two sides of the membrane are equivalent, or at least analogous in their structural buildup; this, however, is by no means neces-

sarily true, as the forces acting upon the two sides of the membrane during the process of drying are not exactly identical. It seems probable that the molecular aggregation in the surface layers should be denser and more regular than in the interior of the membrane where these forces are not operative. Corresponding to this one would find in the surface layers a smaller specific permeability and greater ionic selectivity. According to this view, the membrane would be made up of qualitatively different layers; the surface layers would be mainly responsible for the electrical and general permeability properties of the membrane, the inner layers acting as a more indifferent supporting structure.

This picture agrees well with the experimental results. The steepness of the ascending branches of our curves in the region of the thinnest membranes indicates a very great specific ionic selectivity per unit thickness in this region in a structure conforming in some degree to the picture of Fig. 1. In the addi-

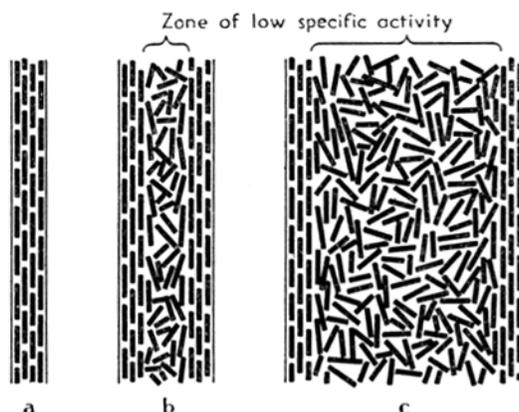


FIG. 4

tional layers of somewhat thicker membranes the selectivity becomes less, hence the rapid flattening out of our curves which is incompatible with equation 4. If the collodion does not happen to be very active, the aggregate selectivity of these layers on the two sides of the membrane is not sufficient to cause maximum concentration potentials. The additional thickness of the membrane is composed of a structure of relatively low specific selectivity, probably due to a somewhat looser state of aggregation of the collodion molecules. These inner layers then would contribute practically nothing to the overall selectivity of the membrane, whatever their thickness may be. These layers thus conform to the picture sketched in Fig. 2.

According to the ideas outlined, membranes above a certain minimum thickness are built up of identical active structures with or without an inactive interlayer. The assumed relationship between a very thin membrane and two constant potential value membranes of different thickness is sketched in Figs. 4 *a*, *b*, and *c*.

From this discussion it can be concluded that the experimental facts can readily be explained by the assumption of a structure which is a combination of the two simplest possible structures which were mentioned in the first part of this paper. The factual state of any given layer of a membrane probably is between the two extremes, a great variety of intermediate states occurring in each membrane. However, until further proof is available, this picture must be considered as entirely hypothetical.

With polylayer membranes, as said before, each previous layer is partially dissolved when one adds another. Here, too, as it appears from the results, the two outermost layers of the membrane are probably responsible for the observed concentration potentials. However, at this time it seems superfluous or at least premature to discuss this possibly more complex case in greater detail.

Further discussion of the significance of the above results with regard to the problem of membrane structure in general must be postponed. Only after additional data concerning water and electrolyte content, conductance, and charge density become available will such a discussion and a comparison with physiological membranes become profitable.

SUMMARY

1. Experiments were carried out to decide whether or not the electromotive properties of dried collodion membranes depend upon their thickness.
2. A number of dried collodion membranes of varying thickness, 3–160 μ , were prepared from collodion preparations of different electrochemical activity. The characteristic concentration potentials across them were measured and the means of these values determined for each thickness.
3. The characteristic concentration potentials across dried collodion membranes are a function of their thickness. The thinnest membranes yield in all cases the lowest concentration potentials; increasingly thicker membranes give increasingly higher potential values, until a constant value is reached which is characteristic of the particular collodion preparation used. With electrochemically active collodion, characteristic concentration potentials approaching the thermodynamically possible maximum are obtained with membranes of only 10 μ thickness, thinner membranes giving appreciably lower values. With two rather inactive commercial collodion preparations the characteristic concentration potential increases from about 30 mv. for membranes 3 μ thick to about 42 mv. for 20 μ membranes; still thicker membranes do not show a significant increase in the potential values. With a highly purified collodion preparation the constant maximum value was found to be about 32 mv., 4 μ thick membranes giving only about 22 mv.
4. These results do not support the homogeneous phase theory as applied to the dried collodion membrane. They are readily compatible with the micellar-structural theory. Several special possible cases of the latter as applied to the dried collodion membrane are discussed.