

THE STRUCTURE OF THE COLLODION MEMBRANE AND ITS ELECTRICAL BEHAVIOR

X. AN EXPERIMENTAL TEST OF SOME ASPECTS OF THE TEORELL AND MEYER-SIEVERS THEORIES OF ELECTRICAL MEMBRANE BEHAVIOR

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I

In several recent publications¹⁻⁶ we have shown experimentally that the acidic groups present in collodion are the primary cause of its electrochemical activity in solutions of strong inorganic electrolytes. The surface concentration of these acidic dissociable groups is assumed to determine the degree of electrochemical activity of any given collodion sample. The abundance of these groups varies with the past history of the collodion from which the membranes are prepared.

This concept of the cause of the electrochemical membrane activity is in general agreement with some newer theories of electrochemical membrane activity, outlined independently by Teorell⁷ and by Meyer and Sievers.⁸ On the basis of these theories it can be concluded that the base exchange capacity of the pore surfaces of a given membrane and its porosity are the factors determining its electrochemical activity. The theory also allows quantitative predictions by which one can link in a definite way base exchange capacity and electromotive behavior.

The empirical correlation between the base exchange capacity of various collodion preparations and their electrochemical activity has been described previously⁴ in connection with studies of the base exchange properties of precipitated fibrous collodion. Such preparations have a very large specific surface and are suitable objects from which to obtain basic information. Our experimental results can be summarized by stating that there is no necessary

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

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

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

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

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

⁶ Sollner, K., and Carr, C. W., *J. Gen. Physiol.*, 1943, **26**, 309.

⁷ Teorell, T., *Proc. Soc. Exp. Biol. and Med.*, 1935, **33**, 282; *Proc. Nat. Acad. Sc.*, 1935, **21**, 152.

⁸ Meyer, K. H., and Sievers, J.-F., *Helv. Chim. Acta*, 1936, **19**, 649, 665, 963.

correlation between base exchange capacity of collodion and its electrochemical activity. There are preparations which combine (a) immeasurably low base exchange capacity and low electrochemical activity, (b) immeasurably low base exchange capacity and high electrochemical activity, (c) measurable base exchange capacity and high electrochemical activity, (the activity in this case is not necessarily higher than in the preceding one).

In later experiments Sollner and Anderman⁹ have made a study of the total acidity, the "acid number," of similar preparations. A qualitative parallelism between the electrochemical activity and total acidity was found; it also was shown that the total acidity did not vary in the same manner as the base exchange capacity of the different collodion samples.

These results were contrary to the original expectation, and, more important, they seemed incompatible with the Teorell⁷ and Meyer-Sievers⁸ theories. The present investigation is an attempt to clarify this situation on a quantitative basis. The base exchange capacity of membranes is compared with what should be an identical or at least a similar value calculated according to the Teorell and Meyer-Sievers theories on the basis of potentiometric measurements.

A necessary condition for the applicability of these theories to membranes of a porous character is their rigidity; *i.e.*, their inability to swell appreciably under the experimental conditions. We have shown previously¹⁰ that both porous and water-wetted dried collodion membranes can be considered rigid structures in solutions of strong inorganic electrolytes.¹¹ They can therefore be used to test the theory.

Before the experiments are described, a short exposition of the Teorell and Meyer-Sievers theories must be given. In substance the two concepts are identical. Teorell has given only brief accounts of his theory; Meyer and Sievers go much more into detail and have tried to corroborate their ideas by experiment. This theory is today the outstanding example of an attempt to put on a rational basis perhaps the most important electrochemical function of membranes, their electromotive action.

Since the Teorell, Meyer-Sievers theory is of a highly involved nature, it is preferable to give a short outline of it as presented by Meyer.¹²

"Consider a membrane consisting of an acid high-molecular substance, for instance of pectin chains, of which the carboxyl groups have been neutralised with metallic

⁹ Sollner, K., and Anderman, J., *J. Gen. Physiol.*, 1944, **27**, 433.

¹⁰ Carr, C. W., and Sollner, K., *J. Gen. Physiol.*, 1943, **27**, 77.

¹¹ Air-dried collodion membranes swell to a slight extent when placed in water, but do not change in structure when transferred from water to solutions of strong electrolytes. Therefore, for the present purpose they can be considered as rigid non-swelling structures.

¹² Meyer, K. H., *Tr. Faraday. Soc.*, 1937, **33**, 1073.

cations, *e.g.*, potassium ions. The membrane then possesses fixed anions and mobile cations. The cations may therefore be displaced if a supply of others is maintained from one side: the membrane is cation permeable. The concentration of the fixed anions, calculated in gram equivalents per litre of the imbibed liquid, is a quantity characteristic for each membrane which we will call the "selectivity constant," A . If now the membrane be immersed in a salt solution, both ions of the salt will penetrate into it; the equilibria then obtaining may be calculated from the Donnan equation: the actual membrane behaves like a solution bounded by two ideal Donnan membranes through which the fixed ions cannot pass. . . ."

"If a current is passed across the membrane, the transport of the electricity will be divided between the two kinds of mobile ions in accordance with the relative numbers of ions passing through the membrane. The ratio, n_c/n_A between the numbers of cations and of anions traversing the membrane, which we will call the ratio of the transport or "traversal" numbers, may be determined by the same methods as those used for the determination of transport numbers in a solution. n_c/n_A depends on the rates of migration of the mobile ions and on their number; as mentioned above, the latter is dependent on the concentration of the ions in the surrounding liquid. We then obtain

$$\frac{n_c}{n_A} = \frac{U_C \cdot (y + A)}{U_A \cdot y} = \frac{U_C \cdot \sqrt{4c^2 + A^2} + A}{U_A \cdot \sqrt{4c^2 + A^2} - A} = \frac{U_C}{U_A} \cdot R,$$

where U_C and U_A are the rates of migration, c the molar concentration of the salt in the surrounding liquid, and A the selectivity constant. . . ." y is the concentration of mobile anions in the membrane.

"The dependence of the selectivity, *i.e.* of the quantity n_c/n_A , on the concentration is expressed by the factor R . Its dependence on the ratio c/A is shown by the following table:

c/A	10	1	0.1	0.01	0.001
R	1.1	2.6	101	10,000	1,000,000

"If we therefore take a membrane with wide pores such that the concentration of the fixed ions in its aqueous parts is normal ($A = 1, c^2/A = c^2$) and surround it with a salt solution the ions of which have equal mobilities, then R will equal the selectivity n_c/n_A . The dependence of n_c/n_A on the external concentration has, as mentioned above, been long known (the "concentration effect"), but so far without having been explained.

"Ionic selectivity is not, however, the sole factor governing ionic permeability: in a network the "sieve effect" can also occur, its importance being the greater the finer the mesh of the net; this will in general be the case with membranes which contain little liquid of imbibition. Finally the "solubility" of the ions in the membrane may also play a part. By this we mean that, as a result of the attractive influence of the organic groups of the membrane, some, say organic, ions may attain a greater concentration in the aqueous liquid of imbibition of an organic membrane than in pure water. The complete equation therefore reads

$$\frac{n_c}{n_A} = \frac{U_C \cdot \sqrt{4c^2 l_C l_A + A^2} + A}{U_A \cdot \sqrt{4c^2 l_C l_A + A^2} - A},$$

where U_c/U_A is the ratio of the rates of migration in the membrane under the influence of the sieve effect, and l_c and l_A the solubility coefficients (partition coefficients) of the ions with respect to membrane and water.

“Now these two essential properties of the membrane—its sieve action with respect to different ions (as expressed by the quotient U_c/U_A) and its selectivity constant, can be determined by measuring the traversal numbers at different concentrations. The potentiometric method is the best; the potential set up when the membrane separates two solutions of the same salt, but of different concentrations is measured, the absolute concentrations being varied in such a way that their ratio is kept constant. When there is no ionic selectivity the potential is determined only by the quantity U_c/U_A , which is dependent on the absolute concentration; the greater the value of A as compared with the external concentration, the more marked will be the ionic selectivity.

“ A , the selectivity constant, and U_c/U_A , which includes the expression for the sieve effect, can be quantitatively determined either by calculation or graphically. We will not here reproduce the complicated formulae required for the calculation, but will merely give a short account of the graphical method.

“Curves are constructed plotting as ordinates the potential differences measured between two solutions of the same binary electrolyte, the concentrations (c_1, c_2) of which are always as 1:2, and as abscissae the quantity $\log \frac{A}{c_1}$. For an electrolyte, the two ions of which have equal mobilities in the membrane (*i.e.*, $U_c/U_A = 1$), a certain curve will then be obtained while other values of U_c/U_A will result in other curves. . . .” (The calculated curve for $U_c/U_A = 1$ is given below in Figs. 1 and 2.)

“To determine A and U_c/U_A for an unknown membrane it will then only be necessary to determine several values of E for different absolute values of c_1 , the concentration c_2 being always kept equal to $2c_1$. The observed values of E are then plotted against c_1 (ordinates) using the same coordinates as before, and then the experimental curve is displaced sideways (parallel to the abscissa) until it has been successfully brought into coincidence with one of the curves already drawn; interpolation may be necessary in this procedure. In this way U_c/U_A is determined, the value depending only on the shape of the curve. The amount of the displacement as read off on the abscissa gives $\log A$, and therefore A”

This quantity, “ A ,” according to Meyer and Sievers can be determined on the basis of potentiometric measurements. Values thus obtained will be designated as A_p throughout this paper.

On the other hand, “ A ” by definition is the concentration of the fixed ions in the aqueous part (pore space) of the membrane, or more correctly the concentration calculated from the number of equivalents of anions fixed immovably to the pore walls, divided by the pore space (in liters) of the same membrane.

Electrically these anions are compensated for by an equivalent quantity of cations. These cations, potassium ions in the example given by Meyer, can be replaced by other cations if the membrane is brought into a suitable electrolyte solution. This actually is the mechanism which according to the theory makes the membrane behave in its characteristic manner with different cations.

In other words, the membrane must show the phenomenon of base exchange in order to exhibit its electromotive properties.

If one is able to determine the base exchange capacity of the membrane, and if one knows its pore space, one is able to calculate the "A" value of the Meyer and Sievers theory,¹³ "A" being the base exchange capacity in equivalents divided by the pore volume in liters. The "A" values which are calculated from base exchange studies will be denoted A_b .

If the theoretical assumptions on which the theory is based are correct, A_p , derived from potential measurements must be identical with A_b , derived from base exchange studies. A comparison of the "A" values obtainable in these two independent ways is the subject of the present investigation.

Before approaching this subject, however, a few critical remarks should be made concerning the Teorell, Meyer-Sievers theory.

Excellent agreement with the experimental facts has been claimed for this theory in several respects, particularly the independence of the "A" value (A_p) of concentration. Actually the constancy of A_p is as good as claimed only in rare cases, as was shown by Fetcher¹⁴ for Meyer and Sievers own experimental data.

The constancy of A_p and its independence of the nature of the electrolyte is bound to so many conditions that it can hardly be expected to hold true. Firstly, it assumes a degree of ionization of the fixed ionizable surface compounds independent of the nature of the counter-ions and of the concentration of the electrolyte solution. This can hardly be the case even when comparing monovalent cations; the hydrogen ion certainly should behave much differently for the dissociation of the acidic surface compounds ("nitrocellulosic" acid with collodion) undoubtedly is much less than that of the corresponding alkali salts.

With membranes having only small pores an additional difficulty arises. The electrolyte content of dried collodion membranes after several days' contact with solutions of different chlorides varies with the cation. With hydrochloric acid and potassium chloride, the electrolyte content of the membranes was found to be about twice as great as with lithium chloride.¹⁵ Presumably

¹³ This procedure involves the assumption that the number of exchangeable, monovalent cations is identical with the number of dissociated, immovable electronegative groups; in other words it assumes complete ion exchange and complete dissociation of the dissociable surface compounds. In view of the completeness of the ion exchange and of the high degree of dissociation of the alkali salts of even weak organic acids these assumptions appear to be permissible. It will be seen below that any error which possibly could be introduced in this manner is too small to affect to a significant extent any conclusions drawn from the experimental results.

¹⁴ Fetcher, E. S., Jr., *J. Physic. Chem.*, 1942, **46**, 570.

¹⁵ Green, A. A., Weech, A. A., and Michaelis, L., *J. Gen. Physiol.*, 1929, **12**, 473.

these membranes contain pores inaccessible for the lithium ion, but accessible for potassium, hydrogen, and chloride ions. There seems to be little doubt that only a part of the pores which are electromotively active with hydrochloric acid and potassium chloride, are electromotively active with lithium chloride. Identity of the A_p values with the various electrolytes would, therefore, be fortuitous, at least from the point of view of the theory.

It must be recognized that at least some of these difficulties could be overcome by proper corrections and additions to the Teorell, Meyer-Sievers theory, which would result in a better agreement between the theoretical and experimental curves.

The main question of general interest which arises is whether the Teorell, Meyer-Sievers theory is inherently a correct representation of the physical facts which lie behind the observable potential-concentration relationships, or whether it is only a formal way of bringing these relations into a fictitious, formally correct framework. It is clear that the planned test of the agreement between the selectivity constants A_p and A_b as established by the two entirely different methods would materially help to decide this question in one or the other way.

II

According to the above outlined plan two kinds of measurements were performed with the same membranes. First the potentiometric studies were made; then the base exchange was determined, and in order to obtain the water content, the wet and dry weights of the membranes were measured. From these data the selectivity constants, A_p and A_b , were obtained as explained in principle above.

In order to cover a wide range of membrane porosities and activities the following kinds of membranes were investigated: (a) membranes prepared from collodion preparations of different activity; (b) "oxidized membranes."³

In the case of the first of these groups "dried" and "porous" bag-shaped membranes were prepared from the collodion preparations characterized in Table I which gives the brand and pre-treatment (if any) of the various preparations together with the data on their electrochemical activity. The membranes were cast in 30×110 mm. test tubes from 5 per cent collodion solutions in absolute ether-alcohol (75:25); the porous membranes were immersed in water after drying for only 20 minutes, the "dried" ones after 24 hours drying time.

The second group of membranes, the "oxidized membranes" were prepared in the following manner. "Dried" membranes cast from commercial collodion were swelled in alcohol of varying (85, 90, and 95 per cent) concentration. The swelled membranes were washed with water, oxidized with 1 M NaOBr for 3 hours, and rewashed thoroughly. In this way a series of oxidized membranes was obtained with water contents of 17, 24, and 62 volume per cent. In all cases at least three membranes of each kind were prepared.

For the *potential measurements* one membrane only of each kind was used since it was shown in preliminary experiments that the variations within each set of identically prepared membranes were negligible. The potentials were

TABLE I
Some Characteristics of Various Collodion Preparations*

1	2 Brand of collodion and pretreatment (All preparations were precipitated from ether-alcohol solutions and dried)	3 Base exchange data (48 hrs.)		5 Acid number 0.01 N KOH per gm. dry collodion (corrected for ash content)	6 Electrochemical activity		8 Characteristic concentration potential 0.1 M KCl/0.01 M KCl (dried membranes†)
		0.01N NaOH per gm. dry collodion on treatment with 0.5 M KCl	pH values on treatment with 0.5 M KCl		Anomalous osmosis (porous membranes‡) Osmotic rise with 0.25 M sucrose	Anomalous osmotic rise with $\frac{M}{512}$ K ₂ SO ₄	
		ml.		ml.	mm.	mm.	mv.
1	Mallinckrodt "Parlodion," boiled 15 hrs. in 90 per cent alcohol	0.01	5.9	1.0	106	15	27
					128	16	28
					136	28	28
2	Baker Collodion U.S.P., commercial preparation	0.03	5.3	1.5	126	50	41
					128	32	42
					130	47	42
3	Oxidized collodion; Baker collodion cotton, "Pyroxilin" oxidized 48 hrs. with 1 M NaOBr and boiled several times with water	0.27	4.2	3.3	118	130	51
					130	142	52
					137	148	53
4	Oxidized collodion (No. 3), washed 16 times with 95 per cent alcohol	0.03	5.0	1.6	132	119	49
					137	128	50
					140	131	52

* The base exchange experiments summarized in Table I were performed with precipitated fibrous collodion as in previous work.⁴ The acid numbers were obtained using the method previously described by Sollner and Anderman.⁹ The anomalous osmosis and concentration potentials were determined as described in previous papers.¹⁻⁴

‡ The porous membranes described in columns 6 and 7 are of course not the same specimens as the dried ones characterized in column 8.

measured with potassium chloride solution of one concentration inside the membrane and a potassium chloride solution of another concentration outside. The concentration ratio was always 2:1 while the absolute concentrations varied between 0.64/0.32 to 0.0050/0.0025 M. In the case of the "porous" membranes, the solutions were stirred vigorously by bubbling air through them

to minimize the effects due to diffusion of electrolyte or movement of solution in bulk (essentially by anomalous osmosis) from the more concentrated solution into the less concentrated one. The solutions were also reversed in a few cases to make sure that the membranes were symmetrical; this was true for all those tested. The results of these potential measurements are plotted in Figs. 1 and 2. Also included in the figures is the curve of Meyer and Sievers calculated for KCl ($U/V = 1$) and $A_p = 1$. As indicated above this is the standard

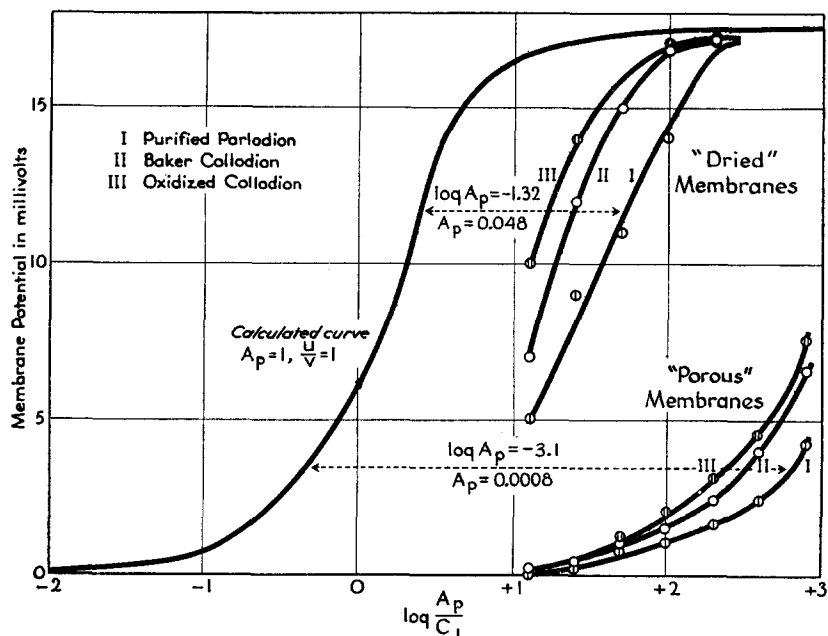


FIG. 1. Potential / $\log \frac{A_p}{C_1}$ curves of "dried" and "porous" membranes prepared from various collodion preparations.

curve, by reference to which A_p for any membrane is determined. The upper three experimental curves in Fig. 1 are for the dried membranes while the lower three are for the porous membranes. Curves for the purified oxidized collodion (No. 4 in Table I) are not shown because they almost coincide with the curves for the unoxidized (Baker) collodion. Fig. 2 shows the results obtained with "oxidized membranes" of varying porosity.

The logarithms of the A_p values can be read directly from the graphs. $\log A_p$ is the horizontal distance between the standard curve and the experimental curve. If these curves are on the right side of the standard curve, this value is negative. Since even the steeply ascending branches of the experimental

curves are not strictly parallel with the theoretical curve a mean A_p value for each curve must be chosen. These A_p values for dried and porous membranes cast from the various collodion preparations (characterized in Table I) are listed in column 8 of Table II, and for "oxidized membranes" in Table III. As will be seen below the uncertainty of the A_p values, which is due to the shape of the experimental curves, is of no consequence for the conclusions which are based upon them.

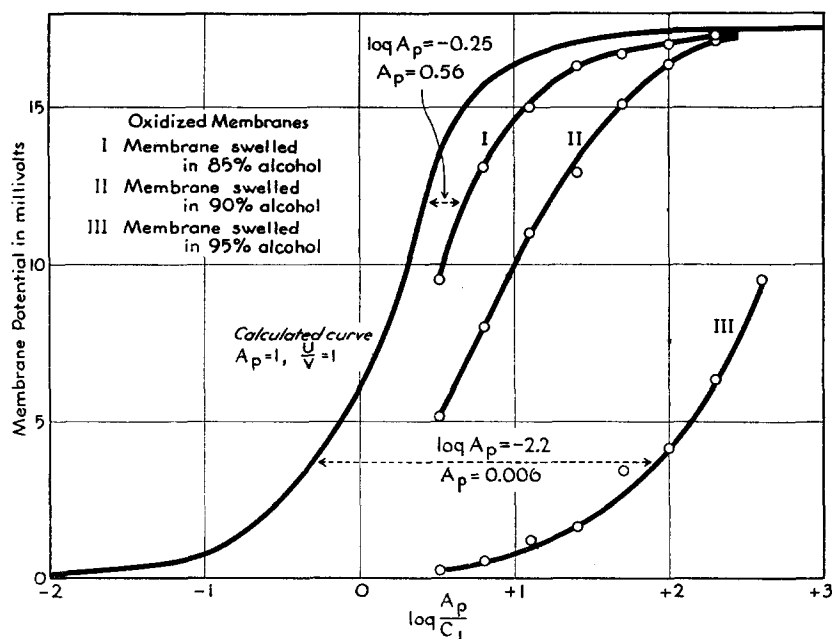


FIG. 2. Potential / $\log \frac{A_p}{C_1}$ curves of "oxidized membranes" of various porosities.

After the potential measurements were completed, the *base exchange capacity of the membranes* was determined. The general principles of the base exchange method and its application to collodion have been discussed in a previous paper⁴ and need no further comment here. The only change in the procedure was that in the present experiments the base exchange capacity of *membranes* was measured, not the base exchange of fibrous collodion as was done previously.

The base exchange experiments were carried out with three membranes of each kind in order to have sufficiently large samples. The membranes that had been used for the potential measurements were first returned to the acidic state as described for fibrous collodion in previous papers.^{4, 5} For the base exchange the membranes were immersed in 25 ml. of 0.5 M KCl solution.

After 24 hours contact with the membranes the pH of the solution was determined with a glass electrode. Control experiments were also run with water in place of the electrolyte solution. The pH values of the KCl solution and of the water are reported in columns 5 and 6 of Tables II and III.

For many of the membranes tested, the change in pH was very small and moreover the same for the water as for the KCl solutions.¹⁶ Nevertheless, in these cases the pH data in column 5 were used in calculating the A_b values.

Finally the *water content* of these membranes was determined. The wet membranes were removed from their glass rings, cut open, blotted dry of surface water, and weighed in a closed weighing bottle. Then they were dried over sulfuric acid and reweighed. The weight loss represents the water content.¹⁷ The water content of the membranes in volume per cent is given in column 3 of Tables II and III. The absolute water content of the various experimental samples is given in column 4.

The calculation of A_b , the base exchange selectivity constant, is based on the following consideration. A_b by definition is equal to the concentration of the fixed ionizable groups in the water contained in the membrane, which is equal to the concentration of the counter-ions of the fixed groups. The counter-ions, H^+ ions in our case, are determined experimentally after exchange with the K^+ ions of a known volume of KCl solution; being contained now in the KCl solution their concentration in the latter is measured electrometrically. The concentration of the counter-ions of the fixed dissociable groups (and therefore the concentration of the latter) in the water contained in the membrane can therefore be calculated from the following equation.

$$C_m \times V_m = C_s \times (V_s + V_m)$$

¹⁶ For detailed discussions of this point see: Sollner, K., Carr, C. W., and Abrams, I., *J. Gen. Physiol.*, 1942, **25**, 411; and Sollner, K., and Anderman, J., *J. Gen. Physiol.*, 1944, **27**, 433.

¹⁷ The water content of collodion membranes represents only a maximum value for the available pore space. Some water, undoubtedly, is "bound" to the collodion and not available for the typical membrane functions. With "porous" membranes of high water content the fraction of "bound" water is negligibly small; with dried membranes the "bound" water may be a sizable fraction of the total water content (Carr, W. C., and Sollner, K., *J. Gen. Physiol.*, 1943, **27**, 77). In the calculations reported below which involve the pore water content of the membranes the assumption is made that the total water content is pore water. If we make the exaggerated assumption that 50 per cent of the water content of the "dried" membranes is "bound" water the figures for cases 1 to 4 in column 7 of Table II would be twice as large as given, and the figures in column 9 would be half of the present values. This, however, would in no way affect the essence of the conclusions which will be drawn below from these figures.

C_m = Concentration of fixed ionizable groups in the water contained in the membrane.

V_m = Volume of H₂O in the membrane (column 4 of Tables II and III).

C_s = Concentration of HCl in the KCl solution (see column 5 of Tables II and III).

V_s = Volume of the KCl solution (25 ml.).

Since by definition $C_m = A_b$,

$$A_b = \frac{C_s \times (V_s + V_m)}{V_m}; \quad (2)$$

as $V_m \ll V_s$ we may use the simplified equation

$$A_b = \frac{C_s \times V_s}{V_m} \quad (3)$$

The base exchange selectivity constants A_b so calculated are recorded in column 7 of Tables II and III.

The fact that many of these A_b values are only maximum values is indicated by a < sign.

Column 9 of Tables II and III gives the end result of the foregoing experiments and calculations, namely the comparison between the potentiometric selectivity constant A_p and the base exchange selectivity constant A_b ; it is given as the ratio $\frac{A_p}{A_b}$.

III

We turn now to the main objective of this paper, namely the comparison of the A_p and A_b values, the ratio of which is given in column 9 of Tables II and III for eleven different cases.

In prior sections of this paper it was pointed out that the Teorell, Meyer-Sievers theory leads to the anticipation of an identity of the selectivity constants, as determined by the potentiometric and base exchange methods. The ratio $\frac{A_p}{A_b}$ should be one, or, considering the uncertainties of the theory, this ratio should not deviate too strongly from unity.

The first glance at the $\frac{A_p}{A_b}$ ratio in the last column of Tables II and III, however, shows that this is by no means the case. The values of the $\frac{A_p}{A_b}$ ratio are spread over three orders of magnitude, varying from 0.08 to 107.

In view of the fact that the agreement between the A_p and A_b values is much better with the "oxidized membranes" (Table III) than with the membranes prepared from various collodion preparations (Table II) we shall treat the two groups separately.

TABLE II
A_b and A_p Values of Membranes Prepared from Various Collodion Preparations

1	2	3	4			5	6	7	8	9
	Brand of collodion (see Table I) and type of membrane	Water content of membranes	Base exchange data			pH of 0.5 M KCl solution after 24 hrs. contact with the membranes	pH of water after 24 hrs. contact with the membranes	<i>A_b</i> calculated from base exchange data (see columns 4, 5, and 6)	<i>A_p</i> obtained from experimental potential curves of Fig. 1	$\frac{A_p}{A_b}$
			Water content <i>V_m</i> of membranes used for base exchange							
		<i>vol. per cent</i>	<i>gm.</i>				<i>equivalents/l. × 10³</i>	<i>equivalents/l. × 10³</i>		
1	Purified "Parlodion," dried membranes	8.2*	0.029	5.8	5.9	<1.4*	48	>34*		
2	Baker Collodion U.S.P., dried membranes	10.5*	0.022	5.9	5.8	<1.5*	100	>67*		
3	Oxidized collodion, dried membranes	10.5*	0.023	5.9	5.9	<1.4*	150	>107*		
4	Oxidized collodion, purified, dried membranes	10.5*	0.021	5.9	6.0	<1.6*	100	>62*		
5	Purified "Parlodion," porous membranes	80	0.821	5.8	5.8	<0.05	0.8	>16		
6	Baker Collodion U.S.P., porous membranes	75	0.626	6.2	6.0	<0.02	1.5	>75		
7	Oxidized collodion, porous membranes	79	0.339	5.4	6.0	0.3	2.0	6.7		
8	Oxidized collodion, purified, porous membranes	77	0.556	6.0	6.2	<0.045	1.5	>33		

* Compare footnote 17.

TABLE III
A_b and A_p Values of Various "Oxidized Membranes"

1	2	3	4			5	6	7	8	9
	Concentration of alcohol used for swelling of membranes	Water content of membranes	Base exchange data			pH of 0.5 M KCl solution after 24 hrs. contact with the membranes	pH of water after 24 hrs. contact with the membranes	<i>A_b</i> calculated from base exchange data (see columns 4, 5, and 6)	<i>A_p</i> obtained from experimental potential curves of Fig. 2	$\frac{A_p}{A_b}$
			Water content <i>V_m</i> of membranes used for base exchange							
	<i>per cent</i>	<i>vol. per cent</i>	<i>gm.</i>				<i>equivalents/l. × 10³</i>	<i>equivalents/l. × 10³</i>		
1	85	17	0.030	3.4	6.0	330	560	1.8		
2	90	24	0.045	3.4	5.9	220	170	0.77		
3	95	62	0.203	3.2	6.1	78	6	0.08		

With the membranes listed in Table II the given A_b values are smaller by one to two orders of magnitude than the A_p values. The discrepancy between the results for the two different methods is in reality greater because the calculation of A_b is based upon experimental data which represent the upper limit of the exchange capacity of the membranes. These values—except with case 7—are, as was explained before, fictitiously high. It is impossible at present to estimate with any degree of accuracy the influence of this factor, but the true base exchange capacity—except in case 7—may be smaller by orders of magnitude; the discrepancy between the two A values would be increased correspondingly.

There is also another factor which tends to increase the discrepancy between A_p and A_b . Sollner and Anderman⁹ have shown that the time required for reaching the maximum base exchange even with fibrous collodion is 24 hours, the base exchange after 30 minutes being only about 5 to 20 per cent of the final value. Evidently a large number of the active groups lie in the interior of the micelles or in dead-end cavities in which the exchange can take place only very slowly. On the other hand, if membrane potentials are measured the final potential values are established after a few minutes of contact with the electrolyte solution. The number of active groups responsible for the potentials, therefore, must be smaller probably by at least one order of magnitude than the number determined by the base exchange after 24 hours upon which our calculations are based. If this time effect is considered, as it must be, the ratio " A_p "/" A_b " becomes larger by at least one order of magnitude than the values given in column 9 of Table II, quite apart from the influence of the above mentioned other factor. The true discrepancy between the A_p and A_b values therefore is not one to two orders of magnitude as indicated in the last column of Table II, A_b is in reality at least two to three orders of magnitude smaller than A_p . If the first of the two factors which tend to increase this discrepancy could be evaluated quantitatively, the disagreement would be found to be still greater.

The results with the "oxidized membranes" in Table III indicate a better agreement between the two methods of determining the selectivity constant than that obtained with the first group of experiments. In one case (No. 3 of Table III) A_b is larger than A_p by a factor of 13.

It must be emphasized that contrary to the situation with the preceding group of membranes, the base exchange values with the "oxidized membranes" are believed to be correct base exchange capacity values, not falsified by any known error. The first factor which in the former cases tended to decrease the A_b values is therefore here not operative. However, the time effect on the base exchange must be considered; if this is done A_b values become much lower. Thus for the one case (No. 3) the agreement between A_p and the corrected A_b value may be satisfactory, but with the other two cases (Nos. 1 and

2), the true A_b value is considerably smaller than A_p , probably by at least one order of magnitude. In any case, however, the discrepancy is much smaller than with the former groups of membranes.¹⁸

If one now considers both groups of experiments together it becomes apparent that the disagreement between the A_p and A_b values is the smaller, the greater the porosity of the membranes and the higher their base exchange capacity; *i.e.*, the greater the charge density of the pore walls. We hope to be able to discuss in a subsequent publication the probable significance of this regularity which obviously must be closely correlated to the basic geometrical and electrical structure of the membranes.

IV

The attempt to verify the Teorell, Meyer-Sievers theory as applied to a variety of porous membranes by the comparison of selectivity constants arrived at on the basis of two different, experimentally independent methods has failed completely. In this section we shall discuss briefly the tentative conclusions which can be drawn from our experimental results concerning the Teorell, Meyer-Sievers theory. The conclusions must be based upon these two facts. On the one hand the theory predicts in a semiquantitative way the shape of the potential-concentration curves on the basis of clear and well defined assumptions; it therefore most likely contains at least a considerable element of basic or at least formal agreement with the reality. On the other hand, the A_p and the A_b values which should be identical according to the theory do not show any regular and reasonable agreement. This can indicate one of several possibilities, foremost amongst them that the attempt to measure A_b values is basically erroneous; or that the theory is basically erroneous; or that the theory, though at least formally correct in some respects (as far as the A_p values are concerned), is not based on a true, but on a one-sided, fictitious picture of the physical facts. It therefore may not permit an application which goes beyond the establishment of formal A_p values.

Of these three main possibilities the first one seems least likely, the theory being founded on the very assumptions which coincide with the definition of our A_b selectivity constant. For the above given reasons we are reluctant to accept the second possibility, namely, that the whole theory is basically erroneous. The greatest inherent probability seems to lie with the third of the above mentioned possibilities, namely, that the theory is built on a basis which though partially correct, neglects some essential features of the real physical

¹⁸ It is interesting to note that there is no parallelism of the change of A_p and A_b with changes in water content. When the water content changed from 17 to 62 per cent, A_p decreases by a factor of 93, whereas A_b decreases by a factor of only 4.2. This is apparently not accidental, for in an analogous experiment with a set of membranes of varying porosity prepared from oxidized collodion, the same trend was found.

situation. This may have something to do with the rather formal character of the Teorell, Meyer-Sievers theory, which does not take into account any structural factors.

In a subsequent publication we shall try to integrate the outlined facts and conclusions with the results of earlier studies on collodion membranes. In this way we hope to move towards a more correct and more concrete picture of the geometrical and electrical structure of porous membranes.

SUMMARY

1. The Teorell, Meyer-Sievers theory characterizes the electrochemical behavior of membranes by their selectivity constant " A_p " which is derived conventionally from concentration potential measurements at various concentration levels. The selectivity constant may, however, be derived also from entirely independent, different experimental data, namely base exchange studies. The constants arrived at in this second way are designated as " A_b ." The selectivity constants derived by these two methods must be in reasonable, at least semiquantitative agreement if the basic assumptions of the theory are correct.

2. The selectivity constants A_p and A_b were determined for eleven different sets of membranes of different electrochemical activity and of different (8.2 to 80 volume per cent) water content.

3. The potentiometric selectivity constants A_p are in most cases several orders of magnitude greater than the corresponding A_b values. With membranes of great porosity and high electrochemical activity the A_b values approach at least in order of magnitude the A_p values.

4. It is concluded that the unexpectedly large discrepancy between the A_p and A_b values is due to some inherent weakness of the Teorell, Meyer-Sievers theory, most likely to its neglect of any structural factors.