

STUDIES ON PERMEABILITY OF MEMBRANES.

VII. CONDUCTIVITY OF ELECTROLYTES WITHIN THE MEMBRANE.

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The present communication deals with the results of measurements of the conductivity of the dried collodion membrane and with some accessory experiments which aid in interpreting the conductivity data.

The measurement of the conductivity of a membrane in equilibrium with an electrolyte solution presents certain difficulties which prevent determinations throughout all ranges of concentration and which limit the number of available electrolytes. Under the conditions of measurement the membrane forms only a small fraction of the whole path of the electric current and the conductivity of the membrane can be determined only when the resistance of all other parts of the system is relatively negligible or when the resistance of the other parts can be measured separately. The latter method is certainly the less dependable and is applicable only when the required correction is small. In collecting our data it turned out to be desirable to use two methods of making measurements, each method having its own field of application.

In the first method the ordinary potentiometer outfit used for recording potential differences was utilized. The applied E.M.F. in millivolts necessary to produce a standard deflection of the galvanometer was compared with the E.M.F. required to produce the same deflection when the membrane system was replaced by a known resistance. The membranes used were of the flat type previously described but in which the membrane was fixed to the end of a straight glass cylinder about 1 inch in diameter instead of over a bell jar. A measurement of the resistance was performed with a glass cylinder carrying no membrane, *i.e.*, with a free open end, and then with a membrane

in place, the electrolyte solution being the same in both cases. The difference between the two readings gave the resistance of the membrane. The membrane was kept constantly in the solution being investigated until readings successively constant over several days indicated that equilibrium had been attained. According to the nature of the solution one or several weeks were required for this purpose. The readings obtained under a given condition did not show any drift from the moment at which the electric current was closed, over a period of several minutes. So it is obvious that we are measuring real ohmic resistance and that no appreciable polarizing counterelectromotive force during the time of reading is established which might produce an additional apparent resistance.

This method proved to be suitable for recording the conductivity in solutions of neutral salts such as KCl and LiCl within a range of concentration from 1.0 N to about 0.01 N. In more dilute solutions the resistance of the solution itself was so high as to render correction unsatisfactory. It became evident that the resistance of the membrane was not a constant proportion of the resistance of the whole system. In high concentrations the membrane resistance was many times greater than that of the adjacent solutions. In very dilute solutions the two figures were of the same order of magnitude. On the other hand in the special case of HCl the membrane resistance was so low even in high dilutions as to make the required correction unsatisfactory. The results of these experiments carried out with eight different membranes have been brought together in Fig. I. The relative resistances of the membranes are plotted as ordinates; the abscissæ give the negative logarithm of the concentration. It will be seen that with HCl in all ranges of concentration the resistance is very low, so low that the relatively large corrections involved rob the figures of any absolute meaning. But it is evident in a striking way that the conductivity with HCl is enormously greater than with either KCl or LiCl. In the experiments with these latter salts it will be seen that the resistance with KCl is always much less than that with LiCl, that with both salts the resistance increases as the concentration decreases and that with neither is there proportionality between the resistance and concentration except, perhaps, in solutions more concentrated than $\frac{1}{3}$ normal. The experiments with very dilute solu-

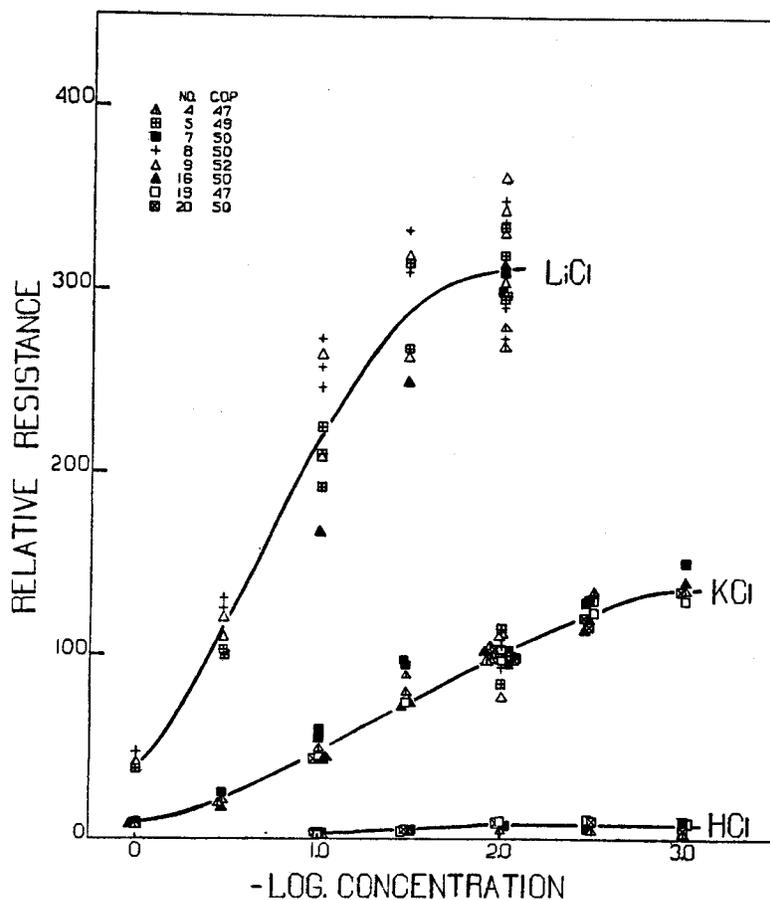


FIG. 1. Showing the relative resistances of the dried collodion membrane in contact with different electrolyte solutions as determined by the first method described in this paper. The experiments from which the figure was drawn were performed with eight different membranes; in most instances more than one determination was made. Since the resistances of these membranes under equal conditions differed widely (25,000–80,000 ohms in 0.01 N KCl) the figures have been brought within the scope of a single chart by setting the average resistance of each membrane in 0.01 N KCl equal to 100 and plotting the points proportionally.

tions have not been included in the chart because of the inaccuracies attending such determinations. Because of the same sources of error it is not desirable to consider the figures obtained as absolute values for the membrane resistances; nevertheless they will prove serviceable when regarded as approximations.

The second method of measuring the membrane resistance was essentially the use of a Kohlrausch bridge with an alternating current produced by a generator of 1,000 cycles. Compensation was effected with the aid of a telephone receiver. In producing a satisfactory tone minimum it was often necessary to balance the capacity involved in the membrane-electrolyte system by means of a variable condenser in the corresponding arm of the bridge. The membrane was one of the usual flat type prepared on a bell jar frame. After complete drying the membrane was cut out and sealed with collodion between two rubber washers. The whole was then clamped between the two halves of the conductivity cell (Fig. 2). Each half cell contained a circular platinum electrode so arranged that when the cell was put together its surface would lie within several millimeters of that of the membrane. The electrode was of such a size as just to allow space at its periphery for free circulation of the solutions under observation. The distance of the electrode from the membrane was as small as possible in order that the resistance of the liquid outside the membrane might form as small a part as possible of the resistance of the whole system. This condition is fulfilled only with membranes of high resistance and is of course totally inapplicable to the more usual type of collodion membrane. The electrolyte solution being investigated was renewed every day until the readings became constant. According to the nature of the solution 3 days to more than a week were necessary for this purpose. The results with any definite solution could be reproduced after some months except for the fact that all resistance data tended to become a little lower as time went on. Obviously the membrane permeability was a little increased in the course of several months. It is surprising that this deterioration was as slight as it was when the long contact with such solutions as 0.5 N HCl is considered.

This method also proved to be applicable only in limited ranges of concentration. Although no upper limit exists there is a very interesting lower limit. For example, with HCl when in the course of weeks

the concentration is lowered more and more a resistance is finally reached which no longer increases with decrease in concentration. Actually in 0.1 N solution a value of 7,150 ohms was obtained, in 0.01 N solution a value of 22,000 ohms and in 0.001 N solution 26,000 ohms. At this point the 0.001 N HCl solution was replaced by distilled water.

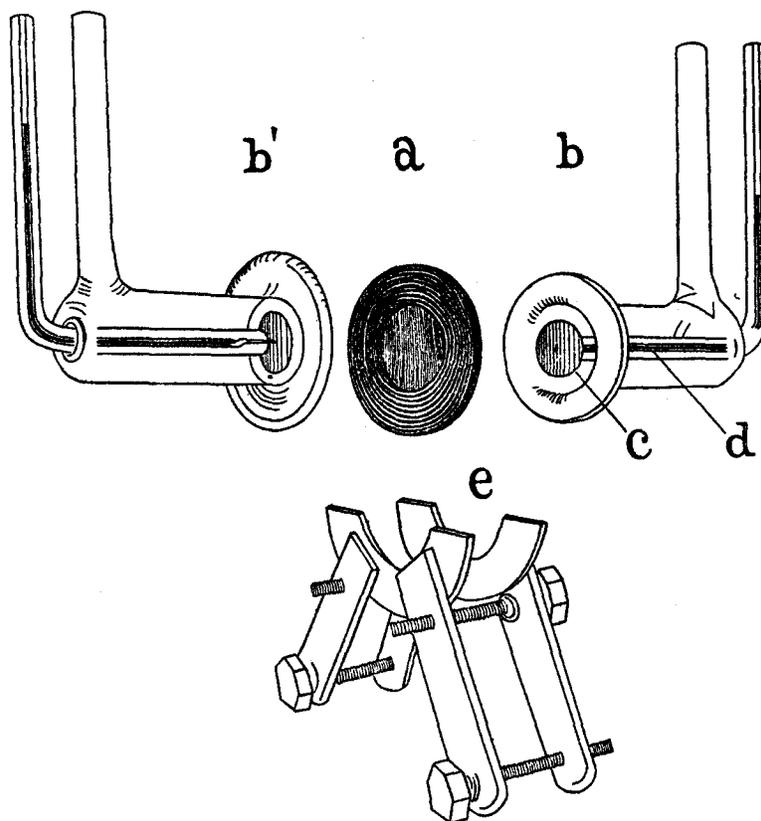


FIG. 2.

An immediate reading of 160,000 ohms was obtained but in the course of some hours this value had decreased to 30,000 ohms. It was then found that no matter how often fresh distilled water was introduced the final resistance of the system after some hours was the same—about 30,000 ohms. The only interpretation possible seemed to be that

some substance liberated by a slow process of disintegration within the membrane was fixing the level of resistance.

Experiments with other electrolytes, KCl, NaCl and LiCl, likewise disclosed a maximum level of resistance but these levels were quite different from each other and all different from that obtained with HCl. The conductivity of the membrane in 0.5 N NaCl was smaller than the limiting value for the HCl solutions regardless of the degree of dilution and that for LiCl was still lower (55,000 ohms). These observations have provided us with the criteria necessary to evaluate our results. They have led us to conclude that it is never justifiable to draw conclusions from conductivity data when the dilution of a particular electrolyte is such that the limiting resistance is approached. For in this case we are no longer dealing with the effect of dilution but with some inherent property of collodion itself.

The results of these experiments have been listed in Table I. With the above mentioned criteria in mind we can state that with HCl in the region of 1.0 N the conductivity is approximately proportional to the concentration. In higher dilutions proportionality no longer exists but because of the limiting resistance which is approached these figures have no satisfactory interpretation. With KCl the resistance is enormously greater than with HCl. Even in a solution as concentrated as 0.5 N a value of 20,000 ohms or more is reached. Although the limiting resistance value for a KCl solution is a little higher than for one of HCl, still the resistance even in the 0.5 N solution is so high that no accurate evaluation of conductivity is possible. But it can be stated that the membrane resistance in a 0.5 N KCl solution is at least 17 times as great as in an HCl solution of the same concentration and probably much more. In the same way we can conclude that the resistance of the same membrane in a 0.5 N LiCl solution is at least 40 times as great as in the corresponding HCl solution.

In reviewing the figures obtained by the two methods just outlined it is evident that the first method yielded little that was not more satisfactorily obtained by the second. In the second method the use of an alternating current assured the absence of even slight polarization effects and the closeness of the platinum electrodes to the membrane surface rendered the resistance of the solution surrounding the membrane negligible as compared with the membrane resistance.

It was thus possible to make measurements with HCl solutions which were not possible by the first method and we became conscious of the limiting resistance values,—values which must have modified the results obtained by the first method. However, because of the cost of the conductivity cell and the length of time (many months) required for a complete series of observations the figures obtained by the second method concern only one sample of membrane. By the first method we were able to work with a number of different samples of membrane. The results obtained by this method when interpreted in the light of the criteria established by the second are quite satisfactory for approximate estimations and show the variations with different specimens of membrane.

TABLE I.
Resistance as Determined by the Second Method (Alternating Current).

	Temperature 23°C.					
	Molar concentration of electrolyte					
	1	1/2	1/4	1/10	1/100	1/1,000
HCl	650	1,240		7,100	22,500	30,000
KCl		22,500	55,000	75,000		
NaCl		41,000				
LiCl		55,000				

A study of all the data obtained leads us to believe that in solutions more concentrated than $N/10$ HCl, $N/4$ KCl or $N/3$ LiCl the conductivity was approximately proportional to the concentration of the electrolyte. It is to be emphasized that this is not the case in the more dilute concentrations. Here, however, the diminishing mobility of the anion, as shown in previous communications, might have altered this proportionality appreciably. Furthermore it is evident that there is an enormous difference in the conductivity of different electrolytes, the conductivity decreasing in the order HCl > KCl > NaCl > LiCl, the differences being many times greater than if no membrane were present.

In attempting to interpret the data obtained we were faced with two questions. (1) Were the differences in conductivity due entirely

to differences in the specific mobilities of the various cations within the membrane? (2) Might not it be that the degree to which an electrolyte could enter the pores of a membrane depended on the nature of the electrolyte? This latter question was especially suggested by the results of our experiments on the diffusion of non-electrolytes. It was here shown that the relatively slow diffusion of a large molecule, such as glucose, when compared with the many times more rapid diffusion of a smaller molecule, such as acetone, was due to the fact that relatively few pores in the membrane were large enough to permit the entry of the larger glucose molecules.

In order to gather data which would enable us to decide between these possibilities it became desirable to determine the actual electrolyte content of membranes after thorough soaking in different electrolyte solutions. After numerous trials the following method was finally adopted. The chlorides of the various cations were selected because of the accuracy with which the electrolyte content could be determined by titration of chlorine. Relatively concentrated solutions (0.5 N) were used in order to obtain a sufficient quantity of electrolyte for satisfactory analysis. A membrane of the ordinary bell jar type was allowed to stand for several days in contact with the particular chloride solution under investigation in order that its pores might become saturated with the electrolyte solution. At the end of this time the membrane and bell jar were thoroughly washed with distilled water to remove all traces of surface solution. We did not believe that washing could remove any appreciable part of the electrolyte within the membrane pores because of the known fact that the diffusion of an electrolyte through these membranes against pure water is extremely slow. This belief was made certain by the analyses which showed the same electrolyte content whether the membrane were in contact with the washing water for 1 or several minutes. The membrane was now placed between two 0.1 N solutions of chloride-free sodium nitrate and an electric current passed by means of platinum electrodes in such a direction that anions would migrate to the interior of the bell jar. During the first minutes of the experiment the only anion carrying current would be Cl^- ; as the experiment continued less and less would be carried by Cl^- and more and more by NO_3^- . We therefore interrupted the experiment from time to time, introduced

fresh nitrate solutions and analyzed the solution from the anode compartment for its content of chlorine. This content became rapidly less with succeeding extractions. From the results we could plot a curve, the asymptote of which represented the original electrolyte content of the membrane for the solution being investigated. As an example

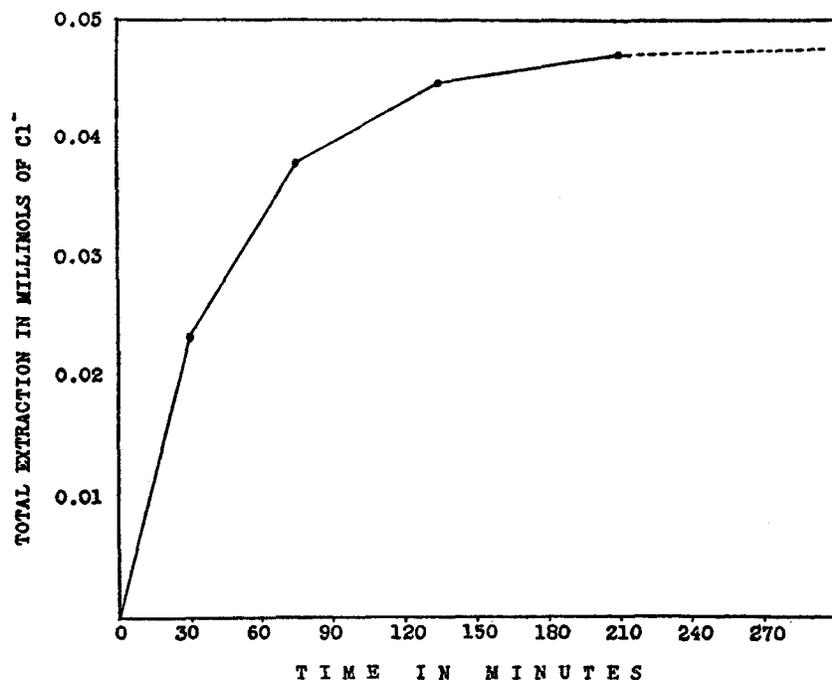


FIG. 3. This chart shows the result of one experiment in which the total electrolyte content of the membrane C-6 was determined after several days contact with a 0.5 N solution of KCl. Repeated extractions of Cl⁻ were made with a current of constant intensity (4×10^{-3} amperes), the sum of these values being plotted as the total Cl⁻ extraction in a given time. The asymptote of the curve represents the value of the electrolyte content.

one of these curves obtained with KCl is shown in Fig. 3. Several experiments were made with each solution in order to establish the constancy of the results. Two membranes were used,—one for comparing HCl and KCl, the other for contrasting KCl and LiCl. The results of individual experiments together with the average results

have been listed in Tables II and III. It will be seen that the electrolyte content of a membrane in equilibrium with 0.5 N HCl is approximately the same as with KCl. With LiCl the content is approximately half that with KCl.

DISCUSSION.

When we bring together the results of conductivity measurements and those concerned with the electrolyte content of the membrane it will be seen that with HCl and KCl there is a great difference in

TABLE II.
Electrolyte Content of Membrane C-6 in Contact with 0.5 N Solutions.

HCl	KCl
<i>millimols</i>	<i>millimols</i>
0.044	0.045
0.041	0.047

Results of experiments with one membrane in which the total electrolyte content was determined after several days contact with 0.5 N solutions of HCl and LiCl. The electrolyte content is essentially the same with the two electrolytes.

TABLE III.
Electrolyte Content of Membrane I-1 in Contact with 0.5 N Solutions.

KCl	LiCl
<i>millimols</i>	<i>millimols</i>
0.019	0.011
0.020	0.011
	0.010

Results of experiments with one membrane in which the total electrolyte content was determined after several days contact with 0.5 N solutions of KCl and LiCl. The electrolyte content of the membrane with KCl is almost the double of that with LiCl.

conductivity whereas the electrolyte content is essentially the same. In this case then we must conclude that the difference in conductivity is due almost entirely to differences in mobility. On the other hand with KCl and LiCl the differences in conductivity correspond fairly

well with the differences in the membrane electrolyte content,—the conductivity and electrolyte content with KCl being roughly the double of that with LiCl. Here it is apparent that no unusual change in mobility need be assumed to explain the result. Inasmuch as for the reasons already given conductivity measurements of the dried collodion membrane do not possess the highest order of accuracy and because the measurements of conductivity and those of the membrane electrolyte content were necessarily made with different samples of membrane, it is not desirable to treat the comparative results in a strictly quantitative way. Nevertheless they are quite sufficient for a few general conclusions concerning the behavior of these membranes with different electrolyte solutions.

An understanding of the facts just presented may be had by considering the same factors used for explaining the differences in the diffusion of non-electrolytes. The pores of the dried collodion membrane are not of uniform size and the membrane is therefore not uniformly permeable to molecular particles of different sizes. When dealing with strong electrolytes the participation of undissociated molecules can be neglected. An anion cannot migrate independently of its cation and therefore a given electrolyte can utilize only those pores large enough to allow the passage of the larger of its ions. Ionic volume is determined not by atomic weight but by the extent to which the particular ions are hydrated. We are aware that according to the Born theory the water shell surrounding an ion does not represent a fixed stoichiometric quantity, but nevertheless all of our concepts of the hydration of ions are based on supposed differences in the volume of the surrounding water shells. We may imagine the sphere of water which sticks so fast to the ion as to resist its separation with a definite force to be different for different kinds of ion. In so far we may speak of differences of volume of the water shell for different ions even though the magnitude of such a volume may not be strictly definable. The results of our experiments are quite in accord with the generally accepted ideas concerning the degree to which the various ions are hydrated. With HCl the H^+ ion is certainly not bigger than the hydrated Cl^- ion and the quantity of HCl entering a membrane is determined solely by the volume of the Cl^- ion. With KCl the volume of the K^+ ion is at least not greater than that of the Cl^- ion and

the latter again determines the quantity of electrolyte which can enter the membrane. In accord with this we found the membrane electrolyte content to be the same with HCl and KCl. On the other hand with LiCl the hydrated Li^+ ion is larger than the hydrated Cl^- ion and it is now the cation which will limit the quantity of electrolyte entering the membrane. In correspondence with this we found the membrane electrolyte content to be much less with LiCl than with either KCl or HCl.

Thus it would seem that two factors are operative in determining the specific conductivity of a membrane in equilibrium with a given electrolyte solution. In the first place the conductivity will depend upon the number of membrane pores large enough to allow the entry of the ions of the electrolyte. But even with different electrolytes which utilize the same membrane pores the ionic mobility and thus the conductivity, because of variations in specific frictional resistance, is much more highly dependent on molecular size than would be true if no membrane were present.

SUMMARY.

Two methods of measuring the electrical conductivity of the dried collodion membrane in contact with an electrolyte solution are described and the results of such measurements with different electrolytes in different ranges of concentration recorded. Some of the difficulties encountered in making these measurements are outlined. Of special interest was the fact that each membrane with each electrolyte showed a maximum level of resistance at a certain point in the dilution scale, a level which was not surpassed by further dilution. It is believed that this level was fixed by the collodion itself rather than by the contiguous electrolyte solution. Its existence limited the results available for reasonable interpretation. In relatively concentrated solutions the conductivity was shown to be approximately proportional to the concentration. With different electrolytes in the same concentration it was shown that the conductivities varied much more than in simple solutions without a membrane and that they fell in the order $\text{HCl} > \text{KCl} > \text{NaCl} > \text{LiCl}$.

A method was described whereby the electrolyte content of a membrane in contact with different chloride solutions could be determined.

It was shown that a membrane saturated with either 0.5 N HCl or 0.5 N KCl had practically the same total electrolyte content whereas the same membrane in contact with 0.5 N LiCl contained only half the quantity. These results were used in interpreting the conductivity data, the evidence presented strongly suggesting that two factors are operative in causing the widely divergent conductivities recorded with different electrolytes. The first factor depended on the quantity of electrolyte which can enter the membrane pores, a quantity dependent on the size of the pores and the volume of the larger of the two hydrated ions of the electrolyte. This factor was the chief one in determining the difference in conductivity between KCl and LiCl. The second factor was concerned with differences in the mobility of the various cations within the membrane brought about by friction between the moving ions and the pore walls. With KCl and HCl the quantity of electrolytes entering the membrane was in each case the same, being determined by the size of the larger Cl^- ion. The widely different conductivity values were explained as due to the changes in the mobility of the two cations within the membrane pores.