

STUDIES ON THE PERMEABILITY OF MEMBRANES.

IV. VARIATIONS OF TRANSFER NUMBERS WITH THE DRIED COLLODION MEMBRANE PRODUCED BY THE ELECTRIC CURRENT.

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In previous papers of this series (1, 2) we have discussed two different methods for determining the transfer number of electrolytes with the narrow pore type of collodion membrane. The first consisted in measuring the P.D. between two electrolyte solutions in a constant ratio of concentration (1:2) in different ranges of concentration. In the second the transfer numbers were calculated directly from electric transfer experiments. It was shown that in general the two methods led to the same result, namely that the transfer number of the anion is always smaller in the membrane than it is in free aqueous solution and that the magnitude of this transfer number largely depends on the concentration. Nevertheless there was a slight but evident discrepancy between the values obtained by the two methods. We also pointed out that the magnitude of the transfer numbers changed a little when several electric transfer experiments were performed in immediate succession with the same membrane. As belief in the validity of the fundamental assumptions is weakened by the presence of unexplained discrepancies, a further investigation of these phenomena was undertaken.

Description of Experiments.

The technique employed in carrying out this series of experiments was essentially the same as has been previously described. The solutions in the anode and cathode compartments were always KNO_3 and KCl respectively. Analyses concerned only the Cl entering the KNO_3 solution.

Two series of experiments were performed. The first series concerned itself with a study of what we shall refer to as a polarization effect. We had previously observed that when a membrane which for several days had been in contact with distilled water was used for two successive experiments the transfer number for Cl obtained by the second experiment was slightly lower than that obtained by the first. The experiments of this series were designed so as to exaggerate this effect as much as possible. Two experiments were always performed successively in which the current strength and length of time were identical (4 milliamperes for 15 minutes) but between the two experiments the membrane was thoroughly polarized by intro-

TABLE I.

Closeness of Agreement between Total Ionic Transfers as Determined by Calculation from the Time and Current Intensity and Directly by Means of an Iodine Coulometer.

Experiment No.	Current intensity	Time	Total transfer by calculation	Total transfer by coulometer
	<i>milliamperes</i>	<i>min.</i>	<i>millimols</i>	<i>millimols</i>
123	2.0	30	0.0373	0.0378
129	2.0	30	0.0373	0.0403
130	2.0	40	0.0498	0.0504
191	4.0	15	0.0373	0.0378
230	0.5	120	0.0373	0.0380
231	0.5	120	0.0373	0.0373

ducing fresh solutions and passing a current of relatively high intensity for several minutes (usually 0.15 amperes for 2 minutes). The experiments were carried out with two membranes of the flat type in 0.5 N, 0.2 N, 0.1 N, 0.05 N, and 0.02 N concentrations.

The second series of experiments was planned so that the effect of varying the current intensity could be studied. In order to eliminate the effect of previous polarization just discussed the experiments of this series were carried out only after considerable polarization had been already established. This was accomplished by performing a third experiment after the completion of the two experiments described in the preceding paragraph. In this experiment the total quantity of current expressed in coulombs was approximately the same as in the

preceding experiments but the current intensity was higher (0.3 amperes) and the duration of the experiments quite brief (10 to 15 seconds). The results obtained by this experiment were then compared with those secured from the second experiment of the first series.

In the first series of experiments the total quantity of current was determined by the method described in the third paper of this series. This consisted in maintaining a current of constant intensity by means of a sensitive milliammeter regulated with a variable resistance and accurately observing the time of application. From this data the total amount of ionic transfer was computed from the formula

$$1 \text{ milliampere} \times 1 \text{ minute} = 0.000622 \text{ milliequivalents of ions.}$$

In the experiments of the second series where the duration was reduced to a few seconds it was not practical to maintain an accurately constant current intensity, especially as the more sensitive milliammeter had to be replaced by a simple ammeter. For this reason a coulometer was used to determine the total amount of ionic transfer.¹ The accuracy of the coulometer was tested by employing it in a number of the experiments of longer duration in which the current intensity and time were easily measured. The results obtained by the two methods were in excellent agreement (Table I).

DISCUSSION.

We may first consider in how far the transfer number calculated from the concentration chain method has agreed with the transfer

¹ An iodine coulometer of the Herroun type as described in Ostwald and Luther's text-book (3) was employed. The arrangement was slightly modified as we found difficulty in obtaining potassium iodide which was free of the iodate. The quantity of KI to be placed in the coulometer was accurately weighed and an identical quantity placed in a similarly shaped tube at the same time and covered with the same solution used in the coulometer. At the conclusion of the experiment the solutions from both tubes were titrated as quickly as possible and the difference between the two titrations taken as the correct result. Furthermore to lessen the amount of spontaneous oxidation of KI the highly acid HCl solution used by Herroun was replaced by a 2 per cent solution of KH_2PO_4 previously boiled to expel all traces of oxygen.

number observed in direct transfer experiments. In the third paper of this series (2) we published a graph² in which the chlorine transfer numbers with KCl as determined by the concentration chain method were compared with the results obtained in twenty-nine electric transfer experiments with the same membrane. Reference to this graph shows that in the more concentrated solutions the observed transfer number was always lower than the calculated. In the lowest

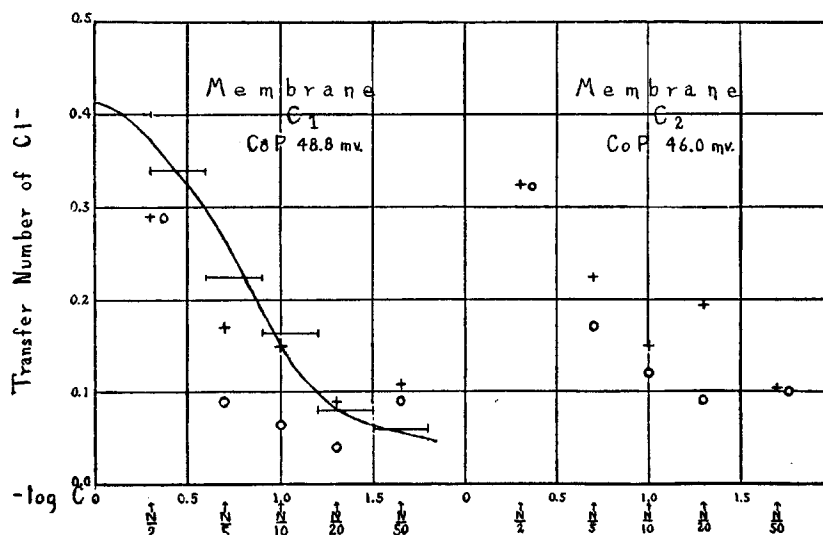


FIG. 1. Showing experimental results in first series of experiments performed with two membranes of the flat type. The transfer number for Cl yielded by the first experiment of each series is represented by +; the transfer number obtained from the second experiment by o. For purposes of comparison the transfer number curve for the membrane C₁ calculated by the concentration chain method has been included.

concentrations the opposite was true. From the present series of experiments it becomes apparent that the observed transfer number rather than being a definite figure depends on the history of the experiment. When in a series of experiments with the same membrane the current intensity and duration of each experiment are kept constant and when several days have been allowed to elapse between experiments, during which time the membrane has been kept in dis-

² Michaelis, Weech, and Yamatori (2), Fig. 1, p. 700.

tilled water, then the transfer numbers observed are in close agreement. But when the time between successive experiments is short, *i.e.* some minutes, as in the experiments of our first series, the second transfer number is often different from the first. This indicates that some kind of polarization remaining from the first experiment has affected the result of the second and suggests that the result even in the first experiment has been more or less disturbed by the same polarization.

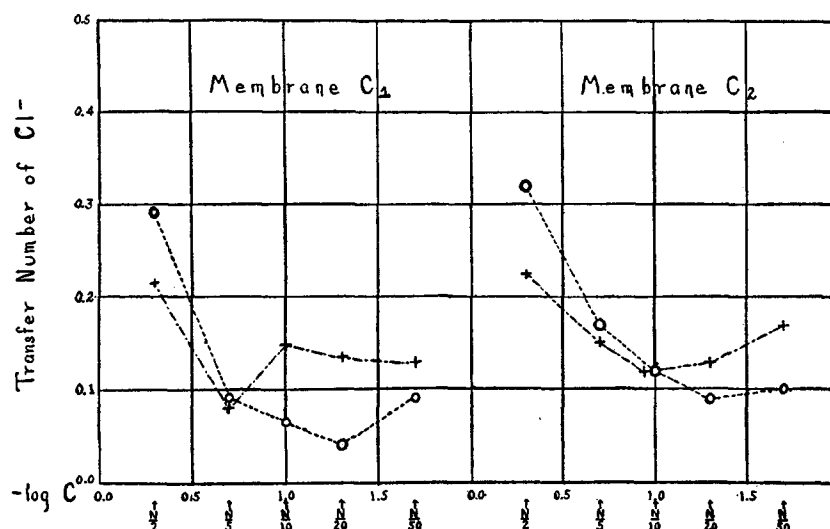


FIG. 2. Showing experimental results in second series of experiments performed with two membranes of the flat type. The transfer number for Cl^- yielded by the first experiment of each series (low amperage) is represented by O ; the transfer number obtained from the second (high amperage) by $+$. In all experiments the total quantity of current (coulombs) was approximately the same.

The direction and magnitude of this polarization disturbance is brought out by the experiments of our first series, the results of which have been summarized in Fig. 1. Here the transfer number of Cl^- has been charted against the logarithmic scale of the concentrations. The figures on the left-hand side of the chart concern one membrane, namely the one with which the graph previously published and mentioned above was prepared. For convenience of comparison the transfer number curve calculated by the concentration chain method

has been included in this chart. The figures on the right-hand side of the chart were obtained with another membrane in which the transfer numbers have not been obtained by the concentration chain method. Both membranes have given essentially the same result. It will be seen that in the experiments of high and of low concentrations, *i.e.* 0.5 N and 0.02 N, there is almost no difference in the transfer numbers obtained from the first and second experiments of the series. In the middle range of concentration there is a considerable difference between the results, the second experiment always yielding the lower transfer number.

In our second series of experiments, the results of which have been summarized in Fig. 2, a study was made of the effect on the transfer number of varying the rate at which the same quantity of electricity was passed through a membrane. Here it can be seen that in the more concentrated solutions (0.5 N) a current of high intensity has always yielded a lower transfer number than one of low intensity, that in dilute solutions the reverse is true, and that a middle range of concentration exists where currents of either high or low intensity give essentially the same transfer number.

An attempt to understand the nature of these two effects has led us to the following considerations. All available data have tended to establish the fact that in our membrane the mobility of Cl is less than that of K and that only the *degree* of the difference is modified by the conditions. Admitting the truth of this fact it follows that the passage of an electric current must be accompanied by a concentration of KCl on the cathode side of the membrane pores and a dilution on the anode side.³ This phenomenon is merely a restatement of the facts

³ As a demonstration of the existence of such a surface boundary concentration would provide a further confirmation of the fundament of this theory we thought it worth while to attempt to show this concentration by experiment. This was accomplished by utilizing a form of membrane similar to our flat bell jar type but in which the collodion was fastened to the end of a straight tube 1 inch in diameter. This form offers less opportunity for mechanical mixing of the different layers of the inside solution. Potassium chloride solutions of equal concentrations were placed on both sides of the membrane and an electric current passed by means of platinum electrodes placed at some distance from the membrane. The inside electrode was always the cathode. At the beginning of the experiment a 1 cc. pipette was placed within the tube and its tip allowed to rest against the membrane.

established by Hittorf, which early led to the concept of a "transfer number." However in our membrane an additional factor has been introduced with which Hittorf did not have to contend. In Hittorf's experiments the transfer number was almost independent of the concentration and hence of changes in concentration brought about by a current. In our experiments the transfer number being a function of the concentration may be altered by changes in concentration resulting only from the current. As the Hittorf effect tends to raise the concentration on one side of the membrane and decrease it on the other it follows that different transfer numbers will obtain in different parts of the membrane. Our analytical results based on Cl determinations concern themselves only with that transfer number holding for the anodic end of the membrane pores. In order to interpret them we must show the effect of the current itself on the concentration at this border.

TABLE II.

Demonstration by Chemical Analysis of the Change in Concentration at One Surface of the Collodion Membrane during the Passage of an Electric Current.

Co P of membrane	Approximate concentration of original KCl solutions	Current intensity	Time	Final Cl concentrations	
				Layer in contact with membrane	Solution distant from membrane
<i>mv.</i>	<i>M</i>	<i>milliamperes</i>	<i>min.</i>	<i>M</i>	<i>M</i>
49.7	0.01	1	30	0.0114	0.0098
50.0	0.01	2	30	0.0111	0.0092
48.3	0.01	2	30	0.0106	0.0091
32.7	0.02	5	20	0.0202	0.0189

After a suitable time the pipette was filled without stirring in order that as much as possible of the solution in direct contact with the membrane might be secured. Immediately thereafter a similar sample was taken from the upper layers of the solution and the two samples titrated for their content of Cl. It is evident that the area of greatest concentration brought about by the electric current must be a film of microscopic thickness coating the membrane surface. By removing an entire cc. merely from this region we did not hope to show the maximal concentration. Nevertheless the results obtained were quite sufficient to support the theory. The solution in contact with the membrane was always the more concentrated (Table II). With the analytical method for determining Cl used the maximum titration error is not above 0.04 cc. of $N/100$ $AgNO_3$ solution or 0.0004 millimols.

The primary effect of the electric current is to lower the concentration at this border. Inasmuch as the concentration here is lower than that originally present the transfer number of the Cl will be lower than would have been expected without polarization. It is likewise evident that the magnitude of this lowering will be greatest in the concentration range where the transfer number is most dependent on the concentration, *i.e.* the middle concentration ranges. In high and in low concentration where the slope of the curve expressing the dependence of the transfer number on concentration is slight the magnitude of this lowering must be minimal. This is in accordance with the observed facts. When a second experiment is performed immediately after a first one in order that polarization may be already established when the second experiment is started then it is observed that the figure obtained from the second experiment is still lower than that secured from the first in the middle ranges of concentrations and in the high and low concentrations essentially no difference between the two experiments can be discovered.

But it is necessary also to consider the change going on at the cathodic border. Here an increase in concentration is being brought about. This increase results in an increase in the transfer number of Cl, so that more KCl can enter the membrane than previously and gradually, as a result of the mutual effect of concentration and transfer number on each other, the whole concentration of KCl within the membrane is increased. Finally this increase will extend even to the anodic border. We shall refer to this as a "secondary effect." At the same time the force of the electric current tending to raise the concentration throughout the membrane is opposed by the force of spontaneous diffusion tending to equalize it throughout the whole system. As a result a stationary condition is reached as long as the current is maintained at constant intensity. Any change in the intensity of the applied current will, however, alter the level of this stationary condition. Inasmuch as this stationary condition may also extend through the membrane even to the anodic border, any change in its level will also alter the transfer number of Cl. To a certain extent the effect will be present even with currents of low intensity but with currents of high intensity it will be greatly exaggerated. Furthermore, if, as in our experiments, the transfer

number obtained with a current of low intensity is contrasted with that given by a current of high intensity, the change in transfer number whether greater or less will indicate the direction of alteration from the transfer number present in the absence of a current. That is, an arrow on the graph shown in Fig. 2 pointing from the result of the weak current experiment toward that of the strong current experiment will indicate the direction of the deviation. Extending this arrow in the opposite direction will indicate the transfer number holding under the initial condition.

Thus we have two contrary effects tending to change the concentration at the anodic border in opposite directions. We regret that we have been unable to form a mathematical representation of the equilibrium resulting from the two forces. We have therefore limited ourselves to some qualitative considerations suitable for an understanding of the total effect.

Thus far we have been talking about changes in the transfer number resulting from simple alterations in concentration. But it must be remembered that the degree of such changes depends greatly on the particular concentration. The rate of change of transfer number with concentration changes is expressed by the slope of the curve indicating the dependence of the transfer number on concentration and is very rapid in the middle ranges of concentration and very gradual in both high and low concentrations.

The combined effect of the two partial effects just discussed which begin at the two borders of the membrane may be expected to be dependent on the particular concentration under consideration.

When an experiment is being carried out in high concentrations there can be no appreciable change in transfer number at the cathodic border where the concentration is increased as further increases in concentration have very little effect on the transfer number. If the current is of low intensity the decrease in concentration at the anodic border will likewise be slight. If this decrease is sufficient to bring the concentration into the range where the transfer number is greatly dependent on concentration the transfer number will be lowered. To a certain extent this lowering may be apparent with currents of low intensity but with currents of high intensity it will be greatly exaggerated. In fact in our experiments in high concentrations the ob-

tained transfer numbers were always somewhat lower than the calculated; when the current was of high intensity the lowering was excessive. Furthermore in the experiments of our first series we obtained no difference in the results between a first and second experiment when an attempt was made to thoroughly polarize the membrane by the intermediate passage of a strong current. This may be explained by the fact that in high concentrations no essential change in transfer number results from the increase in concentration brought about at the cathodic border and there are no gradations of transfer numbers extending throughout the membrane. As no new stationary condition is established within the interior of the membrane a second experiment must give the same result as the first regardless of the intermediate treatment. The changes brought about at the surface layers of the membrane in contact with the fluids and upon which the change in transfer number when the current intensity is greatly increased depends is almost immediately reversible with alterations in the intensity of the applied current. Only changes involving the deeper layers of the membrane can persist any appreciable time after the current has been stopped and only such changes can exert an influence on succeeding experiments.

By a similar process of reasoning it can be shown that the changes going on in the middle range of concentration may lead to lower results than those obtained by a non-electric method. In this range any slight fluctuation in concentration will have a strong effect on the dependent transfer number. In general the primary effect at the anodic border will be greater than the secondary effect beginning at the cathodic border inasmuch as we are measuring the transfer number at this border. That is, when two successive experiments are performed with currents of the same intensity the second experiment will yield the lower result. Sufficient time has elapsed to allow the setting up of the stationary condition within the membrane and the result measured at the anodic border where the concentration becomes lower as the stationary condition is established is to lower the transfer number. The effect of varying the current intensity will be uncertain as the opposing forces acting on the transfer number at the two borders of the membrane are both maximal. In just one concentration the effect of the new stationary condition established by the

stronger current on the transfer number will be obscured because the two forces have neutralized each other. Any variation from this one concentration will cause either a lowering or a raising of the transfer number as one or the other of the two forces becomes more important. The agreement of this theory with the obtained results is evident from inspection of Figs. 1 and 2.

When the concentration under consideration is low it is evident that the decrease in concentration brought about at the anodic border will have little effect on the transfer number and the effects produced at the cathodic border even though secondary will predominate. In our experiments we were not able to show any appreciable difference between successive experiments provided there was no alteration of amperage but when the intensity was increased the transfer numbers became greater. In all experiments the obtained transfer numbers were greater than the calculated.

Thus, even though we have not been able to offer a mathematical presentation of the forces concerned in this series of experiments, it has nevertheless been possible to explain the results in a reasonable way.

SUMMARY AND CONCLUSIONS.

The transfer number of Cl in a KCl solution within the pores of a dried collodion membrane is always lower than 0.5. It depends on the concentration of the solution and decreases in general with decreasing concentration. However, the transfer number for any given KCl concentration has the significance of a definite and constant figure only when an infinitely small amount of coulombs is allowed to pass through the system. For finite durations of electric transfer experiments a polarization effect will always change the original transfer number. This polarization consists in an accumulation of the salt at the one boundary and a diminution at the other boundary of the membrane. Again, as the transfer number strongly depends on concentration, this change in concentration will bring about in its turn a gradual change in the transfer number too. It is shown under what conditions the transfer numbers for the anion as obtained by electric transfer experiments are higher or lower than the ones expected without polarization effect. Thus, by changing the character and magnitude of the force driving the ions across the membranes, and

according to the history of previous treatment of the membrane, the whole character of what we may call the specific permeability for ions of the membrane may be varied without any substantial change of the membrane itself concerning its structure, its chemical composition, or its pore size.

Contemplation of the results obtained in this series of experiments in the light of the theoretical considerations just outlined has impressed us with the fallacy of speaking of the definite permeability of any type of membrane for electrolytes. The behavior of the membrane toward the passage of electrolytes depends on a variety of conditions. It may be recalled that different investigators have reported widely varying results concerning the permeability of certain physiological membranes for electrolytes. Such experiments as have been described in this paper may lead to an understanding of some of the factors responsible for such variations. We are aware that the collodion membrane in its simplicity is scarcely comparable to the extremely complicated biological membranes. Nevertheless any attempts to understand better the behavior of biological membranes may wisely begin with a study of the simplest prototypes.

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