

STUDIES ON THE PERMEABILITY OF MEMBRANES.

III. ELECTRIC TRANSFER EXPERIMENTS WITH THE DRIED COLLODION MEMBRANE.

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1. INTRODUCTION.

In a previous paper (1) an indirect method was described for determining the transfer number of an electrolyte in the dried collodion membrane. To furnish additional evidence in favor of the theory, it has seemed desirable to determine the transfer number by direct transfer experiments with an electric current. For a long time it has been known that the transfer number might be altered by a membrane. A number of investigators had tried to make use of various types of membranes to separate the different regions of the transfer apparatus and thereby avoid mechanical mixture. But as soon as it was recognized that the transfer number might be changed by the membrane, the method was abandoned. In the present investigations, however, this change of the transfer number is the very object of the investigations.

The alteration of transfer numbers by membranes observed by the earlier investigators is discussed by Hittorf (2), who found that only certain membranes, in which what he called the "Schlierenphänomen" could be observed, were able to cause any change. This phenomenon can sometimes be observed when two equal solutions are separated by a membrane and an electric current passed across the

* This investigation was begun by Dr. Yamatori while working in my laboratory in Nagoya, Japan. Due to lack of time he was unable to complete the experiments, but the Baltimore authors are greatly indebted to him for preliminary work in which the difficulties associated with these transfer experiments were recognized and overcome.

membrane in such a way that electroendosmosis occurs. Normally in the phenomenon of electroendosmosis the solution as a whole is forced unchanged through the membrane in the direction of the positive current. But in some cases (especially with membranes of gelatin and dried animal intestine and with electrolytes such as CdCl_2 , CaCl_2 , and HCl , but never with the usual uni-univalent neutral salts) the solution was separated into two different parts by the electroendosmosis. The solution coming through the membrane in the direction of the positive current was of a lower concentration than the original solution and that going in the opposite direction of higher concentration. The two layers could be distinguished with the naked eye because of refractive differences and even better with Töpler's "Schlierenapparat" (3). According to the contention of Hittorf it was only in those membranes which gave rise to this "Schlierenphänomen" that the transfer number differed from the one determined without a membrane. When the phenomenon was absent he believed that the membrane had no influence on the transfer number. Among the membranes showing the "Schlierenphänomen" Hittorf gives brief mention to the collodion membrane. His collodion membranes were in all probability of the dried type used in the present investigations, a fact which can be recognized because of the high electrical resistance which he attributed to them. The more common permeable collodion membranes of the present day when in contact with an electrolyte solution do not offer any conspicuous resistance to the passage of a current. Unfortunately Hittorf's comments on these changes of the transfer numbers are exceedingly brief and the change produced by collodion membranes was not determined. Relatively the observed alterations were small and just great enough to justify the claim that the membrane marred somewhat the accuracy of a transfer number. They did not approach in degree the changes of transfer number by membranes of dried collodion reported in our last paper nor was any note made of dependence on concentration.

Related to the Hittorf phenomenon is the phenomenon described by Bethe and Toropoff (4) which may be regarded as a special case of the more general Hittorf phenomenon. These authors described a sort of hydrolysis brought about by a membrane. When a membrane is interposed between two equal and very dilute solutions of a neutral salt and an electric current allowed to pass, an acid reaction

is brought about immediately adjacent to one side of the membrane and an alkaline on the other. This phenomenon is a special case of the Hittorf phenomenon insofar as a change of concentration of certain ions, namely H^+ and OH^- , is brought about by the membrane. This phenomenon can be observed in an appreciable degree only in salt solutions of such a high dilution that the ions of water participate appreciably in conducting the current within the membrane. As will be shown later this effect is small enough in our experiments to be neglected for the computation of the transfer numbers of the ions of the neutral salt.

The Hittorf effect is likewise closely associated with a phenomenon of electric transfer described by Nernst and Riesenfeld (5). When two equal aqueous solutions of an electrolyte are separated by a third conducting layer which contains the same electrolyte but is not miscible with water and an electric current is allowed to pass through the system, at times the electrolyte becomes concentrated on one side of the third layer and diluted on the other. Nernst and Riesenfeld discerned that this effect must be the result of a difference in the transfer number of the electrolyte in the aqueous and non-aqueous solutions and showed how the transfer numbers could be calculated from such experiments. Riesenfeld (5) made a number of these determinations, using such systems as water-phenol-water, containing electrolytes like KI or KCl in equilibrium throughout the system. The transfer numbers for the cation with KCl were as high as 0.8. He then attempted to determine these transfer numbers by another method; *i.e.*, by measuring the E. M. F. of concentration chains, but was unable to confirm the values obtained in the transfer experiments, the results of the second method giving a figure close to 0.64. A solution of these contradictory results was not attempted by Riesenfeld, nor has anyone undertaken a renewed investigation as far as we know. The membrane used by Riesenfeld differed from ours in being a homogeneous phase working as a solvent for the electrolyte as opposed to our dried collodion membrane which in all probability acts as a sieve. Nevertheless, this phenomenon of Nernst and Riesenfeld¹ observed in homogeneous membranes as well as the

¹ Only a brief discussion of this work by Nernst and Riesenfeld has been inserted here because it is not directly concerned with the properties of porous membranes. A complete review must be left for a more suitable occasion.

phenomenon of Hittorf observed in porous membranes can both be reduced to a difference of transfer numbers of the electrolyte within and without the membrane.

Our own experiments deal with the dried collodion membrane in which the determination of a transfer number is simplified in one respect though complicated in another. It is simpler because the error introduced by spontaneous diffusion, convection, and mechanical stirring is small and usually may be neglected. Separation of the different parts of the fluid is accomplished by the membrane. On the other hand a new source of error is introduced. At times the initial properties of a membrane may be markedly altered by the action of a strong electric current. These changes are partly reversible and partly irreversible; *i.e.*, permanent even after the electric current has been stopped. This action of an electric current on a membrane may be described and a method of obviating the difficulties involved pointed out.

2. *The Behavior of the Dried Collodion Membrane in the Electric Current.*

If two equal solutions of some electrolyte, *e.g.* Na_2SO_4 in 0.1 or 0.01 M concentration, are separated by a bag of completely dried collodion and a rather strong electric current (0.1–1 ampere) is allowed to pass between a platinum electrode inside and another outside the bag, after a certain time a sharp cracking noise will be heard, such as is produced by a spark breaking through an insulator. The noise soon becomes a permanent rattle and on inspection one can see a small leak which is apparent because of a rapid streaming of the liquid through it from one side of the membrane to the other. The stream is visible because of a difference of light refraction. When the leaks are of microscopic size the holes cannot be seen and are recognized only by this phenomenon of refraction. Gradually the leak becomes larger and a macroscopic hole can be seen. Simultaneously with the formation of a leak the intensity of the electric current begins to increase rapidly (unless diminished by the application of an external resistance) due, of course, to the increased conductivity through the hole in the membrane.

The description of this phenomenon as given is far from being complete, and must be studied more thoroughly. However, for the

present purposes it is sufficient to point out that the electric current exerts some influence on the pores of the membranes. Only when the voltage is high will the current strength be sufficiently great to cause an actual break in the membrane. However, when the voltage is lower, the same influence may be present though not great enough to produce a rupture. This supposition is rendered likely by the observation that the $Co P$ of a membrane may be much lower after than before the weak current was passed. For example, one bag membrane with a $Co P$ of 50 millivolts between 0.1 and 0.01 M KCl solutions, showed a P.D. of only 30–40 millivolts after the passage of the current. As a special procedure is necessary for measuring the $Co P$ of membranes after the application of an electric current, a description of this procedure will be inserted here.

When the ordinary dried collodion membrane is placed between two KCl solutions of the same concentration, there is, of course, no P.D. However, after a membrane has been subjected to the passage of an electric current this may no longer be true. A P.D. is established even between two equal solutions. Evidently some kind of polarization has taken place. The distribution of the electrolyte ions within the membrane is no longer homogeneous. One side has become more concentrated, the other more dilute, and hence the P.D. The P.D. tends to fall but the fall is sometimes very slow especially when the membrane has been washed in distilled water. Even after a day of such washing a part of the polarization potential may still remain when the membrane is placed between two 0.01 M KCl solutions. However, it can quickly be diminished by washing with a stronger salt solution instead of pure water. When after washing with water some millivolts are established between two 0.01 M KCl solutions, the P.D. between two 0.1 M KCl solutions is always much smaller. When the membrane is allowed to stand for some minutes in the stronger solution and then replaced in the weaker one, the P.D. will have been definitely diminished. In this way one can depolarize a membrane completely, so that no P.D. will be established between two 0.01 M KCl solutions. Not until this behavior of the membrane has been reached can the P.D. between two *different* KCl solutions (0.1 and 0.01 M) separated by the membrane be measured with any reasonable meaning. With any membrane which has been subjected

to the passage of an electric current the absence of polarization must be strictly proven before its $Co P$ is measured. When the current has been weak (<0.1 milliampere) and the time of exposure short, the polarization potential is usually small and easily overcome.

It is obvious that the permeability of a membrane will change when the pores have been dilated by the electric current. Just as the $Co P$ is diminished, so will the difference in behavior between cations and anions be decreased. It is for this reason that in our first experiments we did not succeed in observing transfer numbers for the anion as low as had been expected. To be sure a transfer number of the anion with KCl close to 0.5 was never found. All experiments tended to confirm a diminished velocity of the anion in the membrane but the diminution was not great enough and not regular enough in the different experiments. When the difficulties had finally been recognized, it became possible to obtain very low transfer numbers for the anion. Those experiments were selected in which the $Co P$ of the membrane turned out not to have been altered by the current. To insure this it was found necessary to apply only weak currents for a short time. As a consequence the quantity of ions transferred was very small and chemical analyses of a high degree of accuracy were not possible. Nevertheless by a slight modification of the procedure, to be described presently, the results of the chemical analyses were in excellent agreement and entirely sufficient for the purpose even though the limits of error were somewhat higher than under more favorable conditions.

Since the development of flat membranes of the type described in a previous paper (1), the difficulties due to alteration of the membrane by the current have been largely abolished. The properties of these membranes, as estimated by the $Co P$, have remained unchanged to the present time, a period of more than 4 months, even though used almost daily for transfer experiments. In the future there should be no difficulty in performing transfer experiments with collodion membranes.

3. Arrangements of Transfer Experiments.

The use of a dried collodion membrane to separate the different solutions in an electric transfer experiment is simple and convenient

when compared with the usual transfer experiments made in electrochemistry. The most simple arrangement is to separate two equal solutions of an electrolyte by the membrane, allow the current to flow, and then determine the change of concentration in the two solutions. This method, however, could not be used because the quantity of current necessary to change the concentrations sufficiently for satisfactory chemical analysis was large and even the most resistant membranes would eventually have been injured, especially when used for a long comparative series of experiments. Fortunately it was possible to modify the procedure so as to furnish better facilities for chemical analysis. Solutions of KNO_3 and NaCl of equal molarity were separated by the membrane, platinum electrodes introduced into each solution, and a current allowed to pass in the direction from KNO_3 to NaCl . In the very beginning of the experiment, before the circuit had been closed, the membrane would contain the ions of both of these two electrolytes. However, within a few moments after the current had been started, the Na^+ and NO_3^- would have been expelled from the membrane, and the current within the membrane conducted entirely by the K^+ and Cl^- ions migrating in opposite directions. The current was furnished by storage cells and regulated by a finely graduated ballast resistance. As a result of polarization taking place at the platinum electrodes the current always tends to fall during the first minutes of the experiment but it is easy to maintain a current of constant intensity (at least within $\frac{1}{2}$ to 1 per cent of the total value) by watching a sensitive milliammeter and varying the amount of ballast resistance by hand. When the membrane itself does not cause trouble due to injury by the current, the necessary change in the applied resistance is quick only in the first few minutes, then a gradual and uniform regulation is required, and finally no essential variation of the resistance is necessary even for a long period.

In the first experiments membranes of the bag form were employed. The electrode inside the bag was a platinum spiral; for the outside electrode a large platinum net bent in such a way as to surround at least half the circumference of the bag was used. It was always kept at a reasonable distance from the membrane (2–3 cm.). The following observations were made.

1. The total quantity of current (calculated from product of milliamperes and seconds). From this the total amount of ionic transfer could be computed from the formula

$$1 \text{ milliampere} \times 1 \text{ minute} = 0.000622 \text{ milli-equivalents of ions.}$$

The accuracy of this method was checked several times by the use of Herroun's iodine coulometer as recommended by Ostwald and Luther² and found to be excellent. With the small amounts of current used in the experiments it proved more satisfactory and convenient than any form of coulometer.

2. The quantity of potassium transferred into the NaCl solution.

3. The quantity of chlorine transferred into the KNO₃ solution.³

4. In some cases the amount of acid developed in the anode chamber.

In these experiments the assumption is necessary that practically all of the current is carried by the ions of the electrolyte and that the water ions do not participate to an appreciable extent even within the membrane. Under this assumption the quantity of H⁺ ions developed in the anode chamber must correspond to the total quantity of current (milliamperes \times seconds) and be equal to the sum of the K and Cl transferred. If it were true that a portion of the current was carried by the water ions this equality would no longer hold for the change of acidity would take place not only at the platinum electrodes but also at the membrane (Bethe-Toropoff effect).⁴ This

² Ostwald, W., and Luther, R., *Hand- und Hilfsbuch zur Ausföhrung physikochemischer Messungen*, Leipsic, 1925, 4th edition, 569.

³ A slight modification of the procedure for determining Cl described in the first paper of this series seemed useful. The solution, which as a rule was acid as a result of the electric transfer, was slightly alkalized by KOH to a slight pink with phenolphthalein, evaporated almost to dryness, acidulated with just sufficient N/10 acetic acid to decolorize the phenolphthalein, then treated with potassium chromate as before described. Approaching the end-point of the titration with N/100 AgNO₃, after each drop of silver solution the liquid was centrifugalized. Under these conditions the first trace of a precipitate of silver chromate could be recognized as a brownish layer above the white AgCl. The increased labor involved in the centrifuging brings increased accuracy. 1 drop of excess of AgNO₃ N/100 results in a striking brown layer.

⁴ The most important paper of Bethe and Toropoff (4) belongs to the same class of phenomena as the Hittorf effect. They are concerned only with the changes in concentrations of H⁺ and OH⁻ ions on both sides of a membrane

effect can be of appreciable magnitude only in very dilute solutions. In our experiments the agreement obtained between total current and sum of migrated electrolyte ions was close enough to indicate that neglecting the Bethe effect introduced no error of greater magnitude than that involved in the chemical analyses.

4. THE EXPERIMENTAL RESULTS.

A. Check of the Method.

The most frequently used arrangement of apparatus in the experiments was as follows:

Large platinum net (anode) | 0.2 M KNO₃ | Membrane | 0.2 M NaCl | Large platinum spiral (cathode)

The intensity of the current was measured with a milliammeter and regulated with a variable resistance. The first problem was to check the soundness of the method by proving that the amount of chlorine transferred in one direction and K in the other was equivalent to the total transfer as estimated from the coulombs applied. It is obvious that no K can be lost during the experiment but it is just possible that a portion of the Cl entering the KNO₃ solution might be oxidized at the electrode and removed from the solution. In view of the small number of Cl⁻ ions in the anode chamber relative to the NO₃⁻ ions, even at the end of the experiment, it does not seem likely that any appreciable amount could be set free at the electrode. Nevertheless, it seems desirable to prove by experiment that the small quantities of Cl found are in reality due to the fact that Cl plays only a minor rôle in carrying the current and not to a loss of Cl.

Table I lists the results of two experiments in which the total ionic equivalent calculated from the coulombs passed is compared with the sum of K and Cl found by analysis. The agreement is very good in view of the analytical difficulties involved and quite sufficient to prove that no appreciable amount of Cl is lost. It also shows that any current transported by water ions (Bethe-Toropoff effect) is too

brought about by an electric current. This change of pH which we called the "Bethe-Toropoff effect" occurs in an appreciable amount only in very dilute electrolyte solutions.

small to produce a measurable error. Having shown that this agreement holds we are justified in using analytical figures for Cl in experiments in which the amount of K or analogous cation was not or could not be determined and the total ionic transfer estimated only from the coulombs passed.

TABLE I.
Potassium Titrations (1/3 of Total Quantity Taken for Analysis).

Experiment No.	N/50 Na oxalate cc. used	KMnO ₄ solution	Corrected by factor to N/100	N/100 KMnO ₄ used	Millimols K	Total K found	Average corrected for K in reagents	Total transfer	
								According to the analyses for K and Cl	According to the coulombs passed
135 (1)	1.40	4.12	4.34	2.94	.01070	.03210	.03186	.03744	.0373
135 (2)	.70	3.86	4.07	3.37	.01226	.03678			
136 (1)	.80	3.86	4.07	3.27	.01190	.03570	.03424	.03982	.0373
136 (2)	.60	3.88	4.08	3.48	.01265	.03795			

Check analyses to determine necessary correction for amount of potassium in NaCl used. .035 millimols K added to 50 cc. N/5 NaCl (amount used in above experiments). 1/3 of total taken for analyses.

1	.60	4.11	4.33	3.73	.01357	.04071	Average	=	.03758
2	1.10	4.11	4.33	3.23	.01175	.03525	Added K present	=	.03500
3	.90	4.06	4.27	3.37	.01226	.03678	K in reagent	=	.00258

Table to show accuracy of agreement between milli-equivalents calculated from the current passed and actual transfer of ions as determined by analysis. N/5 KNO₃ solution surrounding positive electrode. N/5 NaCl solution surrounding negative electrode. Solutions separated by C₁ collodion membrane. Current strength = 0.01 ampere for 6 minutes. Total milli-equivalents of current = .03732 (short time used to avoid error due to diffusion).

In four identical experiments Cl⁻ transferred was .0054; .0054; .0063; and .0052 millimols, respectively. Average figure of .00558 used in calculation of total transfers.

In some of the later protocols similar checks will be found but special care was taken in the experiments of Table I. In these experiments the solutions were in contact with the membrane for less than 7 minutes (total current time 6 minutes) and the time was too short for a measurable error due to spontaneous diffusion. In other experiments where the current intensity was smaller and the current

time was longer, a small correction was necessary for K spontaneously diffused, disturbing somewhat the accuracy of agreement. In none of the experiments could we show that a significant amount of Cl migrated by spontaneous diffusion. Therefore this factor can play no part in disturbing the accuracy of the transfer number for Cl when it is calculated from the Cl found by analysis and the total transfer estimated from the current applied.

B. Protocols of Transfer Experiments.

1. Bag Membrane 31.

a. Characteristics of the Membrane.—*Co P* before the transfer experiment = 52.0 millivolts. After the experiment the membrane was washed in distilled water for 3 days and then the following successive p.d. measurements made.

1. 0.01 M KCl on both sides of membrane 2.3 millivolts.

2. 0.1 M KCl on both sides of membrane 0.0 millivolt.

3. 0.01 M KCl on both sides of membrane . . 0.0 millivolt. (This reading made after solutions had been in contact with membrane for 30 minutes.)

4. *Co P* 47.1 millivolts.

b. The Transfer Experiment.—Outside solution 0.1 M KNO₃; inside solution 0.1 M NaCl; current strength 0.500 milliamperes; time 70 minutes.

K⁺ transferred (analysis of NaCl solution) 0.0182 milli-equivalents.

Cl⁻ transferred (analysis of KNO₃ solution) 0.0045 milli-equivalents.

Total observed transfer (K⁺ + Cl⁻) 0.0227 milli-equivalents.

Total expected transfer 0.0218 milli-equivalent.

$$t_{\text{Cl}^-} = \frac{\text{Cl}^-}{\text{K}^+ + \text{Cl}^-} = 0.20$$

c. Agreement with Transfer Number Determined by the Concentration Chain Method.—After the transfer experiment p.d. measurements were made of the membrane with the following solutions and the transfer numbers calculated according to the method previously described.

0.05 M KCl : 0.1 M KCl — p.d. = 12.8 mv. at 24°C. $t^- = 0.14$

0.1 M KCl : 0.2 M KCl — p.d. = 9.8 mv. at 24°C. $t^- = 0.22$

The transfer number observed in the transfer experiment (0.20) lies between the value of the two average transfer numbers calculated from the concentration chains; *i.e.*, $0.14 < 0.20 < 0.22$.

2. Bag Membrane 100.

a. Characteristics of the Membrane.—*Co P* before the transfer experiment = 52.5 millivolts. Following the experiment and after abolition of the polarization potential *Co P* was only 42.3 millivolts.

b. The Transfer Experiment.—Outside solution 0.01 M KNO₃; inside solution 0.01 M NaCl; current strength 0.125 milliampere; time 150 minutes.

K ⁺ transferred.....	0.0095 milli-equivalents.
Cl ⁻ transferred.....	0.0009 milli-equivalents.
Total observed transfer (K ⁺ + Cl ⁻).....	0.0104 milli-equivalents.
Total expected transfer.....	0.0117 milli-equivalents.

$$t_{\text{Cl}^-} = \frac{\text{Cl}^-}{\text{K}^+ + \text{Cl}^-} = 0.08$$

c. Agreement with Transfer Number Determined by the Concentration Chain Method.—Following the experiment the P.D. of the membrane was measured in the following concentration chains.

KCl 0.005 M : 0.01 M - P.D. = 16.3 mv. at 24°C.	$t^- = 0.039$
KCl 0.01 M : 0.02 M - P.D. = 13.2 mv. at 24°C.	$t^- = 0.126$

The value of t^- as observed in the transfer experiment lies between the values of the two average transfer numbers calculated from the concentration chains; *i.e.*, $0.039 < 0.08 < 0.126$.

3. Bag Membrane 47.

a. Characteristics of the Membrane.—*Co P* before the transfer experiment = 54.3 millivolts. *Co P* after the experiment and after abolition of polarization potential = 50.3 millivolts.

b. The Transfer Experiment.—Outside solution 0.01 M KNO₃; inside solution 0.01 M NaCl; current strength 0.125 milliampere; time 150 minutes.

K ⁺ transferred.....	0.0118 milli-equivalents.
Cl ⁻ transferred.....	<0.0016 milli-equivalents. ⁵
Total observed transfer (K ⁺ + Cl ⁻).....	<0.0134 milli-equivalents.
Total expected transfer.....	0.0117 milli-equivalents.

$$t_{\text{Cl}^-} = \frac{\text{Cl}^-}{\text{K}^+ + \text{Cl}^-} < 0.14$$

c. Agreement with Transfer Number Determined by the Concentration Chain Method.—Following the experiment the P.D. of the membrane was measured in the following concentration chains.

KCl 0.005 M : 0.01 M - P.D. = 16.1 mv. at 24°C.	$t^- = 0.046$
KCl 0.01 M : 0.02 M - P.D. = 15.1 mv. at 24°C.	$t^- = 0.074$

⁵ The amount of Cl⁻ here represented corresponds to 4 drops of the 0.01 M AgNO₃ used in titrating and is too small for accuracy. The quantity recorded must be considered as a maximum value and is probably too high.

The value of t^- as observed in the transfer experiment is slightly greater than that estimated from the concentration chains but of the same order of magnitude and as such, in view of the analytical difficulties, in accordance with expectations.

4. Flat Bell Jar Membrane C_1 .

The results of a long series of transfer experiments with this membrane have been arranged in Table II.

5. DISCUSSION.

The transfer experiments reported in this paper are confirmatory of the results obtained by the indirect method previously described (1), namely that in the membrane the transfer number of the anion is much smaller than that of the cation and that this difference is the most marked in the more dilute solutions. The finding of a membrane with such durable properties as the type with which the experiments of Table II were performed made it possible to carry out a long series of experiments in which the effect of varying the cation and the concentrations could be observed. Here again it will be seen that the transfer number of Cl^- in solutions of equal concentration but with different cations is in the order $\text{Li} > \text{Na} > \text{K} > \text{H}$. Moreover, the transfer numbers regularly become greater as the concentration of the electrolytes is increased. This membrane was also used in a series of 2:1 concentration chain experiments with KCl (1) and it is possible to compare the transfer numbers in the different ranges of concentration as estimated by this method with those actually found in the transfer experiments. The result is shown in Fig. 1. On the whole the agreement is good. Whether the minor discrepancies are the result of some systematic and unrecognized error or due to an additional unknown factor not taken into account in the theory is not clear. In this connection it is desirable to call attention to an observation which was made during the series of experiments and for which no satisfactory explanation is as yet apparent. When the membrane was used in a short space of time for several successive transfer experiments, almost invariably it was found that the transfer number for Cl^- calculated from the results of the first experiment was somewhat higher than the transfer numbers computed from the succeeding experiments. Had the reverse

TABLE II.

Experiment No.	Solution in anode compartment	Solution in cathode compartment	Current strength milliamperes	Time min.	Calculated total transfer <i>milli-equivalents</i>	Millimols K found	Millimols Cl found	Total transfer found	Transfer No. Cl ⁻
A	m/50 KNO ₃	m/50 NaCl	2	15	.01866	.01812	.0023	.02042	0.123
2	m/50 KNO ₃	m/50 NaCl	2	30	.03732		.0045		0.121
3	m/50 KNO ₃	m/50 NaCl	2	30	.03732		.0030		0.080
8	m/50 KNO ₃	m/50 KCl	2	30	.03732		.0039		0.104
143	m/50 KNO ₃	m/50 KCl	6	10	.03732		.0045		0.121
144	m/50 KNO ₃	m/50 KCl	6	10	.03732		.0020		0.054
145	m/50 KNO ₃	m/50 KCl	6	20	.07464		.0045		0.060
30	m/10 KNO ₃	m/10 NaCl	2	35	.04354	.0402	.0043	.04452	0.095
31	m/10 KNO ₃	m/10 NaCl	2	30	.03732	.0405	.0035	.04401	0.094
37	m/5 KNO ₃	m/5 NaCl	2	30	.03732	.0393	.0043	.04362	0.116
39	m/5 KNO ₃	m/5 KCl	2	30	.03732		.0059		0.157
40	m/5 KNO ₃	m/5 KCl	2	32	.03981		.0048		0.122
42	m/5 KNO ₃	m/5 NaCl	4	15	.03732	.0360	.0053	.04135	0.143
43	m/5 KNO ₃	m/5 NaCl	4	15	.03732	.0374	.0047	.04215	0.127
133	m/5 KNO ₃	m/5 NaCl	10	6	.03732	.0414	.0054	.04680	0.145
134	m/5 KNO ₃	m/5 NaCl	10	6	.03732	.0388	.0054	.04420	0.145
135	m/5 KNO ₃	m/5 NaCl	10	6	.03732	.0319	.0063	.03816	0.169
136	m/5 KNO ₃	m/5 NaCl	10	6	.03732	.0342	.0052	.03944	0.139
146	m/5 KNO ₃	m/5 KCl	6	20	.07464		.0175		0.234
147	m/5 KNO ₃	m/5 KCl	6	20	.07464		.0100		0.134
148	m/5 KNO ₃	m/5 KCl	6	20	.07464		.0085		0.114
34	m/2 KNO ₃	m/2 NaCl	2	30	.03732		.0076		0.205

35	m/2 KNO ₃	m/2 NaCl	2	30	.03732	.0068	0.183
131	m/2 KNO ₃	m/2 NaCl	2	30	.03732	.0077	0.206
132	m/2 KNO ₃	m/2 NaCl	2	30	.03732	.0099	0.265
47	m/1 KNO ₃	m/1 NaCl	4	15	.03732	.0108	0.290
139	m/1 KNO ₃	m/1 KCl	6	10	.03732	.0150	0.402
140	m/1 KNO ₃	m/1 KCl	6	11	.04105	.0164	0.400
141	m/1 KNO ₃	m/1 KCl	6	10	.03732	.0146	0.391
1	m/50 NaNO ₃	m/50 NaCl	2	30	.03732	.0082	0.220
6	m/50 NaNO ₃	m/50 NaCl	2	30	.03732	.0065	0.174
7	m/50 NaNO ₃	m/50 NaCl	2	30	.03732	.0057	0.152
13	m/50 NaNO ₃	m/50 NaCl	2	30	.03732	.0100	0.268
14	m/50 NaNO ₃	m/50 NaCl	2	30	.03732	.0077	0.206
15	m/50 LiNO ₃	m/50 NaCl	2	30	.03732	.0131	0.349
16	m/50 LiNO ₃	m/50 LiCl	2	30	.03732	.0099	0.266
17	m/50 LiNO ₃	m/50 LiCl	2	31	.03856	.0113	0.294
18	m/50 LiNO ₃	m/50 LiCl	2	30	.03732	.0097	0.261
19	m/50 LiNO ₃	m/50 LiCl	2	30	.03732	.0056	0.150
23	m/50 LiNO ₃	m/50 LiCl	2	30	.03732	.0083	0.221
24	m/50 LiNO ₃	m/50 LiCl	2	60	.07464	.0196	0.263
27	m/10 LiNO ₃	m/10 LiCl	2	31	.03856	.0124	0.322
28	m/10 LiNO ₃	m/10 LiCl	2	30	.03732	.0112	0.299
4	m/50 HNO ₃	m/50 HCl	2	30	.03732	.0013	0.035
5	m/50 HNO ₃	m/50 HCl	2	35	.04354	.0012	0.028
9	m/50 HNO ₃	m/50 KCl	2	30	.03732	.0017	0.046

Tabulation of results in 46 electric transfer experiments performed with the same dried collodion membrane (C_1 -flat type). Experiments were done during a period of 4 months, the constancy of the properties of the membrane being shown by frequent $C_o P$ determinations. $C_o P$ at beginning of experiments (9-28-26) 48.7 millivolts; (11-8-26) 48.5 millivolts; (12-11-26) 49.0 millivolts; at end of experiments (1-21-27) 49.0 millivolts.

been true and the later experiments given higher transfer numbers we should have supposed that the electroendosmosis had temporarily stretched the membrane pores, lowered its $Co P$, and increased its permeability for the anion. However, the observed findings were the opposite of that which might have been expected. It scarcely seems wise to attempt an explanation until more experimental data has been accumulated. However, the variations in the transfer numbers referred to here were of a minor degree and do not interfere

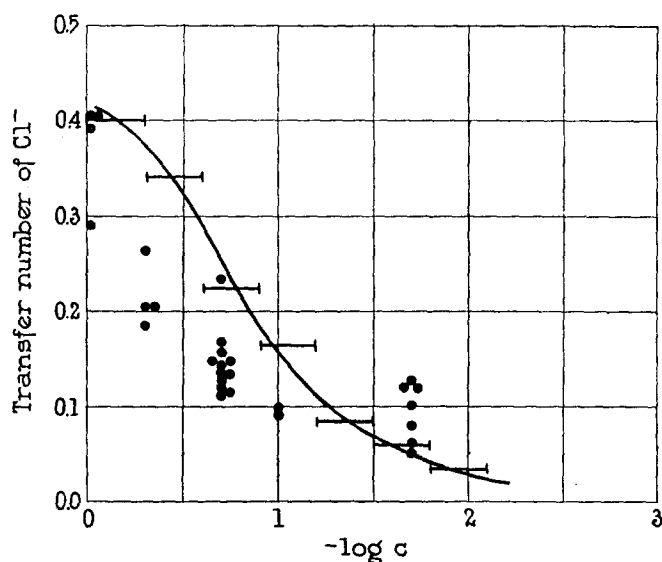


FIG. 1. Shows accuracy of agreement between chlorine transfer numbers with KCl as determined by the concentration chain method (continuous curve) and by electric transfer experiments (separate dots).

with their interpretation in the present communication. The transfer numbers determined in these experiments correspond fairly closely to those calculated indirectly from the concentration chains and furnish an additional reason for maintaining the theory set forth in connection with the latter method. We wish, however, to emphasize that the agreement between the two methods is not complete and that we believe that the range of variation is greater than the limits of error. Obviously the theory in its present state of development is insufficient to explain all data in a really quantitative way.

SUMMARY.

The transfer numbers of the ions of electrolytes in the dried collodion membrane, as determined in a previous paper indirectly from the E.M.F. of concentration chains, can also be determined directly by electrical transfer experiments. It is shown that the difficulties involved in such experiments can be overcome. The transfer numbers obtained by the two methods are in satisfactory agreement. The experimental results obtained in the transfer experiments furnish an additional argument in favor of maintaining the theory that the electromotive effects observed in varying concentrations of different electrolytes with the dried collodion membrane may be referred to differences in the mobilities of the anions and cations within the membrane. As was shown by the method of the previous paper, the transfer number depends largely on concentration. There are some minor discrepancies between the values of the transfer numbers obtained by the two methods which, as yet, cannot be completely explained.

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