# *On the Electro-Osmotic Water Transport Through Cation—Exchange Resin Membranes*

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## Introduction

When ion-exchange resin membranes are used as the ionic permselective diaphragms of electrochemical operations, the movement of water takes place through the membranes simultaneously with the ionic migration. This phenomenon seems important from the practical point of view, since it governs the maximum concentration of the electrolyte solution attainable by means of electrolysis, using the membrane. Also, as it concerns the transport number and electric conductivity of the membrane, the study of the phenomenon is expected to supply valuable clues for clarifying the fundamental properties of the ion-exchange resins.

There are three ways of transference of a solvent through a membrane, according to the driving forces which cause it. They are classified as follows.

(a) Transference due to osmotic pressure.

(b) Transference due to the electric potential difference between the two surfaces of the membrane.

(c) Transference due to the difference of hydrostatic pressure, if present.

The item (a), which takes place in the case where the solutions of both sides of the membrane differ in concentration, was previously studied by the authors and reported elsewhere[1].

As the item (b) seems to be especially important in the ordinary applications, the present work is devoted to its study.

The water transference through a membrane caused by electric potential difference has been known as the electro-osmotic phenomenon and already explored to a considerable extent[2]. These previous works were, however, undertaken using mostly very dilute solutions, and lack the data for the range of comparatively high concentration, up to several normals, despite the fact that the range is expected to be the most prosperous field of applying ion-exchange resin membranes.

Although the electro-osmosis in the case where a membrane is inserted between solutions of different concentrations is important for practical purposes, the present study deals with, as the most simple ones, the cation-exchange resin membranes placed between solutions of the same kind and equal concentration.

## Experimental

**Ion-exchange Resin Membranes**.—The cation-exchange resin membranes used in the experiments are mainly of sulfonated phenol resin type and prepared by Dr. M. Sekino and K. Kōno in the Research Laboratory of Asahi Glass Co. In addition to these a cation-exchange resin membrane of a similar type, Nepton CR-51, which had been furnished by Ionics Inc., U.S.A., was used.

The thickness of the membranes varied from 0.9 to 1.2 mm when swollen.

These membranes were thoroughly equilibrated with the solutions, to be used for measurements at least for 24 hours by repeatedly changing the solution.

**Apparatus.**—A glass cell composed of two half cells as shown in Fig. 1 was used, and a sample membrane was mounted between the flanges, the effective area of the membrane being 5.0 cm². The half cell at the right hand side was provided with a capillary tube which served to indicate the movement of the meniscus due to the liquid transportation from the left half cell to the right one. The inner diameter of the capillary was chosen so as to indicate the volume change as sensitively as possible, and it was calibrated with mercury.

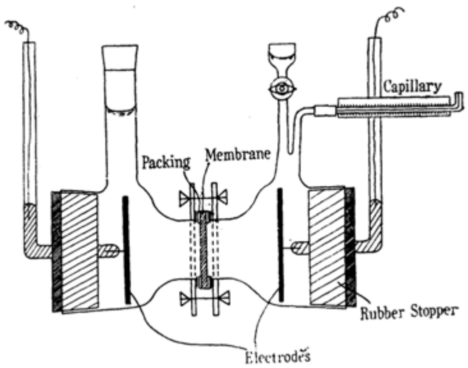

Fig. 1. Apparatus for measurement of electro-osmosis.

The electrodes were Ag and Ag-AgCl for the measurements in chloride solutions, and Pb and Pb-$PbSO_4$ for sulfate solution. Special care was taken for the use of electrodes of ample capacity in order to ensure reversibility of the electrodes.

During the experiments the main part of the cell was dipped into a water thermostat, and the temperature was kept at 25±0.2°C.

## Results

It has been known[3] that the volume of electro-osmosis is proportional to the quantity of electricity flowed, namely the product of current intensity, $I$, and time, $t$.

$$v=\beta\cdot I\cdot t \qquad (1)$$

In the above equation $\beta$ is the amount of electro-osmosis caused by the flowing of the unit quantity of electricity.

The present work was started by examining the above relation when using the cation-exchange resin membranes.

(1) **Liquid Transference in Relation to Time of Electrolysis.**—When the electrical circuit was closed in the apparatus shown in Fig. 1, it was observed that the meniscus in the capillary begins to move, and afterwards showed various tendencies as seen in Fig. 2. In the cases of curve I (Fig. 2) the meniscus retreats at first to the left for a little while and then turns to proceed to the right. On the contrary, in the case of the curve II the meniscus begins to proceed from the start.

Circuit breaking after the current has flowed for some duration causes in the former case a somewhat rapid shift of the

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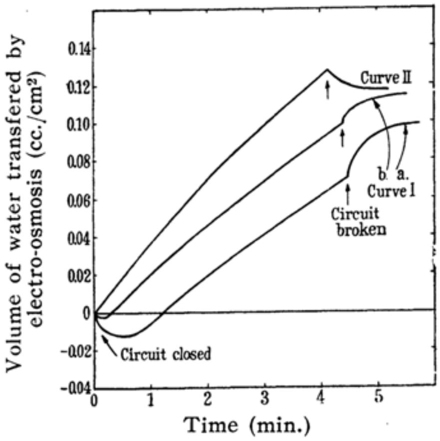
[1] Reports of the Research Laboratory, Asahi Glass Co., Vol. III, No. 2, 180 (1953).

[2] G. Schmid, *Z. Elektrochem.*, **55**, 229 (1951).
K.S. Spiegler, *J. Electrochem.*, **100**, 303C (1953).

[3] E. Manegold and K. Solf, *Kolloid Z.*, **55**, 273 (1931).



Curve I { a. PV-51, 2A/dm², 0.5N NaCl-soln. b. Nepton CR-51, 2A/dm², 1N NaCl-soln.

Curve II Nepton CR-51, 2A/dm², 0.5 N $MgCl_2$-soln.

Fig. 2.

meniscus toward the right to come to a standstill. In the latter case it causes the retreat of the meniscus toward the left for a short time.

The mode of the initial meniscus movement, the type of curve I being more frequently met and curve II rather rarely, appeared to vary according to the stiffness of the membrane, kind and concentration of the equilibrating solution, and other unknown factors. The main cause of this initial anomaly seemed to be attributed to the bending of the membrane due to the applied electric field. But further study will be necessary to explain it in detail.

For the present purpose, however, it is sufficient to find the inclination of the linear part of the curves showing water transference.

**(2) Current Density and Rate of Electro-osmosis.**—The rate of electro-osmosis was calculated from the inclination of the linear part of the curves such as shown in Fig. 2, for several typical cation-exchange resin membranes in sodium chloride solution. The samples employed are of sulfonated phenol resin type, P-4, PV-51, and CR-51, the thickness being 0.10, 0.12 and 0.09 cm. respectively. The latter two are backed by a plastic screen to increase mechanical strength.

As shown in Fig. 3, the rate of electro-osmosis appears to be approximately proportional to the current density except within the region of high current density in case of P-4 membrane.

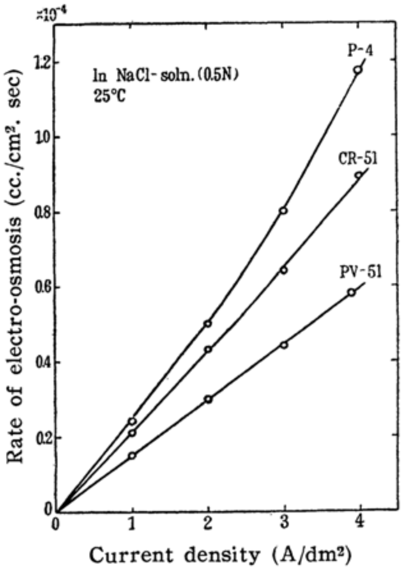
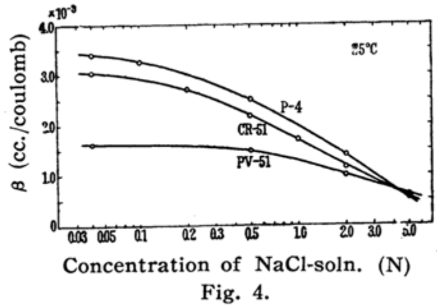


Fig. 3. Current density vs. rate of electro-osmosis.

Since the equation (1) has thus been confirmed to be applicable for the cation-exchange resin membranes, $\beta$ in the equation will be employed hereafter to compare the characteristics of the membranes.

**(3) Electro-osmosis in Relation to the Concentration of the Solution.**—The relations between $\beta$ and the concentration of the equilibrating sodium chloride solution were derived for the three sorts of membrane as shown in Fig. 4.



Concentration of NaCl-soln. (N)

Fig. 4.

In the part of low concentration $\beta$ rises gradually with the decrease in the concentration and approaches a characteristic value, $\beta_0$. There are remarkable differences among $\beta_0$ of the three membranes. As the concentration increases $\beta$ for three membranes converge gradually to come to a nearly equal value at about 5 N.

**(4) $\beta$ and pH of the Solution.**—The change of $\beta$ with varying pH of the sodium chloride solution was measured, keeping the concentration of chlorine ion constant at 0.5 N. The sample employed is PV–51. The result is plotted in Fig. 5.

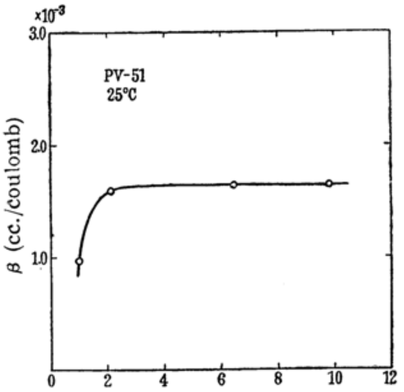
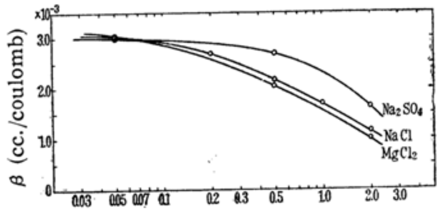


Fig. 5.

From pH 10 to pH 2, $\beta$ remains approximately constant. The influence of pH seems to become remarkable as the concentration of hydrogen ion comes near that of sodium ion.

(5) **Species of Electrolyte and $\beta$.**—Although the present experiments have been carried out using mainly sodium chloride solution, and the cases in other electrolyte solutions will be dealt with in the future, the measurement of $\beta$ in two other electrolyte solutions, i.e., magnesium chloride and sodium sulfate solution, are shown in Fig. 6 in comparison with those in sodium chloride solution. The two electrolytes were chosen in view of the fact that they possess anion or cation in common with sodium chloride.



Normality of solution

Fig. 6.

As shown in the figures, the curves for NaCl- and $MgCl_2$- solution which have a common anion lie very close to each other, while the curve for $Na_2SO_4$ is separated.

## Discussion

Although experimental data are not yet sufficient to allow fully quantitative discussion for the membrane equilibrated with the concentrated solution like those employed in this study, some analyses will be made to interpret the results obtained.

The cation-exchange resins as used in this experiment have as the active groups $\text{-SO}_3\text{H}$ and -OH radicals fixed on the matrix of hydrocarbon, and the former alone is considered to display cation-exchange action in the neutral solutions. The resin equilibrated with a salt solution, swollen to a degree depending on the concentration of the solution and the degree of cross-linkage of the resin matrix, contains cations (exchangeable ions or counter ions), equivalent to the exchangeable polyanionic groups and an equivalent number of cations and anions (non-exchangeable ions). As the concentration of outside solution increases, more salt molecules penetrate into the resin and non-exchangeable ions increase, and at the same time more water within the resin goes out.

Although the cations corresponding to the penetrating neutral salt are called non-exchangeable cations, apparently discriminating them from the exchangeable ones, it will be assumed in the following discussion that there is essentially no distinction between these two kinds of cation in the resin. This assumption does not appear unreasonable, because the cations mix thoroughly with each other due to the thermal motion in such narrow pores[4] as are found within an ordinary ion-exchange resins.

If an electric field is applied to these ion-exchange resin membranes, all the mobile ions migrate to transport electricity in the direction determined by their charges. Water surrounding these ions seems to accompany the migrating ions.

**Transport Number of the Membrane and Electroosmosis.**—If the cationic transport number of a cation-exchange resin membrane is denoted by $n_+$, the volume of the water which moves with a mol of a cation $v_+$ (including the volume of the cations), and the respective values for the anions in the same membrane by $n_-$ and $v_-$, then the volume of the water flow caused by electricity of one Faraday is,

$$\begin{aligned} v = F\cdot\beta &= n_+\cdot v_+ - n_-\cdot v_- \\ &= (v_+ + v_-)n_+ - v_- \qquad (2)^* \end{aligned}$$

From the equation (2), $\beta$ would change linearly with the cationic transport number $n_+$, if $v_+$ and $v_-$ are assumed constant.

In order to compare the equation with the experimental results, the data of $\beta$ in the preceding chapter are plotted in Fig. 7 against the transport number in the membranes cal-

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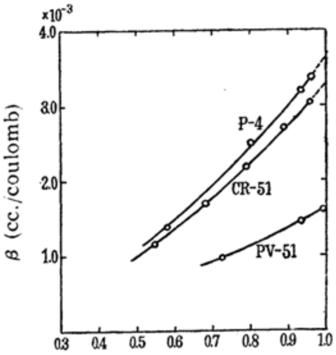
[4] R. Griessbach, *Z. Elektrochem.*, 57, 147 (1953).

* $n_+ + n_- = 1$.



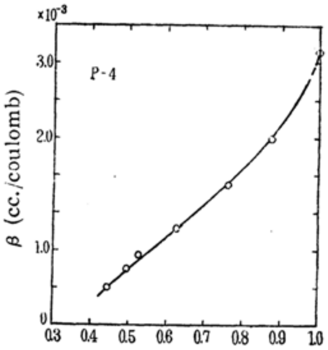
Cationic transport number ($n_+$).
Fig. 7.

culated** from the data reported elsewhere[1].

As shown in the figure, the linear relationship between $\beta$ and $n_+$ appears to hold approximately. But as for the value of $\beta$ corresponding to $n_+=1$, namely $\beta_0$, there is a remarkable discrepancy between the experiment and the theory. Although it is required from the equation (2) that $\beta$ comes to have a constant value, $\beta_0$, regardless of the species of the membrane when $n_+$ approaches 1, the experimental result reveals a very different situation. Also, a constant inclination of the lines which is suggested by the equation (2) is not realized.

The reason for these discrepancies seems to be attributed to the incorrectness of the assumption that $v_+$ as well as $v_-$ is constant.

As a matter of fact, from the experimental results the values of $(v_+ + v_-)$ for the membranes, P-4, CR-51 and PV-51 are found to be 480, 415 and 230 cc./mol. NaCl respectively in the sodium chloride solution (1 N). It is noteworthy that these amounts of water accompanied with the ionic migration through the membrane are decidedly greater than the hydration water of sodium chloride.

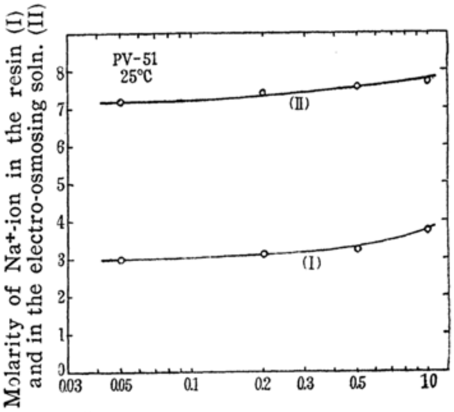


water content of the resin (Na-type) in NaCl-soln.
water content of the resin (Na-type) in distilled water
Fig. 8.

The electro-osmosis seems to depend on the water content of the resin rather than on the hydration water of the migrating ions. The situation can be shown in Fig. 8 in which $\beta$ is plotted against the water content of the resin (P-4).

Therefore in order to discuss the phenomenon further, it will be helpful to compare the concentrations of cation in the solution within the resin and of that in the membrane-permeating solution.

**Concentrations of Cation in the Solution within Cation-exchange Resine Membranes and of that in the Membrane-permeating Solution.**—Molarities of sodium ion in the solution within the cation-exchange resin membrane PV-51, and of that in the solution which passes through the membrane due to electro-osmosis were calculated from the experimental data and compared in Fig. 9.



Concentration of NaCl-soln. ($N$)
Fig. 9.

The former is plotted on the curve (I) and the latter on the curve (II).

Here the procedures of the measurement and the calculation are as follows.

First, in order to measure the water content, small pieces of the cation-exchange resin membrane which have been equilibrated with the solutions of various concentrations are wiped out with filter paper, weighed, dried by means of an Abderhalden's dryer under reduced pressure for 3 hours at 100°C and then weighed again. Second, the cation content of the membranes is determined by

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** Generally the transport numbers in an ion-exchange membrane are measured by inserting the membrane between the two solutions of different concentrations. The data of transport number plotted in Fig. 7 were obtained by extrapolating such data to the case where the concentrations of the two sides are made equal.

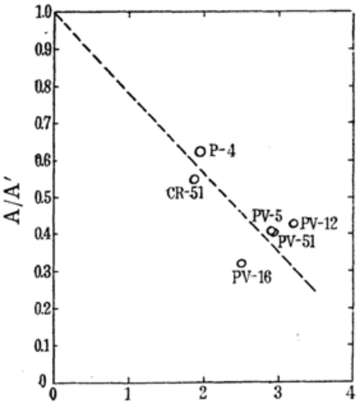
*** It is assumed that the transport number is not affected by the electro-osmosis.

The membrane-permeating solution due to electro-osmosis contains an unbalanced number of cation and anion, dependent on the transport number of the membrane, and is neutralized with the anion coming from the cathode.

measuring the cation-exchange capacity and the amount of non-exchangeable cation which may be taken out by leaching the membrane with a large volume of distilled water. Combining the above measurements, the molarity of the cation based on the water in the resin can be calculated.

On the other hand, the molarity of cation in the membrane-permeating solution can be calculated from the volume of electro-osmosis and the transport numbers of the membrane***.

As shown in Fig. 9, two curves, (I) and (II), are alike in the tendency that they decrease gradually with the lowering of the equilibrating concentration, and approach constant values respectively. There are, however, always a distinct difference between them, namely the electro-osmosing solution appears to be more concentrated in cation than that in the resin.



Molarity of fixed charge (A).
Fig. 10.

To explain the result, an idea of mobile water and fixed water in the resin membrane will be introduced.

**Mobile Water and Fixed Water in the Resin Membrane.**—As described in the early part of this chapter, there are fixed poly-anions, exchangeable cations and non-exchangeable cations and anions in the pores of cation-exchange resin, and all of these ions are supposed to be hydrated. Besides those occupied by these hydrated ions, the pores of the resin have still remaining rooms which is to be filled with water. And its amount depends on the characteristics of the resin and concentration of the equilibrating solution.

Then it will be reasonable to assume that the hydration water of the fixed polyanionic group and the water at the immediate neighborhood of it are fixed and other water moves with ions when an electric field is applied. The former may be called fixed water and the latter mobile water.

Thus considered, the difference between the two curves (I) and (II) in Fig. 9 is readily explained. Since the electro-osmosing solution comes out from the membrane leaving the fixed water in the resin structure, it must necessarily be more concentrated in cation than the solution within the resin.

Now, as the most simple case, the electro-osmosis through a cation-exchange resin membrane containing no non-exchangeable ions will be considered. Such a state can be attained by equilibrating the membrane with a salt solution and then leaching it with a large volume of distilled water.

If we denote the amount of the fixed water in the resin membrane by $\alpha$ (g./meq. fixed ion), the molarity of the fixed charge by $A$, and the molarity of the cation in the membrane-permeating solution by $A'$, the following relationship must exist among them.

$$A=\frac{1}{F\cdot\beta_0+\alpha}=\frac{1}{1/A'+\alpha} \qquad (3)$$

Therefore,

$$A/A'=1-\alpha\cdot A \qquad (4)$$

It is seen in the equation (4) that $A/A'$ plotted against $A$ should be linear, if $\alpha$ is independent of the structure of the resin and the concentration of the equilibrating solution.

The $A/A'$ derived by extrapolation of the curves like those in Fig. 7 to zero concentration are plotted in Fig. 10 for the several membranes of similar type. The results are not yet enough to prove satisfactorily the constancy of $\alpha$, but if we admit the linear relationship in the figure, the amount of the fixed water in the membrane can readily be estimated from the inclination of the line.

In this way $\alpha$ is found to be 10∼15 mol./(eq. fixed ion) in the case of sulfonated phenol resin type in distilled water.

Thus considered, it becomes evident that neither $v_+$ or $v_-$ in equation (2) is constant and is dependent on the properties of the resins.

## Summary

The water transference due to electro-osmosis was studied for several cation-exchange resin membranes of sulfonated phenol resin type, mainly in sodium chloride solution. It was shown that (1) the electro-osmosis depended on the transport number of the membrane and the amount of water

contained in the resin, and (2) the experimental results could be explained by introducing the idea of fixed water and mobile water in the membrane. The fixed water is supposed to be composed mainly of the hydration water attached to the polar groups of the resin.

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