On the Transport Number for Ion-exchange Resin Membranes

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(Received February 24, 1956)

Introduction

The ionic permselectivity of ion-exchange resin membrane has been expressed quantitatively by means of a transport number defined as the fraction of current carried by either cations or anions through it. The transport number for a membrane is generally computed from the membrane potential measurement which arises at a membrane separating two solutions of different concentrations. In this case, the Nernst's equation is generally used for correlating the membrane potentials with the transport number.

$$n_+ = \frac{1}{2}\left(1 + \frac{E_{\text{obs}}}{E_{\text{th}}}\right) \qquad (1)$$

$$E_{\text{th}} = \frac{RT}{nF} \ln \frac{a_2}{a_1} \qquad (2)$$

n_+: transport number (*t. n.*) of cations

E_{obs}: observed value of membrane potential

E_{th}: calculated value of membrane potential by use of Eq. (2)

a_1, a_2: activities of the solutions separated by the membrane. R, T, n, and F have their usual significances.

If an ion-exchange membrane is subjected to an electric field in an electrolyte solution, movement of a definite amount of solvent occurs simultaneously with ion transference[1]. Since the Nernst's equation holds in the case where only ion transference is considered, a correction should be made for the transport number in Eq. (1). This is identical with the "Hittorf transport number", which is calculated from the changes in concentra-

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[1] Y. Oda and T. Yawataya, This Bulletin, 28, 263 (1955).

tion of solution after the passage of the current, without taking account of transport of solvent molecules, and consequently expressed in terms of ionic velocities relative to an imaginary plane moving with the same speed as the solvent.

The errors arising from neglecting the solvent transference were already remarked by A. J. Staverman[2], and G. Scatchard[3], but experimental proof has not yet been reported.

As for the case of ion-exchange resin membranes, the difference between the Hittorf- and true-transport number is comparatively large and plays a very important role for practical applications.

In the present report, the Hittorf- and true-transport numbers of the various cation-exchange resin membranes were determined in sodium chloride solutions and the differences between them were discussed in view of electro-osmotic water transfer.

Experimental

Membranes.—Strong acid cation-exchange resin membranes of sulfonated type, the thickness being about 0.5 and 1.0 mm., and the water contents ranging from 30 to 60%. Prior to the measurement, membranes were thoroughly equilibrated with the solutions to be used. When a membrane is required to be interposed between two solutions of different concentration, as is the case with the membrane potential measurement, it had been equilibrated with the more dilute solution of the two. In such a case at least thirty minutes were needed to attain a stationary state after setting the membrane in the cell.

Hittorf Transport Number.—The potential was measured for a cell shown in Fig. 1, consisting of two glass half cells, a sample membrane, and calomel electrodes. Temperature was regulated at 25±0.2°C.

Calomel electrode	Satd. KCl soln.	NaCl soln. (m_1)	Membrane	NaCl soln. (m_2)	Satd. KCl soln.	Calomel electrode

Fig. 1.

The membrane potential was obtained by making a correction for the liquid junction potential at the boundaries, KCl (satd.) | NaCl (m_1) and NaCl (m_2) | KCl (satd.). This correction amounted to several millivolts under the conditions prevailing in the present experiments. From the membrane potential thus measured, the Hittorf *t. n.* was computed by the Eq. (1).

Although it is desirable to correlate the *t. n.* with the concentration of a solution, the measurement above described has to be made for a membrane placed between two solutions of different concentration. In order to obtain the *t. n.* as a function of a single concentration, an interpolating method was employed as follows. At first, fixing the concentration of a solution in one side of the cell constant, which being a parameter, membrane potentials were measured employing solutions of various concentrations in another side. And, as shown in Fig. 2 the *t. n.* computed therefrom were plotted on a diagram against the varied concentrations respectively for each parameter. Then the *t. n.* corresponding to a single concentration can be obtained by interpolating the curve to a point where the reading of the parameter and the abscissa coincides. In Fig. 2, these points are shown by black solid circles connected with a dotted line.

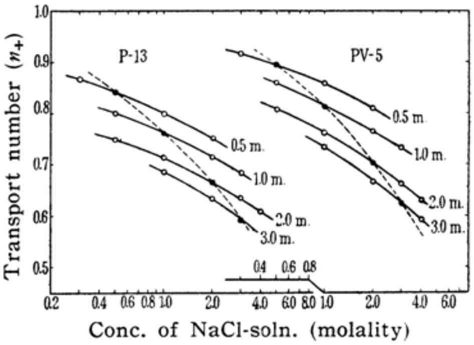

Fig. 2. Transport numbers for cation-exchange resin membranes, determined from membrane potential measurements.

True Transport Number.—A cell made of methyl metacrylate resin was used (Fig. 3). The effective area of a membrane was 4.0 cm². A stirrer was provided in each compartment to keep the solutions as uniform as possible.

Prior to an experiment, the sodium chloride solution was filled in the cell to equilibrate the membrane with it. After the solution was taken out, the remaining solution on the cell wall was wiped out clean with filter paper. A weighed amount of the sodium chloride solution (W_S g.; NaCl: m_S mol.) of the same concentration as previously used, was put in the cell, and silver-silver chloride electrodes (weight of the cathode being W_E) were inserted. Then the circuit was closed, iodine coulometer being connected in series. After a certain amount of electricity (Q coulomb) passed, the solution in the cathode compartment and the cathode itself were taken out separately in dried weighing bottles and their weights were measured rapidly. Let the weight of cathode in wet state be W_E', and that of the solution W_S'. Next, the solution remaining on the cell wall and the membrane inside the cathode cell was blotted rapidly but cautiously with filter paper, and was titrated for chloride ion with silver nitrate standard solution (NaCl: m_S''). Sodium chloride in

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[2] A. J. Staverman, *Trans. Faraday Soc.*, **48**, 176 (1952).

[3] G. Scatchard, *J. Am. Chem. Soc.*, **75**, 2883 (1955).

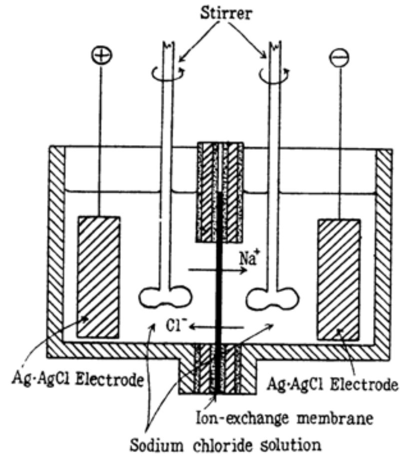

Fig. 3. Apparatus for measuring true transport number.

the main solution taken out from the cathode compartment (m_S') and that imbibed in the cathode material (m_E') were also determined by titration.

Then the material balance in the cathode cell is shown as follows.

NaCl increase $(\Delta m)=(m_S'+m_E'+m_S'')-m_S$

Total weight increase $(\Delta W)=(W_S'+W_E'+W_S'')-(W_S+W_E)$, where, $W_S''=W_S'\cdot\frac{m_S''}{m_S'}$.

From these, the true transport number and the amount of transferred water are computed by the next equations.

$$n_+'=\frac{\Delta m}{Q/F} \tag{3}$$

$$\beta_W=[\Delta W-\Delta m\times M_{Na}+(Q/F-\Delta m)\times M_{Cl}]/Q \tag{4}$$

M_{Na}, M_{Cl}: atomic weight of sodium-and chloride ion

The electrolysis was carried out for about thirty to sixty minutes with the current density of 5 A/dm². By preliminary experiments it was ascertained that the *t.n.* was scarcely dependent on current density over the range from 1 to 6 A/dm².

Since the surface of the solution was inevitably exposed to the atmosphere during the experiment, the amount of water that might be lost by evaporation was not negligible. For this correction, the rate of water evaporation was measured for the same solution in an other vessel.

The β_W computed from the Eq. (4) is the amount of water transferred by one coulomb, i.e. the electro-osmotic water exclusive of solute. In the following part of this report, there will be discussed the relation between β_W and β, volume of transferred solution per unit coulomb, which was determined volumetrically in the previous report[1].

Water Content, Fixed Ion Concentration and the Donnan Absorption.—For the discussion on the transport numbers, measurements were made on water content, fixed ion concentration, along with the concentration of non-exchangeable ions absorbed in membrane due to the Donnan equilibrium, for each membrane in the similar manner to those reported by G. Manecke or W. Juda et al.[4,5].

Results

Transport Numbers.—In Figs. 4 and 5, are shown Hittorf *t.n.* (n_+) and true *t.n.* (n_+')

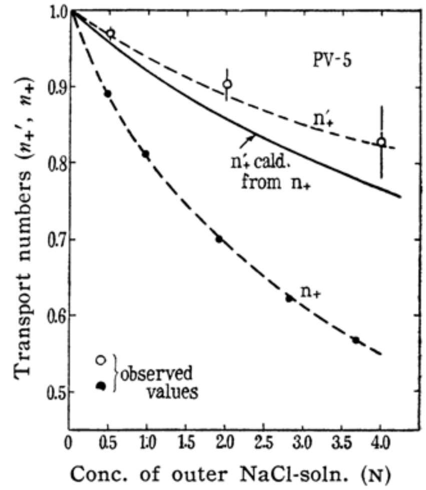

Fig. 4. Transport numbers for cation-exchange resin membrane PV-5.

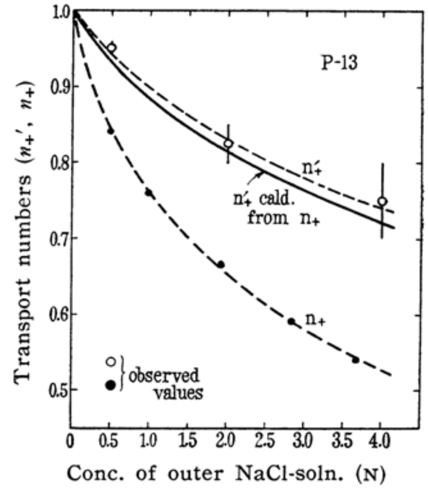

Fig. 5. Transport numbers for cation-exchange resin membrane P-13.

determined by the procedures above described for two typical cation-exchange resin membranes against the concentration of outer solutions. Both *t.n.* show the similar tendency that they decrease with increase in outer concentration, but remarkable differences exist between their absolute values. True *t.n.*, the "dynamic transport number" so to speak, is much higher than Hittorf *t.n.* computed from nearly static thermodynamic membrane potentials.

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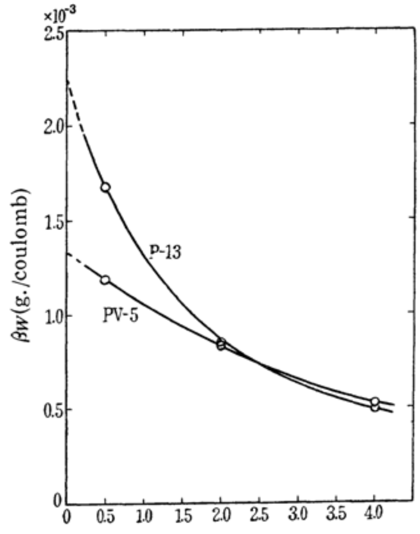
[4] G. Manecke, *Z. phys. Chem.* 201, 193 (1952).

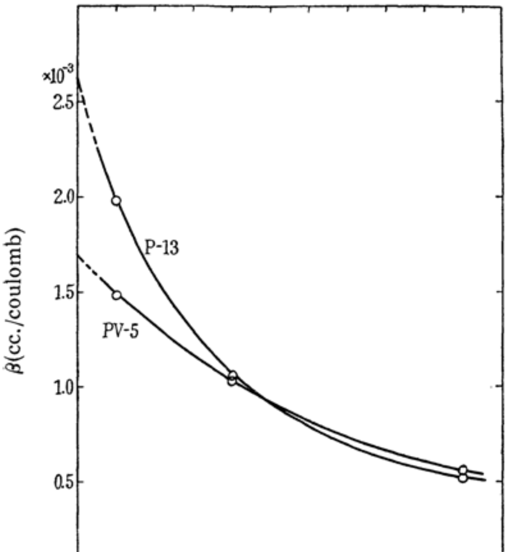
[5] W. Juda et al., *J. Am. Chem. Soc.*, 74, 3736 (1952).

Electro-osmotic Water Transference.—Measured values of β_W are plotted on Fig. 6 against the concentrations of outer solution. For the purpose of comparison, β are shown in Fig. 7.



Conc. of outer NaCl-soln. (N)

Fig. 6. Electro-osmotic water transference of cation-exchange resin membranes.

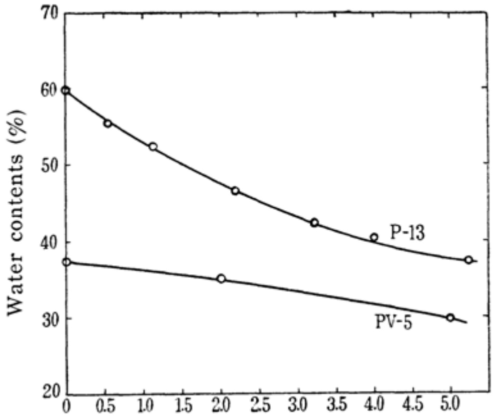


Conc. of outer NaCl-soln. (N)

Fig. 7. Electro-osmosing solution transference of cation-exchange resin membranes.

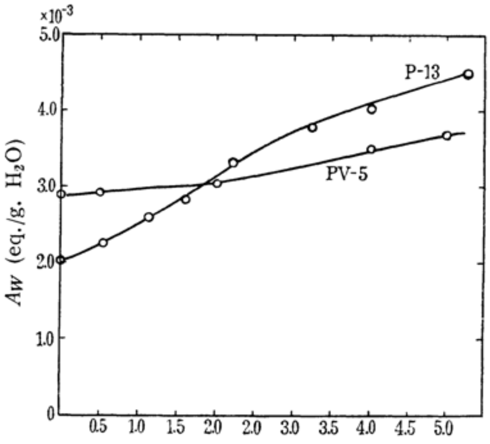
When the concentration of the outer solution was raised from zero concentration upward, β_W and β, irrespective of membrane difference, tend to decrease rather sharply and converge to nearly constant values respectively.

Water Content, Fixed Ion Concentration and the Donnan Absorption.—These are shown in Figs. 8, 9 and 10. Here the Donnan



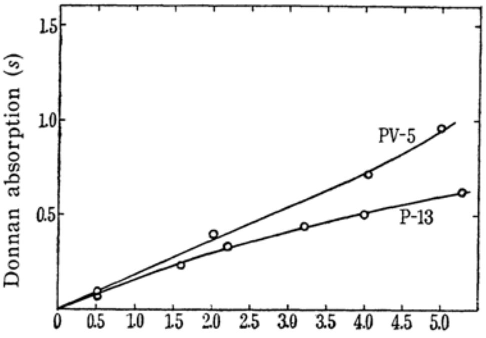
Conc. of outer NaCl-soln. (N)

Fig. 8. Water contents of cation-exchange resin membranes.



Conc. of outer NaCl-soln. (N)

Fig. 9. Fixed ion concentration of cation-exchange resin membranes.



Conc. of outer NaCl-soln. (N)

Fig. 10. Donnan absorption of cation-exchange resin membranes.

absorption (s) is expressed by the ratio of the concentration of absorbed chloride ion to that of fixed ion of the resin, both concentrations being computed in relation either to the weight of water taken up in the resin, or to the swollen volume of the resin.

$$s=[\mathrm{Cl}^-]/[-\mathrm{SO}_3^-]$$

Then, if the fixed ion concentration is expressed by A, which is the content of fixed ion per unit volume of swollen resin, $A(1+s)$ indicates the concentration of Na^+, and $A\cdot s$ that of Cl^-.

Discussion

Transport Numbers.—When a membrane is interposed between two solutions of different concentration, flow of materials takes place across it. Namely, solute molecules diffuse through the membrane from the more concentrated side to the dilute side, and at the same time solvent molecules in the reverse direction. As the membrane potential has to be measured under such a situation, the *t. n.* derived therefrom may cause the erroneous result due to this material transference.

But, the error would be minimized by the application of the " interpolation method " as mentioned above. In fact, R. Schlögl⁶⁾ has shown that the *t. n.* computed from membrane potential measurement* stands in good agreement with that derived from the rate of self-diffusion within a membrane, the latter being determined for the membrane placed between two solutions which are only differentiated with radioactive Na^{24} or Br^{82} on one side.

On the other hand, the water transport due to the current passage across the membrane is so large that its effect on the *t. n.* can never be overlooked.

In order to consider the contribution of electro-osmosis to the passage of the current within a resin membrane, it will be assumed that ions are present in completely dissociated state in the resin. The assumption seems to be not so far from reality because of the strong acidic nature of the sulfonate type cation-exchange resin.

As G. Schmid has already reported⁷⁾, electric conduction within micro-porous membrane consists of electrolytic and convective conduction. If we denote the mobilities of cation and anion relative to the pore wall by u'_+ and u'_-, they are written as,

$$u'_+=u_++u_s,\ u'_-=u_--u_s \tag{6}$$

where u_+ and u_- are the mobilities relative to the solution, and u_s that of the solution.

In this way, ions seem to move in a similar manner to " a walking man on a running vehicle ". In cation-exchange resin membranes, the velocity of cation is accelerated, that of anion retarded.

On this basis, the conductivity of a membrane, k', is derived as,

$$\begin{aligned} k'&=F[A(1+s)u'_++A\cdot s\cdot u'_-]\\ &=FA[(1+s)u_++s\cdot u_-+u_s]. \end{aligned} \tag{7}$$

On the other hand, the conductivity of a membrane, if without any electro-osmosis, is,

$$k=F\cdot A[(1+s)u_++s\cdot u_-]. \tag{8}$$

Therefore, the conductivity rise due to electro-osmosis is,

$$k'-k=F\cdot A\cdot u_s \tag{9}$$

On the basis of a similar concept, the transport numbers may be expressed as,

$$n'_+=\frac{(1+s)u'_+}{(1+s)u'_++su'_-} \tag{10}$$

$$n_+=\frac{(1+s)u_+}{(1+s)u_++su_-}. \tag{11}$$

Thus,

$$n'_+-n_+=(n_-+s)\frac{k'-k}{k'}. \tag{12}$$

Now, if we denote by β_{E} the volume of electro-osmosing solution under unit potential gradient applied to a membrane,

$$\beta_{\mathrm{E}}=\beta\cdot k'=u_sS \tag{13}$$

where S is the total cross sectional area of pores of membrane resin. In this case, the spaces occupied by the hydration water of sulfonate group should be excluded from the pore volume, if it is considered as immobile even under electric field.

Hence, from Eqs. (9), (12) and (13),

$$\begin{aligned} n'_+-n_+&=(n_-+s)\cdot FAu_s/k'\\ &=(n_-+s)\cdot(A/S)\cdot\beta\cdot F\\ &=(n_-+s)\cdot A_{\mathrm{S}}\cdot\beta\cdot F \end{aligned} \tag{14}$$

where A_{S} is the content of fixed ion per unit volume of electro-osmosing solution, i. e. mobile solution in the resin.

In Eq. (14), the term $(n_-+s)\cdot A_{\mathrm{S}}$ expresses the sodium chloride concentration of electro-osmosing solutions. This expression does eventually coincide with " strömende Konzentration "* by G. Schmid⁸⁾, which has been

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6) R. Schlögl, *Z. Elektrochem.*, **57**, 199 (1953).

* He applied the interpolation method on the membrane potential vs. activity of outer solution curves.

7) G. Schmid, *Z. Elektrochem.*, **56**, 181 (1952).

* $C_s=(C_k-n_k\cdot A)=(C_A+n_A\cdot A)=[A(1+s)-n_k\cdot A]$
$=A(1+s-n_k)=A(n_-+s)$

G. Schmid used the notation A as the content of fixed ions per unit volume of solution within resin phase.

8) G. Schmid, *Z. Elektrochem.*, **56**, 35 (1952).

derived for the salt concentration of solution flowing out of a membrane when hydrostatic pressure is applied on one side.

Since it is difficult to determine A_S, a volumetric quantity, experimentally, one had better reform the expression (14) into Eq. (15) by use of gravimetric quantities,

$$n'_+ - n_+ = (n_- + s)A'_W \cdot \beta_W \cdot F \qquad (15)$$

where A'_W is the content of fixed ion per unit weight of the water contained in electro-osmosing solution. The transformation from Eq. (14) to Eq. (15) would be justified when it is considered that the term $A_S \cdot \beta \cdot F$ is a dimensionless quantity.

Here, let us examine the implication of A'_W in a little more detail. There are three kinds of water within ion-exchange resin, (1) hydration water of sulfonate ion, (2) that of free cations and anions, and (3) solvent water. The latter two are "mobile water"[1], and (1) is considered as immobile even under electric field. According to R. H. Stokes and R. A. Robinson[9], the former two have been called "bound water" and (3) "free water".

Basing on this concept, A'_W may be expressed in terms of (2)+(3), since the hydration water of sulfonate ion is considered to be almost indifferent to electro-osmosis. It follows, therefore, that the water which contributes to the "convective conduction" is the mobile water, i. e. (2)+(3).

For these reasons, in order to exactly compute the right-hand term of Eq. (15), it is necessary to know the distribution of water within the exchanger. But, since no satisfactory knowledge on the water distribution is available at present, Eq. (15) is approximately computed by substituting A_W for A'_W, the concentration of fixed ion in the total water within the resin.

In Figs. 4 and 5, the solid line shows the results of computation on n'_+ from observed values of n_+, A_W, β_W and s. The concordance of observed and computed values of n'_+ seems fairly good.

Since the water distribution in ion-exchanger, though neglected in the above treatment, seems very important to account for the nature of ion-exchange resin, it will be examined in more detail in the succeeding paper.

Electro-osmotic Transference of Water, β_W and β.—In the preceding paper the present authors reported on the electro-osmotic water transference through cation-exchange resin membranes. There, employing a volumetric procedure, observed data were expressed by β (cc./coulomb), volume of electro-osmotically transferred solution per unit coulomb.

During current passage, a solution containing excess sodium ion flows into a cathode cell across the membrane, and it is neutralized with chloride ion formed by the cathode reaction with the result that a certain amount of concentrated sodium chloride solution is added to the cathode solution. In this case, although the volume change occurs due to dilution, it may readily be seen that that is negligible for the sensitivity of the present electro-osmotic measurement. Also, the volume change due to the cathode reaction, $AgCl + e \longrightarrow Ag + Cl^-$, may be neglected.

Then, the relation between β_N and β is written as,

$$\beta = \frac{1}{d}(\beta_N + n'_+ \cdot M/F) \qquad (16)$$

where d is the density of the concentrated sodium chloride solution which is added to cathode cell due to electro-osmosis and electrode reaction combined, and M is molecular weight of NaCl.

A difficulty arises to know d, when the electro-osmosing solution is so concentrated in sodium ion that it, combined with chloride ion from cathode, is to form supersaturated solution. In such cases, the values of d were approximately calculated by use of the partial molal volume of sodium chloride at saturation.

In Fig. 11, the value of β calculated from β_W and n'_+ is shown by the solid line in com-

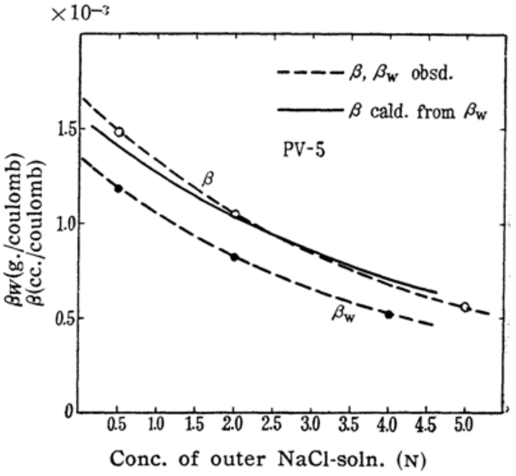

Fig. 11. Relation between β and β_W of a cation-exchange resin membrane.

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9) *Annual Review of phys. Chem.*, **1954**, p. 420.

parison with the experimentally observed values.

Conclusion

The cation transport numbers through cation-exchange resin membranes were determined experimentally by two methods, first, computation from membrane potential measurement, and second from analytical tracing of the concentration change which takes place, on current passage, in the solution separated by the membrane. The former, which is considered as "Hittorf transport number", is found to be far smaller than the latter, the true transport number. The difference between the two sorts of transport number was accounted for on the basis of the concept of convective conduction within the pores of ion-exchange resin.

The electro-osmotic water transference through the membrane was discussed on comparing the results of its volumetric- and gravimetric measurements.

The authors are grateful to Dr. M. Sekino, Dr. S. Uemura and Mr. M. Funaoka for their encouragement in this work.

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