On the Distribution and Behavior of Water in Cation-Exchange Resin Membranes

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Introduction

In the preceding two papers[1,2], we reported on the electro-osmotic phenomena in cation-exchange resin membranes, and discussed to some extent on the distribution of water within the resin. Therein, the water in the resin phase was classified into two groups, i.e., "mobile- and fixed waters". The former was considered to consist of the hydration water of the exchangeable and non-exchangeable ions and the solvent water in the resin, whilst the latter to consist mainly of the hydration water of the structurally bound ions, e. g., sulfonate ions in the cation-exchange resin.

Hitherto several workers have studied the water in the ion-exchange resins basing their studies on different principles.

D. Reichenberg[3], discussing on the exchange rate of sodium- and hydrogen ions in cation-exchange resins of different cross-linkings, calculated the amount of water unavailable as a diffusion medium to find five molecules per equivalent of the resin, and assumed that the ions in the resin were hydrated to this extent.

G. E. Boyd and B. A. Soldano[4], from the study on the water adsorption isotherms for cation- and anion-exchange resins, ascribed one molecule of H_2O to the amount of water which is required by a structurally bond sulfonate ion.

E. Glueckauf[5] has recently determined the hydration number of sulfonate ions as 0.9 in cation exchanger of sulfonated polystyrene type. It was derived on the basis of the thermodynamical concept of electrolyte solution, modified so as to include the effect of co-volume.

According to G. H. Osborn[6], the recent work on the absorption of non-electrolyte by the hydrogen forms of the exchangers has confirmed that there are about four molecules of hydration water per equivalent of sulfonic group.

Referring to these published data, most of which are indicated with numbers of hydration water of total ionic species in the resin, including both fixed and mobile ions, our results[1], about ten molecules water for a sulfonate ion, seems far separated from them.

The difference may be explained that "the fixed water" which does not take part in electro-osmosis would involve not only the hydration water of the fixed ions but a part of water which is hindered to

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

[2] Idem. ibid., **29**, 673 (1956).

[3] D. Reichenberg, *J. Am. Chem. Soc.*, **75**, 589 (1953).

[4] G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).

[5] E. Glueckauf, *Trans. Faraday Soc.*, **51**, 1235 (1955).

[6] G. H. Osborn, "Synthetic Ion-Exchangers," Arrowsmith, London (1955), p. 7.

move due to the network structure of the resin. Thus, the determination of the number of fixed water molecules from the electro-osmotic measurements seems to deserve further discussion. The present paper deals with this problem.

Theoretical

In the first paper of this series[1)], we assumed that the free water in the resin moves with mobility equal to that of the migrating ions.

It would be more reasonable, however, to suppose that in the electro-osmosing solution the mobility of ions differs from that of the solvent water, since the water moves with velocity depending on the balance between the driving force due to ionic migration and the retardation due to the network of resin.

Thus, it will be assumed in this paper that the electro-osmosing water within ion-exchange membrane consists of two sorts with different mobilities: (1) primary shell hydration water of the mobile ions with a mobility equal to that of the ions, and (2) solvent water with smaller mobility than (1). Naturally the transferring velocity of the solvent water would not be uniform over a whole resin pore section, but would have a distribution governed by the hydrodynamic principle. For simplicity, however, it is assumed to have a certain average mobility, u_s.

As was stated previously[2)], the fixed ion concentration A_w based on the total water content in the resin is expressed as follows,

$$\frac{1}{A_w}=h_+\cdot(1+s)+h_-\cdot s+f+\alpha \qquad (1)$$

where, from the definition of A_w, $1/A_w$ means the amount of total water per equivalent of fixed ion. h_+ and h_- are the amount of hydration of mobile cation and anion respectively. And s, f and α are respectively the amount of Donnan absorption, solvent water and fixed water, all these being indicated basing on an equivalent of fixed ion.

When an electric field is applied on a cation-exchange membrane interposed between two solutions of equal concentration, n_+' moles cations enter the cathode cell through the membrane and n_-' moles anions migrate out of the cathode cell into the anode cell for each faraday of electricity. Here, n_+' and n_-' denote* the ture transport numbers of the cation and the anion within the membrane. In this case, the water transference may be considered to take place as illustrated schematically in Fig. 1. The hydration water of cations or anions moves toward cathode or anode with the same mobilities as the respective ions. Whilst, the solvent water, whose amount is f moles per equivalent of fixed ion, or $f\cdot\frac{n_+'}{1+s}$ moles per n_+' moles of the migrating cation, transfers with a mobility u_s/u_+' times as small as that of the cation. Here, u_+' is the mobility of the cation in resin phase.

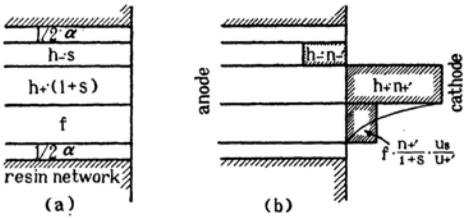

Fig. 1. (a) Distribution of water inside resin-pore
(b) Water transference for passage of one faraday (Shaded areas express the transfered water.)

Therefore, the amount of electro-osmotic water transference, β_w, is correlated with the transport numbers of cation and anion as follows,

$$\beta_w\cdot F=h_+\cdot n'_+-h_-\cdot n'_- +f\cdot\frac{n'_+}{1+s}\cdot\frac{u_s}{u'_+} \qquad (2)$$

$$=\left(h_++f\cdot\frac{u_s}{u'_+}\right)\cdot n'_+ -\left(h_-+f\cdot\frac{u_s}{u'_-}\right)\cdot n'_-. \qquad (2')$$

Cancelling f from (1) and (2), and noting the fact that $n'_++n'_-=1$,

$$\frac{1}{A_w}=\alpha+\frac{\beta_w\cdot F}{u_s/u'_+}\cdot\frac{1+s}{n'_+} +h_+\cdot(1+s)\cdot\left(1-\frac{1}{u_s/u'_+}\right) +h_-\cdot s\cdot\left(1+\frac{1}{u_s/u'_+}\right)$$

$$=\alpha+\frac{\beta_w\cdot F}{u_s/u'_+}\cdot\frac{1+s}{n'_+}+h, \qquad (3)$$

where

$$h=h_+\cdot(1+s)\left(1-\frac{1}{u_s/u'_+}\right)$$

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* The mobility notation with or without a prime refers to the quantity relative to the solution or the resin.

$$+h_{-}\cdot s\cdot\left(1+\frac{1}{u_s/u'_{-}}\right).$$

On the other hand from equations (7), (9) and (12) in the preceding paper[2],

$$\frac{n'_{+}-n_{+}}{n_{-}+s}=\frac{k'-k}{k'}=\frac{u_s}{u'_{+}\cdot(1+s)+u'_{-}\cdot s}$$

$$=\frac{u_s}{u_{+}'}\cdot\frac{1}{1+s}\cdot\frac{u'_{+}\cdot(1+s)}{u'_{+}\cdot(1+s)+u'_{-}\cdot s}.$$

Then, considering the relations of equations (10) and (15) in the previous paper,

$$\frac{n'_{+}-n_{+}}{n_{-}+s}=\frac{u_s}{u_{+}'}\cdot\frac{n'_{+}}{1+s}=A'_w\cdot\beta_w\cdot F. \qquad (4)$$

Therefore, the ratio of the mobility of solvent water to that of cation is,

$$\frac{u_s}{u'_{+}}=\frac{1+s}{n'_{+}}\cdot\frac{n'_{+}-n_{+}}{n_{-}+s}. \qquad (5)$$

By the similar way,

$$\frac{u_s}{u'_{-}}=\frac{s}{n'_{-}}\cdot\frac{n'_{+}-n_{+}}{n_{-}+s}. \qquad (5')$$

Further, from equation (11) in the preceding of paper, the ratio anion's mobility to cation's within the moving solution is obtained as,

$$\frac{u_{-}}{u_{+}}=\frac{n_{-}}{n_{+}}\cdot\frac{1+s}{s}. \qquad (6)$$

The concentration of fixed ion basing on "the mobile water", A'_w, is given, by use of the equation (4), as follows,

$$\frac{1}{A'_w}=\frac{\beta_w\cdot F}{u_s/u'_{+}}\cdot\frac{1+s}{n'_{+}}. \qquad (7)$$

Hence,

$$\frac{1}{A'_w}=\frac{1}{A_w}-\alpha-h. \qquad (8)$$

By means of equations (5) and (5′) values of u_s/u'_{+} and u_s/u'_{-} may be estimated for each membrane from the observed values of n'_{+}, n_{+} and s. These values of u_s/u'_{+} and u_s/u'_{-}, combined with the observed value of β_w, permit an estimation of α by use of equation (3).

Experimental

Membranes.—Two cation-exchange resin membranes were used in the present work. One is of sulfonated polystyrene type (CMA-24), and the other of sulfonated phenol resin type (P-13). The latter is one of the same series as those used previously[2]. Their exchange capacities and water contents are given in Table I.

Measurement.—Of the CMA-24 membrane, measurements were made for true transport numbers (n'_{+}, n'_{-}), Hittorf transport numbers (n_{+}, n_{-}), electro-osmotic water transference (β_w), Donnan absorption (s), and the fixed ions concentration (A_w) in the chloride solutions of 1 :1 valency type such as LiCl, NaCl, NH_4Cl, KCl, CsCl, and HCl of varied concentration. Temperature was regulated at 25±0.2°C. The procedures of the measurements were quite the same as those described previously[2].

Of the P-13 membrane, such measurements were carried out solely in sodium chloride solution.

TABLE I

THE EXCHANGE CHARACTERISTICS OF SAMPLE MEMBRANES (Na-TYPE)

Sample No.	Thickness (mm.)	A°_w m.eq./g. H_2O	A_R m.eq./g.	Water content %
CMA-24	0.3	3.90	1.86	32.3
P-13	0.9	2.02	3.04	60.1

A°_w is the concentration of fixed ions basing on the total water content of the resin equilibrated with distilled water.

A_R is the exchange capacity per one gram of dry resin.

Results

The results are given for CMA-24 membrane unless specified.

The empirically determined true and Hittorf transport numbers of cation (n'_{+}, n_{+}) through the membrane are plotted in Fig. 2 over the concentration range of equilibrating solution from 0 to 4 N. The Hittorf transport number is highest in HCl-solution and decreases in the order, $H^+>Cs^+>K^+>NH_4^+>Na^+>Li^+$. The order is in good accord with that in free aqueous solutions. Such a situation cannot be seen so clearly regarding the true transport number curves, since in this case they

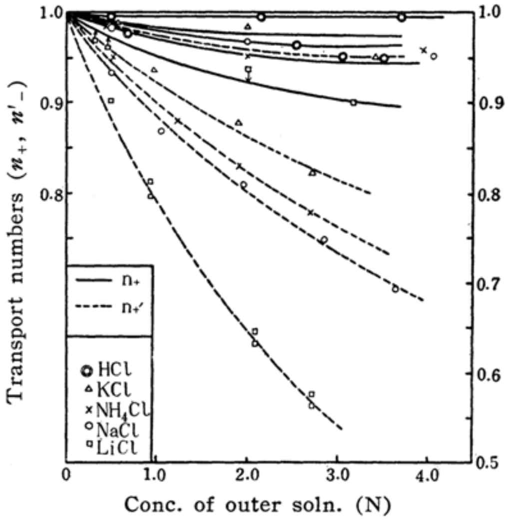

Fig. 2. Transport numbers in cation-exchange resin membrane (CMA-24).

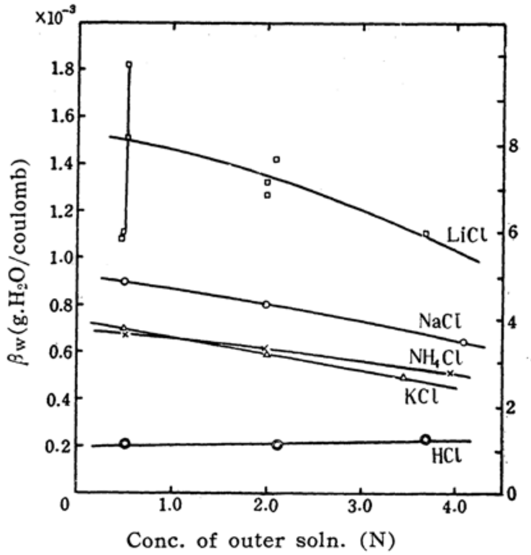

Fig. 3. Electro-osmotic water transference through cation-exchange resin membrane (CMA-24).

come together closely to approach the upper limit line: $n'_- = 1$.

In Fig. 3 are plotted the electro-osmotic water transference, β_w, through the membrane against the concentration of outer solutions. It appears to become large as the hydration of the cation increases, except for the case of HCl-solution. The hydration numbers of the ions concerned are listed below in Table II according to E. Glueckauf. The β_w in HCl-solution is notably and small stays nearly constant over a wide concentration range.

With LiCl-solution the observed values of β_w, particularly in dilute solution region, showed remarkable large fluctuation, and appeared to rise gradually as the duration of electrolysis increased.

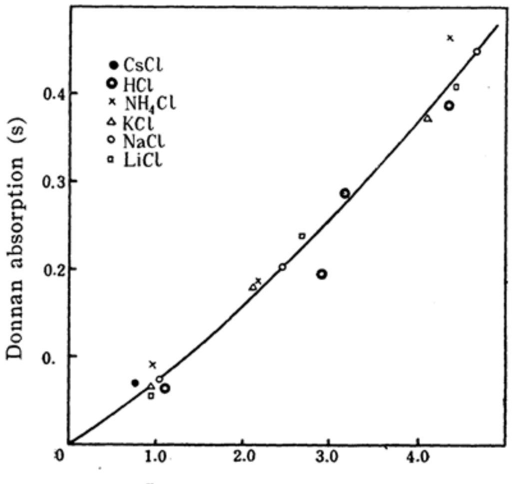

Fig. 4. Donnan absorption (CMA-24).

The Donnan absorptions are given in Fig. 4. They increase with the rise in the concentration of equilibrating solution, and little significant variation can be seen with the difference of cation species.

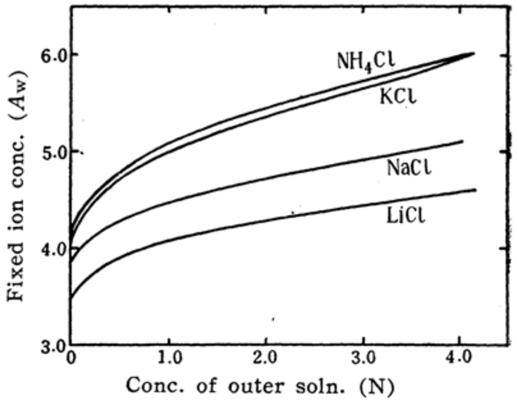

Fig. 5. Fixed ion concentration (A_w) (CMA-24).

Fig. 5 shows the curves of fixed ion concentrations, A_w, plotted against the concentration, of outer solution. As the outer solutions become concentrated, the shrinkage of the resin seems to cause the increase of A_w.

Discussion

The ratios of the mobility of solvent water to that of cation, u_s/u'_+, were cal-

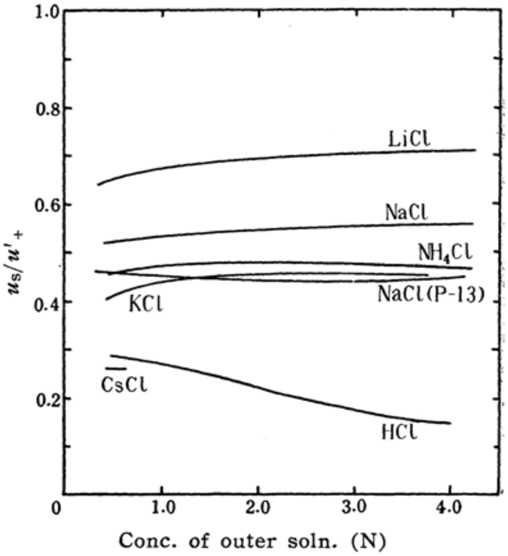

Fig. 6. Mobilities of water relative to cations.

culated by substituting the experimental data obtained above in equation (5). The results are plotted in Fig. 6 against the concentration of outer solution. In this calculation, accuracy decreases as the outer solutions become too diluted, because then the terms $(n'_+ - n_-)$ and $(n_- + s)$ in equation (5) approach zero.

It may be noted that the mobility ratio u_s/u'_+ appears to be almost constant over a wide concentration range of each solution, and that it becomes high to approach the limit line of $u_s/u'_+ = 1$ as the hydration degree of the cation increases, the data for HCl-solution being one exception.

As was seen in Fig. 3, in HCl-solution the electro-osmotic water transference is merely about one mole H_2O per faraday through a membrane, being even smaller than the hydration number of hydrogen ion. These apparently anomalous results with HCl-solution are presumably attributable to the special conduction mechanism of hydrogen ion.

By the similar way, the ratios of anion's mobility to cation's, u_-/u_+, within the electro-osmosing solution were calculated using equation (6), and were shown in Fig. 7. For the sake of comparison, the ratios u_-/u_+ in aqueous solutions were plotted with broken lines in the same figure. It is seen that the u_-/u_+ ratios in electro-osmosing solution tend to approach those in free solutions as the concentration of equilibrating solution rises. This result seems reasonable, for the mobile cations and mobile anions are present in marked unbalance within the resin when the outer solution is dilute, and they tend to approach a balance, which is the case in free solution, as the outer solution, becomes concentrated.

Finally, the values of α, the amount of hydration of sulfonic group, were estimated using equation (3) and plotted in Fig. 8. In this calculation, Glueckauf's data of hydration number of ions were applied for h_+ and h_-. They are given in Table II.

From the result, we are tempted to reach a conclusion that the hydration of a sulfonic group decreases as the effective concentration rises in resin. But the derivation of the values of α is not so precise as to allow it. Though it has been assumed in the above calculation that the hydration degrees of mobile ions are constant irrespective of the concentration of solutions in resin, this seems oversimplified. Also, the determinations of α for the case of very dilute equilibrating solutions are not completely reliable, because as the solutions are diluted both the numerator $(n' - n_-)$ and the denominator $(n_- + s)$ in equation (4) approach zero, resulting in inaccurate values of u_s/u'_+.

Thus, if we take the data around 2N as the comparatively reliable values α may be estimated as 1.5 to 3.5 moles per equivalent. These values of α, though still slightly higher than those found in the literature of the subject, seem much more reasonable as the hydration number of the fixed

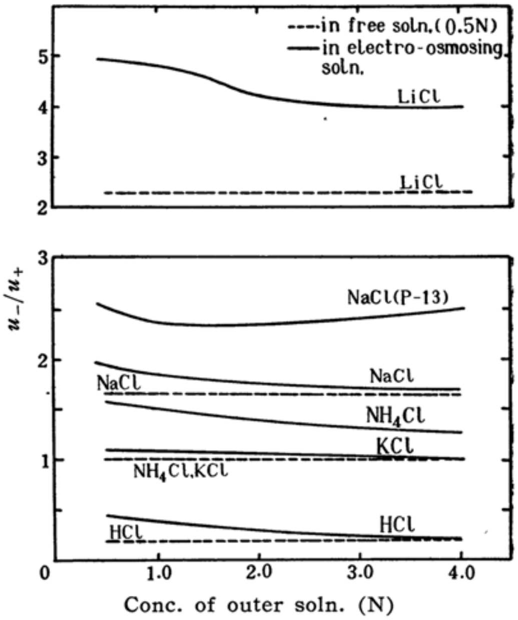

Fig. 7. Mobility ratio of anion's to cation's in electro-osmosing and free aqueous solutions.

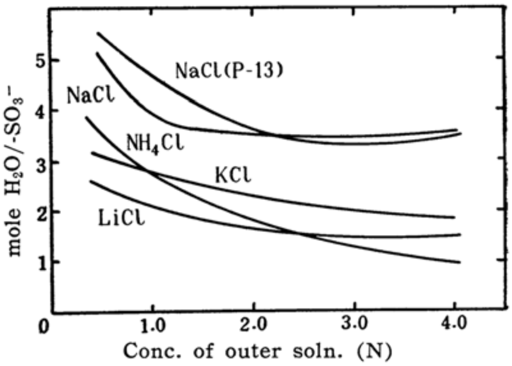

Fig. 8. Amount of hydration of sulfonic group.

TABLE II

	H^+	Li^+	Na^+	K^+	NH_4^+	Cl^-
Primary hydration number	4.0	3.4	2.0	0.6	0.2	0.9

sulfonic group than that reported previously by us.

When the circuitous process of calculation and rather drastic assumptions basing on a simple model in our treatment are considered, the concordance appears comparatively good. But more precise experiments would be desirable for membranes of wide varieties in order to make more strict discussion.

Conclusion

It was assumed for a mechanism of electro-osmosis through ion-exchange resin membranes that (1) the primary shell hydration water of mobile ions transfers with the same mobility as the ions, and (2) the solvent water within the resin phase is dragged by the migrating cations or anions toward anode or cathode, the net result being observed as electro-osmosis. On this view, the mobilities of solvent water relative to those of cations were calculated from the measurements of electro-osmotic properties of cation exchange resin membranes equilibrated with varied concentration of LiCl, NaCl, KCl, NH_4Cl, CsCl and HCl solution. In addition, from these experimental data the amount of hydration of the fixed sulfonate ion was estimated as 1.5 to 3.5 moles per equivalent.

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