The Permeabilities of Hydrogen, Sodium and Calcium Ions in Mixed Solvents across Ion-exchange Membranes

By Manabu SENŌ and Takeo YAMABE

(Received July 19, 1963)

The ion-exchange equilibria in mixed solvents exhibit some different behaviors from those in aqueous solutions. For example, the selectivity coefficient, $K_{\mathrm{H}}^{\mathrm{Na}}$, of the ion exchange of sodium for hydrogen ions increases remarkably with the decrease in the dielectric constants of the media.[1,2] On the other hand, it has been revealed that the selective permeability of ions across ion-exchange membranes is primarily ruled by the concentrations and the mobilities of ions in the membrane phase.[3,4] In this paper, the permeabilities of hydrogen, sodium and calcium ions across ion-exchange membranes in mixed solvents will be examined and discussed. The aim of this investigation is to disclose the behavior of ions in mixed solvents and to give some information on the mechanism of the ion transportation across the membranes.

Experimental

The electrodialysis apparatus is a cell with two compartments separated by a cation-selective membrane and equipped with silver-silver chloride electrodes. The solvent systems examined were water-methanol, water-ethanol and water-acetone, from which the sample solutions were prepared by adding nearly the same equivalent quantities of two kinds of chlorides, hydrogen chloride-sodium chloride, sodium chloride-calcium chloride. The total concentration was nearly 0.1 N. The membranes used were heterogeneous, prepared from pulverized ion-exchange resins (Amberlite IR-120), poly(vinyl chloride), dioctyl phthalate and cyclohexanone.

The electrodialyses were carried out for 90, 60 and 30 min. under the current densities of 5, 10 and 30 mA/cm², respectively. From the analytical data for sample solutions, the coefficient, $T_{\mathrm{B}}^{\mathrm{A}}$, of the permselectivity of ion A for ion B are calculated by

$$T_{\mathrm{B}}^{\mathrm{A}}=\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}}\right)\Big/\left(\frac{C_{\mathrm{A}}}{C_{\mathrm{B}}}\right)$$

where m is the quantity of ions transferred across the membrane and C is the mean concentration in the compartment from which ions flow out. In these calculations, the effect of the concentration diffusion has been disregarded, based on the results of the preliminary experiments.

The electric conductivity of the membranes in each ionic form was measured by the use of a universal bridge, Yokogawa BV-Z-103B. The method, each membrane being sandwiched directly between two mercury electrodes, was employed.

Results and Discussion

The experimental results are shown in Figs. 1 and 2. The premselectivity coefficients, $T_{\mathrm{Na}}^{\mathrm{H}}$

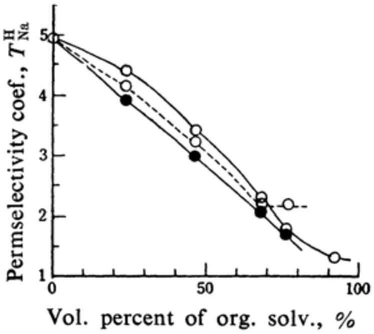

Fig. 1. Relationship between permselectivity coefficient $T_{\mathrm{Na}}^{\mathrm{H}}$ and solvent composition.

—○— Water-methanol
--○-- Water-ethanol
—●— Water-acetone

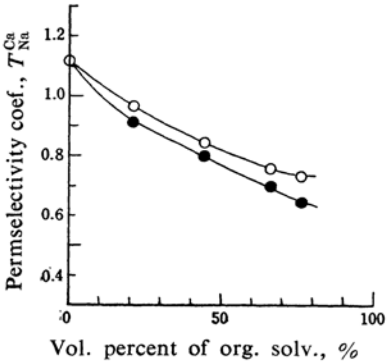

Fig. 2. Relationship between permselectivity coefficient $T_{\mathrm{Na}}^{\mathrm{Ca}}$ and solvent composition.

—○— Water-methanol
—●— Water-acetone

---

[1] T. Sakaki, This Bulletin, **28**, 217 (1955).

[2] T. Yamabe, T. Saito and M. Senō, unpublished.

[3] T. Yamabe, M. Senō, T. Tanaka and I. Kamii, This Bulletin, **33**, 1740 (1960).

[4] M. Senō and T. Yamabe, *Monthly J. Inst. Ind. Sci. Univ. of Tokyo* (*Seisan Kenkyu*), **13**, 433 (1961).

and T^{Ca}_{Na}, decrease upon the addition of the organic solvents. The decrease is approximately linear with the increasing contents of the organic solvents, but it shows a tendency to converge to a limiting value at higher organic contents, especially in the water-ethanol system.

The increase in the current densities decreases the permselectivity coefficients, T^{H}_{Na} and T^{Ca}_{Na}. The effect is pronounced at the lower current densities. An example is shown in Fig. 3.

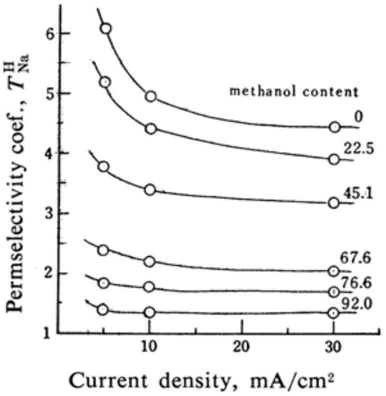

Fig. 3. Dependence of T^{H}_{Na} on current densities.

It is considered that the transport of ions across ion-exchange membranes is effected by both the number of movable ions and the mobility of the ions in the membrane. That is, the coefficient of the permselectivity, T^{A}_{B}, is split into two terms, the mobility terms and the concentration term:

$$T^{A}_{B}=\left(\frac{\bar{u}_{A}}{\bar{u}_{B}}\right)\left(\frac{\bar{C}_{A}}{\bar{C}_{B}}\Big/\frac{C_{A}}{C_{B}}\right)$$

It may readily be shown that, in the limiting region of the lowest current densities, the concentration term approaches the separation factor, S^{A}_{B}, of the ion-exchange equilibria. Moreover, the conductivity ratio, $\kappa_{ACl}/\kappa_{BCl}$, estimated from the electric conductivity of the membranes in each ionic form should be nearly equal to the mobility ratio, if all the ions in the membrane are active in the transportation. The measured values of the separation factor and the conductivity ratio and the product of these values are shown in Tables I and II.

The product, $S^{A}_{B}\cdot\kappa^{A}_{B}$, has characteristics similar to those of T^{A}_{B}. It is considered that the quantitative disagreement between the two values is largely due to the facts that, firstly, the true equilibrium is not attained in the transport process and, secondly, the conductivity ratio estimated from the conductivities of the membranes in each ionic form does not give the true values in the mixture systems. The former results in a concentration ratio nearer to unity, while the latter results in a conductivity ratio nearer to unity, because the slower ions are

TABLE I. CHARACTERISTICS OF HYDROGEN-SODIUM SYSTEM IN MIXED SOLVENTS

Vol. percent of org. solv. %	Separation factor S^{H}_{Na}	Conductivity ratio κ^{H}_{Na} *	Product $S^{H}_{Na}\cdot\kappa^{H}_{Na}$	Coef. of permselectivity T^{H}_{Na}
Water-ethanol				
0	0.82	5.02	4.12	4.95
22.5	0.31	4.53	1.41	4.20
45.1	0.12	4.10	0.49	3.25
67.6	0.025	3.92	0.098	2.25
76.6	0.012	3.68	0.044	2.20
Water-methanol				
0	0.82	5.02	4.12	4.95
22.5	0.38	4.32	1.64	4.50
45.1	0.18	3.50	0.61	3.35
67.6	0.07	3.05	0.21	2.30
76.6	0.051	3.05	0.16	1.72
Water-acetone				
0	0.82	5.02	4.12	4.95
22.5	0.24	4.83	1.16	4.00
45.1	0.093	4.11	0.38	3.20
67.6	0.017	3.60	0.061	2.05
76.6	0.004	3.12	0.013	1.65

* $\kappa^{H}_{Na}=\kappa_{HCl}/\kappa_{NaCl}$

TABLE II. CHARACTERISTICS OF SODIUM-CALCIUM SYSTEM IN MIXED SOLVENTS

Vol. percent of org. solv. %	Separation factor $S_{\mathrm{Na}}^{\mathrm{Ca}}$	Conductivity ratio $\kappa_{\mathrm{Na}}^{\mathrm{Ca}}$	Product $S_{\mathrm{Na}}^{\mathrm{Ca}}\cdot\kappa_{\mathrm{Na}}^{\mathrm{Ca}}$	Coef. of perm-selectivity $T_{\mathrm{Na}}^{\mathrm{Ca}}$
Water-methanol				
0	14.5	0.51	7.38	1.05
22.5	9.2	0.44	4.05	0.96
45.1	5.3	0.39	2.07	0.83
67.6	2.8	0.36	1.01	0.76
76.6	2.0	0.35	0.75	0.74
Water-acetone				
0	14.5	0.51	7.38	1.05
22.5	8.5	0.46	3.93	0.90
45.1	4.1	0.42	1.74	0.80
67.6	2.0	0.35	0.68	0.71
76.6	1.5	0.34	0.51	0.63

accelerated by the faster ions and vice versa. The effect of partial immobilization pointed out by the present authors[3)] is included in the conductivity ratio.

When an ion in the membrane phase has a stronger attractive interaction with the membrane matrix, the concentration of this ion in the membrane phase is higher and its mobility is lower. The concentration and the mobility terms have the opposite effects on the permselectivity.

The decrease in the separation factors, $S_{\mathrm{Na}}^{\mathrm{H}}$ and $S_{\mathrm{Na}}^{\mathrm{Ca}}$, shows that the attractive interaction of hydrogen and calcium ions with the resin matrix becomes smaller than that of sodium ions upon the addition of the organic solvents. This is probably caused by the decrease in the dielectric constant, which results in stronger electrostatic interaction for the smaller hydrated ions. Thus, the permselectivity is in the order $\mathrm{H} \gg \mathrm{Ca} > \mathrm{Na}$ in aqueous solutions, and in the order $\mathrm{H} > \mathrm{Na} > \mathrm{Ca}$ in mixed solvent solutions. This behavior is observed more clearly in solutions with the higher contents of organic solvents or with the solvent of the lower dielectric constant.

The effect of the partial immobilization gives the complicated feature to the conductivity ratio. In the present investigation, the decrease in the conductivity ratio upon the addition of the organic solvents seems to be primarily a result of the partial immobilization. Further investigation is required in this respect.

Under the present experimental conditions, the hydrated state of ions seems not to be affected greatly by the addition of the organic solvents, except for the addition of methanol over 80 percent, where the concentration term changes reversely and the decrease in the permselectivity becomes small.

The Institute of Industrial Science
The University of Tokyo
Azabu, Tokyo