Transport Behavior of Some Inorganic Cations across Ion-exchange Membranes. Preferential Impermeability of Barium Ions across Sulfonic Acid Membrane

By Takeo YAMABE, Manabu SENŌ, Tatuo TANAKA and Ichiro KAMII

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It appears to be generally accepted that the permselectivity of a given ion across ion-exchange membranes is closely related to the selectivity of the ion in the ion-exchange equilibria, while the mobilities of ions in solution and membranes are one of the most important factors that have effects on the permeability. In fact, as shown already by one of the authors[1], the order of the permselectivity of cations across a heterogeneous sulfonated styrene cation-exchange membrane[2] is as follows: $H^+ > K^+ > NH_4^+ > Ca^{2+} > Mg^{2+} > Na^+$, and it was recognized that the ion with the larger mobility and the larger selectivity in the ion-exchange reaction possesses the larger permselectivity. In the present communication, it is reported that barium ions show a peculiar transport behavior in the electrodialyses using ion-exchange membranes. As shown in Table I, barium ions show an extraordinarily small permeability, in spite of their very large selectivity in the ion-exchange equilibria.

TABLE I. PERMSELECTIVITIES OF ALKALI-EARTH METAL IONS

Ions	Permselectivity*	Selectivity of ion-exchange**	Mobility in inf. dil. soln.
M	T^{M}_{Na}	K^{M}_{Na}	cm²/V. sec.
Ca^{2+}	1.24[7]	2.60	5.29×10^{-4}
Mg^{2+}	1.13[1]	1.66	4.66 〃
Ba^{2+}	0.70	5.81	5.70 〃

* Experimental conditions used: Current density 0.02 amp./cm², concentration of stock solution (2-component, ratio 1 : 1) 0.1 N, time 2∼4 hr.

** Data of O. D. Bonner et al. on Dowex 50 X8[8].

This result may be interpreted as follows: The large selectivity of barium ions is owing to the formation of a complex salt with the sulfonated group which dissociates scarecely, resulting in the relatively small concentration of barium ions in unrestricted state[3]. The small concentration of free ions in membranes leads to their small permselectivity. In general, the most predominant factors in determining the permeability of ions across membranes are the mobility and the concentration of unbound ions in membranes, but not the selectivity in the ion-exchange equilibria. The transport behavior of barium ions is one of the confirmative evidences for the deduction and it is also supported by the permeability of some heavy metal ions[6].

The experimental procedure was the same as those given in the preceding papers[1,7], i. e., from the electrodialysis data using a multi-compartment cell with cation- and anion-exchange membranes alternatively, the permselectivity coefficients were calculated according to the equation

$$T^{B}_{A}=\left(\frac{t^{+}_{B}-t^{-}_{B}}{t^{+}_{A}-t^{-}_{A}}\right)\Bigg/\left(\frac{c_B}{c_A}\right)=\frac{r_B-1}{r_A-1}$$

where t^{+}_{A} and t^{+}_{B} are the transport numbers of ion A and B across a cation-exchange membrane, t^{-}_{A} and t^{-}_{B} are those across an anion-exchange membrane, c_A and c_B are concentrations of ion A and B in the stock solution and r_A and r_B are concentration ratios of ion A and B obtained directly from experimental data. If transport numbers of cations across an anion-exchange membrane are small and remain nearly constant, independently of the kind of cations, this coefficient should be a mesure of the permselectivity of given cations across a cation-exchange membrane. It will be permissible to think that this conditions is fulfilled in this experiment.

The Institute of Industrial Science
The University of Tokyo
Yayoi-cho, Chiba (T. Y. & M. S.)

Showa College of Pharmacy
Tsurumaki-cho, Setagaya
Tokyo (T. T. & I. K.)

1) T. Yamabe and Y. Tanaka, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 63, 1342 (1960).

2) This membrane was prepared with pulverized Amberlite IR-120 and the other membranes used in the present experiments were prepared with Amberlite ion-exchange resin powder.

3) It is suggested by the formation of a water-insoluble barium salt with toluenesulfonic acid and is also supported by the swelling behavior[4] and the electric conductivity data[5] of barium-form resin.

4) M. Senō and T. Yamabe, presented at the 9th Annual Meeting of the Society of Polymer Science, Osaka, May 29, 1960.

5) E. Heymann and I. J. O'Donnell, *J. Colloid Sci.*, 4, 405 (1949); A. O. Jakubovic, G. J. Hills and J. A. Kitchener, *Trans. Faraday Soc.*, 55, 1570 (1959).

6) M. Senō, T. Saito and T. Yamabe, This Bulletin, 33, 563 (1960).

7) T. Yamabe, M. Senō and T. Tanaka, *Bull. of Soc. of Salt Sci. Japan* (*Nihon Shio Gakkai-shi*), to be published.

8) It is structurally identical with Amberlite IR-120. Moreover, it was revealed that nearly the same ion-exchange reactions take place for both the heterogeneous ion-exchange membrane and the ion-exchange resin, from which the membrane is prepared.

T. Yamabe and T. Saito, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 63, 1848 (1960).