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Diffusion and Selective Transport of Alkali Cations on Cation-Exchange Membrane

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ABSTRACT

The diffusion coefficients and selective transport for alkali metal cations through a charged polysulfonated ICE-450 ion-exchange membrane were measured as a function of pH at 25°C. The permeability and diffusion coefficients were found to increase in the sequence $Cs^+ \geq K^+ > Na^+ > Li^+$. The relationship between the permeability and the diffusion coefficients, and the hydrated radii of cations in the membrane were shown. This sequence was also explained by considering the hydration of ions in the membrane. The selectivity transport of K–Na and K–Li binary systems at various pH gradients through the membrane were also investigated under various conditions. In the selective transport of metal ions, the selectivity depended on both the hydrated ionic size and the interaction between the fixed groups in the membrane and the metal ions.

INTRODUCTION

Membrane technology has recently become of great practical importance to the chemical and pharmaceutical theories of membrane processes that are well-developed. Ion-exchange membranes are now being used for a variety of processes (1–9), but many questions regarding their transport remain unanswered. In applications of membranes, it is important to develop as detailed an understanding as possible about the underlying relationships between membrane structure and transport properties. Many studies on the diffusion of inorganic ions and molecules and the selective transport of metal ions and anions through ion-exchange membranes have been reported (10–15). Uragami et al. (13, 14) reported that it was possible to transport selectively metal ions through polymer membranes with a fixed specific functional group of the membrane. The functions of specific carriers, such as lactone rings and sulfonic or carboxyl groups, were shown by reversible and rapid changes of chemical structure of their carriers with a change of pH.

Diffusion and permeation of simple salts in polymers are closely related to the ionic transport phenomena in various system, e.g., ion exchange, desalination, dyeing, and biological systems. The transport of ions across membranes is usually regarded as diffusion as it occurs in aqueous bulk solutions. The mechanism of the interaction between simple ions and a charged group of a polymer chain is an interesting subject in ion transport phenomena through charged membranes. It is important to characterize the ion-exchange membranes in different ionic forms. In this study the alkali ions were chosen because they are ions which have vastly differing swelling tendencies in the exchanger and partly because they are ideally suited for testing new exchangers or diffusion techniques due to their large differences in ionic mobility.

ICE-450 polysulfonated ion-exchange membranes offer controlled ion-exchange capacities and excellent mechanical wet strength. Ion-exchange capacity is provided by a new, patented posttreatment process. This new ion-exchange membrane has the necessary chemical stability and ionic transport properties needed for industrial applications as well as various designs. In order to bring these technologies to full commercialization, it is important to develop a thorough understanding of the physical and chemical properties of the membrane for the solution environment in which it is to be used. To investigate this membrane further, it was decided to investigate the transport behavior of alkali metal cations and also of two binary systems. This was partly to investigate the little understood mechanisms of coupling between two counterions within a charged membrane. In this work the permeability of the polysulfonated membrane was investigated to elucidate the permselective transport mechanism of alkali metals.

EXPERIMENTAL

Materials

The salts were analytical grade NaCl, KCl, and standard NaOH and HCl solutions from BDH Ltd.; H_2SO_4 from Merc, Hopkin & Williams; CsCl from Formachem Ltd.; and ICE-450 polysulfonated membrane from Gelman Sciences. Spectrapor Dialysis membrane was used for comparison, and it was obtained from Spectrum Medical Industries Inc.; it consists of wet cellulose dialysis tubing composed of cotton cellulose, 0.05 mm thick, in 1% sodium azide, with a nominal molecular weight cutoff of 3500.

Salt solutions were prepared using deionized water without further purification by dissolving a weighed quantity of Analar salts. Standard solutions were prepared using standard concentrated solutions.

ICE-450 ion-exchange membranes are true microporous membranes. They offer controlled ion-exchange capacities and excellent mechanical wet strength. ICE-450 is a strongly acidic cation-exchange polysulfone with a polyester support membrane and it has an ion-exchange capacity of 0.19 meq per 47 mm disk and a thickness of 152.4 μm in the hydrogen ion form. The polysulfonated membrane disks in the H^+ form were conditioned by a cycle of equilibrations with HCl, distilled water, NaOH, and finally distilled water. The membrane disks were then pretreated with 0.1 M H_2SO_4.

Methods

Transport studies were made in the system aqueous solution (= donor)/ membrane/aqueous solution (= receiver), using two borosilicate half cells. The membrane was mounted between the silicon rubber gaskets and clamped between the two half cells. Appropriate solutions (13 mL) were added into each compartment. The effective membrane area, A, was 2.05 cm^2. The unit was submerged in an incubator and maintained at 25 ± 1°C. The donor solutions were salt chloride solutions and the receiver solutions were the acid solutions applied at different pH ranges. The permeabilities of the ICE-450 membrane were measured in the Li, Na, K, and Cs forms at 0.05 $mol \cdot dm^{-3}$ external concentration. The experiments were repeated using Spectrapor dialysis membranes. The concentrations of metal cations were determined with a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer.

Permeation of liquids across membranes is described in terms of Fick's law. If a planar membrane of area A and thickness l is exposed to a concentration step Δc, the quantity of solute which will have permeated at time t, $Q(t)$, is approximated by Eq. (1) (16):

$$Q(t) = \frac{AD\Delta\bar{c}}{l}\left(t - \frac{l^2}{6D}\right) \qquad (1)$$

where D is the diffusion coefficient and $\Delta\bar{c}$ is the difference in permeant concentration in the membrane phase. From Eq. (1) it is obvious that a plot of $Q(t)$ against time, t, will be linear at large times (when the system is in a steady state) and have a slope of $AD\Delta\bar{c}/l$ and an intercept on the time axis, τ, according to Eq. (2) (17):

$$\tau = l^2/6D \tag{2}$$

For most measurements $Q(t)$ is determined by measurement of concentration in a collecting volume of finite volume, V, since $c = Q(t)/V$.

Permeability, P, can be used to calculate the flow of a penetrated solute across a membrane as a function of driving force. The corresponding diffusion coefficient can be calculated from the hold-up time equation (2).

From the slope $Q(t)$, the steady-state flow, $J = Q(t)/A$, defines the permeability, P:

$$J = D\Delta\bar{c}/l = P\Delta c \tag{3}$$

where

$$P = (D\Delta\bar{c}/\Delta c)/l \tag{4}$$

Selective Transport of Alkali Cations

Selective transport experiments were carried out at 25 ± 1°C under magnetic stirring, using the same diaphragm-type cells. The donor solution was salt chloride solutions such as KCl–NaCl, and KCl–LiCl binary systems, and the receiver solutions were the acid solutions applied at different pH ranges (0–3). The basic design of experiments with the ICE-450 membrane was to determine the transport selectivity for K/Na and K/Li ions in a membrane in which these ions were at equal concentrations (50% in each).

The ratios of transported metal ions from the source phase to the receiver phase through the membrane were calculated from the following equation (13):

$$\text{Selectivity} = \frac{[K^+]_{r,t}/[K^+]_{s,0}}{[Na^+]_{r,t}/[Na^+]_{s,0}} \tag{5}$$

where r,t is the concentration in the receiver phase of the membrane at time t and, s,0 is the initial concentration in the source phase of the membrane.

RESULTS AND DISCUSSION

Steady-state rates were measured by using a diaphragm diffusion cell. The permeability and diffusion coefficients were found to increase in the sequence $Cs^+ > K^+ > Na^+ > Li^+$, as shown in Figs. 1 and 2. This sequence is explained by considering the hydration of the ions in the

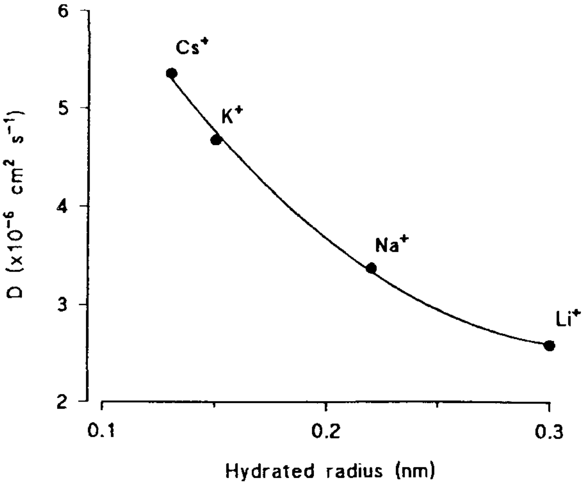

FIG. 1 Diffusion coefficients of alkali cations as a function of hydrated radii on ICE-450 membrane.

membrane. Ionic mobility in the membrane showed the same dependence on the Stokes radius of the cation as that in the bulk aqueous solution (18). There is a significant correlation between the permeability and diffusion coefficients and the hydrated radii of alkali cations. The correlation coefficients are $r = -0.992$ for permeability and $r = -0.978$ for diffusion

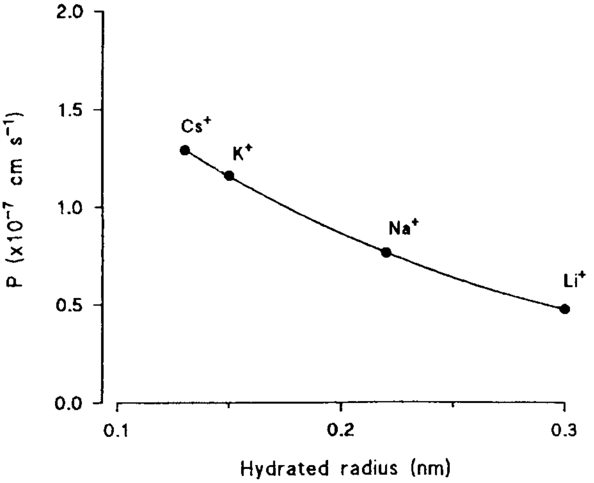

FIG. 2 Permeability of alkali cations as a function of hydrated radii on ICE-450 membrane.

coefficients. The coefficients of determinations means that the hydrated radii the major determinants for the alkali cations tested on the ICE-450 membrane.

The transport properties of charged membranes are infinitely variable since they depend upon the composition and concentration of the electrolyte solutions with which they are in contact and upon the type, magnitude, and direction of the driving forces selected. They are used to characterize a particular membrane system with a series of experiments performed under controlled conditions suitable for the application of interest. Various factors which control the electrolyte permeability through a membrane are the charge on the membrane, its porosity, and the charge and size of the diffusion ion. The process of permeation involves the entry of cations into the membrane phase by ion exchange followed by diffusion to the other side of the membrane. Obviously, the ionic size, hydration, and association are some of the important factors affecting the process.

Most applications of the time-lag method use a mathematical solution valid for an infinite collecting volume (16). In practical applications, changes in pressure or concentration in the collecting volume are used to determine the quantity of permeant diffused, and these are most easily and accurately measured if the collecting volume is small (16). After a sufficient period of time a pseudo-steady state condition was obtained, and the amount of diffused concentration increased linearly with time. This linear portion cut the time axis at $\tau = l^2/6D$ (Eq. 2), and from this cut-off (knowing the membrane thickness, 1 cm), the diffusion coefficient, D, can be found. Results are given in Table 1.

The external solutions were either KCl, NaCl, LiCl, or mixed solutions (0.05 M) which provided well-defined compositions on the membrane surface. When these were different from the receiver phase, which maintained a 50:50 loading in Na and H, an ion-exchange diffusion process was initiated:

$$Na^+ + RSO_3^- H^+ \longrightarrow H^+ + RSO_3^- Na^+$$

There are no comparable data in the literature on this membrane. Charged membranes can include many ions or ionizable groups in their structure. The exclusion of chloride (co-ion) is not involved in the exchange process according to Donnan exclusion. Charge also plays an important role in the transport of simple electrolytes in membrane systems. In such systems the mobility of ions is strongly affected by the fixed charge of the membranes. On the other hand, the diffusion coefficient of chloride anion, which is the common counterion species, increases with increasing Stokes radius of the cations. The interaction between cations and the fixed anion charges is reduced by hydration of the ions.

TABLE 1
Permeability, Diffusion Coefficients and Steady-State Fluxes Obtained from the Time-Lag Method for Alkali Cations on Both ICE-450 Polysulfonated and Spectrapor Dialysis (B) Membranes

Cation	Permeability ($cm \cdot s^{-1} \times 10^{-7}$)	Diffusion coefficient ($cm^2 \cdot s^{-1} \times 10^{-6}$)	Steady-state flux ($mol \cdot cm^{-2} \cdot s^{-1} \times 10^{-5}$)
		ICE-450 Polysulfonated Membrane	
Li	0.477	2.59	2.44
Na	0.761	3.37	3.83
K	1.16	4.68	5.76
Cs	1.29	5.36	6.14

Cation	Permeability ($cm \cdot s^{-1} \times 10^{-7}$)	Diffusion coefficient ($cm^2 \cdot s^{-1} \times 10^{-8}$)	Steady-state flux ($mol \cdot cm^{-2} \cdot s^{-1} \times 10^{-5}$)
		Spectrapor Dialysis Membrane	
Li	3.51	2.79	1.74
Na	3.92	2.95	1.95
K	4.85	4.26	2.40
Cs	5.05	4.35	2.51

Ion exchangers usually exhibit a preference for the counterion species with the smaller volume in the hydrated state. As a consequence of this distribution of ions at the membrane and both solution interfaces, concentration gradients for ion species are formed inside the membrane, and an interdiffusion of these ions takes place. This sequence is the same as the sequence of mobilities in free solution, which is also the sequence of ionic radii. Yet the alkali cations are very similar to each other physically and chemically, and differ mainly in respect to size, the Ladd ionic radii (19).

Relative permeability and diffusion coefficients as a function of hydrated ionic radii of alkali cations are given in Fig. 3, where Li was arbitrarily chosen as a reference ion. P/P_{Li} and D/D_{Li} indicated the relative magnitude of any cation through the membrane.

The permeation selectivity, according to Eisenman (20), depends on the energies of hydration and ion-site interaction. For ion exchangers with fixed charged groupings having field strength, the selectivity sequence is governed by differences in hydration energies of counterions. The curve in Fig. 2 shows that the lower the values of hydration, the higher is the permeability. The effective dielectric properties of solvents are a function of ionic size (primarily), and adsorbability, which is related to polarizabil-

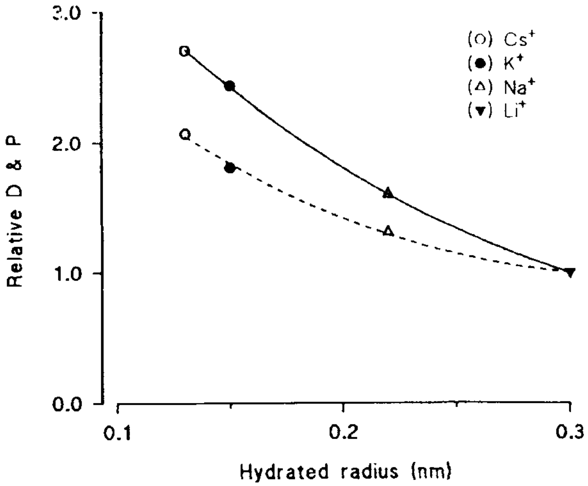

FIG. 3 Relative permeability (——, P/P_{Li^+}) and relative diffusion coefficients (---, D/D_{Li^+}) of alkali cations as a function of hydrated radii on ICE-450 membrane.

ity, also affects diffusion and reduces the effective hydration. As such, the effective dielectric constant and various other thermodynamic parameters of ion hydration are correlated to the permeability of cations.

Selective Transport of Alkali Cations

The selectivity of K^+/Na^+ and K^+/Li^+ binary systems against various pH gradients through the membrane are shown in Fig. 4, where the initial concentrations of KCl and NaCl or LiCl in the source side were kept constant at 0.05 M and that of H_2SO_4 in different pH ranges in the receiver side were changed.

The permeation ratios of K^+ ion to both Na^+ and Li^+ ions changed with the initial pH in the receiver side. The selectivities of K^+/Na^+ and K^+/Li^+ were always greater than unity; that is, K^+ ion permeated preferentially to Na^+ ion or Li^+ ion. If the transport of metal ions was dependent on the reversible adsorption–desorption reaction of metal ions, the selective transportability of metal ions may be governed by the affinity between the membrane and the metal ion. In the former region both K^+ and Na^+ or Li^+ ions diffused without physical interaction with the membrane, such as permeation resistance in the membrane, but in the latter region a frictional resistance between each ion and the membrane occurred because the membrane became denser, and consequently the increase of selectivity was due to the difference of the hydrated size of each ion.

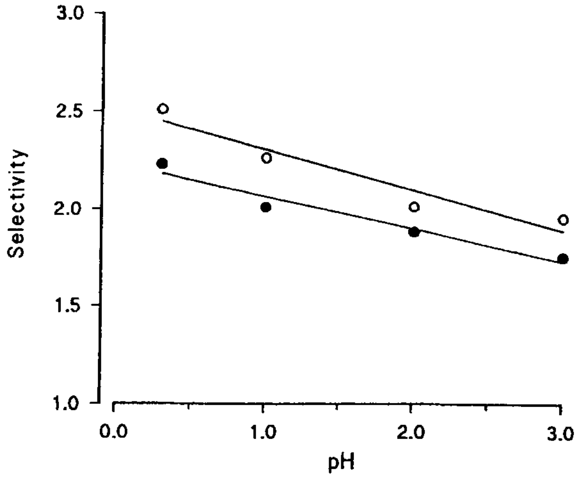

FIG. 4 The effect of the initial pH in the reciver phase on the selectivities of transport of alkali cations across the membrane: (●) K–Na, (○) K–Li binary system.

Selectivity isotherms can be used to predict empirically the permeability for any ion in a given individual situation at a given pH, once the permeability of any other ion under the same conditions has been measured. In all such cases the difference between the free energy of an ion ($\Delta F_{\text{ion/site}}$) and the free energy of hydration ($\Delta F_{\text{hydration}}$) is the equilibrium free energy change ($\Delta F_{\text{transfer}}$) to transfer the ion from water to the carrier, to the ion exchanger, or to the membrane.

$$\Delta F_{\text{transfer}} = \Delta F_{\text{ion/site}} - \Delta F_{\text{hydration}}$$

The selectivity sequences could be related to differences among cations in values of $\Delta F_{\text{transfer}}$, the free energy change in transferring the cation from water to the membrane sites that control permeation. For relatively nondeformable, nonpolarizable ions (alkali ions) and sites, $\Delta F_{\text{ion/site}}$ is likely to be dominated by the electrostatic attractive forces implicit in Coulomb's law.

A decrease of selectivity in treatments with a higher initial pH in the receiver side was caused by the fact that hydrated Na^+ and Li^+ ions are larger than K^+ ions. The relationship between the initial pH in the receiver side and the selectivity of the transport of K^+/Na^+ and K^+/Li^+ ions was calculated from Eq. (5). This result is attributable to the fact that the permeation of K^+ ion was not hindered by the hydrated Na^+ and Li^+ ions which were the most bulky. The selective transportability for the alkali metal ions across the membrane was observed in the following series: $K^+ > Na^+ > Li^+$.

The ionic radius for these metal ions was in the order $K^+ > Na^+ > Li^+$, which agreed with the above selective transportability but was not a measure for the selectivity of the metal ions because, in aqueous solution, the alkali metal ions were certainly hydrated. Therefore, the selective transportability had to be compared with the hydrated ionic radius for the alkali metal ions. Also, a contribution of hydrated ionic size to the selective transportability implies that these physical factors were partly responsible for the selectivity of the metal ions.

When H^+ ions, transferred by the proton-jump mechanism, reach the swollen region in the membrane, they exchange with metal ions and simultaneously the membrane contracts. In this transport system, H^+ ions play the role of the driving force in the transport of alkali ions, and the selectivity depends on both the hydrated ionic size and the interaction between the fixed groups in the membrane and the metal ions.

In these systems the metal ions were transported by both diffusive flow based on the concentration gradient and the transport caused by the pH difference between both sides. The transport of metal ions tended to decrease with an increase in the initial pH in the receiver side of the membrane. The membrane has a distinct selectivity for K^+ ion with respect to Na^+ or Li^+ ions. This is an agreement with the common rule that a cation exchange resin preferably takes up that cation species with the smaller volume in the hydrated state.

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