Simulations of Permselectivity of Ions with Different Valence through a Charged Membrane

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We investigate the effect of the charge density on transport modes of ions through the membrane in a dialysis system consisting of a charged membrane and mixed solutions containing a driving electrolyte and electrolytes with mono-, di- and tri-valent cations by computer simulations. The simulations show that the system has four transport modes in response to membrane charge density changes: (A) all the cations are transported along with their concentration gradient; (B) only tri-valent ions are transported against their concentration gradient between two chambers (*uphill* transport) while the other ions are transported along with their concentration gradient (*downhill* transport); (C) *uphill* transport of di- and tri-valent ions occurs; (D) *uphill* transport of all the cations except for the driving cation occurs. The transport modes also depend on the concentration ratio of the driving electrolyte to the other cations. The results indicate that the transport modes in a dialysis system consisting of mixed electrolyte solutions and a temperature-responsive charged membrane whose charge density changes in response to the temperature can be controlled by changing the temperature.

Key words : Ion, Membrane, Transport mode, Charge density, Selectivity

1. INTRODUCTION

There are many potential applications of external stimuli-responsive gel membranes in drug delivery system [1-3], chemical valve [4-5] etc. Many of the gel membranes undergo changes in volume in response to external stimuli so that the permeability of certain solutes through the membranes can be controlled by these stimuli. However, it would be very useful to control not only permeability but also transport vectors of solutes for some "intelligent" devices such as self-regulating drug delivery, smart sensors and high performance membrane separation systems. Higa et al. [6-7] have reported that transport of muti-valent ions in a dialysis system consisting a charged membrane and mixed electrolyte solutions can be controlled by changing membrane charge density in two ways: *downhill* (the transport along their own concentration gradient in a system) and *uphill* (the transport against their own concentration gradient).

The aim of this study is to simulate the transport of ions in a dialysis system consisting of a negatively-charged membrane and mixed electrolyte solutions containing mono-, di- and tri-valent cations as shown in Figure 1 in order to examine the relationship between the transport modes of ions and membrane charge

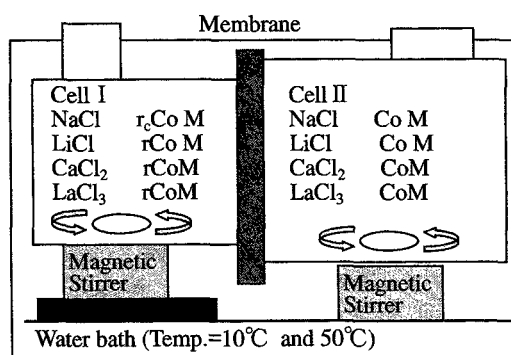density, ionic valence and the ionic composition of the external solutions.

Fig. 1 A dialysis system consisting of a negatively-charged membrane and electrolyte solutions containing mono-, di- and tri-valent cations.

2. SIMULATION METHOD

Ion transport in the dialysis systems shown in Figure 1 is calculated by using the same method as in ref [7,8] under the following assumptions: (a) the surfaces of the membrane are always in a state of the Donnan equilibrium; (b) the boundary effects on the surfaces are negligible; (c) all the electrolytes dissolve perfectly, and

the ionic activity coefficients are unity both in the aqueous solutions and in the membrane; and (d) the standard chemical potential of ions in the membrane is equal to those in the solutions. The electroneutrality condition gives the following equation:

$$\sum z_i (K_s)^{z_i} C_i^R - C_x = 0 \qquad (1)$$

where z_i is the valence of the ith ion and K_s is the Donnan equilibrium constant at the s side surface of the membrane:

$$(K_s)^{z_i} \equiv \frac{\overline{C_i^s}}{C_i^s} = \exp(-z_i F \Delta\phi_{don}^s / RT) \qquad (2)$$

where $\overline{C_i^s}$ and C_i^s are the concentrations of the ith ion in the membrane and external solution at the s side, respectively; F, R and T are Faraday's constant, the gas constant and absolute temperature, respectively; $\Delta\phi_{don}^s$ is the Donnan potential at the s side surface of the membrane. The flux of the ith ion in the membrane, J_i, is given as [7]:

$$J_i = -\frac{RT z_i \overline{\omega_i}}{d} \ln \beta \frac{\overline{C_i^{II}} - \overline{C_i^I} \beta^{z_i}}{\beta^{z_i} - 1} \qquad (3)$$

where d is the thickness; β is defined as [7]:

$$\beta \equiv \exp(-F\Delta\phi_{diff} / RT) \qquad (4)$$

where $\Delta\phi_{diff}$ is the diffusion potential in the membrane. The time evolution of the ionic concentrations in the two cells are given from the following equations:

$$C_{i,t_n+1}^I = C_{i,t_n}^I - J_i S \Delta t / V^I \qquad (5)$$

$$C_{i,t_n+1}^{II} = C_{i,t_n}^{II} + J_i S \Delta t / V^{II} \qquad (6)$$

where C_{i,t_n}^I and C_{i,t_n}^{II} are the ionic concentration at time t_n at cells I and II, respectively; $\Delta t = t_{n+1} - t_n$; S is the membrane area (7.07cm²); V^I and V^{II} are the volume of the cells I (100 cm³) and II (400 cm³), respectively.

3. RESULTS AND DISCUSSION

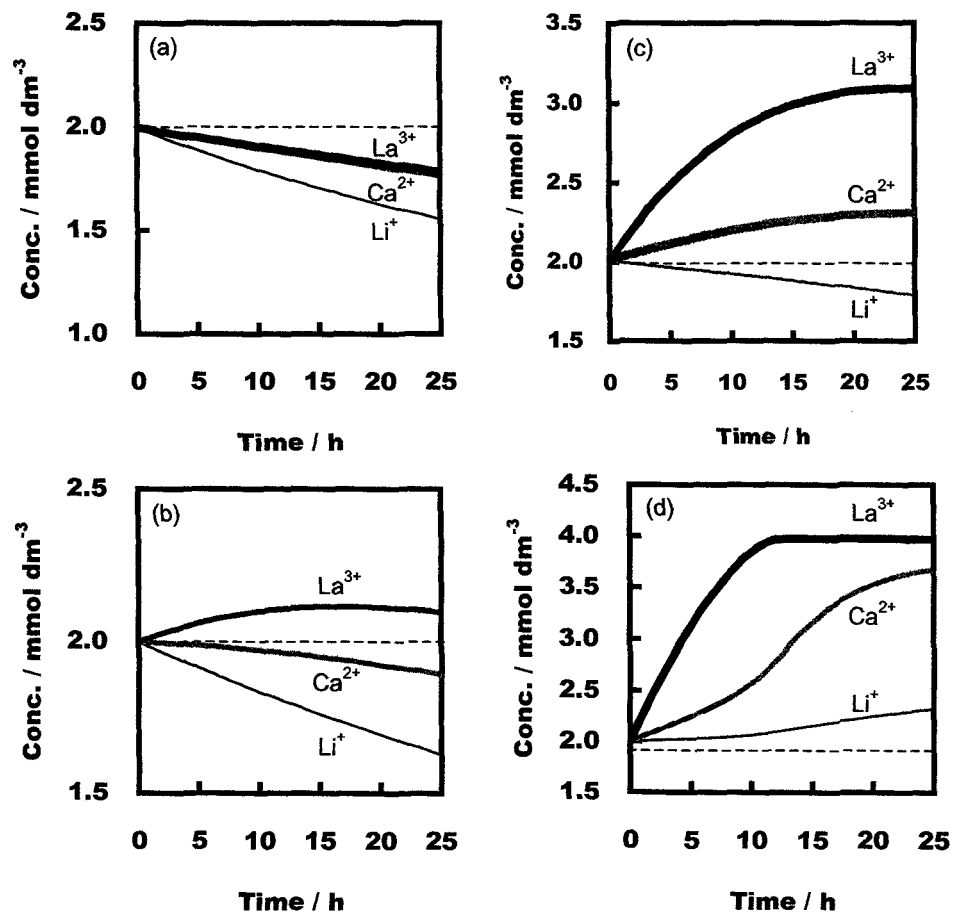### 3.1 The effect of charge density on the transport modes of ions.

Fig. 2 Time-concentration curves of Li⁺, Ca²⁺ and La³⁺ ions at the high concentration chamber in the dialysis system shown in Figure 1, where $Co=5\times10^{-4}$ mol dm⁻³, $r=4$, $r_c=300$ and $H=0.5$.

Cx: (a) 0.035mol dm⁻³, (b) 0.06 mol dm⁻³, (c) 0.12 mol dm⁻³, (d) 0.30 mol dm⁻³.

Part a of Figure 2 shows the time-concentration curves of Li⁺, Ca²⁺ and La³⁺ ions at the high-concentration side in the dialysis system shown in Figure 1 when the charge density is 0.035mol dm⁻³. The concentration of all the cations decreases with time. This means that the caions are transported along with their concentration gradient between the two cells (*downhill* transport). We defined the transport mode as mode *A* as shown in Figure 3.

Part b of Figure 2 shows the time-concentration curves of the cations when the charge density is 0.06 mol dm⁻³. The concentration of just La³⁺ ions increases with time while the concentration of the other cations decreases. This means that La³⁺ ions are transported against their
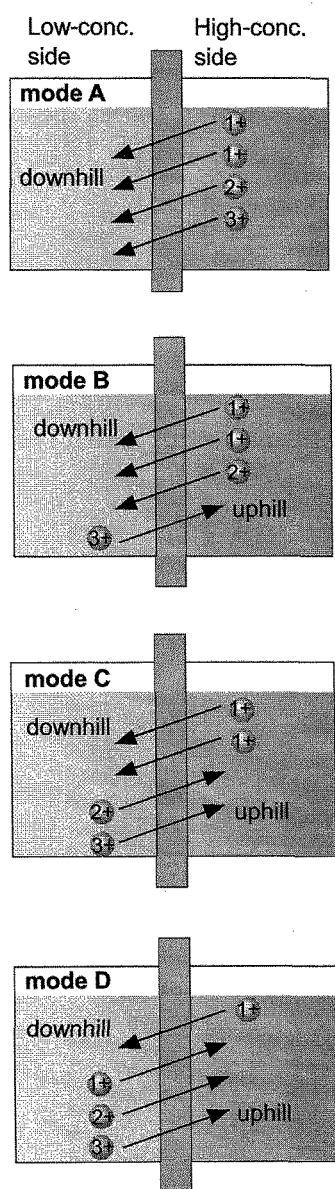

Fig. 3   Four transport modes in the dialysis system shown in Figure 1.

concentration gradient (*uphill* transport). The transport mode in which *uphill* transport of just tri-valent ions occur is defined as mode *B*. The *uphill* transport of La³⁺ ions occurs in the two factors: the conditions that the electric current should be zero, $I \equiv FS\sum z_i J_i = 0$, and the Donnan equilibrium. The electro-neutral condition gives the following equation:

$$J_{Na} - J_{Cl} = -(3J_{La} + 2J_{Ca} + J_K) \qquad (7)$$

The calculations based on the Donnan equilibrium in terms of equations (1) and (2) give that the concentration of the tri-valent ions in the membrane is in opposite direction to that of the two chambers under appropriate conditions [9]. Hence, equation (7) indicates that the *uphill* transport of just La³⁺ ions occurs to compensate the flux of the other cations and the anion. In mode *B*, the slope of the time-concentration curve of the tri-valent ions has a positive value while that of the other cations negative ones. This means permselectivity between the tri-valent ions and the other cations has the infinite value and only tri-valent ions are concentrated at the high-concentration side. The much higher perm-selectivity for tri-valent ions is also due to the Donnan equilibrium: Equation (2) indicates that the concentration of tri-valent ions in the membrane is higher than that of mono- and di-valent ions. The concentration of La³⁺ ions has a maximum value at 20h and decreases with time because the concentration gradient of the driving electrolyte decreases with time. If the system keeps the concentration gradient of the driving electrolyte between the two chambers, the maximum concentration of the tri-valent ions at the high-concentration side will have a higher value by the *uphill* transport of the ions.

Part c of Figure 2 shows the time-concentration curves of the cations when the charge density is 0.12 mol dm⁻³. The concentration of di- and tri-valent ions increases with time while the concentration of mono-valent ions decreases. This means that mode *C* transport shown in Figure 3 occurs under the conditions.

Part d of Figure 2 shows the time-concentration curves of cations when the charge density is 0.30 mol dm⁻³. The concentration of all the cations increases with time. This means that *uphill* transport of mono-, di- and tri-valent ion occurs (mode *D*). Under the conditions, the charge density is mush higher than that in external solution so that the concentration gradient of all the cations in the membrane is opposite to that in external solution due to the Donnan equilibrium in terms of equation (2). The equation also gives that both the concentration and concentration gradient of tri-valent ion in the membrane have the highest value than that of the other cations. These cause that the initial flux and maximum

concentration of the tri-valent ions have the highest values than those of the mono- and di-valent ions. The concentration of the tri-valent ions has a maximum when the permeation time is 12h because almost all of the ions are transported from the low- to the high-concentration side by *uphill* transport. After the tri-valent ions having the maximum concentration, the concentration change of the di-valent ion increases.
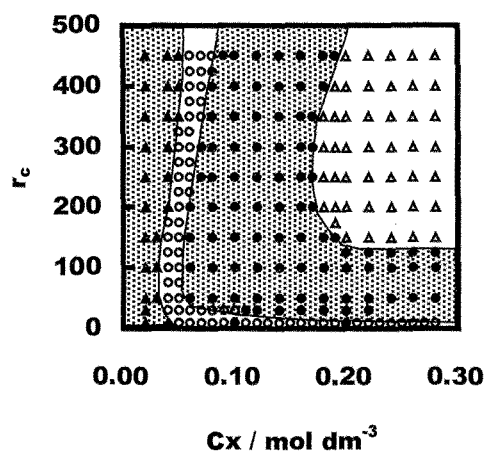

Fig. 4 Transport modes as a function of ratio of driving electrolyte, r_c, and charge density, Cx, where $r=4$. Transport modes, A:($\blacktriangle$), B:($\bigcirc$), C:($\bullet$), D:($\triangle$).

3.2 The effect of the ratio of driving electrolyte and other electrolyte on the transport mode of ions.

Figure 4 shows the modes of the *uphill* transport in the dialysis system as functions of the charge density and the concentration ratio of the driving electrolyte between the two chambers, r_c. Mode D transport does not occur when $r_c < 130$. The transport mode changes from A to D as the charge density increases when $r_c > 130$. The calculations indicate that transport modes in the system can be controlled by changing the charge density. This means that an external-stimuli responsive charged membrane whose charge density changes in response to external stimuli can control the transport modes of ions. We have made a temperature-responsive charged membrane from poly(vinyl alcohol) and poly(N-isopropylacrylamide). The charge density of the membrane changes from 0.03 mol dm^{-3} at 10°C to 0.26 mol dm^{-3} at 50°C in response to the temperature changes. The membrane will control the transport modes of ions in response to the temperature changes [10].

4. CONCLUSIONS

We calculate ionic transport in a dialysis system consisting of a charged membrane and mixed salt solutions containing cations with different values. The calculations show that the system has four transport modes depending on membrane charge density: (A) all the cations are transported along with their concentration gradient; (B) only tri-valent ions are transported against their concentration gradient between two chambers (*uphill* transport) while the other ions are transported along with their concentration gradient (*downhill* transport); (C) *uphill* transport of di- and tri-valent ions occurs; (D) *uphill* transport of all the cations except for the driving cation occurs.

The calculations indicate that a external-responsive charged membrane whose charge density changes in response to external stimuli can control the transport modes of ions.

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