

Determination of the Tracer Diffusion Coefficient in a Cation Exchange Membrane

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Self and tracer diffusion coefficients of sodium ion in a cation exchange membrane (IONICS 61 AZL 389) have been measured. Tracer diffusion coefficients were determined in the Li^+ , K^+ and Mg^{2+} counter-ion states. The concentration of external solution was 0.1 mol dm^{-3} . The method used is based on non-stationary diffusion of radiotracer-sodium ion in the membrane. The results show that the membrane used is essentially uniform and that the magnitude of the tracer diffusion coefficient depends strongly on the counter-ion state of the membrane: the higher the mobility of the counter-ion, the greater is the diffusion coefficient of the tracer ion.

Several studies have been made to measure tracer diffusion coefficients of ions in ion exchange membranes.¹ In most cases the technique used has been the permeation method, which is based on a stationary diffusion process. In the present work a method based on a non-stationary diffusion of a tracer ion in the membrane is presented. The method is simple in technical realization and it also provides some knowledge of the membrane structure.

Theory

The radiotracer ion diffuses into or out of a sheet of a membrane of thickness l as shown in Fig. 1. We make three assumptions:

- The membrane controls the diffusion process. This means that the concentrations of radiotracer ion at the boundaries of the membrane are the same as in the bulk solution.
- The diffusion coefficient is constant.
- The diffusion process is one-dimensional.

With these assumptions the diffusion coefficient of a radiotracer ion in a membrane can be calculated from eqn. (1) for Fick's second law²

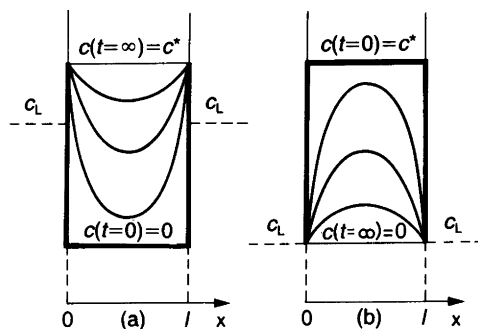


Fig. 1. Concentration profiles of a radiotracer ion diffusing (a) into or (b) out of a membrane. The concentration of radiotracer ion in a membrane is c , which is a function of time and space. The concentration of radiotracer ion in solution is c_L , which is (a) constant or (b) zero. The equilibrium concentration of radiotracer ion in a membrane is $c^* \neq c_L$.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where c is the concentration of radiotracer ion in the membrane and D is the diffusion coefficient of radiotracer ion referred to the membrane.

The solution to eqn. (1) with finite and constant concentration of radiotracer ion outside the membrane, i.e. with initial and boundary values (Fig. 1a) $c = 0$, $0 < x < l$, $t = 0$, and $c = c^*$, $x = 0$ and $x = l$, $t > 0$ has the form³

$$c(x,t) = c^* + \frac{2c^*}{\pi} \sum_{n=1}^{\infty} \frac{\cos n\pi - 1}{n} \sin \frac{n\pi x}{l} e^{-Dn^2\pi^2 t/l^2}. \quad (2)$$

For the corresponding case with zero concentration of radiotracer ion (Fig. 1b), i.e. with initial and boundary values $c = c^*$, $0 < x < l$, $t = 0$, and $c = 0$, $x = 0$ and $x = l$, $t > 0$, the solution to eqn. (1) takes the form³

$$c(x,t) = \frac{4c^*}{\pi} \sum_{n=1}^{\infty} \frac{1}{2n-1} \sin \frac{(2n-1)\pi x}{l} e^{-(2n-1)^2\pi^2 D t/l^2}. \quad (3)$$

For a fixed time ($t = t_k$) we can solve for the total amount of ions inside the membrane by integrating eqns. (2) and (3) across the membrane. If the area of the membrane is A , then the amount of ions is

$$n(t) = A \int_0^l c(x,t) dx$$

and we obtain

$$n(t = t_k) = n^* \left[1 - \frac{8}{\pi^2} \left(e^{-D\pi^2 t_k/l^2} + \frac{1}{9} e^{-9D\pi^2 t_k/l^2} + \dots \right) \right] \quad (4)$$

$$n(t = t_k) = \frac{8n^*}{\pi^2} \left(e^{-D\pi^2 t_k/l^2} + \frac{1}{9} e^{-9D\pi^2 t_k/l^2} + \dots \right). \quad (5)$$

We can approximate the series in eqns. (4) and (5) by taking the first terms only, since these series converge very rapidly. After this we can solve for the diffusion coefficients of radiotracer ion diffusing into the membrane

$$D = \frac{l^2}{t_k \pi^2} \ln \frac{8n^*}{(n^* - n)\pi^2} \quad (6)$$

and out of the membrane

$$D = \frac{l^2}{t_k \pi^2} \ln \frac{8n^*}{n\pi^2}. \quad (7)$$

If we know the total amount of ions inside the membrane (n^*) and the amount of ions inside the membrane at time $t_k(n)$, we can calculate the diffusion coefficient from eqns. (6) or (7), depending on which boundary value is used in the experiment.

Experimental

Experiments were made to determine the self and tracer diffusion of sodium ion in a cation exchange membrane (IONICS 61 AZL 389). The membrane was a circular sheet of thickness 0.12 cm and diameter 1.2 cm. The concentration of the equilibrating solution was 0.1 mol dm⁻³. At this concentration the membrane is not ideal. The co-ion content is about 5 per cent.

Diffusion coefficients were measured in homoionic Li⁺, Na⁺, K⁺ and Mg²⁺ states of the membrane. The experimental set-up is presented schematically in Fig. 2. The diffusion coefficient can be measured in two ways, viz. monitoring diffusion of sodium ion into the membrane or out of the membrane. In the first case, we take a membrane which is equilibrated in electrolyte solution (LiCl, NaCl, KCl or MgCl₂) without ²²NaCl and in the second case, a membrane which is equilibrated in electrolyte solution containing a small amount of ²²NaCl. The membrane is then placed in an equilibrating solution containing a small amount of ²²NaCl (or without ²²NaCl). After stirring the solution with the membrane for a fixed time, we take the membrane out of the solution and dip it into a water solution to remove the solution layers on the surfaces of the membrane. During the stirring, the electrolyte solution is changed so often that the boundary values are valid. Finally, the membrane is placed in a plastic tube and the radioactivity of the membrane is analyzed with a single channel analyzer (AS-11, Wallac). The total activity of the membrane and the background radiation are measured at the end of the experiment.

In order to be sure that there were no disturbing effects in the radiotracer experiments, we measured the capacity of the membrane using

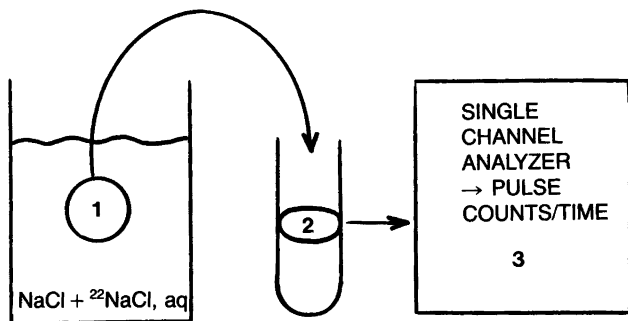


Fig. 2. Apparatus used in self and tracer diffusion experiments. The cation exchange membrane in a well mixed electrolyte solution (1) and in a plastic tube (2), and the tube with the membrane in a γ -ray analyzer (3).

two different methods. To determine the capacity of a membrane with the aid of radiotracer ion, the single channel analyzer must first be calibrated. This can be done with a known volume of NaCl + $^{22}\text{NaCl}$ solution. A membrane is then equilibrated in the solution which was used in the calibrating experiment, after which the activity of the membrane is analyzed and the capacity is calculated. We made capacity studies over a long period of time and the capacity was found to be 0.126 mmol per membrane (0.93 mol per dm^3 membrane) with an accuracy of 4%. In the other

method, the capacity of the membrane was determined by extracting the ion content of the membrane into HCl solution, which was then analyzed.⁴ These two methods gave values for the capacity which agreed to within 5%.

All experiments were carried out at room temperature of $25 \pm 0.5^\circ\text{C}$.

Results

Self diffusion of sodium ion. The self diffusion coefficient of sodium ion was measured when the

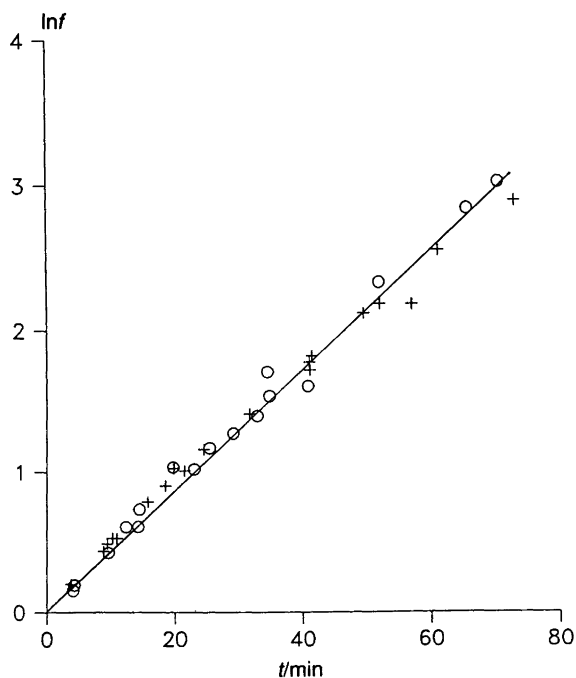


Fig. 3. Experimentally determined time dependence of the functions $f = 8n^*/(n^* - n)\pi^2$ (O) and $f = 8n^*/n\pi^2$ (+) on a logarithmic scale (according to eqns. (6) and (7)). Straight line: the least-squares fit.

Table 1. Self and tracer diffusion coefficients of sodium ion in cation exchange membrane (D) and in aqueous solution (D^*) and ionic conductivities of counter-ions in membrane (λ).

Membrane	$D \times 10^6 / \text{cm}^2 \text{ s}^{-1}$	$\lambda / \text{cm}^2 \Omega^{-1} \text{ mol}^{-1}$	Aqueous solution	$D^* \times 10^5 / \text{cm}^2 \text{ s}^{-1}$
MgR	0.10	0.78		
LiR	0.86	2.0	LiCl	1.18
NaR	1.1	2.9	NaCl	1.23
KR	1.5	4.6	KCl	1.31

radiotracer ion diffuses into or out of the membrane. Experimental results are shown in Fig. 3, in which the functions $\ln 8n^*/(n^*-n)\pi^2$ and $\ln 8n^*/n\pi^2$ are plotted versus time. Plotted points are calculated from experiments where the diffusion was monitored for a period of up to ca. 60 min. During this period of time the membrane has exchanged about 95% of its total capacity. The experimental functions are approximately linear, and we can thus calculate the self diffusion coefficient from the slope. The self diffusion coefficient of Na^+ is $1.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, with an accuracy of 10%.

The same experiment was carried out with two membranes pressed together with the aid of an elastic ring. This measurement gave approximately the same value for the diffusion coefficient as the experiment with one membrane ($1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).

Tracer diffusion of sodium ion. The tracer diffusion coefficient of sodium ion was measured in three environments, viz. in Li^+ , K^+ and Mg^{2+} states of the membrane. The experiments were performed in the same way as for the self-diffusion measurements, but now the equilibrating solution was LiCl, KCl or MgCl_2 instead of NaCl. In all these cases, diffusion of ^{22}Na into and out of the membrane was monitored. The results shown in Table 1 are averaged from these experiments. The reproducibility is 10%.

Discussion

The expressions $8n^*/(n^*-n)\pi^2$ or $8n^*/n\pi^2$ plotted in Fig. 3 are linear with respect to time. This means that the membrane has a constant self and tracer diffusion coefficient. The self diffusion experiment made with two membranes pressed to-

gether proves that the membrane controls the diffusion process and that it is uniform throughout.

The results in Table 1 show that the rate of diffusion of sodium ion increases in the sequence $\text{MgR} < \text{LiR} < \text{NaR} < \text{KR}$. The conductivity of the counter-ion calculated from the homoionic membrane conductivity is also shown in Table 1.⁵ The ionic conductivity increases in the same order as the tracer diffusion coefficient for sodium ion. Assuming that the tracer diffusion occurs from one fixed site to another, the diffusion rate depends, in addition to the concentration gradient, on the exchange reaction between the tracer ion and the counter-ion. Comparing the tracer diffusion and the conductivity data, it can be concluded that the diffusion coefficient of the tracer ion depends strongly on the exchange reaction between the tracer ion and the counter-ion.

Tracer diffusion coefficients of sodium ion in aqueous LiCl, NaCl and KCl solutions (1.0 mol dm^{-3}) are also shown in Table 1.⁶ If we compare these coefficients to those measured in the membrane we notice some interesting facts. Firstly, the diffusion coefficient in the membrane is ten times smaller than that in aqueous solution. This is a known result which is a natural consequence of the structure of the membrane. Secondly, the effect of the environment on the diffusion coefficient in the membrane is similar to that in aqueous solution. If we change the supporting electrolyte from LiCl to KCl, the diffusion coefficient of sodium ion in the solution increases. The same thing happens on changing the membrane from Li^+ to K^+ state. However, in the membrane this effect is much greater than in aqueous solution because the motion of sodium ion in the membrane is more hindered than in solution.

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