

Role of Ion exchange in permeation processes

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Abstract

The single ion transport of transition metal ions like Cu^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} were carried out through the H^+ and alkali metal ion forms of Nafion membrane. These studies showed that the ion exchange selectivity coefficient of the permeating ion had an effect on its transport process. It was found that the diffusion coefficient values (D) were directly proportional to the selectivity coefficient (K). This shows that the initial stage of permeation is governed by ion exchange process (effect of K on D).

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1. Introduction

Study of transport process in membranes is of recent origin but it has been pursued with great vigour ever since a number of synthetic ion exchange resins of high selectivity were synthesized [1–3]. The separation of a metal ion from a multi-ionic mixture by selective transport through membrane processes was of importance from both fundamental and practical viewpoints. For the selective permeation, the desired metal ion in a mixture has to be preferentially sorbed into the membrane phase and then be transported across the membrane phase. Subsequently, such membranes were used for desalination purposes. An appropriate driving force was essential for an uphill transport (building up of the concentration of the permeating ion across the concentration gradient). The driving force could be due to difference in pH of the solutions, concentration difference of the permeating species or an electrical potential. The pH difference was generally responsible for the transport in liquid membrane systems, whereas the electrical potential difference was the driving force for the transport across ion exchange membranes. Donnan dialysis was essentially the transport of the charged species across a membrane due to concentration difference. The combined effect of electrical potential difference and concentration gradient results in the process of electro-dialysis. Ion exchange

membranes, used in electro-dialysis permit the separation of the species, without any change in the phase. Depending on the type of the driving ion used, Donnan dialysis can be applied to the recovery of metal ions from wastewater. There were many studies on the use of ion exchange membranes for Donnan dialysis [4]. Electro-dialysis was principally used for the production of brine from seawater. For this specific application, special cation exchange membranes were often used to reduce the permeability of alkaline earth metal ions with respect to sodium ions [5]. Since ion exchange membranes were used for various purposes, requirements for membranes with specific properties have increased.

Ion exchange membranes find many industrial applications primarily due to their property of perm-selectivity. The term perm-selectivity denotes the difference in permeability between the ions of opposite charges. It is to be mentioned that the perm-selectivity of a membrane is a function of various external parameters. The ion exchange between two solutions separated by a perm-selective cation exchange membrane [6] or an anion exchange membrane [7] has been studied in detail and a few possible analytical applications have been pointed out. There were several reports on the permeation of neutral substances [8], heterocyclic bases [9] and cations [10,11]. Knowledge of the basic transport phenomena of ions in ion exchange membranes was important for the applications of these membranes. Several studies on the development of mathematical models for predicting and correlating the rates were found in literature [12].

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The transport behaviour of various transition metal ions like Cu^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} through the H^+ and alkali metal ion forms of Nafion membrane has been studied in detail. It was expected that there would be a possible effect of the ion exchange selectivity coefficient of the permeating ion on its transport process.

2. Experimental

2.1. Reagents

- i Circular pieces of Nafion membranes (35 mm diameter approximately) were pre-treated in different ways as follows:
 - N: Nafion was immersed in cold 2 M HCl for 3 h.
 - AT: Nafion was refluxed with 1:1 HNO_3 for 1 h, and then boiled with distilled water ($\sim 60^\circ\text{C}$) for 0.5 h.
 - WT: Nafion was boiled with distilled water for 1 h, and then immersed in cold 2 M HCl for 3 h.
 It was then washed well and stored under distilled water till further use.
- ii EDTA solution: 18.6 g of disodium salt of ethylene diammine tetraacetic acid (BDH AnalaR) and dissolved in 500 ml of distilled water to give a stock solution of 0.1 M. A suitable volume of this stock solution was added when required.
- iii Sodium acetate solution: 6.8 g of the salt (E. Merck GR) was dissolved in 500 ml of distilled water to give a stock solution of 0.1 M. This solution was used along with acetic acid for pH adjustments.
- iv Metal ion solutions: the alkali metal ion solutions were prepared by dissolving the appropriate amounts of their chloride salts in distilled water. The transition metal ion solutions were prepared by dissolving suitable amounts of their salts in dilute acid. And these solutions were standardized by EDTA titrations using suitable metallochromic indicators.

2.2. Procedure

The experimental set-up is given in Fig. 1. The permeation experiments were carried out in a U type cell specially designed for this purpose. Two flat ground ends of standard flanged joints FG 15 (Quick Fit, UK) were each connected to a glass tube bent at an angle of 90° . Circular pieces of clean swollen membrane (pre-treated differently) were equilibrated with metal ion solutions for three hours to convert them into desired alkali metal ionic form. These membranes (designated as $\text{M}^{n+}\text{-N}$, $\text{M}^{n+}\text{-AT}$ and $\text{M}^{n+}\text{-WT}$ where M refers to the alkali metal ion and N, AT, WT refer to the type of pre-treatment carried out), with an effective area of permeation of 254 mm^2 , were held tightly in between the joints clamped mechanically to provide a leak proof system. The two compartments on either side of the membrane are designated as the feed (F) and receiving (R) compartments. The feed compartment was filled with a definite volume (20 ml) of solution of the particular transition metal ion of 0.01 M at a pH of 4. The receiving compartment contained an equal volume of solution of EDTA or NaOH of known concentration at a suitable pH. The solutions in both the compartments were continuously

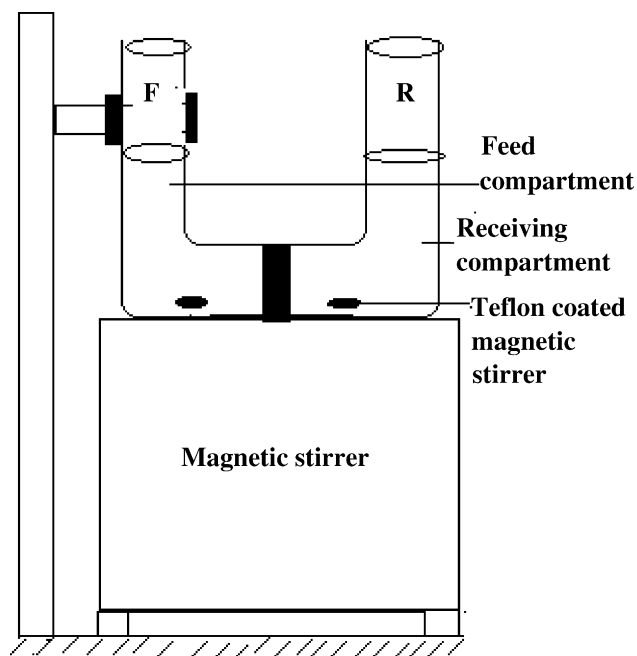


Fig. 1. Permeation Cell.

stirred using magnetic stirrers (s) to reduce concentration polarization.

The concentrations of Cu^{2+} and Ni^{2+} in the receiving compartment were determined spectrophotometrically [13] by measuring the absorbance of the EDTA complexes directly. The concentration of cobalt as its EDTA complex was determined by using phosphomolybdic acid [14]. For the permeation of Zn^{2+} the receiving compartment contained 0.1 M NaOH. The concentration of Zn^{2+} permeated was monitored at regular intervals by withdrawing 1 ml of the receiving solution and treating it with Zincon reagent at pH of 9–10 using ammonia and measuring the absorbance at 580 nm [15].

The absorbance measurements were carried out using a Shimadzu 210 A UV–vis spectrophotometer using a 1 cm quartz cell. The pH measurements were carried out using EIL 7030 pH meter equipped with a combination electrode.

About 0.25 g of Nafion in the H^+ forms were equilibrated with 25 ml of mixture of metal chloride and HCl ($\text{MCl}_2 + \text{HCl}$) (where $\text{M} = \text{Cu}^{2+}$, Ni^{2+} , Co^{2+} , Zn^{2+}) solutions overnight. The concentrations of both MCl_2 and HCl were 0.1 M but the volumes of MCl_2 and HCl in the mixture were varied to give different equivalent fraction in the resin phase. The composition of the metal ions left behind in the aqueous phase was estimated by complexometric titrations with EDTA (sodium salt of ethylenediammine tetraacetic acid) using suitable metallochromic indicators [13]. The equilibrium compositions of the exchanger and solution phases were obtained from the initial composition of the solution, the amount of exchanger used, its capacity and the transition metal ion at equilibrium.

3. Results and discussion

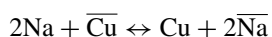
The pendant $-\text{SO}_3\text{H}$ groups in the perfluorinated ionomer form clusters of 40 \AA diameter separated by a distance of 50 \AA

Table 1
Concentration profiles in permeation cell compartments Cu²⁺–AT after 3 h

Feed compartment		Receiving compartment	
Initial [Cu ²⁺] (mol l ⁻¹)	Decrease in [Cu ²⁺] (mol l ⁻¹)	[EDTA] (mol l ⁻¹)	Increase in [Cu ²⁺] (mol l ⁻¹)
NIL	NIL	NIL	<10 ⁻⁵
NIL	NIL	5 × 10 ⁻²	1.0 × 10 ⁻⁴
3 × 10 ⁻³	2.1 × 10 ⁻³	5 × 10 ⁻²	2.0 × 10 ⁻³
1 × 10 ⁻²	4.5 × 10 ⁻³	5 × 10 ⁻²	4.6 × 10 ⁻³

and inter-connected through channels of 10 Å when swollen in water [16,17]. The high acidity of the SO₃H group was responsible for a quantitative neutralization of the membrane by other metal ions. When a cation exchange membrane separates two solutions of a given electrolyte of different concentrations, the cation will permeate from the concentrated to the dilute solution as a result of the concentration gradient.

Since Nafion is a cation exchange membrane, it was thought that the pH of the external solution would affect the affinity of the membrane towards different metal ions. However a high degree of selectivity in the uptake of these metal ions cannot be obtained by controlling the pH alone. The only way to bring about selectivity is to ensure that only the metal ion of interest is present as cationic species. As the permeation of co-ions (anions) across a cation exchange membrane was low (because of the perm-selectivity), the use of complexing agents, which form anionic metal complexes, can prevent the permeation of other cations. Similarly, the complexing agents could be used to prevent the back permeation of metal ion from the receiving phase and thus enhanced the permeation process. Hence, in all the studies, EDTA was used in the receiving side to form anionic metal complexes. The role of EDTA in enhancing the permeation process can be understood from the nature of equilibrium involved in the receiving compartment. This can be represented by the following equation:



Addition of EDTA to this compartment results in the complexation of Cu²⁺ in the solution and so the equilibrium is shifted towards the right. The deficiency of Cu²⁺ concentration in the membrane phase was compensated by further uptake of the metal ion from the feed compartment. This continued till equilibrium was reached. If it is assumed that the cations are transported across the membrane only due to ion exchange process, the permeation of Cu²⁺ would involve the transport of other cations (Na⁺) from the receiving to the feed compartment. The excess of Na⁺ is available from the buffer and also that released due to complexation of Cu²⁺ with EDTA.

The transport behaviour of transition metal ions through Nafion membranes equilibrated with alkali metal ions were carried out to understand the role of ion exchange selectivity on permeation process. It was thought that if permeation were influenced by ion exchange selectivity, there would be a definite correlation between the diffusion coefficients of transition metal ion with respect to its ion exchange selectivity coefficient.

In order to understand the various aspects of permeation, initial experiments were carried out on the permeation of Cu²⁺

across the Nafion membrane in Cu²⁺ form. The results of this experiment are given in Table 1. In this experiment, it was observed that the leaching of Cu²⁺ from the membrane on equilibration with de-ionized water for more than 3 h was negligible while the amount leached with EDTA was quite small but measurable. These observations were quantified from the leaching experiments. The results of mass balance experiments with Cu²⁺ ion in the feed show that the loss in concentration in the feed compartment was equivalent to the gain in the receiving compartment. Any leaching from the membrane phase was automatically compensated by the permeation from the feed. These results show that the self-leaching of Cu²⁺ ion was negligible. Experiments show that the number of moles of Cu²⁺ ion permeated in a given time (after 5 h) was dependant on the initial concentration of the feed solution. These results are given in Table 2. The decrease in permeation could be due to the deviation of the system from Donnan distribution law at high ionic concentration. Moreover, the high cation concentration was likely to block the diffusion pathway and lower the permeation rate.

It was seen that the permeation rate was affected by factors like pH, reagent and buffer concentrations. It was observed that the permeation rate was independent of pH between 3 and 5.5. There was a marginal increase with increase in the concentration of EDTA in the narrow range of 0.025–0.05 M. Since a high EDTA concentration in the receiving compartment results in a simultaneous increase in the Na⁺ concentration, the permeation decreases. Therefore, all the permeation studies were carried out using 0.05 M EDTA as the receiving solution. The concentration of the pure salt solution in the feed was around 0.05 M because the ion exchange studies were carried out under these conditions.

The concentration profiles for the transport of transition metal ions through Nafion equilibrated with alkali metal ions are given in Figs. 2–4. Most of the studies used the Nernst–Planck equation to describe the relation between transfer rates of permeating species and forces acting on the system [18]. The following assumptions were made to arrive at the equation that describe the transport process: (i) system was diffusion-controlled; (ii) under conditions of no current flow, the sum of the fluxes of the

Table 2
Dependence of the amount of permeate on the feed concentration

[Cu ²⁺] (M)	% Permeated
2.5 × 10 ⁻³	75
5.0 × 10 ⁻³	68
7.5 × 10 ⁻³	56
1.0 × 10 ⁻²	51

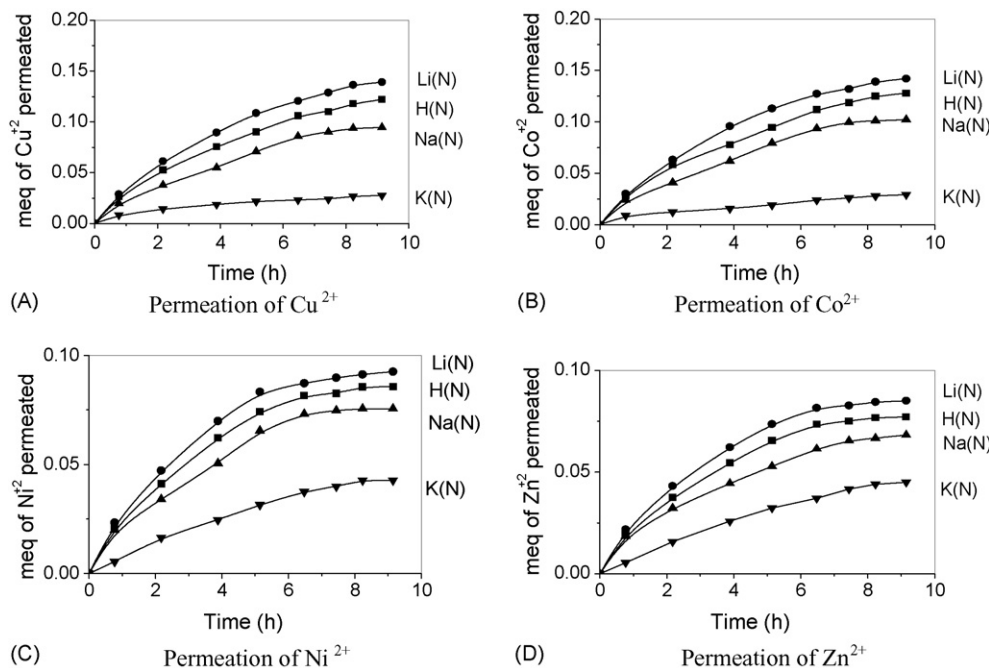


Fig. 2. Concentration profiles of transition metal ions through Nafion sample N.

two ions (in opposite directions) was zero; (iii) amount of co-ions in the membrane was smaller compared to the ion exchange capacity and no co-ions permeate; (iv) thermodynamic equilibrium exists at the membrane-solution interface; (v) osmotic water flow across the membrane can be ignored; (vi) overall electro-neutrality was maintained, i.e. the total concentration of counter ions in the membrane phase was equal to that of fixed ions, which was denoted by the exchange capacity (Q). Eqs. (1) and (2) mathematically represent the conditions (ii) and (vi),

respectively.

$$z_A C_{AM} + z_B C_{BM} = Q \tag{1}$$

$$z_A J_A + z_B J_B = 0 \tag{2}$$

where z_A , C_{AM} and J_A refer to the charge, concentration of the ion in the membrane phase and molar flux of the species A, respectively. Fick's first law can describe the molar flux J of the solute through the membrane [19]. Integration between the

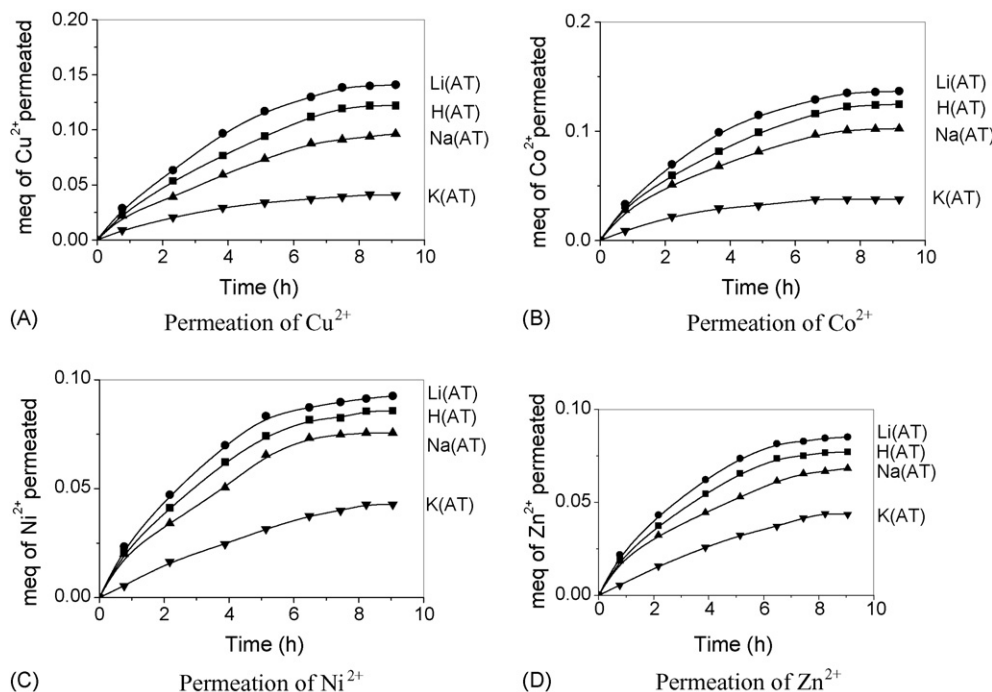


Fig. 3. Concentration profiles of transition metal ions through Nafion sample AT.

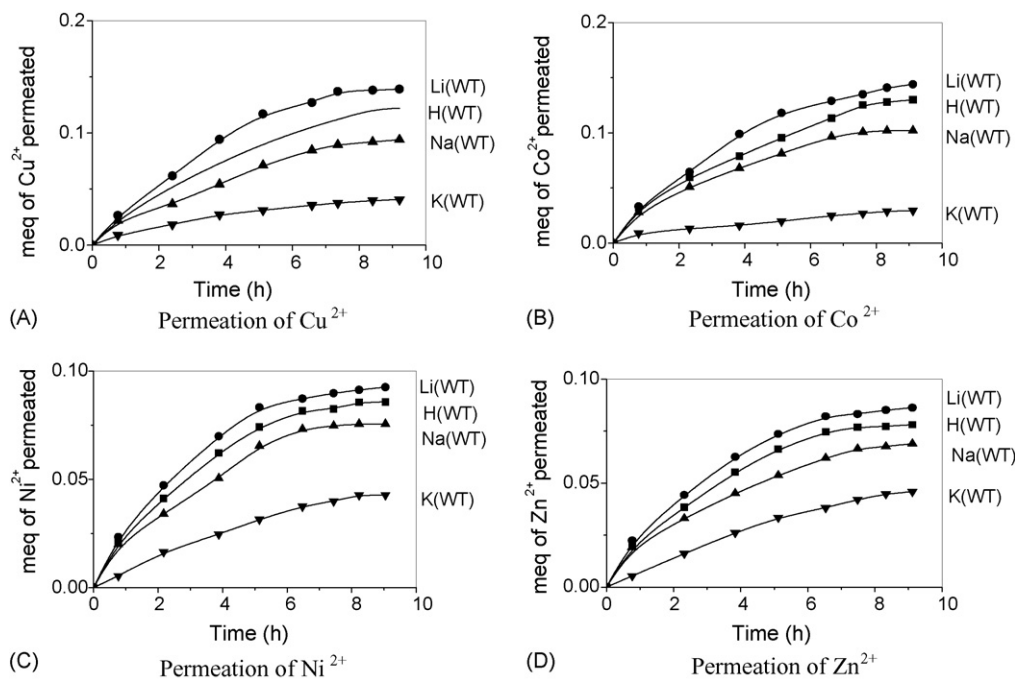


Fig. 4. Concentration profiles of different transition metal ions through Nafion sample WT.

membrane surfaces in contact with the feed and the receiving solutions gives:

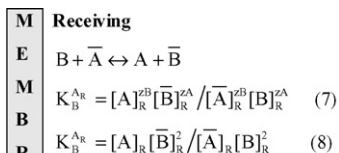
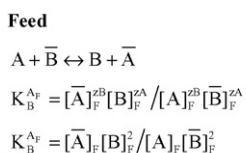
$$J = \frac{D(C_{FM} - C_{RM})}{\delta} \quad (3)$$

where D was the diffusion coefficient of the permeating solute, δ was the thickness of the membrane, C_{FM} and C_{RM} denote the concentrations of the permeating species at the membrane surfaces in contact with the feed and receiving solutions. The flux was also correlated to the change in the concentration of the solute in the receiving phase using the mass balance equation where, V_R and C_R were the volume and solute concentration of the receiving solution and A was the effective area available for permeation.

$$J = \left(\frac{V_R}{A} \right) \times \left(\frac{\delta C_R}{\delta t} \right) \quad (4)$$

Since the C_{FM} and C_{RM} were not easily measured, an equilibrium relationship between the concentration of the solute in the membrane phase and that in the bulk solution was required. It was seen that there exists ion exchange equilibrium on either side of the membrane interface. Taking this into account can help us to calculate the C_{FM} and C_{RM} .

Consider the two sides of the membrane in contact with the ions in solutions.



Here the bars represent the metal ion in the membrane phase.

It was seen that the ion exchange equilibrium operating on the two sides of the membrane were represented by their respective selectivity coefficients, K . If A and B were the same, the effect of these ion exchange reactions will be the same and will not be very obvious. The effect of K will be more pronounced when A and B on the two sides were different. In the experiments carried out in the present permeation study, A was di-valent and B was mono-valent, i.e. $z_A = 2$ and $z_B = 1$.

If a system consists of two solutions of different compositions separated by a cation exchange membrane, there exists a thermodynamic equilibrium [6]. Therefore, the exchange of ions follows a stoichiometric ratio. Using this principle, it was easy to calculate the concentration of Na^+ permeated into the feed compartment. The concentrations of Cu^{2+} on the membrane surface, near the feed and receiving solutions were calculated using Eqs. (6) and (8), respectively, as follows: If the feed contains a solution of Cu^{2+} of known concentration, membrane was in the Na^+ form, and the receiving phase contained Na^+ ion (as EDTA used was in its di sodium form), then the following ion exchange equilibrium would operate at the two sides of the membrane.

Feed compartment:



$$K_{\text{Na}}^{\text{Cu}_F} = \frac{[\bar{\text{Cu}}]_F [\text{Na}]_F^2}{[\text{Cu}]_F [\bar{\text{Na}}]_F^2} \quad (10)$$

The initial concentrations of Cu^{2+} and Na^+ in the feed and receiving compartments were known. From the transport experiments, the concentration of Cu^{2+} in the receiving phase was determined and therefore it is possible to calculate the values of $[\text{Na}]_F$ and also of $[\bar{\text{Cu}}]_F$.

Table 3
Diffusion coefficients ($D \times 10^8$) cm^2/s of permeating transition metal ions

	Cu^{2+}			Co^{2+}			Ni^{2+}			Zn^{2+}		
	N	AT	WT	N	AT	WT	N	AT	WT	N	AT	WT
Li^+	1.87	1.48	9.98	2.44	3.23	7.37	1.47	1.39	2.34	1.24	1.40	2.60
H^+	1.16	1.05	4.59	1.28	2.38	3.38	1.11	1.12	1.37	0.92	1.07	1.85
Na^+	1.13	0.98	4.51	1.43	1.99	3.46	1.40	1.41	1.57	0.75	0.99	1.59
K^+	0.05	0.27	0.59	0.03	0.17	0.19	0.34	0.42	0.24	0.40	0.57	0.95

Receiving compartment:



$$K_{\text{Cu}}^{\text{NaR}} = \frac{[\text{Cu}]_{\text{R}}[\overline{\text{Na}}]_{\text{R}}^2}{[\overline{\text{Cu}}]_{\text{R}}[\text{Na}]_{\text{R}}^2} \quad (12)$$

The concentrations of Cu^{2+} (determined experimentally) and Na^+ in the receiving phase were known. The concentration of Na^+ in the membrane phase was represented as:

$$\overline{\text{Na}}_{\text{R}} = \overline{\text{Na}}_{\text{F}} - \overline{\text{Cu}}_{\text{R}} \quad (13)$$

Therefore, Eq. (12) can be rewritten as:

$$K_{\text{Cu}}^{\text{NaR}} = [\text{Cu}]_{\text{R}} \frac{([\overline{\text{Na}}]_{\text{F}}[\overline{\text{Cu}}]_{\text{R}})^2}{[\overline{\text{Cu}}]_{\text{R}}[\text{Na}]_{\text{R}}^2} \quad (14)$$

Using the above equation, the concentration of Cu^{2+} on the membrane surface adjacent to the receiving solution can be calculated.

Combining the Eqs. (3) and (4), we get

$$\left(\frac{\delta C_{\text{R}}}{\delta t}\right) = D \times A \frac{(C_{\text{FM}} - C_{\text{RM}})}{(V_{\text{R}} \times \delta)} \quad (15)$$

Since all the parameters except D were known, we can use Eq. (15) to calculate D for each transport experiment. The values of D calculated for each of the single ion transport were given in Table 3.

It is seen that when a transition metal ion say Cu^{2+} permeates through Nafion incorporated with alkali metal say Na^+ , then from Eqs. (9) and (10), it is clear that the ion exchange reaction between Cu^{2+} in solution and Na^+ in the resin phase will

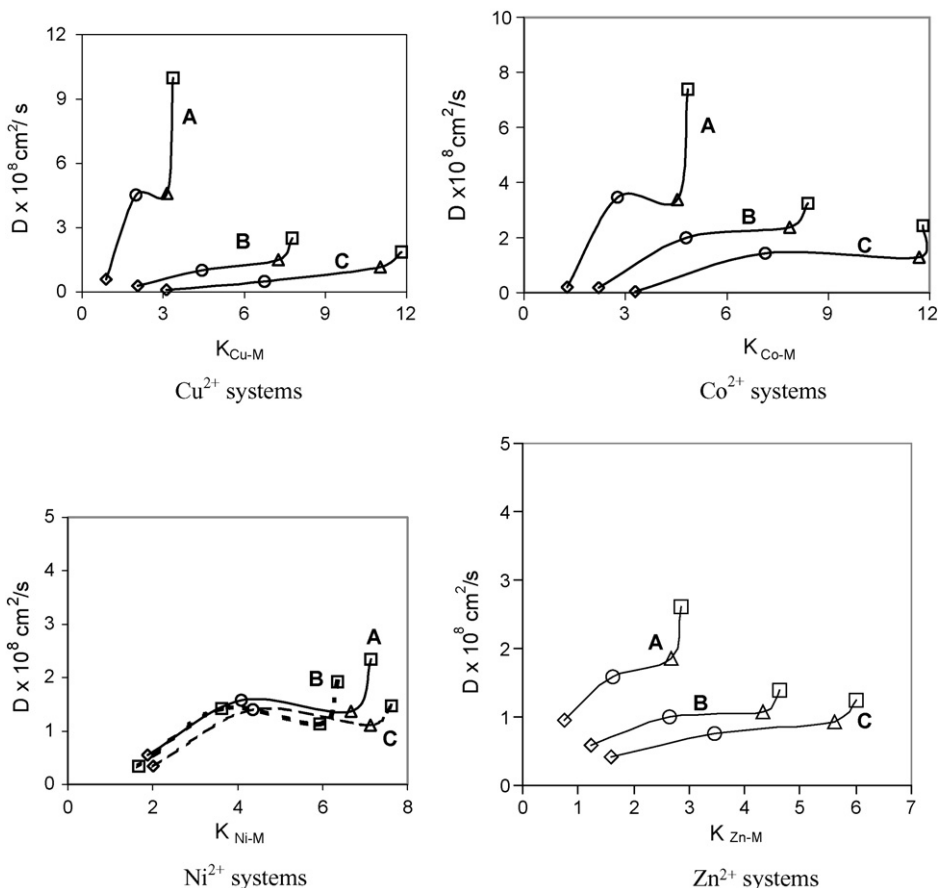


Fig. 5. Plots of D vs. K for different transition metal ions using Nafion. A, B and C refer to the curves for the samples WT, AT and N, respectively. (\square) denotes Li^+ , (\triangle) denotes H^+ , (\circ) denotes Na^+ and (\diamond) denotes K^+ .

definitely affect the transport rate. Hence the ion exchange selectivity of this reaction is expected to affect the D value. It is known that cation exchangers have lower selectivity for Li^+ than that of H^+ . Therefore the ion exchange selectivity K for Cu^{2+} – Li^+ is higher than that of Cu^{2+} – H^+ . Fig. 5 gives the plots of diffusion coefficient (D) versus selectivity coefficient (K). It was seen that the D values were dependent on the K value. As K increases, D also increases. This shows that the initial ion exchange was an important factor, which affects the permeation rate (as given by D). The nature of pre-treatment of Nafion has an effect on its K value and therefore on D . It was seen from that the WT samples have the maximum value for D . This can be understood as follows. After the initial ion exchange with the counter-ion in the membrane phase, the permeating ion was stripped in the receiving phase. Hence if the affinity for the particular ion of the membrane was high, the stripping will be low and therefore the diffusion coefficient value will also be low.

4. Conclusions

It is seen from the above studies that the ion exchange plays a key role in the permeation of ions across cation exchange membrane like Nafion. The pre-treatment of these membranes also affects the ion exchange and therefore the permeation processes as reflected in the D values.

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