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TECHNICAL NOTE

Use of Masking Agents in Promoting Selective Transport of Zn^{2+} through Nafion Membrane

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ABSTRACT

The effect of H^+ ion concentration on the ion-exchange selectivity of Nafion 117 cation-exchange membrane toward Zn^{2+}, Pb^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+} have been studied. A selective transport of any particular metal ion was not possible by controlling the pH alone. However, selective permeation of Zn^{2+} across the membrane could be accomplished by selectively masking the metal ion as the cationic 1,10-phenanthroline complex while the permeation of other interfering ions could be suppressed by masking them as their anionic EDTA complex. About 20% of Zn^{2+} selectively permeated from the mixture in 6 hours and the quantity increased to 67% after 60 hours of permeation.

INTRODUCTION

The perfluoro sulfonic acid cation-exchange membrane Nafion finds wide industrial application (1) due to its high mechanical strength, chemical inertness, and low "co-ion leakage" (2). Because of its tremendous versatility, much effort has been devoted to studying the morphology, transport properties, and mechanical characteristics of the membranes but very little work aimed at characterizing the ion-exchange properties of Nafion has been reported (3, 4). Since Nafion is a cation exchange membrane, the pH of the solution in contact with the membrane is a very important factor in governing the uptake of cations from solution and their subsequent permeation.

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In the present work we studied the affinity of Nafion 117 for Zn^{2+}, Cu^{2+}, Pb^{2+}, Al^{3+}, and Fe^{3+} at different pHs. Since a high degree of selectivity could not be achieved by controlling the pH alone, masking agents were used to ensure selectivity in the permeation of Zn^{2+} across the membrane. Complexation of Zn^{2+} by 1,10-phenanthroline (phen) resulted in the formation of a stable cationic $Zn(phen)_3^{2+}$ complex which selectively permeated through the membrane. Interfering ions like Pb^{2+}, Al^{3+}, and Fe^{3+} were masked as their anionic EDTA complex, and Cu^{2+} was masked by mercapto ethanol.

EXPERIMENTAL

Nafion 117 perfluoro sulfonic acid membrane with an equivalent weight of 1100 g of polymer per mole of SO_3H and a thickness of 0.178 mm was obtained from Du Pont, USA. Circular pieces of membrane (~35 mm diameter) were converted into their acid form by treating with 1 : 1 nitric acid as described elsewhere (5). The disodium salt of EDTA (B.D.H. AnalaR) was weighed and dissolved in deionized water to give a 0.1 M solution. It was standardized by titration with a standard Zn^{2+} solution using hexamine buffer (pH 5.5) and xylenol orange indicator.

Sodium acetate (E. Merck, Germany) in a 0.1 M solution of the reagent in deionized water containing acetic acid was used as a buffer solution in order to adjust the pH to 4.5–5.0.

Metal Ion Solutions. Solutions of Cu^{2+}, Pb^{2+}, Fe^{3+}, and Al^{3+} were prepared by dissolving analytically pure salts in dilute nitric acid. Weighed quantity of zinc granules (B.D.H. AnalaR) were dissolved in dilute hydrochloric acid to give standard 0.1 M Zn^{2+} solution. The concentrations of the metal ions were determined by complexometric titration with EDTA.

Zincon Solution. A 0.01% solution of the reagent was prepared in deionized water.

1,10-Phenanthroline (E. Merck, Germany). A 0.01 M aqueous solution was used. Absorbance was measured with a Shimadzu UV 210A double beam spectrophotometer.

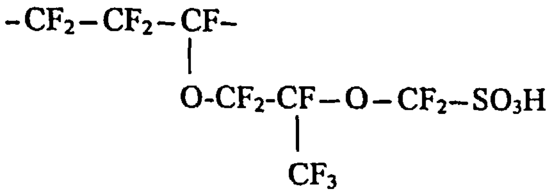
A batch technique was adopted for equilibration of a weighed amount of air-dried Nafion in the Na^+ form with a given metal ion solution of appropriate concentration adjusted to the required pH. The membrane pieces and the solution were stirred constantly for 5–6 hours. The pieces were then filtered out, washed, and the filtrate and washings were analyzed for the metal ions left out by EDTA titration.

Permeation studies were carried out in a U-type cell described elsewhere (5). In a typical experiment the feed solution contained Zn^{2+} (2×10^{-3} M) along with Pb^{2+} (4×10^{-4} M), Al^{3+} (8×10^{-4} M), Cu^{2+} (4×10^{-4} M), Fe^3 (2×10^{-4} M), EDTA (1.35×10^{-2} M), and 1,10-phenanthroline (1.4

$\times 10^{-2}$ M). The pH of the mixture was adjusted to 5.0 with sodium acetate buffer. The volume was made up to 20 mL, and an equal volume of 0.1 M NaOH solution was placed in the receiving compartment. The solutions in both compartments were stirred constantly. The concentration of Zn^{2+} in the receiving solution was monitored at regular time intervals by withdrawing 1 mL of solution and treating with Zincon at pH 9–10 using ammonia and measuring the absorbance at 580 nm (6). The other ions were determined by atomic absorption spectrometry (AAS). Any loss in volume in the receiving compartment was immediately replenished with pure receiving solution.

RESULTS AND DISCUSSION

Nafion 117 can be represented as



It has been established that at ambient temperature the pendant —SO_3H groups attached to the backbone of the polymer in the H^+ form are known to form clusters of 40 Å diameter, separated by a distance of 50 Å and interconnected through channels of 10 Å when fully swollen with water (7). The metal ion, after exchanging with H^+ of the —$SO_3^- H^+$, are accommodated within the ionic cluster and gradually diffuse into the receiving side due to the concentration difference between the membrane phase and receiving solution. Figure 1 shows the affinity of different metal ions for the Nafion membrane at different pHs of the equilibriating solution. The ratio of the number of millimoles (N) of metal ion taken up by W grams of Nafion (i.e., N/W) was plotted against the pH of the equilibriating solution. The weight of the membrane, W, refers to the weight of the air-dried membrane corrected for its approximate water content of 13% as concluded by Koval et al. (8). All the cations studied (namely Zn^{2+}, Pb^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}) showed a high affinity for the membrane throughout the entire pH region. A considerable amount of these ions is taken up by the Nafion even at 0 pH, and at higher pHs the uptake is nearly quantitative. Consequently, a high degree of selectively in the uptake of these ions cannot be obtained by controlling the pH alone. The only alternative way for bringing about selectivity in permeation is to generate a single cationic species of a given metal ion. Selective permeation

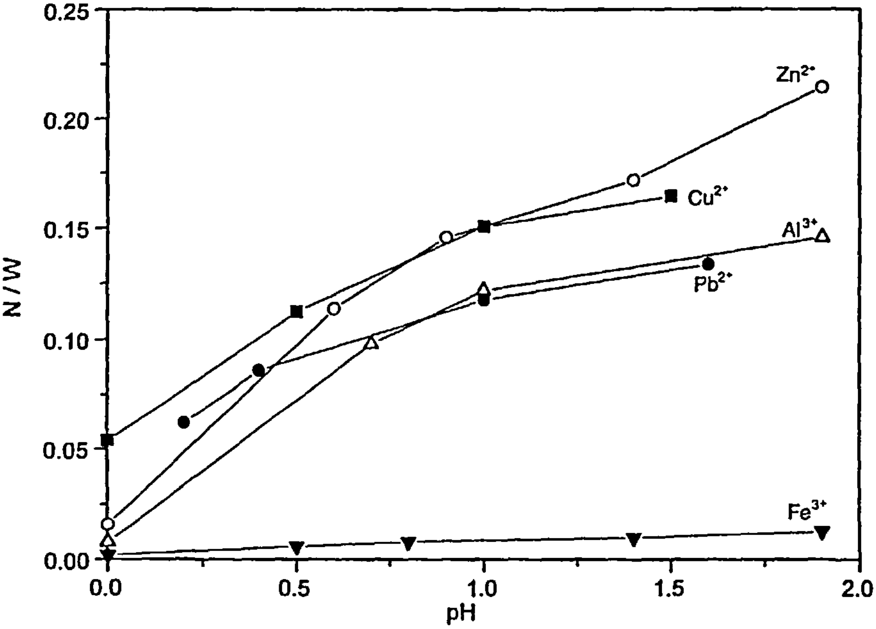


FIG. 1 Variation of *N/W* as a function of pH. *N/W* = moles of metal ion taken up by 1 gram of membrane; *W* = weight of Nafion.

of Zn^{2+} could be achieved by the addition of a mixture of EDTA and 1,10-phenanthroline to the feed solution containing the mixture of metal ions. Phenanthroline forms a stable $Zn(phen)_3^{2+}$ cationic complex with log k = 17.3, and the other metal ions form stable anionic complexes with EDTA. The log k value for Zn $EDTA^{2-}$ is 16.5, and the conditional value of the constant in the presence of 1,10-phenanthroline and buffer anions at pH 5 would be still lower. This will favor complete formation of $Zn(phen)_3^{2+}$ which permeates across the membrane whereas the stable anionic EDTA complexes are prevented from permeating due to Donnan exclusion (9, 10). Based on the quantitative displacement of EDTA by 1,10-phenanthroline, an indirect complexometric method for the determination of Zn^{2+} has been reported (11). The permeation of Zn^{2+} through the membrane was followed by monitoring its concentration in the receiving solution at various time intervals as shown in Fig. 2. It is observed that the transport of Zn^{2+} as a single component (Curve b) is lower than that from a mixture of cations in the feed solution (Curve a). In the absence of other cations, a high concentration of masking agents, particularly mercaptoethanol, reduces the effective concentration of cationic zinc and leads to lower transport. In the receiving compartment, OH^- ions react with the permeated Zn^{2+} to convert it into anionic ZnO_2^{2-}. An equivalent amount of Na^+ permeates across the membrane into the feed solution while ZnO_2^2 remains in the receiving solution due to the negative charge associated with it. This results in an uphill transport of Zn^{2+}. About 20% of Zn^{2+} permeated in 6 hours, but the quantity increased to 67% after 60 hours. The complete transport of Zn^{2+} is expected to take several days at this rate. Thus, the data presented in Fig. 2 for 300 minutes of permeation can be taken as representative for the total permeation process.

The variations in the permeation rates as seen in Fig. 2 are not fully understood. This could be due to some complex equilibria of different cationic species within and outside the membrane phase. High Na^+ concentration in receiving solution is likely to replace $Zn(phen)_3^{2+}$ complex absorbed in the membrane phase rather easily, resulting in a higher transport rate in the initial stage. Then a competitive complex equilibria among Na^+, phenanthroline,

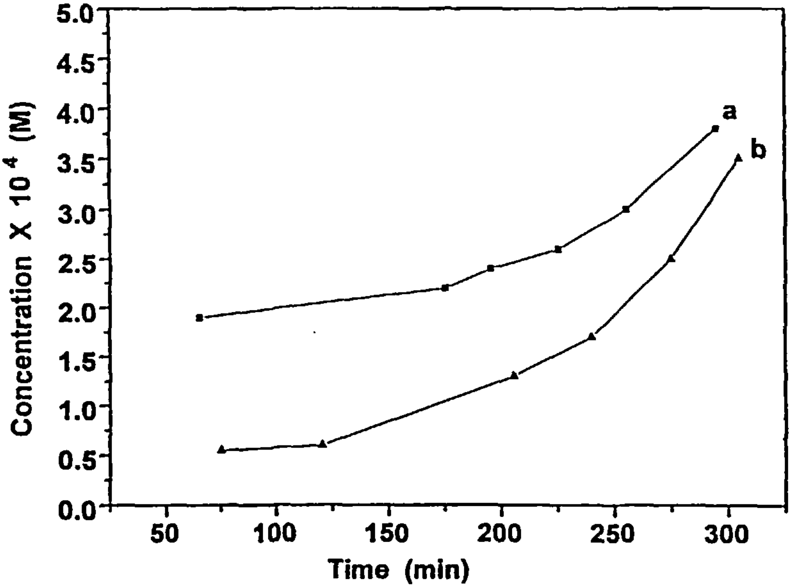


FIG. 2 Variation of Zn^{2+} concentration in the receiving compartment containing 0.1 M NaOH from the feed compartment containing (a) mixture of Zn^{2+} (2×10^{-3} M), Pb^{2+} (4×10^{-3} M), Al^{3+} (8×10^{-4} M), Cu^{2+} (4×10^{-4} M), Fe^{3+} (2×10^{-4} M), EDTA (1.35×10^{-2} M), 1,10-phenanthroline (1.4×10^{-2} M), and mercaptoethanol (1% solution) adjusted to pH 5.0 using acetate buffer; (b) Zn^{2+} (2×10^{-3} M), EDTA (1×10^{-2} M), 1,10-phenanthroline (1.4×10^{-2} M) adjusted to pH 5.0 using acetate buffer.

TABLE 1

Concentration of Different Cations in the Receiving Compartment during the Permeation of Zn^{2+} (initial concentration of Zn^{2+} = 2×10^{-3} M; other metal ions = 4×10^{-4} M each)

Cation	Concentration after 6 hours (M)	Concentration after 60 hours (M)	Percent permeated after 60 hours
Zn^{2+}	4×10^{-4}	1.24×10^{-3}	67
Fe^{3+}	Nd	4.5×10^{-6}	2.25
Al^{3+}	Nd	Nd	—
Pb^{2+}	Nd	Nd	—
Cu^{2+} [a]	Nd	Nd	—

[a] In the presence of mercapto ethanol.

and $Zn(phen)_3^{2+}$ takes place in the membrane phase. This slows down the permeation rate for some time. Since Nafion exhibits a stronger affinity for hydrophobic cation species (3, 4), it can be assumed that phenanthroline or its zinc complex finally dominates the cation-exchange sites of Nafion. The higher transport rate in the last stage can be attributed to the easy absorption of Zn^{2+} and subsequent diffusion/permeation under this condition.

Table 1 shows the concentration of various cations permeated from the feed solution along with Zn^{2+}. The concentrations of the interfering ions in the feed solution were of the same order of magnitude as Zn^{2+} (4×10^{-4} M). Fe^{3+} showed little interference but Cu^{2+} interfered strongly. Interference from Cu^{2+} could be eliminated by the addition of mercaptoethanol to the feed solution. Mercaptoethanol reduces Cu(II) to Cu(I), which forms a very stable complex with the ligand (12). The permeation of this neutral complex through the ion-exchange membrane is negligibly small, and the interference from copper could thus be eliminated. The concentrations of different ions were below their detection limits by AAS ($<10^{-6}$ M), even after 60 hours of permeation (Table 1), so it is imperative that these metal ions do not interfere. Interference from Fe^{3+} could not be totally avoided, but the separation factor is very high. The present study suggests a higher selectivity for Zn^{2+} permeation than observed by Cherif et al. (13).

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