SORPTION OF NICKEL AND IRON ON POLYSULFONE CATION EXCHANGE MEMBRANES

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Sorption of $NiCl_2$ and $FeCl_3$ or di- and trivalent cation salt mixtures on polysulfone or polysulfone polyester-supported cation exchange membranes was investigated as a function of pH and concentration. The sorption of Fe(III) was higher than that of Ni(II) for both types of membranes. The maximum sorption for Fe(III) and Ni(II) ions was observed at pH 2.8 and 4.4, respectively. The selectivity coefficient of Fe(III) was also higher than that of Ni(II). The results were explained by considering the hydration effect and ionic valence.
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Various kinds of separation membranes have been widely studied and utilized industrially in various fields, in particular, ion-exchange membranes have been developed for production of sodium chloride by electrodialytic concentration of seawater[1]. Recently, many applications of ion exchange membrane processes based on the Donnan membrane equilibrium principle have been developed to solve two important environmental problems, recovery or enrichment of valuable ions and the removal of undesirable ions from waste water[2], in particular extract ion of toxic metal ions[3–5].

   In general, membrane transport phenomena are controlled by several factors such as ion concentration within the membrane, charge density of the membrane, composition of the solution, ionic fluxes, water content, *etc.* It has been pointed out that the membrane charge and its density are among the most important factors which characterize membrane properties. The membrane charge plays an important role in transport processes[6,7], and affects the selectivity of the membrane charged molecules[8]. The characterization of charged membranes has been studied both theoretically and experimentally by many researchers[9–11]. Another important point is the nature of the interaction between the membrane matrix and ions in relation

to electrochemical behavior of the membranes. It is known that the ion transport mechanism in membranes is completely different from the transport mechanism in a liquid. The mobility of any particle in the membrane is influenced by interactions with the charged polymer network, friction with water molecules in the electroosmotic flow directed towards the flow of counter-ions and mutual interactions with other transported species[12,13].

In this paper, we attempted to study the sorption of Ni(II) and Fe(III) on polysulfone cation exchange membranes, which are microporous ion exchange membranes having controlled ion-exchange capacity and excellent mechanical wet strength. It is of interest to compare the mobility of di- and trivalent metal mixtures on the membranes, because their structure has to be studied extensively to determine whether they are available as a separation material, particularly for recovery of metals from red mud, which is a by-product in the aluminium plant. Hence, the effect of ion concentration and pH on the sorption of Ni(II) and Fe(III) on polysulfone membranes were investigated and discussed.

EXPERIMENTAL

Cation exchange membranes, ICE-450 polysulfone composition (SA_3S, homogeneous), and polysulfone with polyester support (SA_3T, heterogeneous), from Gelman Sciences were used. The ion exchange capacities for SA_3S and SA_3T membranes are 1.522 and 1.132 mmol/g in the H^+ form, their water contents 40 and 27%, respectively, their pore size 0.45 µm and thickness 152.4 µm. Nickel chloride ($NiCl_2 \cdot 6H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) were of analytical grade, obtained from Merck Co. Darmstadt, Germany.

The membranes were first pretreated by boiling for 60 min in deionized water, followed by 1.0 M HNO_3, NaOH and finally distilled water, and the membrane discs were pretreated with 1.0 M HCl to convert the H^+ form for 24 h. Sorption experiments were carried out by a batch method. Nickel(II) and iron(III) solutions were prepared in distilled water by diluting the prepared stock solution (10^{-2} mol/l) to desired concentrations. Sorption experiments were performed by saturation of the membrane with $NiCl_2 \cdot 6H_2O$ or $FeCl_3 \cdot 6H_2O$ solutions of various concentrations, and the desorption with acid. Membrane samples were soaked in 30 ml of salt solutions of various concentrations for 24 h. Then they were washed in distilled water until no chloride ions were detected in the membranes. The membranes with sorbed Ni^{2+} or Fe^{3+} ions were kept in 30.0 ml 1.0 M HCl solutions for 24 h. The amounts of Ni^{2+} or Fe^{3+} ions desorbed were determined by AAS (Pye Unicam 929). However, the amounts of sorbed metal ions were calculated from the change in the metal concentration in the aqueous solution before and after equilibrium sorption from weight of the dry membrane used. In all cases, mass balance was confirmed. The effect of pH on the q (in mmol/g) values of the membranes was determined in 10^{-3} M Fe^{3+} or Ni^{2+} solutions. The pH values of the solutions were adjusted using HCl or NaOH aqueous solutions and determined with an Orion SA720 pH meter.

The effect of coexisting metal ions in the competitive sorption of nickel and iron was investigated at room temperature. The membranes were equilibrated for 24 h with aqueous so-

lutions of $NiCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ mixtures with the following mole fractions: 0.00, 0.26, 0.35, 0.48, 0.73 and 1.00. The q were measured in salt mixtures as given above. A selectivity coefficient $K_{Ni^{2+}}^{Fe^{3+}}$ of the Fe^{3+} and Ni^{2+} for SA_3S and SA_3T membranes was calculated.

RESULTS AND DISCUSSION

The concentration of Fe^{3+} and Ni^{2+} ions sorbed on the membrane was calculated using the following equation

$$q = \frac{Q}{w_d} , \tag{1}$$

where Q and w_d are the amount (in mmol) of metal ions sorbed on the membrane and the weight (in g) of the dry membrane, respectively.

Single-sorption isotherms of Fe(III) and Ni(II) ions on polysulfone membranes were illustrated in Fig 1, in which a and b represent sorption of Fe(III) and Ni(II), respectively. It can be seen that the q values increased with increasing concentration (C). The steady values approximately were achieved at ion concentrations of 25 mmol/l for Fe^{3+} ions and 20 mmol/l for Ni(II) ions on both the membranes. It is clearly seen from Fig. 1 that both membranes show higher sorption of Fe(III) than that of Ni(II). This is due to the higher valence of Fe^{3+}. When the sorption capacities of both membranes for both ions were compared, the sorption capacity of SA_3S, like its ion exchange capacity, was found to be higher than that of SA_3T. As shown in Fig. 1, the sorption isotherms for metals could be expressed either as Langmuir or Freundlich isotherms. Metal sorption constants and correlation coefficients for Fe(III) and Ni(II) on both the membranes were calculated from Freundlich and Langmuir plots; they are presented in Table I. The sorption data on both membranes were fitted to both Freundlich and Langmuir isotherm equations. The sorption data for both metals and both metals provide an excellent fit to the Langmuir isotherm, giving correlation coefficients in the range 0.989–0.999 Langmuir isotherm; for the Freundlich isotherm they are 0.960–0.993. To test the fit of data, the Langmuir isotherm equation is written as

$$C/q = 1/K_b A_s + C/A_s , \tag{2}$$

where the parameters K_b and A_s are the sorption binding constant (1/mmol) and saturation capacity (mmol metal/g dry membrane), respectively. The Freundlich isotherm equation is written as

$$q = k \, C^{1/n} \, , \tag{3}$$

where k is saturation capacity (mmol metal/g dry membrane) and n is an empirical parameter. The Langmuir and Freundlich isotherm parameters were determined from the least-squares fit of the sorption data in Fig. 1.

The pH dependence of the sorption of Fe^{3+} and Ni^{2+} ions on the SA_3S and SA_3T membranes are presented in Fig. 2, in which a is for Fe(III) and b for Ni(II) ions. They indicate that the sorption amount change with pH. As
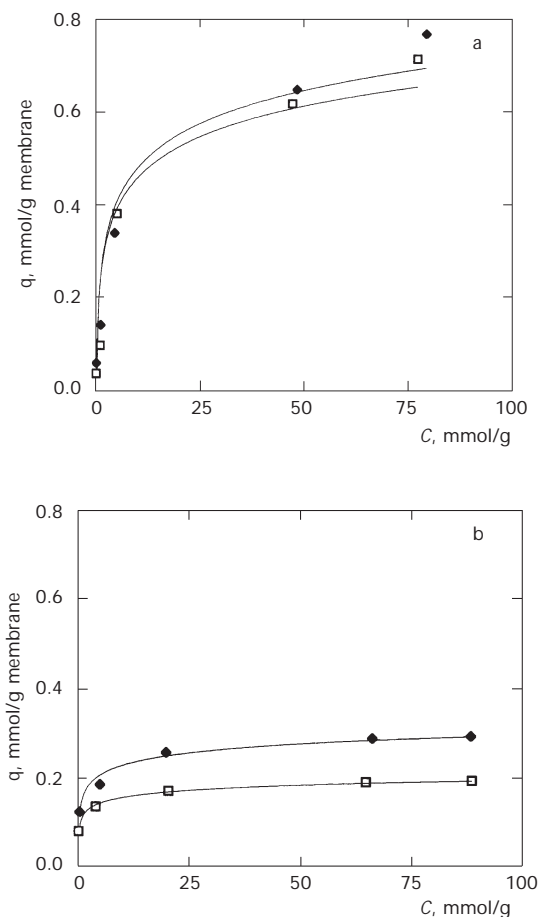

FIG. 1
The sorption isotherms of Fe(III) and Ni(II) ions on the membranes: a Fe(III); b Ni(II). ◆ SA_3S, ◻ SA_3T

seen in Fig. 2, the sorbed amount Fe(III) ion reached a maximum at pH 2.8 and the curve sharply decreased with the increasing pH. In confront, the Ni(II) sorption gradually increases with increasing pH in for pH 4.4 and value then the curve tends to decrease. This case can be explained by the general ion exchange equilibrium on fixed sulfonic acid groups

$$1/n\ M^{n+} + R-SO_3H \qquad R-SO_3(M)_{1/n} + H^+ .$$

This equilibrium is shifted to the left with increasing proton concentration. Consequently, the sorption ability of the polysulfonated membrane decreases. However, the q values of metals also decreased at high pH, owing to the interaction between OH^- and Fe^{3+} or Ni^{2+} ions. Iron(III) ion can exist as Fe^{3+}, $FeOH^{2+}$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$, $Fe(OH)_2^+$, $Fe(OH)_3$ and $Fe(OH)_4^-$ forms depending of pH in solution. These ionic forms will definitely affect the influence of pH on the sorption properties. It was reported that the ionic form of Fe(III) in solution decreases with increasing pH (ref.[14]). Nickel(II) ion forms are Ni^{2+}, $Ni(OH)^+$ (pH $\geq$ 4.5), $Ni(OH)_3^-$ (pH $\geq$ 8.5), $Ni_4(OH)_4^{4+}$ (pH $\cong$ 9–10), $Ni(OH)_2$ (pH $\cong$ 9.5–11.5), $Ni(OH)_4^{2-}$ (pH $\geq$ 10) at various pH of solutions[15].

It is well known that the mobilities of ions within the membrane depend on external concentrations. Therefore, it was decided to start this work by first investigating looking at the equilibrium properties of the membranes with divalent and trivalent salts and then with mixtures of divalent/trivalent salt mixtures to determine permselectivity of the membranes. For an

TABLE I
Parameters of Langmuir and Freundlich isotherms for sorption of metals on SA$_3$S and SA$_3$T membranes

Membrane	Metal	Langmuir isotherm model			Freundlich isotherm model		
		$A_s{}^a$	K_b l/mol	Correlation coefficient	k^a	n	Correlation coefficient
SA$_3$S	Fe^{3+}	0.783	0.218	0.989	0.158	2.698	0.985
	Ni^{2+}	0.303	0.464	0.999	0.154	6.656	0.987
SA$_3$T	Fe^{3+}	0.734	0.217	0.991	0.129	2.395	0.960
	Ni^{2+}	0.200	0.606	0.999	0.110	7.194	0.993

^{a} mmol/g dry membrane

exchanger in equilibrium with two different counterions A and B, the selectivity coefficient K_B^A can be written as in refs[16–18]

$$K_B^A = \frac{(\overline{X}_A)^{1/z_A}}{(\overline{X}_B)^{1/z_B}} \bigg/ \frac{(X_A)^{1/z_A}}{(X_B)^{1/z_B}} , \qquad (4)$$

where $\overline{X}_A$ and $\overline{X}_B$ are the equivalent fractions of the counterions in the membrane and X_A and X_B are the corresponding equivalent fractions of these ions in solution, z_A and z_B are the charges of ions ($\overline{X}_A + \overline{X}_B = 1$ and $X_A + X_B = 1$). The X values of Ni^{2+} and Fe^{3+} ions have been calculated. A plot of metals in the membrane phase versus metals in solution at equilibrium gave a linear curve. The slope of the linear curve defines the selectivity coefficient, K_B^A; the regression lines are given in Fig. 3. It can be seen that both membranes show a high selectivity for Fe(III) ions. The selectivity val-
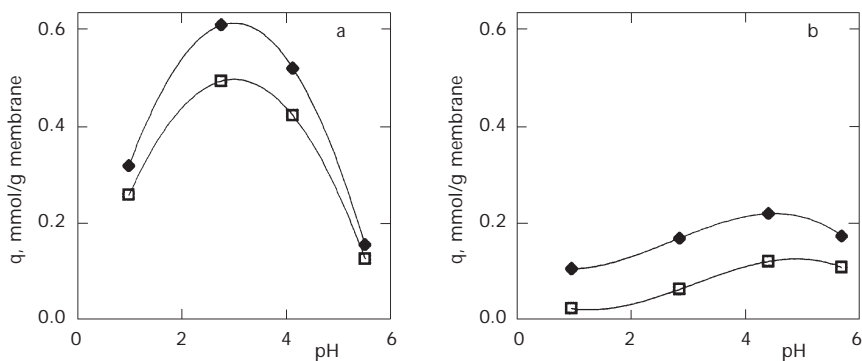

FIG. 2
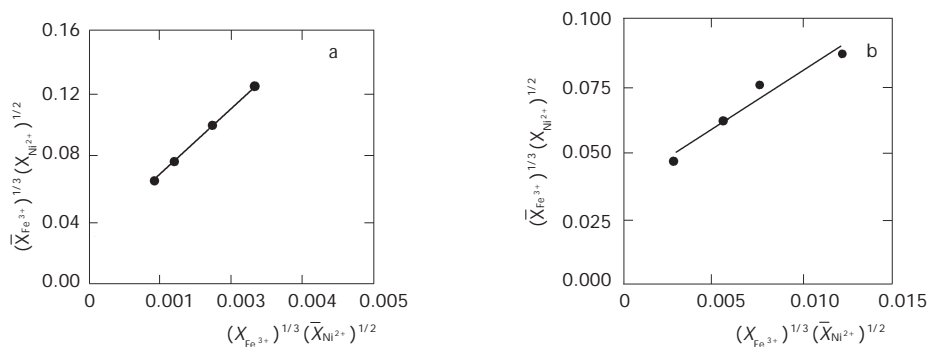The pH dependence of sorption of Fe(III) and Ni(II) ions: a Fe(III); b Ni(II). ◆ SA$_3$S, ☐ SA$_3$T

FIG. 3
The selectivity coefficient of $K_{Ni^{2+}}^{Fe^{3+}}$ for the membranes: a SA$_3$S; b SA$_3$T

ues of SA_3S membrane for Fe(III) ion with respect to Ni(II) ion was found about 33 times higher; for SA_3T, this value was found about 4 times higher. The capability of competitive sorption of Fe^{3+} far exceeds that of Ni^{2+}. It is well known that the attractive force of Fe^{3+} ions is larger than Ni^{2+}, owing to the high charge of Fe^{3+}. For different ionic valences, the capability of competitive sorption of the ions on polysulfone membranes increases with increasing of ionic valence, such as $Ca^{2+} > Na^+$ (ref.[9]) and for the same ionic valences, the capability of competitive adsorption of metal ions on the RC–AC membrane increased with decreasing atomic number, in the order of $Cu^{2+} > Sr^{2+} > Cd^{2+}$ (ref.[19]).

Transport properties of phosphonic acid and sulfonic acid cation exchange membranes were studied and their transport permselectivity for mono- and divalent cations was compared[20]. It was found that the permselectivity of Ca^{2+} in comparison with Na^+ ions for the phosphonic acid membrane was lower than that of the sulfonic acid cation exchange membrane. The relative transport number and ion exchange equilibrium constant of Ca^{2+} and Na^+ ions for phosphonic acid and sulfonic acid cation exchange membranes were found to be 2 and 4, respectively.

The selectivity order in a Nafion perfluorosulfon acid cation exchange membrane was found to be $Cs^+ > Rb^+ > Ba^{2+} > K^+ > Mg^{2+} > Na^+ > H^+ > Li^+$ for a mixture of mono- and divalent cation systems[21]. A similar order was also observed for Neosepta, Selemion, Aciplex and Nafion membranes[22,23]. The selectivity of a binary solution of Ca^{2+} or Cu^{2+} and Na^+ or H^+ in cation exchange membranes was studied and selective uptake of divalent cation species was observed[24]. It was reported that the selective phenomena depend on higher electrostatic attraction between divalent cations and the fixed charge sites within the membrane. This suggests that the hydration radii definitely play a role in the permselectivity of ion exchange membranes and that the permselectivity of any ion can be governed by ion partitioning at the membrane/solution interface.

A multicomponent equilibrium partition coefficient model on a molecular-level basis was formulated by Bontha and Pintaura[25] who reported that the ion with a lower surface charge density (*i.e.*, the monovalent ion with the largest hard-sphere radius) was preferentially adsorbed onto Nafion cation exchange membranes. The divalent/monovalent cation concentration ratio in the membrane was determined and found to be greater than units. Adsorptions of Mg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+} and Pb^{2+} were compared with those of monovalent cations in Dowex 50 poly(styrenesulfonic acid) cation exchange resins, in which the adsorption of divalent cations was found to be higher than that of monovalent cations[26]. The equilibrium partitioning of

Zn^{2+} and Na^+ aqueous solutions in Dowex 50 was investigated the selective uptake of Zn^{2+} was found higher than that of Na^+ (ref.[27]). Divalent cation/hydrogen ion uptake in Nafion membrane was also studied[21,28]; the larger cation is selectively adsorbed. From these observations, it was concluded that the permselectivity of the polysulfone ion exchange membranes depends on, to the ionic valence, on higher electrostatic attraction between metal and fixed charge sites, hydration radii, the ionic forms of cations, pH of the solution, *etc.*

In conclusion, the equilibrium uptake of di- and trivalent cation salt mixtures on polysulfone membranes was investigated. The experimental results show that ion hydration effects, ionic valence and the solution pH affect the sorption behavior of the membranes. The polysulfone membranes, in particular SA_3S, show higher sorption properties for trivalent cations than for divalent cations.

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