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The Effect of Accompanying Anion and the Competitive Transport of Ni(II) and Fe(III) Through Polysulfone Membranes

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ABSTRACT

The effect of accompanying anion on the transport of Ni^{2+} and competitive transport of Ni^{2+} and Fe^{3+} ions through charged polysulfone or polysulfone polyester-supported cation exchange membranes was studied under Donnan dialysis conditions. In the Donnan dialysis process, two electrolyte solutions were separated by ion permeable membrane, the one side (feed solution) initially containing metal salts or their mixtures, the other is HCl and no external potential field is applied. The transport of metal ions through membranes was correlated with the efficiency factor

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(EF) values as well as with fluxes and depended on the interaction between the fixed groups in the membrane and the metal ions. The EF value of Ni^{2+} as a single as well as mixture state was higher than that of Fe^{3+} for both types of membranes. The effect of accompanying anion on the transport of Ni^{2+} was found to be in the following order of $Cl^- > NO_3{}^- > SO_4{}^{-2}$, and the results were correlated with the EF values, as well as with the membrane structure.

Key Words: Donnan dialysis; Charged membranes; Metal transport; Competitive transport; Anion effect.

INTRODUCTION

Donnan dialysis is a membrane-based equilibrium process in which metal ions need to be recovered using hydrogen ions as the "pumping" ion. The principle of Donnan dialysis process is reviewed[1–3] and some applications of the process, such as concentration and removal of cations from hard water[4–8] and diffusion of ions through ion exchange membranes, are reported.[9–14] The permselectivity of these membranes is a consequence of co-ion exclusion, which is conventionally described by the classical Donnan equilibrium equations.[1,13–15] In this process, solute partitioning occurs at two aqueous liquid–membrane interfaces on two sides of an ion permeable membrane. It is not a rate-governed membrane separation process. The separation achieved between feed and receiver solutions is not lost even if the assembly of feed solution–ion permeable membrane–receiver solution is closed to the surrounding, feature characteristic of an equilibrium separation process, such as sorption, solvent extraction, distillation, and so forth.

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,[16] in particular the extraction of toxic metals.[17] The reason for this study is to define the distribution of metals transport and the effect of anions on the transport of Ni^{2+} ion through polysulfonated ion exchange membranes that are different structures as homogenic and heterogenic. Polysulfonated ion exchange membranes are strongly acidic cationic true microporous membranes and patented for trace metal analysis. In an earlier study,[18] the sorption of nickel and iron on these cation exchange membranes were looked at as a function of pH and concentration. Therefore, in this study, the competitive transport of Ni^{2+} and Fe^{3+} ions through a charged membrane was partly investigated.

The results were correlated systematically in terms of the Donnan dialysis conditions.

EXPERIMENTAL

All solutions were prepared with deionized water without further purification and $Ni(NO_3)_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, $NiSO_4{\cdot}6H_2O$, H_2SO_4, and HNO_3 were obtained from Merck (Darmstadt, Germany). NaOH and HCl were obtained BDH (Poole, England). The solutions were not deoxygenated. ICE-450 polysulfonated membranes, which are polysulfone composition (homogenous, SA_3S), and polysulfone with polyester support (heterogonous, SA_3T) were obtained from Gelman Sciences. 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 are 40% and 27%, respectively. Their pore size is 0.45 μm and thickness is 152.4 μm.[19] The membranes were conditioned by cycle equilibrations with 1.0 M HNO_3, NaOH, and, finally, distilled water. The membrane discs were pretreated with 1.0 M of HCl to convert the H^+ form for 24 h. Nickel(II) and iron(III) solutions were prepared in distilled water by diluting from the stock solution (2.0×10^{-2} M) to the desired concentrations.

For the measurement of fluxes of metal ions, a two-compartment cell made of Teflon was used. The membrane was clamped tightly between two compartments of 40 mL capacity and the exposed area of the membrane was 7.07 cm^2. The feed solutions were metal salts (pH was adjusted to 1.0) and the receiver solution was HCl solution applied at constant concentration (1.0 M) for all measurements. The sampling of the solution was carried out at a certain time interval to determine the amount of metal ions transported across the membrane by use of an ICP-AES (Varian, vista\AX CCD Simultaneous ICP-AES). The rotational speed on both compartments was kept constant (500 rpm) with a magnetic stirrer to prevent the formation of significant boundary layers and also to ensure that the concentration of metal was uniform throughout in both solutions. All the measurements were carried out at 25 ± 3°C.

RESULTS AND DISCUSSION

The system to discussed here is a Donnan dialysis with ion exchange membrane separating two solutions initially containing metal salt at one side of membrane and acidic solution at other side. Metal salt solution or their

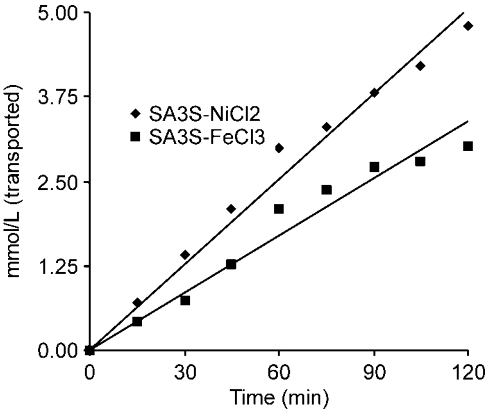

Figure 1. Time course of metal transport across the homogeneous membrane.

mixtures were studied and theoretical treatment for metal transport in Donnan dialysis are discussed in detail elsewhere.[10,13,14,20]

The obtained example of typical curves for both metals in chloride forms on the acidic side vs time are given in Figs. 1 and 2 as a function of metal concentration. To compare the recovery of metals ions, the fluxes were evaluated for the all experimental conditions. The metal flux, J_M can be obtained by using the following equation:

$$J_M = \left(\frac{V}{A}\right)\left(\frac{dM^{n+}}{dt}\right)_{t\to 0} \tag{1}$$

where V is the volume of receiving solution and A is the effective membrane area. In fact, J_M is calculated by differentiating the curve-fit polynomials of the time profiles. Each experiment was at least duplicated and the reproducibility of flux measurements were found mostly within 5% and the calculated fluxes are given in Table 1.

The EF values of transported ion can be determined by using the following relation:

$$\mathrm{EF} = (C_{\mathrm{Fo}} - C_{\mathrm{Ft}})/C_{\mathrm{Fo}} \tag{2}$$

where, C_{Ft} is concentration at t time and C_{Fo} is initial concentration in feed phase of metal. Figures 3 and 4 report the EF values of Ni^{2+} and Fe^{3+} ions with time on the membranes when their accompanying anions are chloride for both membranes. It can be seen that the metal concentration in acid solution increases almost linearly for both metals, but the increase in Ni^{2+} was

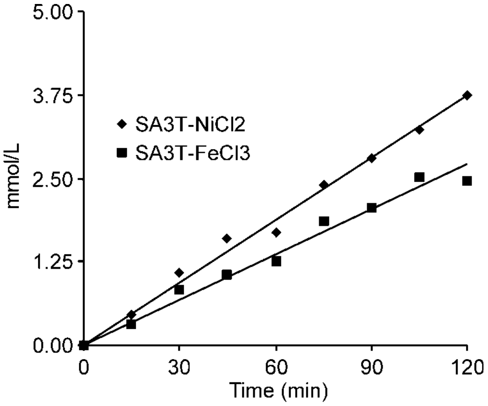

Figure 2. Time course of metal transport across the heterogeneous membrane.

pronounced when compared with Fe^{3+}. The fluxes of Ni^{2+} and Fe^{3+} ions passing through the membranes were estimated by monitoring their concentration in the acidic solutions as a function of time. These data were used to estimate values for fluxes and the procedure for treating experimental data as reported in earlier work.[13,14,18–20]

The EF values of Ni^{2+} ions at different accompanying anions with time are presented in Figs. 5 and 6 for homogeneous and heterogeneous membranes. The effect of accompanying ions was found to be in the order of

Table 1. The flux (J) of the membranes for Ni^{2+} and Fe^{3+}.

	Membrane	
Experiment	SA_3S ($J \times 10^{10}$ (mole cm^{-2} s^{-1}))	SA_3T ($J \times 10^{10}$ (mole cm^{-2} s^{-1}))
$FeCl_3$	19.901 (± 0.016)	15.955 (± 0.007)
$NiSO_4$	21.513 (± 0.005)	19.901 (± 0.002)
$Ni(NO_3)_2$	22.320 (± 0.032)	21.132 (± 0.005)
$NiCl_2$	29.788 (± 0.011)	22.107 (± 0.004)
$(NiCl_2 + FeCl_3)Ni$	12.518 (± 0.003)	10.057 (± 0.002)
$(NiCl_2 + FeCl_3)Fe$	10.905 (± 0.012)	8.911 (± 0.002)

While each metal concentration in feed solution is 1.0×10^{-2} M at pH 1.0, receiver solution is 1.0 M HCl.

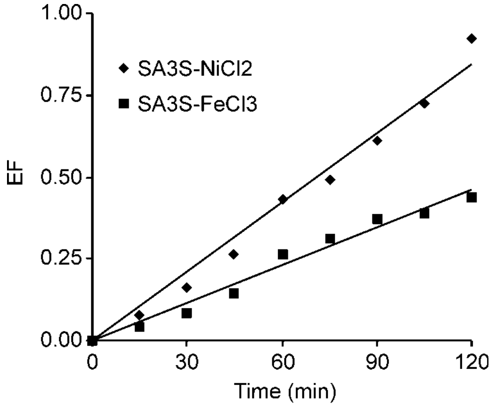

Figure 3. The comparison of EF values of Ni^{2+} and Fe^{3+} with time for homogeneous membrane.

$Cl^- > NO_3^- > SO_4^{-2}$. The thermochemical radii (nm) of anion for Cl^-, NO_3^-, and SO_4^{2-} ions are 0.168, 0.200, 0.281, respectively. If the thermochemical radii values is taken into concentration, the effect of accompanying anion on the transport should be in the order of $Cl^- > NO_3^- > SO_4^{-2}$. The results obtained were agreement with the order of thermodynamic radius of anions.

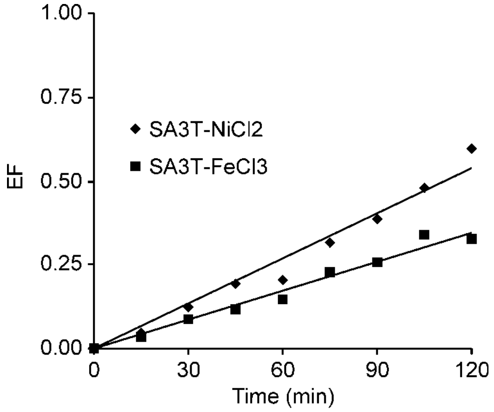

Figure 4. The comparison of EF values of Ni^{2+} and Fe^{3+} with time for heterogeneous membrane.

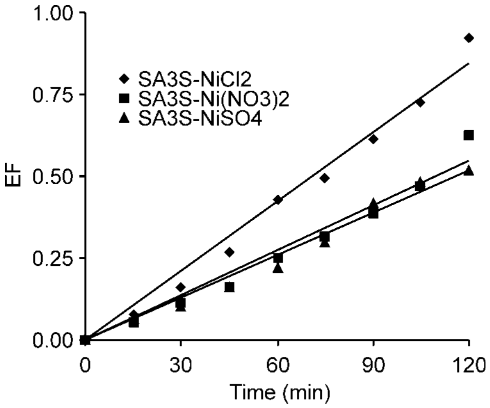

Figure 5. The EF values of the effect of accompanying anion on the transport Ni^{2+} with time for homogeneous membrane.

The observed fluxes of both metals for the homogeneous membrane were found to be nearly two times higher than that of the heterogeneous one. The transport of Ni^{2+} for both membranes was always higher than that of Fe^{3+}, when the feed concentration was 0.01 M and receiver phase was 1.0 M of HCl. The comparison of Ni^{2+} and Fe^{3+} with respect to same membrane is shown in Figs. 3 and 4. This suggests that the metal transport was related with hydrated radii of the metals, the structure of membrane, water contents, and so forth.

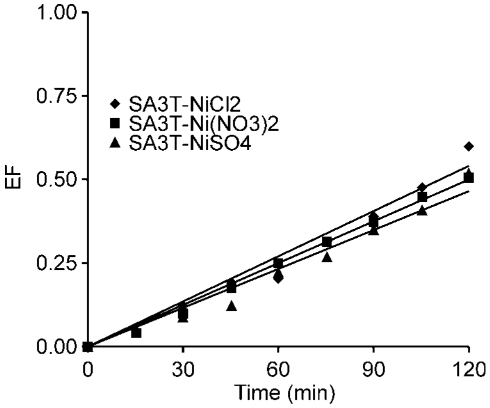

Figure 6. The EF values of the effect of accompanying anion on the transport Ni^{2+} with time for heterogeneous membrane.

In other works, the SA_3S membrane shows a high permselectivity for the bulky ions regarding to its high water content combined with its higher exchange capacity. Its relative high exchange capacity would induce a high selectivity between bivalent and multivalent ions. Moreover, many types of interaction, either between the metals or metal and fixed charges as well as repulsion between them, are involved.

It is well known that the mobility of ions within the membrane depend on external concentrations. Therefore, an earlier work[20] deals with the equilibrium sorption of the membranes with divalent and trivalent salts and mixtures of divalent and trivalent salts to determine the permselectivity of the membranes, which show a high selectivity for Fe^{3+} ions. The selectivity values of SA_3S membrane for Fe^{3+} ion with respect to Ni^{2+} ion was found to be about 33 times higher; in the case of SA_3T, this value was found to be about four times higher. This is the case for higher transport of Ni ions through the membranes. 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. A multicomponent equilibrium partition coefficient model on a molecular-level basis was formulated by Bontha and Pintaura,[21] 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. So, the Fe^{3+} ions was preferentially sorbed on the membranes, on the contrary, its transport has to be lower with respect to Ni^{2+}.

If a counterion is taken from the bulk solution and brought into contact with a fixed group, two types of interaction energy are involved: (1) the electrostatic interaction between the fixed group and the ion, and (2) the free energies required to remove from the fixed group and counterion as many water molecules are as necessary to permit contact of the fixed grouping and counterion. These free energies would be related to the standard free energies of hydration of the counterion and fixed group. In the case of a fixed grouping of high field strength, the exchanger gives preference to the ion with a smaller hydration radius. As a consequence, selectivity in the normal order is governed by the free energies of hydration of the counterion. From these observations, it can be pointed out that the transport ratio of the polysulfone ion exchange membranes depends on the ionic valence, the higher electrostatic attraction between metal and fixed charge sites, hydration radii, the ionic forms of cations, pH of the solution, water contents of the membranes, partition coefficients of the interface, and other factors.

The competitive transports through the polysulfone membranes in the presence of Ni^{2+} and Fe^{3+} at equal mole fraction were investigated when their

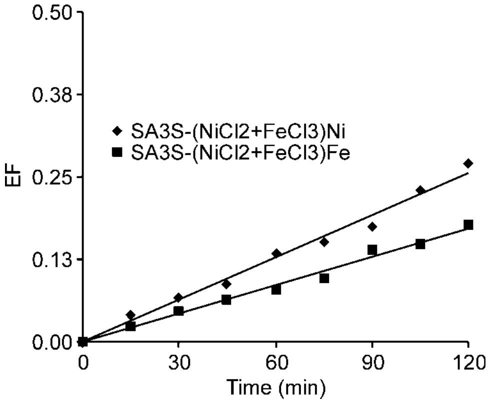

Figure 7. The changes of EF values on the mixture of Ni^{2+} and Fe^{3+} ions with time for homogeneous membrane (the mole fraction of metals was equal as 0.5).

anion was chloride. The EF values for both membranes with time are presented in Figs. 7 and 8. The difference in the behavior of ionic movement is more apparently seen in Figs. 7 and 8. The mobility of H^+, Ni^{2+}, and Fe^{3+} ions in the perfluorosulfonated ionomer membranes were found as $1.33 \times 10^{-7}\, m^2V^{-1}s^{-1}$, $1.65 \times 10^{-8}\, m^2V^{-1}s^{-1}$, and $5.3 \times 10^{-9}\, m^2V^{-1}s^{-1}$, respectively.[22] It was reported that the mobility of H^+ ions depends on the type of foreign cation that coexists in the membrane. In the presence of Fe^{3+} ion, the mobility of H^+

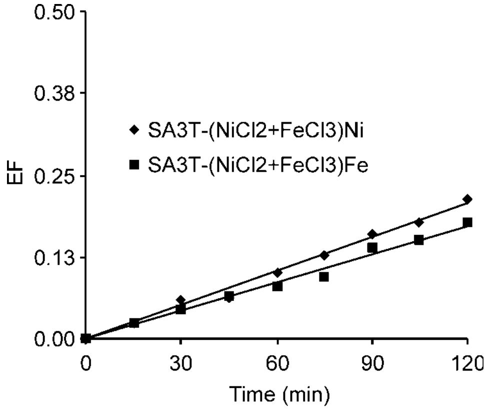

Figure 8. The changes of EF values on the mixture of Ni^{2+} and Fe^{3+} ions with time for heterogeneous membrane (the mole fraction of metals was equal as 0.5).

decreases sharply, but in presence of Ni^{2+}, the mobility of H^+ increases almost linearly of Ni^{2+} and is of intermediate nature and there appears to be little interaction between H^+ and Ni^{2+} ion in the membrane.

In conclusion, our experimental results strongly indicate that the transport process (Donnan dialysis process) of metals through polysulfone cation exchange membranes is driven by hydronium ions. It is clearly seen from Figs. 1 and 2 that the EF values of Ni^{2+} are higher than that of Fe^{3+} and the presence order on the competitive transport is $Ni^{2+} > Fe^{3+}$. The effect of accompanying anions on the transport of Ni were found to be in the order as $Cl^- > NO_3{}^- > SO_4{}^{2-}$.

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