Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Transfer of Monovalent and Divalent Cations in Salt Solutions by Electrodialysis

L. Firdaous[a]; J. -P. Malériat[b]; J. -P. Schlumpf[b]; F. Quéméneur[b]
[a] Laboratoire des Procédés Biologiques, Génie Enzymatique et Microbien, ProBioGem UPRES-EA 1026Polytech' Lille, Villeneuve d'Ascq, France [b] Université de Nantes, Nantes Atlantique Universités, Saint-Nazaire Cedex, France

To cite this Article Firdaous, L. , Malériat, J. -P. , Schlumpf, J. -P. and Quéméneur, F.(2007) 'Transfer of Monovalent and Divalent Cations in Salt Solutions by Electrodialysis', Separation Science and Technology, 42: 5, 931 — 948
To link to this Article: DOI: 10.1080/01496390701206413
URL: http://dx.doi.org/10.1080/01496390701206413

Separation Science and Technology, 42: 931–948, 2007
Copyright © Taylor & Francis Group, LLC
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701206413

Transfer of Monovalent and Divalent Cations in Salt Solutions by Electrodialysis

L. Firdaous
Laboratoire des Procédés Biologiques, Génie Enzymatique et Microbien,
ProBioGem, Polytech' Lille, Villeneuve d'Ascq, France

J.-P. Malériat, J.-P. Schlumpf, and F. Quéméneur
Université de Nantes, Nantes Atlantique Universités, Saint-Nazaire
Cedex, France

Abstract: The selectivity mechanism of transport of Na^+, Ca^{2+} and Mg^{2+} through commercial monovalent-cation permselective membranes is investigated in batch electrodialysis experiments with synthetic salt solutions containing monovalent and divalent cations. The role of hydration energy, steric effect, kinetic effect as well as effects of permselectivity of cation exchange membrane has been elucidated with electrodialysis of single solutions (NaCl, $CaCl_2$, $MgCl_2$). The mechanism of interferences is investigated in (Na^+/Ca^{2+}, Na^+/Mg^{2+}, Ca^{2+}/Mg^{2+} and $Na^+/Ca^{2+}/Mg^{2+}$) mixtures.

Keywords: Electrodialysis, monovalention, ion selective membranes, monovalent and divalent cations mixtures, competitive transport

INTRODUCTION

Traditionally, ion exchange membranes are classified into cation exchange membranes and anion exchange membranes depending on the type of ionic groups attached to the membrane matrix. Cation exchange membranes contain negatively charged groups fixed to the membrane backbone and

Received 23 May 2006, Accepted 10 December 2006

Address correspondence to L. Firdaous, Laboratoire des Procédés Biologiques, Génie Enzymatique et Microbien, ProBioGem UPRES EA 1026, Polytech' Lille, Boulevard Paul Langevin, Cité scientifique, Villeneuve d'Ascq, F-59655, France. E-mail: loubna.firdaous@univ-lille1.fr

allow the passage of cations but reject anions, while anion exchange membranes contain positively charged groups fixed to the membrane backbone and allow the passage of anions but reject cations.

Electrodialysis is a process by which ionic substances permeate through an ion exchange membrane in the presence of an electrochemical potential: to concentrate salt from diluate solution, to desalinate electrolytic solutions, to separate ionic from non-ionic susbstances, to exchange ions across a membrane, etc. A typical electrodialysis cell arrangement consists of a series of anion- and cation-exchange membranes arranged in an alternating fashion between an anode and a cathode to form individual cells. A cell consists of a volume with two adjacent membranes. If an aqueous salt solution is pumped through these cells and an elctrical potential is established between the anode and cathode, the positively charged cations migrate towards the cathode and the negatively charged anions towards the anode. Separation of cations from anions is efficient in electrodialysis. However, ion exchange membranes are generally used in solutions containing multiple ions: electrodialytic concentration and desalination of ionic salt solutions, removal of electrolytes from neutral solutes by electrodialysis, etc. In many cases, selective permeation of specific ions having the same charge through the membrane from a mixture is required. However, conventional ion exchange membranes are ineffective in separating ions having the same charge due to low permselectivity for specific ions. Therefore, various modifications of the ion exchange membranes and improved electrodialysis methods have been proposed and practiced.

For example, the development of monovalent-ion-permselective membranes began in the 1960s (1) with the salt production from sea water by Asahi Co. Since 1972, this technique has been performed in Japan according to a process which combines electrodialytic preconcentration using cationic and anionic membranes which are permselective toward monovalent ions, which allows concentration of NaCl and similtaneous retention of Mg^{2+}, Ca^{2+} and SO_4^{2-}, and crystallisation via vaccum evaporation.

Many attempts to prepare ion exchange membranes having permselectivity for specific ions and to find electrodialysis methods to achieve such a purpose have been performed. Some investigations were made to suppress the transport of divalent ions by introducing exchange groups with a strong affinity for these ions into the membranes (2–4). However, the current efficiency of the resulting membranes decreases due to the strong binding of the exchange groups to divalent cations which causes inactivation of exchange groups (4). Attempts were also made to decrease the charge density on the membrane surface, but results according to this method were ineffective (5, 6).

Since then, a lot of research to improve the permselectivity between ions in electrodialysis has been realized by Sata et al. (7–11) resulting in various membrane modification methods.

Stimulated by the development of new monovalent-ion-permselective membranes with better selectivity and lower electrical resistance, other applications of these permselective membranes apart from the initial edible salt production from sea water (12) have recently gained a broader interest in the removing (from brackich waters or groundwater) of harmful anions such as fluoride (13) or nitrate anions by developping nitrate ion permselective anion exchange membranes (14–16), separation of specific cations in industrial waste water treatment (17) and acid effluents, hydrometallurgy, etc.

However, despite a large number of studies on the modification of ion exchange membranes and electrodialysis methods to permeate specific ions through the membrane, until now not much systematic research has been performed on the investigation on the competitive ion transfer through these membranes.

Monovalent-ion-permselective membranes are, in general, used in solutions containing a number of ions, and permselectivity of ions through the membrane is different according to the ionic species. Monovalent-ion-permselective membranes are important in industry and of interest in academic studies.

The aim of this research is to analyse the mechanism of separation between cations (monovalent and multivalent) of monovalent-ion-permselective membranes, manufactured and commercialized for several electrodialysis applications. Our work is based on a systematic study involving a high number of electrodialysis separation tests.

EXPERIMENTAL

Membranes

Neosepta CMX-S and ACS from Tokuyama Soda Ltd. (Tokyo, Japan) were used. Their properties, given by the manufacturer, are in Table 1. CMX-S membranes are prepared by coating the surface of a standard membrane with a thin polyelectrolyte layer carrying positive charges. The structure of ACS membranes is composed of a PVC internal tissue giving mechanical stability to the membrane which is coated upon it via the so-called "paste

Table 1. Properties of the commercial ion exchange membranes, given by the manufacturer

	Cation exchange membrane	Anion exchange membrane
Trade name	Neosepta CMX-S	Neosepta ACS
Type	Strongly acidic	Strongly basic
Reinforcement	PVC	PVC
Electric resistance ($\Omega \cdot cm^2$)	1.8–3.8	3.0–6.0
Exchange capacity ($meq \cdot g^{-1}$)	1.5–1.8	1.4–2.0

method" (18). A highly cross-linked layer is then deposited according to procedures described in (19).

Equipment

The ED experiments were performed using a laboratory-scale electrodialyser (AQUALYZER P1, Corning EIVS, France). It is equipped with 2 graphite electrodes and a sheet-flow stack containing 20 cation- (CMX-S) and anion- (ACS) exchange membranes for a total membrane surface of $0.27\,m^2$, separated by spacer gaskets. The overall exposed surface area of each electrode was equal to $72.25\,cm^2$, while each geometrical surface area of the membrane was $69\,cm^2$.

The direct current generator could supply voltage and current in the ranges of 0–30 V and 0–5 A respectively. The diluate, concentrate, and electrode rinsing solutions were stored in 1.5 L PVC tanks and recirculated through the ED stack by means of 3 centrifugal pumps with a nominal capacity of $1.3\,m^3 \cdot h^{-1}$.

The basic experimental apparatus was equipped with additional apparatus for temperature, pH, and conductivity measurement.

Temperature was measured by thermocouples inserted in diluate and concentrate circulation tanks and was automatically controlled by varying the temperature of cooling glycol flowing through the coils inserted into each of the above three tanks. In Fig. 1 the experimental setup is displayed.

Experimental Procedure and Operating Conditions

Before starting each electrodialysis experiment, membranes were equilibrated for at least 24 hours with the feed solution. Solutions were realized with analytical-grade powders of NaCl, $CaCl_2$ and $MgCl_2$ dissolved in pure water (Elga, quality II, ISO 3696). All the experiments were conducted in a batch mode by continously recycling the diluate, concentrate and electrode rinsing stream with 1.3 L in each tank:

- The diluate containing the solution to be treated;
- The concentrate and electrode rinsing solution ($10\,g \cdot L^{-1}$ NaCl).

The flow rates were about $200\,L \cdot h^{-1}$. The temperatures were kept at a constant value of 25°C. All experiments were carried out at a constant voltage value of 30 V which corresponds to an initial current density equal to $20\,mA/cm^2$. The runs last 40 min because Na^+ and Cl^- ions are removed from the diluate.

Before applying the electrical field, the pH in each compartment, measured by means of Consort-P902 pHmeter, is controlled by adding a suitable quantity of concentrated NaOH or HCl solutions.

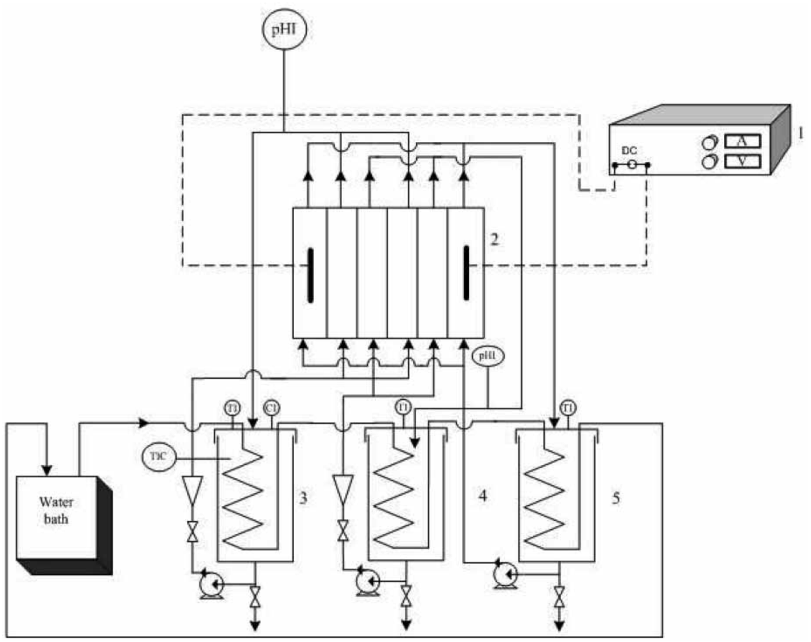

Figure 1. Scheme of the experimental set-up employed for the electrodialysis experiments. 1. power supply, 2. electrodialysis stack, 3. concentrate stream, 4. diluate stream, 5. electrode rinse solution. TI, pHI, CI: temperature, pH and Conductivity indicators.

During the run, the following parameters were recorded: the current (I), the voltage (U), the temperature (T), the conductivity (C), and pH-value (pH) of the diluate and concentrate solutions. Diluate and concentrate streams were sampled at regular time intervals during the course of each experiment for chemical anlysis (5 mL samples).

After each test, the membranes are washed according to the specific procedures reported in (24). The procedure is based on consecutive washings with deionized water, NaOH solution, deionized water, HCl solution and, once again, deionized water.

The physico-chemical characteristics of the studied cations are given in Table 2.

Analytical

For single solutions, ion concentrations were analysed by means of Tacussel-CDM 210 conductivity meter equipped with Radiometer CDC 641T electrode. The measured conductivities were related to salt concentration through calibration.

Table 2. Physico-chemical properties of the studied cations

Ion	Ionic radius (nm)	Hydrated ionic radius (nm)	Hydration energy ($KJ \cdot mol^{-1}$)
Na^+	0.095	0.365	407
Ca^{2+}	0.099	0.349	1584
Mg^{2+}	0.074	0.429	1921

For mixed solutions, concentrations of Na^+, Mg^{2+}, and Ca^{2+} were analysed using ion chromatography (Dionex DX 120) equipped with a CS12A column. The eluate was a solution of H_2SO_4 (14 mM) at flow rate of $1.2\ mL \cdot min^{-1}$.

The concentration of Cl^- was analyzed using ion chromatography (Dionex DX 120) equipped with an AS12A column. The eluate was a solution of $NaHCO_3/Na_2CO_3$ (0.3 Mm/2.7 mM) at a flow rate of $1.5\ mL \cdot min^{-1}$.

Corresponding ion fluxes through membranes were then calculated, in the stationary phase, from the concentration change with time (dC_{ion}/dt) in the diluate compartment:

$$J_{ion} = \frac{V(dC_{ion}/dt)}{A} \qquad (1)$$

where V is the volume of the circulated solution and A is the membrane area.

RESULTS AND DISCUSSION

Electrodialysis of Single Solutions

First, we studied transport of Na^+, Ca^{2+} and Mg^{2+} in each 6 aqueous salt solutions: NaCl ($0.194\ eq \cdot L^{-1}$), NaCl ($0.387\ eq \cdot L^{-1}$), $CaCl_2$ ($0.194\ eq \cdot L^{-1}$), $CaCl_2$ ($0.387\ eq \cdot L^{-1}$), $MgCl_2$ ($0.194\ eq \cdot L^{-1}$) and $MgCl_2$ ($0.387\ eq \cdot L^{-1}$). Fluxes values of theses cations obtained from single solutions electrodialysis are given in Table 3. The evolutions of the concentrations as a function of time have been plotted in Fig. 2.

Table 3. Fluxes of studied cations at two different concentrations

Ion	Flux ($0.194\ eq \cdot L^{-1}$) $10^8\ eq \cdot s^{-1} \cdot cm^{-2}$	Flux ($0.387\ eq \cdot L^{-1}$) $10^8\ eq \cdot s^{-1} \cdot cm^{-2}$
Na^+	16.9	26.5
Ca^{2+}	4.8	6.6
Mg^{2+}	2.6	3.1

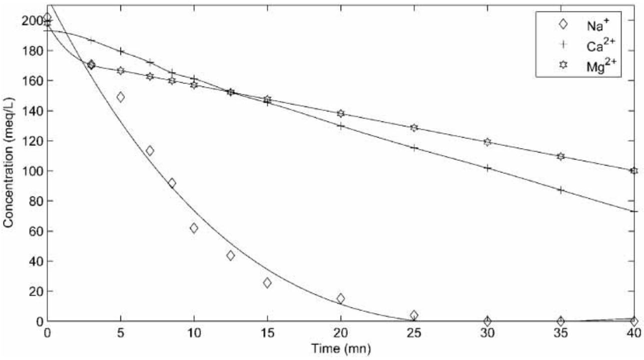

Figure 2. Evolution of Na^+, Ca^{2+} and Mg^{2+} concentrations in the diluate. Electrodialysis of NaCl ($0.194\ eq \cdot L^{-1}$), $CaCl_2$ ($0.194\ eq \cdot L^{-1}$), $MgCl_2$ ($0.194\ eq \cdot L^{-1}$).

For the two studied concentrations, ionic fluxes decrease in the sequence $J_{Na^+} > J_{Ca^{2+}} > J_{Mg^{2+}}$. Furthermore, Na^+, Ca^{2+} and Mg^{2+} transfer flux depends on concentration in the solution but fluxes are not in the ratio of concentrations.

These results are in agreement with those presented by other authors.

Diffusion Inside the Membranes

In their investigations of the selectivity of transport of sodium, calcium and magnesium ions through a heterogenous conventional sulfo-cationite membrane of the type MK-40L, Greben and Rodzik (20) attributed the order of cations decrease removal ($Na^+ > Ca^{2+} > Mg^{2+}$) to their hydration energy (410, 1592 and 1904 KJ/mol, respectively). Indeed, the hydrated cations would be parted from their hydration shell when they introduce the membrane network as proposed by Kotov et al. (21).

Furthermore, Horne (22) confirms the role of the hydration energy by linking the magnitude of hops of an ion with its hydration shell: the ratio (magnitude hydrated ion hop/magnitude no hydrated ion hop) is equal to 0.10, 0.14 and 5.65 for Na^+, Ca^{2+} and Mg^{2+}, respectively. Consequently, the hydrated ions Na^+ and Ca^{2+} would be severely handicapped in their diffusion inside the membrane compared to the dehydrated ions because of the friction of their hydration shell against the polymer matrix of the membrane confirming a diffusion of dehydrated ions depending on Na^+ and Ca^{2+} ions mobility. With a mobility value of $4.39 \cdot 10^{-9}\ cm^2V^{-1}s^{-1}$, Na^+ ions diffuse more easily than Ca^{2+} having a mobility equal to $1.07 \cdot 10^{-9}\ cm^2\ V^{-1}\ s^{-1}$. As for magnesium, strongly polarizing cation by its high charge and its weak ionic radius (0.074 nm), it would produce an electrostatic field sufficiently strong to immobilize it on the negative sites of the cation-exchange membrane, thus preventing it from jumping from site to site (Table 4). But

Table 4. Cation mobilities at 30°C in the cation exchange membrane [24]

Ion	Na^+	Ca^{2+}	Mg^{2+}
Mobility (10^9 cm^2 V^{-1}s^{-1})	4.39	1.07	0.91

the hydration shell would attenuate considerably the electric field on its surface, thereby facilitating the breakage of the electrostatic attraction forces, which would generate the migration of the hydrated Mg^{2+} ions by jumps from site to site with a flux remaining much lower than Ca^{2+} transfer flux due, particularly, to the friction of the hydration shell.

The role of the diffusion inside the membrane is confirmed by Van der Bruggen et al. (23) who carried out a comparative study between the behavior of unmodified membranes (AMV, CMV) and commercial monovalent-ion-permselective ones (ACS, CMS) in the case of single solutions. In their study, they showed that the transfer of the divalent ions is lower than that of the monovalent ones for the two types of membranes. This difference is pronounced in the case of selective membranes. Indeed, during electrodialysis, ions migrate with their hydration shells. Passing the solution-membrane interface requires to overcome an energy barrier caused by the necessity of a partial dehydration of ions (21). The effect of this barrier increases in the case of monovalent-ion-selective membranes since membrane modification is accompanied by hydrophobization of the membrane surface.

One can conclude that the cation transfer would result from the diffusion of the dehydrated Na^+ and Ca^{2+} cations and hydrated Mg^{2+} cations.

The Potential Barrier Effect

The CMX-S membranes owe their permselectivity towards monovalent ions to the presence of a thin positively charged polymeric layer, deposited on their surface. These positive charges enable rejection of divalent ions which have to face a higher electrostatic repulsion than that imposed to monovalent ions (24). That would reinforce the selectivity effect to the profit of Na^+ compared to Ca^{2+} and Mg^{2+} which would be added to the diffusion effects described previously. This is in agreement with the results obtained by Balster et al (25) who find a lower Ca^{2+} flux with the CMS membrane (positively charged coating membrane) compared to other membranes in spite of similar electric properties.

Another Assumption

To explain the weak transfer of Mg^{2+} could be a possible precipitation of $Mg(OH)_2$ resulting in a limited transfer of Mg^{2+}. According to this assumption, the limit of $Mg(OH)_2$ precipitation, calculated from its solubility product ($K_s = 10^{-11}$ $(mol/L)^3$), reaches at pH 8.5 a theoritical value of 1009 g/L of $MgCl_2$ higher than its solubility (550 g/L). As the limit of precipitation varies in opposite direction of the pH, one can affirm a fortiori that the risk of precipitation of $Mg(OH)_2$ is absent in our working area (pH 6.5 to 7.5 and a concentration of $38\ g \cdot L^{-1}$). Besides, one can be concerned with a possible local effect of Mg^{2+} and OH^- concentrationn in the polarization layer of the cation exchange membrane. However, the concentration of Mg^{2+} decreases at this interface. Concerning the possible water splitting at the interface, this phenomenon will enhance the transfer of H^+ ions towards the cathode, thereby eliminating any risk of a local increase of pH.

The Concentration Effect

Table 2 shows that the sensitivity of a cation transfer flux to its concentration in the solution decreases in the sequence $Na^+ > Ca^{2+} > Mg^{2+}$ since for concentration doubling, the ion transfer flux increases by 57% with Na^+, 38% with Ca^{2+} and only 19% with Mg^{2+}. This result suggests that the ion transfer would be a combination of two stages in series. The first would depend on the solution concentration (the crossing of the solution-membrane interface). The second would depend on the cations, physicochemical properties which would contribute to their transfer through the membrane and which would play an increasing part while going from Na^+ to Mg^{2+}: cations diffusion by jumps of site in site whose intensity would vary in opposite direction of their polarizing capacity.

Binary Mixtures

Transport properties of divalent and monovalent ions through monovalent selective ion exchange membranes can be affected by the mutual presence of monovalent and divalent ions in the solution. Hence, the influence of calcium and magnesium on the transfer of the sodium as well as interferences between these two divalent cations were successively examined in various physicochemical conditions. Three binary mixtures (prepared from two salts) have been studied: $NaCl/CaCl_2$ ($0.194\ eq \cdot L^{-1}$, $0.194\ eq \cdot L^{-1}$), $NaCl/MgCl_2$ ($0.194\ eq \cdot L^{-1}$, $0.194\ eq \cdot L^{-1}$) and $MgCl_2/CaCl_2$ ($0.194\ eq \cdot L^{-1}$, $0.194\ eq \cdot L^{-1}$). In these mixtures, combinations of various situations can be observed. Ion fluxes values, obtained in the stationary phase, for all studied systems are reported in Table 5.

Electrodialysis of NaCl-$CaCl_2$ Mixture

This system has been studied to understand the influence of a divalent cation Ca^{2+} on the transfer of Na^+ in the presence of the same co-ion Cl^-. Results

Table 5. Fluxes of studied cations in different ionic systems. Fluxes are expressed in 10^{-8} eq · s^{-1} · cm^{-2}

	Na^+	Ca^{2+}	Mg^{2+}
NaCl	16.9	—	—
$CaCl_2$	—	4.8	—
$MgCl_2$	—	—	2.6
$NaCl/CaCl_2$	11.4	4.6	—
$NaCl/MgCl_2$	8.7	—	2.5
$CaCl_2/MgCl_2$	—	2.4	1.2
$NaCl/CaCl_2/MgCl_2$	10.9	2.4	1.1

obtained with this system are represented in Fig. 3. In this figure, Na^+ transfer flux decreases with its concentration in diluate progressively with the advance of electrodialysis. On the contrary, Ca^{2+} shows a constant transfer flux independent on its concentration decrease. Furthermore, one can note three transfer phases for Na^+:

- A transitory phase of 3 mn (variation compared to the linear phase of decrease) which would correspond to a supplement transfer of Na^+.
- A stationary phase between 3 and 20 mn where we find a transfer flux of Na^+ independent on the concentration and reduced of 33% (11.4. 10^{-8} eq · s^{-1} · cm^{-2} instead 16.9 · 10^{-8} eq·s^{-1}·cm^{-2}) compared to NaCl single solution. It seems that Na^+ transfer is hampered by Ca^{2+} cations.
- Finally, a last asymptotic phase of Na^+ decrease flux. Na^+ are mainly eliminated, leaving in the solution a $CaCl_2$ system. We can note in this phase of

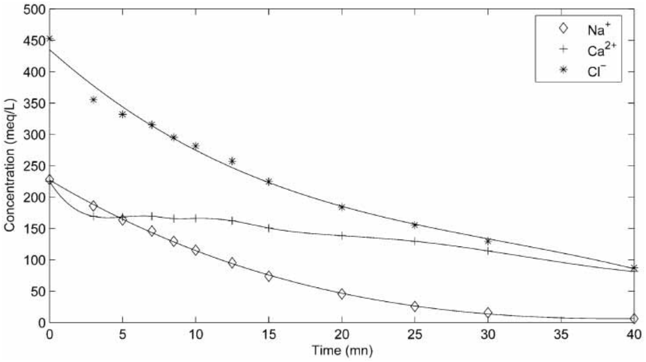

Figure 3. Evolution of Na^+, Ca^{2+} and Cl^- concentrations in the diluate. Electrodialysis of 0.194 eq · L^{-1} NaCl + 0.194 eq · L^{-1} $CaCl_2$.

transfer that Ca^{2+} flux ($4.6 \cdot 10^{-8}$ eq $\cdot$ s^{-1} $\cdot$ cm^{-2}) is close to that of Ca^{2+} in $CaCl_2$ single solution ($4.8 \cdot 10^{-8}$ eq $\cdot$ s^{-1} $\cdot$ cm^{-2}).

For Ca^{2+}, we distinguish 2 stages in the transfer: a transitory stage of 3 min, corresponding to a supplement transfer of Ca^{2+}, followed by a linear stationary phase in the last 30 minutes.

The comparison between the transfer fluxes in the single solutions $CaCl_2$ (0.194 eq $\cdot$ L^{-1}), $CaCl_2$ (0.387 eq $\cdot$ L^{-1}) and in the mixture $NaCl/CaCl_2$ (0.194 eq $\cdot$ L^{-1}, 0.194 eq $\cdot$ L^{-1}) shows that the Ca^{2+} flux is slightly decreased by the presence of Na^+ and slightly sensitive to Ca^{2+} concentration in the solution. Conversly, the comparaison of transfer fluxes in the systems NaCl (0.194 eq $\cdot$ L^{-1}), NaCl (0.387 eq $\cdot$ L^{-1}) and $NaCl/CaCl_2$ (0.194 eq$\cdot$$L^{-1}$, 0.194 eq $\cdot$ L^{-1}) shows that Na^+ transfer flux undergoes an important abatement by the only presence of Ca^{2+}. As described above, CMX-S membranes owe their particular permselectivity to the presence of a thin surface layer of a polymer carrying positive fixed charges which hampers the passing through of divalent cations. Furthermore, the higher dehydration energy for Ca^{2+} cations would impose them a supplementary handicap even though the difference between Na^+ and Ca^{2+} transfer fluxes should be more important with the mixture. But one constate that the presence of Na^+ cations does not influence the Ca^{2+} transfer flux (-4%) and conversly, the presence of Ca^{2+} cations decreases greatly the Na^+ transfer flux (-33%).

This behavior could be the result of the higher electrostatic attraction of Ca^{2+} than Na^+ with the negative fixed charge sites of the cation exchange membrane:

- Ca^{2+} cation with a radius of 0.099 nm and a charge $+2$ is obviously more polarizing that Na^+ with a radius of 0.095 nm and a charge $+1$.
- Chapotot et al (26) showed that divalent cations are prefered by CEMs because of their higher electrostatic attraction with the oppositely fixed charge sites, if no driving force was applied.

The great affinity of Ca^{2+} to the exchange groups of the cation exchange membrane would allow them to occupy a great part of the exchange transfer sites which explains, on the one hand, the weak sensitivity of the Ca^{2+} transfer flux to the presence of Na^+ cations in the solution and the second hand, the sensitivity of Na^+ cations to the presence of Ca^{2+} since they would be affected by a reduction of the number of available exchange sites to their transfer. The great affinity of Ca^{2+} cations to the negative sites of the cation exchange membrane impose them a higher retention time t_r than Na^+ cations. As a result, Ca^{2+} transfer flux would be highly sensitive to the number of the occupied transfer sites. Thus, one can write:

$$flux_{ions} = constante \times \frac{[sites]}{t_r} \qquad (2)$$

Conversly, the weak affinity of Na^+ cations to the ion exchange groups favor them a low retention time which would compensate the small number of available sites for their transfer. This is in agreement with observations made by Balster et al (25) who report that a higher membrane fixed charge density increases the Ca^{2+} transfer flux. They add that this attraction, which increases with increasing charge density of the membrane, seems to have a strong influence on the Ca^{2+} transport through the membrane also when an electric current is applied. On the basis of this assumption, one could understand that the Ca^{2+} transfer flux increases slightly from 25 mn since the removal of Na^+ cations would release new avilable exchange sites for the Ca^{2+} transport.

One could explain the quasi independence of the Ca^{2+} transfer flux on its concentration in solution by the high retention time which would attribute to the cation diffusion through the macromolecular network the role of limiting factor compared to the crossing of the solution-membrane interface.

Electrodialysis of NaCl-$MgCl_2$ Mixture

This mixture has been studied to further elucidate the effect of a divalent cation Mg^{2+} on the transfer of a monovalent cation Na^+. The evolution of the concentrations vs time has been plotted in Fig. 4. As for the mixture $NaCl/CaCl_2$ ($0.194\ eq \cdot L^{-1}$, $0.194\ eq \cdot L^{-1}$), the figure shows a decreasing Na^+ transfer flux as soon as the electrodialysis advances. The concentration curves of the $NaCl/MgCl_2$ system are very similar to the $NaCl/CaCl_2$ ones but they are better characterized. Particularly, Mg^{2+} shows a constant transfer flux, perfectly independent on the concentration with a value very

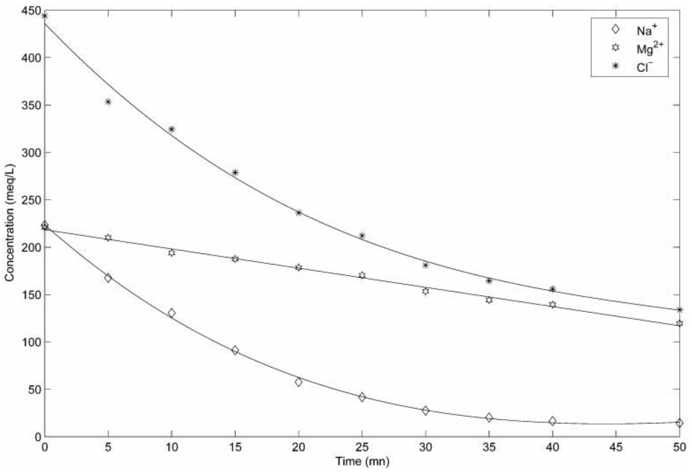

Figure 4. Evolution of Na^+, Mg^{2+} and Cl^- concentrations in the diluate. Electrodialysis of $0.194\ eq \cdot L^{-1}$ NaCl + $0.194\ eq \cdot L^{-1}$ $MgCl_2$.

close to that in the $MgCl_2$ single solution. The transfer of Cl^-, naturally limited by the electroneutrality, is the sum of the two cations fluxes.

The comparison of Na^+ transfer fluxes in the systems NaCl ($0.194\,eq \cdot L^{-1}$) and $NaCl/MgCl_2$ ($0.194\,eq \cdot L^{-1}$, $0.194\,eq \cdot L^{-1}$) shows that Mg^{2+} ions exercise a strong inhibitive action on the Na^+ transfer more important than with Ca^{2+} in $NaCl/CaCl_2$ ($0.194\,eq \cdot L^{-1}$, $0.194\,eq \cdot L^{-1}$). Indeed, the ratio of Na^+ transfer fluxes in $NaCl/CaCl_2$ ($0.194\,eq \cdot L^{-1}$, $0.194\,eq \cdot L^{-1}$) and NaCl ($0.194\,eq \cdot L^{-1}$) $J_{Na} + (NaCl/CaCl_2$, 0.194/0.194)/ $J_{Na} + (NaCl$, 0.194) is equal to 0.67 while it falls to 0.51 with the system $NaCl/MgCl_2$ ($0.194\,eq \cdot L^{-1}$, $0.194\,eq \cdot L^{-1}$). The reason of this behavior could be the fact that Mg^{2+} cations are more polarizing than Ca^{2+} ones: Mg^{2+} has a radius equal to 0.074 nm against a radius of 0.099 nm for Ca^{2+} for the same charge $+2$ what would attribute to the Mg^{2+} cations a stronger affinity than Ca^{2+} for the exchange groups of the cation exchange membrane. Consequently, the Mg^{2+} behavior compared to the Na^+ cations would be *more contrasted* than with the Ca^{2+}. With a stronger affinity, Mg^{2+} would monopolize practically all the transfer sites (more significantly than Ca^{2+} cations): this is why the Na^+ transfer flux is even more weak that with Ca^{2+} and the Mg^{2+} transfer flux is not sensitive to the presence of Na^+ (the Mg^{2+} transfer flux is reduced from $2.6 \cdot 10^{-8}\,eq \cdot s^{-1} \cdot cm^{-2}$ to $2.5 \cdot 10^{-8}\,eq \cdot s^{-1} \cdot cm^{-2}$).

The very low sensitivity of the Mg^{2+} transfer flux to its concentration would be the result of *a rate of crossing* of the double electrostatic barrier-dehydration on the level at the solution-membrane interface not very determining in the Mg^{2+} transfer rate compared to the slower Mg^{2+} diffusion which would impose its kinetic.

At the end of the Na^+ electrodialysis, the increase of Mg^{2+} transfer flux, which would be due to the released transfer sites by the Na^+ removal, would be compensated by a flux reduction at the solution-membrane interface resulting from the division of $MgCl_2$ concentration by 2. But this double phenomenon would concern only one marginal Mg^{2+} quantity because of the high activation energy of Mg^{2+} in the crossing of the electrostatic repulsion barrier. However, asymptotic evolution of Na^+ concentration with the time shows that Na^+ migration in the solution remains a limiting factor in the Na^+ transfer.

Electrodialysis of $CaCl_2$-$MgCl_2$ Mixture

This system has been studied to observe the interferences between two divalent cations Ca^{2+} and Mg^{2+}. The obtained results with this mixture are represented on Fig. 5. With this system, we also observe a transitory phase of 3 mn for the two cations corresponding to a Ca^{2+} and Mg^{2+} surplus transfer. The shape of the curves in the stationary phase is practically the same for the two cations Ca^{2+} and Mg^{2+}, suggesting a similar behaviour of these cations with a difference in the intensity of the transfer.

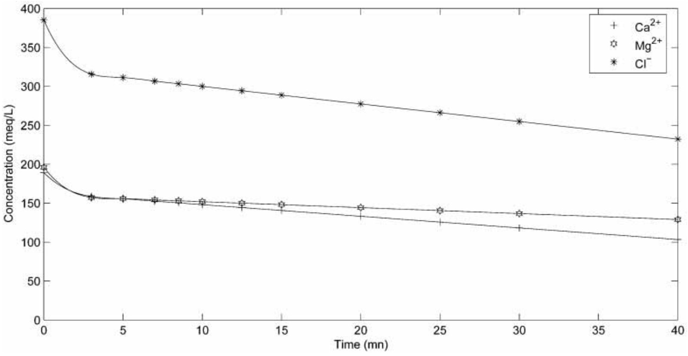

Figure 5. Evolution of Ca^{2+}, Mg^{2+} and Cl^- concentrations in the diluate. Electrodialysis of $0.194\ eq \cdot L^{-1}$ $CaCl_2 + 0.194\ eq \cdot L^{-1}$ $MgCl_2$.

The comparison of transfer fluxes in the single solutions $CaCl_2$ ($0.194\ eq \cdot L^{-1}$), $MgCl_2$ ($0.194\ eq \cdot L^{-1}$) and in the mixture $CaCl_2/MgCl_2$ ($0.194\ eq \cdot L^{-1}$, $0.194\ eq \cdot L^{-1}$) shows that Ca^{2+} and Mg^{2+} transfer fluxes are divided by two but with a higher relative abatement with Mg^{2+} $(2.6/1.2) = 2.2$ compared to Ca^{2+} $(4.8/2.4) = 2$. As described above, Ca^{2+} and Mg^{2+} have both a strong affinity to the negative fixed charge sites of the cation exchange membrane. When mixed together, the macromolecular network sites dividing between Ca^{2+} and Mg^{2+} should change. It would be more equilibrated than with Na^+ in both binary systems $NaCl/CaCl_2$ ($0.194\ eq \cdot L^{-1}$, $0.194\ eq \cdot L^{-1}$) and $NaCl/MgCl_2$ ($0.194\ eq \cdot L^{-1}$, $0.194\ eq \cdot L^{-1}$) but with an advantage with the Mg^{2+} which should occupy more exchange sites than Ca^{2+} due to its great affinity to negative fixed charge of the membrane. However the retention time in expression 2 would reverse the ratio of transfer fluxes. Indeed the migration of Ca^{2+} cations, being done without the hydration shell, would be faster than the hydrated Mg^{2+} cations subjected to more significant frictions as can be seen in their single solutions where they have the same number of the exchange sites respectively whereas the Mg^{2+} transfer flux is definitely lower than Ca^{2+}.

The weak concentration effect on the respective Mg^{2+} and Ca^{2+} transfer fluxes in their single solutions shows that the crossing of the solution-membrane interface should play a minor role with however an advantage for the Ca^{2+} cations.

Ternary Mixture

In order further to emphasize the specific effects related to ion characteristics when mixed together, we studied the ternary mixture $NaCl/CaCl_2/MgCl_2$ ($0.129\ eq \cdot L^{-1}$, $0.129\ eq \cdot L^{-1}$, $0.129\ eq \cdot L^{-1}$) (a system containing a monovalent cation and two divalent cations) with a total salt concentration of $0.387\ \mathrm{eq \cdot L^{-1}}$.

In Fig. 6, ions concentration (Na^+, Ca^{2+}, Mg^{2+} and Cl^-) in the diluate are represented vs time. In this mixture, we distinguish clearly two phases of mobile cation transfer; a first fast phase with a Na^+ transfer flux equal to $10.9 \cdot 10^{-8}\ \mathrm{eq{\cdot}s^{-1} \cdot cm^{-2}}$ located between fluxes observed in the $NaCl/CaCl_2$ and $NaCl/MgCl_2$ systems and a second asymptotic phase translating the Na^+ depletion in the solution. As regards the rejected cations, after a transitory stage of 3 mn, a transfer flux can be noted equal to $2.4 \cdot 10^{-8}\ \mathrm{eq \cdot s^{-1} \cdot cm^{-2}}$ for Ca^{2+} and a transfer flux equal to $1.1 \cdot 10^{-8}\ \mathrm{eq \cdot s^{-1} \cdot cm^{-2}}$ for Mg^{2+}, both perfectly constant in the time. The comparaison of Ca^{2+} and Mg^{2+} transfer fluxes in the binary system $CaCl_2/MgCl_2$ ($0.194\ \mathrm{eq \cdot L^{-1}}$, $0.194\ \mathrm{eq \cdot L^{-1}}$) and the ternary mixture $NaCl/CaCl_2/MgCl_2$ ($0.129\ \mathrm{eq \cdot L^{-1}}$, $0.129\ \mathrm{eq \cdot L^{-1}}$, $0.129\ \mathrm{eq \cdot L^{-1}}$) shows that Ca^{2+} transfer flux remains the same ($2.4 \cdot 10^{-8}\ \mathrm{eq{\cdot}s^{-1}{\cdot}cm^{-2}}$) despite the presence of Na^+ and the salt concentration variation ($0.129\ \mathrm{eq \cdot L^{-1}}$ instead $0.194\ \mathrm{eq \cdot L^{-1}}$) and the Mg^{2+} transfer flux decreases slightly ($1.2 \cdot 10^{-8}\ \mathrm{eq \cdot s^{-1} \cdot cm^{-2}}$ to $1.1 \cdot 10^{-8}\ \mathrm{eq \cdot s^{-1} \cdot cm^{-2}}$) which demonstrate that the rejected cations flux would not depend greatly on crossing of the solution-membrane interface.

Dividing the Na^+ concentration by 2 in the single solution involves a transfer flux reduction equal to 36%. Thus theoretically a concentration of $0.194/2 = 0.097\ \mathrm{eq \cdot L^{-1}}$ should give a transfer flux equal to $10.8. 10^{-8}\ \mathrm{eq \cdot s^{-1} \cdot cm^{-2}}$. In the Na^+, Ca^{2+} and Mg^{2+} system, one finds this Na^+ flux value but with a concentration of $0.129\ \mathrm{eq \cdot L^{-1}}$. Thus the Na^+ flux is decreased by the presence of the rejected cations Ca^{2+} and Mg^{2+} which would play an inhibiting role. This behavior could be explained by a monopolization of the transfer sites by Ca^{2+} and Mg^{2+} not compensated by the high diffusion rate of Na^+ as in the $NaCl/CaCl_2$ and $NaCl/MgCl_2$

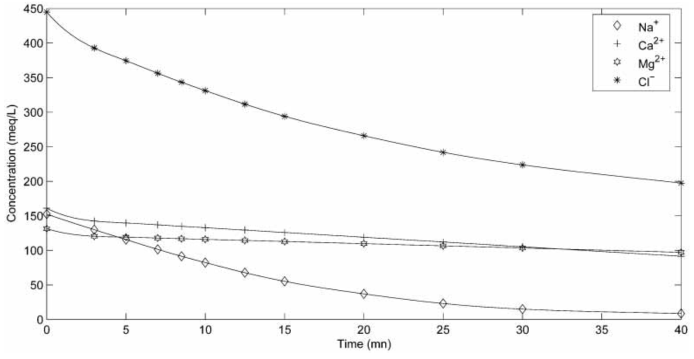

Figure 6. Evolution of Na^+, Ca^{2+}, Mg^{2+} and Cl^- concentrations in the diluate. Electrodialysis of $0.129\ \mathrm{eq \cdot L^{-1}}$ $NaCl$ + $0.129\ \mathrm{eq \cdot L^{-1}}$ $CaCl_2$ + $0.129\ \mathrm{eq \cdot L^{-1}}$ $MgCl_2$.

binary systems. The NaCl/MgCl$_2$ (0.129 eq $\cdot$ L^{-1}, 0.129 eq $\cdot$ L^{-1}) system should provide a Na$^+$ transfer flux lower than $8.7 \cdot 10^{-8}$ eq $\cdot$ s^{-1} $\cdot$ cm^{-2}. One can note that the contribution of CaCl$_2$ with a concentration equal to 0.129 eq $\cdot$ L^{-1} increases the Na$^+$ transfer flux at $10.9 \cdot 10^{-8}$ eq$\cdot$s^{-1} $\cdot$ cm^{-2}. The Ca^{2+} cations, less attached than Mg^{2+} to the negative exchange sites of the membrane network, would allow an unbalanced division of sites in favour of the Na$^+$ cations. In conclusion, Mg^{2+} would block the transfer sites for them.

CONCLUSION

The main purpose of the experimental study done was to understand the mechanism according to which divalent-ion repulsion takes place in commercial monovalent-cation-permselective membranes (Neosepta CMX-S by Tokuyama Soda Co). These membranes owe their particular permselectivity to the presence of a thin surface layer of the same charge of the permeating cations which hampers the passing through of plus valent cations owing to electric repulsion forces. Different experimental behaviours have been observed and well characterized between Na$^+$ on the one hand and the Ca^{2+}, Mg^{2+} cations on the other hand.

- A very low sensitivity of Ca^{2+} and Mg^{2+} transfer fluxes to the presence of Na$^+$ in the solution. Conversly, a strong abatement of Na$^+$ transfer flux involved by the presence of Ca^{2+} and Mg^{2+} in solution.
- A very low sensitivity of Ca^{2+} and Mg^{2+} transfer fluxes to their concentration in the solution contrary to Na$^+$ whose transfer flux is very sensitive to its concentration in solution.
- Always with Ca^{2+} and Mg^{2+}, a very strong effect of mutual abatement of their mutual respective transfer fluxes.

The principal phenomenon governing the transfer of Ca^{2+} and Mg^{2+} cations would be the cation diffusion through the ion exchange membrane macromolecular network, controlled by the strong affinity to the negative exchange sites of the membrane. This effect would impose its transfer rate (the slowest) in a process with two stages in series: the crossing of the electrostatic barrier followed by the diffusion through the macromolecular network. This strong affinity for the sites would reduce the number of sites used by the Na$^+$ cations.

The Na$^+$ cations, which remain sensitive to the concentration in solution, would profit from a weak repulsion energy at the solution-membrane interface and from a weak affinity towards the negative exchange sites, therefore of a great mobility from which a large diffusivity compensating the low number of available sites for their transfer, what would enable them to maintain a transfer flux higher than the two other cations.

In conclusion, the effect of electrostatic repulsion is not the only phenomenon nor even most significant of the Ca^{2+} and Mg^{2+} transport. And paradoxically, it should play with the Na^{+} cations a role relatively larger compared to internal diffusion.

REFERENCES

1. Nishiwaki, T. (1972) *Industrial Process with Membranes*; Wiley-Interscience: New York.
2. Onoue, Y., Mizutani, Y., Yamane, R., and Takasaki, Y. (1961) Studies on ion exchange membranes. II. Selectivity of cation exchange membranes for NaCl-$CaCl_2$ system. *J. Electrochem. Soc. Jpn*, 30: 155.
3. Yamane, R., Mizutani, Y., and Onoue, Y. (1961) Studies on ion exchange membranes. IV. Permselectivity of Anion Exchangers for NaCl-Na_2SO_4 System. *J. Electrochem. Soc. Jpn*, 30: 220.
4. Sata, T., Yoshida, T., and Matsusaki, K. (1996) Transport properties of phosphonic acid and sulfonic acid cation exchange membranes. *Journal of Membrane Science*, 120: 101.
5. Hani, H., Nishihara, A., and Oda, Y. (1961) Cation exchange membrane having permselectivity between cations with different valency. Japan Pat. 3164.
6. Mihara, K., Misumi, T., Yamagoshi, Y., and Tsuzura, K. (1969) Preparation method of cation exchange membrane. Japan Pat. 8985.
7. Sata, T. (1994) Studies on ion exchange membranes with permselectivity for specific ions in electrodialysis. *Journal of Membrane Science*, 93: 117.
8. Sata, T., Yamaguchi, T., and Matsusaki, K. (1995) Effect of hydrophobicity of ion exchange groups of anion exchange membranes on permselectivity between two anions. *J. Phys. Chem.*, 99: 12875.
9. Sata, T., Teshima, T., and Yamaguchi, T. (1996) Permselectivity between two anions in anion exchange membranes crosslinked with various diamines in electrodialysis. *Journal of Polymer Science*, 34: 1475.
10. Sata, T. (2000) Studies on anion-exchange membranes having permselectivity for specific anions in electrodialysis—effect of hydrophilicity of anion exchange membranes on permselectivity of anions. *Journal of Membrane Science*, 167: 1.
11. Sata, T., Sata, T., and Yang, W. (2002) Studies on cation-exchange membranes having permselectivity between cations in electrodialysis. *Journal of Membrane Science*, 206: 31.
12. Tomita, A. (1988) Salt and chlor-alkali plant in Kuwait by all membrane process. Nippon Kaisui Gakkaishi. *Bull. Soc. Sea Water Sci. Jpn*, 42: 28.
13. Amor, Z., Malki, S., Taky, M., Bariou, B., Mameri, N., and Elmidaoui, A. (1998) Optimization of fluoride removal from brackich water by electrodialysis. *Desalination*, 120: 263.
14. Korose, K., Janowski, F., and Shapshnik, V.A. (1997) Highly effective electrodialysis for selective elimination of nitrates from drinking water. *Journal of Membrane Science*, 127: 17.
15. Oldani, M., Killer, E., Miquel, A., and Schock, G. (1992) On the nitrate and monovalent cation selectivity of ion exchange membranes used in drinking water purification. *Journal of Membrane Science*, 75: 265.

16. Hell, F., Lahnsteiner, J., Frischherz, H., and Baumgartner, G. (1998) Experience with full-scale electrodialysis for nitrate and hardness removal. *Desalination*, 117: 173.
17. Saracco, G., Zanetti, M.C., and Onofrio, M. (1993) Novel application of monovalent-anion- permselective membranes to the recovry treatment of an industrial wastewater by electrodialysis. *Ind. Eng. Chem. Res.*, 32: 657.
18. Mizutani, Y. (1990) Ion exchange membranes with preferential permselectivity for monovalent ions. *Journal of membrane Science*, 54: 233.
19. Yamane, R., Mizutani, Y., Motomura, H., and Izuo, R. (1964) Studies on ion exchange membranes. XXI. Preparation of SO_4^{2-} non-permselective anion exchange membranes. *J. Electrochem. Soc. Jpn*, 32: 134.
20. Greben, V.P. and Rodzik, I.G. (2005) Selectivity of transport of sodium, magnesium and calcium ions through a sulfo-cationite membrane in mixtures of solutions of their chlorides. *Russian Journal of Electrochemistry*, 41: 888.
21. Kotov, K.K., Peregonchaya, O.V., and Selemenev, V.F. (2002) Electrodialysis of binary electrolyte mixtures with membranes modified by organic species. *Russian Journal of Electrochemistry*, 38: 927.
22. Horne, R. (1969) *Marine Chemistry*; Wiley: New York.
23. Van der Bruggen, B., Koninckx, A., and Vandcasteele, C. (2004) Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration. *Water Research*, 38: 1347.
24. Saracco, G. (1997) Transport properties of monovalent-ion-permselective membranes. *Chemical Engineering Science*, 52: 3019.
25. Balster, J., Krupenko, O., Pnt, I., Stamatialis, D.F., and Wessling, M. (2005) Preparation and characterisation of monovalent ion selective cation exchange membranes based on sulphonated polyether ether ketone). *Journal of Membrane Science*, 263: 137.
26. Chapotot, A., Pourcelly, G., and Gavach, C. (1994) Transport competition between monovalent and divalent cations through cation-exchange membranes. Exchange isotherms and kinetic concepts. *Journal of Membrane Science*, 96: 167.