

A mathematical model of multicomponent mass transfer in electro dialysis

L. Firdaous^{1*}, T. Saheb, J-P. Schlumpf¹, J-P. Malériat¹, P. Bourseau² and P. Jaouen¹

¹ GEPEA UMR-CNRS 6144, 37 boulevard de l'université, BP 406, 44602 Saint-Nazaire Cedex, France

² LT2E, Rue Saint Maudé Lorient, 56321 Lorient Cedex, France

*loubna.firdaous@univ-nantes.fr

Abstract

A mathematical model has been developed which describes the mass transfer across monovalent-ion-permselective membranes as used in an electro dialysis cell. The mass transfer model is based on the Stefan-Maxwell transport equations. The latter are derived in the membrane phase with two unstirred layers on each side. Donnan equilibrium is used to describe the concentration and the potential discontinuity on the membrane-solution interface by means of sorption measurements. The combination of the mass transfer model and the equilibrium model enables the prediction of concentration and potential profiles across the electro dialysis stack once the model parameters are available which are obtained from literature, separate experiments or existing correlations.

Keywords : Electro dialysis; Modelling; Stefan-Maxwell theory

1 Introduction

Electro dialysis is a process by which ionic substances with molecular weight below several hundreds dalton permeate through a membrane in the presence of an electrochemical potential : to concentrate salt from dilute solution, to desalinate electrolytic solutions, to separate ionic from non-ionic substances, to exchange ions across a membrane, etc. The principle of this technique is illustrated in Figure 1 which shows a schematic representation of a typical electro dialysis cell arrangement consisting 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 electrical potential is established between the anode and cathode, the positively charged cations migrate

towards the cathode and the negatively charged anions towards the anode. The cations pass easily through the negatively charged cation-exchange membrane but are retained by the positively charged anion-exchange membrane. Likewise, the negatively charged anions pass through the anion-exchange membrane, and are retained by the cation-exchange membrane. Separation of cations from anions is efficient in

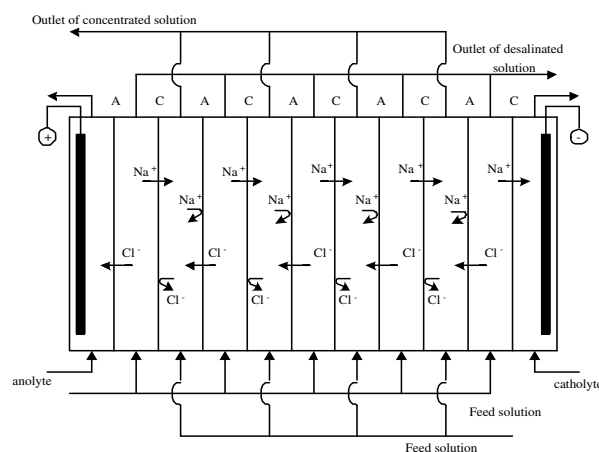


Figure 1: Schematic diagram illustrating the principle of an electro dialysis stack. C : Cation exchange membrane; A : anion exchange membrane.

electro dialysis. However, in many cases, selective permeation of specific ions, having the same charge, through the membrane from a mixture is required. Therefore various modifications of the ion exchange membrane have been proposed and practiced, like ion exchange membranes having monovalent ion permselectivity [14, 15]. Electro dialysis through these membranes has found a wide range of applications such as edible salt production from sea water [18], selective demineralization of brackish and saltwaters [10] and acid effluents treatment. Even though they are widely used in practice, the understanding and modelling of their mass transfer behaviour has

not yet been completely elucidated.

To supply theoretical explanation of monovalent-ion-permselective membrane phenomena, Nikonenko et al [11] proposed a model based on the Nernst-Planck equations. To take into account surface modification, they introduced phenomenological conductivity coefficients. Saracco et al [12, 13] analysed transport phenomena through these membranes on the basis of a combination of both a kinetic approach and the conventional solution-diffusion approach. In this paper, we describe our attempts to model an electro dialysis process on the basis of the non-equilibrium thermodynamics.

2 Process model

2.1 Schematic description of the membrane flux model

Figure 2 shows a scheme of the membrane system. The system under study consists of five main regions : two stagnant film-layers and two equilibrium points, on either side of the membrane, and the membrane itself. The two bulk regions contain the boundary conditions, which are the known concentrations. The situation is one-dimensional with Z , the direction of transport.

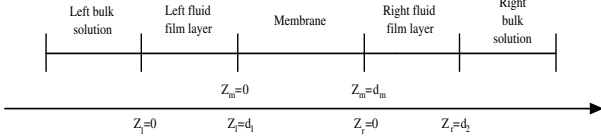


Figure 2: Schematic picture of the membrane flux model

2.2 Transport equations

To model the movement of ions and water in multi-component electrolyte-membrane system considered, we have chosen to apply the Stefan-Maxwell theory to our system. Transport equations according to this theory allow to include the effect of non-idealities in the chemical potential gradients and ion-ion friction interactions into the mass transfer model. For an n component mixture, for each component i , the Stefan-Maxwell equation can be formulated, which can be represented as [17] :

$$c_i \nabla \mu_{T,P} = RT \sum_{j=1}^n \frac{c_i c_j}{c_T D_{i,j}} (v_j - v_i) = RT \sum_{j=1}^n \frac{x_i N_j - x_j N_i}{D_{i,j}} \quad (1)$$

The left hand side of equation 1 represents all driving forces exerted on a species i in the system, the right hand side contains the friction forces between the species i and other moving species in the system. The set of Stefan-Maxwell equations for n components was re-written by Hogendoorn et al [5] in such a way that the current density can be used as an input parameter in the model. The resulting transport equations leading to $(n-2)$ independent Stefan-Maxwell equations are [5] :

$$(N) = [A](\nabla C) - [\beta]C \quad (2)$$

here N is the matrix of fluxes, the contents of the matrices A and β are given in the appendix. Only $(n-2)$ fluxes could be obtained by equation 2, hence, more relations and constraints are needed. Electroneutrality in the diffusion film :

$$\sum_{i=1}^n z_i c_i = 0 \quad (3)$$

Electroneutrality inside the membrane :

$$\sum_{i=1}^n z_i c_i + z_m c_m = 0 \quad (4)$$

The volume continuity equation in the diffusion film :

$$\sum_{i=1}^n \bar{V}_i c_i = 1 \quad (5)$$

The volume continuity equation inside the membrane :

$$\sum_{i=1}^n \bar{V}_i c_i + \bar{V}_m c_m = 1 \quad (6)$$

Electrical current density expression :

$$I = \mathcal{F} \sum_i z_i N_i \quad (7)$$

Finally, for each component there is a component mass balance. Under the steady state assumption, the equation of continuity is :

$$\nabla N_i = 0 \quad (8)$$

To solve the system of Eqs. (2)-(8), it is easier to use dimensionless variables. To this end the following relations are used:

$z' = \frac{z}{\delta}$	$c' = \frac{c}{c_0}$	$[A'] = \frac{[A]}{D_0}$
$[\beta'] = \frac{\delta}{D_0} [\beta]$	$\tau = \frac{D_0 t}{\delta^2}$	$(N') = \frac{\delta}{c_0 D_0} (N)$

To describe the transport through the all membrane system, the set of differential equations have to be expressed in diffusion film layers and the membrane and need to be linked to each other by means of the interfacial equilibrium. On the boundary between the fluid film and the membrane, a thermodynamic equilibrium is assumed. Then, for each species, we can define an electrochemical equilibrium between liquid and membrane phase :

$$\mu_i^{0m} + RT \ln a_i^m + z_i \mathcal{F} \phi^m = \mu_i^{0s} + RT \ln a_i^s + z_i \mathcal{F} \phi^s \quad (9)$$

Rearranging of equation 9 gives the electrical potential difference between the membrane and the adjacent solution to :

$$\phi^m - \phi^s = \frac{RT}{z_i \mathcal{F}} \ln \frac{a_i^s}{a_i^m} = \phi_{Don} \quad (10)$$

ϕ_{Don} is the potential difference between the membrane and the solution and referred to as Donann potential [2]. Equation 10 permits to describe distribution of ions at the interface between the solution and the membrane. Given the multicomponent character of the electro dialysis electrolytes and the membranes phase, the activity coefficients of the individual ions were evaluated by the multicomponent Bromley model [1] :

$$\log_{10} \gamma_i = \frac{-0.509 z_i^2 \sqrt{I}}{1 + \sqrt{I}} + F_i \quad (11)$$

For a specific cation C and an anion A , the term F_i becomes :

$$F_C = \sum_a \left(\frac{(0.06+0.6B_{ca})|z_c z_a|}{\left(1+\frac{1.5I}{|z_c z_a|}\right)^2} + B_{ca} \right) \left(\frac{z_c + |z_a|}{2} \right)^2 m_a$$

$$F_A = \sum_c \left(\frac{(0.06+0.6B_{ca})|z_c z_a|}{\left(1+\frac{1.5I}{|z_c z_a|}\right)^2} + B_{ca} \right) \left(\frac{z_c + |z_a|}{2} \right)^2 m_c$$

Here B_{ca} is the Bromley constant of the electrolyte under consideration and I is the ionic strength. To describe mass transport in aqueous phase, the film thickness of the polarisation layer must be known and depends on the flow rate. We evaluated it, in our case, by the correlation presented in [16] :

$$Sh = 1.9 Re^{1/2} Sc^{1/3} \left(\frac{h}{\Delta l} \right)^{0.5} \quad (12)$$

The model equations involves a set of non-linear equations. To overcome discontinuity occurring on the membrane-solution interface, the numerical resolution

strategy is as follows. Equations were solved numerically in the individual sections by an implicit finite difference method using the following boundary conditions :

- Bulk concentrations of the left- and right-side electrolytes,
- at the phase transition between the fluid film and the membrane, equation 10 and sorption measurements results were used to describe distribution of ions at the interface. The membrane water concentration at interfaces was calculated as a function of the external salt concentration. Besides, the volume continuity (5, 6) , electroneutrality (3, 4) and continuity (8) equations are part of the system of equations.

Finally, to calculate solution concentrations at left and right interfaces ($C_{i,l}^s$ and $C_{i,r}^s$), we defined an optimisation criterion in which the difference between species fluxes at interface is minimised :

$$J = \min \sqrt{\left(N_{i,l}^s - N_i^m \right)^2 + \left(N_{i,r}^s - N_i^m \right)^2} \quad (13)$$

with following constraints :

$$C_{i,l}^s > 0 \quad (14)$$

$$C_{i,r}^s > 0 \quad (15)$$

We plotted the evolution of J according to $C_{i,l}^s$ and $C_{i,r}^s$. Figure 3 shows that there is unique minima which was obtained by applying numerical optimisation using a fast algorithm for nonlinearly constrained optimisation calculations [8, 9].

3 Experimental

Membranes studied in this work are Neosepta ACS and CMX-S provided by Tokuyama Soda Co. ACS are monovalent-anion-permselective membranes, the permselective layer is made of a highly cross-linked resin, whereas in CMX-S (monovalent-cation-permselective membranes) the thin layer is positively charged.

For the electro dialysis mass transfer model, membrane diffusion coefficients and membrane composition have to be known as a function of concentration. Therefore, three types of experiments are performed.

1. Measurement of internal water concentration at different external concentrations.

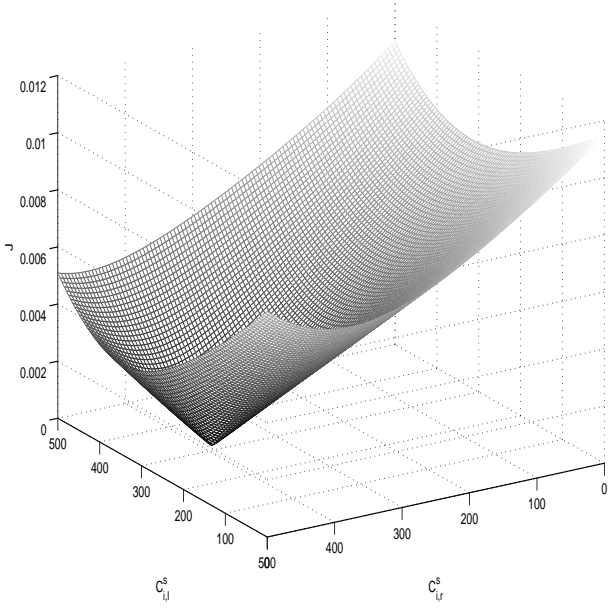


Figure 3: Evolution of the optimisation criterion versus solution concentrations at the interface

2. Co-ion uptake by means of ion exchange equilibrium measurements.
3. Diffusion dialysis.

Prior to any measurement, the membranes are stabilized according to French standards [3].

3.1 Membrane water content

The internal water concentration was measured in NaCl solutions at 0.1, 0.2, 0.3, 0.4 and 0.5 M. Samples of membrane of 4×4 cm are soaked in the agitated solution at a given concentration and then removed from the solution. After drying only the membrane surface by wiping, the wet weight of the membrane is determined. The dry weight of the membrane is obtained after drying the membrane at 60°C in a exsiccator until a constant weight was attained. The water mass fraction of the membrane is calculated from :

$$\varepsilon_w = \frac{m_{wet} - m_{dry}}{m_{wet}} \quad (16)$$

The internal water concentration then follows from :

$$\bar{c}_w = \frac{\rho_m \varepsilon_w}{M_w} \quad (17)$$

ρ_m is the membrane density determined from both the wet masses and volumes involved.

3.2 Sorption measurements

Ion exchange equilibrium measurements were performed for both cation and anion exchange membrane.

To determine the ion-exchange capacity and the Cl^- co-ion uptake in the CMX-S membrane, each sample of membrane is immersed into 1 M NaCl solution to convert the membrane into Na^+ form. To remove the co-ions Cl^- , samples are put into pure water until end of pH variation. Then these are equilibrated in NaCl solution of 0.1, 0.2, 0.3, 0.4 and 0.5 M.

After being rinsed carefully the membranes with distilled water to eliminate electrolyte adhering to the membrane surface, the membranes were put into 0.5 M NaNO_3 solution. The amounts of the Cl^- exchanged by NO_3^- ions are analysed by ionic chromatography (Dionex DX 120 equipped with a CS 12 A for cations or an AS 12 A column for anions). Afterwards, the membranes are equilibrated in 0.5 M HNO_3 solution. This procedure was repeated three times to be sure that all Na^+ ions in the membrane were exchanged by H^+ ions. Na^+ ions concentration was determined using a VARIAN AA 220 atomic absorption spectrophotometer.

Knowing the masses and volumes involved in the experiment, the co-ion concentration in the membrane can be calculated. The ion exchange capacity of the membrane in Na^+ form is simply the difference between the calculated Na^+ concentration and Cl^- concentration.

To measure the ion-exchange capacity and the co-ion Na^+ uptake of the anion exchange membrane, the same concentrations of NaCl were used. To replace the co-ion Na^+ and to keep the fixed charges in Cl^- form, 0.5 M HCl was used. Total internal concentration of Cl^- was determined by immersing the sample of membranes in 0.5 M HNO_3 . The calculation of the fixed-charge concentration and the co-ion uptake is analogous to cation exchange membrane.

3.3 Diffusion dialysis

To determine binary diffusivities inside the membrane, diffusion dialysis experiments are conducted in a membrane cell. Tested membrane separates two compartments : concentrated electrolyte (initial concentration equal to 0.4 M) and pure water. The starting volume of each solution is 500 mL. The circulation of solutions is made by two gear pumps. After 72 h, the dialysis is stopped and the solutions are sampled. By means of conductivity measurements and solution weighing, concentrations and volumes were determined.

$C_s(\text{mol/m}^3)$	$C_w(\text{mol/m}^3)$	$n_{\text{Cl}^-}^m(\text{mol})$	$n_{\text{Na}^+}^m(\text{mol})$	$\bar{m}_{\text{Cl}^-}(\text{mol/kg})$	$\bar{m}_{\text{Na}^+}(\text{mol/kg})$	γ_s^m
100	15519,78	$6,34 \cdot 10^{-6}$	$0,408 \cdot 10^{-3}$	0,019	1,212	0,671
200	15073,53	$8,73 \cdot 10^{-6}$	$0,434 \cdot 10^{-3}$	0,027	1,354	0,685
300	14671,36	$34,79 \cdot 10^{-6}$	$0,419 \cdot 10^{-3}$	0,104	1,247	0,686
400	14198,01	$63,52 \cdot 10^{-6}$	$0,393 \cdot 10^{-3}$	0,189	1,167	0,667
500	14760,25	$93,17 \cdot 10^{-6}$	$0,415 \cdot 10^{-3}$	0,277	1,233	0,642

Table 1: Equilibrium properties of the cation exchange membrane as a function of the external concentrations of NaCl.

$C_s(\text{mol/m}^3)$	$C_w(\text{mol/m}^3)$	$n_{\text{Cl}^-}^m(\text{mol})$	$n_{\text{Na}^+}^m(\text{mol})$	$\bar{m}_{\text{Cl}^-}(\text{mol/kg})$	$\bar{m}_{\text{Na}^+}(\text{mol/kg})$	γ_s^m
100	13580,00	$0,462 \cdot 10^{-3}$	$0,091 \cdot 10^{-3}$	2,020	0,397	0,318
200	12902,10	$0,500 \cdot 10^{-3}$	$0,021 \cdot 10^{-3}$	2,084	0,087	0,279
300	12611,99	$0,544 \cdot 10^{-3}$	$0,031 \cdot 10^{-3}$	2,357	0,134	0,328
400	12298,00	$0,582 \cdot 10^{-3}$	$0,072 \cdot 10^{-3}$	2,479	0,307	0,312
500	11548,12	$0,553 \cdot 10^{-3}$	$0,207 \cdot 10^{-3}$	2,526	0,947	0,252

Table 2: Equilibrium properties of the anion exchange membrane as a function of the external concentrations of NaCl.

4 Results

4.1 Membrane characterisation

Membrane water content and ion exchange equilibrium measurements permit us to obtain an insight into properties of the cation-exchange membrane. These properties are the internal water concentration \bar{C}_w , total co-ion molality \bar{m}_{Cl^-} and counter-ion molality \bar{m}_{Na^+} . The situation with the anionic membrane is analogous. The last column of tables 1 and 2 gives the values of the mean activity coefficient of the electrolyte in the membrane phase γ_s^m calculated using co-ion, counter-ion values and equation 10. Donnan thermodynamic equilibrium model was applied to the results. Figures (4) and (5) show results for the co-ion sorption in the studied membranes. The deviation of the model lines from the measured points follow directly from experimental errors.

4.2 Diffusion coefficients

Description of mass transport according to the Stefan-Maxwell equations requires knowledge of binary diffusivities $D_{i,j}$ which measure the interaction between each component i with another component j in the system. For a system with n components, $\frac{n(n-1)}{2}$ diffusivities are required. A distinction should be made between the diffusivities in the diffusion films and the membrane phase. In NaCl aqueous solution, diffusivities are obtained from transport numbers, activity coefficients and equivalents conductivities of Na^+ and Cl^- ions. This information is available in literature [7].

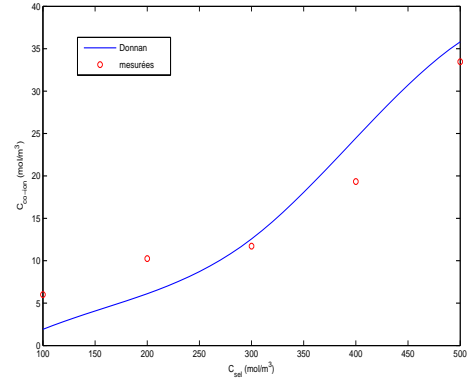


Figure 4: The co-ion concentration in CMX-S membrane as a function of external NaCl concentration.

$D_{\text{Na}^+,w}$ and $D_{\text{Cl}^-,w}$ depend little on concentration and both have values of around $10^{-9} \text{ m}^2/\text{s}$, in model calculation we used the following values : $D_{\text{Na}^+,w} = 1.333 \times 10^{-9} \text{ m}^2/\text{s}$ and $D_{\text{Cl}^-,w} = 2.033 \times 10^{-9} \text{ m}^2/\text{s}$. $D_{\text{Na}^+, \text{Cl}^-}$ is much smaller and can be determined by an empirical relation given in [19] :

$$D_{\text{Na}^+, \text{Cl}^-} = \frac{D_{\text{Na}^+,w} + D_{\text{Cl}^-,w}}{2} \frac{i^{0.55}}{|z_+ z_-|^{2.3}} \quad (18)$$

For the studied membranes, no Stefan-Maxwell diffusivity data is reported in literature. The NaCl-membrane system involves six membrane diffusivities ($D_{\text{Na}^+,m}^m, D_{\text{Cl}^-,m}^m, D_{\text{Na}^+, \text{Cl}^-}^m, D_{w,m}^m, D_{\text{Na}^+,w}^m, D_{\text{Cl}^-,w}^m$) in both cation and anion exchange membranes. In order to reduce this set of diffusion coefficients, we first carried out a sensitivity analysis in CMX-S membrane to analyse the effect of each diffusivity on the variation

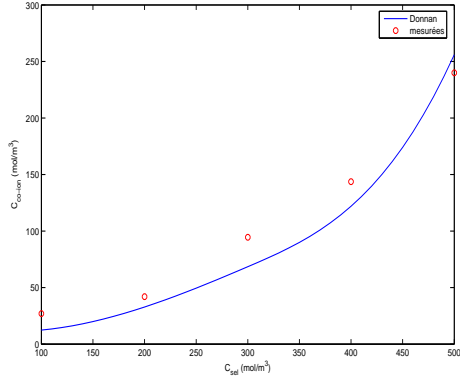


Figure 5: The co-ion concentration in ACS membrane as a function of external NaCl concentration.

of water and ion fluxes. Diffusivities which had a substantial influence on fluxes were considered as important diffusivities. This sensitivity analysis showed that D_{Cl^-,Na^+}^m and $D_{Cl^-,m}^m$ could be considered as "unimportant" diffusivities then reducing the number of diffusivities to determine to 4 instead of 6. Latters were evaluated using independent dialysis measurements and empirical relations. Wesselingh et al [20] have presented some methods to predict interactions with water, the method being based on the values of the diffusivities in free solution [20] :

$$D_{i,j}^m = \varepsilon^{1.5} D_{i,j}^s \quad (19)$$

where ε is the membrane void ratio and $D_{i,j}^s$ is the diffusivity in free solution.

Remaining diffusivities were obtained from diffusion dialysis experiments which have to be described by the same model outlined in section 2 with a difference that no current is applied. Diffusivities in ACS membrane are analogous, inimportant diffusivities are $D_{Na^+,m}^m$ and D_{Na^+,Cl^-}^m . Results of sensitivity study showing the effect of the diffusivities in membrane for both CMX-S and ACS membranes are represented in figures (6) and (7). "Interesting zone" in figures shows interval in which diffusivities lead to electrolyte and water fluxes in opposite directions.

The results for NaCl and water fluxes for both CMX-S and ACS membranes are shown in table 3.

Membrane	$N_{NaCl}(\text{mol}/\text{m}^2 \cdot \text{s})$	$N_{water}(\text{mol}/\text{m}^2 \cdot \text{s})$
CMX-S	$4,69 \cdot 10^{-6}$	$1,77 \cdot 10^{-3}$
ACS	$16,1 \cdot 10^{-6}$	$4,09 \cdot 10^{-3}$

Table 3: Measured NaCl and water fluxes through CMX-S and ACS membranes.

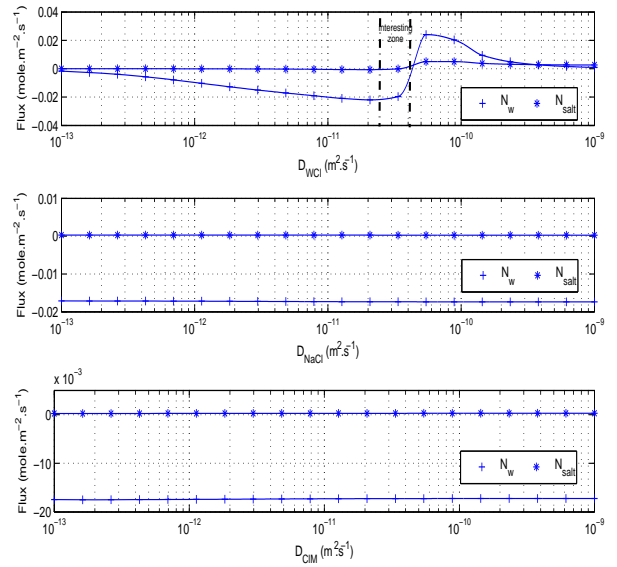


Figure 6: Sensibility study of CMX-S membrane.

Measured fluxes have been used to calculate membrane diffusivities by applying a numerical optimisation using the Marquardt-Levenberg method. Table 4 contains the values of all diffusivities estimated and calculated using empirical relations.

Diffusivities	CMX-S		ACS	
$D_{Na^+,w}$	1,37	$\times 10^{-10}$	7,366	$\times 10^{-11}$
$D_{Cl^-,w}$	3,874	$\times 10^{-11}$	1,82	$\times 10^{-10}$
D_{Na^+,Cl^-}	7,743	$\times 10^{-12}$	7,848	$\times 10^{-12}$
$D_{Na^+,m}$	1,37	$\times 10^{-11}$	1	$\times 10^{-10}$
$D_{Cl^-,m}$	1	$\times 10^{-10}$	1,81	$\times 10^{-11}$
$D_{w,m}$	2,11	$\times 10^{-10}$	2,33	$\times 10^{-10}$

Table 4: Diffusion coefficients.

4.3 Model calculations

In the present work, we simulate salt and water fluxes in the stationary state through CMX-S and ACS membranes in an electro dialysis cell containing the cation and anion exchange membranes with two boundary layers and well mixed solution. Temperature is 298 K. The thickness of polarisation layers was $100 \mu\text{m}$, all layers being assumed the same thickness. The distance between membranes was 0.4 mm. Membrane thickness is 1.7×10^{-4} m for CMX-S membrane and 1.3×10^{-4} m for ACS membrane. Mean concentration of fixed functional groups $c_M = 1500 \text{ mol}/\text{m}^3$ and their valence $z_M = -1$

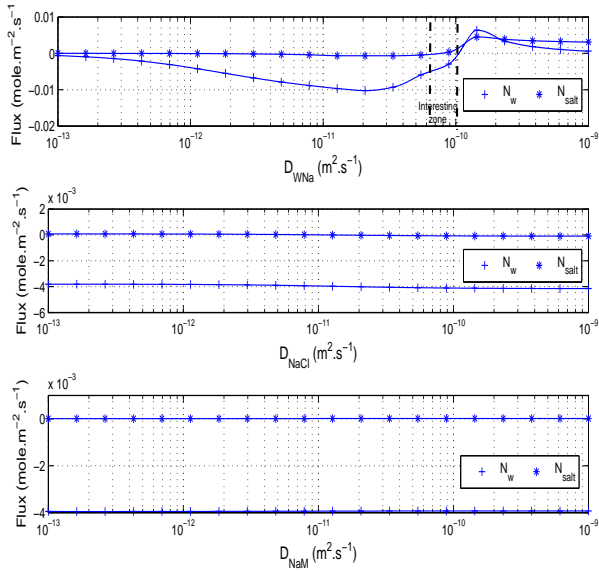


Figure 7: Sensibility study of ACS membrane.

and $z_M = 1$ for CMX-S and ACS membranes respectively were used in the present study. The following values of partial molar volumes were considered [6] : $\bar{V}_{Na^+} = 4.4 \times 10^{-6} \text{ m}^3/\text{mol}$, $\bar{V}_{Cl^-} = 1.2 \times 10^{-5} \text{ m}^3/\text{mol}$ and $\bar{V}_w = 1.8 \times 10^{-5} \text{ m}^3/\text{mol}$. The partial molar volume for membranes were fitted with the model. In figure 8 the calculated concentration profiles across the membranes placed in an electro dialysis cell are given. These profiles are obtained for a current density of 37 A/m^2 . As can be seen in figure 8, counter-ions in cationic and anionic membrane behave differently. Na^+ ions concentration in cation exchange membrane is distinctly much higher than fixed charge concentration, while Cl^- ions concentration in anion exchange membrane is scarcely above the fixed anion concentration in the membrane. When applying an electrical current through the electro dialysis cell in NaCl solution, boundary layers are formed on each side of membranes with a higher gradient at the concentrating side.

5 Conclusion

The electro dialysis of NaCl solution was modelled using the Stefan-Maxwell formalism which offers a suitable way to describe mass transport and provides interesting information on the ion distribution inside membranes. Model parameters were obtained from existing correlations and independent measurements. Diffusion dialysis was used to estimate some membrane diffusivities, it is interesting to set up experiments using different driving forces to find more accurately mem-

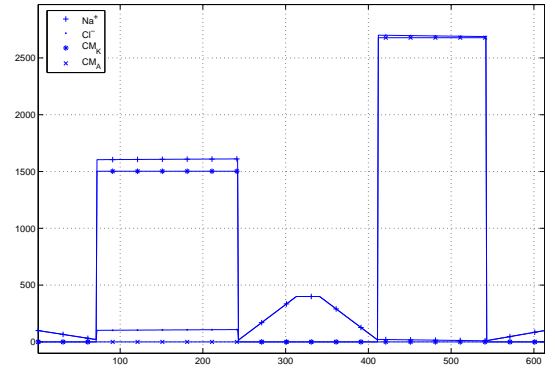


Figure 8: Calculated concentration profiles in an electro dialysis cell containing CMX-S and ACS membranes.

brane diffusion coefficients.

6 List of symbols

A	matrix with diffusivities, non idealities and transference numbers	
a_i	activity of species i	(mol.m^{-3})
B^{n*}	matrix with diffusivities	
c	molar concentration	(mol.m^{-3})
C_m	ion exchange capacity	(mol.m^{-3})
c_T	total concentration	(mol.m^{-3})
$D_{i,j}$	Stefan-Maxwell diffusivity	$(\text{m}^2.\text{s}^{-1})$
h	distance between membranes	(m)
i	ionic strength	(mol.m^{-3})
I	current density	(A.m^{-2})
Δl	distance between successive eddy promoters	(m)
N	molar flux density	$(\text{mol.m}^{-2}.\text{s}^{-1})$
P	pressure	(Pa)
R	universal gas constant	$(\text{J.K}^{-1}.\text{mol}^{-1})$
T	temperature	(K)
v	average species velocity	(m.s^{-1})
\bar{V}_i	partial molar volume	$(\text{m}^3.\text{mol}^{-1})$
x	mole fraction	$(-)$
z_i	ionic charge of species i	$(-)$
$Z^\#$	matrix with electrical coefficients i	$(-)$

Dimensionless criterions

Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number

Subscripts and exponents

A	anion
C	cation
m	membrane
s	salt solution
w	water

Greek letters

γ	activity coefficient	(-)
\mathcal{F}	Faraday constant	(96487 C.mol ⁻¹)
ϕ	electrical potential	(V)
μ	electrochemical potential	(J.mol ⁻¹)
ε	void ratio	(-)
ε_w	water mass fraction	(-)

Appendix.

Content of matrix A and β

Matrices A and β are defined in [5], we point out here their contents.

$$[A] = [B^{n*}]^{-1}[\Xi^*] \quad (20)$$

Matrix β contains diffusivities and the current density :

$$[\beta] = [B^{n*}]^{-1}[Z^\#] \quad (21)$$

- Matrix with frictions $[B^{n*}]$:

$$B_{i,j}^{n*} = B_{i,j}^n - B_{i,n-1}^n \frac{z_j}{z_{n-1}} \quad i = 1, \dots, n-2 \quad (22)$$

with

$$B_{i,j}^n = \frac{c_i}{c_T D_{i,j}} \quad i \neq j \quad (23)$$

- Matrix with thermodynamic non-idealities and transference numbers $[\Xi]$:

$$\Xi_{i,j}^* = \Xi_{i,j} - \Xi_{i,n-1} \frac{z_j - z_n}{z_{n-1} - z_n} \quad i = 1, \dots, n-2 \quad (24)$$

With:

$$\Xi_{i,j} = \Gamma_{i,j} - c_i z_i \sum_{k=1}^{n-1} \Gamma_{k,j} \frac{t_k^n}{z_k c_k} \quad (25)$$

$$\Gamma_{i,j} = \delta_{i,j} + c_i \frac{\partial \ln \gamma_i}{\partial c_j} \quad (26)$$

$$t_j^n = \frac{z_j c_j \mathcal{F}^2}{\kappa} \sum_{k=1}^{n-1} L_{j,k}^n z_k c_k \quad (27)$$

$$\kappa = \mathcal{F}^2 \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} z_i z_j c_i c_j L_{i,j}^n \quad (28)$$

$$L^n = -[M^n]^{-1} \quad (29)$$

Matrix M is defined by :

$$M_{i,j} = K_{i,j} \quad i \neq j = 1, 2, \dots, n \quad (30)$$

$$M_{i,i} = K_{i,i} - \sum_{k=1}^n K_{i,k} \quad i = 1, 2, \dots, n \quad (31)$$

$$K_{i,j} = RT \frac{c_i c_j}{c_T D_{i,j}} \quad (32)$$

- Matrix with diffusivities and current density $Z^\#$:

$$Z_{i,j}^\# = 0 \quad i \neq j = 1, 2, \dots, n-2 \quad (33)$$

$$Z_{i,i}^\# = \left(\frac{z_i \mathcal{F}}{RT \kappa} + \frac{1}{\mathcal{F} c_T D_{i,n-1} z_{n-1}} \right) I \quad i = 1, 2, \dots, n-2 \quad (34)$$

References

- [1] L.A. Bromley, "Thermodynamic properties of strong electrolytes in aqueous solutions" *AICHE* 19 (1973), 313-320.
- [2] F.G. Donnan and E.A. Guggenheim, "Exact thermodynamics of membrane equilibrium" *Z. Phys. Chem. A* 162 (1932), 346-360.
- [3] French standard NF X 45-200, "Membranes polymères échangeuses d'ions : caractéristiques et méthodes d'essais des membranes homopolaires." AFNOR, Paris, (1995).
- [4] B. Hamrouni and M. Dhabbi, "Activity coefficient calculation. Application to salt aqueous solutions" *Entropie* 237 (2002), 52-59.
- [5] J.A. Hogendoorn, A.J. van der Veen, J.H.G. van der Stegen, J.A.M. Kuipers and G.F. Versteeg, "Application of the Maxwell-Stefan theory to the membrane electrolysis process - Model development and simulations" *Computers and Chemical Engineering* 25 (2001) 1251-1265.
- [6] H.D.B. Jenkins and M.S.F. Pritchett, "Absolute ionic partial molal hydration volumes in water at 298 K" *Phil. Mag. B* 48 (1983) 493-503.
- [7] V.M.M. Lobo, "Handbook of electrolyte solutions". Elsevier Science, (1990).
- [8] M.J.D. Powell, "A fast algorithm for nonlinearly constrained optimization calculations", Numerical Analysis, ed. G.A. Watson, Lecture Notes in Mathematics, Springer Verlag, 630 (1978).

- [9] M.J.D. Powell, "The Convergence of variable metric methods for nonlinearly constrained optimization calculations" *Nonlinear Programming 3* (O.L. Mangasarian, R.R. Meyer, and S.M. Robinson, eds.), Academic Press, (1978)
- [10] F. Quéméneur, J-P. Schlumpf, L. Firdaous, M. Stitou, J-P. Malérial and P. Jaouen, "Modification of ionic composition of natural salt-waters by electrodialysis" *Desalination* 149 (2002) 411-416.
- [11] V.V. Nikonenko, V.V. Zabolotskii and K.A. Lebedev, "Model for the competitive transport of ions through ion exchange membranes with a modified surface" *Russian Journal of Electrochemistry* 32 (1996) 234-236.
- [12] G. Saracco, "Transport properties of monovalent-ion-permselective membranes" *Chemical Engineering Science* 52 (1997) 3019-3031.
- [13] G. Saracco and M.C. Zanetti, "Ion transport through monovalent-anion-permselective membranes" *Ind. Eng. Chem. Res* 33 (1994) 96-101.
- [14] T. Sata, "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 (2000) 1-31.
- [15] T. Sata, T. Sata, W. Yang, "Studies on cation-exchange membranes having permselectivity between cations in electrodialysis" *Journal of Membrane Science* 206 (2002) 31-60.
- [16] A.A. Sonin and M.S. Isaacson, "Optimization of flow design in forced flow electrochemical systems, with special application to electrodialysis" *Ind. Eng. Chem., Process Des. Develop.*, 13 (1974) 241-248.
- [17] R. Taylor and R. Krishna, "Multicomponent Mass Transfer". Wiley : New York (1993).
- [18] A. Tomita, "Salt and chlor-alkali plant in Kuwait by all membrane process" *Nippon Kaisui Gakkaishi. Bull. Soc. Sea Water Sci, Jpn.* 42 (1988), 28-32.
- [19] J.A. Wesselingh and R. Krishna, "Mass transfer in multicomponent mixtures." Delft University Press : The Netherlands (2000).
- [20] J.A. Wesselingh, P. Vonk and G. Kraaijeveld, "Exploring the Maxwell-Stefan description of ion exchange" *The Chemical Engineering Journal* 57 (1995) 75-89.