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Modeling of Solvent and Ionic Fluxes in Electronanofiltration

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ABSTRACT

Electronanofiltration (ENF) is a new membrane separation process that uses an additional electric field between the permeate and retentate sides during nanofiltration. A recently published pioneering work gives the performance with single and mixed ionic solutions containing one monovalent cation and one or two anions (mono- or/and divalent). It appears that the electric field leads to a net increase of cation flux and a decrease of anion permeation at the same time if the cathode is placed on the permeate side. In relation with the well-known dependence of solvent flux on transmembrane pressure, these data open up potential applications of ENF for new integrated operations of ion separation/concentration. In this paper a semiempirical model accounting for permeate and ionic fluxes is proposed. Based on the Stefan–Maxwell approach, a simple set of linearized equations is developed that fits experimental data at various transmembrane pressure (ΔP), electric fields (ΔU), and concentrations (C).

Key Words. Nanofiltration; Electrophoresis; Ion transport; Modeling

INTRODUCTION

Nanofiltration is a new membrane separation technique intermediate between reverse osmosis and ultrafiltration for pore diameters around 1 nm and applied transmembrane pressure in the 5–30 bars range (2) that appears more and more attractive for the treatment of ionic solutions. This is especially

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when electric charges present on membrane materials strongly interact with specific charges of ions and thus control rejection performance. If organic membranes ordinarily present a fixed charge, inorganic materials exhibit changing behaviors that mainly depend on pH and ionic strength of solutions due to their amphoteric nature (3). In the past few years much research has been devoted to the study of inorganic (4) or organo-inorganic (5) elements which can work with strong basic or acid solutions.

In a previous paper (1) we presented a new application of an organo-inorganic nanofiltration membrane that consists in applying an external electric field during nanofiltration. The same idea had been presented earlier for electroultrafiltration with a view both to increase solvent flux by preventing polarization and fouling, and to control macromolecule rejection. In some cases a selective separation of different species had been observed (6–8). With nanofiltration, the function of the electric field is to control ionic movements, the solvent flux mainly depending on transmembrane pressure. Thus simultaneous ion concentration/separation may be imagined, unlike a simple nanofiltration process (where the electric effects control permeation of salts rather than of individual ions in order to preserve solution electroneutrality) or electrodialysis (where there is no solvent flux). As an example, with simple or mixed solutions of NaCl and/or Na_2SO_4, a net increase of cation concentration in the permeate may be observed while the anion permeation is lowered by using an external cathode.

A few works devoted to modeling fluxes during nanofiltration of charged species have been published recently (9–12). The Stefan-Maxwell approach that sets equilibrium conditions between the various driving and friction forces acting on ions is usually used as a basis for equation design (13, 14). In this paper, following the same idea, we endeavor to elaborate a set of semiempirical linear equations that correctly account for the influence of transmembrane pressure (ΔP), external electric field (ΔU), as well as the concentrations and compositions of salt solutions.

MATERIALS AND METHODS

Because we will use previously published data (1), we will only briefly recall the experimental conditions.

Experimental Set-up

The membrane is an organo-inorganic tubular element made from an α-alumina macroporous support, an intermediate mesoporous titania substrate, and a very thin microporous film of negatively charged nation (pore diameters, respectively, of 200, 10–15, and 1.2 nm) (5, 15).

The experimental set-up is a classical nanofiltration plant equipped with two stainless steel electrodes connected to a D.C. electric power supply unit. The anode is a rod located on the axis of the tubular membrane. The cathode is a cylindrical wire netting stuck on the ceramic support.

Solutions

Single salt and mixed solutions of Na_2SO_4 and NaCl were studied. Most of them presented a constant counterion concentration—$[Na^+] = 10\ mol\cdot m^{-3}$—and different values of $\alpha = [Na_2SO_4]/[NaCl]$, the salt concentration ratio. In a few runs the influence of the total concentration was checked by making $[Na^+] = 50\ mol\cdot m^{-3}$ at $\alpha = 1$ ($[Cl^-] = [SO_4^{2-}]$).

Operating Conditions

Permeate and retentate were continuously recycled to operate under constant bulk concentration. The cathode was placed at the outside of the membrane in order to promote a "pumping effect" of Na^+ through the porous medium.

Special attention was paid in this work to the effect of pressure and electric field, the two main driving forces (1) of performance. Thus, various transmembrane pressures and voltages ranging between 5–30 bars and 0–7.5 volts were tested.

On the other hand, the temperature was fixed at 303 K and the fluid velocity at $3\ m\cdot s^{-1}$, which guaranteed a turbulent regime.

Notations

J ($m\cdot s^{-1}$) and J_i ($mol\cdot s^{-1}\cdot m^{-2}$) are the solvent and ionic fluxes respectively. R_i (%) is rejection of the i species:

$$J_i = JC_{pi} \tag{1}$$

$$R_i = 100\left(1 - \frac{C_{pi}}{C_{ri}}\right) \tag{2}$$

with C_{pi} and C_{ri} the concentrations in the permeate and retentate, respectively.

PRINCIPLES OF MODELING

What Does the Stefan–Maxwell Approach Predict for Mass Transfer through Pores?

Each ionic species moves in the pores of the membrane at a velocity v_i ($m\cdot s^{-1}$) under the simultaneous action of driving—chemical, electrical, and pressure—and friction—with the other species—forces.

In the case of dilute solutions, the activity a_i is roughly equal to the concentration C_i, and the driving forces (m^{-1}) may be written:

Composition:

$$-\frac{1}{C_i}\frac{dC_i}{dz} \tag{3}$$

Pressure:

$$-\frac{\upsilon_i}{RT}\frac{dP}{dz} \tag{4}$$

Electric:

$$-\frac{Fz_i}{RT}\frac{d\phi}{dz} \tag{5}$$

with z the space variable (m) and υ_i the molar volume of i ($\mathrm{m}^3\cdot\mathrm{mol}^{-1}$).

With dilute solutions, the friction term reduces to

$$\frac{v_i}{\theta_i}+\frac{v_i}{\Gamma_i} \tag{6}$$

with θ_i the free diffusivity of i in water and Γ_i the friction factor with the membrane. For simplicity a unique "hindered" coefficient, D_i ($\mathrm{m}^2\cdot\mathrm{s}^{-1}$), which accounts for both θ_i and Γ_i, is used in what follows.

Thus at steady-state:

$$\frac{v_i}{D_i}=-\frac{1}{C_i}\frac{dC_i}{dz}-\frac{\upsilon_i}{RT}\frac{dP}{dz}-\frac{Fz_i}{RT}\frac{d\phi}{dz} \tag{7}$$

For the calculation of ionic fluxes, J_i, a term uC_i must be added to the term v_iC_i because of the convective transport of solvent due to ΔP. Ordinarily solvent fluxes are expressed as regards the total surface of the membrane S rather than the total open surface of pores S_p. Thus:

$$J_i=(v_i+u')C_i \tag{8}$$

with

$$u'=u(S_p/S)$$

The diffusional part of the transfer in pores is small with the membrane used in this work, as previously demonstrated by Rios et al. (13). Moreover, the pressure term may be neglected due to the low specific volume of solutes. As a consequence:

$$J_i=u'C_i-\frac{D_iC_iFz_i}{RT}\frac{d\phi}{dz} \tag{9}$$

By integrating this equation on the membrane thickness, *e*, the following expression of J_i may be proposed:

$$J_i = u' C_i^* - \omega_i z_i C_i^* \frac{\Delta\phi F}{RT} \quad (10)$$

with $\omega_i = D_i/e$ and C_i^* the *i*-average concentration.

Toward Simple Semiempirical Equations for ENF

Starting from Eq. (10), a relationship easier to work with may be obtained by introducing:

- C_{ri} instead of C_i^*. In fact, C_{ri} represents the feed solution concentration that can be related to C_i^* by a partition coefficient.
- The permeate flux J rather than the solvent flux u', the two values being connected by a membrane–solute interaction (or "reflection") factor.
- $[-\Delta U]$† the applied voltage instead of $\Delta\phi$, the actual transmembrane voltage. The difference is mainly due to electrochemical reactions that develop in the immediate vicinity of the electrodes.

This leads to the general equation involving two coefficients K_i' and K_i'':

$$J_i = JK_i' C_{ri} + z_i K_i'' C_{ri} \frac{\Delta UF}{RT} \quad (11)$$

According to this equation, ionic transport through membrane pores is made up of two parts. The first, J_i', mainly relates to the transmembrane pressure through J, and the second, J_i'', is directly dependent on the applied electric field:

$$J_i = J_i' + J_i'' \quad (12)$$

with

$$J_i' = JK_i' C_{ri} \quad (13)$$

$$J_i'' = z_i K_i'' C_{ri} \frac{\Delta UF}{RT} \quad (14)$$

It is worth recalling at this stage of the presentation that the membrane used in this work is constituted of two parts acting in parallel: a microporous part through which both cation and anions are able to flow together by convection and migration, and a dense part negatively charged through which only cation can move under an electric field as in electrodialysis‡ (Fig. 1). This model looks like ones already presented by Gierke and Eisenberg for electrodialysis membranes (16, 17), but the water contained inside fixed clusters, embedded

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†$\Delta U > 0$ with an outside cathode.

‡Diffusion will be neglected due to the very small thickness of the polymer layer [less than 1 μm (5, 15)].

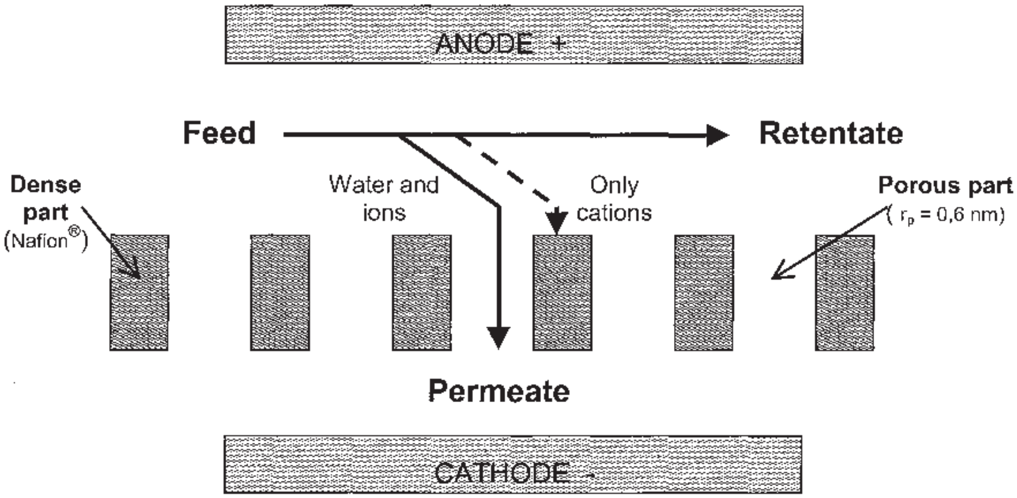

FIG. 1 Schematic representation of ENF membrane behavior (bicompartimental model).

in the dense material according to these authors, is here replaced by solvent moving through pores.

As a consequence, it will be necessary to distinguish clearly between anions and cation, especially when regarding J_i''. For anions, K_i'' will just account for the transport through membrane pores. For cation, by extending the use of Eq. (11), it will also cover migration through dense material.

In this presentation, following a classical assumption, the polarization effect is neglected due to low ionic concentrations ($C < 10^{-2}$ mol·L^{-1}).

MODEL IDENTIFICATION AND DISCUSSION

Permeate Flux, *J*

The clear dependence of J on ΔP may be checked from the data points reported in Fig. 2. One can also observe that flux slightly decreases when ΔU increases. There is also a variation with C_{Na^+} (1).

Starting from the classical relation $J = K\Delta P$, the assumption is made of a linear variation of K as a function of ΔU and C_{Na^+} in the range investigated:

$$K = E + FC_{\mathrm{Na}^+}\Delta U \tag{15}$$

By calculating the average values of K for nanofiltration ($\Delta U = 0$ V) with a constant C_{Na^+} concentration (10 mol·m^{-3}), and $(K - E)/(C_{\mathrm{Na}^+}\Delta U)$ at $\Delta U \neq 0$ V, E and F may be identified as follows:

$$J_{\mathrm{calc}} = (1.71 \times 10^{-6} - 2.7 \times 10^{-9}\, C_{\mathrm{Na}^+}\Delta U)\Delta P$$

For $\alpha = 1$ (Fig. 2), the relative error between calculated, J_{calc}, and measured, J_{mes}, values is less than 10%.

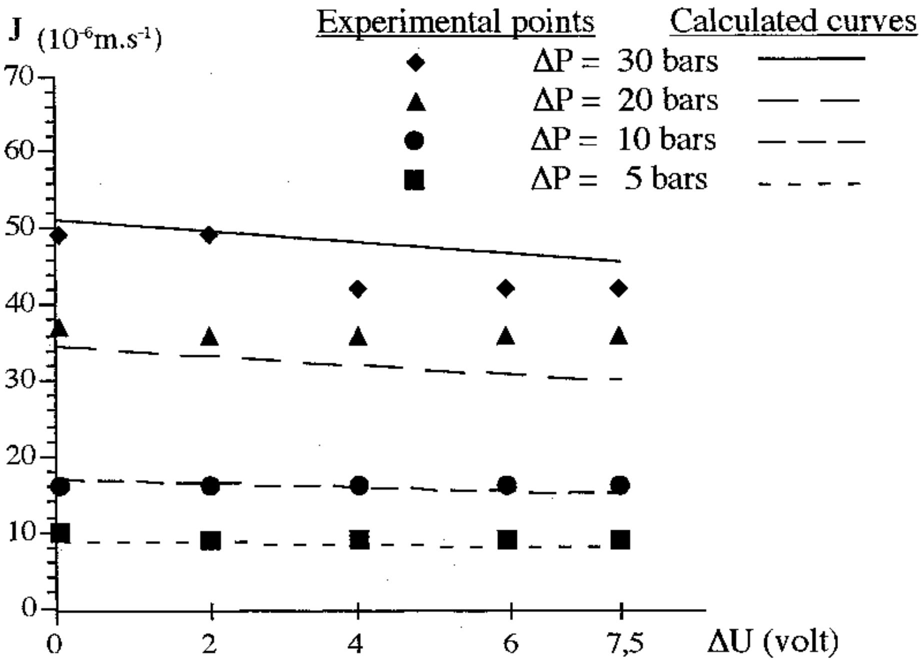

FIG. 2 J versus ΔP and ΔU. $\alpha = 1$; ΔP variable; $C_{Na^+} = 10\ \text{mol·m}^{-3}$.

Other data referring to other α values confirm these trends and also indicate that, even above $\Delta U = 4$ V, there is a continual decrease of J vs ΔU, in good agreement with model predictions.

J' Component

At $\Delta U = 0$ V, $K = E$ and Eq. (11) reduces to:

$$J_i = J_i' = E\Delta P K_i' C_{ri} \tag{16}$$

In Table 1 the average values of $K_i' = J_i/E\Delta P C_{ri}$ are reported for each ion. There is only a small gap between values obtained at $C_{Na^+} = 10\ \text{mol·m}^{-3}$ and

TABLE 1
Average Value of K_i' (—) with α Variable, $\Delta U = 0$ volt, C_{Na^+} Variable (mol·m^{-3})

α	C_{Na^+}	Na^+	Cl^-	SO_4^{2-}
0	10	0.8	0.79	—
1		0.59	1.15	0.24
4		0.42	1.09	0.1
∞		0.2	—	0.3
1	50	0.78	1.07	0.52

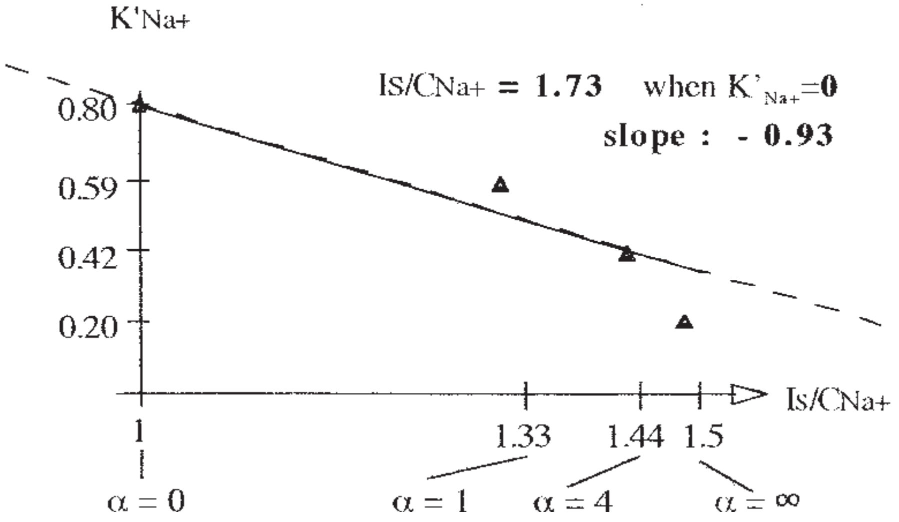

FIG. 3 K'_{Na^+} versus I_S/C_{Na^+}.

$C_{\mathrm{Na}^+} = 50\ \mathrm{mol{\cdot}m}^{-3}$ with $\alpha = 1$. To order to express the steeper variation versus composition, the ratio I_S/C_{Na^+} of ionic force to cation concentration* has been chosen. For simplicity, the assumption has been made that the variation of K'_i versus I_S/C_{Na^+} as reported in Fig. 3 is linear. Thus, smoothing data for the three ions gives:

$$K'_{\mathrm{Na}^+} = 1.73 - 0.93 I_S/C_{\mathrm{Na}^+}$$

$$K'_{\mathrm{Cl}^-} = -0.07 + 0.85 I_S/C_{\mathrm{Na}^+}$$

$$K'_{\mathrm{SO}_4^{2-}} = 1.29 - 0.66 I_S/C_{\mathrm{Na}^+}$$

The K'_i terms measure the selectivity of the membrane as regards *i*-species in the same way as reflection coefficients do in nonequilibrium thermodynamics.

Thus the following equations result for J'_i :

$$J'_{\mathrm{Na}^+} = C_{r\mathrm{Na}^+}(1.73 - 0.93 I_S/C_{\mathrm{Na}^+}) \times (1.71 \times 10^{-6} - 2.7 \times 10^{-9}\, C_{\mathrm{Na}^+}\Delta U)\Delta P$$

$$J'_{\mathrm{Cl}^-} = C_{r\mathrm{Cl}^-}(-0.07 + 0.85 I_S/C_{\mathrm{Na}^+}) \times (1.71 \times 10^{-6} - 2.7 \times 10^{-9}\, C_{\mathrm{Na}^+}\Delta U)\Delta P$$

$$J'_{\mathrm{SO}_4^{2-}} = C_{r\mathrm{SO}_4^{2-}}(1.29 - 0.66 I_S/C_{\mathrm{Na}^+}) \times (1.71 \times 10^{-6} - 2.7 \times 10^{-9} C_{\mathrm{Na}^+}\Delta U)\Delta P$$

J'' Component

As indicated previously, J'' will be dealt with separately for the cation and anions.

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*For fixed α, this ratio does not depend on C_{Na^+}.

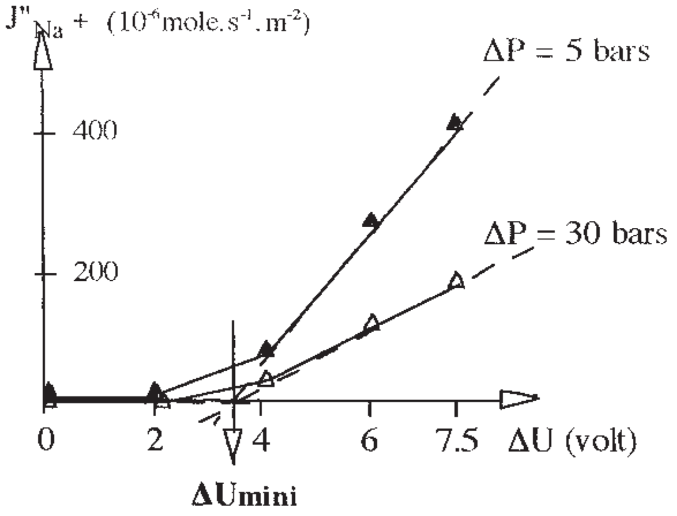

FIG. 4 Calculation of ΔU_{mini}. $\alpha = 1$; $\Delta P = 5$ or 30 bars; $C_{\mathrm{Na}^+} = 10\ \mathrm{mol \cdot m^{-3}}$.

Cation

Experimental data, such as those reported in Fig. 4, suggest that the assumption of a linear variation of J''_{Na^+} versus ΔU may be done above a nearly constant boundary value $\Delta U_{\mathrm{mini}} = 3.4$ V (Table 2).* Below this value, J''_{Na^+} remains close to zero. This leads to

$$J''_{\mathrm{Na}^+} = 0, \qquad \text{if } \Delta U < \Delta U_{\mathrm{mini}} \tag{17}$$

$$J''_{\mathrm{Na}^+} = z_{\mathrm{Na}^+} K''_{\mathrm{Na}^+} C_{r\mathrm{Na}^+} \frac{(\Delta U - \Delta U_{\mathrm{mini}})F}{RT}, \qquad \text{if } \Delta U \geq \Delta U_{\mathrm{mini}} \tag{18}$$

TABLE 2
Calculation of ΔU_{mini} (V) with
α Variable, ΔP Variable,
$C_{\mathrm{Na}^+} = 10\ \mathrm{mol \cdot m^{-3}}$

α	ΔP	ΔU_{mini}
0	10	3.48
	30	3.4
1	5	3.36
	10	3.48
	20	3.91
	30	3.66
4	5	3.21
	10	3.35
	20	3.2
∞	10	3.21
	Average =	3.4

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*At $C_{\mathrm{Na}^+} = 50\ \mathrm{mol \cdot m^{-3}}$, ΔU_{mini} is slightly lower.

Figure 4 also indicates that the slope of J''_{Na^+} versus ΔU is not the same at different ΔP: it is steep for low ΔP and drops when ΔP increases. This variation may result from a slight deformation of the microporous polymeric layer under the effect of pressure. That is why we propose to write

$$K''_{\mathrm{Na}^+} = A_{\mathrm{Na}^+} + B_{\mathrm{Na}^+}\Delta P \tag{19}$$

well in agreement with the data of Fig. 5.

From a thorough investigation of the experimental data, it follows that

$$A_{\mathrm{Na}^+} = 2130 \times 10^{-10}\ \mathrm{m\cdot s^{-1}}$$

$$B_{\mathrm{Na}^+} = (60 - 70.2 I_S / C_{\mathrm{Na}^+}) 10^{-10} \mathrm{m\cdot s^{-1}\cdot bar^{-1}}$$

So that

$$J''_{\mathrm{Na}^+} = z_{\mathrm{Na}^+} C_{r\mathrm{Na}^+} \left[2130 + \left(60 - 70.2 \frac{I_S}{C_{\mathrm{Na}^+}} \right) \Delta P \right] \times 10^{-10} \frac{F \Delta U}{RT} \Lambda_{\mathrm{Na}^+}$$

with $\Lambda_{\mathrm{Na}^+} = 0$ when $\Delta U < 3.4$ V, $\Lambda_{\mathrm{Na}^+} = 1 - 3.4/\Delta U$ when $\Delta U \geq 3.4$ V.

By summing the electrochemical standard potential of water (1.23 V), as well as the oxygen oxidation and hydrogen reduction overvoltages at the anode (0.8 V) and cathode (0.3 V), respectively, a theoretical value of the minimum voltage for electrolysis is obtained (2.33 V). It is always lower than ΔU_{mini}, the practical value at which water hydrolysis takes place at the electrodes. Above this limit the voltage actually applied between the two limiting surfaces

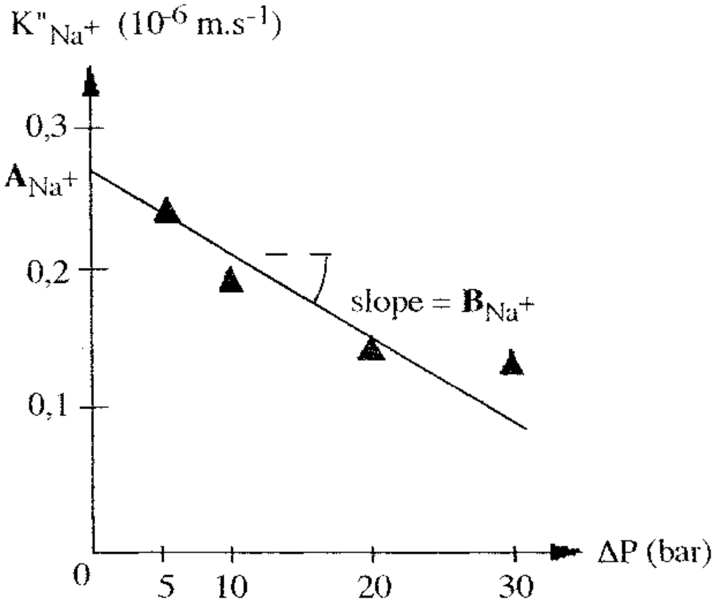

FIG. 5 Calculations of A_{Na^+} and B_{Na^+}. $\alpha = 1$; $\Delta P = 10$ bars; $C_{\mathrm{Na}^+} = 10\ \mathrm{mol\cdot m^{-3}}$.

of Nafion strongly increases, leading to an improved migration of Na$^+$ through the dense part of the membrane. As already explained, this phenomenon will depend on ΔP.

Finally, it appears that

$$J_{\mathrm{Na^+}\,\mathrm{calc}} = C_{r\mathrm{Na^+}}\left(1.73 - 0.93\,\frac{I_{\mathrm{S}}}{C_{\mathrm{Na^+}}}\right) \times (1.71\times 10^{-6} - 2.7\times 10^{-9}C_{\mathrm{Na^+}}\Delta U)\Delta P + z_{\mathrm{Na^+}}C_{r\mathrm{Na^+}} \times \left[2130 + \left(60 - 70.2\,\frac{I_{\mathrm{S}}}{C_{\mathrm{Na^+}}}\right)\Delta P\right] \times 10^{-10}\,\frac{F\Delta U}{RT}\,\Lambda_{\mathrm{Na^+}}$$

As an example, data points and model curves corresponding to $C_{\mathrm{Na^+}} = 10$ mol·m^{-3} and $\alpha = 1$ are reported in Fig. 6. It may be observed that the estimation is acceptable within ±25%. For other values of composition and/or concentration, it is always acceptable within less than ±40%.

Anions

The same procedure as the one previously described for $J''_{\mathrm{Na^+}}$ was also applied to $J''_{\mathrm{Cl^-}}$ and $J''_{\mathrm{SO_4^{2-}}}$. However, with anions the variation of ionic fluxes with the electric field are smooth (there is no marked change in the transport mechanism around ΔU_{mini}), so that $\Lambda_{\mathrm{Cl^-}} = \Lambda_{\mathrm{SO_4^{2-}}} = 1$. $K''_{\mathrm{Cl^-}}$ and $K''_{\mathrm{SO_4^{2-}}}$ values

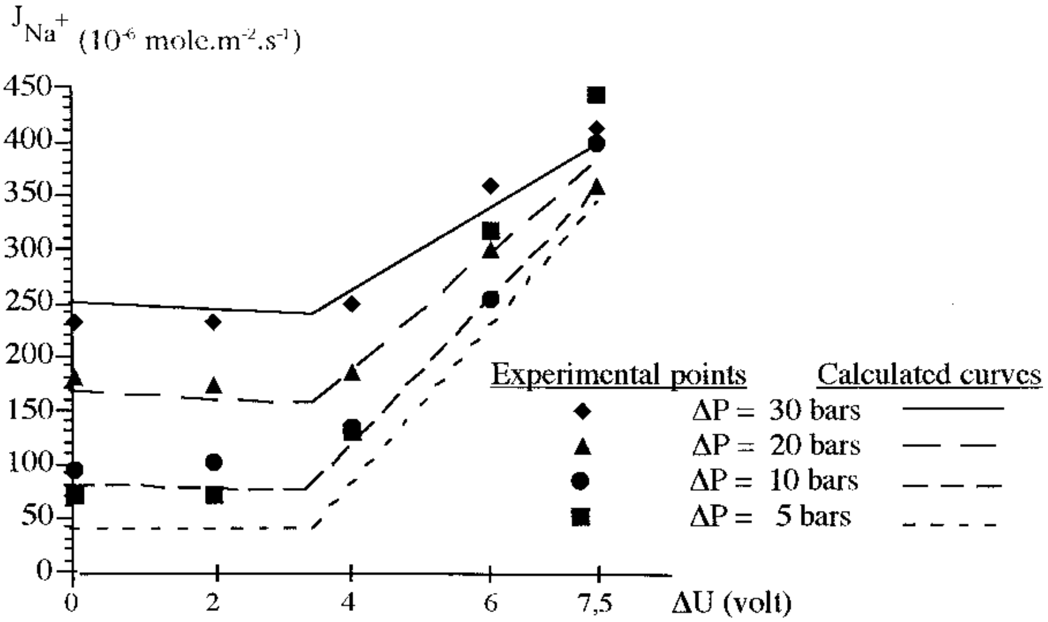

FIG. 6 $J_{\mathrm{Na^+}}$ versus ΔP and ΔU. $\alpha = 1$; ΔP variable; $C_{\mathrm{Na^+}} = 10$ mol·m^{-3}.

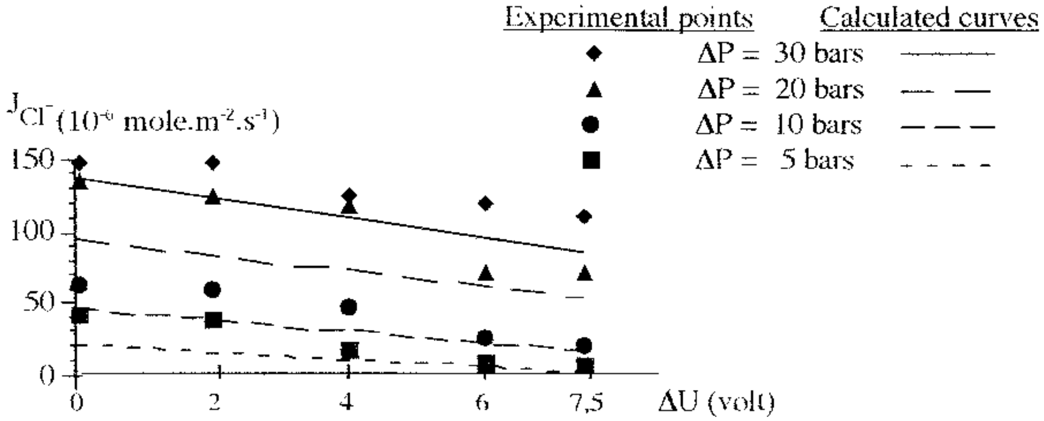

FIG. 7 J_{Cl^-} versus ΔP and ΔU. $\alpha = 1$; ΔP variable; $C_{\mathrm{Na}^+} = 10\ \mathrm{mol}\cdot\mathrm{m}^{-3}$.

seem to depend on ΔP in the same way as does K''_{Na^+}. The same physical meaning as the one already proposed for the cation may be put forward. Thus the expression $K''_i = A_i + B_i\Delta P$ holds. The identification of A and B values leads to

$$A_{\mathrm{Cl}^-} = 164 \times 10^{-10}\ \mathrm{m}\cdot\mathrm{s}^{-1}$$

$$A_{\mathrm{SO}_4^{2-}} = -27 \times 10^{-10}\ \mathrm{m}\cdot\mathrm{s}^{-1}$$

and:

$$B_{\mathrm{Cl}^-} = 8 \times 10^{-10} + 10^{-10}\ I_{\mathrm{S}}/C_{\mathrm{Cl}^-}\ \mathrm{m}\cdot\mathrm{s}^{-1}\cdot\mathrm{bar}^{-1}$$

$$B_{\mathrm{SO}_4^{2-}} = -24 \times 10^{-10} + 9\ 10^{-10}\ I_{\mathrm{S}}/C_{\mathrm{SO}_4^{2-}}\ \mathrm{m}\cdot\mathrm{s}^{-1}\cdot\mathrm{bar}^{-1}$$

As a consequence:

$$J''_{\mathrm{Cl}^-} = z_{\mathrm{Cl}^-}\ C_{r\mathrm{Cl}^-}\ [164 + \left(8 + \frac{I_{\mathrm{S}}}{C_{\mathrm{Cl}^-}}\right)\Delta P] \times 10^{-10}\ \frac{F}{RT}\Delta U$$

$$J''_{\mathrm{SO}_4^{2-}} = z_{\mathrm{SO}_4^{2-}} C_{r\mathrm{SO}_4^{2-}} \left[-27 + \left(-24 + 9\,\frac{I_{\mathrm{S}}}{C_{\mathrm{SO}_4^{2-}}}\right)\Delta P\right] \times 10^{-10}\ \frac{F}{RT}\Delta U$$

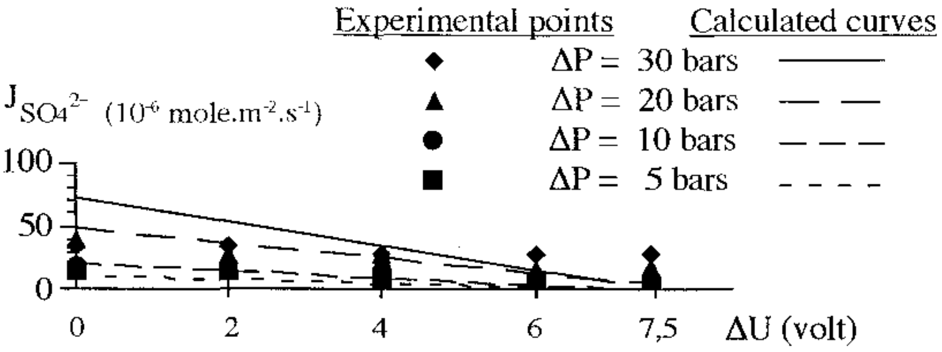

FIG. 8 $J_{\mathrm{SO}_4^{2-}}$ versus ΔP and ΔU. $\alpha = 1$; ΔP variable; $C_{\mathrm{Na}^+} = 10\ \mathrm{mol}\cdot\mathrm{m}^{-3}$.

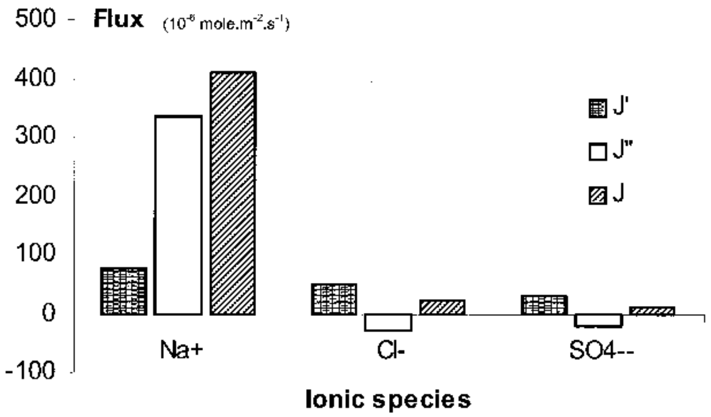

FIG. 9 J_i, J_i', and J_i''. $\alpha = 1$; $\Delta P = 10$ bars; $\Delta U = 7.5$ V.

and

$$J_{\mathrm{Cl^-calc}} = C_{r\mathrm{Cl^-}}\left(-0.07 + 0.85\,\frac{I_{\mathrm{S}}}{C_{\mathrm{Na^+}}}\right)(1.71\times10^{-6} - 2.7\times10^{-9}\,C_{\mathrm{Na^+}}\Delta U)\Delta P + z_{\mathrm{Cl^-}}C_{r\mathrm{Cl^-}}\left[164 + \left(8 + \frac{I_{\mathrm{S}}}{C_{\mathrm{Cl^-}}}\right)\Delta P\right]\times 10^{-10}\,\frac{F}{RT}\Delta U$$

$$J_{\mathrm{SO_4^{2-}calc}} = C_{r\mathrm{SO_4^{2-}}}\left(1.29 - 0.66\,\frac{I_{\mathrm{S}}}{C_{\mathrm{Na^+}}}\right)(1.71\times10^{-6} - 2.7\times10^{-9}C_{\mathrm{Na^+}}\Delta U)\Delta P + z_{\mathrm{SO_4^{2-}}}C_{r\mathrm{SO_4^{2-}}}\times\left[-27 + \left(-24 + 9\,\frac{I_{\mathrm{S}}}{C_{\mathrm{SO_4^{2-}}}}\right)\Delta P\right]\times 10^{-10}\,\frac{F}{RT}\Delta U$$

Figures 7 and 8 clearly show that anion fluxes decrease when ΔU is increased as a consequence of improved migration of negatively charged species toward the central anode. The gap between measured and calculated values is larger for divalent than for monovalent anions, probably due to lower fluxes and thus a loss in precision with sulfate. As a whole, the estimations are acceptable within an average of ±30%.

In Fig. 9 it can be seen that whatever the ionic species, there is a net transport of ions through the membrane: the sum (J_i) of convection (J_i') and migration (J_i'') terms remains positive.

CONCLUSIONS

The bicompartimental model developed in this work considers the microporous Nafion membrane to be made of two parts: a dense part negatively charged and only permeable to a cation under the influence of the electric field, and a porous part where all species can move by convection or migration. This model, which gives a good account of experimental data obtained during ENF of single or mixed ionic solutions, represents a good compromise between those classically proposed for NF with microporous membranes and ED with dense layers.

As deduced from the Stefan–Maxwell approach of mass transfer, the model equations state that ionic fluxes may be written as the sum of two terms: one that linearly varies with J (the permeate flux) and another that is mainly dependent on the electric field. The permeate flux is controlled by the transmembrane pressure.

In agreement with the idea of two cells acting in parallel, the second term does not have the same meaning and expression for the cation and anions. Indeed, for anions, flux varies smoothly with ΔU while for the cation there is a clear change above ΔU_{mini}, the practical value of voltage at which water hydrolysis takes place, thus modifying the distribution of electrical resistances between electrodes.

The use of linear approximations for more complex phenomena leads to quite easy-to-use relations only valid for the range investigated. But it is worth noting that the general pattern and ideas proposed for modeling in this study can be easily extended to other areas.

SYMBOLS

C_{pi}	ion concentration in permeate ($\mathrm{mol \cdot m^{-3}}$)
C_{ri}	ion concentration in retentate ($\mathrm{mol \cdot m^{-3}}$)
C_i^*	i-average concentration in the membrane ($\mathrm{mol \cdot m^{-3}}$)
D_i	diffusivity of i ($\mathrm{m^2 \cdot s^{-1}}$)
F	Faraday number ($\mathrm{C \cdot eq^{-1}}$)
I_s	ionic strength of the solution ($\mathrm{mol \cdot m^{-3}}$)
J	solvent flux ($\mathrm{m \cdot s^{-1}}$)
J_i	ionic flux ($\mathrm{mol \cdot s^{-1} \cdot m^{-2}}$)
K	membrane permeability ($\mathrm{m \cdot s^{-1} \cdot bar^{-1}}$)
R	gas constant ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)
R_i	ion rejection (%)
S	membrane surface ($\mathrm{m^2}$)
S_p	total open surface of pores ($\mathrm{m^2}$)
T	absolute temperature (K)
u	fluid velocity referred to the membrane surface ($\mathrm{m \cdot s^{-1}}$)
u'	fluid velocity referred to the total pore surface ($\mathrm{m \cdot s^{-1}}$)

v_i	velocity of i referred to the membrane surface ($m \cdot s^{-1}$)
z	space variable (m)
z_i	ionic valence (—)

Greek

α	salt concentration ratio (= $[Na_2SO_4]/[NaCl]$)
Γ_i	friction factor of i with the membrane ($m^2 \cdot s^{-1}$)
ΔP	transmembrane pressure (bar)
ΔU	voltage (volt)
θ_i	free diffusivity of i in water ($m^2 \cdot s^{-1}$)
υ_i	molar volume of i ($m^3 \cdot mol^{-1}$)
$A_i, B_i, E, F, K_i', K_i''$	empirical coefficients in various model equations

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