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Electronanofiltration: A New Process for Ion Separation

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ABSTRACT

Nanofiltration (NF) is a new pressure-driven process which typically concerns the separation of species having a size of about 1 nanometer. Applications have been proposed in the fields of biotechnology, drinkable water production, and brackish water treatment. As regards size exclusion of neutral solutes, NF membranes have characteristics intermediate between those for ultrafiltration and reverse osmosis. Most of them also have a charge density which explains their typical use in salt solution filtration. Thus nanofilters can distinguish ionic species according to their size and/or valence. This pioneering work aims to study the influence of an additional electric field on NF performance in the case of single or mixed ionic solutions. This is the so-called "electronanofiltration (ENF) process," here experimented with using a new type of organo-inorganic membrane. Results are given in terms of fluxes, ion rejections, pH of solutions, and current densities. General trends are emphasized and discussed.

Key Words. Nanofiltration; Electric field; Ion rejection; Organo-inorganic membrane

INTRODUCTION

The most classical membrane processes for the treatment of salt and ionic solutions are electrodialysis (ED) and reverse osmosis (RO) (1). Both

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of them allow the dilution or concentration of solutions, but only ED uses an external adjustable electric field that leads to ion selection.

A few years ago, the idea of coupling two driving forces—pressure and electric field—was proposed as a way to reduce concentration polarization. This is the so-called electrofiltration (EUF) process that was applied to the concentration and/or separation of charged molecules (2–4) or particules (5, 6).

More recently, it has been shown that nanofiltration (NF) membranes (7, 8) also provide a good mean for salt separation due to their own electrical charge, but there is no direct control of the transmembrane voltage that naturally develops during the process (streaming potential).

In this paper, after a short review of ED and pressure-driven processes, the first results obtained by superimposing an electric field on a classical nanofiltration operation are presented. This is the new "electronanofiltration" (ENF) process.

Electrodialysis

This voltage-driven process aims to promote the selective transport of either anions or cations through dense semipermeable membranes with an opposite charge (anion-exchange or cation-exchange membranes, respectively (9). The membranes are not permeable to the solvent, which is usually water for salt solutions (10). Donnan exclusion constitutes the main mechanism for ion separation. ED membranes require high electrical conduction, a moderate degree of swelling, and good chemical stability. Because not all these constraints are easy to fulfill, there are just a few commercially available membranes on the market. As a whole, the process energy consumption is low.

Pressure-Driven Processes

Ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF) are pressure-driven processes where the membrane retains molecules or ions. Basically, in RO the objective is to remove water from a salty solution. In UF, ions and small molecular weight solutes are separated from macromolecules such as proteins. In NF, the separation may involve ions and/or small neutral solutes.

Two kinds of membranes can be distinguished (11): dense membranes in RO and NF, and porous membranes for UF and NF. Another distinction can be made between organic and inorganic materials (1, 12). While organic polymers present a fixed electric charge, amphoteric inorganic ceramics exhibit different behaviors. They may be positively or negatively charged depending on whether the pH of the bulk solution is below or beyond the isoelectric point (PIE) of the material (12).

Contrarily to ED, there is no anion/cation selection with pressure-driven processes, but the solvent flux may be easily varied by changing the transmembrane pressure, thus leading to the purification or concentration of charged solutes.

In this work, using the same apparatus designed for EUF (13, 14), a radial electric field has been superimposed on the transmembrane pressure during NF experiments. The possibility of sorting and concentrating ions in a single step has been explored with this device.

EXPERIMENTAL

Experimental Setup

The membrane is an organo-inorganic tubular element created from an α-alumina macroporous support, an intermediate mesoporous titania substrate, and a very thin microporous film of negatively charged Nafion (15). Its useful length and diameter are 1.32×10^{-1} m and 6.8×10^{-3} m, respectively (membrane surface area: 2.82×10^{-3} m^2).

The experimental setup 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 (diameter: 3×10^{-3} m). The cathode is a cylindrical wire netting stuck on the ceramic support Figs. 1 and 2.

Solutions

Single salt and mixed solutions of Na_2SO_4 and NaCl were successively tested. Most of them presented a constant counterion concentration—$[Na^+] = 10$ mol·m^{-3}—and different values of $\alpha = [Na_2SO_4]/[NaCl]$, the salt concentration ratio (Table 1). However, the influence of the total concentration was checked by making $[Na^+] = 50$ mol·m^{-3} at $\alpha = 1$.

The anion and cation concentrations were measured by high performance liquid chromatography (Dionex QIC Analyser) and atomic absorption (Atomic Absorption Spectrometer: SpectrAA-20), respectively.

Operating Conditions

Experiments were carried out at a fixed temperature ($T = 303$ K) under a constant bulk concentration (permeate and retentate were continuously recycled to the feeding tank). Various transmembrane pressures (5, 10,

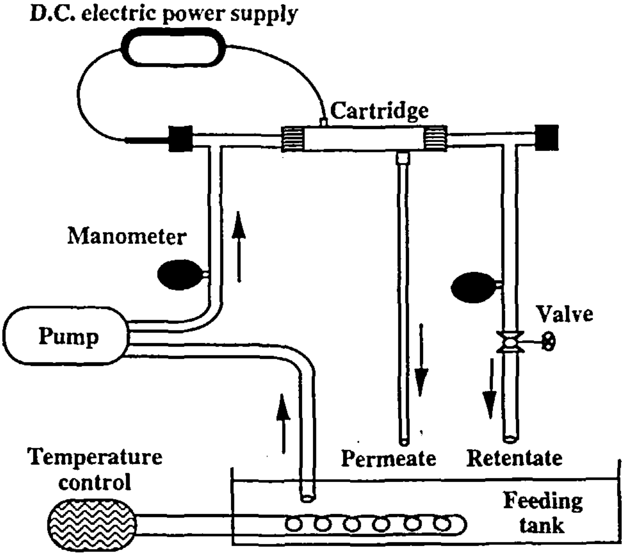


FIG. 1 Pilot plant.

20, and 30 bar) were successively tried. The tangential fluid velocity was 3 $m \cdot s^{-1}$, which corresponds to a feed flow rate of about 8.78×10^{-5} $m^3 \cdot s^{-1}$. The volume of the feeding tank was around 10^{-2} m^3.

Because the membrane was negatively charged, it was first decided to set up the anode inside the membrane and the cathode outside the mem-

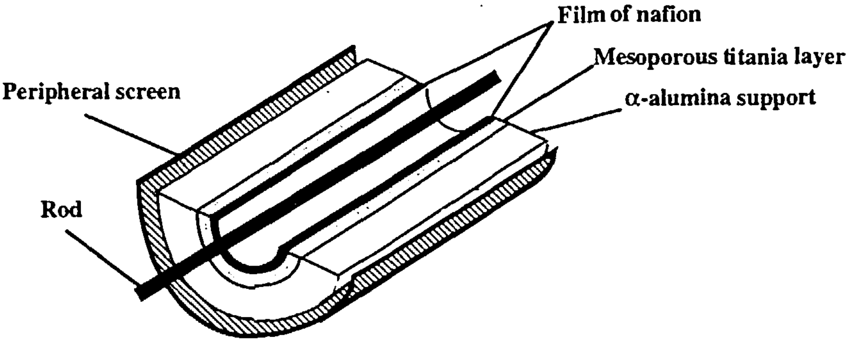


FIG. 2 Nanofiltration membrane and electrodes setup.

TABLE 1
Ion Concentrations of Feed Solutions C_i (10^{-6} mol·m^{-3})

	Solutions		
α	C_{Cl^-}	$C_{SO_4^{2-}}$	C_{Na^+}
0	10	0	10
0.25	6.67	1.67	10
1	3.33	3.33	10
4	1.11	4.44	10
16	0.33	4.85	10
∞	0	10	10

brane in order to promote a "pumping effect" of Na^+ through the porous medium. In what follows, the process performance is examined in relation to this objective.

The electric field was progressively increased from a fixed transmembrane pressure, ΔP, always starting from the previous equilibrium conditions. The maximum value of the electric voltage, ΔU, was fixed at 6 or 7.5 V to prevent electrode damage with high ($C = 50$ mol·m^{-3}) and low ($C = 10$ mol·m^{-3}) concentrated solutions.

The influence of ΔP, ΔU, and α on the fluxes of solvent, J (m·s^{-1}), or ions, J_i (mol·s^{-1}·m^{-2}), as well as on the rejections R_i (%) and selectivities $S_{i/j}$ (between the two species i and j) was investigated using the following equations:

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

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

$$S_{i/j} = \frac{100 - R_i}{100 - R_j} = \frac{C_{rj}}{C_{ri}} \cdot \frac{C_{pi}}{C_{pj}} \tag{3}$$

where C_{pi} and C_{ri} are the ion concentrations in the permeate and retentate, respectively.

The current, I(A), and pH values were also recorded.

RESULTS AND DISCUSSION

NF and ENF Performances

The rejections by nanofiltration, shown in Fig. 3, are in good agreement with other data previously reported in the literature (16–19). The divalent

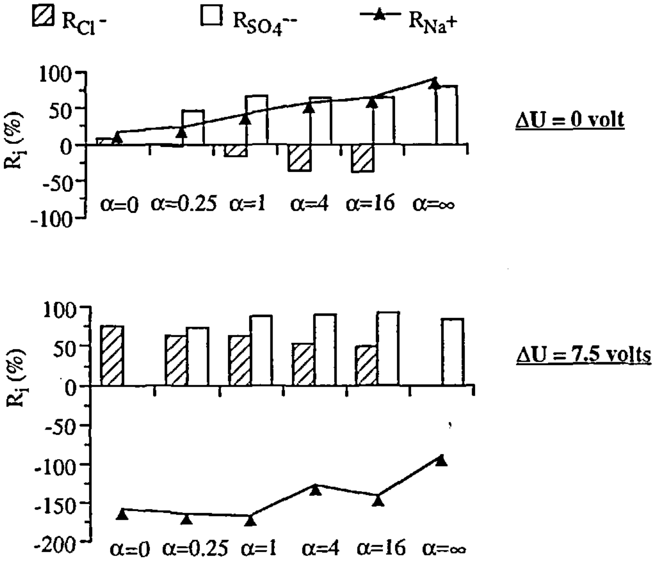


FIG. 3 Ion rejections for NF and ENF (ΔP = 10 bars; C = 10 mol·m^{-3}).

co-ion, SO_4^{2-}, is retained more than the monovalent anion, Cl^-, and the rejection of sodium and sulfate increases with α while chloride rejection goes down to negative values at $\alpha \geq 0.25$. These results have all been previously interpreted taking into account electrical effects: Donnan equilibrium at interfaces or streaming potential inside the pores (19, 20).

For ENF (ΔU = 7.5 V), the same trends prevail: the rejection of the counterion (Na^+) increases with α while the chloride rejection decreases, but the values of R_{Na^+} are considerably lower than for NF and well below zero. Conversely, anion rejections are always positive. As a whole, the permeate becomes more (less) concentrated in counterions (co-ions) than the retentate. There is a clear "pumping effect" of sodium in the presence of the electric field.

As shown in Table 2, the selectivity between chloride and sulfate increases with α for both NF and ENF but the causes are different. At ΔU = 0 V there is a continuous increase in $(1 - R_{Cl^-})$ while at ΔU = 7.5 V $(1 - R_{SO_4^{2-}})$ progressively approaches zero. That is the reason why S(NF) > S(ENF) at $\alpha \leq 1$ and S(NF) < S(ENF) at $\alpha \geq 4$.

Finally, it may be added that the solvent flux does not depend on α and varies slightly under electric field conditions: 1.41×10^{-5} m·s^{-1} for NF against 1.31×10^{-5} m·s^{-1} for ENF.

TABLE 2
Anion Selectivity $S_{SO_4^{2-}/Cl^-}$ versus α and ΔU
($C = 10\ \text{mol·m}^{-3}$)

α	Solutions NF ($\Delta U = 0$)	 ENF ($\Delta U = 7.5$)
0	—	—
0.25	1.9	1.4
1	3.4	3.1
4	3.8	4.6
16	4.0	7.3
∞	—	—

Effect of Voltage

Variations of R_i versus ΔU are the same whatever the value of α. In what follows, data points refer to $\alpha = 1$.

The most glaring effect of an electric field is the cation (anion) rejection decrease (increase). This "pumping effect" of Na^+ is clearly expressed by means of selectivities S_{Na^+/Cl^-} and $S_{Na^+/SO_4^{2-}}$ that continuously increase with ΔU, as reported in Table 3, but $S_{Cl^-/SO_4^{2-}}$ remains nearly constant.

As indicated in Fig. 4, sulfate rejection increases slightly with ΔU, while chloride retention is considerably modified (from − 17% at $\Delta U = 0$ V to 63% at $\Delta U = 7.5$ V at $C = 10\ \text{mol·m}^{-3}$). Moreover, counterion rejec-

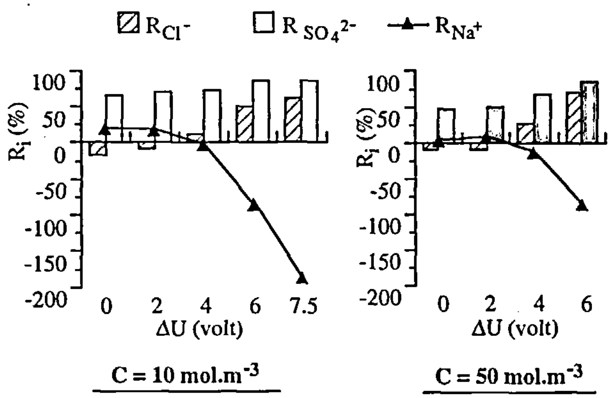


FIG. 4 Ion rejections versus ΔU ($\alpha = 1$; $\Delta P = 10$ bars).

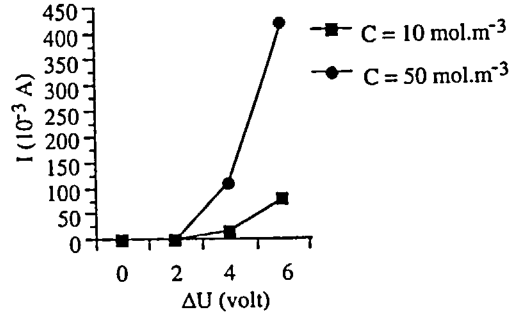


FIG. 5 I versus ΔU (α = 1; ΔP = 10 bars).

tion starts decreasing sharply between 2 and 4 V. At the same time, a rapid increase in current density (Fig. 5) and strong variations of pH values (Fig. 6) are recorded.

All these results may be explained by electrode reactions generating protons (and chloride) at the anode and hydroxyl ions at the cathode:

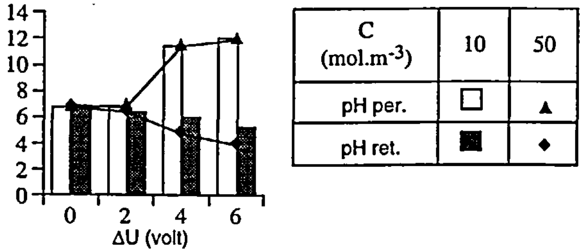
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \text{ (at the anode)}$$

$$(2Cl^- \rightarrow Cl_2 + 2e^-)$$

and

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \text{ (at the cathode)}$$

It is worth recalling that the normal oxidation-reduction potential of water is 1.23 V (pH 0, T = 298 K). For the process under consideration, the ohmic resistance of the liquid phase, the overvoltage on stainless steel electrodes, as well as the pH and temperature working conditions must maintain the boundary value between 2 and 4 V.



C (mol.m^{-3})	10	50
pH per.	□	▲
pH ret.	■	◆

FIG. 6 pH versus ΔU (α = 1; ΔP = 10 bars).

Effect of Feed Concentration

In Fig. 4, R_i versus ΔU has been drawn at $C = 10$ mol·m^{-3} and $C = 50$ mol·m^{-3} ($\alpha = 1$). It may be seen that the directions of the variations are independent of C. Anion rejections increase and cation rejections decrease from 0 to 6 V.

The difference between sulfate and chloride rejections, and thus their selectivity (Table 3), decreases when C increases. This is particularly true for NF, as already explained by Rios et al. (19). At high voltage, sodium and sulfate rejections are practically independent of C; only chloride rejection varies from 50% ($C = 10$ mol·m^{-3}) to 70% ($C = 50$ mol·m^{-3}) at $\Delta U = 6$ V.

At $C = 50$ mol·m^{-3} the electric current increases logarithmically (Fig. 5), but pH values vary only slightly (Fig. 6). Indeed, in terms of OH^- concentration, a ratio of just about 5 is obtained when the total concentration is increased from 10 to 50 mol·m^{-3}.

According to Fig. 7, the solvent flux decreases as ΔU is increased. Variations are all the more important when the concentration is higher. This could be due to a larger electroosmosis flow that would logically lead to lower J values when C is increased. Conversely, for nanofiltration ($\Delta U = 0$ V), the flux is all the higher as the concentration is larger. One can think that in micropores the fixed Stern layer thickness diminishes as C is increased, thus giving a larger free cross-section surface area for flow (19).

Effect of Transmembrane Pressure

Figure 8 shows the variations of R_i as a function of ΔP at 0 and 7.5 V ($\alpha = 1$).

It appears that rejections for NF and ENF are all the more different as ΔP is lower. At $\Delta P = 5$ bar R_{Na^+} strongly decreases from 30 to −367%

TABLE 3
Selectivities versus ΔU and C ($\alpha = 1$)

	S_{Na^+/Cl^-}		$S_{Na^+/SO_4^{2-}}$		$S_{Cl^-/SO_4^{2-}}$	
ΔU (V)	$C = 10$	$C = 50$	$C = 10$	$C = 50$	$C = 10$	$C = 50$
0	0.5	0.7	1.7	1.5	3.4	2.1
2	0.6	0.7	2.1	1.5	3.6	2.2
4	1.0	1.3	3.1	2.9	3.2	2.3
6	3.3	5.5	11.9	11.1	3.6	2.0
7.5	6.9	—	20.6	—	3.0	—

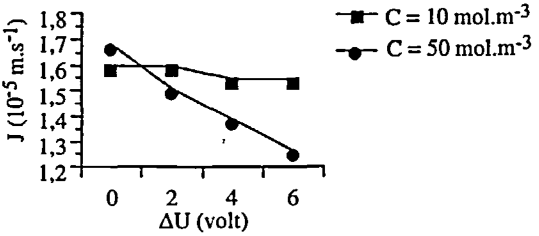


FIG. 7 J versus ΔU (α = 1; ΔP = 10 bars).

when changing from NF to ENF working conditions, while anion rejections increase from −27 to 81% for chloride and from 56 to 90% for sulfate.

All the curves seem to reach a plateau value at high pressure. This could indicate that rejections become less dependent on ΔU. The flux of solvent logically increases with ΔP (Table 4).

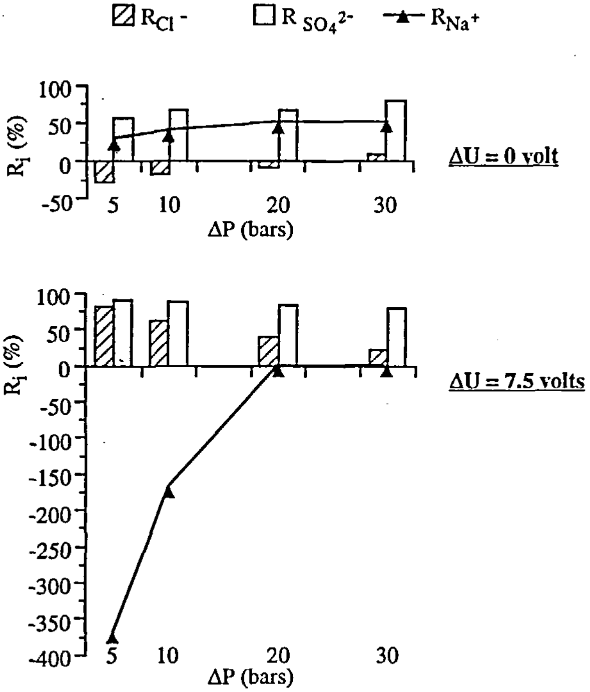


FIG. 8 Ion rejections versus ΔP (α = 1; C = 10 mol·m^{-3}).

TABLE 4
Solvent Flux J (10^{-6} m·s^{-1}) versus ΔP
($\alpha = 1$; $C = 10$ mol·m^{-3})

	ΔP (bar)			
ΔU (V)	5	10	20	30
0	10	16	37	49
7.5	9	16	36	42

As a whole, the variations of ion fluxes versus ΔP are less pronounced under ENF conditions (Fig. 9). In that case, J_{Na^+} is considerably higher than J_{Cl^-} and $J_{SO_4^{2-}}$. The similarity of the J_{Na^+} and I curves suggests that sodium constitutes the main current carrier.

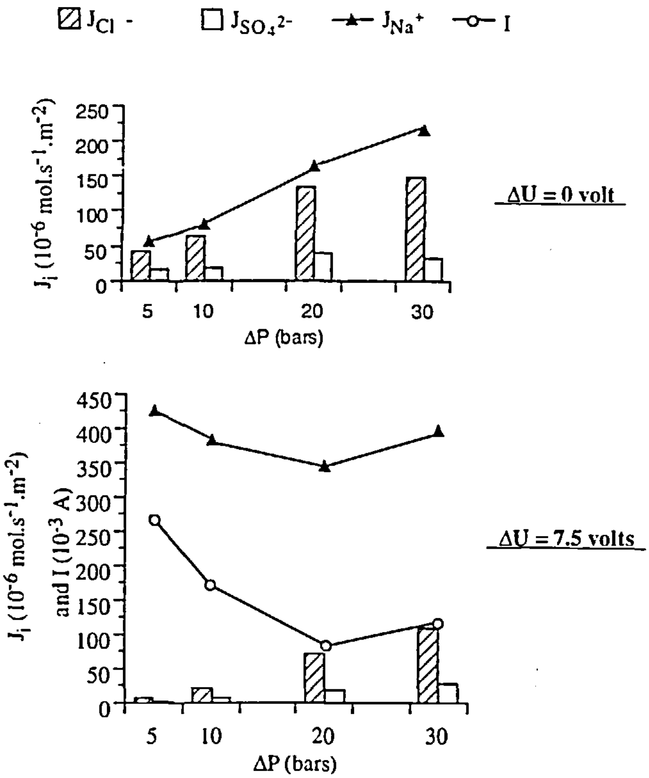


FIG. 9 Ion molar fluxes J_i and current density I versus ΔP ($\alpha = 1$; $C = 10$ mol·m^{-3}).

The pH values are not significantly modified by changing ΔP.

Process Energy Consumption

The parts of energy consumption respectively due to voltage, E_U (W), and transmembrane pressure, E_P (W), may be written

$$E_U = I\Delta U \tag{4}$$

$$E_P = J\Delta P \tag{5}$$

As shown in Table 5, their sum, $E = E_U + E_P$, increases with ΔP at low voltage ($\Delta U \leq 2$ V), but E_U becomes very high compared to E_P above 4 V, and the total energy consumption goes in the direction opposite of ΔP. In fact, there is an increase in convection with ΔP. Thus, the difference between anion and cation permeations is reduced as is the current density value.

The flux of salt ions through the membrane, which corresponds to the electric current conveyed by Na^+, Cl^- and SO_4^{2-}, may be written

$$I_{ion.} = FS \sum_i z_i J_i \tag{6}$$

TABLE 5

Energy Consumption E_P, E_U, and E versus ΔU and ΔP ($\alpha = 1$; $C = 10\ \text{mol·m}^{-3}$)

		ΔP (bar)			
ΔU (V)		5	10	20	30
0	E_P	0.01	0.05	0.21	0.41
	E_U	0	0	0	0
	E	0.01	0.05	0.21	0.41
2	E_P	0.01	0.05	0.20	0.41
	E_U	0.00	0.00	0.00	0.00
	E	0.02	0.05	0.21	0.42
4	E_P	0.01	0.05	0.20	0.35
	E_U	0.14	0.08	0.07	0.08
	E	0.15	0.12	0.28	0.43
6	E_P	0.01	0.04	0.20	0.35
	E_U	0.93	0.49	0.30	0.33
	E	0.94	0.54	0.50	0.68
7.5	E_P	0.01	0.04	0.20	0.35
	E_U	2.03	1.28	0.60	0.86
	E	2.04	1.33	0.80	1.22

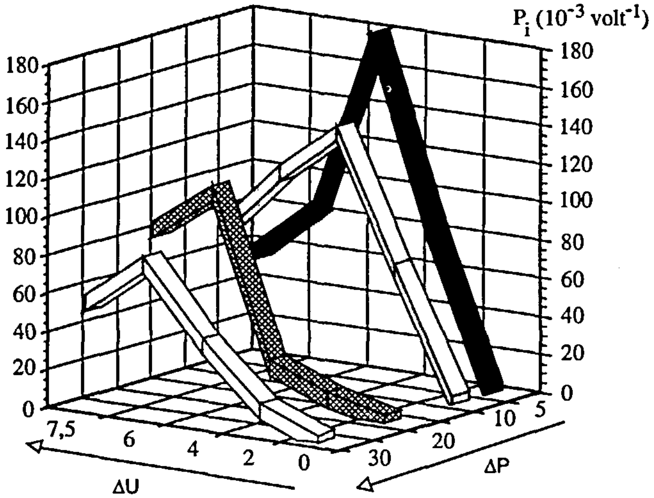


FIG. 10 P_i versus ΔU and ΔP ($\alpha = 1$).

with F the number of Faradays (C·eq^{-1}) and S, the membrane surface (m^2). $I_{\text{ion.}}$ increases with ΔU because of the "pumping effect" of sodium, and it decreases with ΔP, which generates a stronger anion permeation (Fig. 9).

Optimum working conditions associated with reduced electrochemical reactions at electrodes are found when the separation coefficient P_i (volt^{-1}), defined as

$$P_i = I_{\text{ion.}}/E \tag{7}$$

is maximum. From Fig. 10 it appears that $\Delta U = 4$ V; $\Delta P = 5$ or 10 bar, and $\Delta U = 6$ V, $\Delta P = 20$ or 30 bar, agree well with this objective.

CONCLUSION

In this paper a new process has been presented that consists of superposing on a classical nanofiltration operation a radial electric field to induce ion separation and concentration at the same time. Experiments were carried out using an hybrid tubular membrane constituted from a microporous Nafion top layer deposited on a ceramic support. As expected, the experimental results clearly indicate that the electric field strongly modifies the kinetics of ionic transport through the membrane.

The transport of cations through the wall is increased while anions are trapped inside the tubular element. The combination of the actions of the electric field and the transmembrane pressure effectively allows ion separation and concentration in either permeate or retentate depending on ion valency.

The general trends of variations for ion rejection, pH value, or current are not modified by changing the ratio of anion concentrations in the feed solution. Even with a high electric field ($\Delta U = 7.5$ V), the selectivity between mono- and divalent co-ions is unchanged.

Assessment of the process energy consumption indicates that optimal working conditions that correspond to reduced electrochemical reactions at the electrodes may be found. Other studies involving different species are now in progress. They aim to clarify the basic process mecanisms of the process, as well as to fit data with appropriate models.

SYMBOLS

C	feed concentration ($mol \cdot m^{-3}$)
C_{pi}	ion concentration in permeate ($mol \cdot m^{-3}$)
C_{ri}	ion concentration in retentate ($mol \cdot m^{-3}$)
I	current (A)
$I_{ion.}$	current conveyed by salts (A)
E	total power consumption (W)
E_U	power consumption due to voltage (W)
E_P	power consumption due to transmembrane pressure (W)
F	number of Faraday ($C \cdot eq^{-1}$)
J	solvent flux ($m \cdot s^{-1}$)
J_i	ion flux ($mol \cdot s^{-1} \cdot m^{-2}$)
P_i	separation coefficient (V^{-1})
R_i	ion rejection (%)
S	membrane surface (m^2)
$S_{i/j}$	selectivity between i and j
ΔP	transmembrane pressure (bar)
ΔU	voltage (V)

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