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C. Gavach, J. Bribes, A. Chapotot, J. Maillols, G. Pourcelly, et al.. Improvements of the selectivity of ionic transport through electrodialysis membranes in relation with the performances of separation electromembrane processes. *Journal de Physique IV Proceedings*, 1994, 04 (C1), pp.C1-233-C1-243. 10.1051/jp4:1994117 . jpa-00252459

HAL Id: jpa-00252459

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Submitted on 4 Feb 2008

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Improvements of the selectivity of ionic transport through electro dialysis membranes in relation with the performances of separation electromembrane processes

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Abstract

Separation electromembrane processes such as electro dialysis or electro-electro dialysis are being applied to bioindustries and to the treatment of industry waste waters. For these purposes, the selectivity of ion transport has to be improved in order to obtain performances of the process which are compatible with the technico-economical conditions. In this paper, we examine four particular cases where the analysis of the ion transport selectivity has been developed in relation with better performances of the electromembrane processes:

- (i) Reduction of the proton leakage through anion exchange membranes in contact with acidic solutions.
- (ii) Specific transport of protons through cation exchange membranes in contact with solutions containing both an acid and a bivalent metallic ion.
- (iii) Reduction of cation leakage through bipolar membranes.
- (iiii) Loss of permselectivity of cation exchange membranes due to the poisoning of the membrane by organic ions

INTRODUCTION

Electromembrane processes are not only a part of applied electrochemistry (membrane electrolysis, fuel cells, storage batteries etc...), but they also belong to the field of separation techniques through electro dialysis (ED) and electro-electro dialysis (EED). ED has been developed for several years, essentially for desalting brackish waters and reconcentrating brine from sea water. Nowadays, EED remains at the pre-industrial step of development but the perspective of this technology, as well those of ED are very exciting because they can be applied to the environment protection (depollution and recycling of chemicals) and to bioindustries (food, pharmacy and biotechnology). ED is already used at a large industrial scale in dairy industries for demineralization of whey.

For these new kinds of applications, special membranes have been elaborated showing adapted selectivity in ion transport under an electrical driving force. The synthesis of new membrane material involves the knowledge of the physicochemical mechanisms at the basis of the selectivity of ion transport in the membrane. Among the recent progresses in ED and EED resulting from an improvement of the ionic transport selectivity, one can mention:

- (i) Recovery and purification of acid from metallurgy effluents;
- (ii) Chemical recycling of salt effluents with the production of acids and bases;
- (iii) Extraction and reconcentration of charged biomolecules from protein hydrolyzates and fermentation broths.

This paper is a short review of the results obtained by our research group in the frame of studies which have been undertaken for these purposes. Four special cases have been examined and are schematically represented in Fig. 1:

(i) **Reduction of the proton leakage through anion exchange membranes (AEM) in contact with acidic solutions.** ED membranes are swollen polymeric ion exchangers. Due to the presence of sorbed water, AEM are proton conductors. That is the reason why, up to now, ED was not applied to the treatment of acidic solutions. For this purpose, ideal AEM must be only permeable to anions and not to protons (Fig. 1a).

(ii) **Specific transport of protons through cation exchange membranes (CEM) in contact with solutions containing both an acid and a bivalent metallic ion.** Combining an ideal CEM only permeable to proton and not to the metallic cation (Fig. 1b), and an AEM with no proton leakage, it will be possible to apply ED to the treatment of metallurgy effluents for obtaining concentrated and purified acids.

(iii) **Reduction of cation leakage through bipolar membranes (BPM).** A bipolar membrane is composed of a cation exchange layer (CEL) and an anion exchange layer (AEL). When this membrane is placed between two salt solutions and submitted to an electrical field, a cation leakage takes place across the BPM, leading not only to a loss of current efficiency for the proton and hydroxyde ion generation, but also to a lower degree of purity of the produced acid (Fig. 1c).

(iiii) **Loss of permselectivity of CEM due to the poisoning of the membrane by organic ions.** During ED experiments with solutions containing organic ions, fouling phenomena are observed, giving rise to a loss of permselectivity of the membrane and an increase of its electrical resistance [1-3]. These effects are due to a poisoning of the membrane by hydrophobic or amphiphilic ions penetrating into the membrane material. For the application of ED to the extraction of an organic cation, the ideal CEM should be only permeable to the cation and not to the inorganic anion (Fig. 1d).

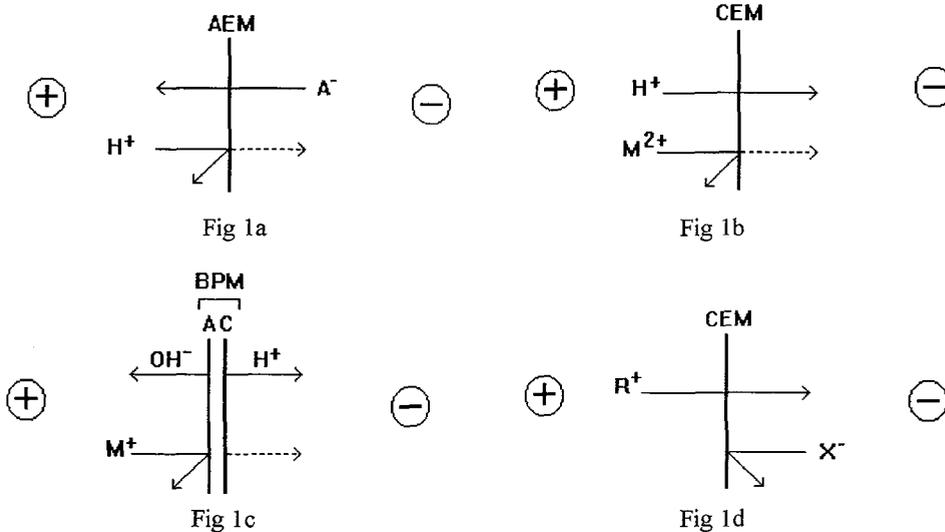


Figure 1: Four cases of selectivity for homopolar or bipolar membranes.

EXPERIMENTAL

For all the studied homopolar membranes, the following parameters have been measured: thickness, water content, amount of sorbed species, electrical conductivity and self-diffusion or unidirectional fluxes by means of the radiotracers technique. All these classical techniques have been already described elsewhere [4,5]. Moreover, Raman spectroscopy, which is a technique able to determinate the nature and the amount of sorbed species, has been applied and is the object of a particular development. For the bipolar membranes, two main characteristics have been measured: the transmembrane potential difference under a given applied current density [6] or the co-ion leakage by means of the radiotracers technique.

RESULTS AND DISCUSSION

Raman spectroscopy

Vibrational spectroscopy is known as a valuable tool to characterize various materials. Infrared absorption technique is generally most widely used than Raman scattering. However, in the investigation of ion exchange membranes immersed in aqueous solutions, the major advantage of Raman spectroscopy is the easy measurement of the fundamental vibrational spectra of these materials. Besides, industrial ion exchange membranes are polymeric films with a thickness between 100 and 200 μm on account of mechanical constraints. Thereby, only Raman measurements can be carried out under these experimental conditions. The main contribution of Raman spectroscopy to investigate this type of membranes have already been emphasized [7,8], giving informations about the macroscopic membrane homogeneity, the relative grafting rate, the overall degree of ionization and the intrinsic pK (weak ion exchanging sites).

Another interesting possibility provided by Raman technique is to allow the detection of some molecules or molecular ions in the interstitial phase of the membranes in contact with electrolyte solutions. When the ARA membrane, which is an AEM for acid reconcentration, is immersed in sulfuric acid solutions, the signals belonging to HSO_4^- and SO_4^{2-} ions present within the membrane phase can be detected as seen in Fig.2. Using these signals, the ratio R of the amount of hydrogenosulfate ions over sulfate ions can be determined as a function of the external concentration of the sulfuric acid (Fig.3). The results obtained show a difference in the variation in these ratio compared to that in the external solution. Analysis of these data shows that R first increases in the 0.25-1M external concentration range, opposite to the aqueous solution behaviour. This fact confirms that HSO_4^- ions are already present in the membrane in the close vicinity of ion exchanging sites (vinylpyridinium), at low external concentration, as indicated by radiotracer measurements [9].

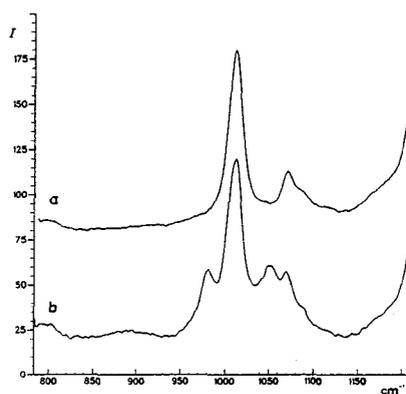


Figure 2: Raman spectra of the ARA membrane
(a) immersed in 1M HCl solution;
(b) immersed in 0.25M H_2SO_4 solution

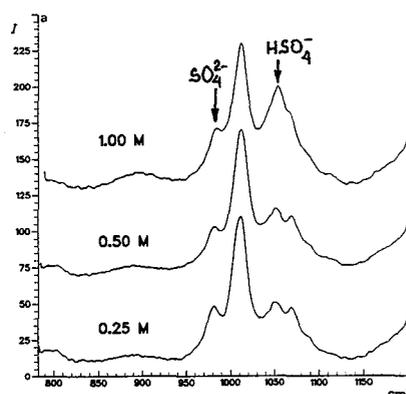


Figure 3: Raman spectra of the ARA membrane immersed in H_2SO_4 aqueous solution of increasing molar concentration.

Anion exchange membranes designed for the recovery of acids by electro dialysis

New commercial membranes showing a reduced proton leakage have been specially manufactured for the recovery of acids: the AAV Selemion membrane produced by Asahi Glass, the ACM Neosepta from Tokuyama Soda and the ARA membrane from Morgane. The study of the mechanisms of the selectivity of these anion exchange membranes is carried out in HCl solutions and can be divided into two parts:

(i) The equilibrium properties i.e. when the membrane is not submitted to an electrical driving force. In this case, the measurements of exchange capacity, sorption, water-content, ionic composition of the interstitial phase, electrical conductivity and self-diffusion flux lead to the determination of the ionic mobilities.

(ii) The non-equilibrium properties, i.e. when the membrane is submitted to an electrical driving force. In this case, the measurements of the transport numbers of the mobile species allow the determination of both the concentration profiles within the diffusion layers and the kinetic parameters of the ionic interfacial transfer. The study is limited to the case where the membranes are interposed between symmetrical HCl aqueous solution in order to prevent the transport of acids by dialysis.

Mobilities of ions within the membrane phase

The species present within the membrane phase are the Cl^- ions balancing the exchange sites and the Cl^- and H^+ ions resulting from the dissociation of the sorbed HCl. Raman spectroscopy measurements had shown that no molecular HCl species was present within the membrane phase for external HCl concentrations ranging from 0.1M to 6M [10]. For each HCl concentration of the equilibrating solution, the ionic composition of the membrane phase, the electrical conductivity and the self-diffusion flux of the chloride ions measured by the radiotracer technique are known. Assuming a proportional contribution of both the Cl^- ions balancing the exchanging sites and the Cl^- ions in the interstitial region to the self-diffusion flux of the chloride ions, the individual ionic mobilities of ions can be calculated (Fig.4).

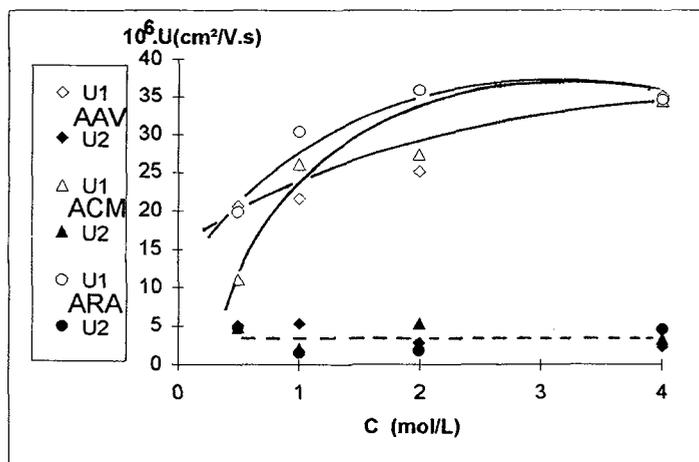


Figure 4: Calculated values of the individual mobilities of the chloride ions within the membrane phase: u_1 : Cl^- ions balancing the exchanging sites (active region); u_2 : Cl^- ions resulting from the dissociation of sorbed HCl (interstitial region).

The mobility of the Cl^- counter-ions in the vicinity of the exchanging sites is always higher than that of chloride sorbed species. The conduction mechanisms seem to be very different in the two regions. These results are corroborated by the results of sorption measurements. The experimental sorption curves are completely different from that predicted by the Donnan relation on the basis of the gel-model i.e. the membrane is assimilated to an homogeneous polyelectrolyte. So, we have to consider the region of the membrane material where ion movements take place, as composed of two distinct phases, on one hand, an "active region", located in the close vicinity of the exchanging sites and, on the other hand, an "interstitial region" containing the dissociated acid. In the active region, the counter-ions move by an hopping mechanism, the elementary step being a transfer reaction from the vicinity of one exchanging site to another, while the migration of Cl^- and H^+ within the interstitial region can be considered as a dragging mechanism with which friction against the polymeric chains must be taken into account, at least for the chloride ions.

Transport number of the counter-ion and kinetic parameters of the interfacial transfer.

The transport number of the Cl^- counter-ion under an applied current density of $100\text{mA}\cdot\text{cm}^{-2}$ is calculated from unidirectional flux measurements. Fig.5 shows that the ARA and the AAV present a reduced proton leakage with respect to the ACM membrane.

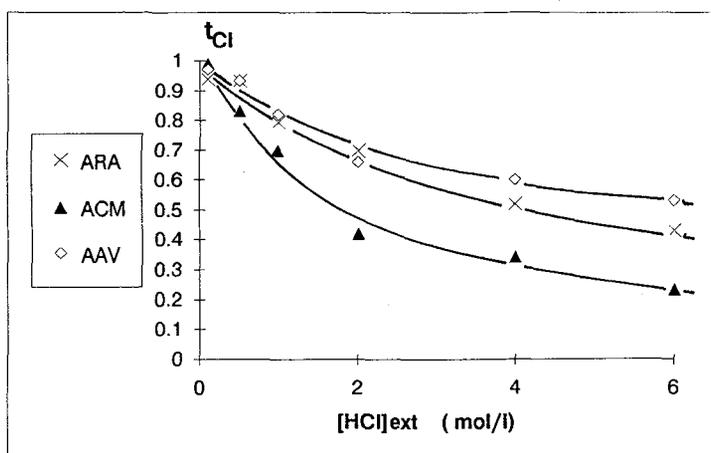


Figure 5: Transport number of the chloride ion through the three anion exchange membranes vs the concentration of the HCl solution ($j=100\text{mA}\cdot\text{cm}^{-2}$).

The determination of both the thickness of the unstirred layer and the concentration profiles allow to calculate the concentration of the counter-ion at the extreme end of this unstirred layer. From the values of the unidirectional fluxes of Cl^- and H^+ ions in the same direction of the electrical driving force, the apparent rate constants of the interfacial transfer have been calculated [11]. Table 1 shows that, for low HCl concentration, this apparent rate constant is higher for Cl^- than for H^+ . When the HCl concentration increases, the apparent rate constant for Cl^- decreases while that for H^+ remains practically constant. These results suggest that the mechanisms of the interfacial ionic transfer reaction are different for the two ions. For protons, a Grotthus mechanism of hopping from one molecule of water to another may be envisaged while for the chloride ions, a transfer with a modification in its solvation state would be more suitable.

Table 1: Values of the calculated apparent rate constant k'_- and k''_+ of the penetration of chloride ions and protons in the ARA membrane phase ($j=100\text{mA/cm}^2$).

C_{HCl} (mol/L)	0.5	1.0	2.0	4.0
k'_- (10^4cm/s)	68	13	4.6	1.6
k''_+ (10^4cm/s)	0.98	1.62	1.34	1.17

Cation exchange membranes preferentially permselective to monovalent cations

In order to obtain cation exchange membranes preferentially permselective to monovalent cations when they are immersed in solutions containing monovalent and bivalent cations, two ways can be used:

(i) the first method consists in manufacturing an homopolar CEM by adjusting the fabrication parameters such as time, concentrations of cross-linking agent and inhibitor in the grafting solution etc...

(ii) the second one consists in creating a thin anion exchange layer on the surface of the CEM. Indeed, the positive charges introduced on the surface create a potential barrier and bivalent cations require greater energy than monovalent cations to overcome this potential barrier [12]. Various possibilities concerning the modification of membrane surfaces have already been described. For example, we can mention the immersion of a membrane in a surface-active agent solution [13] or in a cationic polyelectrolyte solution [14-17], the electrodeposition method [18], the layer formation on a CEM by acid-amid bonding [19], the modification of CEM surface by plasma process [20-22] or the photo-induced polymerization on the surface of a membrane [23]. We have chosen the method consisting in an immersion of the CEM in an aqueous solution of polyethyleneimine in order to adsorb it on the membrane surface.

The membrane used for this immersion method is the CRA membrane supplied by Morgane Co. It bears sulfonic exchanging groups and its polymeric matrix is fluorinated. Polyethyleneimine (PEI) has a molecular weight between 6×10^5 - 10^6 (Fluka Chemika). The preferential selectivity of the so-obtained modified membranes is characterized by electro-electrodialysis experiments with a mixed solution (0.5M NiSO_4 - $0.5\text{M H}_2\text{SO}_4$) in the anodic compartment and a $1\text{M H}_2\text{SO}_4$ solution in the cathodic compartment.

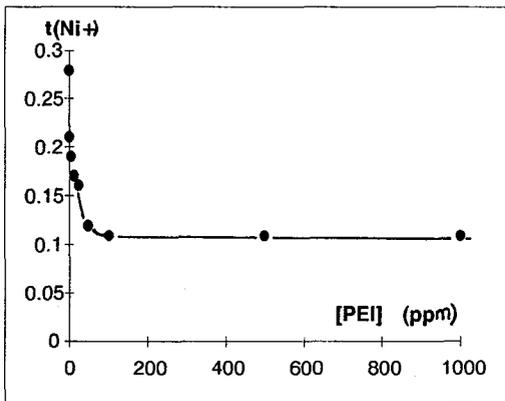


Figure 6: Variation of the transport number of the nickel cation vs concentration of PEI.

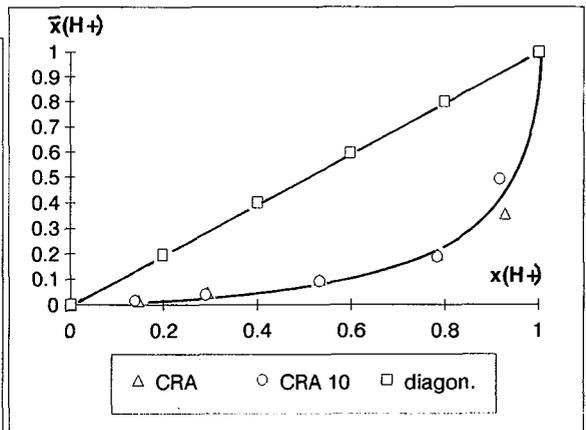
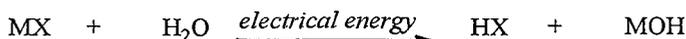


Figure 7: Ion exchange isotherm of modified and non-modified membranes; (exchange H^+ , Cu^{2+}).

From the measured values of the transport number of the nickel cation, it appears that this parameter decreases from 0.28 to 0.10 when the PEI concentration of the treatment solution increases. However, above a PEI concentration close to 100ppm, the transport number of the nickel ion remains equal to 0.10 (Fig.6). Concerning equilibrium properties, the ion-exchange isotherms have been studied with mixed solutions of $\text{CuCl}_2\text{-HCl}$ such as the total concentration of the equilibrating solutions are equal to 0.1 equiv./L. For both the modified and the non-modified membranes, plots of the equivalent ionic fraction \bar{x}_{H^+} of the H^+ counter-ion in the membrane vs the equivalent fraction x_{H^+} in the solution (Fig.7) show that the surface modification does not affect the ion exchange equilibrium. The ion-exchange isotherm is positively curved and falls below the diagonal i.e., the bivalent cation is preferred to the monovalent one by the membrane. As expected, the modification of the membrane surface therefore affects the interfacial transfer properties under an electrical driving force and not the equilibrium properties.

Bipolar membranes

A bipolar membrane (BPM) allows the decomposition of a salt into an acid and a base according to the schema:



A bipolar membrane is composed of three parts, an anion exchange layer (AEL), a cation exchange layer (CEL) and an hydrophilic junction located at the interface of the two previous layers. When an electrical current is passed across this kind of membrane, electrical conduction is achieved by the transport of protons and hydroxyl ions obtained from the dissociation of water. This phenomenon is named water-splitting [24]. In order to reach a maximum efficiency, the BPM should have a good permeability towards water and a weak co-ion leakage of its two selective layers. In this study, we show that hydrodynamical conditions may also have an influence on the current efficiency. For this purpose, a BPM having a co-ion leakage has been synthesized from an ETFE film irradiated under an electron beam, then grafted with styrene and cross-linked with divinylbenzene. Further chemical treatments allow to create an AEL (with quaternized ammonium groups as exchanging sites) and a CEL (with sulfonic groups as exchanging sites). When the BPM is immersed in NaCl solutions, radiotracers are used to quantify the co-ion leakage by permitting the determination of the unidirectional flux values of both sodium ions, J_{Na^+} through the AEL and chloride ions, J_{Cl^-} through the CEL, following the method described elsewhere [4,5]. Experimental results show that the co-ion leakage concerns the sodium ions through the AEL and not the chloride ions through the CEL. From Fig. 8, it appears that J_{Na^+} reaches a limiting value for an applied current density $j > 150 \text{mA}\cdot\text{cm}^{-2}$. No superlimiting current is yet detectible at this current density. Thus, no electroconvection effect or water-splitting contribution at the AEL-solution interface affects the value of J_{Na^+} . The transfer of sodium ions across the AEL is therefore the rate-limiting step of the water-splitting.

The current efficiency R of the water dissociation is defined by $R = nF/q$, with n the number of H^+ or OH^- ions generated by the BPM, q , the amount of transferred electrical charges and F the Faraday constant. The values of the transport numbers of sodium ions and R are collected in Table 2.

Three important facts have to be pointed out:

- (i) Taking into account an experimental error estimated to be 2%, the sum of t_{Na^+} and R remains very close to unity. This result confirms that the chloride leakage through the CEL is negligible.
- (ii) For a given current density, t_{Na^+} increases with the external NaCl concentration.
- (iii) For each NaCl concentration, t_{Na^+} decreases as the current density increases.

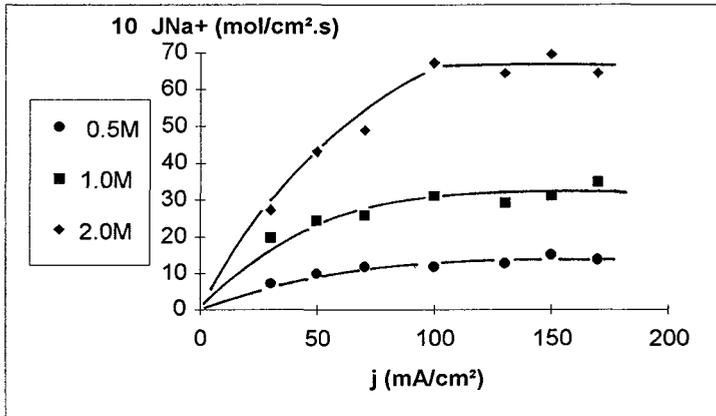


Figure 8: Unidirectional flux of sodium ions through the BPM vs current density for different concentrations of the NaCl solution.

Table 2: Values of the co-ion leakage across the AEL, expressed as the transport number of the sodium ion t_{Na^+} . Current efficiency R of the water dissociation, determined by acido-basic titration.

j (mA/cm ²)	30	50	70	100	130	150
<u>C(NaCl)=0.5M</u>						
t_{Na^+}	0.23	0.20	0.17	0.12	0.09	0.09
R	0.77	0.79	0.81	0.87	0.90	0.91
<u>C(NaCl)=1.0M</u>						
t_{Na^+}	0.63	0.48	0.36	0.29	0.22	0.20
R	0.36	0.50	0.62	0.70	0.76	0.79
<u>C(NaCl)=2.0M</u>						
t_{Na^+}	0.88	0.84	0.68	0.65	0.48	0.45
R	0.10	0.15	0.31	0.33	0.51	0.52

The current density j is the sum of j_G carried by the ions generated from the water dissociation and j_L due to the co-ion leakage. The current efficiency R is defined by $R = j_G / (j_G + j_L)$. R increases therefore when j_L decreases. The flux of sodium ions through the AEL reaches limiting values as for a classical phenomenon of concentration polarization (Fig.8). The values of the limiting current carried by the sodium ion depend on the thickness of the diffusion layer and, therefore, on hydrodynamic conditions. Effectively, this prediction has been experimentally confirmed. For an applied current density of $j=100\text{mA}\cdot\text{cm}^{-2}$ and symmetrical NaCl concentrations, R varies from 0.87 to 0.77 for $C(\text{NaCl})=0.5\text{M}$, from 0.70 to 0.63 for $C(\text{NaCl})=1.0\text{M}$ and from 0.33 to 0.23 for $C(\text{NaCl})=2.0\text{M}$, when the mechanical stirring is stopped in the two compartments.

The current efficiency of water dissociation in a BPM depends therefore not only of both the selectivity of the two exchanging layers and the hydrophilic nature of their junction, but also on hydrodynamic conditions. Unfavourable hydrodynamic conditions increase the efficiency of the water-splitting.

Co-ion leakage associated with the transport of hydrophobic ions.

Poisoning of ion-exchange membranes is one of the major limits of ED when this technique is applied to a medium containing organic (hydrophobic or amphiphilic) ions. This phenomenon has been experimentally observed by several authors [1,25-27], who have shown that the transport properties of the membrane were modified: the electrical resistance was increased and the permselectivity was lowered.

Here, we investigate the behaviour of a CEM (Selemion CMV from Asahi Glass) widely used in ED in contact with aqueous solutions containing both sodium chloride and arginine chlorhydrate. The concentrations range from 0.001M to 0.1M and the pH value is maintained at pH7 where the arginine molecule bears positive charges. The values of the electrical resistance, the number of arginine ions (mmole per gram of dry membrane) and the percentage of water content (P_w) are collected in Table 3. These results can be analysed taking into account the hydrophobic character of arginine molecules. When the organic ions penetrate into the membrane, water is partly excluded from the membrane and the conductivity decreases. Fig.9 shows the correlation between the mobility of sodium ion, calculated from the Stokes-Einstein and Helfferich equations [28], and the water content of the membrane.

Table 3: Electrical resistance , number of arginine ions and water content inside the CMV membrane

NaCl /M	0.1					
ArgCl /M	0	0.001	0.01	0.03	0.05	0.1
R / $\Omega.cm^2$	1.9	3.8	6.6	9.6	15	79
$n_{Arg^+}/mmol.g^{-1}$	0	0.08	0.44	0.87	1.05	1.49
$P_w /%$	33	33	32	30.4	29.7	28.6

Using radiotracers, the values of the individual fluxes of sodium and arginine counter-ions and also those of chloride co-ions crossing the membrane are obtained. From these values, the transport numbers of each species present in the aqueous solution are calculated. The results of Table 4 and Fig.10 show that, for the 0.1M ArgCl concentration, the CMV membrane becomes anion-selective.

Table 4: Electrical resistances and ionic fluxes ($mol.cm^{-2}.s^{-1}$) under an applied current density of $20mA.cm^{-2}$ with the CMV membrane.

ArgCl /M	0.1					
NaCl /M	0	0.001	0.01	0.03	0.05	0.1
R / Ωcm^2	2317	2125	1367	500	290	79
$10^8 J_{Na^+}$	0	0.18	2.3	8.2	9.8	13.3
$10^8 J_{Arg^+}$	11.3	11	10	7.2	6.21	4.6
$10^8 J_{Cl^-}$	9.61	9.3	8.17	5.59	4.35	3.32

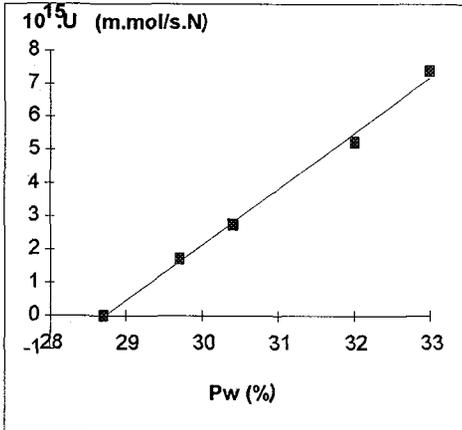


Figure 9: Mobility of the sodium ion vs water content inside the CMV membrane

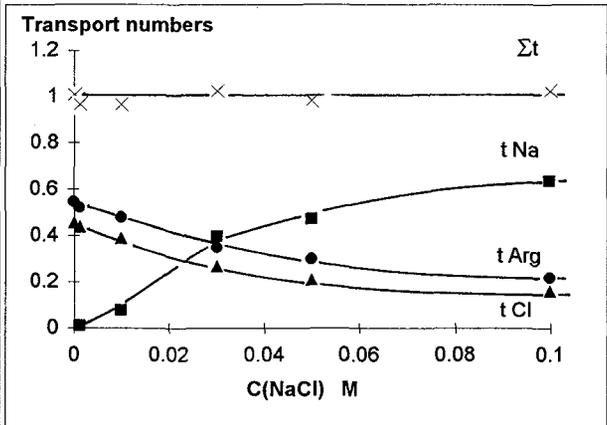


Figure 10: NaCl concentration dependence of the transport numbers of Na^+ , Arg^+ , Cl^- ions.

This study shows the high affinity of the CMV membrane for arginine ions, presumably related to their hydrophobic character. That gives rise to a decrease in water content and an increase in electrical resistance. On the other hand, the presence of arginine molecules inside the membrane catalyses the entry of co-ions. This phenomenon is at the basis of the loss of permselectivity of the ion-exchange membrane in the presence of organic ions.

CONCLUSION

Combining several experimental approaches, the study of the physicochemical mechanisms of the ionic transfer in various membrane-solution systems shows that improvements of the process performance, due to a better membrane selectivity, can be obtained by new membrane materials and also by surface modification and adapted hydrodynamic conditions.

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