The Apparent Selectivity of Different Counter-Ions through a Cross - linked Ion Exchange Membrane

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In this paper it was studied the apparent selectivity of different counter ions like H^+ Na^+ and Mg^{2+} through a polymer electrolyte membrane which was cross linked with a haloalkyl. The best apparent transport numbers, over 0.86, were recorded for H^+, Na^+ using as electrolytes HCl and NaCl.

Keywords : counter-ions, PEM, conductivity, selectivity, ionic exchange membrane , transport number

The interest for the applications of various types of membrane is continuously growing during the past decades. One of these applications is the separation of ions [1, 2]. Today, the separation membranes have become essential materials not only in industries, but also for the daily life. Thus, various membranes have been developed: membranes for reverse osmosis, nanofiltration, ultrafiltration, microfiltration, pervaporation processes, ion exchange membranes, membranes for medical use such as an artificial kidney, etc. [3, 4]. Among these membranes, the ion exchange membranes are one of the most advanced separation membranes. Ion exchange membranes can be subdivided into cation exchange membranes, which contain negatively charged groups, and anion exchange membranes, containing positively charged groups fixed to the polymer matrix [3]. Ion exchange membranes are used for separating electrolyte solutions when an electrical potential gradient is used as the driving force for the chemical species transport [4]. When placed into an electrolyte solution, the affinity of an ion exchange membrane for the ions in the solution is different. The cations, the positively charged ions in the solution, are able to penetrate a cation exchange membrane due to the negatively charged fixed groups in the membranes. In contrast, the anions are more or less excluded from the polymer matrix because of their electrical charge which is identical to that of the fixed groups. The mobile ions with opposite charge to the fixed groups are called counter-ions, while the mobile ions with the same charge are called co-ions. Basically, the ion exchange membranes separate cations from anions and anions from cations. As a result of extensive studies, the separation between cations and anions has attained almost an ideal level in any concentration of solutes [2-9]. The ion exchange membranes have been mostly used in solutions containing multi-components, such as electrodialytic concentration of sea water to produce sodium chloride, demineralization of saline water, desalination of cheese whey solutions, etc. In some cases, because the particular ions should be concentrated or removed from the mixture, the ion exchange membranes having permselectivity for specific ions have been used industrially: monovalent ion permselective ion exchange membranes [5–8], proton permselective ion exchange membranes [9, 10].

Permselectivity among components in a mixture through non-porous separation membranes is governed by the difference of the affinity of respective component with the membrane and the difference of the migration rate of the component in the membrane phase, e.g., gas separation membranes, membranes for pervaporation process, membranes for diffusion dialysis, which are similar with the reverse osmosis membranes [3]. The anions' permselectivity through an electrodialysis anion exchange membranes is also governed by the affinity of the anions with membranes (ion exchange equilibrium constant) and the difference of the migration rate of the respective anions (anions mobility ratios). To simplify the system, a standard anion is also decided by the permeation equivalent ratio for a given anion and a standard anion [4].

A potential difference could be observed and measured for each membrane, at least partly ionic permselective, in contact with two solutions for the following cases: (1)the same electrolyte at different concentrations; and (2) the same ionic strength but different counter-ions or co-ions. The former is called concentration potential and the latter bi-co-ionic/bi-counter-ionic potential [11, 12]. These potentials are of great interest for the analysis of effective charge, the ionic transport number, and selectivity as well as for the interaction between the charged species and membranes in both single charged membrane and bipolar membranes [13–16]. At most occasions, such as electrodialysis and diffusional dialysis, the mobility or diffusivity of single ionic species through the membrane is less important than the diffusivity ratio or permselectivity of different ionic species [16].

Polymer electrolyte membranes have found a broad application in a number of processes, as those from the fuel cells, which, due to energy concerns, became a main focus of the worldwide scientific community. Relatively little attention has been paid to the use of these materials in electrochemical and separation production processes [14].

The transport number is a measure of the permselectivity of counter-ions through the ion exchange membrane. This is related both to the ratio of the concentration of ion exchange groups in the membrane (fixed ion concentration) and to the concentration in the outer solution. There are two methods used to measure the transport number; its calculation from the membrane potential (static state transport number) and by electrodialysis (dynamic state transport number, Hittorf method of current efficiency). Because the transport

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Concentration [mol/L]	Right compartment	0.05	0.1	0.2	0.5	1
	Left compartment	0.1	0.2	0.5	1	1.5
Electrodes		Ag|AgCl electrodes			Hg|Hg$_2$SO$_4$ electrodes	
Electrolyte		HCl	NaCl	MgCl$_2$	Na$_2$SO$_4$	MgSO$_4$

number based on the membrane potential is easy to measure, this method is used to evaluate the membrane preparation methods and for checking the membrane manufacturing processes, when the transport number relative to that of standard product is compared. The membrane potential is generally measured using sodium chloride or potassium chloride solutions, which have nearly equal cation and anion mobilities [13, 15, 17].

In this paper, the transport number and selectivity of counter-ions were evaluated for a synthetic reticulated ionic exchange membranes.

Experimental part
Materials and methods

The used ion exchange membrane was prepared by cross-linking poly (styrene sulfonic acid-co-4-vinylpyridine) with 1,10-dibromodecane. The main characteristics of the used membrane were IEC=0.78 meq/g dry membrane, σ=136 S/cm, the water content 2.6. The solutions used to measure the apparent selectivity are hydrochloric acid, sodium chloride, magnesium chloride, sodium sulphate and magnesium sulphate.

Experimental procedure

The apparent selectivity was measured by the static method between solutions of an electrolyte at different concentration. The film was equilibrated in the concentrated solution at least for 12 h. Then it was mounted in a bicameral electrolytic cell (fig. 1) where the membrane separated the two compartments which were filled as follows: in the right compartment with the less concentrated electrolyte and in the left compartment with the more concentrated electrolyte. Also, there were two Ag\|AgCl reference electrodes on each side of the membrane. All the experiments were conducted at room temperature (25 and 28 ºC). The two compartments were rinsed once with solutions of the same concentration as used in the actual measurement to reduce influences on the solution concentrations and to test the membrane integrity.
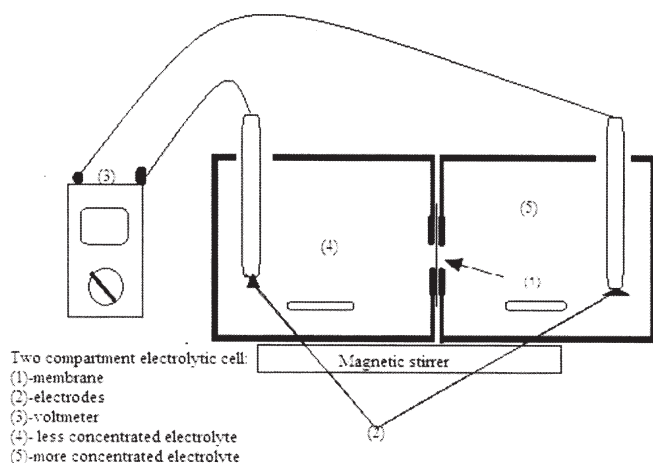

Two compartment electrolytic cell:
(1)-membrane
(2)-electrodes
(3)-voltmeter
(4)- less concentrated electrolyte
(5)-more concentrated electrolyte

Fig.e 1. Bicameral electrolytic cell

For HCl, NaCl and MgCl$_2$ electrolytes were used Ag\|AgCl reference electrodes and for Na$_2$SO$_4$ and MgSO$_4$ were used Hg\|Hg$_2$SO$_4$ electrodes. The Hg\|Hg$_2$SO$_4$ electrodes were kept in a H$_2$SO$_4$ concentrated solution. Silver chloride was deposited electrolytically on a silver or platinum wire and it was then immersed in a solution containing chloride ions.

The potentials between the two compartments were measured using Ag\|AgCl reference electrodes or Hg\|Hg$_2$SO$_4$ electrodes that were connected to a digital voltmeter [18-21].

Membrane resistance

The membrane resistance was measured under atmospheric pressure and through membrane thickness, using as electrolyte different solutions in a cylindrical glass holder at 25 ºC. The membrane was mounted as sandwich between two wire electrodes which were directly connected to a LCR meter (fig. 2). The voltage used was 7.5 mV and before any measurement the membrane was equilibrated for at least 30 min [20,21].
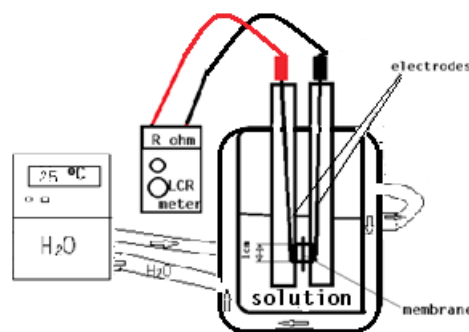

Fig. 2. Proton conductivity measurement installation scheme

The membrane resistance (R) was calculated by subtracting the electrolyte resistance (here R$_{el}$ is the resistance of electrolyte in the cell measured without any membrane) from the membrane resistance equilibrated in electrolyte solution (R$_{memb}$), according to the equation

$$R = Rmemb - Rel, \tag{1}$$

The proton conductivity was calculated by measuring the impedance R (ohm) of the membrane using a LCR meter. The proton conductivity of the membrane was calculated:

$$\sigma = \frac{L}{R \times A}, \tag{2}$$

where σ is the proton conductivity [Scm^{-1}], L is the membrane thickness [cm] , A is the membrane section area [cm^2] which is 1 cm diameter and R is the impedance [ohm] measured at a frequency of 1 KHz and direct current.

Results and discussions

The ion transport number quantifies the amount of charge that is transported through the ion exchange membrane by that specific ion. Several methods are available to determine the ion transport number.

The apparent selectivity (t^+_{app}) is a measure for the preferable transport of counter-ions in the membrane, thus, it is related to the ion fluxes in the membrane. The electric potential difference, E, between the reference electrodes is measured and the apparent selectivity t^+_{app} is calculated as follows (3):

$$t^+_{app} = \frac{E_m}{E_{id}} \quad , \qquad (3)$$

$$t^-_{app} = 1 - t^+_{app} \qquad (4)$$

where: E_m is the mean membrane potential, t^+_{app} is the apparent transport number of the cation in the membrane, t^-_{app} is the apparent transport number of the anion in the membrane and E_{id} is the ideal potential.

In the case of an ideal membrane ($t^+=1$) [17] between two reversible electrodes:

$$E\,id = \frac{v}{v_+ z_+} \frac{RT}{F} \; ln(\frac{a^2_\pm}{a^1_\pm}), \qquad (5)$$

where:
- R = 8.314 J.K⁻¹.mol⁻¹ is the Universal Gas Constant
- F = 96485 C.mol⁻¹is the Faraday's Constant
- T is the temperature in Kelvin (K = °C + 273.15)
- $a^2_\pm$, $a^1_\pm$ is the mean ionic activity of the electrolyte of the more concentrated solution and respectively, the less concentrated solution
- z_+, z_- are the ions' charge
- $v = v_+ + v_-$, v_+, v_- are the stoichiometric number of ions.

In figure 3 and 4 are represented the apparent transport number of counter-ions H⁺ Na⁺ and Mg²⁺ in HCl, NaCl, MgCl₂, Na₂SO₄, MgSO₄ electrolytes .

From figure 3 and 4 it is observed that the apparent transport number of counter-ions H⁺ Na⁺ and Mg²⁺ increases with the electrolyte concentration decreasing.

Both figures show that the apparent transport number of counter-ions H⁺ Na⁺ and Mg²⁺ is almost double in the electrolytes containing chloride than those containing sulphates.

One could observe that the counter-ion apparent transport number is higher for H⁺ is almost equal to 1. Also, from figure 3 and 4 it could be seen that $t_{app}^{H+} > t_{app}^{Na+} > t_{app}^{Mg2+}$.
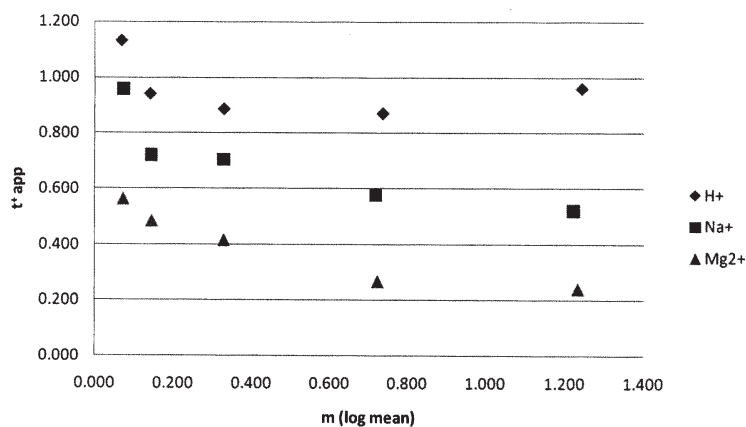

Fig. 3. Apparent transport number of H⁺,Na⁺ and Mg²⁺ through the membrane equilibrated in HCl, NaCl and respectively in MgCl₂ solutions
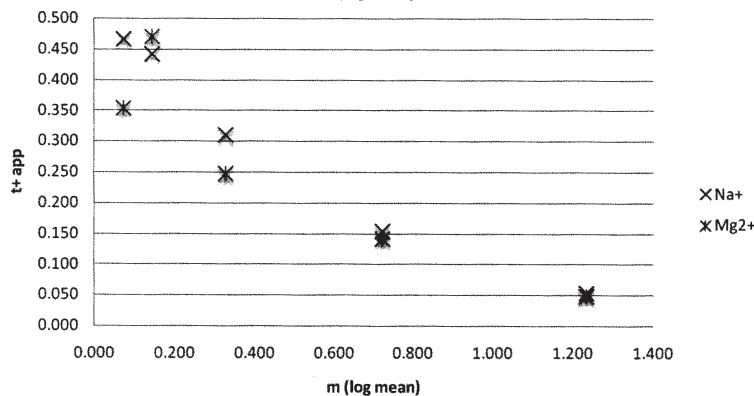

Fig. 4. Apparent transport number of Na⁺ and Mg²⁺ through the membrane equilibrated in Na₂SO₄, respectively in MgSO₄ solutions
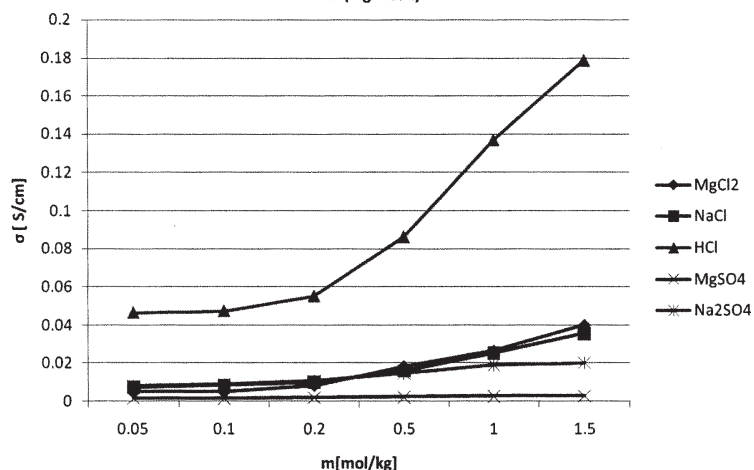

Fig. 5. Comparation between membrane proton conductivity in different electrolyte solutions

The resistance of the membrane was measured separately (at 25°C) in the same electrolytes used for ion mobility (HCl, NaCl, MgCl$_2$, Na$_2$SO$_4$, MgSO$_4$) and the same concentration for each solution (0.1 mol.L^{-1}, 0.2 mol.L^{-1}, 0.5 mol.L^{-1}, 1 mol.L^{-1} and 1.5 mol.L^{-1}).

In figure 5 it is shown the proton conductivity of the membrane immersed in all the electrolytes and concentrations mentioned before. As we can see the membrane proton conductivity increases with the concentration. The best proton conductivity is demonstrated to be recorded for HCl electrolyte.

Conclusions

In this paper it was studied the apparent selectivity of a few inorganic cations such as H$^+$, Na$^+$ and Mg^{2+} through a synthetic ion exchange membrane, obtained from poly (styrene sulfonic acid-co-4-vinylpyridine) cross- linked with a haloalkyl 1,10-dibromodecane.

The used membrane had IEC=0.78 meq/g dry membrane, σ=136 S/cm and a water content of 2.6 g H$_2$O/g dry membrane.

It was observed that the counter-ion apparent transport number was higher for H$^+$, and that the counter-ion apparent transport number is varying as follows: $t_{app}^{H+} > t_{app}^{Na+} > t_{app}^{Mg2+}$

This study reaffirms that ion-exchange membranes could be used for an efficient separation of various chemical species from liquid mixtures without changing the membrane in the electrolytic cell used.

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