Study the Transport Properties of Anion and Cation Exchange Membranes toward Various Ions Using Chronopotentiometry

Ashrafi, Amir Mansoor*+; Mustakeem, Mustakeem•, David, Nedela

Membrain Innovation Center, Pod Vinicí 87, 471 27 Stráž pod Ralskem, CZECH REPUBLIC

ABSTRACT: *The transport properties of various anion and cation exchange membranes were studied in different electrolyte solutions using chronopotentiometry technique to get insight about the influence of the counter ion on the transport properties of the membranes. The investigated samples include heterogeneous ion exchange membranes varying in the functionality of fixed charged groups, physical properties of the polymer and the preparation procedure. Chloride and nitrate were investigated as counter-ion in their sodium salts for anion exchange membranes while sodium, calcium, potassium, and magnesium were selected as counter-ion in their chloride salts to study cation exchange membranes transport properties. First the current – voltage curve of an ion exchange membrane in a given solution was recorded to obtain the limiting current, then a constant current above the limiting current was used for chronopotentiometry measurement. In all the studied membranes the potential across the membrane remained constant for a time interval called the transition time τ when a constant current was applied. Then the potential increased rapidly to reach the steady state potential. The permselectivty and the transport number of a membrane were calculated using the corresponding transition time.*

KEYWORDS: *Ion exchange membranes, Permselectivity, Chronopotentiometry, Transport number.*

INTRODUCTION

Electrically driven membrane processes are an interface between applied electrochemistry (fuel cells, storage batteries, etc.) and the separation techniques through electrodialysis, electrodeionization.

Furthermore, producing the membranes with various properties allows the electrodialysis to be implemented in diverse applications including treatment of drinking water [1], depolluting and recycling of chemicals [2], food and pharmacy [3]. In some of these applications

the membrane must be selective in ion transport toward particular ions to achieve the highest energy efficiency and the purity of the products. It is the point which one of critical characteristics of the ion exchange membranes appears, the permselectivity to particular ions, when given specific ions should be concentrated or removed from a solution. As instances; low membrane permeability to divalent ions respects to monovalent [4], a very low permeability to hydroxyl ions (membranes

for the chlor-alkali electrolysis) [5], a very low permeability to protons (membranes for treatment of used acids) [6] and membrane through which large organic ions like ionic surface active agents cannot permeate [7], etc. Therefore in manufacturing the membrane, produced for a given application, it is essential to know the transport properties of the membranes.

Recently, the selectivity of the ion exchange membrane toward a specific ion has been playing an important role. As an instance; as reported the excess use of artificial fertilizer resulted in an increase in nitrate ions concentration in groundwater in parts of some European countries which is a serious danger for human health because nitrate ions are harmful. Electrodialysis is one of the potential candidate methods to solve this problem if a nitrate ion permselective anion exchange membrane is developed [8]. Other applications of selective separation can be mentioned as; protein separation from milk whey [9-11], and ion exchange membranes used in gas separation [12]. Hence, in addition to the traditional characteristics such as high chemical, mechanical and thermal stability the ion exchange membrane must meet new demanded characteristics.

The permselectivity can be determined by the static membrane potential measurement. The test system consists of two cells separated by the membrane sample, two reference electrodes placed into the solutions on either side of the membrane to measure the potential difference across the membrane while the cell compartments are filled with the solutions of the same salt but different concentration. The permselectivity of the membrane is the ratio of the measured potential difference (ΔV_{meas}) and the potential difference calculated for a 100% permselective membrane (ΔV_{calc}). The obtained permselectivity of the membrane using this method includes water transport as well, therefore it is called appearance permselectivity [13].

Another method which can be used for calculating the permselectivity of an ion exchange membrane is the chronopotentiometry. The transition time obtained with chronopotentiometric measurement of the membrane under investigation is given by equation:

$$\tau = \frac{\pi D}{4}\left(\frac{C_0 zF}{\overline{t_i} - t_i}\right)^2 \frac{1}{i^2} = \frac{\pi D}{4}\left[\frac{C_0 zF\left(1 - t_i\right)}{P}\right]^2 \frac{1}{i^2} \qquad (1)$$

Where $P = \dfrac{\overline{t_i} - t_i}{1 - t_i}$

Thus the transition time for an ideally permselective membrane is calculated using the same equation in which $\overline{t_i}$ is substituted by 1. Hence, the permselectivity is determined using the ratio of the transition time calculated for a 100% permselective membrane, τ_{ideal} over the measured transition time τ_{meas}:

$$P = \sqrt{\frac{\tau_{ideal}}{\tau_{meas}}} \qquad (2)$$

Moreover, since in chronopotentiometry measurement both of the cell compartments are filled with the same salt solution with the same concentration therefore, osmotic water transport does not contribute to the calculated permselectivity, resulted in more precise determination of the transport number of the ion in the membrane $\overline{t_i}$ and subsequently the precise permselectivity [14-18].

The aim of the present paper was to calculate the permselectivity of the various ion exchange membranes either anion exchange or cation exchange membranes toward different ions using chronopotentiometry technique.

EXPERIMENTAL SECTION
Chemicals
All the salts used in the experiments were analytical grade and purchased from Merck, Germany. The solutions were prepared with deionized water produced in the MemBrain Innovation center (Straz pod Ralskem, Czech Republic).

Apparatus
The electrochemical measurement, hydrodynamic galvanometry and chronopotentiometry, were carried out with a modular electrochemical analyzer BioLogic equipped with SP-300 controlled by EC-Lab software (BioLogic, France). The solution was thermostated using a Julabo thermostat (Germany).

The specially designed cell composed of two equally sized compartments (30 mL) was used for the electrochemical measurements. The conical shape of the cell allows the homogeneous current flow through the membrane and minimizing the border effect. The membrane was placed in a hole separating two halves of the cell and
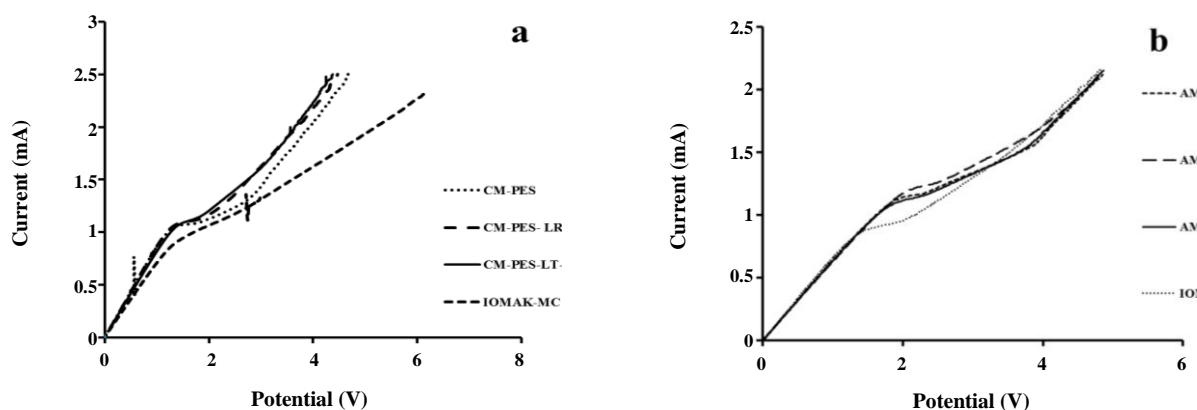
***Fig. 1: Current –voltage curve of ion exchange membranes in 0.01 M NaCl a: cation exchange membranes
b: anion exchange membranes.***

tightened when two compartments connected together. In order to minimize the surface polarization of the membrane the stirring with a constant speed was utilized in both compartments. The current was applied to the Pt electrodes while the potential was measured with two calomel electrodes (3 M/ KCl).

Measurements

The dependency of the voltage across the ion exchange membrane upon the applied current (current-voltage curve) was investigated using galvanodynamic technique. To briefly explain, the membrane was placed between two cell compartments which were filled with 0.01 M of the desired solution, and thermostated at 25 °C, the current was scanned from 0 to 15 mA and the potential drop across the membrane was measured and recorded with reference electrodes locating next to the both sides of the membrane. The scan rate of the current was 10 μAs^{-1}. For each solution the measurement was performed one time without the membrane to observe the solution behavior under the same condition.

For the chronopotentoimetric measurement a direct current equals to 1.5 mA which was above the limiting currents of all the studied membranes in all the solutions, was applied to the Pt electrodes and the potential change across the membrane was recorded within a given time interval every half second.

Ion exchange Membranes

MC 40 and MA 40 are the heterogeneous membrane produced by Russian producer JSC Shchekinoazot. IONAC MC-3475 and IONAC MA-3470 are heterogenous

ion exchange membranes with strong acid cationic and strong base anionic functionality produced by Sybron Chemicals Inc. Ralex® AM(H)-PES and Ralex® CM(H)-PES are heterogeneous membrane in which the polymer composite is highly filled with fine milled ion-exchange resin, anchored in polymer matrix and reinforced by the fabric which improves the mechanical properties of the membrane. Ralex® AM(H)-PES LR and Ralex® CM(H)-PES LR are the low electrical resistance heterogeneous type of anionic and cationic exchange membrane designated for desalination of high saline content solutions. Their unique properties lead to energy voltage consumption. Ralex® AM(H)-PES LT and Ralex® CM(H)-PES LT are the heterogeneous type of ion exchange membranes. Due to their decreased thickness more pairs of the membrane can be placed in the ED stack, which resulted in an increase in the ED module capacity and consequently an increase in overall performance of ED.

RESULTS AND DISCUSSION

The current-voltage curves of the cation and anion exchange membranes are shown in Fig. 1. (a and b). Although the current - voltage curve of the blank solutions were linear indicating the ohmic behavior of the solutions (not shown), as can be seen (Fig. 1) three regions are recognizable in membranes voltammograns. With increasing the current, voltage also increases in low currents. Since voltage and current are in linear relationship, this region is called ohmic region. At higher currents the concentration polarization becomes more pronounced, thus the resistance increases because
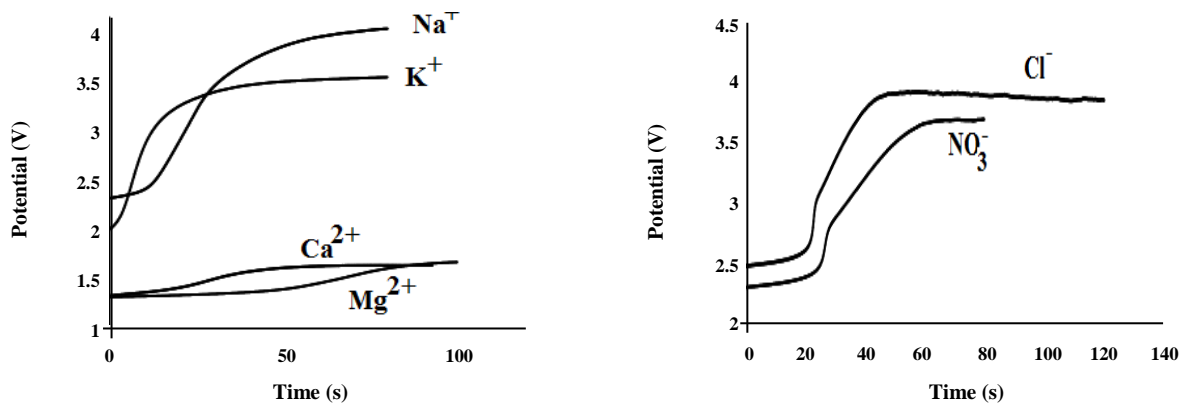
***Fig. 2: Recorded chronopotentiograms a: Iomac Mc in 0.01 M of the studied cations with common chloride co-ion
b: Iomac Ma in 0.01 M the studied anions with Na+ as co-ion.***

of the concentration drop in dilute boundary layer, resulting in a deviation of the linear behavior. At limiting current, because of the ion depletion in boundary layer next to the dilute side, a plateau is observed. After the plateau, due to the presence of water dissociation products again voltage and current have a linear relationship [19]. For all the membranes in various investigated solutions the limiting current was distinct and below 1.5 mA. Hence, 1.5 mA was selected as the applied current for the chronopotentiometry measurements.

The obtained chronopotentiograms are displayed in Fig. 2. As it is observed the potential of the membranes increased rapidly when the current was applied. This rapid increase in membrane potential is attributed to the ohmic resistance of the membrane and the adjacent solution. Then the concentration gradient which is caused by the concentration polarization is developed in the vicinity of the membrane. After a time interval τ, called transition time the membrane surface concentration reaches zero, resulted in a rapid increase in the membrane potential until the steady state potential is achieved [20]. The transition time is determined by the intersection of parts **a** and **b** of the curve, shown in Fig. 3.

The observed initial potential for a given cation exchange membrane in various solutions of chloride with different counter-ions increased in the order $Mg^{2+} \lesssim Ca^{2+} < K^+ < Na^+$. Considering the values of the equivalent conductance of the cations in infinite dilute aqueous solution (Na^+; 50.1, Mg^{2+} ;53.1, Ca^{2+}; 59.5 and K^+ 73.5 cm²/ohm) [21-22], it might be concluded that in the case of KCl large columbic interaction of K^+ and Cl^- causes the large potential drop.
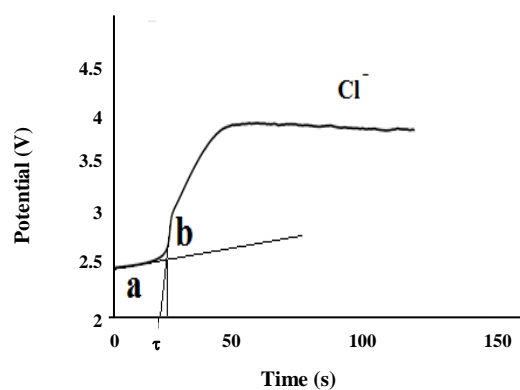

Fig. 3: The method to determine the transition time in the obtained chronopotentiogram.

Moreover, the observed transition times in all the studied cations were sharp and distinctive. At t = τ the flow of counter ion, going from interfacial layer to the membrane surface has the highest rate, causes the maximum difference from the rate of counter ion flow from the bulk solution into the interfacial layer.

Concerning the investigated cation exchange membranes as can be seen in Fig. 2, τ was much early in NaCl followed by KCl, delayed in CaCl₂ and the latest in MgCl₂. The larger value of τ for Ca^{2+} and Mg^{2+} could be attributed to delayed concentration gradient due to higher charge density. The permselectivity and the transport numbers of the cations are shown in the Table 2 while the diffusion coefficients and solution transport numbers for various ions are displayed in Table 1.

It is worth notice that in CEM-PES and CEM-PES LR the permselectivity of all the studied cations are close

Table 1: Diffusion coefficient and transport number in solution for the studied ions[21-22].

Ion	D x 10^5	t_i
Na^+	1.40	0.39
K^+	1.78	0.49
Ca^{2+}	1.22	0.43
Mg^{2+}	1.16	0.37
NO_3^-	1.36	0.60
Cl^-	1.40	0.61

Table 2: Calculated permselectivity and the transport number of the cation exchange membranes towards studied cations.

Membrane	Na^+		K^+		Ca^{2+}		Mg^{2+}	
	P%	$\bar{t}_i$	P%	$\bar{t}_i$	P%	$\bar{t}_i$	P%	$\bar{t}_i$
MC 40	73	0.82	83	0.91	65	0.80	54	0.71
IOMAC MC	77	0.84	179	1.4	86	0.92	51	0.69
CM-PES LR	69	0.79	71	0.85	70	0.83	60	0.75
CM PES	78	0.85	76	0.88	69	0.82	64	0.77
CM PES LT LR	85	0.89	100	1.00	69	0.82	62	0.76

while MC 40, Ionac and particularly CEM-PES-LT-LR show different permselectivity towards various cations. Hence, based on the desired application the appropriate cation exchange membrane can be selected and utilized. The value of the permselectivity of K^+ and consequently its transport number is greater than unity in Ionac-MC which may be because of complexing tendency with the fixed charges of the membrane that was reported before [20].

Considering the anion exchange membranes, the initial potential is higher in $NaNO_3$ in all the membranes studied, resulted in higher resistance of the membrane in this electrolyte solution compared to NaCl. It may be explained by their corresponding equivalent conductance, Cl^-; 76.36, and $NaNO_3$; 71.44 cm^2/ohm.

Furthermore, all of the anion exchange membranes showed a distinct transition time in both of the investigated electrolyte solutions. In addition, all of the membranes have a reasonable permselectivity towards Cl^- and NO_3^- expect Ionac-MA which shows a very high permselectivity (~ 1) for both of the anions. Therefore particular attention must be paid specially in the processes which NO_3^- ion transport through the membrane is not favorable. The calculated transport number and permselectivity of anion exchange membranes toward the sample anions are represented in Table 3.

COLCUSIONS

The chronopotentimetry technique was utilized to study the ion transport through the ion exchange membranes in dilute aqueous solution of various counter-ions having a common co-ion. The ion transport number and the permselectivity were calculated using the transition time in the related chronopotentiograms. The observed transport numbers and permselectivities confirmed the relation between the permselectivity of a particular membrane and the counter- ion.

As represented in the Table 2. The studied cation exchange membranes show different transport properties toward various counter-ion. Thus it is possible to select the appropriate membrane based on the aim of electrodialysis. As instance, if the electrodialysis is used to separate the monovalent cations (Na^+ and K^+) from the divalent ones (Mg^{2+} and Ca^{2+}), CM-PES LT LR seems to be a good choise, since it shows high difference between the transport numbers of the studied monovalent and divalent cations. On the other hand CM-PES does not seem to be so much efficient for that porpuse.

Table 3: Calculated permselectivity and the transport number of the anion exchange membranes towards studied anions.

Membrane	Cl⁻		NO₃⁻	
	P%	$\overline{t}_i$	P%	$\overline{t}_i$
IOMAC MA	100	1.00	100	1.00
AMH-PES LR	72	0.89	75	0.90
AMH PES	73	0.89	75	0.90
AMH PES LT LR	74	0.90	77	0.91

In contrary to the cation exchnage membranes, the studied anion exchange membrane did not show so mcuh differences in their transport properties toward the sample counter-ions (Cl^- and NO_3^-) indicating that the separation of the chloride and nitrate is not efficient using the investigated membranes.

The used method was easy to perform, rapid and the obtained data were precise since the osmotic water transport is also taken into account. Moreover the initial potential was used to estimate the resistance of the membrane. In most of the studied counter-ions an agreement exists between the obtained resistance and the equivalent conductance of the counter ions.

However, the experiments must be continued to study the relationship between the permselectivity of a particular membrane with its structural and morphological, and other electrochemical properties. It is desired to get insight about the ion exchange membranes in order to modify a given membrane to have the highest permselectivity towards a particular counter-ion while the least permselectivity towards unfavorable ones.

Acknowledgment

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