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Evaluation of Calcium Ion Transport Number through A Cation Exchange Membrane by Chronopotentiometry

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Abstracts: In this research work, the transport properties of calcium ions (Ca2+) in a heterogeneous cation exchange membrane (IEM) MK-40 of Schekinoazot. Aqueous solutions of sodium chloride (NaCl) and calcium chloride (CaCl2) of 0.01 M and 0.02 M concentration, respectively, were used. The limit current density and transport numbers were evaluated by means of the chronopotentiometry technique, applying electric current pulses, obtaining electric potential differences, from which the chronopotentiograms were obtained. Then, plots of electric potential difference variation with respect to time were constructed to find the transition time. A linear fit of the transition time with the square of the inverse of the inverse of the electric current density was performed based on the modified Sand equation to determine the Ca2+ transport number. The results showed the Ca2+ transport numbers in the cation exchange membrane and in solution are 0.976 and 0.437, respectively. The limiting current density was also found for both membrane-solution systems. We conclude that chronopotentiometry is an accurate and fast technique for the determination of the ion transport number in systems consisting of ion exchange membranes and electrolyte solutions.

Keywords: Cation Exchange Membrane, Chronopotentiometry, Limiting Current Density, Transport Number.

1. INTRODUCTION

Water is one of the most valued and important resources in industrial production. However, the discharge of industrial wastewater is one of the main causes of pollution to the environment, and wastewater treatment has become a major problem[1]. Water hardness is generally due to the presence of calcium cations(Ca2+). The World Health Organization recommended maintaining Ca2+ ion concentrations below 75 mg/L in drinking water[2]. In recent years, there has been a growing interest in wastewater treatment using environmentally friendly processes, especially membrane processes[3]. Electrodialysis is an electrochemical separation technique that uses electrical potential as a driving force to move ions across selective ion exchange membranes and separate them from other molecules in aqueous solutions[4].For the technical feasibility of an electrodialysis process, it is useful to know about ion exchange membranes, their electrochemical behavior, stability, conductivity, selectivity, ion transport number and associated transport phenomena such as limiting current density [5]. If, in an electrodialysis process, the current density used exceeds the limiting current density, operational problems such as precipitation of inorganic salts, destruction of the membrane and an increase in energy consumption may occur, leading to a decrease in process efficiency[6]. Ion exchange membranes (IEM) are the main part of electrodialysis cells, being polymers with fixed charges in their structure. These charges show electrostatic affinity towards oppositely charged ions and repulsive forces against ions having the same charge sign (electrolyte coions). Cation exchange membranes (CEM) have negatively charged fixed groups and anion exchange membranes have negatively charged fixed groups. (AEM) have fixed groups with positive charges [7]. The fixed charge groups commonly present in CEMs are sulfonic acid ($-SO3-$), carboxylic acid ($-COO-phosphonic\ acid$($-PO3H-$) and in AEMs, the most common fixed charge groups are ammonium ($-NH3+$), secondary amine (($-NRH2+$), tertiary amine ($-NR2H+$) and quaternary amine (($-NR3+$) [8]. Regarding the heterogeneity of the membrane structure, there are two different types of membranes: homogeneous and heterogeneous [7]. In homogeneous membranes, the fixed functional groups are uniformly distributed throughout the polymer matrix, whereas in heterogeneous membranes, the fixed groups are not uniformly distributed and are separated by uncharged binding polymers, which increases the mechanical strength of the membrane [9]. Figure 1 shows a homogeneous membrane and a heterogeneous membrane [7].

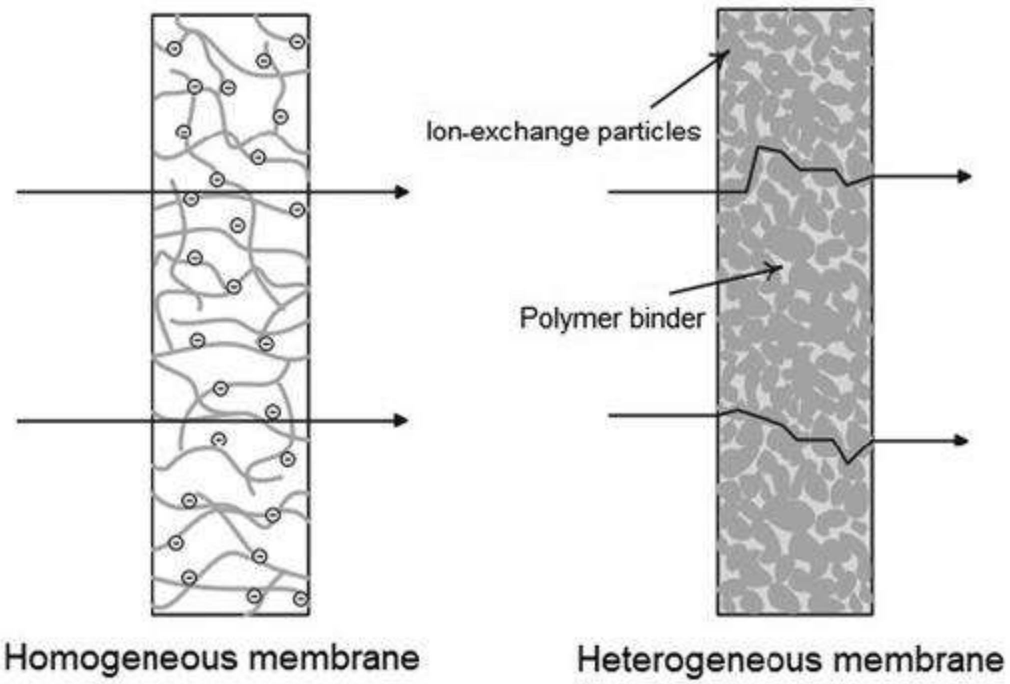

Figure 1. Schematic drawing illustrating a counter-ion pathway through homogeneous and heterogeneous ion-exchange membranes (Adapted from ref.[7]).

Chronopotentiometry is a very effective technique for investigating different types of phenomena occurring in electrode and membrane systems[10] [11]. This technique makes it possible to determine the ion transport number in the membrane [12]. An experimental technique in which a constant electric current is applied to a solution-membrane system, and its electric potential difference (E) is measured as a function of time [13]. Chronopotentiograms are used to evaluate the dynamic behavior of membranes and to determine some properties, such as transition time, transport number of ions in the membrane and apparent fraction of conducting área [14]. The transition time corresponds to the time at which ion depletion occurs at the membrane surface due to the intense onset of concentration polarization [7]. Concentration polarization is a well-known phenomenon involved in studies of membrane processes. The result of concentration polarization is the decrease of the electrolyte concentration on the depletion side of the membrane almost to zero [13]. The time required for the system to reach this sudden increase in voltage drop from the start of the current load application is called the transition time [13]. Depending on the magnitude of the applied electric current, the development of diffusion boundary layers is more or less severe and E evolves differently during the application of electric current pulses.The increase in electric current can reach a limiting condition when the concentration of counterions near the membrane surface approaches zero. The depletion of ions near the membrane surface implies an increase in the electrical resistance of the solution-membrane system and a pronounced increase in E is recorded, and the time at which this occurs is called the transition time .The electric current density at which counterion depletion occurs near the membrane surface is commonly referred to as the limiting current density $ilim$ [15]. Transition times can be predicted theoretically by the Sand equation. The theory that gives rise to the Sand equation is based on solving a non-stationary unidirectional diffusional problem in an electrolyte solution on the side of the membrane where counterion depletion occurs[13]. The transition time, τ, can be calculated from the equation in Sand (1)

$$\tau=\pi Ds4(c0zjFtjm-tjs)21i2 \quad (1)$$

where Ds is the diffusion coefficient of the electrolyte in solution, C0 is the concentration of the electrolyte in solution, zj is the charge number of the counterion, F is Faraday's constant, i is the current density, tjm and tjs are the transport numbers of the counterion in the membrane and in solution, respectively. Choi y Moon [16] modified Sand's equation and included a term relating to the apparent fraction of the conducting area(ε).This equation is widely used in chronopotentiometric studies to determine the apparent fraction of the conducting area or the transport number of counterions in heterogeneous MIIs [17]. The form of the equation of Choi y Moon is as follows:

$$\tau=\varepsilon 2\pi Ds4(c0zjFtjm-tjs)21i2 \quad (2)$$

It is widely known that IEMs exhibit a nonlinear current-voltage curve characteristic of ion-selective systems [18]. Three typical regions can be clearly distinguished in this curve, which are called (i) below the limit current, (ii) limit current and (iii) overcurrent [19]. Figure 2 shows the electric current density versus electric potential curve applied to an electrolyte solution and ion exchange membrane system. In region 1, also called ohmic region, the current density and the electric potential difference show a linear relationship. In this case, the ion flux through the membrane increases proportionally with the electric field, following a quasi-ohmic behavior [7]. The curve reaches region 2, where the current density remains practically constant with increasing electric potential difference. At the inflection of the curve, i.e. at the intersection of the tangents of regions 1 and 2, the limit current density is reached [20]. In region 3, transport mechanisms such as water dissociation, gravitational convection and electroconvection are activated, which increase ionic transfer across the membrane. [21]. In this work by means of chronopotentiometry the current-voltage curves were studied, and the transport numbers and limiting current densities were determined for the systems NaCl 0.01 M - CEM and CaCl2 0.02 M - MIC, where the concentration of the latter is on the order of a groundwater.

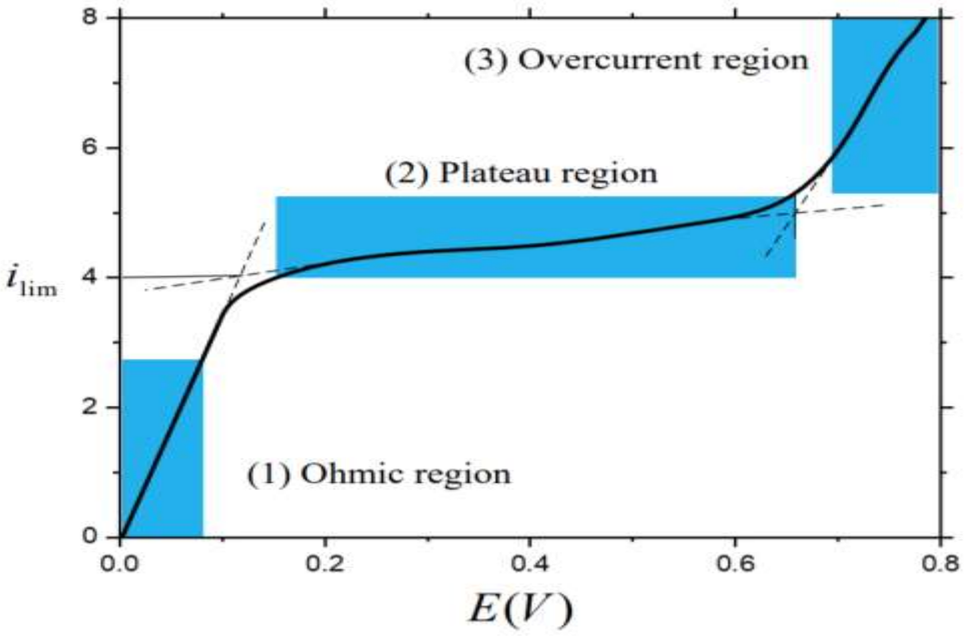

Figure 2. Current–voltage curves [21]

2. MATERIEL AND METHODS

2.1. Ion-Exchange Membranas

The work used heterogeneous IEM produced by Schekinoazot (Russia), being a cation exchange membrane (MK-40) and an anion exchange membrane (MA-41), both with a working area of 3.14 cm2. Before each experiment, the membranes were immersed in the working solutions for 24 hours. Some of the main characteristics of the membranes are shown in Table 1.

Table 1. Main characteristics of the membranes used [22], [23]

Membrane	Type	Thickness of wet membrane, microns	Exchange capacity, mmol g$_{-1}$ wet	Density, g cm$_{-3}$ wet	Surface resistance Escriba aquí la ecuación.Ω. cm$_2$	Transport number
MK-40	Cation-exchange	520 ± 20	1.52 ± 0.08	1.13	≤10.0	≥0.98
MA-41	Anion-exchange	530 ± 20	1.18 ± 0.06	1.06	≤10.0	≥0.98

2.2. Solutions

Pure analytical grade chemicals, solid sodium chloride (NaCl) and solid calcium chloride (CaCl2), and ultrapure water of 18.2 MΩ.cm were used in the preparation of the solutions. Electrolyte solutions of 0.01 M NaCl and 0.02 M CaCl2 were prepared.

2.3. Chronopotentiometric experiments

The equipment used for the chronopotentiometric experiments was similar to that used in previous work. [24]. The experimental apparatus is composed of three compartments, each with a capacity of 130 mL. The CEM and AEM were placed between each compartment. Two graphite electrodes used as cathode and anode are placed at the ends of the cell. To measure the potential difference on the adjacent faces of the cationic membrane, two reference electrodes of Ag/AgCl contained in capillaries of Luggin. A potentiostat/galvanostat was used (PGSTAT 128N, Autolab) to apply the current pulses to the membrane-solution system. All experiments were performed at the temperature of 20.2 °C Figure 3 shows the schematic of the experimental equipment used to obtain the chronopotentiograms. (1) potentiostat-galvanostat; (2) cathode; (3) anode; (4) cation exchange membrane(CEM); (5) Luggin capillaries; (6) Ag/AgCl electrodes; (7) anion exchange membrane(AEM) and three compartments (I, II and III).

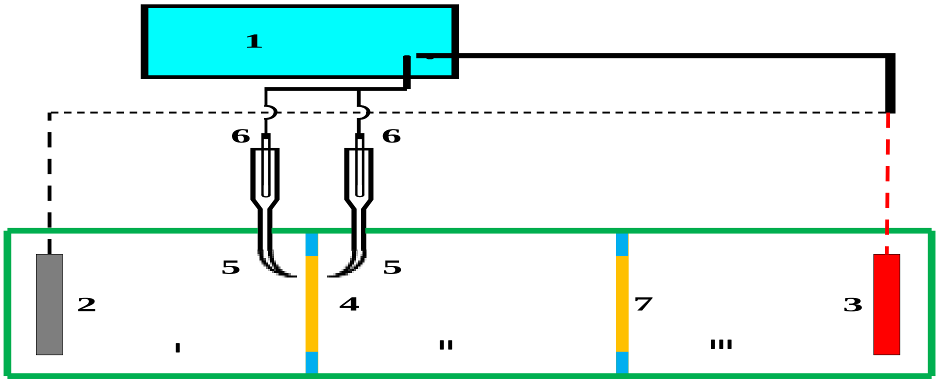

Figure 3. Schematic diagram of the three compartment electrochemical cell used to obtain chronopotentiometric curves.

3. RESULTS AND DISCUSSIONS

3.1. Limit current density

The current-voltage curves for the NaCl 0.01 M - IEM system were obtained with the application of currents in the range of 0.5 to 10 mA. The chronopotentiograms above the limit current density (0.42 mA/cm2) were selected, see Figure 4, to determine graphically the transition times, as shown in Figure 6. The same procedure was followed for the CaCl2 0.02 M - MIC system, obtaining a higher limit current density (1.42 mA/cm2), as shown in Figure 4

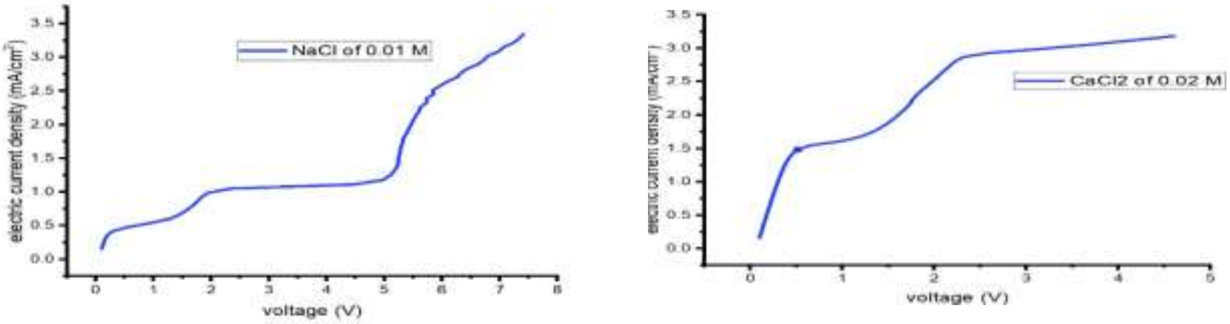

Figure 4. Electric current density - voltage curve

3.2. Transport number

To determine the Ca2+ transport number across the CEM, the apparent fraction of conducting area of the CEM was first evaluated. This was obtained from literature data [23]. The number of Na+ transport at low concentrations across a cation exchange membrane. MK-40 es tm + ≈ 1. The transport number of Na+ in the solution was calculated and the following was obtained ts + =0.395 and then related transition times (τ) to the square of the current density(1/i)2 by a linear fit, using Equation 2, obtaining the apparent fraction of the conductive area of the MIC, ε = 0.7955. The Ca2+ transport number in the solution was calculated and the following was obtained ts 2+ = 0.437, and considering the value of ε, the transport number of Ca2+ in the CEM was obtained using equation 2, resulting in tm 2+ = 0.976. The transport number obtained tells us that MIC has a good selectivity to separate Ca2+ from the solution under study. According to [22] the transport number for a 0.02 M CaCl2 - CEM (MK-40) system is close to 0.98, which is in agreement with the present work.

3.2. Transition Time

The chronopotentiometric curves obtained for the 0.01 M NaCl at current densities of (0.605, 0.668, 0.732 ,0.796, 0.859, 0.923, 0.987 y 1.05 mA/cm2) are presented in Figure 6. It was observed that at all current densities used in the first 20 seconds, the electric potential has been slowly increasing with time. The first stage is due to the electrical ohmic resistance of the system- solution. The second stage shows a marked increase in the electric potential during the transition period, then the potential stabilizes in the third stage. The transition time is determined by the intersection of the tangents with the first and second stages of the curve. The transition times of the CEM (MK-40) were 39.2 and 8.5 s, respectively, at a current density of 0.605 mA/cm2 and 1.05 mA/cm2. Previous work with other membranes has shown that the transition time decreases with increasing applied current density [25]. This is due to increased ion flux depletion at the interface of the membrane-solution system with increasing current density[25].

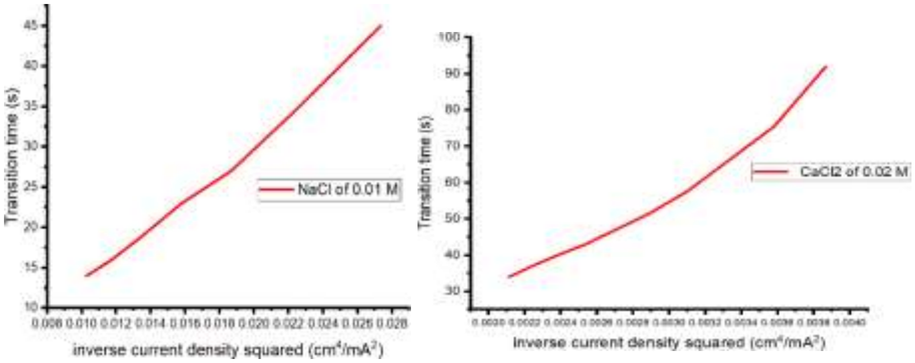

Figure 5. Transition time, r, as a function of $1/i2$ for the MK-40 membrane

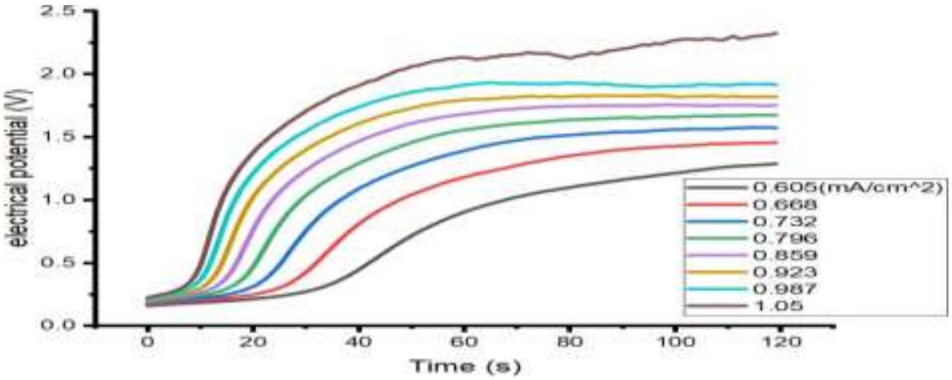

Figure 6. Chronopotentiometric curves for the MK-40 membrane in contact with a 0.01 M NaCl solution at various applied currents.

CONCLUSIONS

The current-voltage curves were obtained from the chronotenograms and the values of the limiting current density of the membrane-solution systems were determined. Also, the difference between the transport number of the counterion in the membrane and in solution were studied. The apparent fraction of conductive area of the CEM was determined. (ε = 0.7955) in 0.01 M NaCl solution using chronopotentiometry, confirming that not all of the MIC surface participates in counterion transport. Finally, for the CaCl2 0.02 M - CEM (MK-40) system, the limiting current density was determined. (1.42 mA/cm2) and the transport numbers of Ca2+ in the solution (ts 2+ = 0.437) and in the membrane (tm 2+ = 0.976). It is concluded that the fraction of electric current density carried by Ca2+ in solution is lower than that carried by Cl-, but it is much higher in MIC. According to Sarapulova et. al. [22] the transport number for a CaCl2 0.02 M - CEM (MK-40) system is close to 0.98 which is in agreement with the present study.

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