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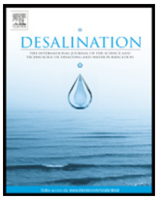

Electrochemical characterization of the CMX cation exchange membrane in buffered solutions: Effect on concentration polarization and counterions transport properties

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HIGHLIGHTS

- The ohmic region resistance is constant whatever the acetic acid concentration.
- The plateau slopes (1/Rpol) increase linearly with the counter-ion concentration.
- The concentration polarization theory is insufficient to explain these results.

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ABSTRACT

In the present work, the combination of both properties of buffer and weak electrolyte solutions and their effects on concentration polarization phenomena, particularly on the limiting current density and the ohmic region resistance (R_{ohm}) is investigated. Acetic acid (pKa = 4.75) plays the role of weak electrolyte while at the same time buffers the pH of the system with acetate co-ions. In order to better understand the effect of the counterion nature and the pKa of the buffer acid/base pair, different electrolyte solutions are studied. The current–voltage curve characteristic values such as the limiting current density, the ohmic resistance (R_{ohm}) and the polarization plateau resistance (R_{pol}) are determined and discussed according to the classical concentration polarization theory. However, it remains insufficient to explain the most important result obtained: The addition of acetic acid increases linearly the limiting current density while the ohmic resistance remains constant whatever the acetic acid concentration is.

1. Introduction

Electrodialysis is an electrical potential driven process to concentrate or to remove ions from an electrolyte solution through alternating cation and anion exchange membranes. It is applied in many fields, such as drinking water treatment, wastewater treatment, demineralization of amino acid, demineralization of whey, treatment of organic substances, removal and recovery of heavy metals and other inorganic toxic substances [1–5]. In all processes, it is desirable to work at the highest possible current density in order to achieve fast desalination with the lowest possible effective membrane area. However, in practice the operating currents are restricted by the occurrence of the concentration polarization phenomena due to the existence of the limiting current density [3,6–12].

The current–voltage curve (CVC) of an ion exchange membrane (IEM) can be divided into three regions, as shown in Fig. 1. At low current densities, the first region (A) generally called the ohmic region presents a linear relationship between the current and the voltage drop. When the current increases, the concentration near the membrane surface on the diluted side decreases, at a certain current density this concentration reaches zero and a limiting current density is reached (region (B)), after that the current density increases again in the so-called the over-limiting current region (C).

If the applied current density exceeds the limiting one, operational problems occur, such as inorganic salt precipitation on the membrane surface, destruction of the membranes and an increase in the energy consumption decreasing the process efficiency. So, the limiting current density is an important parameter to make decisions regarding which membrane is the most appropriate and what is the maximum current density that can be used for a given application [3,9–11,13]. According to the classical depletion layer theory of concentration polarization the limiting current density could be expressed by the following equation:

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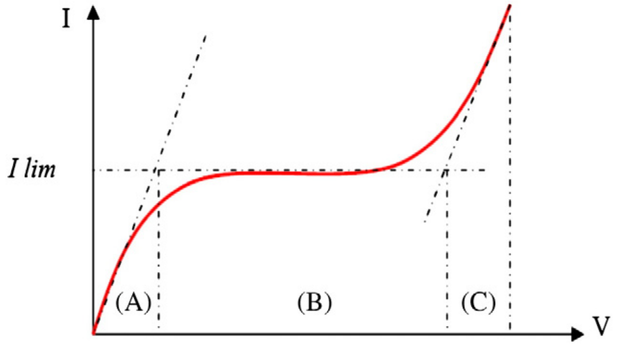

Fig. 1. Typical current–voltage curve of a mono-polar ion exchange membrane.

$$I_{lim} = (C \cdot D \cdot F)/[(t_s - t_m)\delta] \quad (1)$$

where: I_{lim}: the limiting current density (A/m^2), C: the solution concentration (mol/L), D: the salt diffusion coefficient (m^2/s), δ: the boundary layer thickness (m), t_s: the counterion transport number in the solution, t_m: the counterion transport number in the membrane and F: the Faraday constant (A·s/mol).

According to Eq. (1), the limiting current density is a function of: the solution concentration C, the salt nature which fixes the transport number in the solution t_s, the diffusion coefficient D, the membrane permselectivity which fixes the transport number in the membrane and the hydrodynamic conditions of the system which affect the boundary layer thickness δ. In the literature, several theoretical and experimental studies are reported on the effect of these parameters on the limiting current density [6,12–22].

In previous works, the effect of buffer solutions and weak electrolytes on the concentration polarization phenomena was determined [23,24]. The buffer solution increases the polarization plateau length but the addition of weak electrolytes reduces it without affecting the limiting current density values.

The aim of this study is to investigate the combination of both properties and their effect on concentration polarization, particularly on the limiting current density and the ohmic region resistance. In this case acetic acid (pKa = 4.75) plays the role of weak electrolyte and at the same time buffers the pH of the system with acetate co-ions. To better understand the effect of the counterion nature and the pKa of the buffer acid/base pair, different electrolyte solutions are studied. The current–voltage curve characteristic values, such as the limiting current density, the ohmic resistance (R_{ohm}) and the polarization plateau resistance (R_{pol}) are determined and discussed according to the classical concentration polarization theory.

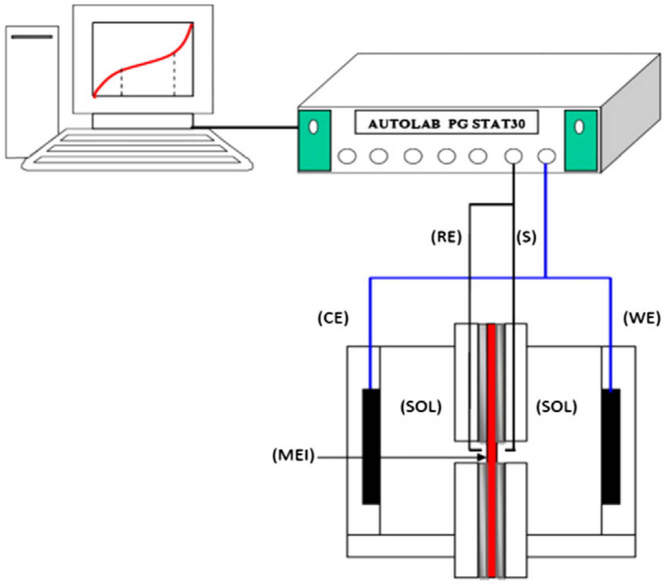

Fig. 2. Schematic description of the experimental setup. RE: reference electrode, S: sensor electrode, CE: counter electrode WE: working electrode, SOL: solutions, MEI: ion exchange membrane.

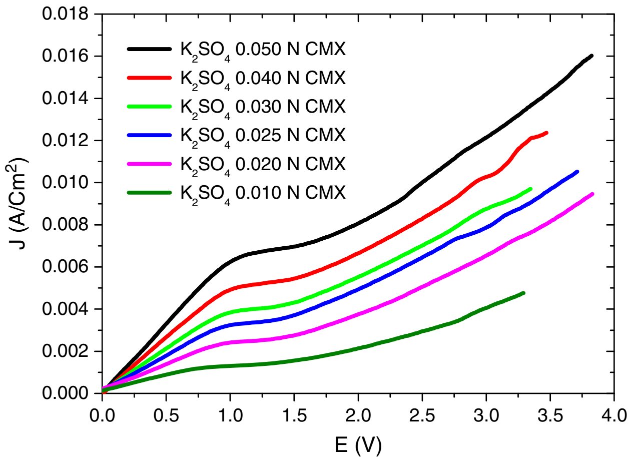

Fig. 3. Influence of K_2SO_4 concentration on the I–V curves of CMX membrane.

2. Experimental

2.1. Cation exchange membrane and chemicals

The ion exchange membrane used in this work is the CMX cation exchange membrane (Neosepta CMX, Tokuyama Soda, Japan). This is a homogenous membrane containing sulfonic acid groups as fixed charges, it is produced from the sulfonation of cross-linked styrene–divinylbenzene copolymer (PS-DVB) and reinforced with polyvinyl chloride (PVC) fiber. The membrane was conditioned according to the NF X 45-200 standards of the French Normalization Association (AFNOR) for IEM, then the experiments are carried on after a membrane equilibration period of at least 24 h in a solution with the same characteristics used in the experiments (100 ml / 10 cm^2 membrane). The solutions are prepared dissolving analytical grad reagents in distilled water.

2.2. Electrochemical cell and current–voltage measurements

The current–voltage curves are obtained using a two compartment electrochemical cell as shown in Fig. 2. This cell is composed of two

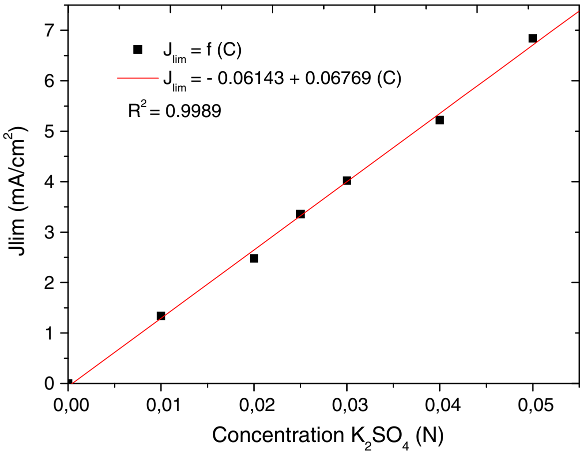

Fig. 4. Limiting current density as a function of K_2SO_4 concentration for CMX membrane.