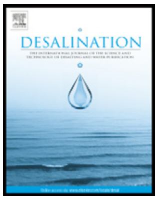
Desalination 263 (2010) 118–121

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



Transport properties of tartrate ions through an anion-exchange membrane

Mónica Lucía Vásquez-Garzón *, Giancarlo Bonotto, Luciano Marder,
Jane Zoppas Ferreira, Andréa Moura Bernardes

LACOR, PPGEM, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, Setor 4, Prédio 74, Campos do Vale, 91501-970, Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:
Received 16 December 2009
Received in revised form 16 June 2010
Accepted 20 June 2010
Available online 14 July 2010

Keywords:
Tartrate ions
Current–voltage curves
Anion-exchange membrane
Electrodialysis

ABSTRACT

In this study, the transport properties of tartrate ions through an anion-exchange membrane were evaluated by current–voltage curves. The values of the limiting current density were determined using these curves, to estimate the transport number of tartrate ions through the anion-exchange membrane. The influence of tartrate ion concentration, ethanol content in solution and solution pH were investigated. The results obtained, typically revealed three regions of current–voltage curves for potassium tartrate solutions with concentrations between 0.01 and 0.05 mol/L. The estimated transport number of tartrate ions through the membrane for this concentration range was 0.9. Neither the ethanol present in the potassium tartrate solution nor the solution pH affected the shape of the current–voltage curves. However, the limiting current density values were greatly influenced by the ethanol content and solution pH.

1. Introduction

Ion-exchange membrane processes, as in electrodialysis, are separation methods used in various industrial fields. It is therefore important to know the transport properties of the ions through the ion-exchange membranes [1] to ensure good performance of this process. One of the common methods used to characterize the transport across the ion-exchange membranes is to study the current–voltage curves corresponding to the membrane system. The typical shape of these curves is related to the concentration phenomenon that occurs when an electric current passes through a solution–membrane interface. According to the classical theory of polarization, in principle the electric current circulating through the membrane system increases linearly with voltage increase. Later, this increase slows down, and finally the electric current reaches a certain limit, i_{lim}, which the value is expressed by Eq. (1):

$$i_{lim} = \frac{C_0 D z_j F}{\delta\left(t_j^m - t_j^s\right)} \tag{1}$$

where C_0 is the concentration corresponding to the bulk solution, z_j is the charge of the counter-ion, δ is the thickness of the diffusion boundary layers, D is the salt diffusion coefficient, F is the Faraday constant, t_j^s and t_j^m are the transport numbers of the counter-ion in the solution and in the membrane, respectively.

In practice, such a limiting value is not observed, although the current–voltage curves show the characteristic shape on which the three regions can be clearly distinguished: (I) a region of ohmic behavior; (II) a second region, where the current varies very slowly with voltage (plateau corresponding to the limiting current), and (III) a third region, of rapid current increase [2]. This rise in current is attributed to several effects like water splitting, gravitational convection and electro-convection [3,4].

The transport properties of inorganic ions through the ion-exchange membranes have been extensively studied over the recent years and much information is available in the literature [5–12]. However, studies and available experimental data on ion-selective membranes in contact with organic anions are relatively limited [13,14]. As some electrodialysis processes, such as the tartaric stabilization of wines [15], require the removal of organic anions, in this study, transport properties of tartrate ions through a commercial anion-exchange membrane were evaluated by current–voltage curves. The influence of tartrate ion concentration and ethanol content in solution were investigated.

2. Experiment

The solutions utilized in this work were prepared by dissolving potassium tartrate ($C_4H_4K_2O_6.1/2H_2O$) in deionized water. Solutions with potassium tartrate concentrations between 0.01 and 0.05 mol/L were employed. Besides, 0.03 mol/L potassium tartrate solutions with 5, 10 and 15% of ethanol were also used. The potassium tartrate solutions revealed pH between 6.0 and 6.5, at which value, the tartrate ion in solution is usually present as a bivalent ion, $C_4H_4O_6^{2-}$ [16]. In addition, a 0.03 mol/L tartaric acid solution prepared by dissolving tartaric acid ($C_4H_6O_6$) in deionized water was also tested. Analytical grade reagents and the IONICS 204-SXZL-386 anion-exchange membrane were utilized. The study was conducted using the classical two-compartment

---

* Corresponding author. Tel.: +55 51 328647; fax: +55 51 33089427.
E-mail address: monicavasquezg@gmail.com (M.L. Vásquez-Garzón).

0011-9164/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2010.06.047

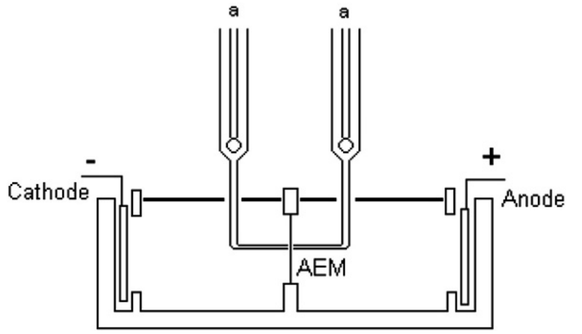


Fig. 1. Two-compartment electrochemical cell. (AEM: IONICS 204-SXZL-386 anion-exchange membrane; a: Ag/AgCl reference electrodes immersed in Luggin capillaries).

electrochemical cell (Fig. 1). It comprises two 180 mL symmetrical half-cells, between which the anion-exchange membrane was clamped. The membrane surface area was 12.6 cm^2. Two electrodes, titanium coated with titanium and ruthenium oxide were used to set up the current. Two Ag/AgCl reference electrodes immersed in Luggin capillaries were used to measure the potential drop through the membrane.

The current–voltage curves were obtained by a step-wise increase in the current, measuring the potential drop through the membrane after a stabilization period (typically 120 s). All experiments were conducted at room temperature and without stirring. In both cell compartments, solutions of identical concentration and composition were utilized. The experiments were accomplished after a membrane equilibration period of at least 24 h, with a solution of the same characteristics used in the experiments.

3. Results and discussion

Fig. 2 shows the current–voltage curve obtained for a 0.03 mol/L potassium tartrate solution (K_2T). In this figure a typical current–voltage curve can be observed, with all the three characteristic regions (ohmic, plateau, and over-limiting), as well as the limiting current density, determined by the intersections of the tangents corresponding to the first and second regions of the curve. The limiting current density values were also determined by plotting voltage/i versus 1/i [17]. The obtained results have given similar limiting current density values.

From the limiting current density value obtained in Fig. 2, the transport number of the tartrate ions through the membrane was estimated. According to Eq. (1), if C_0, z_j, δ, D and t_j^s are known, then t_j^m can be estimated by the limiting current density value. Under natural gravitational convection conditions, for a vertical plate, the effective thickness of the diffusion boundary layer δ, is a function of the diffusion coefficient, and can be estimated from the Levich equation [18]:

$$\delta \approx \frac{L^{1/4}}{0.7Sc^{1/4}\left(\frac{g\Delta C_g}{4\upsilon^2}\right)^{1/4}} \tag{2}$$

where L is the membrane height, g is the gravitational acceleration, $Sc = \nu/D$ is the Schmidt number, ν is the solution viscosity and ΔC_g is the concentration drop in the boundary layer between the interface and solution bulk, expressed in g/cm^3.

Assuming that for the diluted solution used in this study the kinematic viscosity is 10^{-2} cm^2/s, the thickness of the diffusion boundary layer was estimated from Eq. (2). The value obtained was 3.8×10^2 µm. The potassium tartrate diffusion coefficient data ($D = 1.3 \times 10^{-5}$ cm/s) was obtained from the equivalent conductivity data λ, at infinite dilution using the Nernst–Einstein equation. The tartrate transport number in the solution ($t_j^s = 0.5$) was also calculated by employing the equivalent conductivity data [19].

The tartrate transport number obtained through the anion-exchange membrane, calculated by Eq. (1) and assuming that the tartrate ion is on divalent ion form, was 0.9, which represents a good selectivity of the ion-exchange membrane for this ion. Of an electrochemical membrane process point of view, as electrodialysis, this aspect is greatly favorable, since it indicates that almost all of the electrical current within the ion-exchange membrane is carried out by the counter-ion, that is essential to assure a good performance of this electrochemical membrane process.

3.1. Influence of potassium tartrate solution concentration

Fig. 3 shows the current–voltage curves obtained for the potassium tartrate solutions with concentrations between 0.01 and 0.05 mol/L. Fig. 3 reveals that the current–voltage curves for all the solutions show the three characteristic regions. By relating the limiting current densities obtained to the potassium tartrate concentration (Fig. 4) it is observed to increase linearly with solution concentration. This behavior follows the trend of Eq. (1). Assuming that D, δ, t_j^s and t_j^m remain constant, this equation predicts a linear relationship between the limiting current density and the solution concentration. According to these results therefore, it can be estimated that the transport number of the tartrate ions through the ion-exchange membrane remains constant for the solution concentration range studied.

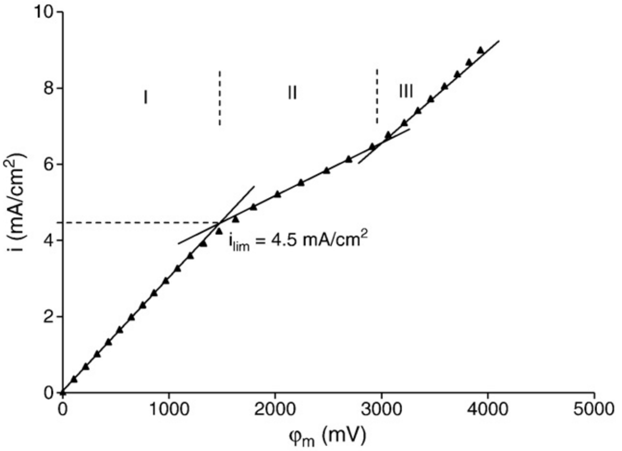


Fig. 2. Current–voltage curve obtained for a 0.03 mol/L potassium tartrate solution (K_2T).

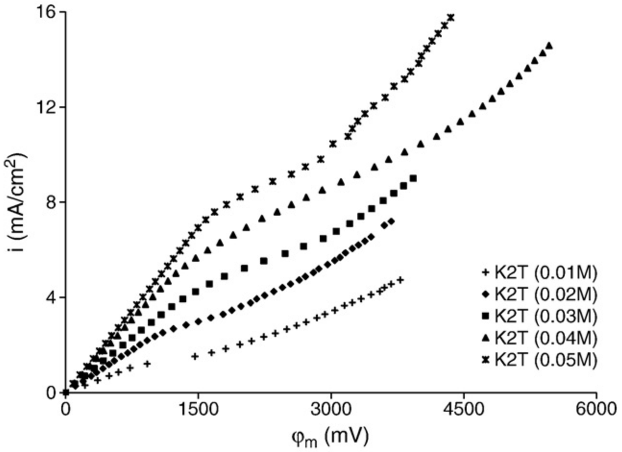


Fig. 3. Current–voltage curves obtained for the potassium tartrate solutions (K_2T) with concentrations between 0.01 and 0.05 mol/L.