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Salt diffusion through cation-exchange membranes in alcohol–water solutions

M.A. Izquierdo-Gil*, V.M. Barragán, M.P. Godino, J.P.G. Villaluenga, C. Ruiz-Bauzá, B. Seoane

Department of Applied Physics I, University Complutense of Madrid, 28040 Madrid, Spain

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ABSTRACT

The salt flow through several commercial cation-exchange membranes separating two NaCl alcohol–water solutions with the same alcohol concentration, but different NaCl concentration was investigated. Homogeneous (Nafion-115) and heterogeneous (MK-40 and CR65-AZL-412) membranes were used in this work. The integral permeability coefficient was determined from the temporal evolution of the concentration in the dilute solution. The results showed that the integral permeability coefficient depends on both the solution alcohol concentration and the type of alcohol. It is observed that this dependence is function of the membrane structure. In general, for the heterogeneous membranes, the integral permeability coefficient is less sensible to alcohol concentration than for the homogeneous membrane at low and intermediate values of the alcohol percentage in the solutions.

1. Introduction

Ion-exchange membranes find applications in many processes like electrodialysis, dialysis, reverse osmosis, membrane electrolysis, fuel cells, etc. In all these processes, the behaviour of the membrane is of the greatest importance to the viability and performance of the process. For this reason, the preparation and the characterization of ion-exchange membranes have been well developed in these former decades. The issue is different depending on the application, but a common factor in the present researches is the development of new economically attractive membranes with specific characteristics to resolve satisfactorily the technical limitations. Therefore, the focus of much recent research has been the development of alternative membranes with specific properties. As it is well known, there is an essential difference between homogenous and heterogeneous membranes used in electromembrane processes. Therefore, in this challenge, the understanding of the influence of the membrane structure on its transport properties is fundamental. A knowledge of the electrokinetic properties of a particular membrane type could prove to be a major contribution factor behind the decision to implement that membrane for a specific separation process.

When two electrolyte solutions of the same nature at the same pressure and temperature, but of different concentrations are placed on both sides of a membrane, a salt flow through the membrane (electrolyte permeation) is observed. This phenomenon has been widely studied by other researchers [1–6]. Electrolyte permeability belongs to the basic characteristic of membranes dedicated to dialysis or electrodialysis techniques because of the knowledge of transport rates of electrolytes in ion-exchange membranes is necessary for designs in different systems. For this reason, a lot work has been carried out in this sense [7–10].

The diffusion process through the membrane is a non-steady state process. The salt flow causes the concentration difference between both sides of the membrane to decrease with time, and as a consequence of it, the electrolyte permeation velocity also decreases. The higher the value of the integral permeability coefficient of the system (formed by the membrane and the two diffusion boundary layers flanking it), the former effect will be the more pronounced. The determination of the integral permeability coefficient is very useful because its knowledge allows to obtain some internal characteristics of the membrane system.

Today ion-exchange membranes are receiving considerable attention. They are successfully applied for desalination of sea and brackish water, and for treating industrial effluents. Up to now, electromembrane processes, specifically electrodialysis, have been mainly applied in aqueous media [11]. In the last years, however, the development of direct methanol fuel cell and electrodialysis in organic media has got electrochemical applications of membranes in hydro-organic media to be a relatively new research and development domain [12–17]. For this reason the study of the electrolyte permeation in this kind of media is also crucial.

In order to gain a better understanding of the influence of the membrane morphology on its permeation characteristics, salt

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* Corresponding author. Tel.: +34 91 3944458; fax: +34 91 3945191.
E-mail address: amparo@fis.ucm.es (M.A. Izquierdo-Gil).

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transport properties of different sulfonated cation-exchange membranes in water and different alcohols have been investigated. To this end, our work used a method which allows the determination of the integral permeability coefficient directly from the fitting of the dilute chamber concentration experimental data as a function of the time. The influence of alcohol nature, alcohol percentage and membrane morphology on the integral permeability coefficient has been analysed. The salt diffusion through three commercial cation-exchange membranes with different structures has been studied. The aim of this work is to establish relations between the salt diffusion and the membrane structure in alcohol–water media. Three kinds of sulfonated cation-exchange membranes of different structures have been chosen. The membranes studied were: Nafion-115 (perfluorinated polyethylene with pendant ether-linked side chains terminated with sulfonated groups), MK-40 (microparticles of polystyrene-divinylbenzene with sulfonic groups randomly dispersed in a polyethylene matrix) and CR65-AZL-412 (crosslinked sulfonated copolymer of styrene-divinylbenzene). Nafion-115 is selected as being reference membrane for direct methanol fuel cell, and MK-40 and CR65-AZL-412, references for electrodialysis.

2. Basic equations

The salt flux through the membrane (J) from a mass balance is given by

$$J = \frac{V}{A}\frac{dc_1}{dt} = -\frac{V}{A}\frac{dc_2}{dt} \tag{1}$$

where c_1 and c_2 are the salt concentrations in chambers 1 and 2 (with $c_2 > c_1$), V is the volume of each chamber and A is the effective membrane area.

The integral permeability coefficient of the system is defined by

$$P_{\mathrm{ms}} = \frac{J}{c_2 - c_1} \tag{2}$$

From Eqs. (1) and (2), assuming that both volumes are equal and constant, the following equation can be obtained for $c_1(t)$ (concentration in the dilute chamber as a function of the time) [18]:

$$c_1(t) = \frac{c_1^0 + c_2^0}{2} - a\frac{\Delta c^0}{2}\exp\left(-\frac{2AP_{\mathrm{ms}}t}{V}\right) \tag{3}$$

where c_1^0 and c_2^0 are, respectively, the initial concentration in the dilute and concentrate chambers, Δc^0 is the initial concentration difference. The parameter a is introduced as a time origin correction, which considers the possibility that the diffusion process beginning time and the starting time of chronometer were not exactly the same. In general, the value of a will be very close to unity. Eq. (3) allows us to obtain P_{ms} directly from the fit of the experimental data of c_1 as a time function.

3. Experimental

3.1. Membranes and materials

The membranes used in this work are three sulfonic cation-exchange membranes, with similar electric properties but different structure.

A commercial cation-exchange membrane type Nafion-115 (hereafter named NF115), manufactured by DuPont Inc., was used in this study. This type of membrane consists of a polytetrafluoroethylene backbone (or matrix) and regularly spaced perfluorovinylether side chains ending in sulfonic acid groups. According to the data provided by the manufacturer, this membrane has a nominal equivalent weight of 1100 g equiv.$^{-1}$ and dry thickness of 127 μm. The maximum water uptake, the ion-exchange capacity, and the density are 41%, 0.996 kmol m^{-3} and 2 g/cm^3, respectively.

MK-40 membrane (hereafter named MK40), produced by Shchekinoazot Ltd., is a heterogeneous membrane with sulfonic groups as fixed sites. This membrane is manufactured by grinding of the KU-2-8 cationic resin (sulfonic groups, polystyrene-divinylbenzene copolymer as matrix) followed by mixing of the resin powder with polyethylene, fixing the mixture between two sheets of caprone gauze (reinforcing fabric) and molding such a sandwich under temperature and pressure. MK40 is a heterogeneous sulphocationic membrane with an ion-exchange capacity, a dry thickness, a density, and a maximum water uptake of 1.64 kmol/m^3, 510 μm, 1.12 g/cm^3 and 40%, respectively.

The cation-exchange membrane CR65-AZL-412 (hereafter named CR65), produced by Ionics Inc., is a type web supported styrene-divinylbenzene-based membrane with sulfonic acid functional groups. According to the data provided by the manufacturer, this membrane has 1.2 kmol/m^3 sulfonated groups and it is mainly hydrophilic. The dry thickness, the density, and the maximum water content are 570 μm, 0.877 g/cm^3 and 43 wt.%.

Pure pro-analysis grade methanol and ethanol (Panreac), Pro-analysis NaCl (Merck) and bidistilled pure water were used in this study.

3.2. Conductivity measurements

Data on the electrical conductivity of NaCl aqueous solutions can be found in the literature [19]. However, data about the electrical conductivity of NaCl alcohol–water solutions have not been found in literature in the range of interest. For that reason the first step was to measure the conductivity of NaCl alcohol–water solutions (at alcohol 25, 50 and 75 wt.%) for both alcohols. The salt concentration range for the calibration procedure was 0.001–0.003 M. The solutions were finely thermostatized at 25 °C (by using a thermostat Techne TU-16D together with a Techne Refrigerated bath RB-12A), and then the conductivity was measured by using the electronic device described below (Section 3.3).

3.3. Permeability measurements

The experimental device used for the permeability measurements is similar to one used in previous works [20–22]. The membrane cell has two PTFE independent chambers of an approximate volume of 5.64×10^{-5} m^3 separated by the membrane. The effective membrane area was 2.61×10^{-3} m^2. The membranes were used as received, without any previous treatment, with the exception of membrane NF115 that was previously boiled in deionized and bidistilled water for 1 h. Each chamber had two orifices communicating to the exterior, they were used as solution inlet and outlet.

Two glass reservoirs of 0.5×10^{-3} m^3 of capacity were used to contain the circulating solution in both chambers. Each reservoir was provided with three orifices. Two of them were used as solution inlet and outlet. In the third one, a conductivity and temperature probe was introduced in order to measure the solution concentration. For this purpose an electronic device (Oakton PH/CON 510 series) with an accuracy of ±0.1 °C was used. In each probe orifice, one L-shape capillary tube was also introduced to avoid the pressure difference built-up between the reservoirs. These capillary tubes were kept at the same height. The reservoir had a glass made jacket where water was recirculated by means of a Techne TU-16D thermostat. This water was recirculated in order to maintain constant the solution temperature. The solutions were circulated between the cell and the reservoirs by means of a peristaltic pump (Heidolph Typ 52100). The solution circulation velocity was