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Liquid transport through sulfonated cation-exchange membranes for different water–alcohol solutions

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ABSTRACT

The aim of this work was to study the sorption and transport of different water–alcohol solutions (methanol, ethanol, 1-propanol and 2-propanol solutions) when a Nafion 117 membrane is separating them. It was observed that methanol permeability remains constant when varying the composition of the mixture. However, the permeability for the other alcohol solutions decreases from alcohol concentrations that are different for each alcohol. In addition, it was aimed to compare the behavior of membranes with different morphologies when they were separating water and water–alcohol solutions. Nafion 117 membrane and two sulfonated cation-exchange membranes (CR65-AZL-412 and MK-40) were used. Measurements of sorption and liquid transport were made using methanol and ethanol solutions. The uptake values for Nafion 117 membrane were higher than those obtained for CR65-AZL-412 and MK-40 membranes. The results reveal that, in contrast to Nafion membrane, a non-negligible water flux through CR65-AZL-412 and MK-40 membranes was observed along with the alcohol diffusion through them. For these two latter membranes the permeability could not be calculated since the alcohol diffusion is not the only physical process that should be considered. In spite of it, the alcohol and water fluxes through CR65-AZL-412 and MK-40 were estimated; turning out that the water flux was higher than alcohol flux.

1. Introduction

One of the most used ion-exchange membranes in analytical chemistry and in industry is Nafion membrane. The wide-ranging applications of this membrane are due to its excellent properties, as can be good water ion exchange, high electrical conductivity, excellent thermal and chemical stability and low gas permeability. Attending to these properties, Nafion membrane has one of its main uses in direct methanol fuel cell (DMFC), where it is commonly used as electrolyte. DMFC is hindered by methanol diffusion from anode to cathode side through the polymer electrolyte membrane [1–5], but this is not the only difficulty that has been found but also the slow kinetic of the oxidation reaction of methanol at the anode [6]. To overcome these problems some different solutions have been proposed. One of the solutions has been to replace methanol by other alcohols, mainly ethanol [7,8]. Although direct ethanol fuel cells (DEFCs) present some advantages over DMFC, higher energy density and non-toxicity, the diffusion of the alcohol through the membrane is not avoided. It seems clear that the understanding of the alcohol crossover through the membrane should be one of the major issues at the study of Nafion 117. This is one of the aims of the present work. To address it, we study the sorption and the permeation characteristics of different alcohols when a Nafion membrane is separating water and water–alcohol solutions. They have been using methanol and ethanol water solutions because they are the most employed with the Nafion membrane. But they have been also added 1-propanol and 2-propanol solutions to the study because their physical and chemical properties are different enough to those of methanol and ethanol solutions and have been less used with this membrane.

Not only Nafion but also other ion-exchange membranes are extensively used in an important number of processes in chemical and biochemical industry. Up to now, these transport processes in ion-exchange membranes were mainly developed in aqueous media. However the use of this kind of membranes in hydro-organic media allows the opening of new and important applications, which demand the development of new ion-exchange membrane solving the important technical and commercial limitations of the current ion-exchange membranes [9–12]. This is an important research domain, which involves the study of the influence of the membrane morphology in the transport coefficient in this kind of media. The membranes can be classified attending to different aspects, one of them is their structure. According to this aspect, ion-exchange membranes are divided into two major categories, the first one comprises homogeneous membranes that are polymers with ion-exchange groups bound to the polymer backbone. The second one consists of heterogeneous membranes that are neutral

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Table 1
Membranes characteristics: thickness (Th), maximum water uptake (MWU) and ion-exchange capacity (IEC).

	Th (μm)	MWU (%)	IEC (mequiv./g)
Nafion 117	183	35	0.941
MK-40	510	40	2.60
CR65-ALZ-412	570	43	2.1

polymer matrices randomly filled with micron size ion-exchange particles.

The structural differences are responsible for different behaviors under the same conditions. In a previous paper [13] liquid uptake and permeation fluxes as a function of the applied pressure difference were reported. It was obtained that both, the liquid uptake and the permeation show an important dependence on the structure of the ion-exchange membrane. In order to achieve a better understanding of the influence of the membrane morphology on the factors controlling sorption and permeability, different cation-exchange membranes separating water and water–alcohol solutions have been investigated. Two different alcohols, methanol and ethanol, and three sulfonated cation-exchange membranes of different structures have been selected. Nafion 117 is chosen as its significant use for direct fuel cell, and CR65-AZL-412 and MK-40 as being reference membranes for electrodialysis.

2. Experimental part

2.1. Membranes and materials

The first kind of membrane used was a Nafion 117 (Nafion) produced by Dupont Inc., and its nominal equivalent weight is 1.1 kg/equiv. Prior to testing, the Nafion membrane was introduced in a 0.25 M HCl solution during 48 h, at room temperature, for its complete conversion to an H+ form. Then, the membrane was washed with deionized bidistilled water. The properties and morphology of Nafion membrane have been at length studied in the literature [14,15]. Based on these studies, it is known that the membrane consists of a matrix (polytetrafluoroethylene backbone) and regularly spaced perfluorovinylether side chains ending in sulfonic acid groups. It has been proposed that the membrane would be understood as hydrophilic areas made up of the sulfonic acid groups clustered in spherical domains (4–5 nm) connected by channels to a hydrophobic perfluorocarbon matrix.

The cation-exchange membrane MK-40 (MK40) produced by OAO ShchekinoAzort is a heterogeneous membrane with sulfonic groups as fixes sites. According to the data provided by the manufacturer, the cross-linking degree of the membrane is 8%. This membrane was used as received without any previous treatment. In accordance with the literature [16], these membranes consist of ion-exchange particles (sulfonated groups chemically attached to polystyrene/divinylbenzene copolymer chains) dispersed in the polymer matrix. The membrane surface areas corresponding to the exit of ion-exchange resin particles have linear dimensions within the range from 10 to 30 μm.

CR65-ALZ-412 membrane (CR65) produced by Ionics Inc. is a type web supported styrene-divinylbenzene (DVB)-based membrane with sulfonic acid functional groups. In the membrane manufacture, styrene and DVB are copolymerized using an initiator (BPO) to get a homogeneous viscous polymer solution. Attending to the data provided by the manufacturer, the membrane is mainly hydrophilic. CR65 was used without any previous treatment.

The thickness, maximum water uptake and ion-exchange capacity, given for the manufacturer, for the three membranes are shown in Table 1.

Table 2
Physical and chemical properties of water, methanol, ethanol, 1-propanol and 2-propanol at 25 °C and 10^5 Pa. Density (ρ), viscosity (μ) and molar mass (M).

	ρ (g/cm^3)	μ (mPa s)	M (g/mol)
Water	0.9970	0.890	18
Methanol	0.7865	0.541	32
Ethanol	0.810	1.0774	46
1-Propanol	0.799	1.938	60
2-Propanol	0.781	2.070	60

Pure pro-analysis grade methanol, ethanol, 1-propanol, 2-propanol (Panreac) and bidistilled pure water were used in this work. Their main physico-chemical characteristics are given in Table 2 [17].

2.2. Determination of liquid uptake in the membrane

In order to determine the water–alcohol solution uptake, a sorption study with Nafion membrane was performed by using aqueous mixtures of methanol, ethanol, 1-propanol and 2-propanol at different concentrations. The study was made using aqueous methanol and ethanol solutions for the two other membranes (MK40 and CR65). In this case, the investigation was not extended to 1-propanol and 2-propanol since at the permeability study these alcohols were not employed.

Before the experiments, the membrane samples were dried in a vacuum oven at 100 °C during 24 h. After that, the samples were weighed and then immersed in a close bottle containing a known mass of the corresponding solution and allowed to equilibrate at room temperature. After 48 h of immersion, the swollen membranes were taken out of the solution, dried with filter paper and weighed again. The liquid uptake degree, S, was calculated according to the following formula:

$$S = \frac{m_\mathrm{w} - m_\mathrm{d}}{m_\mathrm{d}} \tag{1}$$

where m_w and m_d are the masses of the swollen (dried with filter paper) and dry membrane (dried in a vacuum oven), respectively.

The density of the solution in the bottle, before and after membrane immersion, was measured in order to estimate whether a component of the solution, water or alcohol, is preferentially sorbed by the membrane. It was obtained that the results were reproducible for all the membrane at any alcohol concentration.

2.3. Concentration change measurements

The experimental device is only briefly summarized here, since it is similar to the ones used in previous works [18–20]. Basically, the membrane was housed at a PTFE cell, consisting of two independent chambers with an approximate volume of 10^{-4} m^3, the active membrane area was 25.3×10^{-4} m^2. Two glass reservoirs of capacity of 0.5×10^{-3} m^3 were employed to contain the circulating solution in both chambers. Both, in the cell and in the glass reservoir, temperature probes were introduced in order to control the temperature inside and outside the chamber. The solutions were circulated between the cell and the reservoirs by means of a peristaltic pump (Masterflex L/S model, Cole–Parmer).

Water was introduced in one reservoir and the water–alcohol solution in the other one. When a temperature of 25 °C is achieved in both chambers, the solutions were circulated through the cell. The chamber that contained pure water was placed over a mass balance (Sartorius BL3100 model) so the mass changes as a function of the time could be measured. The accuracy in the mass measurements was $\pm 10^{-4}$ kg.

The density of the water–alcohol solution was measured in the reservoir at the beginning and every hour during the exper-