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Comparative study of liquid uptake and permeation characteristics of sulfonated cation-exchange membranes in water and methanol

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ABSTRACT

Liquid permeation and uptake measurements of pure water and methanol were carried out using three commercial cation-exchange membranes: Nafion-117 (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 CR61-CZL-412 (crosslinked sulfonated copolymer of styrene–divinylbenzene). Methanol uptake by the Nafion-117 membrane was higher than that of water, in contrast, for MK-40 and CR61-CZL-412 membranes the opposite behavior is observed. Differences in the water and methanol liquid uptakes by the membranes were discussed in terms of the chemical interaction between the liquids and the polymers, and also on the size of the liquid molecules. On the other hand, the methanol permeation flow values through the membranes were higher than those of water for all the studied membranes.

1. Introduction

Ion-exchange membranes play an important role in an increasing number of processes in chemical and biochemical industry. They are used, e.g., in electrodialysis and as separators in electrolytic cells and fuel cells [1–3]. Most commercial ion-exchange membranes can be divided, according to their structure, into two major categories: (1) homogeneous membranes, which are composed of crosslinked polymers having ion-exchange groups bound to the polymer backbone; (2) heterogeneous membranes, which consist of neutral polymer matrix randomly filled with micron-sized ion-exchange particles [4,5]. Methods of preparing these membranes are different and available in open literature [6].

The investigation of transport and equilibrium phenomena in ion-exchange membranes has been studied in a number of papers [7–11]. It has been recognized that, although a homogeneous ion-exchange membrane indicates a chemically homogeneous polymer, there is microheterogeneity in the membrane morphology. There are several approaches allowing description of the transport properties of these systems, e.g., capillary models [12–14], and the microheterogeneous model [15,16]. In the first approach, the membrane is idealized assuming that is a porous medium containing parallel and cylindrical pores of the same radius. In the second approach, the membrane is presented as a microheterogeneous multiphase system and the transport modeling consists in describing the properties of the membrane as a function of different phases properties.

The sorption and permeation of liquid water–methanol mixtures containing different dissolved chloride salts in a Nafion-117 membrane were reported in a previous paper [17]. It was observed that both the permeation flow through the membrane and the membrane liquid uptake increase significantly with the methanol content of the solutions. These facts are attributed to the increase in wet membrane porosity, which brings about the increase of the mobility of solvents in the membrane, besides the increase of the mobility of the polymer pendant chains. In contrast, the influence of the type of electrolyte on the membrane porosity and permeability was not very important, with the exception of the CsCl solutions, which was probably due to the small hydration ability of the Cs^+ ion. We also investigated the transport properties of Nafion-117 membranes towards binary solutions of water and methanol under the actions of temperature gradients [18]. It was reported that the thermoosmotic flux through the membrane, which goes from the low temperature side to the high temperature side, increases linearly with the temperature difference across the membrane. The effect of the composition of the water/methanol mixtures on the thermoosmotic properties of the membrane is not straightforward, because the total flux through Nafion membrane can be larger than the fluxes of pure solvents. It was observed that the thermoosmotic coefficient increases with increasing the methanol content of the solutions. This behavior was attributed to the variation of the solvent uptake by the membrane and the solvent mobility in

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the membrane as a function of the mixture composition. The volume flow of methanol–water potassium chloride solutions through a Nafion-117 membrane originated by the simultaneous action of a pressure and electric potential differences was also measured [19]. The application of the irreversible thermodynamics theory, which includes second order terms, allowed the determination of the different phenomenological coefficients. The influence of the methanol content of the solutions on both the electroosmotic permeability and the mechanical conductance was similar; both decrease with increasing methanol content. The obtained results indicated that the simultaneous action of the pressure and electric potential differences originates a flow different than the sum of the individual flows due to the each force acting separately. The coupling effect makes that the total volume flow decreases when aqueous solutions are used, whereas for methanol–water solutions an increase is observed.

In order to gain a better understanding of the influence of the membrane morphology on its liquid permeation characteristics, transport and equilibrium properties of different sulfonated cation-exchange membranes in water and methanol have been investigated. To this end, our work includes the determination of the permeation flows through the membranes as a function of the applied pressure difference, and the liquid uptake of the membranes. Three kinds of sulfonated cation-exchange membranes of different structures have been chosen. Nafion-117 is selected as being reference membrane for direct methanol fuel cell, and MK-40 and CR61-CZL-412, references for electrodialysis.

2. Experimental

2.1. Membranes and materials

Three sulfonic cation-exchange membranes are investigated in the present work. Their main characteristics are presented in Table 1. The membranes were used for liquid uptake and permeation measurements as received in the acid form.

A commercial cation-exchange membrane type Nafion-117 (hereafter named NF117), produced by DuPont Inc., was used in this study. The ion-exchange capacity and nominal equivalent weight provided by the manufacturer for this membrane are 1.13 kmol/m^3 and 1100 g/mol of fixed charge, respectively. This type of membrane consists of a polytetrafluoroethylene backbone (or matrix) and regularly spaced perfluorovinylether side chains ending in sulfonic acid groups. The preparation and properties of commercial NF117 membrane are well described in the literature [20,21]. The morphology of Nafion has been extensively studied, and although the presence of ion clusters is understood, there are some ambiguity as to their shape and size. Various models have been proposed which describe its structure as a network of hydrophilic ionic clusters (4–5 nm), connected by channels, within a hydrophobic perfluorocarbon matrix. Although Nafion is mechanically strong, it is not crosslinked, and the size of ionic clusters and hydrophobic regions may vary according to the solvent, the temperature and counter-ions nature and concentration [15].

Table 1
Main characteristics of the sulfonated cation-exchange membranes investigated

Membrane	l (μm)	ρ (g/cm^3)	S	IEC (kmol/m^3)
NF117	183	1.98	0.35	1.13
MK40	510	1.12	0.40	1.64
CR61	570	0.877	0.43	1.16

Dry thickness (l), density (ρ), maximum water uptake (S) and ion-exchange capacity (IEC).

MK-40 membranes (hereafter named MK40), produced by NOP Plastmassy, are heterogeneous membranes with sulfonic groups as fixed sites. They are 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. The crosslinking degree of the membrane, according to the data provided by the supplier, is 8%. MK40 is a heterogeneous sulphocationic membrane with an ion-exchange capacity of 1.64 kmol/m^3. The properties of commercial MK40 membrane are well described in the literature [5]. The structure of the MK40 membrane consists of ion-exchange particles (sulfonated groups chemically attached to polystyrene/divinylbenzene copolymer chains) dispersed in the polyethylene matrix. The main part of the heterogeneous membrane surface is coated by polyethylene. The surface regions corresponding to the exit of ion-exchange resin particles on the surface are distributed sufficiently uniformly. Their linear dimensions are within the range from 10 to 30 μm.

The cation-exchange membrane CR61-CZL-412 (hereafter named CR61), produced by Ionics Inc., is based on poly(styrene-co-divinylbenzene) with sulfonic acid functional groups. Styrene–divinylbenzene (DVB)-based membranes have been stated to be the best for use in electrodialysis [4] because the crosslinked polystyrene has more phenyl rings that act as reactive sites for functionalization reactions like nitration, chloromethylation, and sulfonation. In the preparation of the membrane, styrene and DVB are copolymerized using an initiator (BPO) to get a homogeneous viscous polymer solution. Here DVD acts as crosslinking agent. Then, the CR61 cation-exchange membrane was prepared by the sulfonation of polymer in solution, with concentrated sulfuric acid in dichloroethane using the silver sulfate as catalyst. The crosslinking degree of the membrane, according to the data provided by the manufacturer, is 10%. The CR61 membrane has 1.16 kmol/m^3 sulfonated groups and it is mainly hydrophilic. The maximum water content is 43 wt.% corresponding to 17 mol of water per mol of sulfonic group.

Microphotographs (scanning electronic microscope images) of NF117, MK40, and CR61 cross-sections are shown in Fig. 1.

The liquids used were analytical grade methanol and deionized bidistilled water. Their main characteristics are given in Table 2.

2.2. Liquid uptake

In order to determine the total liquid uptake by each membrane type, a liquid swelling study was performed by using pure water and methanol. Before experiments, a membrane sample was dried in a vacuum oven at 100 °C for 6 h. After that, the sample was weighted and, then, immersed in a closed bottle containing the corresponding liquid and allowed to equilibrate. The bottle was placed in an oven thermostatted at 25 °C. After 1 week of immersion (when no more liquid is sorbed and the swelling is considered to be completed), the swollen membrane was taken out of the liquid, wiped carefully with filter paper and weighted again. The increase in weight was equal to the weight of the liquid sorbed by the membrane. The liquid uptake (S) by the membranes was calculated by the following equation:

Table 2
Physico-chemical properties of water and methanol

Solvent	ρ (g/cm^3)	μ (mPa s)	M (g/mol)	σ (Å^2)
Water	0.9970	0.890	18	10.6
Methanol	0.7865	0.544	32	17.6

Density (ρ), viscosity (μ), molar mass (M), and diffusion cross-section (σ).