

Fluid Flow Modeling in a Sulfonated Cation-Exchange Membrane

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ABSTRACT: Liquid permeation measurements of water, methanol, and 2-propanol were carried out using a commercial cation-exchange membrane Nafion-117 (perfluorinated polyethylene with pendant ether-linked side chains terminated with sulfonated groups). The experimental permeation data are treated and analyzed using the capillary

model, leading to the determination of equivalent pore radius of the membrane structure. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1412–1416, 2009

Key words: permeation; cation-exchange membrane; capillary model; nafion

INTRODUCTION

The investigation of transport and equilibrium phenomena in ion-exchange membranes has been studied in a number of articles.^{1–5} 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,^{6–8} and the microheterogeneous model.^{9,10} In the first approach, the membrane is idealized assuming that it 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.

To gain a better understanding of the influence of the membrane morphology on its liquid permeation characteristics, transport properties of a sulfonated cation-exchange membrane in water, methanol, and 2-propanol have been investigated. To this end, this work includes the determination of the permeation flows through the membrane as a function of the applied pressure difference, and the liquid uptake of

the membrane. A sulfonated cation-exchange Nafion-117 membrane is chosen as being reference membrane for direct methanol fuel cell.

EXPERIMENTAL

Membrane and materials

A commercial cation-exchange membrane type Nafion-117 (hereafter named NF117), produced by DuPont Inc., was used in this study. The main characteristics of the NF117 membrane are given in Table I. 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.^{11,12} 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. When the membrane is in contact with a solution, the size of ionic clusters and hydrophobic regions may vary according to the solvent, the temperature and counter-ions nature and concentration.⁹ All the membrane samples used in this work were dried in a vacuum oven at 100°C during 24 hours. It is well known that the treatment of the NF117 membrane at elevated temperatures results in better evacuation of secondary synthesis products and in larger opening of pores.⁹ In this

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TABLE I
Main Characteristics of the NF117 Membrane Reported by the Manufacturer. Dry Thickness (l), Density (ρ), Maximum Water Uptake (S) and Nominal Equivalent Weight (EW)

Membrane	l (μm)	ρ (g/cm^3)	S	EW (g/mol)
NF117	178	1.98	0.35	1100

study, this pretreatment of the membranes was found to be efficient to ensure the reproducibility of the measurements. Therefore, the membrane samples were in the H^+ form.

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

Liquid uptake

To determine the total liquid uptake by the membrane, a liquid swelling study was performed by using pure liquids. The membrane 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 several days 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.

Permeation measurements

The liquid permeation flux through the membrane was determined by using an experimental set-up reported elsewhere.¹³ Basically, the main part of the experimental device was a cell, which consisted of two equal cylindrical glass chambers. The membrane with an effective surface area of 5.7 cm^2 was mounted in a Teflon holder, which was positioned between the two chambers. The right chamber was connected to an air reservoir and a digital pressure gauge. The pressure in this chamber was varied over the atmospheric pressure, thus, the reading of

TABLE II
Physico-Chemical Properties of Water, Methanol, and 2-propanol. Density (ρ) at 25°C , Viscosity (η) at 25°C , Molar Mass (M), Dielectric Constant (ϵ) at 25°C , and Molar Volume (V)

Solvent	ρ (g/cm^3)	η (mPa s)	M (g/mol)	ϵ	V (mol/cm^3)
Water	0.9970	0.890	18	78.4	18.0
Methanol	0.7865	0.544	32	33.0	40.7
2-Propanol	0.79996	2.038	60	18.3	75.0

the pressure gauge gives the pressure difference between the two chambers. When the system was stabilized at the selected temperature (25°C), the right chamber was pressurized up to the desirable pressure value. For each pressure difference, the measurement consisted of following the displacement of the liquid meniscus in a L-shaped capillary tube introduced into the left chamber, as a function of time. The volume flux (J) through the membrane was estimated from the time evolution of the volume in the left chamber, $V(t)$, in the steady state region, by using the following expression:

$$J = \frac{dV}{dt} \quad (1)$$

RESULTS AND DISCUSSION

The volume flux values of water, methanol, and 2-propanol are shown in Figure 1 as a function of hydrostatic pressure difference across the membrane. It is found that the flux through the cation-exchange membrane follows the sequence: 2-propanol > methanol > water. The analysis of data in Figure 1 shows a linear dependence between the permeation flux and the hydrostatic pressure difference. According to irreversible thermodynamics, the liquid volume flow dependence on the hydrostatic pressure difference can be described by the following equation:

$$J = L_P \Delta P \quad (2)$$

where L_P (m^3/sPa) is the permeability coefficient of the liquid, and ΔP (Pa) is the hydrostatic pressure difference across the membrane. The values of permeability coefficients are given in Table III. It is

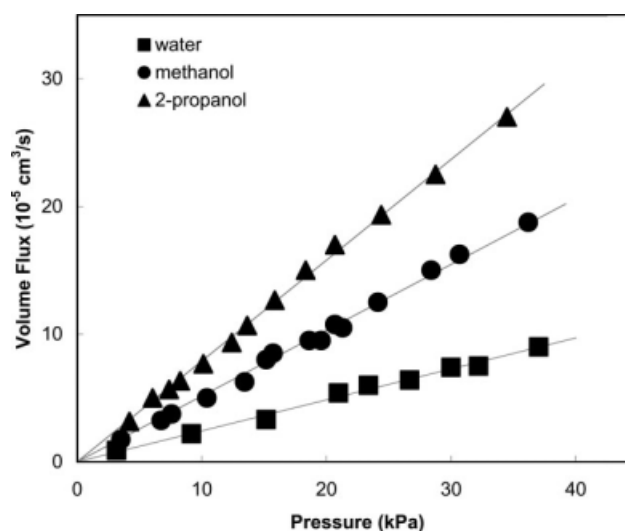


Figure 1 Liquid volume flux vs. pressure difference for the cation-exchange membrane studied.

TABLE III
Permeability Coefficient (L_P) of the Liquids, Membrane Liquid Uptake (S), Wet Membrane Porosity (ϵ), and Equivalent Pore Radius (r) Values for the NF117 Membrane

	Water	Methanol	2-Propanol
L_P (m^3/sPa)	7.5×10^{-16}	2.8×10^{-15}	1.1×10^{-14}
S	0.11	0.22	0.17
ϵ	0.19	0.33	0.29
R (nm)	3.1	3.4	14

known that irreversible thermodynamics approach treats the membrane as a black box ignoring the structure of the membrane or any transport mechanism. The interpretation of the experimentally determined L_P coefficient can be made if a transport model is assumed. In general, the liquid transport in dense membranes, such as NF117, may be described in terms of solution-diffusion mechanism. However, there are experimental evidences showing that, in highly swollen membranes like used in this study, the liquid forms an independent phase embedded in the polymer matrix.¹⁴ Then, in the course of liquid transport across the membrane, the liquid molecules collide with each other more often than with the polymer molecules. Hence, a convective contribution to the liquid transport in the membrane should be considered. Effectively, highly phase separated ionomer membranes like NF117 can be interpreted as porous media consisting of the sponge-like hydrophobic polymer backbone, which surrounds the well-connected hydrophilic domains allowing for species transport.^{15,16} In this study, the modeling of the liquid transport behavior exhibited by the membrane NF117 was made by the uniform-pore model,^{7,17} in which the membrane is modeled as an equivalent pore structure containing an array of parallel cylindrical pores of identical radius. This model is not physically realistic because membrane pores are tortuous and interconnected, and have a variable cross-section area.¹⁸ However, the idealized uniform-pore model provides a simple framework to estimate the radius of the pores, often called the equivalent pore radius.¹⁷ The expression of the pressure gradient driven flux through the cation-exchange membrane derived from Darcy's law is given by the following equation¹⁹⁻²³:

$$J = \frac{n\pi r^4 \Delta P}{8\eta l} \quad (3)$$

being n , the number of pores in the membrane; r , the pore radius; η , the viscosity coefficient of the liquid; and l , the membrane thickness. It should be pointed out that this equation was derived by neglecting other contributions to the driving force, such as local capillary pressures and elastic forces

exerted by the polymer matrix, and also tortuosity effects. If the effective cross-sectional area A of the membrane is considered, the equation of the flux through the membrane can be given as follows

$$J = \frac{Ar^2 \Delta P}{8\eta l} \quad (4)$$

where $A = n\pi r^2$. It is worth mentioning here that the membrane effective surface area available for liquid permeation is assumed to be proportional to the wet porosity V_P of the membrane. As was shown,²⁴ the hydrophilic pores in Nafion-type membranes appear normally as a result of contact with water and other polar liquids penetrating to its ionogenic groups. Then, the flux is given by

$$J = \frac{V_P Ar^2 \Delta P}{8\eta l} \quad (5)$$

It is known that a certain portion of the liquid sorbed by the membrane is bounded on the ionogenic groups of the polymer structure, hence the mobility of this liquid is lower than that of free liquid in the membrane. In addition, there are cooperative motions among the liquid molecules and strong interaction with the ion-exchange groups.¹¹ Here, it is assumed that the whole liquid in the Nafion membrane contributes to the fluid flow.

The equivalent pore radius can be estimated from eqs. (2) and (5) as follows

$$r = \left(\frac{8\eta l L_P}{V_P A} \right)^{1/2} \quad (6)$$

The wet membrane porosity, which is defined as the volume of the liquid within the membrane per unit volume of the wet membrane, can be obtained by the following expression^{21,25}:

$$V_P = \frac{\Delta V}{1 + \Delta V} \quad (7)$$

where ΔV designates the volume increase of the membrane upon sorption of the liquid per unit of dry membrane volume. This quantity is also calculated from membrane liquid uptake data using the following equation

$$\Delta V = \frac{(m_W - m_D)\rho_M}{m_D\rho_L} \quad (8)$$

where ρ_M and ρ_L are the density of the dry membrane and the density of liquid that enters into the membrane. The masses of the swollen, m_W , and dry membrane, m_D , were determined experimentally as described in the experimental section. The liquid uptake values of the membrane are 0.11, 0.22, and 0.17, expressed in gram of sorbed liquid per gram of

dry membrane, for water, methanol, and 2-propanol, respectively. Probably due to possible differences in the membrane pretreatment, the liquid uptake values obtained in this study are lower than those reported by others. As an example, the solubilities in NF117 reported by Rivin et al.²⁶ are as follows: water, 0.22 g/g; methanol, 0.492 g/g; propanol, 0.486 g/g. In NF117, the polytetrafluoroethylene backbone is highly hydrophobic, whereas the sulfonic groups are very hydrophilic. In the presence of a polar solvent, this gives rise to some hydrophobic/hydrophilic separation. It is known that water reside completely in the hydrophilic domains of the polymer, whereas alcohols are also soluble to a certain extent in the hydrophobic fluorocarbon backbone. This fact would explain the higher sorption value of methanol and 2-propanol compared with that of water. It is well known that the sorption of a liquid not only depends on the specific chemical affinity between the liquid molecules and the polymer but also on free volume available in the membrane, and the molecular size of the liquid. In this sense, dielectric constant is often used as a factor of solvent polarity, whereas the molar volume informs about the space hindrances exerted by the solvent during sorption and transport through the membrane. When methanol and 2-propanol sorption values in NF117 are compared, it can be seen that increasing molar volume and decreasing polarity of the alcohol resulted in the decreasing membrane swelling.

Membrane porosity values for the NF117 membrane are given in Table III. The porosity values of the methanol and 2-propanol-swollen membranes are nearly the same, whereas the wet porosity in water is much smaller than in alcohols. The behavior observed for the NF117 membrane is in agreement with that reported by others,^{21,27,28} which found that the dimensions of channels connecting the swollen clusters and the size of the clusters were larger for an alcohol-swollen membrane than that for a water-swollen membrane. Moreover, the NF117 membrane porosity values obtained in this study when using methanol and water seem reasonable, taking into account the data reported by other authors.^{8,21,25} As an example, water porosity for Nafion-type membranes ranges from 0.114 to 0.385.

Values of the pore radius estimated using eq. (6) for the membrane are given in Table III, assuming that the liquid viscosity in the membrane is the same as for bulk liquid. It is found that the equivalent pore radius of the membrane swollen in water and methanol are nearly the same, whereas the value in 2-propanol is much larger. The calculated membrane pore radius for water and methanol is in reasonable agreement with data reported by others,

taking into account the different assumptions made in the capillary model. As an example, for low angle X-ray diffraction measurements, the pore radius reported by a water-swollen NF117 membrane is 2.75 nm.²⁹ The pore radius, based on the measurement of electroosmotic flow, reported by a NF117 membrane is 1.28 nm.¹⁷ On the other hand, the equivalent pore radius estimated from 2-propanol data seems to conflict with reported data. The main cause of the greater value of the pore radius in the propanol-swollen membrane could be related to its relatively larger permeability coefficient. It can be speculated that the mobility of 2-propanol molecules increases with its content in the membrane, as the membrane is more and more plasticized. However, beyond a certain content, the propanol molecules form clusters inside the membrane due to its high viscosity, and its mobility becomes strongly increased. On the other hand, it is well known that, in nanoscale range as that encountered in this study, the viscosity of liquids is different from their bulk viscosity because of the effect of confined geometry.¹⁴ In nanopores it has been reported that the viscosity is either enhanced or decreased relative to the viscosity of bulk liquid for a number of systems. In spite of this, bulk viscosity values are considered in most of articles on membrane transport. It seems that this effect would be more important when using a liquid with a larger viscosity like 2-propanol. In such cases, the estimation of the equivalent pore radius from measurement of the hydrodynamic flux would not be a convenient method.

According to a cluster-pore model, the different values of the pore radius of the NF117 membrane for the liquids used in this study, indicates that the size and the number of channels depend on the liquid content of the membrane. It is well known that NF117 membrane is characterized by the formation of clusters, which are structural units of 4–10 nm size containing the solvent and the functional sites on the walls. As discussed before, the clusters are linked by more or less wide channels (1–6 nm in diameter) forming a connected network. Therefore, in this work, the equivalent pore radius value is in the order of magnitude to those of average channels radius for the NF117 membrane given in the literature.^{9,22,18,30,31} It is worth mentioning that Eikerling et al.¹⁴ investigated the pore-size distribution for hydrated Nafion membranes, and they reported the existence of pores of up 10.5 nm in size. This result was interpreted as the possibility for small pores to fuse into larger-size pores in the case of soft polymer matrix, such as NF117 membrane. On the other hand, Wijmans and Baker³² suggested that the transition between diffusive and convective regimes occurs for membranes with pores in the range of

0.5–1.0 nm diameter. Using this basis, as the values of pore size for NF117 membrane are larger than that of the predicted transition between regimes, the liquid permeation in the membrane is better described by a pore-flow mechanism.

CONCLUSIONS

The liquid permeability of a sulfonated cation-exchange NF117 membrane is studied using water, methanol, and 2-propanol. It is observed that the membrane is more permeable to alcohols than to water. It is found a linear dependence between the permeation flux and the hydrostatic pressure difference. The irreversible thermodynamics allows the estimation of the permeability coefficient of the liquids in the membrane. It is observed that the permeability coefficient follows the sequence: 2-propanol > methanol > water. The NF117 membrane is swollen by water and alcohols; the liquid uptake follows the sequence: methanol > 2-propanol > water. It can be seen that increasing molar volume and decreasing polarity of the alcohol resulted in the decreasing membrane swelling.

The modeling of the liquid transport in the membrane was made by the uniform-pore model, in which the membrane is interpreted as an idealized porous media characterized by an equivalent pore radius. The equivalent pore radius of the NF117 membrane was estimated from the permeability coefficient of the liquids and the wet membrane porosity. The calculated pore radii for water and methanol swollen membranes, which are 3.1 and 3.4 nm, respectively, are similar to data reported by others, using different methods of measurement. In contrast, the resultant equivalent pore radius of the propanol-swollen membrane is too large to be realistic, which may be due to a viscosity effect. It can be stated that, to avoid this inconvenient, the choice of the liquid is crucial to obtain accurately the equivalent pore radius in charged membranes based on the measurement of the hydrodynamic flow.

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