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SIMULTANEOUS TRANSPORT OF WATER AND ORGANIC MOLECULES THROUGH A PROTON-CONDUCTING MEMBRANE

D. Rivin*, G. Meermeier, N.S. Schneider
USA SBCCOM (Natick Soldier Center)
Natick, MA 01760

ABSTRACT

Proton-conducting polymers are used as compartment separators in fuel cells etc., and are also of interest as permselective diffusion barriers in protective fabrics. This study explores the concentration-dependent interaction between water and hydrophilic solvents in a perfluoroionomer under both permeation and immersion conditions. Permeation of vapor mixtures causes a large decrease in water flux and a proportionally smaller enhancement in organic flux. These effects arise from morphological changes in the swollen polymer.

1. INTRODUCTION

Ongoing work in our laboratory is concerned with characterizing polymer membranes which can provide protection against chemical warfare agents, while permitting high water vapor permeation to minimize heat stress in protective clothing. Nafion® a perfluoro ionomer, is of particular interest because of its exceptionally high water transport promoted by sulfonic acid terminated, perfluoroether side chains. The polymer is phase segregated with the ionic component, comprising one-third of the polymer, distributed in a fluorocarbon matrix. It was expected that the importance of ionic species in promoting transport of water and the fully fluorinated composition might lead to favorable permselective barrier properties for various classes of organic molecules, including chemical warfare agents. In unpublished permeation studies we found that Nafion® in acid form is not a good barrier for the nerve agent simulant, dimethyl methylphosphonate, DMMP. However, by substitution with multivalent cations the barrier properties of Nafion® are markedly enhanced. In fact, separately determined permeation rates of water vapor and DMMP vapor for calcium (+2) and iron(+3) modified Nafion® indicate a remarkable improvement in barrier performance with only a modest reduction in water vapor permeability. Based on this data, a cation modified Nafion® thin film or coating would be a superior permselective barrier if the material cost could be substantially reduced. However, separately

determined permeabilities are not a sufficient test of permselective performance, since barrier properties may be influenced by interactions between water and the hazardous chemical. In the present work, simultaneous permeation and solubility measurements have been made with mixtures of water and DMMP, a dipolar, aprotic, water soluble solvent, and with 1-propanol, a hydrogen bonding, protic solvent.

2. EXPERIMENTAL

Permeation measurements were conducted at selected vapor activities, generated by diluting a nitrogen stream saturated with water and/or organic vapor with additional nitrogen, in ratios set with electronic mass flow controllers. In counter-current flow, water vapor and organic vapor feed streams entered on opposite sides of the membrane, whereas a single mixed feed stream was used in co-current flow. Water vapor concentrations were determined with auto sampling instrumentation employing an etched GC column and thermal conductivity detector (MTI M200H) or, in a few cases, with a humidity detector (Vaisala HMI 32-HMP 35). Propanol concentrations were also determined with the MTI detector using an alternative GC column. DMMP vapor concentrations were recorded with a flame ionization detector (SRI Model 110). The permeation cell exposes a rectangular sample area 3.2 x 4.4 cm, with the membrane forming a pressure seal between the two halves of the cell. Flow rates for challenge and sweep were 60 cc/min. Vapor generators and permeation cell were housed in a constant temperature cabinet maintained at 30 ± 0.1 °C. Boundary layer resistance was determined from fluxes measured with multilayer microporous perfluoroethylene films extrapolated to zero film thickness. Reported membrane fluxes are calculated from net membrane resistance corrected by subtraction of the boundary layer resistance. Immersion sorption was determined gravimetrically on blot dried samples. The concentrations of sorbed water and DMMP were determined by weight loss (water) over molecular sieve (3A), followed by aqueous extraction of DMMP. Sorbed water and

propanol were measured by thermal desorption GC.

3. RESULTS

Measurements with DMMP and water vapor: The boundary layer corrected flux of water in NafionH, increases rapidly with activity from 2000 at activity 0.3 to 16500 g/day-m² at activity 0.9. The introduction of DMMP vapor, even at low activities, reduces the water flux, from 4000 to about 1000 g/day-m² at water activity of 0.3 and from 16500 to about 4000 g/day-m² at activity of 0.9. The effect is comparable in co-current and counter-current flow and almost independent of DMMP activity over the measured range, 0.1 to 0.5. Water vapor has the opposite effect on DMMP permeability, causing a rapid increase with water activity in co-current flow, but only a minor increase in counter-current flow. According to Fick's law the steady state flux equals the product of a diffusion coefficient and a solubility. Directly measured water and DMMP concentrations in the membrane are close to values for the individual vapor solubilities, or higher, if corrected for the concentration gradient in the film. These solubility results imply that the reduced water flux is not due to reduction of sorbed water but a result of competitive diffusion interaction with DMMP. On the other hand, the increase in DMMP flux in cocurrent flow could well be due to the increased solubility. Solubility measurements were also conducted from liquid mixtures at 5 to 80 weight percent DMMP in water. Water solubility goes through a maximum with increasing DMMP from 31% at 5% DMMP, which is about 1.5 times the solubility of pure water, to 41% at 20% DMMP then decreases to 16% at 80% DMMP. The increase in water sorption at low DMMP concentrations is consistent with evidence from vapor sorption measurements. DMMP immersion sorption increases nearly linearly with DMMP concentration.

Ca(+2) and Fe(+3) forms of Nafion® are excellent barriers to DMMP in the absence of water, and this improvement is maintained at low water concentrations. As an example, at DMMP activity of 0.3 and water activity of 0.5, the flux of 449 g/day-m² for acid Nafion® is lowered to 8 g/day-m² in NafionCa and is too low to measure in NafionFe. However, high activity water, near saturation, severely compromises barrier performance with DMMP. Substitution with the multivalent cations also affects water vapor permeability, resulting in a four-fold reduction at activity 0.9 from 16500 to 3800 g/day-m². DMMP at activity 0.5 causes an additional 25% reduction in water flux with NafionCa but has

little effect with NafionFe. For dry DMMP, 48 hours is required for breakthrough with NafionCa and several days with NafionFe. Breakthrough times decrease with concurrent water permeation, but values were not recorded in the permeation runs.

Measurements with 1-propanol and water: The flux of pure propanol increases from 790 g/day-m² to 5400 g/day-m² in the range of activities from 0.3 to 0.9. Water vapor at activity 0.5, increases propanol flux to 1360 g/day-m² at activity 0.3, but flux then remains nearly constant with increasing propanol activity, decreasing slightly to 1050 g/day-m² at propanol activity of 0.9. With an increase in water activity to 0.9, the flux at propanol activity of 0.5 doubles and is also about 50% higher in co-current than counter-current flow. Sorbed propanol concentration following permeation runs with water was independent of water activity. Uptake was about 25% lower than values determined for the pure vapor but could be as much as 1.5 times higher due to the concentration gradient in the film. Propanol severely depresses the water flux, by a factor of 4 to 5, but the effect at water activity of 0.5 is insensitive to propanol concentration or co-current flow. Weight uptake determined under immersion conditions goes through a maximum of 250% at 40% propanol in the mixed solvent. It is interesting that the concentration of sorbed water increases in a parallel fashion reaching a maximum of 164% at 30% propanol. These results are an indication of strong mixed water/alcohol interactions with Nafion®, which lead to high degrees of swelling and to dissolution of Nafion® at higher temperatures.

CONCLUSIONS

Simultaneous permeation measurements of water and water-soluble organic molecules through Nafion®, a phase segregated ionomeric membrane, show a significant decrease in water flux, compared to pure water vapor, and a smaller increase in organic flux relative to dry vapor. The magnitude of these interactions is affected only slightly by the relative direction of transport of the individual permeants. Nonlinear flux additivity with mixed vapor challenge is due to specific interactions with ionic and polar components of Nafion® and changes in morphology due to swelling, which alters diffusion pathways. Calcium(+2) and iron(+3) modified Nafion® demonstrate excellent permselectivity, especially, at the low concentrations characteristic of chemical agent vapor exposure.