Pervaporation removal of water from ionic liquid solutions using Nafion membranes

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ABSTRACT

We report a pervaporation process to remove water from a solution containing ionic liquid (IL) + solvent + water. Specifically, Nafion-based membranes were employed for the separation, and tributylmethylammonium dimethylphosphate and N-methyl-2-pyrrolidone (NMP) were the IL and solvent, respectively. Membrane swelling in contact with the IL–NMP–H₂O solution was accommodated by judicious use of gaskets and membrane supports. The pervaporation fluxes of water and NMP increased with temperature and flow rate of the permeate sweep gas. Among the membranes examined, a commercially available Nafion membrane (XL, Ion Power) provided the highest water (10 mg h⁻¹ cm⁻²) and NMP (182 mg h⁻¹ cm⁻²) fluxes. The results show that pervaporation separation is a technologically feasible method to decrease the water content of an IL–NMP–H₂O solution from 1 to 0.5 wt%.

Introduction

Cellulose is the most abundant organic compound in the world.[1,2] Cellulose and its derivatives are extensively used in industries such as textiles, polymers, coatings, membranes, and pharmaceuticals due to attractive properties such as biocompatibility, biodegradability, and chemical stability.[3] However, difficulty in dissolving cellulose in water and common organic solvents hinders its application as a biorenewable feedstock. In 2002, Rogers and co-workers[4] reported cellulose dissolution without derivatization in high concentrations using ionic liquids (ILs). Since then, interest in developing and using ILs to dissolve and react cellulose has grown.[5–12] Because of the high viscosity of ILs, however, a solvent is commonly used to allow practical processing, and the IL solution becomes contaminated by reactants, by-products, and impurities during use and requires purification.[14] Example contaminants include carboxylic acids, water, aliphatic alcohols, and salts. These contaminants may negatively affect the dissolution/reaction of cellulose and must be removed completely or controlled at an acceptable level. Furthermore, ILs are expensive and essentially their complete recovery is needed for economical biomass processing.

A small number of studies have been reported on purification of ILs. Raines and co-workers[15] used ion-exclusion chromatography in batch operation to recover ILs, glucose, and xylose with yield >95, 94, and 88%, respectively. Holmes and co-workers[16] used a solvent extraction technique, based on a boronic acid membrane, to extract glucose, xylose, and cellulose from aqueous mixture of ILs with yields up to 90%, resulting in a solution of fermentable sugars and facilitating the recovery of ILs. Koo and co-workers[14] reported that simulated moving bed (SMB) chromatography, equipped with an ion-exclusion column, can be used to separate ILs, glucose, and xylose from their aqueous solution with yields of 99, 71, and 99%, respectively. Nevertheless, little is known about processing of IL–H₂O mixtures with membranes.[17]

Dehydration of IL solutions (<0.5 wt% water) may be achieved by distillation/molecular-sieves[18,19] and extraction methods.[20] The drawback of distillation is its high energy consumption. It may require a temperature which causes thermal degradation of some ILs. Liquid–liquid extraction has several disadvantages including limited selectivity, difficulty of automation, and emulsions. Other difficulties are (1) it needs costly amounts of organic solvents and generates large volumes of organic waste and (2) the process can be time consuming, especially if attainment of equilibrium is slow.

Nafion, a sulfonated fluoropolymer (Fig. 1), has a variety of commercial applications, but mainly as the membrane/separators in chlorine-alkali cells and polymer electrolyte
membrane fuel cells (PEMFCs). In the early 1990s, Nafion membrane dryers were introduced to remove moisture from a wet gas. In recent years, research has been reported on the development of Nafion-IL composites for various applications; however, none we found are related to water removal from ILs. It is noteworthy that the Nafion-IL composites are reported to be chemically and mechanically stable.

Pervaporation is a processing method to separate mixtures of liquids by vaporization of the component through a membrane. Studies reporting pervaporation separation of alcohol/water mixtures using Nafion hollow fibers and membranes have been published. To our knowledge, no research has been reported on the use of Nafion to remove water from ILs. It is our hypothesis that a Nafion-based pervaporation membrane process may be employed to remove water efficiently from IL solutions (Figure S1), and the present study was exploratory with an objective to demonstrate feasibility of a pervaporation process to remove water from an IL + solvent + water solution. Specifically, Nafion-based membranes were employed and tributylmethylammonium dimethylphosphate and N-methyl-2-pyrrolidone (NMP) were the IL and solvent, respectively. Based upon conversation with the sponsor of our work, an aim was set to lower water content of an IL+NMP+H₂O solution (wt ratio IL:NMP @ 7:3) from 1 to 0.5 wt% water: The composition of feed solution includes 69.3 wt% IL, 29.7 wt% NMP, and 1.0 wt% H₂O. Moreover, pervaporation operates at moderate temperature (<100°C) and may be more cost effective than alternative separation processes. These advantages may enable an economical IL recovering process and thereby advance cellulose technology.

### Experimental

#### Chemicals and membranes

NMP was purchased from BDH Chemicals. Potassium chloride (KCl) and Karl-Fischer reagent (HYDRANAL®-Coulomat AG) were obtained from Sigma-Aldrich. IL studied in this research is tributylmethylammonium dimethylphosphate, provided by Eastman Chemical Company. This IL has a melting point of 60°C; however, with water content >1 wt% it is a liquid at room temperature. Nine ionomer membranes were evaluated: (a) six commercially available Nafion-based membranes (Ion Power) and (b) three proprietary W. L. Gore & Associates membranes (Gore). Table 1 summarizes properties of the membranes. Membranes with thicknesses ranging from 10 to 183 μm are divided into three types based on composition: (1) plain (neat) Nafion (membranes composed solely of Nafion without additive or reinforcement), (2) fiber-reinforced Nafion, and (3) composite (Nafion + other polymeric material). Composite membrane indicates that the membrane was reinforced by combining pristine ionomer with a chemically stabilized polymer; Ion Power and Gore do not report details of their proprietary membranes.

### Membrane pretreatment and solution uptake

As-received membranes are in proton form and were used without pretreatment, except for two plain Nafion membranes, N115 and N117, which were also studied with K⁺ as the counterion. The K⁺ form of the membrane was prepared by submerging membrane in a 1 M KCl solution at room temperature for 12 h. After KCl treatment, the membrane was rinsed and soaked in deionized water for 24 h. Membrane solution-uptake studies were performed for four liquids: NMP, IL–NMP (wt ratio IL:NMP @ 7:3), IL, and H₂O at room temperature. IL–NMP solution shows water content from 0.03 to 0.07 wt% IL contains >1 wt% water. Membrane samples with a size of 6 cm² were dried at 45°C and then soaked in the solutions at 20°C for 24 h and 1 month. The containers used for the uptake experiment were sealed by parafilm. Membrane uptake was determined by measuring the weight difference of the membrane before and after immersing in the solutions. Uptake (%) was calculated as

![Figure 1. Chemical structure of Nafion.](image)

**Table 1. Nine ionomer membranes evaluated in this study.**

| Membrane | Manufacturer | Type    | Thickness (μm) | EW (g) |
|----------|--------------|---------|----------------|--------|
| N117     | Ion Power    | Plain   | 183            | 1100   |
| N115     | Ion Power    | Plain   | 127            | 1100   |
| NR212    | Ion Power    | Plain   | 51             | 1100   |
| N324     | Ion Power    | Reinforced | 152*          | 1100/1500 |
| XL       | Ion Power    | Composite | 27*        | NA     |
| HP       | Ion Power    | Composite | 20*        | NA     |
| Gore A   | Gore        | Composite | 10*        | NA     |
| Gore B   | Gore        | Composite | 10*        | NA     |
| Gore C   | Gore        | Composite | 10*        | NA     |

*Thickness data provided by manufacturers. *EW: Equivalent weight is weight of Nafion per mole of sulfonic acid. *N324 membrane contains PTFE fiber reinforcement. *Thickness of the composite membrane includes Nafion and reinforced polymer. NA: Not available.
Uptake (%) = \frac{wt_{\text{wet}} - wt_{\text{dry}}}{wt_{\text{dry}}} \times 100\% \quad (1)

where \( wt_{\text{wet}} \) and \( wt_{\text{dry}} \) are the mass of wet and dried membranes, respectively. Each uptake measurement was performed in triplicate using three membrane samples.

**Pervaporation experiment**

Pervaporation experiments were performed in a closed-loop system consisting of an IL-solution reservoir (165 mL), a liquid pump, a flat-sheet membrane in a plate-and-frame cell (2.5 cm\(^2\) permeation zone), and a dry gas (\(N_2\)) as extractant. The IL-solution evaluated in this study consists of 69.3 wt% IL, 29.7 wt% NMP, and 1.0 wt% \(H_2O\).

Figure 2 is a schematic of the apparatus used in the study, and the cell was operated in differential-conversion mode; that is, the gas and liquid flow rates were set to be significantly higher than pervaporation rates of \(H_2O\) and NMP. All gas and liquid lines were heat-tape traced and temperature controlled. A heating mantle set the temperature of the IL-solution reservoir and a cartridge heater maintained temperature of the plate-and-frame pervaporation cell. The parameter space explored included 11 membrane types, gas-sweep rate from 50 to 200 mL min\(^{-1}\), and temperature from 60 to 100°C. The water content in the IL solution decreased linearly with time as its concentration dropped from 1 to 0.5 wt% and this is the rate reported herein. The average mass flux of the permeate over the course of the experiment was calculated using the total weight of the permeate at the end of a batch experiment. The NMP is absorbed by Nafion and NMP is also volatile, although with a much lower vapor pressure than water; thus, NMP pervaporates in addition to water. Hence, an important measure determined in the work is the selectivity of the pervaporation process to water.

The plate-and-frame cell (Fig. 3 and S2) has a sandwich-type structure and consists of two graphite plates with machined-in serpentine flow channels for liquid and gas flows, two gaskets for accommodating membrane swelling and providing a seal between graphite plate and membrane, a support layer to improve membrane mechanical stability, and a membrane. The width and depth of the serpentine channel are 0.8 and 1.0 mm, respectively. Using Karl-Fischer titration (Mettler-Toledo, KF coulometer DL 39), we measured water content of the IL solution during the course of a batch run and the water content of the permeate [condensate from refrigerated bath (\(-20°C\))] at the end of a run. After refining experimental protocols, a mass balance on water removed from the IL solution and collected in the permeate would typically close within ±6%. The ionic resistance of the IL solution and permeate were measured using electrochemical impedance spectroscopy (EIS)\(^{[38]}\). The AC impedance measurement is performed using a VersaSTAT 4 potentiostat (Princeton Applied Research) and using a frequency range of 10\(^5\) to 10 Hz and perturbation voltage amplitude of 5 mV.

Table S1 lists the resistivity data of various solutions studied. Rheology experiments were performed at 25°C on a stress-controlled rheometer (AR-2000, TA Instruments) using 40-mm flat plates. Viscosity was determined by averaging steady-shear viscosity values in the Newtonian regime.

**Results and discussion**

**Membrane uptake properties**

Membrane chemical and mechanical stability in contact with the IL–NMP–\(H_2O\) mixtures is critical and was studied before evaluating the feasibility of the pervaporation process itself. We performed a series of
membrane-uptake studies at room temperature in four solutions: NMP; IL–NMP (wt ratio IL:NMP @ 7:3); IL (IL contains >1 wt% water and is in liquid state); and H₂O. Uptake results provide not only information about membrane stability but also membrane swelling behavior. Membrane (H⁻ form) uptake results along with standard deviation based on results of three membranes are summarized in Table 2. For the plain membranes, such as N115, N117, and NR212, solution uptake decreased in following order:

\[ \text{NMP} > \text{IL} > \text{H}_2\text{O} > \text{IL} \]  

Plain membranes showed no notable weight gain after immersion in IL for 24 h. However, the average uptake amount increased to 7% after 1 month. ILs are known to be hygroscopic and water accumulates slowly over time to saturation corresponding to the ambient humidity. Therefore, the observed increase in uptake of the membranes may be caused by water absorption into the IL from the air atmosphere to which the containers were exposed. We tried to affirm the supposition by performing an IL uptake experiment under a low humidity condition. Unfortunately, the experiment failed due to a high melting point (60°C) of the IL and it solidified at room temperature. Most importantly, Nafion membranes are chemically and mechanically stable in IL as reported by other researchers. No sign of membrane degradation was visually observed during the uptake experiments. Composite membranes (XL, HP, and Gore A) absorbed less than 30% of their initial weight in IL–NMP solution, which indicates higher stability and limited swelling relative to the plain membranes. Moreover, composite membranes showed higher solution uptake than the plain membranes in IL and may be attributed to absorption in the polymer used in the composite. The uptake results indicated NR212 and Gore B membranes were unstable in IL–NMP: they showed weight loss after one month and other experiments showed pinholes were formed during their use in pervaporation experiments. NMP is a common solvent used in the dispersion-cast process for synthesizing membrane such as NR212. These dispersion-cast membranes showed poor stability and slowly dissolved in IL–NMP solution during the uptake experiments.

It is well known that the counterion has significant effect on swelling behavior of Nafion membranes. Gebel and co-workers proposed that two factors affect solvent uptake amount including (1) cation radius and (2) cation softness (Table S2). In our study, the H⁺ form N115 and N117 membranes were ion-exchanged into K⁺ form. The K⁺ form of N115

Table 2. Solution uptake results of membranes (proton form) at room temperature.

| Membrane  | NMP 24 h | NMP 1 mo. | IL-NMP* 24 h | IL-NMP* 1 mo. | IL² 24 h | IL² 1 mo. | H₂O 24 h | H₂O 1 mo. |
|-----------|----------|-----------|--------------|---------------|----------|----------|----------|----------|
| N115      | 56 ± 1   | 68 ± 1    | 52 ± 1       | 48 ± 1        | Ne.      | 6 ± 1    | 16 ± 1   | 21 ± 1   |
| N117      | 57 ± 1   | 67 ± 1    | 44 ± 1       | 47 ± 1        | Ne.      | 5 ± 1    | 25 ± 1   | 26 ± 1   |
| NR212     | 87 ± 2   | 126 ± 2   | 70 ± 1       | 62 ± 1        | Ne.      | 8 ± 4    | 8 ± 1    | 8 ± 1    |
| NR324     | 51 ± 1   | 53 ± 1    | 7 ± 1        | 17 ± 1        | Ne.      | 2 ± 1    | 8 ± 1    | 8 ± 1    |
| XL        | 82 ± 1   | 104 ± 2   | 23 ± 1       | 26 ± 1        | 6 ± 1    | 10 ± 1   | 6 ± 1    | 11 ± 1   |
| HP        | 67 ± 2   | 92 ± 1    | 23 ± 1       | 27 ± 1        | 5 ± 1    | 18 ± 1   | 2 ± 1    | 6 ± 1    |
| Gore A    | 23 ± 1   | 26 ± 3    | 25 ± 1       | 27 ± 1        | 7 ± 1    | 15 ± 2   | Ne.      | Ne.      |
| Gore B    | 79 ± 2   | 113 ± 2   | 51 ± 2       | 43 ± 1        | 9 ± 1    | 34 ± 1   | Ne.      | Ne.      |
| Gore C    | 26 ± 3   | NA        | 30 ± 1       | NA            | 8 ± 1    | NA       | Ne.      | NA       |

*Membranes were dried at 45°C and then soaked in solution at 20°C for 24 h and 1 month. N = 3. *The weight ratio between IL and NMP is 7:3. *IL contains >1 % H₂O. Ne.: Negligible. NA: Not available.
showed a factor of four decrease of the absorption of IL +NMP at room temperature from 52 to 13 wt% in comparison to the H⁺ form of Nafion (Table 3). Similar phenomena were observed for the K⁺ form of N117. Yeo and Cheng⁴⁰ reported uptake ability of Nafion membrane for most solutions they studied decreased with the membrane in K⁺ form, which is in agreement with our measurements. Interestingly, both K⁺ forms of N115 and N117 membranes absorbed only 3% less NMP than the H⁺ forms of the membranes.

### Preliminary studies

A screening protocol ( pervaporation performed at 80°C with liquid and gas flow rates of 5 and 50 mL min⁻¹, respectively) was used to evaluate 11 membranes. The following observations were made: (1) for the plain membranes, thinner membranes provide greater permeate fluxes by assuming the solution-diffusion mechanisms in Nafion behaves more or less the same for the two thicknesses investigated; the H₂O flux across N115 (127 μm) was larger than that across N117 (183 μm). (2) The K⁺ form of Nafion reduced membrane swelling, and the H⁺ form of Nafion resulted in a larger H₂O flux (Table 4). (3) The swelling of the membranes in IL–NMP mixture caused significant pressure drops in the flow channel and a large trans-membrane pressure difference. This membrane swelling was accommodated in the cell design by increasing the gasket thickness (from 254 to 762 μm). (4) The NR212 and Gore B membranes were unstable in IL–NMP: they showed weight loss in static solution-uptake experiments and pinholes were formed during pervaporation experiments. (5) Gore C membrane was unstable at a pervaporation temperature of 100°C and pinholes formed during pervaporation. (6) The HP membrane formed an unknown surface film during the pervaporation process and showed the lowest water flux, we presume the unknown film formed due to a reaction between the proprietary reinforcing layer of the HP membrane and the IL mixture. (7) The pervaporation results using XL and Gore A membranes were promising: Both membranes showed reasonable mass fluxes, limited swelling, and were stable during the pervaporation experiments. Therefore, XL and Gore A membrane were chosen to examine more thoroughly the effects of temperature, support type, and gas-sweep rate on water and solvent pervaporation rates.

### Effect of temperature and gas-sweep rate on pervaporation rates

Temperature effect was studied using the XL membranes. The water flux increases 2.5 times to 10 mg h⁻¹ cm⁻² when the cell temperature increased from 80 to 100°C. Despite the high water flux, an XL membrane in a cell without a membrane support was unstable and formed pinholes during the pervaporation experiments at the higher temperature. Post-run examination of the membranes indicated they swelled considerably at the higher temperature and essentially thinned to failure in an extrusion-like process.

In an effort to prevent dimensional distortion of the swollen membrane, a metal grid with a 500-μm opening was used as a support to improve mechanical stability of membrane. The results indicated the XL membrane was stable during the pervaporation experiment at 100°C. The water content in the IL–NMP–H₂O solution decreased linearly as its concentration dropped from 1 to 0.41 wt% within a period of 56 h. The water and solution fluxes are 7.2 and 117 mg h⁻¹ cm⁻², respectively. (Solution flux is the total permeate flux and includes both H₂O and NMP.) An important parameter determined in this work is the selectivity of the pervaporation process to water. Water selectivity is listed in the last column of the Table 3 and is defined as

\[
H_2O selectivity = \frac{\text{wt}_\text{H}_2\text{O}/\text{wt}_\text{NMP}}{\text{Reservoir}} \cdot 100
\]

where \((\text{wt}\text{H}_2\text{O}/\text{wt}_\text{NMP})_{\text{Reservoir}}\) and \((\text{wt}\text{H}_2\text{O}/\text{wt}_\text{NMP})_{\text{Permeate}}\) are the mass ratio of H₂O to NMP initially in the IL-solution reservoir and at the end-of-run in the permeate, respectively. Even though the IL solution initially contains ~30 wt% NMP and ~1 wt% H₂O,
the pervaporation result shows a high H$_2$O selectivity of 1.9. Figures S3(a) and (b) are images of the IL solution at the end-of-run and permeate liquid, respectively. They show a distinct difference in color: IL–NMP–H$_2$O solution is brownish and permeate solution is clear. These images indicate the permeation of IL through the membrane is negligible. The IL was confined by the membrane and remained on the liquid side of the cell. This claim was further confirmed by the conductivity measurement. The resistivities of the IL–NMP–H$_2$O and permeate were 2.7 × 10$^5$ and 1.2 × 10$^6$ Ω cm, respectively. The high resistivity of the permeate indicated that no IL was presence in the solution. Furthermore, these results indicate a support improves membrane stability and prevents pinhole formation.

The effect of temperature on pervaporation rates was investigated using XL and Gore A membranes (Table S4). We found that heating IL over long periods of time at high temperatures (110°C) caused a discoloration, most likely due to Hofmann elimination: tributylmethylammonium (quaternary amine) decompose into a tertiary amine and an alkene. Therefore, pervaporation performances were measured from 60 to 100°C, with the upper limit set to prevent IL degradation. The H$_2$O and solution fluxes (H$_2$O and NMP) and H$_2$O selectivity are shown in Fig. 4 as a function of the pervaporation temperature. The H$_2$O and NMP mass fluxes using the XL or Gore A membranes increased with over the 40°C temperature increase, water flux increased 3.5 times from 2 to 7 mg h$^{-1}$ cm$^{-2}$ and solution flux increased around 5 times for XL membranes. But H$_2$O selectivity shows a minimum with temperature around 80 and 90°C for XL and Gore A membranes, respectively.

Figure 5 and Table S5 compare the effect of gas-sweep rate on pervaporation rates using Gore A membrane at 100°C. At these conditions, gas flow rate affected pervaporation performance. High gas-sweep rate resulted in an increase in H$_2$O and NMP fluxes but a decrease in H$_2$O selectivity: H$_2$O flux increases from 7 to 10.4 mg h$^{-1}$ cm$^{-2}$, solution flux increase from 106 to 185 mg h$^{-1}$ cm$^{-2}$, and water selectivity decreases from 2 to 1. At a flow rate of 200 mL min$^{-1}$, Gore A membrane leaked after 30 h of use, presumably from pinholes formed due to an increase in pressure difference between the gas and liquid sides of the membrane. Table 5 compares pervaporation results collected using XL and Gore A membranes at 100°C with liquid and gas flow rates of 5 and 150 mL min$^{-1}$, respectively. Both membranes were stable in the pervaporation process and successfully lowered the water content to <0.5 wt % with high H$_2$O and NMP fluxes. Moreover, the XL membrane provided the highest water (10 mg h$^{-1}$ cm$^{-2}$) and NMP (182 mg h$^{-1}$ cm$^{-2}$) fluxes of all membranes examined in this study.

Conclusions

Eleven types of membranes were used in a pervaporation process to remove water from an IL solution containing IL + solvent + water. Upon examining membranes after use in preliminary experiments, we found swelling of unsupported membranes in the IL–NMP mixture was problematic and the volume increase of the membrane required accommodation. The swelling was manifested as a significant increase of liquid-side pressure, presumably due to blockage of the flow channels, and subsequent membrane pinholes and trans-membrane leakage of the IL solution. Membrane mechanical stability was improved by providing a porous support layer for the membrane. Pervaporation temperature and gas-sweep rate play important roles in the pervaporation process. Higher temperature and gas flow rate result in larger H$_2$O and NMP fluxes. The
best results measured provide a water flux of ~10 mg h$^{-1}$ cm$^{-2}$ and a NMP flux of ~180 mg h$^{-1}$ cm$^{-2}$. The results from this study show pervaporation is a technologically feasible method to dry an IL-solution and could be used in an IL recovery process to lower water content of an IL–NMP–H$_2$O mixture from 1 to 0.5 wt%.

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