Testing and evaluation of room temperature ionic liquid (RTIL) membranes for gas dehumidification

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ABSTRACT

Membranes studied for gas dehumidification, drying, or dehydration historically included polymers, tri-ethylene glycol, and aqueous LiCl. RTILs are hydroscopic liquids with negligible vapor pressures that form stable supported liquid membranes. This work evaluated the potential of RTIL-membranes as dehumidification membranes. The work studied the dehumidification of both nitrogen and methane. It tested the role of diffusion (RTIL viscosity) and water solubility (RTIL-anion) in water vapor permeation. The procedures also evaluated the performance and stability of both water immiscible and water miscible RTILs from 0% to >90% relative humidity (rH). In contrast to polymer-based membranes that can have water permeabilites that increase with rH, RTIL-membrane water permeances do not change with rH. Water/methane selectivities are constant with rH for the water immiscible RTIL-membranes tested; however, for the water miscible RTIL-membrane the selectivity decreased with increasing rH from 8100 to 5800. Both water miscible and immiscible RTIL-membranes were stable when operated at rHs up to at least 90%. Taken together, this preliminary evaluation of RTIL-membranes for gas dehumidification encourages further research especially in those applications where they are competitive with existing membrane materials such as, the treatment of bio-methane from anaerobic digesters, flue gas dehydration, and building ventilation systems.

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1. Introduction

Membrane-based gas dehumidification (or drying) can have technical, energy, and economical advantages over other dehumidification technologies, such as absorption, adsorption, and refrigeration depending on the application [1]. The advantages of simple installation, ease of operation, low process cost allow successful applications to dehumidification of N_2, O_2, and compressed air [1]. Other applications include combustion flue gas drying to prevent acid gas corrosion [2], methane [3–6], and other hydrocarbon gas conditioning [7]. Outside of chemical processing, building ventilation latent heat recycling can use water vapor permeable membranes [8–10].

Typically membrane-based gas dehumidification uses hydrophilic polymer membrane materials, such as polydimethylsiloxane (PDMS) and cellulose acetate (CA) [2]. Table 1 reports the permeabilities, permeances, and water selectivities for polymers typically used for gas dehumidification along with some novel membranes recently proposed in the literature. In hydrophilic polymers, water molecules occur in two states: water bound to the polymer via hydrogen bonds and unbound water occurring in clusters on the molecular scale [7]. The water permeability of the polymers increases as the ratio of the water clusters to bound water increases, since water clusters are more mobile than bound water [7]. In general, polymer-based dehumidification membranes have the following performance characteristics: increasing water permeability with gas relative humidity (rH) [1,7], solubility determined selectivities [1], and support resistance dominated permeances [11]. The support resistance dominance comes from the high water permeabilities common to hydrophilic polymers (Table 1).

Room temperature ionic liquids (RTILs) are salts that are liquid at room temperature and have no measurable solvent loss due to volatilization. RTIL-membranes or supported ionic liquid membranes (SILMs) have advantageous performance for the separations of the gas pairs CO_2/CH_4 and CO_2/N_2 [12]. Literature also proposes the use of SILMs for olefin/paraffin [13–15], sulfur dioxide [16], carbon monoxide [17], and hydrogen [18] separations. To the best of our knowledge, water permeability in SILMs is unreported. There may be an unexploited potential for SILMs as dehumidification membranes, since all RTILs are hydroscopic [19] and, as liquids, have higher solute diffusivities than polymers [20]. Therefore, the motivation for the work reported here is to evaluate the potential for SILMs (RTIL-membranes) as dehumidification membranes.

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Table 1
Polymers "conventionally used for gas dehumidification" along with some novel membranes recently proposed in the literature. Permeability given as permeability coefficient (1 barrer = 3.348 × 10^{-16} mol/[m Pa s]) or as permeance (2.988 GPU = 1 × 10^{-9} mol/[m^2 Pa s]).

Material/membrane	Water permeability (barrer) or permeance (GPU)	Selectivity vs. N$_2$ (air)	Selectivity vs. methane	Comments	Reference
Dense film polymers					
Polydimethylsiloxane (PDMS)	40 000 barrer	140			[2]
Cellulose acetate (CA)	60 000 barrer	24 000			[2]
Sulfonated polyethersulfone (SPES)	15 000 barrer	210 000			[2]
Polyethylene oxide (PEO-PBT)	100 000 barrer	52 000			[2]
Sulfonated poly(ether ether ketone) (SPEEK)	30 000 barrer; 1500 GPU	300 000		rH < 50% and 30 C	[2]
Poly(vinylalcohol)–EDTMPA	997.7 GPU				[7]
Polyimide	10 000 barrer				[28]
Polyimide with tetrabutylammonium naphthalenesulfonate	36 000 barrer				[28]
Polyimides with fluorine-containing 6FDA dianhydride	2450–4400 barrer		5000–30 000	Ideal selectivity	[5]
Polyether–polyurethanes–PU 400	1760 barrer		29 300	Ideal selectivity	[4]
Polyether–polyurethanes–PU 2000	23 400 barrer		2600	Ideal selectivity	[4]
Polyvinylalcohol doped with LiCl					[32]
Stabilized liquid					
Triethylene glycol	2690–4030 barrer	2000			[29]
Aqueous LiCl					[30]

1.1. RTIL/water mixture physical chemistry

RTILs are liquids in the absence of water and SILM separations do not depend on the presence of water [12]. There are both water miscible and immiscible RTILs. The primary determination of water miscibility is the anion [21]. Both miscible and immiscible RTILs are hydroscopic [19] with the uptake of water decreasing the RTIL viscosity [21]. The molecular states of water absorbed by RTILs depend on the source fluid's state (gas vs. liquid). Cammarata et al. studied the uptake of water from gases with less than 70% rH and found that absorbed water in both miscible and immiscible RTILs occur as H-bonded to the anion [19]. They concluded that water molecules are not associated into clusters. In contrast, Fortunato et al. studied RTIL uptake of water from contact with aqueous solutions [22,23]. They concluded that water molecules begin to cluster on the molecular level after the water in the RTIL exceeds a critical concentration. After the formation of clusters, the transport of a third component through the RTIL/water mixture becomes dominated by the chemistry of the clusters [23]. Combining the studies of Cammarata et al. and Fortunata et al., we hypothesize that the critical concentration for water cluster formation is anion dependent and is higher for the water miscible RTILs compared to the water immiscible RTILs.

In the studies of other vapor separations using RTIL-membranes (SILMs), the following are the key performance factors quoted from Ref. [13]. "Solubility selectivity dominates the permeability selectivity in SILMs. The fact that diffusion selectivity does not play a major role gives a theoretical basis for the experimental observations that SILM mixed gas selectivities are approximately equal to the single gas or ideal selectivities. For CO$_2$ separations, there are two critical RTIL properties that affect SILM performance: RTIL molar volume and RTIL viscosity. The permeability selectivity is a function of RTIL molar volume while the CO$_2$-permeability is a function of viscosity."

1.2. Experimental objectives and plan

Based on the previous discussion, the following are the key objectives for the work presented in this paper:

- Determine if water vapor permeability is a function of RTIL viscosity and if water/gas selectivity is a function of RTIL molar volume.
- Determine the functionality of water permeabilities in SILMs vs. gas relative humidity (rH). Will they mimic the behavior of polymer membranes with the water permeabilities increasing with gas rH or will they be constant? This objective will also com-

ment on the role of diffusion in water permeance since water adsorption exponentially reduces RTIL viscosity [21].
- Determine the water separation selectivity vs. gas rH relationship. Will the selectivities remain constant similar to the behavior of SILMs in mixed gas carbon dioxide separations from nitrogen and methane [12].
- Determine the performance and stability of water immiscible vs. water miscible RTIL-membranes in conditions that exceed 70% rH.

The experiments described below have these objectives as their goal along with the goal of evaluating the SILMs' potential as dehumidification membranes. Specifically, the experiments tested the roles of diffusion (RTIL viscosity) and water solubility (RTIL-anion) in water vapor separations using SILMs. The procedures also evaluated the performance and stability of both water immiscible and water miscible RTILs from 0 to >90% rH.

Table 2 shows the RTILs used to fabricate the SILMs tested in this work along with their properties relevant to membrane stability/formation (surface tension, melting points, and thermal decomposition) or membrane performance (water miscibility, viscosity, and molar volume). Using the abbreviations given in Table 2, [emim][Tf$_2$N] was the baseline-SILM because it used the lowest viscosity water immiscible RTIL previously reported to form stable SILMs [13]. The [emim][Tf$_2$N]-membranes, historically, form the highest permeability SILM for both inorganic and organic permeating gases [13]. The inclusion of [N(4)111][Tf$_2$N] tested the role of diffusivity in water vapor membrane separation since [N(4)111][Tf$_2$N] has a higher viscosity (71 cP vs. 26 cP) while keeping the same RTIL-anion and similar RTIL molar volume. This 2.7 times greater viscosity should result in gas diffusivities 60% of the [emim][Tf$_2$N] diffusivities [20]. [N(4)111][Tf$_2$N] also has a literature reported methane permeability approximately one-half of that of [emim][Tf$_2$N] (63.1 barrer vs. 139.2 barrer [13]).

To test the role of water solubility, we initially chose, [emim][dca], an RTIL with similar viscosity to [emim][Tf$_2$N] (21 cP vs. 26 cP) but with a water miscible anion. Unfortunately [emim][dca] does not form a stable SILM in the same porous supports used to form the [Tf$_2$N]-membranes [12]. So the [emim][dca]-membrane data cannot be quantitatively compared with the [Tf$_2$N]-membranes. We do include the [emim][dca]-membrane dehumidification performances in qualitative discussions. Additionally, we included [emim][BF$_4$] for quantitative comparisons since it will form stable SILMs using the same supports as the two [Tf$_2$N]-membranes. [emim][BF$_4$] is a