Pore Wetting Behavior of Ionic Liquids in Polymeric Membranes

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Bioastronautics

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Introduction

Supported ionic liquid membranes (SILMs), comprised of an ionic liquid (IL) suspended in the pores of a thin physical membrane support, have potential for use in gas separations. SILMs can continuously and selectively transport target gases from feed side of the membrane to the permeate side without the need for liquid sorbent flows or temperature-pressure cycling to regenerate solid or liquid sorbents. These complexity-reducing and power-saving advantages, combined with the stability of ILs in low-pressure environments, makes SILM-facilitated gas separations attractive for use in space applications. SILM construction requires the imbibition of an IL into the pores of a membrane, a process governed by complex surface chemistry.

Contact angle of ILs on the outside surface a membrane has been suggested as a guideline to predict pore wetting behavior.[1] However, pore wetting can be modeled as fluid flow in small capillaries – suggesting that outside surface roughness does not actually determine pore wettability for SILMs as two membranes with significantly different pore sizes can have the same roughness factor. The Washburn Law for capillary imbibition in tubes and pores describes the length of liquid in the capillary with respect to time as proportional to the square root of capillary radius.[2]

In this poster we describe wetting phenomena on rough and porous surfaces and extend the lessons learned to pore imbibition in SILMs focusing on implications for initial wetting, mass transfer performance, and long-term stability. We report results of pore wetting behavior of the ionic liquid 1-butyl-3-methylimidazolium acetate ([bmim][Ac]) on different membrane supports and the effect of surface and environment modifications on wettability.

Materials and Methods

Two different wetting tests were conducted. The first varied the presence of vacuum and the use of a pretreatment using low-surface tension solvent (LSTS) during the wetting process of [bmim][Ac] (IoLiTech, 99%; denoted "IL" in table 1) in polypropylene and nylon membranes (Sterlitech, nominal pore size 0.1 µm). Membrane samples were placed in a glass dish with enough IL to completely cover the membrane surface. LSTS-pretreated samples were first wetted through with the LSTS before being placed in the glass dish. The dish was then placed into a thermal vacuum chamber and heated to 40°C. If vacuum was applied, the pressure was below 5.0×10^{-2} torr. After 24 hours, the chamber was repressurized and the samples were removed. Excess IL was wiped off the surface before weighing the membranes. In the case of LSTS-pretreated, non-vacuum samples, one week was allowed before removal to ensure that all the LSTS had evaporated before weighing. The results of this first test are shown in Table 1.

The second test examined wetting of polypropylene and nylon membranes with IL at room temperatures (22°C) and pressures (760 torr). Pore sizes were varied. Each sample was placed in a glass dish with enough IL to cover the membrane surface and left on a tabletop for 24 hours. No LSTS was used in this test. The membranes were weighed before and after this process, and the results of this second test are shown in Table 2.

Sample	Initial Mass (g)	Mass Uptake (g)	Percent change (%)
Polypropylene, IL	0.0847	0.0018	2.125
Polypropylene, IL, Vacuum	0.1336	0.0043	3.21
Polypropylene, IL, LSTS	0.0895	0.2505	279.8
Nylon, IL	0.1675	0.2496	149.9
Nylon, IL, LSTS	0.1922	0.2503	130.0
Nylon, IL, Vacuum	0.1402	0.3237	230.9

Table 1: First test results. Initial mass and mass gain before and after wetting procedure. Samples are described by their membrane material, IL, and whether an LSTS or vacuum was present. Pore size 0.1 µm for all membrane samples.

Sample (Pore Size)	Initial Mass (g)	Mass Uptake (g)	Percent gain (%)
Polypropylene (1.2 um)	0.0399	0.1127	282.4561
Polypropylene (0.45 um)	0.0378	0.0982	259.7884
Polypropylene (0.2 um)	0.0219	0.0324	147.9452
Nylon (10.0 um)	0.0189	0.0307	162.4339
Nylon (0.8 um)	0.019	0.0296	155.7895
Nylon (0.45 um)	0.0171	0.0255	149.1228

Table 2: Second test results. Initial mass and mass gain before and after wetting procedure at ambient conditions.

Discussion of Results

At the 0.1 µm pore size, 1-butyl-3-methylimidazolium acetate does not readily wet polypropylene, as shown in table 1. Results are very different when the LSTS pretreatment is done - mass uptake of polypropylene matches that of nylon, which readily wets with IL at ambient conditions. LSTS pre-treatment decreased percent mass gain relative to the nylon-IL sample with no vacuum. The presence of LSTS reduces the effective IL concentration, making it more difficult for the same mass of IL to enter the pores. The presence of vacuum had a strong positive effect on infiltration in nylon; evacuating air trapped in the pore matrix allows the IL to more easily advance along the length of the pore without having to displace air molecules. Results of the second test (table 2) indicate that increasing pore size will significantly increase the amount of IL infiltrated; however, further testing is required to understand the stability and bubble-point pressures of large-pore SILMs.

Since membrane materials differ greatly in density and porosity, mass uptake and percent gain are not sufficient metrics to assess the level of liquid infiltration. For example, the first test presented in this study used membrane pieces of roughly the same geometric size, but the polypropylene membranes had significantly less mass than the nylon membranes. The mass uptake representing the mass of IL trapped in the pores is almost identical for the LSTS-pretreated polypropylene and both non-vacuum nylon samples, but percent change in the polypropylene sample is much higher (279.8 compared with 149.9 and 130.0). Without further characterization of the membranes' physical properties, we cannot be sure if the similar mass uptake signifies that all membranes contain roughly the same pore volume and have been fully infiltrated with liquid, or if the polypropylene sample has truly achieved a higher level of infiltration than the nylon samples.

Future analysis should normalize for the pore volume in each sample by including a metric that expresses extent of infiltration as the fraction of the total pore volume that is filed with the liquid. Pore size distribution should also factor into the analysis – a wider distribution will extend the range of pore diameters available for liquid to enter and will affect capillary imbibition behavior. Pore volume can be obtained through mercury porosimetry and when combined with BET surface area data, we can define the pore size distribution and tortuosity of the membranes.

References

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Acknowledgements and Funding The authors thank Cody Bahan for assistance in data collection and acknowledge funding from the NASA Space Technology Graduate Research Opportunities Fellowship (Grant #80NSSC21K1289).

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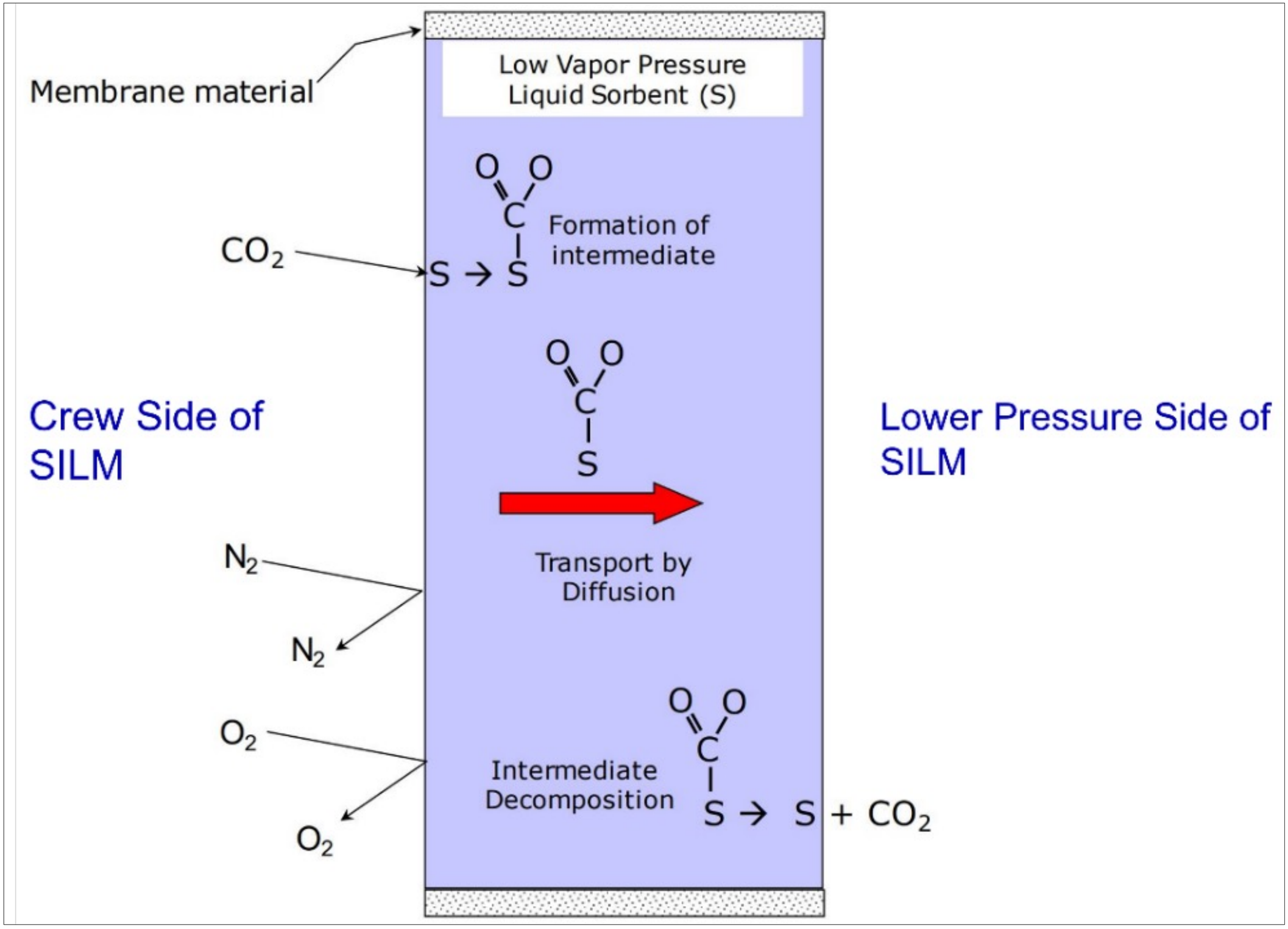
Mechanism of CO_2 transport in a liquid-filled membrane pore. Reproduced from Wickham et al.



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