



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

The bubble point of supported ionic liquid membranes using flat sheet supports

David Hopkinson^{a,*}, Matthew Zeh^{a,b}, David Luebke^a^a National Energy Technology Laboratory, 3610 Collins Ferry Rd, Morgantown, WV 26507, USA^b Oak Ridge Institute for Science and Education, 3610 Collins Ferry Rd, Morgantown, WV 26507, USA

ARTICLE INFO

Article history:

Received 28 February 2014

Received in revised form

21 May 2014

Accepted 24 May 2014

Available online 2 June 2014

Keywords:

Supported ionic liquid membrane

Stability

Bubble point

Laplace–Young equation

Contact angle

ABSTRACT

Supported ionic liquid membranes were tested to determine the maximum pressure drop that can be withstood before expulsion of the liquid from the membrane pores, also known as the bubble point. Bubble point was measured using two ionic liquids, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]) and 1-ethyl-3-methylimidazolium ethyl sulfate ([emim][EtSO₄]), and four porous flat sheet supports, including anodic alumina, track etched polyester, nylon, and polysulfone. These supports represented a variety of pore morphologies that ranged from straight and cylindrical to highly tortuous, interconnected and irregularly shaped. An effective maximum pore size and pore size distribution were determined for each porous support using gas–liquid displacement porometry with isopropanol as a wetting fluid. From this it was possible to accurately predict the bubble point for ionic liquids using the Laplace–Young equation, but only if a contact angle of zero was assumed for all combinations of liquids and supports. Also, the effects of surface tension, pore size, and temperature on the bubble point were evaluated. It was found that a judicious combination of support structures and ionic liquids can lead to a very stable system which can satisfy many membrane applications.

Published by Elsevier B.V.

1. Introduction

It has long been assumed that supported ionic liquid membranes have limited use in practical applications due to a lack of mechanical stability, although the envelope of possible operating conditions has not been well defined for these materials. A supported ionic liquid membrane (SILM) is a composite structure that consists of a porous support in which the pores have been filled with an ionic liquid (IL). The IL acts as the primary gas transport medium while the support, often a polymeric material, gives structure to the liquid membrane. Ionic liquids are salts that typically contain bulky organic cations and inorganic anions, are liquid at room temperature, and have a negligible vapor pressure. Functional groups can be added to free sites in IL cations or anions in order to enhance their gas solubility and other physical properties; for example, amine groups may be added to facilitate chemical complexing with carbon dioxide [1]. In an SILM, it is common for the ionic liquid to have gas permeabilities that are two orders of magnitude higher than typical selective polymers, which is a compelling reason to use a liquid as a membrane [2].

Supported ionic liquid membranes have been the subject of gas separation research for several decades due to their impressive gas

transport properties [3,4]. However, they have yet to find their way into practical applications, largely because of concerns over the mechanical stability of the membranes. In operation, if the trans-membrane pressure exceeds the capillary pressure that retains the ionic liquid inside of the support pores, then the liquid will be expelled from the support and the membrane will lose selectivity. Recently, research groups have begun to study supported ionic liquid membranes in a hollow fiber configuration, which is an important step towards realizing their use in applications [2,5]. Therefore, there is a need to determine the precise range of operating conditions in which SILMs can be used, and if necessary, develop strategies to improve the stability of the membranes.

Some researchers have attempted to overcome instability issues associated with SILMs by modifying the ionic liquid component into a solid or semi-solid. For example, in one study the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]) was made into a gel through reaction with a gelator, 12-hydroxystearic acid [6]. This process resulted in a slightly higher mechanical stability compared with the neat IL, coupled with a slightly reduced permeability for CO₂ and N₂ and approximately the same CO₂/N₂ selectivity. In another method, a thin film was solution cast from a mixture of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]) and the polymer poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [7]. As the proportion of

* Corresponding author. Tel.: +1 304 285 4360.

E-mail address: david.hopkinson@netl.doe.gov (D. Hopkinson).

ionic liquid was increased, gas permeabilities (CO_2 , He, H_2 , O_2 , CH_4 , N_2) increased while Young's modulus of the film decreased. In a third method, various styrene and acrylate based ionic liquids were polymerized using a photoinitiated cross-linking agent [8]. In this case it was reported that the solubility for CO_2 was improved in the polymerized ILs over the neat ILs, but diffusivity decreased and resulted in a net reduction in permeability. Previous attempts to quantify the stability of SILMs have included methods such as measuring compositional changes over time using scanning electron microscopy with energy dispersive X-rays (SEM-EDX); immersing the SILM in de-ionized water and measuring ion concentration changes in the aqueous solution; using X-ray photon spectroscopy (XPS) to study the composition of an SILM submerged in de-ionized water; and measuring changes in permeance or selectivity as a function of time or trans-membrane pressure [3,9–14]. Alternatively, the bubble point method is a well-established, simple, and useful tool for measuring the maximum trans-membrane pressure that a supported liquid membrane can withstand. In this method, pressure is slowly increased to one side of the membrane using a compressed gas such as air or nitrogen. When the liquid begins to empty out of the pores, gas bubbles can be observed on the permeating side of the membrane, and the flow rate becomes non-zero [15–17]. Since practical membranes always have a distribution of pore sizes, the largest pore will empty first as predicted by the Laplace–Young equation:

$$\Delta p_c = 4\gamma \cos \theta / d_p \quad (1)$$

where Δp_c is the critical trans-membrane pressure (the bubble point), γ is the surface tension of the liquid–gaseous interface, θ is the contact angle at the liquid and solid surface interface, and d_p is the largest pore diameter [18,19]. The bubble point only depends on the largest pore in the support since this pore has the lowest capillary force to retain fluids. If pressure is further increased beyond the bubble point, then smaller size pores also empty out, and the gas flow rate increases accordingly. Comparing the flow rate versus pressure profile of a dry membrane with that of a wetted membrane can be used to determine the pore size distribution by gas–liquid displacement porosimetry [17,20,21].

The Laplace–Young equation can only be used to predict the bubble point if the largest pore diameter is known. This value may not be immediately obvious for practical membranes because pores may change diameter along their lengths, may not be circular, and may interconnect with other pores. Adjustments have been suggested to the model for non-ideal cases such as fibrous supports and pores with non-circular cross sections and non-uniform diameters [16,22]. These methods are useful for accurately estimating the pore size distribution, but if the primary objective is to predict the bubble point, then a simpler method to account for non-ideal pores is to experimentally measure an effective maximum pore size for the support, as is explained in this work.

Determining the contact angle for Eq. (1), which is a boundary condition of the liquid/pore wall interface, poses some additional problems. The magnitude of the contact angle results from a balance between the cohesive attraction of liquid molecules with

each other and the adhesive attraction of liquid molecules with the solid surface. For gas–liquid displacement porosimetry experiments, it is common to use wetting liquids such as isopropanol or perfluoropolyethers that have relatively low surface tension and readily wet most surfaces, resulting in a contact angle of zero and the cosine of the contact angle equal to one. On the other hand most ionic liquids have higher surface tensions and will not exhibit perfect wetting with a surface. Consequently, the contact angle found in Eq. (1) cannot be so easily ignored. However, measuring the contact angle of an IL with the inside of a membrane pore wall is not a practical option. Besides the obvious difficulty of measuring contact angles in a confined space at very small length scales, the pore wall will also have some roughness that influences its contact angle. At macroscopic scales, rough surfaces can cause a wetting liquid to appear to have a different contact angle (an apparent contact angle) than it would on an ideal, flat surface of the same solid material (the intrinsic contact angle, Fig. 1a). A liquid that is in contact with a rough surface can exist in two states: the Cassie–Baxter state (Fig. 1b), in which the liquid phase bridges the peaks of a surface and rests on top of air gaps, and the Wenzel state (Fig. 1c), in which the liquid is in full contact with the uneven surface [23,24].

At least two studies have suggested that the contact angle for a fluid confined within a small pore should be considered zero [25,26]. Interestingly, though, these were due to different mechanisms. By contrast, other references make the traditional assumption that the contact angle formed by the liquid/solid interface inside of a pore wall is non-zero and an applicable boundary condition [27]. Good and Mikhail studied the contact angle of mercury in pore walls when it is forced into a porous material using mercury intrusion porosimetry [25]. According to Wenzel's theory, the intrinsic contact angle, θ_i , is related to the apparent contact angle, θ_a , by the ratio of the surface roughness, r , where

$$r = \frac{\cos \theta_a}{\cos \theta_i} \quad (2)$$

From this relationship, a rough surface ($r > 1$) will cause the apparent contact angle to be larger than the intrinsic contact angle if $\theta_i > 90^\circ$, and smaller if $\theta_i < 90^\circ$. Wolansky and Marmur showed that this relationship is most accurate when the size of the liquid drop is much larger than the scale of the surface roughness [28]. In Good's study using mercury as the wetting liquid, the intrinsic contact angle will be greater than 90° for most surfaces and therefore roughness causes the apparent contact angle to increase. If, for example, the intrinsic contact angle was $\theta_i = 135^\circ$ and there was a moderate level of roughness $r > 1.41$, then the apparent contact angle would be $\theta_a = 180^\circ$. Good suggests that most practical porous materials will have a high enough roughness inside the pores to make the apparent contact angle always equal to 180° . Similarly, if the intrinsic contact angle is much less than 90° and there is at least a moderate amount of roughness, then the apparent contact angle will become 0° .

Piatkiewicz and co-authors have also made a case that the contact angle should be considered zero for measurements in which gas pressure is used to force a wetting liquid out of the pores of a support. According to their work, this phenomenon

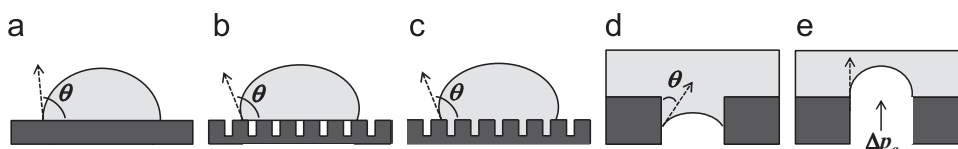


Fig. 1. (a) The intrinsic contact angle of a droplet on a smooth, ideal surface; (b) the apparent contact angle of a liquid droplet on a rough surface in the Cassie–Baxter state; (c) the apparent contact angle of a droplet on a rough surface in the Wenzel state; (d) the contact angle of the meniscus of a liquid inside a pore; (e) the contact angle between the liquid and pore when pressurized at the critical pressure just before releasing a gas bubble.

Download English Version:

<https://daneshyari.com/en/article/633448>

Download Persian Version:

<https://daneshyari.com/article/633448>

[Daneshyari.com](https://daneshyari.com)