Natural gas purification using supported ionic liquid membrane

Mamoun Althuluth [a,b], Johan P. Overbeek [c], Hans J. van Wees [c], Lawien F. Zubeir [b],
Wim G. Haije [c], Abdallah Berrouk [a], Cor J. Peters [a,b], Maaike C. Kroon [b]

[a] The Petroleum Institute, Chemical Engineering Department, P.O.Box 2533, Abu Dhabi, UAE
[b] Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Separation Technology Group,
Den Dolech 2, 5612 AZ Eindhoven, The Netherlands
[c] Energy Research Center of the Netherlands, Sustainable Process Technology, P.O. Box 1, 1755 ZG Petten, The Netherlands

ABSTRACT

This paper examines the possibility of the application of a supported ionic liquid membrane (SILM) for natural gas purification. The ionic liquid (IL) 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)tri-fluorophosphate ([emim][FAP]) was impregnated successfully in the γ-alumina layer of a tubular porous asymmetric membrane. The pure gas permeability of natural gas components, such as carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) were tested through the SILM at a trans-membrane pressure of 0.7 MPa and temperature of 313 K. The following trend of pure gas permeability was observed for the SILM in this study: $P_{CO2} > P_{CH4} > P_{C2H6} > P_{C3H8}$. Moreover, the CO_2/CH_4 ideal permselectivity was calculated. Mixed gas permeability and permselectivity for the binary mixture of CO_2/CH_4 (50/50%, v/v) was also measured. The mixed gas permselectivity ($\alpha=1.15$) was found to be much lower than the ideal permselectivity ($\alpha=3.12$). The performance of the SILM was significantly affected by the presence of water, which is also generally present in natural gas. Even though [emim][FAP] is an excellent alternative absorbent with high CO_2 absorptive capacity and ideal solubility selectivity for CO_2/CH_4 ($S=9.69$), the incorporation of this IL in a SILM is less promising for the removal of CO_2 from natural gas streams, because the permselectivity for CO_2/CH_4 is low.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Knowledge on the solubilities and diffusivities of gases in ionic liquids (ILs) is important for the design of absorption processes, such as the gas sweetening process. The solubilities of carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) in several ILs have been studied intensively [1–5]. From these solubility studies, it can be concluded that ILs are promising absorbents for the removal of CO_2 from natural gas streams [6–8]. Especially interesting for CO_2 capture is the IL 1-ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate ([emim][FAP]), because of its high bulk solubility for CO_2 compared to the much lower bulk solubilities of CH_4, C_2H_6 and C_3H_8 as measured previously using a synthetic method with the Cailletet apparatus [1,2,6].

On the contrary, the transport of gases in ILs has been much less investigated. Only limited experimental data are available in the literature [9–12]. It was found that diffusion coefficients of CO_2 in most ILs near ambient temperature are in the order of 1×10^{-10} m^2/s, which is slower than CO_2 diffusion in traditional solvents [13]. Diffusion coefficients of small hydrocarbons in ILs were even lower [11].

Recently, new ILs were discovered that can absorb CO_2 much quicker [14–16]. For example, it took only 4 min for polymerized-ILs to reach their 90% absorption capacities and about 30 min to reach their full capacities [14]. Moreover, CO_2 absorption in protic ILs could be almost completed within 5 min [15]. In mixed IL+aqueous amine solutions 90% of the absorption capacity was reached within 15 min, and the chemisorption was completed after 25 min [16]. It should be noted that these rate measurements were done using different experimental set-ups, so that quantitative comparison is difficult. However, it is clear that it takes much more time (about 3 h) to reach equilibrium for most other ILs absorbing CO_2 physically [17].

The properties of ILs, specifically the viscosity, have an effect on the gas absorption rate. Morgan et al. [18] reported that the diffusivity of gases relates inversely to the viscosity of ILs. Thus, ILs with a high viscosity lead to low absorption and desorption rates in comparison to conventional chemical absorbents (e.g., aqueous amine solutions) and physical absorbents (e.g., Selexol). Moreover, ILs are generally more expensive than conventional solvents. Therefore, it can be difficult to apply ILs in conventional absorption columns.

For this reason, researchers have given much attention to create new cost-effective technologies using small amount of low-viscous ILs. One technology that has attracted interest is the use of supported ionic liquid membranes (SILMs) for gas sweetening [19,20]. SILMs are produced by impregnating a porous membrane with a small amount of IL. This process may be economically competitive with the chemical or physical CO_2 absorption process. The main challenge for liquid membranes is that the liquid phase can evaporate over time [21]. The very low volatility of the IL [17] is beneficial for its incorporation in a SILM, but probably not enough to completely get rid of the evaporation problem.

In this work, the permeabilities of pure CO_2, CH_4, C_2H_6 and C_3H_8 through a SILM consisting of γ-alumina impregnated with the IL [emim][FAP] were measured. These measurements were calculated the permselectivity and diffusivity. Also, diffusivities were measured and correlated using a suitable model [18]. Furthermore, mixed gas permeability and permselectivity for the binary mixture of CO_2/CH_4 (50/50%, v/v) were measured and compared to the calculated ideal permselectivity. Finally, the influence of the presence of water on the permselectivity was investigated.

2. Experimental

2.1. Preparation of SILM

The IL [emim][FAP] was provided by Merck Chemical Company with a purity of ≥ 99.0% and was used as such. The viscosity and density of [emim][FAP] were measured in triplicate at 0.1 MPa in the temperature range from 293.15 to 363.15 K using an Anton Paar SVM 3000 facility. Standard deviations less than ± 0.20 mPa.s in the viscosity and ± 0.1 kg m^{-3} in the density were obtained, respectively. Surface tension measurements were performed in triplicate using a Kruss K11Mk4 tensiometer with a standard deviation ± 0.070 mN m^{-1}.

The [emim][FAP] was impregnated in the top two γ-alumina layers of a tubular porous asymmetric membrane support. The support consists of a coarse α-alumina commercial support on which two less coarse α-alumina layers (porosity ~35%) and two γ-alumina layers (porosity ~50%) are applied by ECN (Energy research Center of the Netherlands) using the dip coating technique. The γ-alumina layers have an average pore size of ~4 nm and maximum pore size of ~14 nm. The thickness of both impregnated γ-alumina layers together is ~2.64 μm (Fig. 1).

Impregnation of the IL was done using a sponge filled with IL. The sponge was placed inside a coating vessel. This coating vessel moves with a speed of 15 mm/s along the membrane to impregnate it with the IL.

The impregnated SILM was analyzed using Scanning Electron Microscopy (SEM), type Hitachi 3700. Fig. 2 shows the presence of fluorine atoms, originating from the IL [emim][FAP], as light blue spots in the SILM. From Fig. 2 it can be concluded that the γ-alumina layers
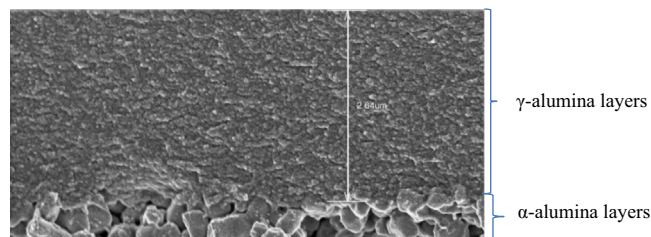

Fig. 1. Asymmetric membrane with the γ-alumina layers at the top with an average pore size of ~4 nm.
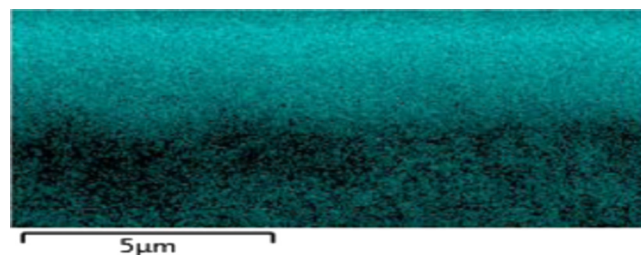

Fig. 2. SEM picture showing the fluorine atoms (from [emim][FAP]) as light blue spots in the γ-alumina layers and the top part of the intermediate α-alumina layers of the support of the SILM. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

are fully impregnated with the IL and that some traces of the IL are also present in the top part of the intermediate less course α-alumina layers of the support.

2.2. Gas permeation set-up

Single gas permeabilities of He (quality test) purity 99.995%, CO_2, CH_4, C_2H_6 and C_3H_8 (all with purity of > 99.5% and provided by Air Liquid Co.) through the SILM have been determined using a gas permeation set-up. The membrane was placed inside a module in which tubular membranes of 10 cm length can be housed using graphite sealings. This module was fixed horizontally inside an oven to control the experimental temperature value at 313 K ± 2.5 K; the trans-membrane pressure was set at 0.7 MPa ± 0.5%. The stability of the membrane under these conditions was first established. The maximum capillary pressure p of a SILM can be calculated using the Young–Laplace Equation.

$$\Delta p = \frac{4 \gamma \cos\theta}{d} \tag{1}$$

where γ is the surface tension of the IL (34.6 mN/m at T=313 K), θ is the contact angle (θ=0, because complete wetting is assumed), and d is the pore diameter of γ-alumina layer (4 nm). Then, the maximum pressure difference that can be used in the SILM is 34 MPa. Even though the real maximum pressure difference could be lower than the calculated pressure (because the pore size distribution of γ-alumina layer is non-uniform), it is still much higher than the transmembrane pressure used in this study (0.7 MPa). Therefore, the IL will not be pushed out of the pores. The stability of SILM was confirmed by constant gas permeance over time (~30 h).

Prior to any permeation experiment, the graphite ring for sealing the membrane in the module and the membrane itself were checked for gas leaks by placing a fresh SILM with graphite seal in the system and pressurizing it to 0.3 MPa using a He gas flow. The permeate flow through the SILM was monitored. A constant low permeate flow value (5–15 mL/min ± 0.5%) was an indication that the system was completely sealed (no leaks). Then, the measurements were conducted automatically by providing set pressures and temperatures. The pressure difference between the feed and permeate was controlled depending on the pressure difference required. The results (flows, pressures and time) were stored in a database.

The permeance P (mol m^{-2} s^{-1} Pa^{-1}) of the gas permeating through the membrane can be defined as:

$$P = \frac{J}{\Delta P \, A} \tag{2}$$

where J is the gas flow through the membrane (mol s^{-1}), Δp is the trans-membrane pressure (pressure difference between feed and permeate stream (Pa)), and A is the exposed area of the membrane (m^2).