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Room temperature ionic liquid/ZIF-8 mixed-matrix membranes for natural gas sweetening and post-combustion CO_2 capture

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ABSTRACT

We have investigated the effects of zeolite imidazolate framework-8 (ZIF-8) nanoparticles in miscible ionic liquid blend systems for natural gas sweetening and post-combustion CO_2 capture. The miscible blend systems consists of a polymerizable room temperature ionic liquid (poly(RTIL)) and a “free” room temperature ionic liquids (RTILs). The poly(RTIL) is 1-vinyl-3-butyl imidazolium-bis (trifluoromethylsulfonyl) imidate ([vbim][NTf_2]), while the RTIL is either (i) 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), (ii) 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide ([emim][NTf_2]) or (iii) 1-ethyl-3-methylimidazolium tetracyanoborate ([emim][$B(CN)_4$]). Experimental results show that the free ionic liquids are miscible with poly(RTIL), while ZIF-8 are uniformly dispersed in the MMMs. The presence of ZIF-8 nanoparticles in the MMMs considerably improves gas permeability without much scarifying CO_2/N_2 and CO_2/CH_4 selectivities as compared to their poly(-RTIL)/RTIL counterparts. The gas permeability of P[vbim][NTf_2]/[emim][$B(CN)_4$]/ZIF-8 comprising 25.8 wt% ZIF-8 exhibits a threefold increase in gas permeability. Both the semi-logarithmic addition and Maxwell equations are employed to analyze the transport mechanisms across the newly developed MMMs. The permeability vs. ZIF-8 content of P[vbim][NTf_2]/ZIF-8, P[vbim][NTf_2]/[emim][NTf_2]/ZIF-8 follows exactly the Maxwell prediction, indicating these blend membranes are intrinsically heterogeneous with well dispersed ZIF-8 nanoparticles. However, an interesting phenomenon was observed in the P[vbim][NTf_2]/[emim][$B(CN)_4$]/ZIF-8 system where the homogeneous poly(RTIL)/RTIL phase turns into a more heterogeneous phase upon the adding of ZIF-8. As a result, a double employment of Maxwell equation is applied to analyze the enhanced gas permeability when a higher ZIF-8 loading is utilized. The P[vbim][NTf_2]/[emim][$B(CN)_4$]/ZIF-8 system with 25.8 wt% ZIF-8 exhibits impressive performance for post-combustion CO_2/N_2 (50/50 mol%) separation. It has a CO_2 permeability of $906.4 \times 3.348 \times 10^{-19}$ kmol m/(m^2 s pa) (906.4 barrer) and a CO_2/N_2 selectivity of 21 at 35 °C and 3.5 bar.

1. Introduction

The issues of environmental change and global warming have attracted ceaseless debates on carbon dioxide (CO_2) emission, its effects and consequential treatments. Human factors are the major contributors to the escalation of annual global CO_2 emission with 80% increase from 1970 to 2004 [1]. Integrated gasification combined cycle (IGCC) projects like ZeroGen and FutureGen have been proposed aiming at near-zero CO_2 emission [2]. Various CO_2 capture methods must be developed in order to (1) control the CO_2 emission and (2) implement end-of-pipe storage and further CO_2 utilizations [3]. Besides the well-established cryogenic and absorption processes [4], membrane technology has been suggested because of its advantages on energy saving, small foot print, easy scale-up and ambient operation [5–9]. Membrane technology is a proven technology for natural gas sweetening. For instance, it has already occupied 20% of the CO_2/CH_4 separation market in 2009 [10]. Unexploited separation opportunities from petrochemical and refinery industries to various post-combustion CO_2 capture not only open up new prospects for gas separation membranes but also call for the discovery of high performance membrane materials [11].

There is a trade-off between permeability and selectivity for gas separation membranes [8,12]. Permeability is a unit flux that a membrane allows certain gas molecules to pass through, which is normalized with factors such as pressure, temperature and thickness. Permeation happens as a result of the difference in the chemical potential across the membranes, which means in most cases the driving force for permeation is the difference in gas concentration. Given the complexity of the system, permeability

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is not a single property but a product of diffusivity and selectivity as follows:

$$P = SD \tag{1}$$

where P denotes the permeability, S stands for the solubility coefficient and D refers to the diffusion coefficient. Solubility coefficient is mainly influenced by (i) the condensability of the penetrant, (ii) the free volume of the polymer, and (iii) the interaction between the penetrant and the polymer, while diffusion coefficient is determined by (i) the size and shape of the penetrant, (ii) the free volume and free volume distribution of the polymer, and (iii) the chain flexibility of the polymer [8,12].

Selectivity is the ratio of permeation rates for different pure gases across the membrane. It can be defined as follows for gas species A over B:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A}{S_B}\frac{D_A}{D_B} \tag{2}$$

where $\alpha_{A/B}$ denotes the ideal selectivity, while S_A/S_B and D_A/D_B are solubility selectivity and diffusion selectivity, respectively.

Room temperature ionic liquids (RTILs) have drawn considerable attention for CO_2 capture because they can be designed to possess high CO_2 affinity. RTILs are organic salts that remain in the liquid state at room temperature. Since they also possess high thermal stability, negligible vapor pressure and nonflammable characteristics, RTILs have been considered as a new generation green material [13,14]. Blanchard et al. [15] first reported in 1999 that CO_2 has a relatively high solubility in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]). Subsequent studies from the same group revealed that RTILs comprising anions that contain fluoroalkyl groups exhibited high CO_2 solubility [16]. Since then, a new research direction of gas separation using various ionic liquids was initiated.

Supported ionic liquid membranes (SILMs) were thereafter proposed to take advantage of specific ionic liquids which have high CO_2/N_2 or CO_2/CH_4 selectivities [17]. Other research groups also fabricated Nafion matrix, Nylon and Mitex based membranes consisting of RTILs to achieve CO_2/CH_4 separation [18,19]. Applying SILMs still faces challenges such as long-term stability under extreme conditions because RTILs with high viscosities tend to be immobilized on the surface or external layer of the membranes instead of deep inside the pores [20,21].

To overcome the immobilization and stability problems, polymerizable room temperature ionic liquids (poly(RTILs)) were proposed for CO_2 sorption in 2005 [22], followed by studies on gas separation [23–26]. However, in comparison with their liquid analogs, poly(RTILs) have smaller free volume, less mobility and subsequently reduced gas permeability. Therefore, the poly(RTIL)/RTIL system which contains free RTILs within the PILs was invented in 2008 to enhance the permeability [27]. Recent studies from our group also showed that the permeability of this system could be further improved without sacrificing CO_2 permeability by increasing the loading of free ionic liquids [28,29].

In light of the aforementioned situation, mixed-matrix membranes (MMMs) that comprise both polymerizable and free RTILs, and nanoparticles were proposed to improve the membrane performance. The first MMM was invented in 1988 [30]. The amalgamation of inorganic and polymeric materials in MMMs aims to synergetically combine both strengths as well as minimize each other's shortcomings such as the relatively low permeability of organic membranes and the high cost and difficulties of fabricating inorganic membranes [31–34]. Contemporary research on poly(RTILs) based MMMs is relatively limited. To the best of our knowledge, only poly(RTILs)/SAPO-34 and poly(RTIL)/RTIL/SAPO-34 zeolite MMMs have been investigated for CO_2 separation [35,36].

In fact, the fabrication of defect-free MMMs with appropriate adhesion between polymers and molecular sieves is not a trivial task [32,34]. The voids as well as rigidified interface between the organic and inorganic components affect the separation performance significantly. Gas molecules usually bypass the sieves and transport directly through the voids and polymer matrix, while chain rigidification and pore blocking often take place to reduce the overall gas permeability [34,37,38]. However, with the unique fluidity and charge characteristics of RTILs, Hudiono et al. have demonstrated that RTILs can behave like a wetting agent in poly(RTILs)/zeolite-based MMMs and mitigate the aforementioned issues [35,36]. A similar observation has been found in polymer blends comprising poly(vinylidene fluoride) (PVDF) and a RTIL, 1-ethyl-3-methylimidazolium tetracyanoborate ([emim][$B(CN)_4$]), where the optical observation confirmed the heterogeneous nature of these mixtures, while their gas transport properties followed the Maxwell predictions [39].

Recently, we have developed MMMs consisting of zeolitic imidazolate frameworks (ZIFs) nanoparticles and polybenzimidazole (PBI) polymer and the ZIF particles significantly enhanced both solubility and diffusion coefficients [40–42]. ZIFs belong to a subgroup of metal-organic frameworks (MOFs) with excellent chemical and thermal stability [43] and there is a belief that MOFs may have better affinity and interaction with polymeric materials [44]. These positive factors inspired us to examine the MMMs made of polymerizable and free RTILs together with ZIFs for natural gas sweetening and post-combustion CO_2 capture from CO_2/CH_4 and CO_2/N_2 streams. So far, Ultem®/ZIF-8 and Matrimid®/ZIF-8 have been studied [45–47]. Both systems maintain CO_2/N_2 selectivity values at around 30, while their CO_2 permeability values were generally below $100 \times 3.348 \times 10^{-19}$ kmol m/(m^2 s pa) (100 barrer).

ZIF-8 ($Zn(2\text{-methylimidazole})_2$) with the accessible cavity diameter of 3.4 Å was chosen in this study because it has a proper pore size for CO_2/N_2 separation and its basic physicochemical properties have been intensively studied [48–50]. Fig. 1A illustrates

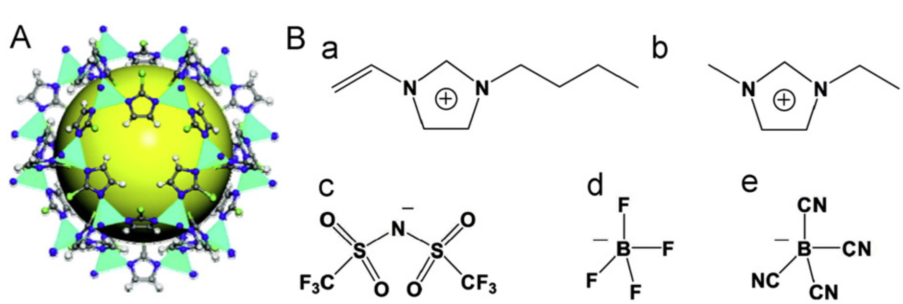

Fig. 1. (A) Structure of ZIF-8 with labeled elements. N: blue; C: gray; Zn: light blue; methyl: green and H: white. (Reprinted with permission from Li et al. [51]. Copyright @ 2009 American Chemical Society.) (B) Structures of cations and anions used in this study: (a) $[vbim]^+$, (b) $[emim]^+$, (c) $[NTf_2]^-$, (d) $[BF_4]^-$ and (e) $[B(CN)_4]^-$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)