



Supported ionic liquid membranes with high carrier efficiency via strong hydrogen-bond basicity for the sustainable and effective olefin/paraffin separation

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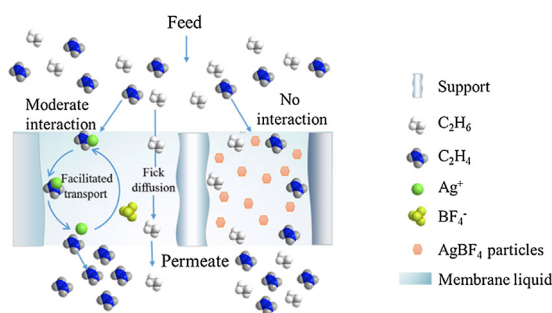
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HIGHLIGHTS

- Supported ionic liquid membranes (SILMs) with high carrier efficiency were designed and fabricated.
- The strong hydrogen-bond basicity of AILs greatly increased the number of carriers and enhanced the carrier efficiency.
- The effect of interactions in membranes on the carrier activity were revealed at the molecular level.
- The gas solubility was measured and described by a first-order equilibrium model quantitatively.
- The SILMs obtained good C₂H₄ permeability, high C₂H₄/C₂H₆ selectivity and acceptable stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 April 2018

Received in revised form 21 August 2018

Accepted 31 August 2018

Available online 1 September 2018

Keywords:

Ionic liquids

Hydrogen bond basicity

Olefin/paraffin separations

Supported ionic liquid membranes

Thermodynamic analysis

ABSTRACT

Supported ionic liquid membranes (SILMs) constitute a radical advance in olefin/paraffin separation membranes. Unfortunately, the applications of SILMs are vastly hindered by low carrier efficiency. Herein, SILMs with high carrier efficiency via strong hydrogen-bond basicity were designed to carry out efficient ethylene/ethane separation. The strong hydrogen-bond basicity of ILs not only endowed the membranes with high carrier concentration, but also effectively favored for the good disassociation of carrier to form solvated free ions through coordinative interactions between IL and carrier, which greatly increased the number of carrier and enhanced the carrier efficiency. Benefiting from the high carrier efficiency, both ethylene permeability and ethylene/ethane selectivity were significantly elevated, which could reach up to 100 Barrers and 40, respectively, surpassing most of results reported in the open literature. Meanwhile, the ethylene and ethane solubility data in the carrier/ILs were measured in a pressure range from 0 to 3.5 bar at 298.15 K, a first-order equilibrium model based on the formation carrier-ethylene complex species has been developed to describe the physical and chemical dissolving behaviors of ethylene and the equilibrium constants were obtained accordingly. Moreover, the membrane separation process was optimized, confirming that ethylene permeability and ethylene/ethane selectivity increased with the increase of carrier concentration due to the combined effects of gas solubility and diffusion. It was notable that the selectivity of as-prepared SILMs was more effective at lower transmembrane pressures and operating temperatures, which contributed to designing the energy-efficient and

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sustainable membrane processes. This study opens a new route for the utilization of the IL properties to manipulate the carrier efficiency for developing high performance SILMs.

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1. Introduction

The expansion of world energy demands have driven a critical appetite for the development of energy-efficient and sustainable technology in the petrochemical industry (Sun et al., 2017b). Light olefins are essential building blocks for a large number of useful products (Jiang et al., 2016). Light olefins are primarily produced via the pyrolysis or catalytic cracking of the crude oil component, such as naphtha, light diesel and other petroleum products. Among the mentioned processes, the olefins usually exist as the olefin/paraffin mixtures and are subsequently separated by cryogenic distillation technology. However, because of their low boiling point and the close relative volatility, traditional cryogenic distillation technology is operated at very high pressures and extremely low temperatures, which is the most costly and energy intensive process (Cadiou et al., 2016). Therefore, it is highly desirable to develop more efficient and sustainable olefin separation technology.

The introduction of the “Green Chemistry” concept has triggered ionic liquids (ILs) to the spotlight (Capela et al., 2017). Supported ionic liquid membranes (SILMs) based on facilitated transport mechanism combine the outstanding properties of ILs with the advantages of the carrier-facilitated transport, which have triggered revolutionary changes in olefin separation processes (Jiang et al., 2017a, 2017b, 2017c). Besides the technical advantages of small-sized equipment, low energy consumption and environmental friendliness, the SILMs also possess high stability and structural designability due to the solvent properties of ILs (Abdelrahim et al., 2017; Ilyas et al., 2017). Inspired by the structure and facilitated transport properties of cell membranes, SILMs introduce the active carriers distributed within the IL matrix (Li et al., 2015). The vehicle-like carriers facilitate the olefin transport (Sun et al., 2017a), and ILs as the continuous phase manipulate higher permeability due to the fast olefin diffusion in ILs (Pitsch et al., 2012).

Recently, Bin et al. firstly utilized IL analogues as the membrane liquids to fabricate SILMs for the olefin/paraffin separation, these membranes exhibited good selectivity but the gas permeability was still low (Deng et al., 2017; Jiang et al., 2017b). Then, Dou et al. reported protic IL based SILMs for the ethylene/ethane separation, the good gas permeability, selectivity and stability were obtained (Dou et al., 2018a, 2018b). However, the poor thermal stability and operational safety of the NO_3^- based protic ILs are the great obstacles for the practical applications. Compared with protic ILs, aprotic ILs (AILs), have excellent thermal stability and good operational safety. However, up to now, only two studies reported the utilization of silver salt/AIL based SILMs for the olefin/paraffin separation. Previous studies only evaluated the possibility of SILM fabrication with $[\text{Bmim}][\text{BF}_4]$, $[\text{Emim}][\text{BF}_4]$, $[\text{Emim}][\text{TF}_2\text{N}]$ (Fallanza et al., 2012; Kasahara et al., 2013). Although the potential of AIL based SILMs to separate the olefin/paraffin mixtures was demonstrated, the application of AIL based SILMs was still confined by the unsatisfactory separation performances because of low carrier efficiency, including the low carrier concentration and poor carrier activity.

Therefore, the exploration of novel AILs or careful selection of reported AILs to obtain high carrier concentration as well as understanding the effect of interactions between AIL and silver salt on the carrier activity is highly desirable. Some investigations have

been focused on the enhancement of solubilities of inorganic salts in AILs by designing novel AILs during recent fifteen years (Branco et al., 2002; Chiappe et al., 2010; Ghareh Bagh et al., 2013; Kuzmina et al., 2016; Lui et al., 2011; Pereiro et al., 2012). However, their results indicated that the solubilities of metal salts in the AILs were much lower than those in the molecular solvents. Intrigued by the excellent solubilities of most metal salts in water due to its high solvent strength, the solvent strength of ILs may give us an effective criteria for seeking AILs for the fabrication of SILMs with high carrier concentration. The polarity of ILs is the simplest indicator of solvent strength (Aki et al., 2001), embodying their ability to dissolve and stabilize dipolar or charged species (Schade et al., 2014). The polarity of ILs can be described quantitatively by Kamlet-Taft solvent parameters (α , β , π^*) (Ab Rani et al., 2011).

Based on the values of IL polarity, AILs (1-ethyl-3-methylimidazolium dimethylphosphate $[\text{Emim}][\text{Me}_2\text{PO}_4]$ and 1-ethyl-3-methylimidazolium diethylphosphate $[\text{Emim}][\text{Et}_2\text{PO}_4]$) were selected for the fabrication of SILMs due to their high polarity, especially their high hydrogen-bond basicity (Ab Rani et al., 2011), which was expected to obtain high carrier efficiency. The select AILs display very attractive physicochemical properties with great technical potential, such as their easy and cost-effective preparation, high stability toward hydrolysis and moderate viscosity (Fukaya et al., 2008). As expected, the select AILs exhibited good dissolving capacity for AgBF_4 , which favored for the fabrication of SILMs with high carrier concentration.

In this study, a series of SILMs with high carrier efficiency were successfully fabricated by impregnating the Ag/AILs into the microporous polyvinylidene fluoride (PVDF) support, which obtained high C_2H_4 permeability, $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ selectivity and excellent stability. The interactions between the silver salt (AgBF_4) and AILs were intensively characterized by the nuclear magnetic resonance (^1H NMR), Fourier transform IR spectrometer (FTIR), Fourier transform Raman spectrometer (FT-Raman), electrospray ionization mass spectroscopy (ESI-MS), which revealed the effect of interactions on carrier efficiency at the molecular level. The gas solubility in the Ag/AILs was measured and the absorption equilibrium was described by a mathematical model. The separation process was optimized systemically, namely silver salt concentration, the trans-membrane pressure and the operating temperature. Finally, our experimental results were compared with those reported in previous studies.

2. Experimental

2.1. Chemicals

C_2H_4 and C_2H_6 gases ($\geq 99.9\%$) were purchased from Tianjin Tang Dynasty Gas Co., LTD (China). $[\text{Emim}][\text{Me}_2\text{PO}_4]$ ($\geq 99.8\%$), and $[\text{Emim}][\text{Et}_2\text{PO}_4]$ ($\geq 99.8\%$), were supplied by Shanghai Cheng Jie Chemical Co. LTD (China). AgBF_4 ($\geq 99.5\%$) was purchased from Shanghai Titan Technology Co., Ltd. (China). The microporous PVDF support was obtained from Haining Zhongli Filtering equipment Corporation (China), which is a 75% porous hydrophilic PVDF membrane with a nominal pore size of 0.1 μm and 75 mm in diameter. The thickness of PVDF membrane was determined using a digital micrometer, being the average value of 125 μm . The PVDF support was selected because it showed good wettability, chemical

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