

論文 / 著書情報  
Article / Book Information

論題(和文)	
Title(English)	Gas and Vapor Permeation through Liquid Membrane Using Ionic Liquid
著者(和文)	山之内宣博, 段 淑紅, 伊東 章
Authors(English)	Nobuhiro YAMANOUCHI, Shuhong DUAN, Akira ITO
出典(和文)	, Vol. 29, No. 7, pp. 3299-3302
Citation(English)	Transactions of the Materials Research Society of Japan, Vol. 29, No. 7, pp. 3299-3302
発行日 / Pub. date	2004, 11

Transactions of the Materials Research Society of Japan, **29**(7), 3299-3302(2004)  
Gas and Vapor Permeation through Liquid Membrane Using Ionic Liquid

Nobuhiro Yamanouchi, Shuhong Duan and Akira Ito

Department of Chemistry and Chemical Engineering, Niigata University, Niigata 950-2181, Japan

Fax: 81-25-262-6789, e-mail: aito@eng.niigata-u.ac.jp

Ionic liquids are salts in liquid state at room temperature. This new material is expected to be applied to separation processes. Ionic liquids are particularly promising material for supported liquid membrane process, because they are non-volatile and can solve other salts as separation agents. In this study, A liquid membrane using an ionic liquid, 1-propyl-3-methylimidazolium iodide, was applied to gas and vapor separation of CO<sub>2</sub>, water vapor from air and aromatic hydrocarbon vapors. A supported liquid membrane of the ionic liquid was placed on a hydrophobic microporous membrane. The thickness of the liquid membrane was 35-55  $\mu\text{m}$ . Since the ionic liquid is non-volatile, hydrophilic and high surface tension, the liquid membrane could be applied to gas and vapor permeation with vacuum at permeate side. Overall permeation property, permeabilities, was similar to that of a triethylene glycol liquid membrane. The membrane of the ionic liquid showed selectivity of 20 for CO<sub>2</sub> over CH<sub>4</sub>, 1000 for water vapor over air and 20 for benzene vapor over cyclohexane vapor. The membrane of the ionic liquid is promising for dehumidification and the separation of CO<sub>2</sub>, VOC and aromatic hydrocarbons. The high selectivity for water vapor may be caused by the hydrophilic property of the ionic liquid. By adding alkaline salt to the liquid membrane, the selectivity for CO<sub>2</sub> was enhanced.

Key words: Membrane separation, Liquid membrane, Ionic liquid, Dehumidification, Permeability

## 1. INTRODUCTION

Room temperature Ionic liquids (RTILs) are salts which melt near room temperature. The RTILs consist large, organic cations and a variety of anions. This new material has attracted for application to reaction solvents as replacements for traditional organic solvents [1]. The RTILs are non-volatile and dissolve inorganic salts and organic compounds. These special features of RTILs suggest new applications for separation processes, such as extraction, absorption and membrane separation. The research on a separation process using RTILs was recently started. Scovazzo et. al. [2] first applied a supported liquid membrane using RTIL to CO<sub>2</sub> separation. Sorption and permeation properties of CO<sub>2</sub> and N<sub>2</sub> were reported through a liquid membrane of the most popular RTIL, [bmim][PF<sub>6</sub>]. They stated a potentiality for RTIL liquid membrane development for gas separation.

We have reported gas and vapor permeation through a triethyleneglycol (TEG) liquid membrane, which was placed on a hydrophobic microporous membrane. Since TEG is non-volatile and hydrophilic, the TEG liquid membrane is stable on top of the hydrophobic microporous membrane under transmembrane pressure conditions. This double-layer construction enabled a vacuum-mode permeation of gas and vapors through the TEG liquid membrane. The liquid membranes using TEG and a mixture of TEG with inorganic salts were applied to dehumidification [3], CO<sub>2</sub>/CH<sub>4</sub> separation [4], propane/propylene separation [5], and

aromatic vapor separation [6].

In this study, we use a RTIL for liquid membrane material. The vacuum mode permeation experiments through the liquid membrane were conducted by feed gas or vapors of air/water-vapor mixture (dehumidification), CO<sub>2</sub>/CH<sub>4</sub> mixed gas and aromatic/cyclohexane mixed vapor. The separation performances of the RTIL liquid membrane were illustrated by concentration change between feed and permeate. The permeabilities of gases through the RTIL liquid membrane were evaluated from the permeation data and were compared with that of other membranes.

## 2. EXPERIMENTAL

An RTIL, 1-propyl-3-methylimidazolium iodide ([pmim][I]) (Shikoku Kasei Ltd., Japan), was used in

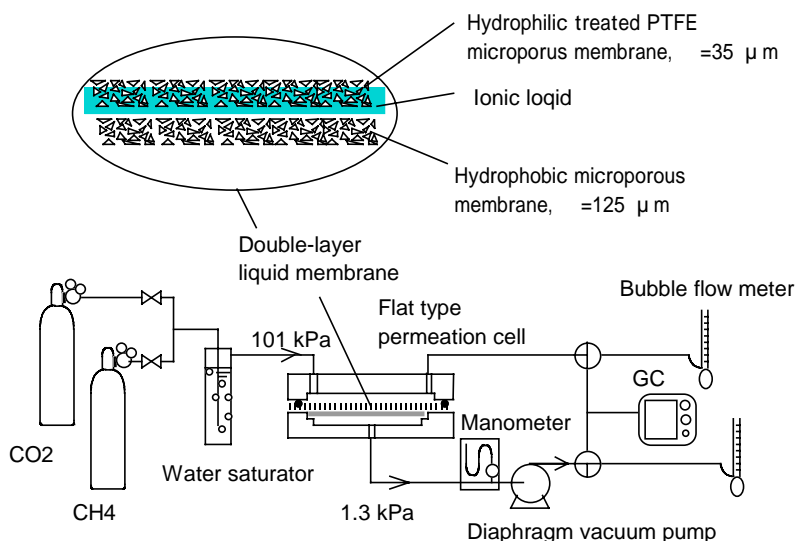


Figure 1. Membrane construction and experimental apparatus.

this study. This RTIL has a hygroscopic property and a high surface tension (approximately 50 dyn/cm), which are comparable to the properties of TEG.

The liquid membrane construction and experimental setup for CO<sub>2</sub>/CH<sub>4</sub> permeation are shown in Figure 1.

The liquid membrane had a double-layer construction. The top layer was a conventional supported liquid membrane. A hydrophilic treated polytetrafluoroethylene (PTFE) microporous membrane of 1  $\mu$ m pore size, 35  $\mu$ m thickness and 83% porosity was soaked in the ionic liquid, or its salt mixture. The thickness of the liquid membrane was 20–60  $\mu$ m, which was comparable or more to the supporting membrane thickness. The supported liquid membrane of the ionic liquid was placed on another microporous membrane, a Durapel membrane (Millipore). Durapel membrane is surface-treated microporous polyvinylidene fluoride (PVDF) membrane and has a highly-hydrophobic surface. This membrane has developed for medical use of de-gassing from water. A Durapel membrane of 0.1  $\mu$ m pore size, 125  $\mu$ m thickness and 70% porosity was used throughout this study. Since the RTIL is hydrophilic and high surface tension, the liquid layer is supported on the surface of the hydrophobic microporous membrane under a transmembrane pressure of over 200 kPa.

The membrane cell was flat-type with a 24 cm<sup>2</sup> permeation area. The feed side was atmospheric pressure. The feed gas, CO<sub>2</sub> and CH<sub>4</sub> mixture, was saturated by water vapor. The downstream pressure was maintained 1.3 kPa by a diaphragm vacuum pump. All measurements were at room temperature.

The liquid membrane and membrane cell were same for the dehumidification and the aromatic/aliphatic vapor permeation. In the dehumidification experiment, feed gas was humid air. The downstream pressure was maintained 0.1 kPa by a oil rotary vacuum pump. The humidity change between feed air and retentate air was measured using a humidity meter (HMP230, VAISALA).

In aromatic/aliphatic hydrocarbon mixed vapor permeation, saturated vapors in carrier gas, N<sub>2</sub>, fed to the membrane cell. No water vapor was contained in the feed. The downstream pressure was maintained 0.1 kPa by a oil rotary vacuum pump. The permeate vapor and the retentate vapor were collected in cold traps at 233 K.

### 3. RESULTS AND DISCUSSION

#### 3.1 Separation of carbon dioxide

Figure 2 shows the results of CO<sub>2</sub>/CH<sub>4</sub> mixed gas permeation, in which CO<sub>2</sub> concentration in the permeate is plotted versus that in the feed. The feed gas was saturated with water vapor. The RTIL Ionic liquid membrane has CO<sub>2</sub> selectivity of 20 over CH<sub>4</sub>. This selectivity for CO<sub>2</sub> is comparable to a TEG liquid membrane [4] and a 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]) liquid membrane [2]. Water content in the RTIL liquid membrane may increase the solubility and selectivity for CO<sub>2</sub> [2]. In this study, the liquid membrane of [pmim][I] can absorb 0.6 g-water/1 g-liquid in 95%RH air. The absorbed water in the membrane play role to CO<sub>2</sub> separation.

Ionic liquid can dissolve other salt. When K<sub>2</sub>CO<sub>3</sub> was mixed to 40wt% with the ionic liquid membrane,

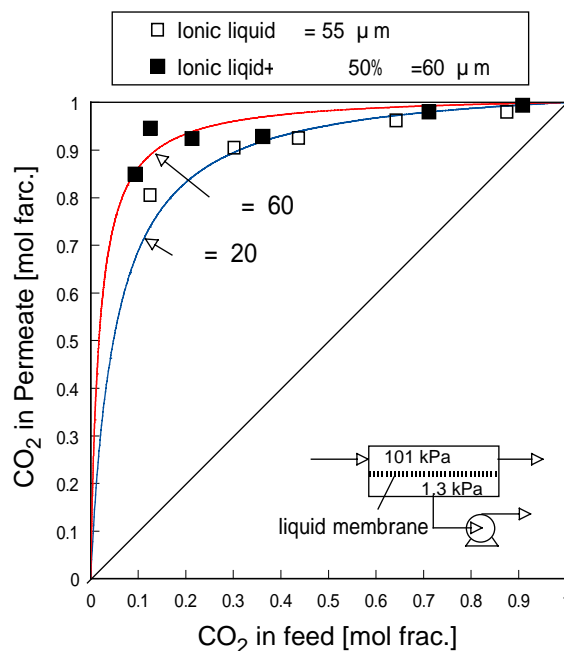


Figure 2. Separation of CO<sub>2</sub>/CH<sub>4</sub>.

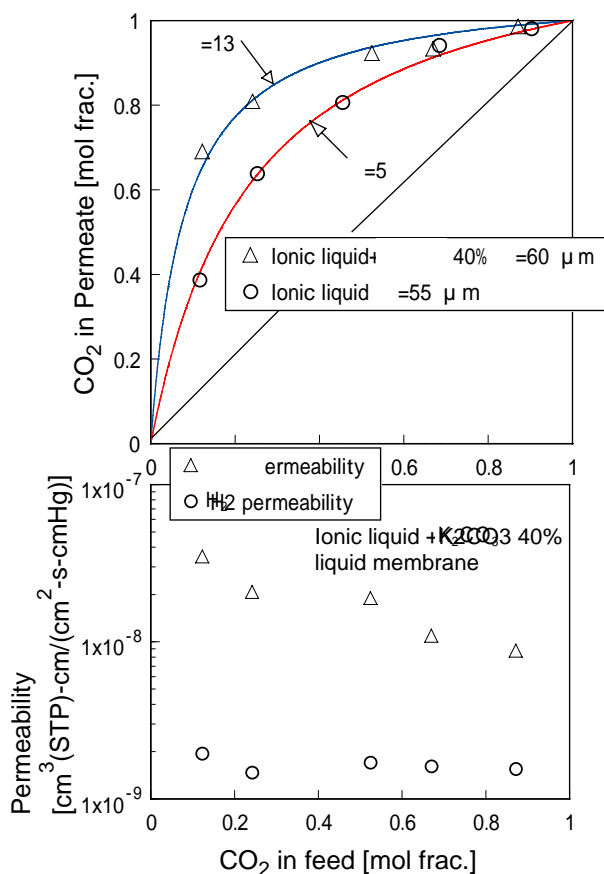


Figure 3. Separation of CO<sub>2</sub>/H<sub>2</sub>.

the selectivity for CO<sub>2</sub> improved to 60 at the low concentration range of CO<sub>2</sub> as shown in the figure. It may caused by a facilitated transport effect between the alkaline salt and CO<sub>2</sub>. In ionic liquid with water, a high carrier concentration of alkaline salt and ionic field

causes effective CO<sub>2</sub> transport to the permeate side. This results illustrate a potential of RTILs as base materials of facilitated transport membranes for CO<sub>2</sub> separation [2].

Figure 3 shows permeation result of CO<sub>2</sub>/H<sub>2</sub> mixed gas through the [pmim][I] liquid membrane contained 40wt% of K<sub>2</sub>CO<sub>3</sub>. CO<sub>2</sub> concentration of permeate gas and permeabilities of each components are plotted versus CO<sub>2</sub> concentration of feed gas. CO<sub>2</sub> also preferentially permeated in this process. The separation factor for CO<sub>2</sub> over H<sub>2</sub> was 13. The lower permeability of light gas, H<sub>2</sub>, than CO<sub>2</sub> means that the gas permeation mechanism through the RTIL liquid membrane is controlled by solution process to the membrane material. There also shown a increase of CO<sub>2</sub> permeability at the low concentration range due to a facilitated transport effect for CO<sub>2</sub> by alkaline salt.

### 3.2 Dehumidification using RTIL liquid membrane

The dehumidification performance of the RTIL liquid membrane was demonstrated by humidity change of feed air through the membrane cell. Figure 4 shows the dehumidification results, where the tested liquid membrane were of TEG, RTIL and a mixture of RTIL with hygroscopic salt, LiBr. The vertical axis shows that humidity of the feed air decreases from 60%RH at the inlet to 20-30%RH at the outlet of the membrane cell. Permeation rate of air was negligibly small. The driving force of the water vapor permeation is the partial pressure difference between feed side and permeate side. In the experimental condition, feed side partial pressure of water was corresponding to an average humidity between inlet and outlet of 30-40%RH. Permeate side partial pressure was much lower than 0.1 kPa. Since the absolute permeation rate of water vapor was nearly constant, the outlet humidity decreases with small feed air rate. The RTIL liquid membrane has a comparable dehumidification property to the TEG liquid membrane [3]. This results due to high hygroscopicity of the [pmim][I] ionic liquid.

To improve the dehumidification performance, a hygroscopic salt, LiBr, was mixed to the RTIL liquid membrane. The water absorption of the ionic liquid increases from 0.6 g-water/1 g-liquid to 1.5 g-water/1 g-liquid in 95%RH air with 25wt% mixing of LiBr. Using this mixed liquid membrane, outlet air humidity decreased compare to the pure ionic liquid membrane as shown in Figure 4. It may caused by a increased water content at the membrane surface faced to the feed air.

### 3.3 Separation of aromatic hydrocarbons

The RTIL is expected to have affinity to aromatic hydrocarbons for its large polarity. Aromatic/aliphatic mixed vapor permeation was tested thorough the RTIL liquid membrane. Saturated vapors of benzene/cyclohexane (C6), toluene/heptane (C7) or m-xylene/n-octane (C8), in carrier gas, N<sub>2</sub>, fed to the membrane cell. In Figure 5, the aromatic vapor mole fractions in the permeate vapors are plotted versus that in the feed vapors. Aromatic vapors passed preferentially through the RTIL membrane. Benzene(C6) selectivity was 20 over cyclohexane. When the number of carbon increased from C6 to C8, aromatic selectivity decreased. Vapor flux was about

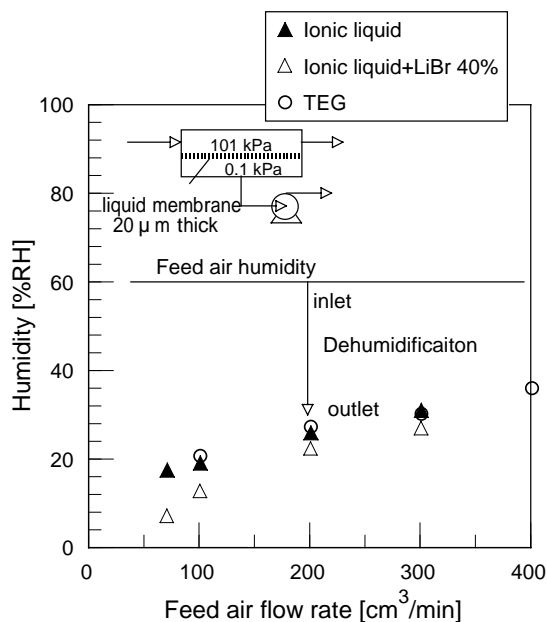


Figure 4. Dehumidification of air.

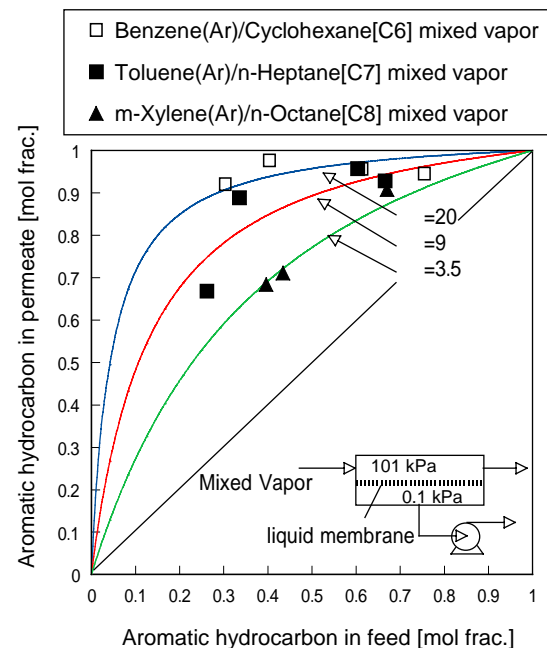


Figure 5. Aromatic hydrocarbon separation.

0.02 kg/(m<sup>2</sup>-h). It was larger than that of polymers, and smaller than triethylene glycol (TEG) liquid membrane or KI mixed TEG liquid membrane [6].

There has been no literature on selectivity or affinity of RTILs to aromatic hydrocarbon. It remains uncertain on mechanism of preferentially permeation or facilitated transport for aromatics through RTILs. In researches on facilitated transport of liquid membrane, which are normally aqueous solution, silver nitrate, AgNO<sub>3</sub>, is well known as a facilitating agent for permeation of olefin and aromatic hydrocarbons [5, 6]. Propylene or benzene vapor will preferentially permeate through a liquid membrane of aqueous AgNO<sub>3</sub> solution. In this separation process, the metal ion, Ag<sup>+</sup>, is considered to be a carrier for the facilitated transport. The affinity of

an olefin with a metal cation result from the interaction of the olefin  $\pi$ -orbital with the  $\sigma$ - and  $\pi$ -orbitals of the metal. The selectivity of the RTIL liquid membrane to aromatic vapor in this study may due to a similar mechanism that the cation part of the ionic liquid has an interaction to aromatic hydrocarbons.

### 3.4 Gas permeability through RTIL liquid membrane

Figure 6 indicates the comparison of gas permeability among the RTIL liquid membrane, the TEG liquid membrane[3, 4] and silicone rubber membrane. Permeability of liquid membranes was evaluated from permeation rate, partial pressure difference of the component across the liquid membrane and liquid membrane thickness. The permeation resistance of the Durapel microporous membrane could be ignored. For the RTIL membrane, the permeabilities of condensable gas,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , are larger than other gases. It means the permeation through the RTIL membrane is controlled by the solution step of gas into the membrane material. This permeation property is similar to TEG liquid membrane and silicone rubber.

The gas permeabilities through the ionic liquid as a whole are lower than that through the TEG liquid membrane. The difference in permeabilities due to the difference in viscosity of the liquids, because diffusivity in the liquid depends on viscosity. The viscosity of the [pmim][I] ionic liquid is greater than 100 mPa·s and the viscosity of TEG is 39 mPa·s at room temperature. This viscosity difference affects permeabilities for the two liquid membranes.

From Figure 6, we can see advantages for a ionic liquid to be used as a liquid membrane material. One advantage of the RTIL is low permeability of  $\text{N}_2$  and  $\text{CH}_4$ . The RTIL liquid membrane is expected to apply to the separation between air and condensable gas, e.g. dehumidification and VOC removal from air. Another advantage of the RTIL is that it dissolves other salt or organic compounds as facilitation transport agent. As shown in Figure 3,  $\text{CO}_2$  selectivity of the RTIL was improved by incorporation of alkaline salt. Dehumidification performance was enhanced by incorporation of hygroscopic salt into the ionic liquid membrane. The potential of RTIL liquid membrane development exists in a facilitated transport membrane for a special gas or vapor to be separated.

### 4. CONCLUSION

An application of the room temperature ionic liquid was proposed and reported experimentally as a new material for separation process of gas and vapor. A liquid membrane using an ionic liquid, 1-propyl-3-methylimidazolium iodide, was applied to gas and vapor separation of  $\text{CO}_2$ , water vapor from air and aromatic hydrocarbon vapors. A supported liquid membrane of the ionic liquid was placed on a hydrophobic microporous membrane. Since the ionic liquid is non-volatile, hydrophilic and high surface tension, the liquid membrane could be applied to gas and vapor permeation with vacuum at permeate side. Overall

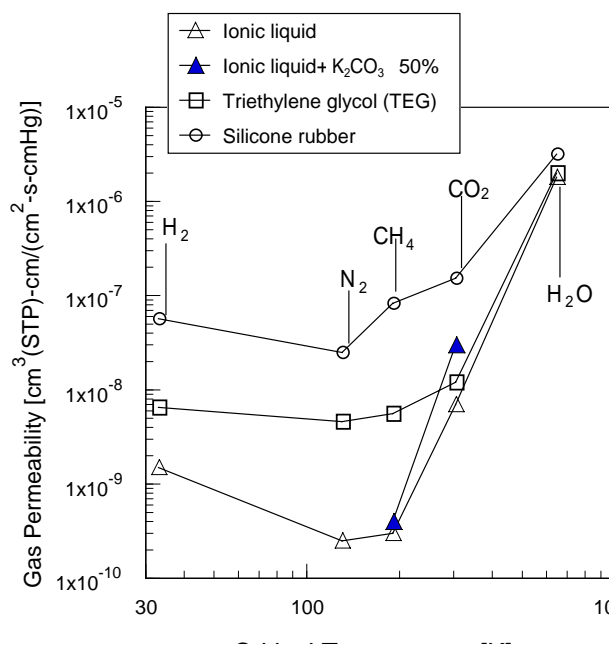


Figure 6. Comparison of gas permeabilities.

permeation property, permeabilities, was similar to that of a triethylene glycol liquid membrane. The membrane of the ionic liquid showed selectivity of 20 for  $\text{CO}_2$  over  $\text{CH}_4$ , 1000 for water vapor over air, and 20 for benzene vapor over cyclohexane vapor. The membrane of the ionic liquid is promising for dehumidification and the separation of  $\text{CO}_2$ , VOC and aromatic hydrocarbons. The high selectivity for water vapor may be caused by the hydrophilic property of the ionic liquid. By adding alkaline salt to the liquid membrane, the selectivity for  $\text{CO}_2$  was enhanced. The use of ionic liquids as a liquid membrane material for gas and vapor separation has advantage that ionic liquids have variety of sorption properties by combination of anion and cation. Since ionic liquids can dissolve other inorganic salts and organic solvents, future applications of facilitated transport membrane are expected by mixing of a facilitation agent to an ionic liquid.

### REFERENCES

- [1] P. Wasserscheid and T. Welton (Eds.), "Ionic Liquid in Synthesis," Wiley-VCH, Berlin (2003).
- [2] P. Scovazzo, A. E. Visser, J. H. Davis Jr., R. D. Rogers, C. A. Koval, D. L. DuBois and R. D. Noble, *ACS Symp. Ser.*, 818, 69-87 (2003).
- [3] A. Ito, *J. Membrane Sci.*, 175, 35-42 (2000).
- [4] A. Ito, S. Duan, Y. Ikenori and A. Ohkawa, *Sep. Purif. Technol.*, 24, 235-242 (2001).
- [5] S. Duan, A. Ito and A. Ohkawa, *J. Membrane Sci.*, 215, 53-60 (2003).
- [6] N. Yamanouchi, A. Ito and K. Yamagiwa, *J. Chem. Eng. Japan*, 36, 1070-1075 (2003).