[Review Paper]

CO₂ Absorption Property of Ionic Liquid and CO₂ Permselectivity for Ionic Liquid Membrane

Takashi MAKINO* and Mitsuhiro KANAKUBO*

National Institute of Advanced Industrial Science and Technology, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, JAPAN

(Received April 4, 2016)

The aim of this review is to provide some information on the CO₂ absorption property of ionic liquids and the CO₂ permselectivity for the separation membranes using ionic liquids. Ionic liquids are a unique solvent, of which the characteristics are non-volatile, non-flammable, miscible with various chemicals, and so on. The CO₂ capture using ionic liquids is a promising technology, and a variety of studies have been reported on the natures of the ionic liquid absorbents and membranes. This review presents some fundamental data on the following three topics: (1) the CO₂ solubility in the ionic liquid physical absorbents; (2) the high-pressure CO₂ absorption behavior for the ionic liquid chemical absorbents; (3) the CO₂ permselectivity for the inclusion membranes with ionic liquids and polymers. The first two topics describe the effects of the chemical structures of ionic liquids on the CO₂ solubility, in particular, in terms of the oxygen containing groups and the interionic interactions. The second topic also contains how amino acid anions affect the physical and chemical absorptions under high CO₂ pressure conditions. The last topic reported that the CO₂ and N₂ permeations in the inclusion membranes depend on the composition and kind of polymers.

Keywords

Ionic liquid, Carbon dioxide, Physical absorption, Chemical absorption, Membrane separation

1. Introduction

CO₂ separation is an important process for petrochemical industry, like the purification of syngas, the production of energy resources, and so on. There are some options for the CO₂ capture, absorption, adsorption, and membrane separation, depending on throughput, composition, pressure, and temperature for gas mixture sources^{1),2)}.

Absorption process is applicable to a variety of separation targets, and many kinds of absorbents have been investigated. Ionic liquids (ILs) also have attracted much attention as a promising CO₂ absorbent because they can overcome some critical issues of conventional absorbents composed of molecular liquids: the high energy-consumption for absorption/desorption and the loss and flammability of absorbent itself. ILs are a salt, of which the melting point is at or below the ambient temperature. They have some unique characteristics as absorbents: negligible vapor pressure, non-flammability, and low heat capacity. Some ILs can selectively absorb acidic gases like CO₂, SO_x, and NO_x, while they do not dissolve in gas phase even at high

pressures as demonstrated elsewhere³⁾. Because of these features, ILs have drawn much attention as an energy-efficient and environmentally-friendly CO₂ absorbent.

It is also expected that ILs are a promising material for the gas separation membrane. The membrane separation can generally reduce the operation energy and the footprint of equipment compared to other separation technologies. Supported ionic liquid membranes (SILMs), composed of porous organic or inorganic materials filled with IL, have been studied well. SILMs are stable for a much longer time than the supported liquid membranes using organic solvents because of their non-volatile nature. Furthermore, it is reported that some SILMs of ILs with the fluorinated anions show the comparable or higher CO₂ permeability and selectivity than the conventional polymer membranes^{4),5)}.

For ILs in the absorption and adsorption technologies are required not only the high CO₂ capacity but also its large pressure and/or temperature variations, since the ILs are reused, in general, by depressurization and/or heating. On the other hand, the membrane separation technology demands the ILs with the high CO₂ solubility over a wide temperature range, because the gas permeation rate depends strongly on the gradient of gas concentration in the membrane. High kinetic properties

DOI: dx.doi.org/10.1627/jpi.59.109

* To whom correspondence should be addressed.

* E-mail: makino.t@aist.go.jp (TM), m-kanakubo@aist.go.jp (MK)

are essential for each technology to absorb, desorb, and transport CO₂ rapidly. The physicochemical and gas absorption properties can be tuned for individual applications by the chemical modification and the combination of cation and anion. A great number of studies have been performed to understand the effects of chemical modifications, so far.

Our research group has investigated the density, viscosity, electrical conductivity, and heat capacity of neat ILs and the CO₂ solubilities in various ILs over the wide ranges of temperature and pressure. In particular, we measured not only the mole fraction based solubility but also the molarity based solubility. A lot of experimental data on two-phase equilibria for CO₂ + IL systems have been reported at various temperatures and pressures, however, the mole fraction scaled solubilities or Henry constants were only reported in many cases. These parameters are a measure of the CO₂ absorption property in ILs, but they exclude the molecular volume/weight of ILs themselves. More important information for the engineering design in the CO₂ separation is the CO₂ capacity, *i.e.* the molarity or molality scaled solubilities of CO₂^{8)~10)}. Pressure-volume-temperature-composition (*pVTx*) relations for the binary systems are required to obtain the molarities/molalities of CO₂, however, there have been a small number of experimental data on the *pVTx* relations, compared to the *pTx* behaviors. Very limited information is available for the effect of chemical modifications on the CO₂ capacities in ILs.

This review describes some fundamental data about the effect of chemical modifications on the CO₂ absorption property based on our previous studies. There are three topics, the ionic liquid physical absorbent, the ionic liquid chemical absorbent, and the inclusion membrane of ionic liquid and polymer. **Figure 1** summarizes the chemical structures and abbreviations of the ionic species presented in this review.

2. Physical Absorbent

2.1. Effects of Oxygen-containing Groups

Some research groups reported that the fluorine atom improves the CO₂ solubility in ILs^{6)~8)}. It is also pointed out that this enhancement is mainly due to the Lewis acid-base interaction between the acidic carbon atom of CO₂ and the basic fluorine atom. However, the fluorination sometimes increases the viscosity of ILs dramatically⁸⁾. The worse transport property causes the depression of CO₂ absorption and desorption kinetics as mentioned in introduction. We focused on the oxygen-containing groups, *i.e.* the ether, ester, and hydroxyl groups^{9)~12)}. It was expected that these functional groups interact strongly with CO₂ because the oxygen atom is Lewis basic as well as the fluorine atom. Actually, the similar enhancements were reported in the

Fig. 1 Chemical Structures and Abbreviations of the Ionic Species Presented in This Review

earlier studies on the CO₂ + polymer systems^{13)~16)}. In addition, it was demonstrated that the ether modification decreases the viscosity of ILs^{17)~21)}.

Table 1 lists the physical properties of ILs and the CO₂ solubilities with the related thermodynamic parameters of solution for physical absorbents. Since the lengths of side chain in the cations are very similar between the functionalized and analogous pairs, *i.e.*, [N_{112,20CO1}][Tf₂N]-[N₁₁₂₅][Tf₂N], [N_{112,202O1}][Tf₂N]-[N₁₁₂₇][Tf₂N], and [Pyr₁₃][Tf₂N]-[Pyr_{1,101}][Tf₂N], respectively, the differences of values in **Table 1** can be mainly interpreted by the effects of ester and ether functionalization. The ether group on cation slightly increased the mole fraction scaled solubility (smaller k_H^∞), while the ester group decreased it (larger k_H^∞). The increment of CO₂ solubility by the ether modification was also observed in the sulfates ([6SO₄]⁻, [102SO₄]⁻, and [102O2SO₄]⁻). Although the alkyl sulfate shows the poorer CO₂ solubility than the fluorinated anions like [Tf₂N]⁻, the ether moiety successively improved it. The thermodynamic parameters indicate that the ether and ester modifications in ammonium cations strengthened the intermolecular interaction

Table 1 Density ρ , Molar Volume v_m , Concentration of Ionic Species c_2° , and Viscosity η of and Henry Constant at Infinite Dilution k_H^∞ , Enthalpy of Solution $\Delta_{\text{sol}}H^\infty$, Entropy of Solution $T \cdot \Delta_{\text{sol}}S^\infty$, and Slope of Molarity Scaled Solubility of CO_2 Δc_1 for ILs

	$\rho^{\text{a)}}$ [kg m ⁻³]	$v_m^{\text{a)}}$ [cm ³ mol ⁻¹]	$c_2^{\circ \text{a)}}$ [mol dm ⁻³]	$\eta^{\text{a)}}$ [mPa s]	$k_H^{\infty \text{a)}}$ [MPa]	$\Delta_{\text{sol}}H^{\infty \text{b)}}$ [kJ mol ⁻¹]	$T \cdot \Delta_{\text{sol}}S^{\infty \text{b)}}$ [kJ mol ⁻¹]	$\Delta c_1^{\text{a)}}$ [mol dm ⁻³ MPa ⁻¹]
[N ₁₁₂₅][Tf ₂ N] ⁽¹¹⁾	1341	316.4	3.161	128	3.12	-12.8	-22.4	0.99
[N _{112,20CO1}][Tf ₂ N] ⁽¹¹⁾	1459	301.9	3.312	208	3.38	-13.7	-23.6	0.96
[N ₁₁₂₇][Tf ₂ N] ⁽¹¹⁾	1291	350.5	2.853	168	2.96	-12.8	-22.3	0.98
[N _{112,202O1}][Tf ₂ N] ⁽¹¹⁾	1391	328.1	3.048	58.6	2.90	-13.6	-23.1	1.07
[Pyr ₁₃][Tf ₂ N] ⁽¹²⁾	1428	286.0	3.497	61.5	3.35	-14.0	-23.9	1.01
[Pyr _{1,101}][Tf ₂ N] ⁽¹²⁾	1483	276.8	3.613	40.6	3.29	-13.5	-23.3	1.08
[Pyr _{1,101}][FSA] ⁽¹²⁾	1405	220.8	4.529	28.5	4.05	-14.3	-24.7	1.08
[P _{444,2O1}][6SO ₄] ⁽¹³⁾	1075	411.6	2.430	1628	4.82	-	-	0.512
[P _{444,2O1}][1O2SO ₄] ⁽¹³⁾	1078	386.4	2.580	491	4.30	-	-	0.663
[P _{444,2O1}][1O2O2SO ₄] ⁽¹³⁾	1078	427.1	2.341	359	3.66	-	-	0.703
[emim][Tf ₂ N] ⁽²⁹⁾	1519	246.0	4.065	33.0	3.45 (6.11 ^{c)})	-13.7	-23.6	1.08
[emim][TCB] ⁽²⁷⁾	1036	218.1	4.585	18.1	3.27 (5.83 ^{c)})	-13.9	-23.7	1.41
[eimH][Tf ₂ N] ⁽²⁹⁾	1574	239.9	4.168	60.0	3.90	-15.0	-25.3	1.07
[P ₄₄₄][Pro] ⁽⁴²⁾	971.1	384.7	2.599	1025	6.8 ^{c,d)}	-	-	0.380 ^{c)}
[P ₄₄₄][MePro] ⁽⁴²⁾	-	-	-	-	7.0 ^{c,d)}	-	-	0.338 ^{c)}
[P ₄₄₄][Gly] ⁽⁴²⁾	963.0 ⁽⁴³⁾	346.3 ⁽⁴³⁾	2.888 ⁽⁴³⁾	426 ⁽⁴⁴⁾	8.1 ^{c,d)}	-	-	0.336 ^{c)}
[P ₄₄₄][Tf ₂ N] ⁽⁴⁵⁾	-	-	-	-	2.5	-	-	-

a) 298.15 K. b) 313.15 K. c) 333.15 K. d) The proportional constant of CO_2 physically dissolved in the AAILs like the Henry constant.

between CO_2 and ILs (smaller $\Delta_{\text{sol}}H^\infty$). They caused simultaneously the negative entropic effect (smaller $T \cdot \Delta_{\text{sol}}S^\infty$). Unlike the ether modified ammonium, the pyrrolidinium with the ether group showed the opposite trend.

According to the earlier reports, the micro phase separation occurred between the polar and apolar phases in ILs, and CO_2 dissolves preferentially in the polar phase^{(22),(23)}. In addition, the carbon atom of CO_2 interacts strongly with the Lewis basic atoms. Thus, the ether and ester modifications expand the CO_2 -philic space where CO_2 can dissolve. It is considered that these effects are related to the enthalpic term caused by the functional groups on ammoniums. The alternative interpretation of CO_2 dissolution at molecular level was proposed in the theoretical study: the rearrangement of coordination position between the cation and anion to create a “cavity” for CO_2 ⁽²⁴⁾. This means that the structure of solution changes before and after CO_2 dissolution, *i.e.*, leading to the change of entropy. It is considered that the ester group on the ammonium makes this rearrangement more difficult compared to the ether group. On the other hand, the ether modification of the pyrrolidinium resulted in the easier change of the coordination. It is not clear what brings about the difference between the ether modified ammonium and pyrrolidinium at present. One possible reason might be the distance between the charge center (the nitrogen atom) and the oxygen atom, two carbons for the ammonium and one carbon for the pyrrolidinium.

Figure 2 presents the CO_2 solubility in molarity scale c_1 as a function of pressure p . The CO_2 capacity increased almost linearly with the pressure increment, which is a typical behavior for IL physical absorbents.

Open triangle, [N₁₁₂₅][Tf₂N]⁽¹¹⁾; closed triangle, [N_{112,20CO1}][Tf₂N]⁽¹¹⁾; open circle, [N₁₁₂₇][Tf₂N]⁽¹¹⁾; closed circle, [N_{112,202O1}][Tf₂N]⁽¹¹⁾; open diamond, [Pyr₁₃][Tf₂N]⁽¹²⁾; closed diamond, [Pyr_{1,101}][Tf₂N]⁽¹²⁾; gray diamond, [Pyr_{1,101}][FSA]⁽¹²⁾; gray square, [emim][Tf₂N]⁽²⁹⁾; closed square, [emim][TCB]⁽²⁷⁾; open square, [eimH][Tf₂N]⁽²⁹⁾; asterisk, [P_{444,2O1}][6SO₄]⁽¹³⁾; plus, [P_{444,2O1}][1O2SO₄]⁽¹³⁾; cross, [P_{444,2O1}][1O2O2SO₄]⁽¹³⁾.

Fig. 2 Pressure p —molarity scaled solubility of CO_2 c_1 projection for the CO_2 + IL binary systems at 298.15 K

The slopes $\Delta c_1 \equiv \partial c_1 / \partial p$ are also summarized in **Table 1**. Generally, the physisorption separation is operated by pressure swing, and thus, a solvent with larger Δc_1 is a better physical absorbent. The values of Δc_1 for the ether functionalized ammonium and pyrrolidinium were

7–11 % larger than those for the non-functionalized ones, although the Henry constants for the former ILs were only ~ 2 % better than those for the latter ones. This is due to the smaller molar volume v_m for the ILs with the ether group as listed in **Table 1**. On the other hand, the ester modified IL showed the smaller value of Δc_1 than its analogue despite the smaller v_m . The decrement in Δc_1 is derived from the worse k_H^∞ for $[\text{N}_{112,20}\text{CO}_1][\text{Tf}_2\text{N}]$. The more pronounced improvement of ether group was observed in the sulfonate salts. The values of Δc_1 for $[\text{P}_{444,201}][\text{IO}_2\text{SO}_4]$ and $[\text{P}_{444,201}][\text{IO}_2\text{O}_2\text{SO}_4]$ were 29 % and 37 % larger than that for $[\text{P}_{444,201}][6\text{SO}_4]$. The better k_H^∞ for the ether sulfates mainly caused this enhancement. In addition, $[\text{Pyr}_{1,101}][\text{FSA}]$ had the worse k_H^∞ and the higher c_2° than $[\text{Pyr}_{1,101}][\text{Tf}_2\text{N}]$, resulting in the same value of Δc_1 for the two ILs. We also investigated the effect of hydroxyl group (data is not shown) and found that the functionalization caused the worse k_H^∞ and Δc_1 as well as the higher viscosity⁹.

2. 2. Effects of Interionic Interactions

We described in the former section that not only the enthalpic effect but also the entropic effect are important to improve the CO_2 solubility in addition to the smaller molar volume. The entropic term can be related to the rearrangement of coordination, and thus, the interionic interaction between the cation and anion is of primary importance for the improvement of the entropy of solution. It is reported that the interaction energies for a pair of ILs between $[\text{emim}]^+$ and different anions increased in the following order: $[\text{BF}_4]^- < [\text{PF}_6]^- < [\text{Tf}_2\text{N}]^- < [\text{TCB}]^-$ ²⁵. This trend is in a good agreement with the experimental CO_2 solubilities for the three $[\text{bmim}]^+$ ILs, $[\text{bmim}][\text{BF}_4] < [\text{bmim}][\text{PF}_6] < [\text{bmim}][\text{Tf}_2\text{N}]$ ²⁶. Therefore, we investigated the phase equilibria for the $\text{CO}_2 + [\text{emim}][\text{TCB}]$ system²⁷. **Table 1** lists the k_H^∞ values of $[\text{emim}][\text{TCB}]$ and $[\text{emim}][\text{Tf}_2\text{N}]$, which indicates that the mole fraction based solubility in the former IL was slightly larger than that in the latter IL. The enthalpies suggest that $[\text{TCB}]^-$ interacts with CO_2 as strongly as $[\text{Tf}_2\text{N}]^-$, implying that the CN group is also presumably CO_2 -philic (Lewis basic). Actually, the nitrogen atoms in $[\text{TCB}]^-$ have large negative partial charges²⁸. The entropies reveal that the coordination change caused by CO_2 dissolution in $[\text{emim}][\text{TCB}]$ is similar to that in $[\text{emim}][\text{Tf}_2\text{N}]$. Although ILs with smaller anions like $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ generally show more negative entropic values, the weaker interaction of $[\text{TCB}]^-$ leads to the favorable entropic effect. The c_1 data for $[\text{emim}][\text{TCB}]$ are also plotted in **Fig. 2**. The c_1 is almost proportional to the pressure and the slope for $[\text{emim}][\text{TCB}]$ is $1.41 \text{ mol dm}^{-3} \text{ MPa}^{-1}$, which is ~ 31 % higher than that for $[\text{emim}][\text{Tf}_2\text{N}]$. This increment is attributed to the higher concentration of ionic species as summarized in **Table 1**. The molarity of CO_2 in $[\text{emim}][\text{TCB}]$ is the

largest in the IL physical absorbents investigated previously, and the more rapid absorption and desorption are expected because of its low viscosity (see **Table 1**).

We also studied the effect of interionic interaction *via* proton in a protic ionic liquid (PIL), which is a subclass of IL²⁹. PILs have an advantage over the conventional ILs in the cost of production, because PILs are synthesized by simple neutralization of an acid with a base. PILs have proton-acceptor and -donor sites in the cation and anion, which can form an extended intermolecular network^{30–32}. The spectroscopic study pointed out that the intermolecular interaction between the cation and anion in PILs is generally stronger than that in ILs³³. The stronger interaction increased both the density and viscosity for PILs. The example results for $[\text{eimH}][\text{Tf}_2\text{N}]$ are shown in **Table 1**. k_H^∞ for $[\text{eimH}][\text{Tf}_2\text{N}]$ is larger than that for the corresponding IL, $[\text{emim}][\text{Tf}_2\text{N}]$. The entropic term for $[\text{eimH}][\text{Tf}_2\text{N}]$ is smaller than for $[\text{emim}][\text{Tf}_2\text{N}]$. This unfavorable effect is partially compensated by the smaller enthalpy. The stronger solution structure in $[\text{eimH}][\text{Tf}_2\text{N}]$ makes the cavity formation more difficult. The protic nature, *i.e.* the electro positive and negative sites can interact with the negative oxygen and positive carbon atoms of CO_2 , resulting in the better enthalpic effect. **Figure 2** plots the relations of p - c_1 for $[\text{eimH}][\text{Tf}_2\text{N}]$ at 298.15 K. The CO_2 capacities in the PIL and the corresponding IL are almost the same. This is due to the smaller molar volume of $[\text{eimH}][\text{Tf}_2\text{N}]$ compared to that of $[\text{emim}][\text{Tf}_2\text{N}]$. The intermolecular interaction *via* proton makes a negative contribution to the physical properties, in particular, the transport properties, but not to the molarity scaled solubility of CO_2 .

3. Chemical Absorbent

Unlike the physical absorbent, the chemical absorbent absorbs CO_2 through the chemical reaction. Generally, the chemical absorption is saturated at lower pressures and the contribution of physical absorption becomes larger at higher pressures. Most of the earlier studies investigated the CO_2 solubility at limited pressures lower than $\sim 0.2 \text{ MPa}$. However, some CO_2 separation processes are operated at much higher pressures of CO_2 . To understand whether IL chemical absorbents are applied to high CO_2 pressure sources or not, it is important to investigate the CO_2 solubility at high pressures and the effect of chemical modifications on both chemical and physical absorptions.

Some kinds of IL chemical absorbents have been reported so far^{34–41}, and we focused on the amino acid ILs (AAILs) with tetrabutylphosphonium⁴². One of the advantages of AAILs is high CO_2 solubility; one mole of AAILs absorb an equimolar amount of CO_2 through a 1 : 1 stoichiometric reaction. In the conventional amine solutions and other amine functionalized

Closed circle, $[P_{4444}][Pro]^{42)}$; open circle, $[P_{4444}][MePro]^{42)}$; closed square, $[P_{4444}][Gly]^{42)}$; closed triangle, $[emim][TCB]^{27)}$; open triangle, $[emim][Tf_2N]^{29)}$.

Fig. 3 Pressure p —mole fraction scaled solubility of CO_2 x_1 projection for the CO_2 + AAIL binary systems at 333.15 K

ILs, two moles of amines are consumed for one mole of CO_2 through a 2 : 1 reaction. **Figure 3** presents the CO_2 solubility in mole fraction x_1 as a function of pressure at 333.15 K. The values of x_1 are 0.45–0.50 at 0.10 MPa, *i.e.*, each AAIL absorbed 0.9–1.0 moles of CO_2 per mole of AAIL. x_1 increased steeply at pressures up to ~ 0.15 MPa and gradually increased at higher pressures. The $[P_{4444}][Pro]$ + CO_2 solution at atmospheric pressure was analyzed using NMR, and we identified that CO_2 was absorbed chemically as a carbamate ($[Pro-CO_2]^-$). The amount of CO_2 absorbed chemically in $[P_{4444}][Gly]$ was the smallest and those in $[P_{4444}][Pro]$ and $[P_{4444}][MePro]$ are almost the same. The theoretical study revealed that the 2 : 1 reaction, *i.e.* the formation of dianion ($[Pro-CO_2]^- + [Pro]^- \rightarrow [Pro-CO_2]^{2-} + [ProH]$) also occurs simultaneously, although the dianion is less stable thermodynamically³⁸⁾. It is suggested that the 1 : 1 reaction is promoted in $[Pro]^-$ compared to $[Gly]^-$, and the methylation of $[Pro]^-$ does not influence significantly the CO_2 chemisorption.

Figure 4 is the plot of the molarity scaled solubility c_1 against the pressure p . To understand the effect of the amino acid anions on high-pressure CO_2 solubility, c_1 was deconvoluted into the two contributions of physical and chemical absorptions. The molarities of physically absorbed CO_2 $c_{1,p}$, and chemically absorbed CO_2 $c_{1,c}$ are also plotted in **Fig. 4**. The v_m value for $[P_{4444}][Pro]$ is larger than that for $[P_{4444}][Gly]$, however, the slope of $c_{1,p}$ for $[P_{4444}][Pro]$ is the largest in these AAILs. The proportional constant like the Henry constant was calculated based on the deconvolution result, of which the values are summarized in **Table 1** with

Circle, $[P_{4444}][Pro]^{42)}$; diamond, $[P_{4444}][MePro]^{42)}$; square, $[P_{4444}][Gly]^{42)}$; triangle, $[emim][TCB]$ (physical absorption)²⁷⁾; cross, $[emim][Tf_2N]$ (physical absorption)²⁹⁾. Gray, total absorption; open, chemical absorption; closed, physical absorption.

Fig. 4 Pressure p —molarity scaled solubility of CO_2 c_1 projection for the CO_2 + AAIL binary systems at 333.15 K

some literature values^{43)–45)}. $[Pro]^-$ is a better anion for the increment of physisorption than $[Gly]^-$; however, these anions are less effective than the typical anions like $[Tf_2N]^-$. The $[P_{4444}]^+$ salt shows the smaller k_H than the $[emim]^+$ salt (*ex.* 2.5 MPa for $[P_{4444}][Tf_2N]$ and 3.45 MPa for $[emim][Tf_2N]$ at 298.15 K). Nevertheless, k_H for the amino acid ILs are larger than $[emim][Tf_2N]$ at 333.15 K as summarized in **Table 1**. The methyl group on $[MePro]^-$ does not affect significantly the physisorption. The values of $c_{1,c}$ increased dramatically at low pressures and decreased gradually after that. This decrement is attributed to the slight volume expansion arising from the physisorption. Unlike the mole fraction based solubility of CO_2 absorbed chemically ($[P_{4444}][Gly] < [P_{4444}][Pro] \sim [P_{4444}][MePro]$), $c_{1,c}$ in $[P_{4444}][Gly]$, $[P_{4444}][Pro]$, and $[P_{4444}][MePro]$ decreased in this order. The difference in the order between x_1 and $c_{1,c}$ is due to the smaller molar volume in $[P_{4444}][Gly]$ as listed in **Table 1**.

4. Ionic Liquid + Polymer Membrane

4.1. Poly(ethyleneglycol) Based Polymer

SILMs can be optimized for individual application by modifying the chemical structures of ILs as described in the previous sections. However, there is a serious drawback: SILMs are not stable under pressurized conditions because ILs easily drop out from the porous material. The polymer inclusion and ion gel membranes are possible materials for overcoming this disadvantage. The rigid polymer matrixes commonly restrict the gas diffusion, which leads to the lower per-

Square, P_{CO_2} ; circle, $P_{\text{CO}_2}/P_{\text{N}_2}$. Closed, Tetra-PEG + [emim][Tf₂N] membrane; open, [emim][Tf₂N] SILM. Feed and sweep gases were a CO₂/N₂ mixture, of which the CO₂ composition was 50 mol%, and He, respectively. Total pressures of the mixture and He were both 101 kPa. Neither of the feed and sweep gases contained water.

Fig. 5 Temperature T —permeability of CO₂ P_{CO_2} and selectivity of CO₂ $P_{\text{CO}_2}/P_{\text{N}_2}$ ⁽⁵¹⁾

meability in the inclusion membranes compared to that in SILMs. Therefore, an IL membrane with a low polymer content is more favorable for the gas separation. Some research groups reported such membranes for the CO₂ separation^{(46)–(50)}.

We investigated the CO₂ permselectivity and solubility for the tetra-armed poly(ethylene glycol) (Tetra-PEG) + [emim][Tf₂N] ion gel⁽⁵¹⁾. The previous study reported that the gel is mechanically robust (the maximum breaking strength by compression reaches 18 MPa) and thermally stable (up to 300 °C) even at 6 wt% polymer content⁽⁵²⁾. **Figure 5** shows the CO₂ permeability and selectivity for the Tetra-PEG + [emim][Tf₂N] membrane (94 wt%-IL) and the [emim][Tf₂N] SILM as a function of temperature. One important finding is that P_{CO_2} for the ion gel membrane is 37–57 % higher than that for the SILM. The high permeation for the ion gel membrane might be ascribed to the larger cross sectional area where gas molecules dissolve in the IL. The porosity of the support filter is 68 %, and thus, the ideal permeability of the SILM is estimated to become 1.47 times, which agrees well with the difference in the permeabilities. The other finding is almost the same selectivities for both membranes. According to the solution-diffusion transport mechanism, an ideal selectivity of CO₂ to N₂ mainly depends on the solubility c and diffusion coefficient D , $P_{\text{CO}_2}/P_{\text{N}_2} = (c_{\text{CO}_2}/c_{\text{N}_2})(D_{\text{CO}_2}/D_{\text{N}_2})$. The present results imply that both solubilities and diffusion coefficients of CO₂ and N₂ in the ion gel are not so far from those in the SILM. Thus, the support polymer, Tetra-PEG, does not hinder the gas separation performance.

Circle, c_1 ; square, ΔV . Closed, Tetra-PEG + [emim][Tf₂N] ion gel; open, [emim][Tf₂N].

Fig. 6 Temperature T —molarity scaled solubility of CO₂ c_1 and volume expansion of liquid or gel phase ΔV ^{(29),(51)}

We also investigated the CO₂ absorption behavior for the ion gel under high-pressure conditions, which is the first demonstration as far as we know. **Figure 6** shows the pressure dependence of the CO₂ solubility (molarity scale) and the volume expansion at 298.15 K. The ion gel expands without solvent seeping-out even at 3 MPa. The volume expansion for the ion gel is practically equal to that for the neat [emim][Tf₂N]. In addition, the ion gel can absorb CO₂ physically as much as the corresponding neat IL. These results indicate that Tetra-PEG does not interfere CO₂ absorption and liquid-like absorption occurs even in the solid-state ion gel. In conclusion, the Tetra-PEG + IL gels are promising materials applicable to the CO₂ separation over the wide range of temperatures (up to 300 °C) and pressures (at least up to 3 MPa).

4.2. Poly(vinylidene fluoride) Based Polymer

In earlier studies, the polymers do not contribute to the CO₂ selective permeation (in other words, the polymers are only a “container”), and the maximum performance of inclusion membrane is determined by only the property of ILs. However, if the polymers can enhance the CO₂ solubility in the inclusion membranes, the CO₂ permselectivity would be improved compared to the SILMs according to the solution-diffusion model. We investigated the effect of poly(vinylidene difluoride) (PVDF) and poly(vinylidene difluoride-co-hexafluoropropylene) (PVDF-HFP) on the CO₂ permselectivity⁽⁵³⁾. These conventional polymers contain the fluorine atoms, which can favorably interact with the Lewis acidic carbon atom on CO₂ as mentioned before.

The Raman spectra for the inclusion membranes are summarized in **Fig. 7**. We observed the drastic change of Raman spectra, in particular, at 800–900 cm^{−1}

Fig. 7 Raman Spectra for the [bmim][TfO] + PVDF and + PVDF-HFP Inclusion Membranes⁵³⁾

by adding [bmim][TfO]. According to the literatures^{54)~57)}, this spectral change is interpreted as the conformational transition of polymer from non-polar α -phase to polar β -phase. The conformational transition, *i.e.*, the plasticization was also indicated by the thermal analyses for the present membranes (the data are not shown). Commonly, the polar polymer is more CO_2 -philic than the non-polar polymer due to the quadrupole moment of CO_2 . It is expected that the plasticized (polar β -phase) PVDF and PVDF-HFP can enhance the CO_2 solubility in the inclusion membrane compared to the non-plasticized polymers (non-polar α -phase).

Figure 8 presents the CO_2 permeability and selectivity for the [bmim][TfO] + PVDF and + PVDF-HFP membranes. The inclusion membranes with 25 wt%-IL showed the smaller P_{CO_2} and $P_{\text{CO}_2}/P_{\text{N}_2}$ than the [bmim][TfO] SILM. This might be due to the slower diffusion and the decrement of solubility of gas components. The addition of polymer generally increases the viscosity of IL, resulting in the worse diffusivity. In addition, the non-polar polymers do not have the CO_2 affinity as mentioned above. On the other hand, the values of P_{CO_2} and $P_{\text{CO}_2}/P_{\text{N}_2}$ for the inclusion membranes with 75 wt%-IL are higher than those for the SILM (*e.g.*

Diamond, PVDF-HFP + [bmim][TfO] (25 wt%-IL); square, PVDF-HFP + [bmim][TfO] (75 wt%-IL); triangle, PVDF + [bmim][TfO] (25 wt%-IL); circle, PVDF + [bmim][TfO] (75 wt%-IL). Closed, P_{CO_2} ; open, $P_{\text{CO}_2}/P_{\text{N}_2}$. Plus, P_{CO_2} for [emim][Tf₂N] SILM; cross, $P_{\text{CO}_2}/P_{\text{N}_2}$ for [emim][Tf₂N] SILM. Feed and sweep gases were a CO_2/N_2 mixture, of which the CO_2 composition was 50 mol%, and He, respectively. Total pressures of the mixture and He were both 101 kPa. Neither of the feed and sweep gases contained water.

Fig. 8 Temperature T —permeability of CO_2 P_{CO_2} and selectivity of CO_2 $P_{\text{CO}_2}/P_{\text{N}_2}$ for the PVDF (a) and PVDF-HFP (b) inclusion membranes⁵³⁾

P_{CO_2} for the inclusion membrane was 2.1 times higher than that for the SILM), although the diffusion of gas species would be slower. The cross sectional area where gas species pass through for the inclusion membrane was higher than that for the SILM, as mentioned in the section 4. 1. Again, the ideal permeability of the SILM is 1.47 times as high as its experimental permeability. This value is still smaller than the ratio mentioned above (2.1 times), which suggests that the CO_2 solubility in the membrane was higher than that in the IL itself. This upgrading is derived from the enhanced interaction between the polar polymer and the CO_2 molecule. In conclusion, the appropriate compo-

sitions of IL and fluorinated polymer successfully improves the performance of IL membrane.

5. Conclusion and Outlook

We described the effects of chemical modifications on the CO₂ absorption and physical properties for ILs. The strong interactions between CO₂ and ILs, the weak electrostatic cation-anion interactions, and the smaller volume are required to improve the CO₂ physisorption in ILs. On the other hand, the information for the IL chemical absorbents is still limited. It has been reported the effective chemical structures for the improvement of CO₂ chemisorption at atmospheric pressure and room temperature. However, it is unclear how the chemical modifications influence other properties, such as the high pressure CO₂ solubility, the temperature dependence of CO₂ chemisorption, and so on. These properties are also essential to design various chemisorption processes. Thus, we have presented a new analytical method to evaluate both the chemical and physical absorption capacities in ILs over an extended pressure range. The bio-compatibility and -degradability for both kinds of IL absorbents must be considered for the commercial use; however, a limited number of reports is available. Although the ether group, as introduced in this review, is a possible choice to improve the biodegradability, further investigations should be performed in the future,

The modified ILs can be applied to not only the absorption but also the membrane separations. The ion gels with low polymer contents are a good candidate for the gas separation membranes under various temperature and pressure conditions. The ion gel membranes have the superior permselectivity to the SILMs because of its large cross sectional areas where gas species pass through, though the manufacturing of “special” polymers is disadvantageously still cost-intensive. Another approach is the improvement of membrane performance using conventional polymers as presented in this review. In both cases, the compatibility between the polymer matrixes and the IL molecules is the key factor. In spite of some literatures available, the more deep insights should be provided for diverse combinations of polymer and IL.

Acknowledgment

The authors would thank Ms. Eriko Niitsuma, Mr. Atsuhiko Oguni, and Ms. Kaori Takeshita for their assistance with the measurements in the present study.

Nomenclatures

c	: molarity	[mol m ⁻³]
D	: diffusion coefficient	[m ² s ⁻¹]
$\Delta_{\text{sol}}H$	: enthalpy of solution	[J mol ⁻¹]

k_H	: Henry constant	[Pa]
P	: permeability	[Barrer]
p	: pressure	[Pa]
$\Delta_{\text{sol}}S$	: entropy of solution	[J mol ⁻¹ K ⁻¹]
T	: temperature	[K]
v_m	: molar volume	[m ³ mol ⁻¹]
ΔV	: volume expansion rate	[-]
x	: mole fraction	[-]
<Greeks>		
η	: viscosity	[Pa s]
ρ	: density	[kg m ⁻³]
<Subscripts>		
1	: CO ₂	[-]
2	: IL	[-]
c	: chemical absorption	[-]
p	: physical absorption	[-]
<Superscript>		
o	: neat IL	[-]
∞	: infinite dilution	[-]

References

- 1) Bara, J. E., Camper, D. E., Gin, D. L., Noble, R. D., *Acc. Chem. Res.*, **43**, 152 (2010).
- 2) Ramdin, M., de Loos, T. W., Thijs Vlugt, J. H., *Ind. Eng. Chem. Res.*, **51**, 8149 (2012).
- 3) Blanchard, L. A., Hancu, D., Beckman, E. J., Brennecke, J. F., *Nature*, **399**, 28 (1999).
- 4) Scovazzo, P., *J. Membr. Sci.*, **343**, 199 (2009).
- 5) Bara, J. E., Carlisle, T. K., Gabriel, C. J., Camper, D., Finotello, A., Gin, D. L., Noble, R. D., *Ind. Eng. Chem. Res.*, **48**, 2739 (2009).
- 6) Anthony, J. L., Anderson, J. L., Maginn, E. J., Brennecke, J. F., *J. Phys. Chem. B*, **109**, 6366 (2005).
- 7) Muldoon, M. J., Aki, S. N. V. K., Anderson, J. L., Dixon, J. K., Brennecke, J. F., *J. Phys. Chem. B*, **111**, 9001 (2007).
- 8) Almantariotis, D., Gefflaut, T., Padua, A. A. H., Coxam, J.-Y., Costa Gomes, M. F., *J. Phys. Chem. B*, **114**, 3608 (2010).
- 9) Makino, T., Kanakubo, M., Umecky, T., Suzuki, A., *Fluid Phase Equilib.*, **357**, 64 (2013).
- 10) Makino, T., Kanakubo, M., Umecky, T., Suzuki, A., Nishida, T., Takano, J., *Fluid Phase Equilib.*, **360**, 253 (2013).
- 11) Makino, T., Kanakubo, M., Umecky, T., *J. Chem. Eng. Data*, **59**, 1435 (2014).
- 12) Kanakubo, M., Makino, T., Taniguchi, T., Nokami, T., Itoh, T., *ACS Sustainable Chem. Eng.*, **4**, 525 (2016).
- 13) Kazarian, S. G., Vincent, M. F., Bright, F. V., Liotta, C. L., Eckert, C. A., *J. Am. Chem. Soc.*, **118**, 1729 (1996).
- 14) Fink, R., Hancu, D., Valentine, R., Beckman, E. J., *J. Phys. Chem. B*, **103**, 6441 (1999).
- 15) Kilic, S., Michalik, S., Wang, Y., Johnson, J. K., Enick, R. M., Beckman, E. J., *Ind. Eng. Chem. Res.*, **42**, 6415 (2003).
- 16) Beckman, E. J., *Chem. Commun.*, 1885 (2004).
- 17) Sato, T., Maruo, T., Marukane, S., Takagi, K., *J. Power Sources*, **138**, 253 (2004).
- 18) Zhou, Z.-B., Matsumoto, H., Tatsumi, K., *Chem. Eur. J.*, **11**, 752 (2005).
- 19) Ferrari, S., Quartarone, E., Mustarelli, P., Magistris, A., Protti, S., Lazzaroni, S., Fagnoni, M., Albini, A., *J. Power Sources*, **194**, 45 (2009).
- 20) Makino, T., Kanakubo, M., Umecky, T., Suzuki, A., Nishida, T., Takano, J., *J. Chem. Eng. Data*, **57**, 751 (2012).
- 21) Makino, T., Kanakubo, M., Umecky, T., Suzuki, A., *J. Chem. Eng. Data*, **58**, 370 (2013).
- 22) Kanakubo, M., Umecky, T., Hiejima, Y., Aizawa, T., Nanjo, H., Kameda, Y., *J. Phys. Chem. B*, **109**, 13847 (2005).

- 23) Canongia Lopes, J. N. A., Pádua, A. A. H., *J. Phys. Chem. B*, **110**, 3330 (2006).
- 24) Huang, X., Margulis, C. J., Li, Y., Berne, B. J., *J. Am. Chem. Soc.*, **127**, 17842 (2005).
- 25) Babarao, R., Dai, S., Jiang, D., *J. Phys. Chem. B*, **115**, 9789 (2011).
- 26) Aki, S. N. V. K., Mellein, B. R., Saurer, E. M., Brennecke, J. F., *J. Phys. Chem. B*, **108**, 20355 (2004).
- 27) Makino, T., Kanakubo, M., Masuda, Y., Mukaiyama, H., *J. Sol. Chem.*, **43**, 1601 (2014).
- 28) Koller, T., Rausch, M. H., Ramos, J., Schulz, P. S., Wasserscheid, P., Economou, I. G., Fröba, A. P., *J. Phys. Chem. B*, **117**, 8512 (2013).
- 29) Makino, T., Kanakubo, M., Masuda, Y., Umecky, T., Suzuki, A., *Fluid Phase Equilib.*, **362**, 300 (2014).
- 30) Greaves, T. L., Drummond, C. J., *Chem. Rev.*, **108**, 206 (2008).
- 31) Miran, M. S., Kinoshita, H., Yasuda, T., Hasan Susan, M. M. A. B., Watanabe, M., *Chem. Commun.*, **47**, 12676 (2011).
- 32) Shen, Y., Kennedy, D. F., Greaves, T. L., Weerawardena, A., Mulder, R. J., Kirby, N., Song, G., Drummond, C. J., *Phys. Chem. Chem. Phys.*, **14**, 7981 (2012).
- 33) Fumino, K., Fossog, V., Wittler, K., Hempelmann, R., Ludwig, R., *Angew. Chem., Int. Ed.*, **52**, 2368 (2103).
- 34) Bates, E. D., Mayton, R. D., Ntai, I., Davis Jr., J. H., *J. Am. Chem. Soc.*, **124**, 926 (2002).
- 35) Zhang, Y., Zhang, S., Lu, X., Zhou, Q., Fan, W., Zhang, X., *Chem. Eur. J.*, **15**, 3003 (2009).
- 36) Yokozeki, A., Shiflett, M. B., Junk, C. P., Grieco, L. M., Foo, T., *J. Phys. Chem. B*, **112**, 16654 (2008).
- 37) Carvalho, P. J., Álvarez, V. H., Schröder, B., Gil, A. M., Marrucho, I. M., Aznar, M., Santos, L. M. N. B. F., Coutinho, J. A. P., *J. Phys. Chem. B*, **113**, 6803 (2009).
- 38) Gurkan, B. E., de la Fuente, J. C., Mindrup, E. M., Ficke, L. E., Goodrich, B. F., Price, E. A., Schneider, W. F., Brennecke, J. F., *J. Am. Chem. Soc.*, **132**, 2116 (2010).
- 39) Goodrich, B. F., de la Fuente, J. C., Gurkan, B. E., Zadigian, D. J., Price, E. A., Huang, Y., Brennecke, J. F., *Ind. Eng. Chem. Res.*, **50**, 111 (2011).
- 40) Wang, C., Luo, H., Li, H., Zhu, X., Yu, B., Dai, S., *Chem. Eur. J.*, **18**, 2153 (2012).
- 41) Seo, S., Quiroz-Guzman, M., DeSilva, M. A., Lee, T. B., Huang, Y., Goodrich, B. F., Schneider, W. F., Brennecke, J. F., *J. Phys. Chem. B*, **118**, 5740 (2014).
- 42) Makino, T., Kanakubo, M., Matsuki, T., Kamio, E., Takaba, H., Matsuyama, H., *Fluid Phase Equilib.*, in press (DOI: 10.1016/j.fluid.2016.02.013).
- 43) Zhou, G., Liu, X., Zhang, S., Yu, G., He, H., *J. Phys. Chem. B*, **111**, 7078 (2007).
- 44) Kasahara, S., Kamio, E., Otani, A., Matsuyama, H., *Ind. Eng. Chem. Res.*, **53**, 2422 (2014).
- 45) Zhang, X., Liu, Z., Wang, W., *AIChE J.*, **54**, 2717 (2008).
- 46) Gu, Y., Lodge, T. P., *Macromolecules*, **44**, 1732 (2011).
- 47) Jansen, J. C., Friess, K., Clarizia, G., Schauer, J., Izák, P., *Macromolecules*, **44**, 39 (2011).
- 48) Li, P., Pramoda, K. P., Chung, T.-S., *Ind. Eng. Chem. Res.*, **50**, 9344 (2011).
- 49) Kasahara, S., Kamio, E., Ishigami, T., Matsuyama, H., *Chem. Commun.*, **48**, 6903 (2012).
- 50) Tomé, L. C., Mecerreyes, D., Freire, C. S. R., Rebelo, L. P. N., Marrucho, I. M., *J. Membr. Sci.*, **428**, 260 (2013).
- 51) Fujii, K., Makino, T., Hashimoto, K., Sakai, T., Kanakubo, M., Shibayama, M., *Chem. Lett.*, **44**, 17 (2015).
- 52) Fujii, K., Asai, H., Ueki, T., Sakai, T., Imaizumi, S., Chung, U., Watanabe, M., Shibayama, M., *Soft Matter*, **8**, 1756 (2012).
- 53) Makino, T., Kanakubo, M., Uragami, T., *Int. J. Membr. Sci. Technol.*, **2**, 14 (2015).
- 54) Kobayashi, M., Tashiro, K., Tadokoro, H., *Macromolecules*, **8**, 158 (1975).
- 55) Tashiro, K., Kobayashi, M., *Polymer*, **29**, 426 (1988).
- 56) Zheng, J., He, A., Li, J., Han, C. C., *Macromol. Rapid Commun.*, **28**, 2159 (2007).
- 57) Tao, M., Liu, F., Ma, B., Xue, L., *Desalination*, **316**, 137 (2013).

要 旨

イオン液体の CO₂ 吸収特性およびイオン液体膜の CO₂ 透過選択性

牧野 貴至, 金久保 光央

(国研)産業技術総合研究所, 983-8551 仙台市宮城野区苦竹4-2-1

本稿では、イオン液体の CO₂ 吸収特性およびイオン液体分離膜の CO₂ 透過選択性について、我々の研究成果を中心に概説する。イオン液体は室温近傍以下に融点を持つ液体の塩であり、不揮発性、難燃性、多様な物質の溶解能力等の従来の有機溶媒にない特徴を有する。イオン液体を用いた CO₂ 分離回収は有望な技術として注目されており、主にイオン液体を吸収液

および分離膜として利用することが提案されている。本稿では、特に (1) 酸素原子を含む物理吸収イオン液体の CO₂ 吸収特性、(2) 化学吸収イオン液体の高圧 CO₂ 雰囲気下における化学吸収および物理吸収特性、(3) イオン液体+高分子膜の CO₂ 透過選択性に対する高分子種および高分子濃度の影響、に焦点を絞って紹介する。