Improvements in the CO₂ permeation selectivities of amino acid ionic liquid-based facilitated transport membranes by controlling their gas absorption properties

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Abstract

A series of amino acid ionic liquids (AAILs) composed of different cations of different sizes, including trihexyl(tetradecyl)phosphonium glycinate, tetrabutylphosphonium glycinate and triethyl(pentyl)phosphonium glycinate have been synthesized for the carrier of CO₂ facilitated transport membrane. Their physical properties, including their viscosity, density, molar volume and N₂ absorption amount were investigated. The amount of N₂ absorption decreased as the size of the cation of the AAIL decreased. Facilitated transport membranes containing these AAILs were prepared, and their CO₂ and N₂ permeabilities were measured. The N₂ permeabilities were systematically investigated both experimentally and theoretically with the aim of improving the selectivity of the CO₂ permeation of the AAIL-based facilitated transport membrane. As expected, the CO₂ permselectivity was improved using triethyl(pentyl)phosphonium glycinate, which contained the smallest cation of the AAILs investigated in this study. We have proposed a methodology for improving the CO₂ selectivity of AAIL-based facilitated transport membranes based on reducing their N₂ permeabilities.

Keywords

Gas separation; Carbon dioxide; Facilitated transport membrane; Amino acid ionic liquid; Gas absorption property

1. Introduction

The fabrication of a high performance gas separation membrane represents an important challenge in gas separation technology because membranes of this type would allow for a reduction in the membrane requirements for gas separation and lead

directly to more compact processing equipment and lower capital costs. The performance of a membrane for gas separation is principally given by its permeability and selectivity. In general, high performance membrane shows high gas permeability and high selectivity, as shown in Robeson's plot [1]. In CO₂ separation, in particular, facilitated transport membranes (FTMs) are well known as high performance membranes [2-4]. It has been reported that FTMs show high CO₂ permselectivity, which goes far beyond the upper bound shown in Robeson's plot [4]. The high CO₂ permselectivities of FTMs occur as a consequence of the CO₂ carrier included in the FTM which can chemically react with only CO₂. In our previous study, we explored our interest in the high CO₂ permselectivities of FTMs and investigated the permeation properties of various FTMs [2,5-8]. In this study, we have attempted to develop a series of different guidelines for improving the CO₂ permselectivities of FTMs. In general, the gas permeability can be described by multiplying the concentration gradient of the solute in the FTM, which corresponds to the absorbed gas amount, and the diffusion coefficient of the solute. Many studies have attempted to improve the CO₂ selectivity of FTMs against other gases by enhancing the CO₂ permeability of the FTMs. As an alternative strategy, reducing the N₂ permeability can be also used as an effective methodology. In this study, we have attempted to improve the CO₂ selectivity of FTMs by reducing their N₂ permeabilities.

Two methods are available for decreasing the N₂ permeability of FTMs to improve their CO₂ selectivity, including (1) a reduction in the N₂ amount in a solvent of the FTM; and (2) reducing the diffusion coefficient of the FTM. The second of these two methods is the least preferable because its implementation would also lead to a decrease in the CO₂ permeability. In contrast, the amounts of CO₂ and N₂ absorbed in the solvent in the FTM can only be independently varied in the FTM. CO₂ is absorbed in the solvent in the FTM via a chemical reaction, and the amount of CO₂ absorbed is mostly dependent on the amount of CO₂ carrier included in the FTM. In other words, CO₂ absorption is not so influenced by a molecular structure of the solvent. In contrast, N₂ is absorbed in the solvent without a chemical reaction. The amount of N₂ absorbed in the solvent depends on a molecular structure of the solvent, such as molar volume.

The N₂ absorption properties of room temperature ionic liquids (RTILs) have recently been investigated by many researchers [9-12]. RTILs have an inherent designer nature, in that many of their physicochemical properties, including their gas absorption properties, can be tuned by making appropriate variations to the cation and anion pair comprising the solvent. Camper et al. [9] proposed that the amount of N₂ absorbed in a RTIL is strongly dependent on its molar volume. This molar volume of

RTILs can be easily changed by changing the size of their cation or anion. Therefore, if an RTIL was used as the solvent for a FTM, the N₂ permeability of the membrane could be reduced by controlling the cation and/or anion sizes of the RTILs.

We previously reported the use of amino acid ionic liquid (AAIL)-based membranes as FTMs [13,14]. The AAILs allowed for a large amount of CO₂ absorption because they possess a CO₂ reactive amine group [15-17], and the AAIL-based FTMs therefore showed high CO₂ permeability. With regard to N₂ permeation, the N₂ permeability could be controlled by designing the structure of the AAIL because AAILs are ionic liquids, i.e. “designer solvents” [18].

In this work, we have proposed a methodology for improvement of the CO₂ selectivity of AAIL-based FTMs by reducing N₂ permeability. AAILs with a series of cation size were synthesized and the effects of the cation size on the amount of gas absorption in the AAIL and gas permeability of the AAIL-based FTM were systematically investigated both experimentally and theoretically.

2. Experimental

2.1. Reagents

Tetrabutylphosphonium hydroxide ([P₄₄₄₄][OH], 40 wt% in water), trihexyl(tetradecyl)phosphonium bromide ([P₆₆₆₁₄][Br], ≥ 95%), acetonitrile (> 99.9%) and anion exchange resin (OH type) were purchased from Sigma Aldrich (St. Louis, MO, USA). Glycine was purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Methanol (99.8%) was purchased from Wako Pure Chemicals Industry Ltd. (Osaka, Japan). Triethyl(pentyl)phosphonium bromide ([P₂₂₂₅][Br], 50 wt% in water) was purchased from Nippon Chemical Industrial Co., Ltd. (Tokyo, Japan). All of the reagents were used as received. CO₂ and N₂ gases of 99.9% purity were used for the gas permeation tests. A hydrophilic polytetrafluoroethylene (PTFE) microporous membrane with an average pore size of 0.1 μm and a film thickness of 37.5 μm was purchased from Sumitomo Electric Industries Ltd. (Osaka, Japan) and used as a support for the AAIL-based membranes.

Tetrabutylphosphonium glycinate ([P₄₄₄₄][Gly]) was synthesized according to a previously reported neutralization procedure [15]. An aqueous solution of [P₄₄₄₄][OH] (50.0 g) was added to an aqueous solution of glycine containing 1.05 molar equivalent of the appropriate glycine to prepare the [P₄₄₄₄][AA] salts. The product was collected by filtration and dried in vacuo for 12 h at 313 K. The material was then added to a mixture of acetonitrile/methanol to allow for any unreacted glycine to be removed by sequential crystallization and filtration, and the resulting filtrate was collected and

evaporated to remove solvents. The reaction ratio of $[P_{4444}][Gly]$ was 99.9%.

Trihexyl(tetradecyl)phosphonium glycinate ($[P_{66614}][Gly]$) was synthesized using a previously reported anion exchange and neutralization procedure [16]. $[P_{66614}][Br]$ (40.0 g) was dissolved in methanol (80.0 g), and the resulting solution was treated with a basic anion exchange resin (142.0 g) to form $[P_{66614}][OH]$. The mixture was then filtered before being treated with the appropriate glycine (1.1 molar equivalents) and stirred for 24 h at room temperature. Cold acetonitrile was added to the mixture to precipitate any unreacted glycine, which was removed by filtration, and the resulting filtrate was evaporated to remove solvents. The reaction ratio of $[P_{66614}][Gly]$ was 91.2%.

Triethyl(pentyl)phosphonium glycinate ($[P_{2225}][Gly]$) was synthesized by similar procedure to $[P_{66614}][Gly]$ except the source solution. A commercial aqueous solution of $[P_{2225}][Br]$ (50.0 g) was used as the source solution and treated with a basic anion exchange resin (190.0 g). The reaction ratio of $[P_{2225}][Gly]$ was 91.9%.

The structures of the resulting $[P_{66614}][Gly]$, $[P_{4444}][Gly]$ and $[P_{2225}][Gly]$ products were confirmed by 1H -NMR and FT-IR analyses, as shown in the electronic supplementary material. The chemical structures of the different AAILs are shown in Fig. 1.

2.2. Measurement of AAILs properties

The viscosities of the AAILs were measured before and after CO_2 absorption with an ElectroMagnetically Spinning Sphere Viscometer (EMS-1000W, Kyoto Electronics Manufacturing Co., Ltd., Kyoto, Japan), using a metallic sphere at a constant rotating speed of 1000 rpm. The CO_2 saturated AAILs for the viscosity measurements were prepared by bubbling CO_2 through the AAILs at room temperature. The viscosities were measured at temperatures in the range of 303 to 373 K.

The densities of the AAILs were measured using a density/specific gravity meter (DA-650, Kyoto Electronics Manufacturing Co., Ltd.). The densities were measured at temperatures in the range of 303 to 363 K.

2.3. Absorption of N_2 in AAILs

The apparatus used to measure N_2 absorption isotherms is illustrated in Fig. 2. The temperature of the system was controlled by a water bath (T-105B, Thomas Kagaku Co., Ltd., Tokyo, Japan) at constant temperature with an accuracy of ± 0.1 K. The equipment consisted of stainless steel tubes, and reference and sample cells. The volumes of both the reference and sample cells were determined by the following experiments. The reference cell was pressurized to the desired pressure with N_2 and the sample cell was

evacuated by closing the valve separating the two cells. The experiments basically consisted of measuring the pressure drop when the valve was opened. The measurements were conducted with and without a stainless ball, which acted as a known volume, placed in the sample cell. Using the measurements from these experiments, it was possible to generate two equations with two unknowns:

$$P_1 V_{\text{ref}} = P_2 (V_{\text{ref}} + V_{\text{sam}}) \quad (1)$$

$$P_1' V_{\text{ref}} = P_2' \{V_{\text{ref}} + (V_{\text{sam}} - V_{\text{ball}})\} \quad (2)$$

Where P_1 (or P_1') (Pa) and P_2 (or P_2') (Pa) are the pressure before and after opening the valve. V_{ref} (m^3) and V_{sam} (m^3) are the reference and sample cell volumes. V_{ball} (m^3) is a known volume of the stainless ball. These equations were subsequently solved for both the reference and sample cell volumes of the apparatus.

To begin the absorption experiments, AAIL (5.0 g) was added to the sample cell, and the experiments were conducted according to the following procedure. The reference and sample cells were evacuated and the valve separating the two cells was then closed. The reference cell was pressurized with a known amount of N_2 and the temperature was kept constant. After the N_2 was charged, the stirrer was turned on and the AAIL was stirred at a constant rate throughout the experiment. The N_2 absorption was started when the valve connecting the two cells was opened. Once the valve was opened, the N_2 in the reference cell was transferred into the sample cell, bringing the N_2 into contact with the AAIL. This mixing led to a drop in the pressure which was caused by the absorption of N_2 in the AAIL. The pressure was measured by a digital pressure gauge (MODEL AM-756 digital manometer, GE Sensing & Inspection Technologies CO., Ltd., Tokyo, Japan). The pressure was monitored until it became constant for more than 1 h, with equilibration generally being achieved within 30 min. After the system reached equilibrium, the final pressure was measured and the amount of N_2 absorption was determined from the observed pressure change.

2.4. Preparation of AAIL-FTMs

The AAIL-based membranes were prepared as follows. A hydrophilic PTFE microporous membrane was immersed into the synthesized AAILs (i.e., $[\text{P}_{66614}][\text{Gly}]$, $[\text{P}_{4444}][\text{Gly}]$ and $[\text{P}_{2225}][\text{Gly}]$) and immediately decompressed for 1 h to allow for the air in the PTFE membrane to be completely exchanged with ionic liquid. The ionic liquid impregnated in the PTFE membrane was taken out and the excess ionic liquid was wiped from the surface.

2.5. Gas permeability measurements

A diagram of the experimental setup is shown in Fig. 3. The gas permeability of the membrane was measured using a flat-type permeation cell placed in a thermostat oven (Yamato Scientific Co., Ltd., Tokyo, Japan), which was adjusted to the desired temperature. The permeation cell was made of stainless steel and had an effective permeation area of 2.88 cm². The N₂ and CO₂ flow rates were controlled by mass flow controllers (Hemmi Slide Rule Co., Ltd., Tokyo, Japan). A model feed gas was prepared by mixing N₂ and CO₂ with specific flow rates. No water vapor was added to the feed gas. The total flow rate of the feed gas was adjusted to 1.49×10⁻⁴ mol/s at a temperature of 298 K and a pressure of 101.3 kPa. The feed gas was pre-heated with a coiled heat exchanger and introduced into the cell. The pressure on the feed side was kept constant at atmospheric pressure. Helium was supplied to the permeate side of the cell as a sweep gas through a coiled heat exchanger at a flow rate of 2.98×10⁻⁵ mol/s at a temperature of 298 K and a pressure of 101.3 kPa. The sweep side pressure was also kept constant at almost atmospheric pressure. The flow rates of the dried streams were measured using soap-film flow meters (Horiba Stec Ltd., Kyoto, Japan). The dried sweep gas was sent to a gas chromatograph (GC-8A, Shimadzu Co., Kyoto, Japan) equipped with an activated carbon column (1 m) to determine the composition of the permeate. Each test was performed for more than 3 h until the differences in the peak areas for N₂ and CO₂ measured by GC became less than 1%.

3. Result and discussion

3.1. Viscosity measurement of AAILs

In solution-diffusion model, gas permeation through a membrane can be described by multiplying the concentration gradient of the gas in the membrane by the diffusion coefficient [19]. The flux of gas permeation, J , can then be expressed as follows:

$$J = \frac{\varepsilon}{\tau} \frac{D}{\delta} (C_f - C_p) \quad (3)$$

Where ε (-), τ (-) and δ (m) are the porosity, tortuosity and thickness of the support membrane, respectively, D (m²/s) is the molecular diffusion coefficient of the solute in the membrane, and C_f (mol/m³) and C_p (mol/m³) are the concentrations of the gas near the surface of the membrane at the feed and permeate sides, respectively. In this study, we wanted to focus on the effect of the amount of gas absorption. Thus, it was necessary to select a preferred set of experimental conditions which would have a relatively small effect on the diffusion coefficient of the gas permeability of the AAIL-based FTM. It has been reported that the viscosities of AAILs increase significantly with CO₂ absorption

[19]. It is also well known that the diffusion coefficient is strongly dependent on the viscosity. The viscosities of the AAILs synthesized in this study were therefore measured and investigated before and after CO₂ absorption to establish experimental conditions that were capable of revealing small differences in the viscosities among three synthesized AAILs. Fig. 4 shows the effect of temperature on the viscosities of the AAILs before and after CO₂ absorption. It has been reported that the viscosities of ILs can be adequately described by the modified Vogel-Fulcher-Tammann (VFT) equation [20,21]:

$$\eta = AT^{0.5} \exp\left(-\frac{k}{T-T_0}\right) \quad (4)$$

Where A , k and T_0 are fitting parameters and T (K) is the temperature. The fitting parameters were obtained for three AAILs based on the data shown in Fig. 4 and are listed in Table 1. Within a wide temperature range, the modified VFT equation can be used to estimate not only the viscosities of the pure ILs but also the viscosities of two-component liquids, regardless of their composition. The predicted viscosities obtained using the modified VFT equation are shown in Fig. 4 together with the experimental data. As shown in Fig. 4, the viscosities of [P₆₆₆₁₄][Gly], [P₄₄₄₄][Gly] and [P₂₂₂₅][Gly] increased with CO₂ absorption, and these increases were attributed to the formation of hydrogen bonding networks between the AAIL-CO₂ complexes [22,23]. Following the CO₂ absorption, the viscosities of the different AAILs were reduced significantly with increasing temperature because the hydrogen bonding networks were being broken by heating. It is also noteworthy that the viscosities of the AAILs after CO₂ absorption showed almost the same value at 373 K, which indicated that the effect of the diffusion coefficient on the gas permeability was relatively small for three AAILs at 373 K. Based on these results, our work towards improving the N₂ barrier properties by controlling the amount of N₂ absorbed in the AAILs was investigated at 373 K.

3.2. Density and molar volume of AAILs

It has been reported that the amount of N₂ absorbed in an RTIL is predominantly dependent on its molar volume if the temperature is kept constant [9-12]. It is therefore necessary to measure the molar volume at 373 K to predict the amount of N₂ absorbed at 373 K. The molar volume can be calculated by multiplying the molecular weight by the reciprocal of density. In this study, the densities of the AAILs at 373 K were estimated using the linear relationship between the density and the temperature. Fig. 5(a) shows the effect of temperature on the density. As shown in Fig. 5(a), the densities

of the AAILs were of the order $[P_{2225}][\text{Gly}] > [P_{4444}][\text{Gly}] > [P_{66614}][\text{Gly}]$ at all of the temperatures studied. The densities of the AAILs became higher as the size of the cation decreased. This result is reasonable because the amount of molecule per unit volume increases as the size of the molecule decreases. From the results shown in Fig. 5(a), we were able to establish a linear relationship between the density of the AAILs and the temperature. The molar volumes of the AAILs were then calculated using the molar weight and density values. Fig. 5(b) shows the effect of temperature on the molar volume of the AAILs. As shown in Fig. 5(b), the molar volumes were of the order $[P_{66614}][\text{Gly}] > [P_{4444}][\text{Gly}] > [P_{2225}][\text{Gly}]$ at all of the temperatures studied, including 373 K, and it was assumed that the order of the N_2 absorption amounts would be $[P_{66614}][\text{Gly}] > [P_{4444}][\text{Gly}] > [P_{2225}][\text{Gly}]$ at 373 K.

Based on these results, it appears plausible to suggest that the molar volume of an AAIL can be successfully controlled according to the size of the cation used in the AAIL. It therefore follows naturally that the N_2 absorption amount could also be controlled in the same way.

3.3. N_2 absorption test

Fig. 6 shows the experimental for the N_2 absorption isotherms of the different AAILs. In general, the physical dissolution can be described according to the following equation:

$$C_{\text{N}_2} = H_{\text{N}_2} p_{\text{N}_2} \quad (5)$$

Where H_{N_2} is the Henry's constant ($\text{mol}/(\text{m}^3 \cdot \text{kPa})$), and C_{N_2} and p_{N_2} are the concentration of N_2 in the AAIL and the partial pressure of N_2 , respectively. The H_{N_2} values were determined for each AAIL to demonstrate a good correlation between the lines calculated according to Eq. 5 and the experimental absorption isotherms. The calculated Henry's constants are listed in Table 2. As shown in Fig. 6, the AAILs absorbed different amount of N_2 in the order $[P_{66614}][\text{Gly}] > [P_{4444}][\text{Gly}] > [P_{2225}][\text{Gly}]$ at every temperature. This order was the same as that obtained for the molar volumes of the AAILs, as shown in Fig. 5(b). In this study, it was not possible to conduct an N_2 absorption test at 373 K because of the limitations of our experimental apparatus, and the N_2 absorption isotherm at 373 K was therefore theoretically predicted. To predict the amount of N_2 physically absorbed at 373 K, the thermodynamic constants of the entropy for the physical absorption (ΔS_{N_2}) and the enthalpy for the physical absorption (ΔH_{N_2}) were determined using the following van't Hoff relationships:

$$\ln H_{\text{N}_2} = -\frac{\Delta H_{\text{N}_2}}{RT} + \frac{\Delta S_{\text{N}_2}}{R} \quad (6)$$

The plots based on Eq. 6 for [P₆₆₆₁₄][Gly], [P₄₄₄₄][Gly] and [P₂₂₂₅][Gly] are shown in Fig. 7. As shown in Fig. 7, all of these plots showed linear relationships. The ΔS_{N_2} and ΔH_{N_2} values were determined from the intercept and slope, respectively, and are listed in Table 3. The N₂ absorption isotherms of [P₆₆₆₁₄][Gly], [P₄₄₄₄][Gly] and [P₂₂₂₅][Gly] at 373 K were calculated using the thermodynamic parameters summarized in Table 3. In addition, the calculated Henry's constants for all three of the AAILs at 373 K are shown in Table 2. Fig. 8 shows the calculated isotherms for all three of the AAILs at 373 K. As was the case at the other temperatures, the amount of N₂ absorbed in the AAILs also decreased as the size of the cation decreased at 373 K. From these results, it is plausible to suggest that the N₂ absorption amount can be successfully controlled by controlling the size of the cation. It was envisaged that a CO₂ separation membrane with high N₂ barrier properties could be fabricated using an AAIL with a small cation such as [P₂₂₂₅][Gly].

3.4. Gas permeation properties of AAIL-based FTMs

The effect of CO₂ partial pressure on the gas permeation properties of the AAIL-based FTMs was investigated. The experimental conditions for the gas permeation test are shown in Table 4 and the corresponding results are shown in Fig. 9. As shown in Fig. 9(a), the order of the N₂ permeability for the three AAIL-based FTMs was [P₆₆₆₁₄][Gly] > [P₄₄₄₄][Gly] > [P₂₂₂₅][Gly]. This order was identical to that observed for the amount of N₂ absorbed in each AAIL (Fig. 8). In contrast, as shown in Fig. 9(b), the CO₂ permeabilities for the three AAIL-based FTMs were of the order [P₂₂₂₅][Gly] > [P₄₄₄₄][Gly] > [P₆₆₆₁₄][Gly]. This increase in the CO₂ permeability with decreasing cation size in the AAILs was attributed to increases in the CO₂ absorption amount, because this amount would increase as the number of amine groups per unit volume increased. Consequently, the [P₂₂₂₅][Gly]-FTM showed better CO₂/N₂ selectivity, as shown in Fig. 9(c).

Instead of focusing on the dependence of the CO₂ partial pressure on the CO₂ permeability, the CO₂ permeability of the AAIL-based FTMs underwent significant reduction with increasing CO₂ partial pressure. This trend was attributed to the carrier in the FTM becoming saturated with CO₂ [2]. In contrast, no discernible changes were noted in the N₂ permeability of the AAIL-based FTMs following increases in the CO₂ partial pressure because the permeation mechanism is the solution-diffusion mechanism. In conclusion, it was suggested that the CO₂ separation performances of the AAIL-based FTMs could be improved by controlling the molar volumes of the AAILs, which contribute to both the N₂ barrier property and CO₂ permeability of the FTMs.

Finally, the N₂ permeation behaviors through all three of the AAIL-based FTMs were investigated using theoretical considerations. According to Eq. 3, the diffusion coefficient and transmembrane concentration gradient would be required to predict the N₂ permeability through the membrane. The concentration of dissolved N₂ can be determined using Henry's law (Eq. 5). Therefore, by substituting Eq. 5 into Eq. 3, the flux and permeability of N₂ through an AAIL-based FTM can be expressed according to Eqs. 7 and 8, respectively.

$$J_{N_2} = \frac{\varepsilon}{\tau} \frac{D}{\delta} H_{N_2} (p_{N_2,f} - p_{N_2,p}) \quad (7)$$

$$R_{N_2} = D_{\text{eff}} H_{N_2} \quad (8)$$

Where the subscripts “f” and “p” denote the feed and permeate sides, respectively, and D_{eff} is the effective diffusion coefficient, which takes into account the effects of porosity and tortuosity.

$$D_{\text{eff}} = \frac{\varepsilon}{\tau} D \quad (9)$$

A general form for the effective diffusion coefficients of the RTILs has been given as follows [24-27]:

$$D_{\text{eff}} = B \frac{V_{\text{IL}}^a}{\eta_{\text{IL}}^b V_1^c} \quad (10)$$

Where B , a , b and c are the fitting parameters, η_{IL} is the viscosity of the RTIL, V_{IL} is the molar volume of the IL (cm³/mol), and V_1 is the molar volume of the gas dissolved in the IL. By substituting Eq. 10 into Eq. 8, it was possible to calculate the N₂ permeabilities for different CO₂ partial pressures when B , a , b and c are obtained. The calculated lines are shown in Fig. 9(a). In the calculation, the values of B , a , b and c were 2.3×10^{-9} (-), 0.5, 0.5 and 0.5 for all AAILs, respectively. V_1 was 31.2 cm³/mol as the molar volume of N₂. The calculated effective diffusion coefficients are listed in Table 5. The difference of the effective diffusion coefficients was caused from the differences of the molar volume and the viscosity of the AAILs with different cation size. However, it can be considered that the effect of viscosity was much smaller than the effect of molar volume under the experimental condition of the gas permeation tests because the viscosities of each AAIL at 373 K were almost same as shown in Fig. 4. Therefore, the molar volume of the AAILs mainly affected the difference of the effective diffusion coefficient among the AAIL-based FTMs. As shown in Fig. 9(a), the calculated results for the N₂ permeabilities of the AAIL-based FTMs were in good agreement with the experimental data. The ratio of Henry's constants and that of diffusion coefficients for each AAIL were

calculated to confirm each contribution of solubility change and diffusivity change to the N₂ permeability change. The calculated ratio of the Henry's constants and the effective diffusion coefficients for each AAIL were listed in Table 6. As shown in Table 6, the decrease of the solubility with the decrease of AAIL size was almost same as that of effective diffusion coefficient. This means that the decrease of both solubility and effective diffusion coefficient with decreasing the AAIL size brought about the N₂ permeability decrease. Concerning them, the decrease of the diffusion coefficient is not preferable for improvement of the selectivity because the decrease of the N₂ diffusion coefficient also cause the decrease of the CO₂ diffusion coefficient. In contrast, the N₂ solubility of the AAILs can be separately controlled from their CO₂ solubility because N₂ is dissolved physically, while CO₂ is dissolved chemically. With this in mind, the decrease of the N₂ permeability with controlling the gas solubility which easily controlled by designing the cation size in the AAILs is preferable methodology for improving the selectivity of the AAIL-based FTMs.

4. Conclusion

AAILs with containing a series of cations of different sizes were synthesized and the effects of the cation size on their gas absorption and gas permeability properties were systematically investigated. Their physical properties, including viscosity, density and molar volume were also determined. The use of an AAIL with a small cation could lead to a reduction in the N₂ permeability, whereas the CO₂ permeability kept at high value. Among three AAILs used in this study, [P₂₂₂₅][Gly]-FTM showed the best N₂ barrier property and CO₂/N₂ selectivity at high temperature. The amount of N₂ absorbed in [P₂₂₂₅][Gly] was remarkably small compared to the other AAILs investigated in this study because the [P₂₂₂₅][Gly] had the smallest molar volume. In addition, the effective N₂ diffusivity was also smallest in the case of [P₂₂₂₅][Gly]. These two factors brought about the low N₂ permeability and high CO₂ selectivity. As mentioned above, we showed that the AAIL-based FTMs with both high N₂ barrier and high CO₂ permeation properties could be fabricated by decreasing the size of the cation in the AAILs.

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Figures

Fig. 1. Chemical structures of the amino acid liquids used in this study ([Px][Gly]; X=tetrabutyl, trihexyl(tetradexyl) and triethyl(pentyl)).

Fig. 2. Schematic diagram of the apparatus used for the gas absorption tests.

Fig. 3. Schematic diagram of the apparatus used for the gas permeation tests.

Fig. 4. Effect of temperature on the viscosity of the AAILs. (a) before CO₂ absorption and (b) after CO₂ absorption. The points and lines show experimental data and results calculated according to the modified VFT model, respectively.

Fig. 5. Effect of temperature on the properties of the AAILs. (a) density and (b) molar volume.

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Fig. 8. Calculated N₂ absorption isotherms of the AAILs at 373 K.

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Tables

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Table 1

Fitting parameters for the VFT equation.

	Before CO ₂ absorption			After CO ₂ absorption		
	A	k	T_0	A	k	T_0
[P ₆₆₆₁₄][Gly]	0.0245	725	200	0.00550	800	248
[P ₄₄₄₄][Gly]	0.0450	600	203	0.135	530	252
[P ₂₂₂₅][Gly]	0.0120	680	208	0.0170	647	216

Table 2

Henry's constant for the AAILs.

	Henry's constant (mol/(m ³ kPa))				
	313 K	323 K	333 K	343 K	373 K
[P ₆₆₆₁₄][Gly]	0.31	0.25	0.20	0.17	0.10 ^a
[P ₄₄₄₄][Gly]	0.29	0.22	0.17	0.14	0.074 ^a
[P ₂₂₂₅][Gly]	0.27	0.20	0.15	0.12	0.060 ^a

^aCalculated parameters from Eq. 6.

Table 3Thermodynamic constants the N₂ absorption into the AAILs.

	ΔH_{N_2} kJ/mol	ΔS_{N_2} J/(K·mol)
[P ₆₆₆₁₄][Gly]	-18.1	-125.0
[P ₄₄₄₄][Gly]	-21.8	-137.6
[P ₂₂₂₅][Gly]	-24.3	-146.1

Table 4

Experimental conditions for the gas permeation test.

Conditions		
Temperature		373 K
Pressure	Feed	101.3 kPa
	Sweep	101.3 kPa
Partial pressure difference	CO ₂	2.5, 5.0, 10, 25, 35, 50 kPa
Pressure difference		0 kPa
Gas flow rate (dry base)		
Feed	Total	200 mL/min
	CO ₂	5, 10, 20, 50, 70, 100 mL/min
	N ₂	balance
	He	40 mL/min
Sweep		

Table 5

Calculated effective diffusion coefficients for the AAILs at 373 K.

	[P ₆₆₆₁₄][Gly]	[P ₄₄₄₄][Gly]	[P ₂₂₂₅][Gly]
D_{eff} (m ² /s)	7.04×10^{-10}	5.12×10^{-10}	4.50×10^{-10}

Table 6

Calculated ratio of Henry's constants and effective diffusion coefficients for the AAILs.

	i=[P ₂₂₂₅][Gly] j=[P ₄₄₄₄][Gly]	i=[P ₂₂₂₅][Gly] j=[P ₆₆₆₁₄][Gly]
$H_{N2,i}/H_{N2,j}$	0.81	0.60
$D_{eff,i}/D_{eff,j}$	0.88	0.64