Effect of the amino-group densities of functionalized ionic liquids on the facilitated transport properties for CO₂ separation

Shohei Kasahara,[†] Eiji Kamio,[†] Abdul Rajjak Shaikh,[†] Tatsuya Matsuki,[†] and Hideto Matsuyama^{*,†}

[†]Center for Membrane and Film Technology, Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe, Hyogo 657-8501, Japan

*Corresponding author. Tel: +81-78-803-6180; Fax: +81-78-803-6180; Email: matuyama@kobe-u.ac.jp

Abstract

Amino acid ionic liquids (AAILs) composed of different sizes and numbers of amino groups, including tetrabutylammonium glycinate, tetramethylammonium glycinate, and 1,1,1-trimethylhydrazinium glycinate, were synthesized as CO₂ carriers for facilitated transport membranes. The physical properties of the fabricated AAILs, such as density, viscosity, and N₂ and CO₂ absorption capacities, were measured, and the fractional free volume was calculated using molecular dynamics (MD) simulations. The results showed that the molar and fractional free volumes decreased with decreasing AAIL size, which caused increased CO₂ absorption and decreased N₂ absorption. In addition, the CO₂ absorption increased with higher numbers of amino groups in the AAILs. The gas permeation properties of facilitated transport membranes containing the synthesized AAILs were investigated. The small AAILs with two amino groups showed better CO₂ permeability and N₂ barrier properties under humid conditions. We propose that ionic liquids optimized as CO₂ carriers for facilitated transport membranes under humid conditions should have high amino-group density, which could be realized by decreasing the molecular size and introducing more amino groups in the molecule.

Keywords

Gas separation, Carbon dioxide, Facilitated transport membrane, Amino acid ionic liquid, Gas absorption properties

1. Introduction

With the growing awareness of global warming and serious climate change, energy-efficient and cost-effective technology for CO₂ separation is urgently required. The most widely used technology for CO₂ separation is an amine-based absorption process. However, aqueous-amine absorption

processes have disadvantages, including high energy costs, solvent loss, and corrosion effects. Recently, membrane technology has gained importance as a potential alternative to conventional technologies because of its advantages such as low capital and operating costs, low energy consumption, and ease of operation.[1] However, practical application of CO₂ separation membranes remains challenging despite extensive research in this field. Poor separation performance, in particular, low CO₂ permeability, is a weakness of membranes that restricts their industrial application. The fabrication of a high-performance membrane for CO₂ separation would reduce membrane requirements and lead to more compact processing equipment and lower capital costs. The CO₂ separation performance is determined by CO₂ permeability and other gas barrier properties. Therefore, from a practical perspective, it is necessary to design and fabricate a membrane with high CO₂ permeability and other gas barrier properties.

With respect to polymer membranes, a trade-off exists between the CO₂ permeability and CO₂ selectivity versus other gases; this results in an upper limit to membrane performance.[2] The CO₂ separation membranes utilizing ionic liquids as a CO₂ separation medium in a membrane, which have attained great attention recently, have the same trade-off and almost same upper limit as the polymer membranes.[3] That is because the CO₂ permeation mechanism of the membranes are based on solution-diffusion mechanism. On the other hand, a membrane containing CO₂-reactive compounds can achieve very high CO₂ permeation through significant enhancement of CO₂ absorption while maintaining low permeability to other gases. Such special membranes, which are known as facilitated transport membranes (FTMs), have considerable potential for applications that require good CO₂ separation,[4-10] and have shown membrane performance beyond the upper limits.

Recently, we developed a new class of FTM containing amino acid ionic liquids (AAILs), which are a type of amine-functionalized ionic liquid, and reported their excellent CO₂ permeability and CO₂/N₂ selectivity.[11-14] The advantages of AAILs as a component of FTMs include high CO₂ absorption and lack of volatility.[15-17] In addition, the molecular structures of AAILs are flexible for versatile design. Therefore, it is easy to tune the chemical structures of AAILs to be suitable for CO₂ transport in FTMs. For example, we proposed an FTM containing an AAIL composed of a compact cation and anion pair. Using the compact AAIL, the CO₂ selectivity was successfully improved owing to the considerable N₂ barrier properties resulting from the small free volume of the AAIL.[13] From the CO₂ permeation perspective, there remain many options to increase the CO₂ permeability by tuning the molecular structure of AAILs. Herein, we propose an AAIL with high amino-group density as an effective CO₂ carrier in FTMs. Increasing the amino-group density is a promising methodology to enhance both the CO₂ absorption and permeability of the FTM.

To enhance the amino-group density, we designed an AAIL composed of a pair of the smallest anion and cation containing amino groups. The compact cation and anion pair not only decreases the

free volume of the AAIL but also increases the number of amino groups per unit of AAIL volume. Although typical AAILs contain an amino group in the anion, the introduction of an additional amino group in the cation, i.e., dual amino-functionalization, is a straightforward way to increase the amino-group density and CO₂ absorption capacity of the AAILs. It was reported that the CO₂ absorption of dual amino-functionalized AAILs (dual AAILs), which have two amino groups on the cation and anion, increased two-fold over that of an AAIL with only one amino group in the anion.[18] Accordingly, we synthesized a dual AAIL constructed using small cations and anions on the basis of the above guidelines and investigated the resultant CO₂ absorption properties of the dual AAIL and CO₂ permeation properties of the dual AAIL-based FTM.

2. Experimental

2.1 Reagents

Glycinate was chosen as the anion for the AAILs because it is the smallest amino acid. Tetrabutylammonium glycinate ([N₄₄₄₄][Gly]) was synthesized as a basic AAIL. Tetramethylammonium glycinate ([N₁₁₁₁][Gly]) and 1,1,1-trimethylhydrazinium glycinate ([aN₁₁₁][Gly]) were used as a small AAIL with low N₂ absorption ability and small dual AAIL with high CO₂ and low N₂ absorption abilities, respectively. The chemical structures of these three AAILs are shown in Fig. 1.

Tetrabutylammonium hydroxide ([N₄₄₄₄][OH], 40 wt% in water), tetramethylammonium hydroxide ([N₁₁₁₁][OH], 25 wt% in water), 1,1,1-trimethylhydrazinium iodide ([aN₁₁₁][I], ≥97%), 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%) and ethanol (99.5%) were purchased from Wako Pure Chemicals Industry Ltd. (Osaka, Japan). All reagents were used as received. [N₄₄₄₄][Gly] and [N₁₁₁₁][Gly] were synthesized according to a previously described neutralization procedure (see Supplementary material).[16] [aN₁₁₁][Gly] was synthesized using a previously described anion exchange and neutralization procedure (see Supplementary material).[17] The structures of the resulting [N₄₄₄₄][Gly], [N₁₁₁₁][Gly], and [aN₁₁₁][Gly] products were confirmed by ¹H NMR (Bruker Advance 500, Bruker BioSpin, Kanagawa, Japan) and FT-IR (ALPHA FT-IR Spectrometer, Bruker Optics, Tokyo, Japan) spectroscopy (see Supplementary material and Fig. S1).

CO₂ and N₂ gases with 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 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.

2.2 Physicochemical properties of the AAILs

2.2.1 Density and viscosity measurements

Samples for density and viscosity measurements were prepared by drying the synthesized AAILs for 12 h at 343 K. The densities of the AAILs were measured using a density/specific gravity meter (DA-650, Kyoto Electronics Manufacturing Co., Ltd., Kyoto, Japan). The densities were measured at temperatures in the range of 303 to 363 K.

The viscosities of the AAILs were measured using an electromagnetically spinning sphere (EMS) viscometer (EMS-1000W, Kyoto Electronics Manufacturing Co., Ltd.) using a metallic sphere at a constant rotation speed of 1000 rpm. Using the EMS viscometer, the viscosity of the liquids in an environment with the desired gas composition in which the liquids absorbed the contacting gases can be measured. In this study, the viscosities of the AAILs in contact with humid CO₂ in a sample vessel were continuously measured. For the measurements, the gas inlet and outlet channels were placed at the top of the sample vessel. A schematic illustration of the viscosity measurement system is shown in Fig. 2.

For the viscosity measurements of the AAILs in the absence of CO₂, a certain portion of the AAIL sample was introduced into the vessel, and then the gas inlet and outlet channels were closed. For the investigation of the temperature, dried AAILs were used. The measurements were carried out at temperatures in the range of 303 to 373 K. The effect of the water content of the AAILs was investigated using AAILs containing a certain amount of pure water. The measurements were performed at 373 K.

During the investigation of the effect of water vapor on the viscosities of CO₂-absorbed AAILs, the viscosity was continuously measured during subsequent introductions of dry and humid CO₂. In this case, the inlet and outlet channels were opened, and the gas was continuously introduced into the sample vessel. The concentration of CO₂ and relative humidity (RH) of the humid gas was adjusted by controlling the flow rate of CO₂ and water vapor using a mass-flow controller (Hemmi Slide Rule Co, Ltd., Tokyo, Japan) and a reciprocating metering pump (Nihon Seimitsu Kagaku Co. Ltd., Japan), respectively. The RH of the gas was adjusted by introducing the desired amount of water, which was completely vaporized. The experiments were carried out at 373 K.

2.2.2 Gas absorption properties of the AAILs

The apparatus used to measure the gas absorption isotherms is illustrated in Fig. 3. This apparatus has a water injection port to measure the gas absorption under saturated water vapor conditions. The temperature of the system was controlled by a water bath (T-105B, Thomas Kagaku Co., Ltd., Tokyo, Japan) with an accuracy of ± 0.1 K. The pressure was monitored by a digital pressure gauge (MODEL AM-756 digital manometer, GE Sensing & Inspection Technologies Co., Ltd., Tokyo, Japan). The equipment consisted of stainless steel tubes along with reference and sample cells. The volumes of both the reference and sample cells were determined before the

absorption experiments.[14] In this study, CO₂ and N₂ absorption tests were carried out under different conditions. Each test was conducted according to the following procedures.

2.2.2.1 CO₂ absorption tests

The CO₂ absorption test was carried out at 343 K at 100% RH. Initially, AAIL (1.5 g) was added to the sample cell. The reference and sample cells were evacuated, and the valve separating the two cells was then closed. A known amount of water that was sufficient to achieve 100% RH was added to the reference cell. The pressure was monitored until it became constant. The pressure increase was confirmed to be equal to the saturated water vapor pressure. The valve separating the two cells was then opened to allow contact between the water vapor and AAIL. After the AAIL fully absorbed the water vapor, the valve was closed. The remaining amount of water in the reference cell was calculated from the amount of water added and saturated water vapor pressure, and the actual volume of the cells excluding water was recalculated. The reference cell was then pressurized to the desired pressure by introducing CO₂ from a CO₂ cylinder. After the CO₂ was charged, the stirrer was turned on, and the AAIL was stirred at a constant rate throughout the experiment. CO₂ absorption began when the valve connecting the two cells was opened. Once the valve was open, the CO₂ in the reference cell transferred into the sample cell, bringing the CO₂ into contact with the AAIL. This mixing led to a drop in pressure caused by absorption of CO₂ by the AAIL. The pressure was monitored until it remained constant for more than 1 h, with equilibration generally achieved within 3 h. After the system reached equilibrium, the final pressure was measured, and the amount of CO₂ absorption was determined from the observed pressure change.

2.2.2.2 N₂ absorption tests

In this study, we focused on the CO₂ permeation properties of AAIL-FTMs under humid conditions. Therefore, it was preferable to measure the N₂ absorption properties under humid conditions. However, under humid conditions, both water and nitrogen are present in the system. Because the N₂ absorption of the AAILs was quite low, the pressure drop upon N₂ absorption would also be very small. Therefore, the relative pressure fluctuation caused by water evaporation and condensation cannot be neglected; accordingly, we cannot accurately measure the amount of N₂ absorbed under humid conditions. Hence, the N₂ absorption tests were carried out under dry conditions.

The N₂ absorption test was performed at 343 K. A known amount of the AAIL was added to the sample cell, and the N₂ absorption test was carried out using a similar procedure to that used for the CO₂ absorption test, except that no water was added.

2.3 Molecular dynamics simulations to evaluate absorption under humid conditions

Owing to the experimental limitations described above, we could not investigate the N₂ absorption of each AAIL under humid conditions. However, it is important to determine the N₂

absorption under humid conditions in order to confirm our proposed guideline for the structure of AAILs with superior N₂ barrier properties. It has been reported that the amount of N₂ physically absorbed in room temperature ionic liquids (RTILs) correlated well with the free volume of ionic liquids.[19, 20] Thus, we calculated the fractional free volume (FFV) using MD simulations and investigated the amount of N₂ absorbed in the AAILs under humid conditions. The relationship between the amount of N₂ absorbed and FFV of the AAILs was presumed via the relationship under dry conditions.

The structures were built using Material Studio version 6.1.[21] Quantum chemistry calculations were performed using the Gaussian 09 program.[22] Vibrational analyses of all calculated structures revealed a lack of imaginary frequencies, confirming the presence of true minima on the potential energy surface. The electrostatic potential surface was generated by the Merz-Kollman method at an HF/6-31G(d) level of theory, which is typical for Amber-like force fields, followed by multiconfigurationally two-stage relaxed electrostatic potential (RESP) fitting. The software code R. E. D. IV was used for the RESP fitting.[23] We used the Amber force field to determine the intra- and inter-molecular force constants for the cations and anions of the ionic liquids.[24]

2.3.1 Simulation details

We generated initial configurations of the ionic liquid using the Packmol program.[25] All simulations reported here were performed using the Gromacs 4.5 simulation program.[26] The simulated systems were composed of 384 ion pairs. Under humid conditions, we added 384 water molecules to the ionic mixture using Packmol. The configurations were then optimized by Gromacs using an energy minimization routine. The MD simulations were performed at 300 K for the neat ionic liquid to reproduce the experimental density and validate the model. Production simulations were carried out using the isothermal-isobaric (NPT) ensemble for 25 ns. The temperature and pressure were controlled with coupling times of 5 and 1 ps using the velocity-scaling [27] and Berendsen methods [28], respectively. The equations of motion were integrated with the leapfrog algorithm with a time step of 2.0 fs. The full electrostatic interactions were accounted for using the particle mesh Ewald summation.[29] Coulomb and van der Waals cutoffs of 1.2 nm were used. Periodic boundary conditions in all directions were used to mimic the bulk behavior. The bond lengths were constrained with the LINCS algorithm. After the simulation, the physical properties were characterized using Gromacs analysis tools, and the structures were visualized by visual molecular dynamics.[30] A similar procedure was followed for the ionic liquid–water mixtures.

2.3.2 Binding energy calculations

To investigate the strengths of the interactions between the cations and anions in the gas and solvent phases, density functional theory (DFT) calculations were carried out with the B3LYP

functional and 6-31+G(d,p) basis set using the Gaussian 09 program.[22] Different possible orientations of the cation and anion interactions were considered, and the minimum energy conformation was selected for the single-point energy calculations. Frequency calculations were performed to ensure that the ionic pairs were indeed at their minimum energy. Starting with an optimized geometry, single-point energy calculations were carried out using the 6-311+G(3df,2p) basis set and M05-2X functional routine. Previous studies have demonstrated that the DFT method is suitable for calculations on ILs using the method described above.[31, 32] The solvent effects were mimicked using the SMD solvation model.[33]

2.3.3 Free volume calculations

The equilibrated structures obtained after the MD simulations were selected for FFV calculations. The FFV was calculated using the following method:[34]

$$FFV = \frac{V_m - V_{vdW}}{V_m}$$

where V_{vdW} is the van der Waals volume of the molecule and V_m is the molar volume. The van der Waals radii according to Bondi were used for this calculation and were calculated using the Material Studio program.[21, 35]

2.4 Gas permeability measurements

The AAIL-based membranes were prepared as follows. A hydrophilic PTFE microporous membrane was immersed into the synthesized AAILs, i.e., $[N_{444}][Gly]$, $[N_{111}][Gly]$, and $[aN_{111}][Gly]$, and immediately decompressed for 1 h to allow complete exchange of the air in the PTFE membrane with the ionic liquid. The AAIL-impregnated PTFE membrane was removed, and the excess AAIL on the surface was wiped off.

The gas permeabilities of the AAIL-based membranes were measured according to a previously reported procedure.[11-14] In this study, the CO_2 partial pressure and relative humidity dependencies on the gas permeability was examined using the apparatus shown in Fig. 4. Details of the experimental procedure are described in the Supplementary material. The experimental conditions are listed in Table 1.

3. Results and discussion

3.1 Densities, molar volumes, and viscosities of the synthesized AAILs

It has been reported that the N_2 permeabilities of the AAIL-based FTMs as well as amounts of N_2 absorbed by AAILs depend strongly on the molar volume and free volume of the AAILs.[13] We also previously reported that the CO_2 permeabilities of AAIL-based FTMs increased with decreasing size of the AAILs.[13] Accordingly, it was suggested that the amount of CO_2 absorbed in the AAILs

increases with decreasing size of AAILs, which leads to an increase in the amount of amino groups per unit volume of AAILs. To evaluate the effect of the molecular sizes of the AAILs on their CO₂ and N₂ absorption, their molar densities and molar volumes were investigated. The densities of the AAILs at various temperatures were measured and their molar densities and molar volumes were calculated.

Fig. 5(a) shows the effect of temperature on the molar density of the AAILs. As shown in Fig. 5(a), the molar densities of the AAILs were in the following order: $[a\text{N}_{111}][\text{Gly}] \approx [\text{N}_{1111}][\text{Gly}] > [\text{N}_{4444}][\text{Gly}]$. If each type of AAIL molecule has the same number of amino groups, this order would directly relate to the order of amino-group density in the AAILs. However, the number of amino groups per molecule of $[a\text{N}_{111}][\text{Gly}]$ is twice that of the others. Therefore, the amino-group densities of the AAILs are in the following order: $[a\text{N}_{111}][\text{Gly}] > [\text{N}_{1111}][\text{Gly}] > [\text{N}_{4444}][\text{Gly}]$. If all the amino groups in each AAIL can react with CO₂, the amount of CO₂ absorbed in the AAILs should follow the same order as the amino-group density of the AAILs.

The molar volumes of the AAILs, which would strongly affect N₂ absorption, are shown in Fig. 5(b). $[\text{N}_{4444}][\text{Gly}]$, which has a large cation, showed the highest molar volume at all temperatures. The molar volumes of $[\text{N}_{1111}][\text{Gly}]$ and $[a\text{N}_{111}][\text{Gly}]$ were similar because the sizes of $[\text{N}_{1111}]^+$ and $[a\text{N}_{111}]^+$ are similar. From these results, it can be predicted that the amount of N₂ absorbed in the AAILs would be in the following order: $[\text{N}_{4444}][\text{Gly}] > [\text{N}_{1111}][\text{Gly}] \approx [a\text{N}_{111}][\text{Gly}]$.

The viscosities of the AAILs, which strongly affect the diffusivity of gases in AAIL-based FTMs, also affect the membrane performance when AAILs are used as the CO₂ carrier in FTMs. Figs. 6(a) and (b) show the effect of temperature and water content of the AAILs, respectively, on their viscosity. As shown in Figs. 6(a) and (b), the viscosities of the AAILs decreased with increasing temperature or water content of the AAILs and were in the following order: $[\text{N}_{4444}][\text{Gly}] > [a\text{N}_{111}][\text{Gly}] > [\text{N}_{1111}][\text{Gly}]$. In previous studies, it was revealed that the viscosities of AAILs after CO₂ absorption were dramatically higher than those of neat AAILs under dry conditions around room temperature.[14] The dramatic increase of the viscosity along with CO₂ absorption would be due to the formation of an intermolecular hydrogen bond network among the AAIL-CO₂ complexes.[14, 36, 37] Therefore, the viscosity of the AAIL in contact with CO₂ was the dominant factor in determining the CO₂ permeation properties of AAIL-FTMs when used under dry conditions around room temperature. However, under humid conditions, the intermolecular hydrogen bonding would be weakened by intercalation of water between the complexes. Therefore, it is expected that, under humid conditions, the marked increase in viscosity of the AAIL-CO₂ complex would be prevented. In this study, we investigated the effect of the RH on the viscosities of AAILs during contact with CO₂. The viscosity change of $[a\text{N}_{111}][\text{Gly}]$ was measured with changing water vapor content in CO₂, and the results are shown in Fig. 7. As shown in Fig. 7, the viscosity of $[a\text{N}_{111}][\text{Gly}]$ gradually increased during contact with pure CO₂; this was due to the formation of CO₂- $[a\text{N}_{111}][\text{Gly}]$

complexes and a hydrogen bonding network between the complexes. However, upon the introduction of water vapor, the viscosity drastically decreased. This was caused by destruction of the hydrogen bonding networks between the complexes because of the intercalation of water molecules. From these results, the AAIL-based FTMs would preferably be used under humid conditions.

3.2 Gas absorption tests

3.2.1 N₂ absorption

Applications of AAILs in CO₂ separation membranes involve the presence of CO₂, N₂, and water vapor around the AAILs. It is therefore reasonable to measure the amount of gas absorbed by the AAILs under such conditions to elucidate the CO₂ and N₂ permeation properties from the gas absorption abilities. However, we cannot accurately measure the amount of N₂ absorbed in the AAILs under such conditions, as described above. In this study, therefore, we calculated the FFVs of the AAILs via MD simulations and discussed the N₂ absorption in light of the computational results.

The FFVs and densities of the AAILs calculated from MD simulations, ρ_{calcd} , are listed in Table 2. First, to check the validity of the computational results, the densities before CO₂ absorption calculated from the simulation under dry conditions were compared with the experimental results; from Table 2, it is evident that the calculated and experimental densities of the neat AAILs at 300 K are nearly equal. Thus, it was confirmed that the computational results calculated in this study were reasonable.

Subsequently, we considered the FFVs of the AAILs shown in Table 2. Before CO₂ absorption under dry conditions, [N₄₄₄][Gly] had the highest FFV, i.e., about 1.6 times larger than those of [N₁₁₁][Gly] and [aN₁₁₁][Gly]. In the case of [N₁₁₁][Gly] and [aN₁₁₁][Gly], the FFVs were very similar. To investigate the relationship between the FFV and amount of N₂ absorbed, the computational results for the FFVs under dry conditions were compared with the experimentally obtained N₂ absorption amounts measured under dry conditions. The FFVs have been reported to correlate with the molar amount of N₂ absorbed per unit volume of RTIL.[19] Therefore, we used the following units to describe the amount of N₂ absorbed in the AAILs: mol-N₂/dm³-AAIL. As shown in Fig. 8(a), [N₄₄₄][Gly] absorbed the most N₂, i.e., about 1.9 times more than those of the other AAILs. [N₁₁₁][Gly] and [aN₁₁₁][Gly] absorbed very similar amounts of N₂. These tendencies were almost the same as those of the FFVs under dry conditions. From these results, it was confirmed that the amounts of N₂ absorbed strongly correlated with the FFVs of the AAILs. This correlation between FFV and amount of N₂ absorbed should also occur under humid conditions. Therefore, the amounts of N₂ absorbed by [N₄₄₄][Gly], [N₁₁₁][Gly], and [aN₁₁₁][Gly] after CO₂ absorption under humid conditions were then investigated under humid conditions. As shown in Table 2, the FFVs of the AAIL-CO₂ complexes formed after CO₂ absorption under humid conditions were in the

following order: $[N_{4444}][Gly] > [aN_{1111}][Gly] \approx [N_{1111}][Gly]$. Hence, the amounts of N_2 absorbed under humid conditions would also be in that order. From these results, it is evident that the amount of N_2 absorbed in the AAILs after CO_2 absorption under humid conditions could be reduced by decreasing the size of the AAILs.

3.2.2 CO_2 absorption

Figs. 8(b) and (c) show the amounts of CO_2 absorbed by $[N_{4444}][Gly]$, $[N_{1111}][Gly]$, and $[aN_{1111}][Gly]$ at 100% RH. In this study, we attempted to increase the amount of CO_2 absorbed by AAILs by increasing the number of amino groups per unit volume of AAIL, i.e., amino-group density. As mentioned before, the amino-group densities of the AAILs synthesized in this study are in the following order: $[aN_{1111}][Gly] > [N_{1111}][Gly] > [N_{4444}][Gly]$. Therefore, if all of the amino groups in the AAILs reacted with CO_2 , the amounts of CO_2 absorbed by the AAILs should be in the same order. The CO_2 absorption isotherms for each AAIL are shown in Fig. 8(b). $[N_{1111}][Gly]$ absorbed more CO_2 than $[N_{4444}][Gly]$, which is in agreement with the prediction from the molar densities of these AAILs. Here, it is worth noting that the amount of CO_2 absorbed by $[aN_{1111}][Gly]$ was higher than that absorbed by $[N_{1111}][Gly]$; this results from the dual amino-functionalized effect of $[aN_{1111}][Gly]$ and suggests that both amino groups in $[aN_{1111}][Gly]$ contribute to CO_2 absorption. The effect of dual amino-functionalization on the amount of CO_2 absorbed can be easily evaluated by comparing the molar amount of CO_2 absorbed per unit mole of the AAILs. As shown in Fig. 8(c), $[aN_{1111}][Gly]$ exhibited the highest CO_2 absorption because of the presence of two amino groups in each molecule. On the other hand, the CO_2 absorptions of $[N_{1111}][Gly]$ and $[N_{4444}][Gly]$ were approximately equal; this shows that the amino groups in $[N_{1111}][Gly]$ and $[N_{4444}][Gly]$ have the same CO_2 absorption properties. From these results, the superior CO_2 absorption properties of the dual amino-functionalized ionic liquid were confirmed.

Based on the above results, $[aN_{1111}][Gly]$ has suitable gas-absorption properties for application as a carrier in CO_2 separation membranes. It is expected that $[aN_{1111}][Gly]$ -based FTMs would have better CO_2 permeation properties than $[N_{4444}][Gly]$ - and $[N_{1111}][Gly]$ -based FTMs.

3.3 Gas permeation properties of AAIL-FTMs

To confirm the facilitated transport mechanism of the $[aN_{1111}][Gly]$ -based FTM, we examined the CO_2 partial pressure dependency on the CO_2 permeability. As shown in Fig. 9(a), the CO_2 permeability strongly depended on the CO_2 partial pressure. This behavior is a general trend of FTMs which is caused by the saturation of CO_2 carrier under high CO_2 partial pressure conditions. From this result, it was confirmed that $[aN_{1111}][Gly]$ -based FTM permeated CO_2 based on the facilitated transport mechanism. On the other hand, as shown in Fig. 9(b), the N_2 permeability was not depended on the CO_2/N_2 mixed gas composition because the N_2 permeation through the

membrane was based on solution-diffusion mechanism. Regarding the CO₂ permeability around 10 kPa of CO₂ partial pressure, it remained about 1000 barrer with about 50 of CO₂/N₂ selectivity as shown in Fig. 9(a) and (c), respectively. It is worthy to note that the CO₂ flux of the membrane in whole CO₂ partial pressure range investigated in this study was not depended on the CO₂ partial pressure at all. In the practical operation using a membrane module, the CO₂ partial pressure in the feed gas continuously decreased along with the CO₂ permeation in the membrane module from the upstream to the downstream because of the CO₂ permeation. In the case using normal CO₂ separation membrane of which CO₂ permeation is based on solution-diffusion mechanism, the CO₂ flux continuously decreases with the decrease of the CO₂ partial pressure in the module. However, [aN₁₁₁][Gly]-based FTM can keep its CO₂ flux in spite of the decrease of CO₂ partial pressure. That means the CO₂ flux could be kept constant in whole position in the membrane module. This is advantageous property to make the process simple.

To confirm the effect of amino group introduced in the cation of the [aN₁₁₁][Gly], the gas permeation performances of the [aN₁₁₁][Gly]-based FTMs were tested under humid conditions and compared with those of the [N₁₁₁₁][Gly]- and [N₄₄₄₄][Gly]-based FTMs. Under humid conditions, the hydrogen bonding networks between AAIL-CO₂ complexes would be only loosely formed. As a result, with increasing the humidity, the viscosities of the AAILs after CO₂ absorption would gradually decrease and become almost constant under highly humid conditions. In other words, under highly humid conditions, the gas absorption properties, and not CO₂-complex diffusion, play a key role in determining the CO₂ separation properties of the AAIL-FTMs.

As shown in Fig. 10(a), the CO₂ permeabilities of all AAILs increased with increasing RH at low RH ranges. These results suggest that the dominant factor that affects CO₂ permeation is trans-membrane diffusion of the CO₂ complex because of the relatively high viscosity under low RH conditions. On the other hand, under high RH conditions, the CO₂ permeation properties were significantly different for the AAIL types used. The CO₂ permeabilities of the FTMs containing [N₁₁₁₁][Gly] and [N₄₄₄₄][Gly] were almost constant above 50% RH. Under high RH conditions, the water contents of the AAILs increased above 10 wt%.[12] As shown in Fig. 6(b), the viscosities of the AAILs became lower than 10 mPa·s; therefore, the variation of viscosity with increasing RH became negligible. Furthermore, the trans-membrane concentration gradient of the CO₂ complex was constant over the entire RH range because the amino groups of the glycinate anions in [N₁₁₁₁][Gly] and [N₄₄₄₄][Gly] can fully react with CO₂ regardless of the RH. Therefore, the CO₂ permeabilities of [N₁₁₁₁][Gly]- and [N₄₄₄₄][Gly]-based FTMs became almost constant under high RH conditions. However, the [N₁₁₁₁][Gly]-based FTM showed higher CO₂ permeability than the [N₄₄₄₄][Gly]-based FTM; this is due to differences in the CO₂ absorption amount resulting from differences in the amino-group densities of the AAILs, as shown in Fig. 8(b).

For the [aN₁₁₁][Gly]-based FTMs, the relationships between the CO₂ permeability and RH

differed from the other two AAIL-based FTMs. Although the CO₂ permeability of the [aN₁₁₁][Gly]-based FTMs under low RH conditions indicated almost the same trend as that of the [N₁₁₁₁][Gly]-based FTMs, it continuously and monotonically increased with increasing RH even under high RH conditions. This result could be explained by the effect of the additional amino group in the cation of [aN₁₁₁][Gly]. As shown in Fig. 8(c), the amino groups in the cation and anion of [aN₁₁₁][Gly] would react with CO₂ under saturated water vapor pressure conditions. Therefore, the CO₂ permeability of the [aN₁₁₁][Gly]-based FTM was higher than that of the [N₁₁₁₁][Gly]-based FTM under high RH conditions. In contrast, under low RH conditions, the CO₂ permeabilities of [aN₁₁₁][Gly]- and [N₁₁₁₁][Gly]-based FTMs were almost equivalent. From this trend, it could be suggested that one of the amino groups in [aN₁₁₁][Gly] might not react with CO₂ and therefore not affect CO₂ permeation in the low RH region.

The effect of RH on the CO₂ reactivity of [aN₁₁₁][Gly] can be elucidated by evaluating the difference between the amounts of CO₂ absorbed under dry and humid conditions in the CO₂ absorption tests. However, it was quite difficult to measure the CO₂ absorption under dry conditions because the viscosity of [aN₁₁₁][Gly] markedly increased with CO₂ absorption. Therefore, we investigated the effect of RH on the reactivities of the AAILs with CO₂ using DFT studies. Regarding [aN₁₁₁][Gly], the formation of three types of [aN₁₁₁][Gly]-CO₂ complexes is possible: 1) COM_C, which could form via a reaction between CO₂ and the amino group in the cation of [aN₁₁₁][Gly] (Fig. S2(a)); 2) COM_A, which could form via a reaction between CO₂ and an amino group in the anion of [aN₁₁₁][Gly] (Fig. S2(b)); and 3) COM_{CA}, which could form via a reaction between CO₂ and the amino groups in both the cation and anion of [aN₁₁₁][Gly] (Fig. S2(c)). The binding energies of these complexes under dry and humid conditions were calculated via DFT, and we investigated the structures of the complexes under each condition on the basis of the structural stability predicted from the binding energy. The binding energies of the three complexes under dry and humid conditions are listed in Table 3; the results show that the binding energies under both dry and humid conditions were in the following order: COM_C < COM_{CA} < COM_A. In general, it is well known that a structure with a smaller binding energy (large negative value) is more stable. Therefore, the stabilities of the complexes under both dry and humid conditions were in the following order: COM_C > COM_{CA} > COM_A.

Based on the above explanations, the binding energies of COM_A and COM_{CA} were significantly different from that of COM_C under dry conditions. The binding energy difference between COM_C and COM_A under dry conditions was −36.48 kcal/mol, and that between COM_C and COM_{CA} was −16.87 kcal/mol. In contrast, the binding energy of COM_{CA} was similar to that of COM_C and much smaller than that of COM_A under humid conditions. The binding energy difference between COM_C and COM_{CA} under humid conditions was only −3.71 kcal/mol. From these results, COM_C would preferentially form under dry conditions, while COM_C and COM_{CA} would co-exist under humid

conditions. Thus, the amount of CO₂ absorbed in [aN₁₁₁][Gly] is expected to increase due to the formation of COM_{CA} under high RH conditions, which leads to the observed continuous increase in CO₂ permeability. The continuous increase in the CO₂ permeability of [aN₁₁₁][Gly]-FTM above 50% RH shown in Fig. 10(a) was caused by this additional reaction of CO₂ with COM_C to form COM_{CA}.

In contrast, as shown in Fig. 10(b), the N₂ permeabilities of the AAIL-FTMs monotonically increased with RH; this is because the viscosities of each AAIL decreased with increasing water content in the AAILs, as shown in Fig. 6(b). The N₂ permeabilities of the [N₁₁₁₁][Gly]- and [aN₁₁₁][Gly]-based FTMs were similar at all RH values and lower than that of the [N₄₄₄₄][Gly]-based FTM. The difference in the N₂ permeabilities is caused by a difference in the N₂ absorption amount, which is dependent on the FFVs of the AAILs (Fig. 8(a)). Regarding CO₂/N₂ selectivity, as shown in Fig. 10(c), the [aN₁₁₁][Gly]- and [N₁₁₁₁][Gly]-based FTMs showed higher CO₂/N₂ selectivity than the [N₄₄₄₄][Gly]-based FTM owing to their smaller FFVs and higher amino-group densities compared to those of [N₄₄₄₄][Gly]. Under high RH conditions, the CO₂/N₂ selectivity of the [aN₁₁₁][Gly]-based FTM was higher than that of the [N₁₁₁₁][Gly]-based FTM, which was caused by the increased CO₂ absorption by the second amino group under highly humid conditions.

From the results of this study, the following design criteria for AAILs as effective CO₂ carriers in FTMs under humid conditions are proposed: (1) Multi-amino-functionalization of AAILs, which enhances CO₂ permeability, and (2) small molecular size, which not only decreases N₂ permeability but also enhances CO₂ permeability. Because the [aN₁₁₁][Gly]-based FTM developed in this study was a supported ionic liquid membrane in which [aN₁₁₁][Gly] was impregnated in a porous support membrane by weak capillary force, there still remains challenge on the improvement of low pressure resistance and the achievement of long term stability. Recently, we developed a tough gel membrane containing a large amount of AAILs with high pressure resistance and long term stability.[38] The tough gel technology could be used to prepare [aN₁₁₁][Gly]-based gel membrane with high pressure resistance and good stability. Fabrication of a tough gel membrane containing a large amount of [aN₁₁₁][Gly] for practical application is our next target.

4. Conclusions

Three AAILs with different numbers of amino groups and different molecular sizes were synthesized, and their gas absorption properties were investigated. The FFVs of the AAILs before and after CO₂ absorption were calculated using MD simulations, and the amounts of N₂ absorbed were evaluated on the basis of their FFVs. Based on computational and experimental studies, it was determined that the FFVs and molar volumes of the AAILs decreased with decreasing size of the ionic liquids. [aN₁₁₁][Gly], which is small and contains two amino groups, showed high CO₂ and low N₂ absorptions with a low viscosity under humid conditions, as aided by water molecules.

AAIL-based FTMs were prepared and their gas permeation properties were investigated. Based on the experimental and computational results, it was suggested that an additional [aN₁₁₁][Gly]-CO₂ complex can form via a reaction with the second amino group at higher RHs. The [aN₁₁₁][Gly]-based FTM showed high CO₂ permeability and high CO₂ selectivity against N₂ over a wide RH range. This membrane selectively permeated CO₂ based on the facilitated transport mechanism. Therefore, it is expected that this membrane can effectively separate CO₂ from not only N₂ but also O₂, CH₄ and H₂, which permeate through the membrane based on the simple solution-diffusion mechanism. From the investigations, as the design criteria for AAILs as suitable CO₂ carriers for FTMs under humid conditions, compact and multi-amino-functionalized AAILs are recommended.

Acknowledgements

This work was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI (Grant No. 25•4070) and Japan Science and Technology Agency-Advanced Low Carbon Technology Research and Development Program (JST-ALCA).

References

- [1] B. Li, Y. Duan, D. Luebke, B. Morreale, Advances in CO₂ capture technology: A patent review, *Appl. Energy*, **102** (2013) 1439-1447.
- [2] L.M. Robeson, The upper bound revisited, *J. Membr. Sci.*, **320** (2008) 390-400.
- [3] Z. Dai, R. D. Noble, D. L. Gin, X. Zhang, L. Deng, Combination of ionic liquids with membrane technology: A new approach for CO₂ separation, *J. Membr. Sci.*, **497** (2016) 1-20.
- [4] M. Teramoto, K. Nakai, N. Ohnishi, Q. Huang, T. Watari, H. Matsuyama, Facilitated Transport of Carbon Dioxide through Supported Liquid Membranes of Aqueous Amine Solutions, *Ind. Eng. Chem. Res.*, **35** (1996) 538-545.
- [5] A.S. Kovvali, H. Chen, K.K. Sirkar, Dendrimer Membranes: A CO₂-Selective Molecular Gate, *J. Am. Chem. Soc.*, **122** (2000) 7594-7595.
- [6] J. Huang, J. Zou, W.S.W. Ho, Carbon Dioxide Capture Using a CO₂-Selective Facilitated Transport Membrane, *Ind. Eng. Chem. Res.*, **47** (2008) 1261-1267.
- [7] H. Kreulen, C.A. Smolders, G.F. Versteeg, W.P.M. Swaaij, Selective removal of hydrogen sulfide from sour gases with microporous membranes. Part II. A liquid membrane of water-free tertiary amines, *J. Membr. Sci.*, **82** (1993) 185-197.
- [8] M.G. Shalygin, D. Roizard, E. Favre, V.V. Teplyakov, CO₂ transfer in an aqueous potassium carbonate liquid membrane module with dense polymeric supporting layers: Influence of concentration, circulation flow rate and temperature, *J. Membr. Sci.*, **318** (2008) 317-326.
- [9] L.A. El-Azzami, E.A. Grulke, Carbon dioxide separation from hydrogen and nitrogen, *J. Membr. Sci.*, **328** (2009) 15-22.

- [10] A.S. Kovvali, K.K. Sirkar, Dendrimer Liquid Membranes: CO₂ Separation from Gas Mixtures, *Ind. Eng. Chem. Res.*, **40** (2001) 2502-2511.
- [11] S. Kasahara, E. Kamio, T. Ishigami, H. Matsuyama, Amino acid ionic liquid-based facilitated transport membranes for CO₂ separation, *Chem. Commun. (Cambridge, U. K.)*, **48** (2012) 6903-6905.
- [12] S. Kasahara, E. Kamio, T. Ishigami, H. Matsuyama, Effect of water in ionic liquids on CO₂ permeability in amino acid ionic liquid-based facilitated transport membranes, *J. Membr. Sci.*, **415-416** (2012) 168-175.
- [13] S. Kasahara, E. Kamio, H. Matsuyama, Improvements in the CO₂ permeation selectivities of amino acid ionic liquid-based facilitated transport membranes by controlling their gas absorption properties, *J. Membr. Sci.*, **454** (2014) 155-162.
- [14] S. Kasahara, E. Kamio, A. Otani, H. Matsuyama, Fundamental Investigation of the Factors Controlling the CO₂ Permeability of Facilitated Transport Membranes Containing Amine-Functionalized Task-Specific Ionic Liquids, *Ind. Eng. Chem. Res.*, **53** (2014) 2422-2431.
- [15] K. Fukumoto, M. Yoshizawa, H. Ohno, Room Temperature Ionic Liquids from 20 Natural Amino Acids, *J. Am. Chem. Soc.*, **127** (2005) 2398-2399.
- [16] J. Zhang, S. Zhang, K. Dong, Y. Zhang, Y. Shen, X. Lv, Supported absorption of CO₂ by tetrabutylphosphonium amino acid ionic liquids, *Chem. - Eur. J.*, **12** (2006) 4021-4026.
- [17] B.F. Goodrich, J.C. de la Fuente, B.E. Gurkan, Z.K. Lopez, E.A. Price, Y. Huang, J.F. Brennecke, Effect of Water and Temperature on Absorption of CO₂ by Amine-Functionalized Anion-Tethered Ionic Liquids, *J. Phys. Chem. B*, **115** (2011) 9140-9150.
- [18] Y. Zhang, S. Zhang, X. Lu, Q. Zhou, W. Fan, X.P. Zhang, Dual amino-functionalised phosphonium ionic liquids for CO₂ capture, *Chem. - Eur. J.*, **15** (2009) 3003-3011.
- [19] M.S. Shannon, J.M. Tedstone, S.P.O. Danielsen, M.S. Hindman, A.C. Irvin, J.E. Bara, Free Volume as the Basis of Gas Solubility and Selectivity in Imidazolium-Based Ionic Liquids, *Ind. Eng. Chem. Res.*, **51** (2012) 5565-5576.
- [20] T.C. Lourenco, M.F.C. Coelho, T.C. Ramalho, D. van der Spoel, L.T. Costa, Insights on the Solubility of CO₂ in 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide from the Microscopic Point of View, *Environ. Sci. Technol.*, **47** (2013) 7421-7429.
- [21] Modeling and Simulation Solutions for Chemicals and Materials Research, Materials Studio (Version 6.1), Accelrys software Inc., San Diego, USA (2013) www.accelrys.com.
- [22] G.W.T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K.aghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M.

- Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc.: Wallingford, CT, (2009).
- [23] F.-Y. Dupradeau, A. Pigache, T. Zaffran, C. Savineau, R. Lelong, N. Grivel, D. Lelong, W. Rosanski, P. Cieplak, The R.E.D. tools: advances in RESP and ESP charge derivation and force field library building, *Phys. Chem. Chem. Phys.*, **12** (2010) 7821-7839.
- [24] T.A.D. D. Case, T. E. Cheatham, C. Simmerling, J. Wang, R. Duke, R. Luo, M. Crowley, R. Walker, W. Zhang, K. M. Merz, B. Wang, S. Hayik, A. Roitberg, G. Seabra, I. Kolossvary, K. F. Wong, F. Paesani, J. Vanicek, X. Wu, S. Brozell, T. Steinbrecher, H. Gohlke, L. Yang, C. Tan, J. Mongan, V. Hornak, G. Cui, D. H. Mathews, M. G. Seetin, C. Sagui, V. Babin and P. Kollman, Amber 11. .San Francisco, CA: University of California; 2010.
- [25] L. Martinez, R. Andrade, E.G. Birgin, J.M. Martinez, PACKMOL: A package for building initial configurations for molecular dynamics simulations, *J. Comput. Chem.*, **30** (2009) 2157-2164.
- [26] E.L. D. van der Spoel, B. Hess, A. R. van Buuren, E. Apol, P. J. Meulenhoff, D. P. Tieleman, A. L. T. M. Sijbers, K. A. Feenstra, R. van Drunen and H. J. C. Berendsen, Gromacs User Manual version 4.5.6, www.gromacs.org (2010).
- [27] G. Bussi, D. Donadio, M. Parrinello, Canonical sampling through velocity rescaling, *J. Chem. Phys.*, **126** (2007) 014101-014107.
- [28] H.J.C. Berendsen, J.P.M. Postma, W.F. Van Gunsteren, A. DiNola, J.R. Haak, Molecular dynamics with coupling to an external bath, *J. Chem. Phys.*, **81** (1984) 3684-3690.
- [29] U. Essmann, L. Perera, M.L. Berkowitz, T. Darden, H. Lee, L.G. Pedersen, A smooth particle mesh Ewald method, *J. Chem. Phys.*, **103** (1995) 8577-8593.
- [30] W. Humphrey, A. Dalke, K. Schulten, VDM: visual molecular dynamics, *J. Mol. Graphics*, **14** (1996) 33-38.
- [31] V.S. Bernales, A.V. Marenich, R. Contreras, C.J. Cramer, D.G. Truhlar, Quantum Mechanical Continuum Solvation Models for Ionic Liquids, *J. Phys. Chem. B*, **116** (2012) 9122-9129.
- [32] E.I. Izgorodina, U.L. Bernard, D.R. MacFarlane, Ion-Pair Binding Energies of Ionic Liquids: Can DFT Compete with Ab Initio-Based Methods?, *J. Phys. Chem. A*, **113** (2009) 7064-7072.
- [33] A.V. Marenich, C.J. Cramer, D.G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions, *J. Phys. Chem. B*, **113** (2009) 6378-6396.
- [34] W.M. Lee, Selection of barrier materials from molecular structure, *Polym. Eng. Sci.*, **20** (1980) 65-69.
- [35] A. Bondi, van der Waals volumes and radii, *J. Phys. Chem.*, **68** (1964) 441-451.

- [36] B.F. Goodrich, J.C. de la Fuente, B.E. Gurkan, D.J. Zadigian, E.A. Price, Y. Huang, J.F. Brennecke, Experimental Measurements of Amine-Functionalized Anion-Tethered Ionic Liquids with Carbon Dioxide, *Ind. Eng. Chem. Res.*, **50** (2011) 111-118.
- [37] K.E. Gutowski, E.J. Maginn, Amine-Functionalized Task-Specific Ionic Liquids: A Mechanistic Explanation for the Dramatic Increase in Viscosity upon Complexation with CO₂ from Molecular Simulation, *J. Am. Chem. Soc.*, **130** (2008) 14690-14704.
- [38] M. Moghadam, E. Kamio, A. Yoshizumi, H. Matsuyama, An Amino Acid Ionic Liquid-based Tough Ion Gel Membrane for CO₂ Capture, *Chem. Commun.*, **51** (2015) 13658-13661.

Table 1 Experimental conditions for the gas permeation tests(a) CO₂ partial pressure dependency measurement

Temperature		373 K
Pressure	Feed	101.3 kPa
	Sweep	101.3 kPa
Partial pressure difference	CO ₂	2, 2.5, 5, 10 and 25 kPa
	N ₂	98, 97.5, 95, 90 and 75 kPa
Total pressure difference		0 kPa
Gas flow rate (dry base)		
Feed	Total	200 cm ³ /min
	CO ₂	4, 5, 10, 20, 50 cm ³ /min
	N ₂	Balance
	He	40 cm ³ /min
Sweep		40 cm ³ /min
Relative humidity		0% (dry condition)

(b) relative humidity dependency measurement

Temperature		373 K
Pressure	Feed	101.3 kPa
	Sweep	101.3 kPa
Partial pressure difference	CO ₂	1 kPa
Total pressure difference		0 kPa
Gas flow rate (dry base)		
Feed	Total	200 cm ³ /min
	CO ₂	2 cm ³ /min
	N ₂	Balance
	He	40 cm ³ /min
Sweep		40 cm ³ /min
Relative humidity		0, 2.7, 5.3 10–90% (every 10%)

Table 2 FFVs and densities of the AAILs from molecular dynamics simulations at 300 K

	Before CO ₂ absorption under dry condition			After CO ₂ absorption under humid condition	
	FFV (SD [†])	ρ_{calcd} (g/cm ³)	ρ_{exp} [‡] (g/cm ³)	FFV (SD [†])	ρ_{calcd} (g/cm ³)
[N ₄₄₄₄][Gly]	0.19 (0.0058)	0.905	0.955	0.16 (0.012)	1.022
[N ₁₁₁₁][Gly]	0.12 (0.010)	1.058	1.076	0.050 (0.0058)	1.311
[aN ₁₁₁][Gly]	0.12 (0.010)	1.123	1.126	0.070 (0.010)	1.403

[†] SD means standard deviation. [‡] The ρ_{exp} is the experimentally obtained density under dry condition at 303 K.

Table 3 Binding energies of [aN₁₁₁][Gly]-CO₂ complexes

Complex	Dry condition ΔE (kcal/mol)	Humid condition ΔE (kcal/mol)
COM _C	-130.54	-16.00
COM _A	-94.06	-1.05
COM _{CA}	-113.67	-12.29

Fig. 1 Chemical structures of (a) 1,1,1-trimethylhydrazinium glycinate ($[aN_{111}][Gly]$), (b) tetramethylammonium glycinate ($[N_{1111}][Gly]$), and (c) tetrabutylammonium glycinate ($[N_{4444}][Gly]$).

Fig. 2 Schematic diagram of the viscosity measurement system used in this study.

Fig. 3 Schematic diagram of the apparatus used for the gas absorption measurements.

Fig. 4 Schematic diagram of the apparatus for the gas permeation tests.

Fig. 5 Effect of temperature on the (a) molar densities and (b) molar volumes of [N₄₄₄₄][Gly], [N₁₁₁₁][Gly], and [aN₁₁₁][Gly].

Fig. 6 Effect of (a) temperature and (b) water content on the viscosities of [N₄₄₄₄][Gly], [N₁₁₁₁][Gly], and [aN₁₁₁][Gly]. The temperature dependency (a) was measured under dry conditions. The effect of water content (b) was investigated at 373 K.

Fig. 7 Effect of RH on the viscosity of [aN₁₁₁][Gly] in contact with CO₂ at 373 K.

Fig. 8 Absorption isotherms of (a) N₂ (mol/dm³), (b) CO₂ (mol/dm³), and (c) CO₂ absorbed per mole of AAIL molecules (mol CO₂/mol AAIL) at 343 K.

Fig. 9 CO₂ partial pressure dependency on permeability and flux of (a) CO₂ and (b) N₂ and (c) CO₂/N₂ selectivity and CO₂ purity in the permeate of [aN₁₁₁][Gly]-based FTM. Experimental conditions: $T = 373$ K, Total pressure was atmospheric pressure and the relative humidity in feed gas was 0 % (dry condition).

Fig. 10 Effect of relative humidity on the (a) CO₂ permeabilities, (b) N₂ permeabilities, and (c) CO₂/N₂ selectivities of [aN₁₁₁][Gly]-, [N₁₁₁][Gly]-, and [N₄₄₄₄][Gly]-based FTMs ($T = 373$ K, $p_{\text{CO}_2} = 1$ kPa).