Ionic Liquid Mixtures for Direct Air Capture: High CO₂ Permeation Driven by Superior CO₂ Absorption with Lower Absolute Enthalpy

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ABSTRACT: This paper reports a series of liquid materials suitable for use as high-performance separation membranes in direct air capture. Upon mixing two ionic liquids (ILs), namely N-(2-aminoethyl)ethanolamine-based IL ([AEEA][X]) and 1-ethyl-3-methylimidazolium acetate ([emim][AcO]), the resulting mixtures with a specific range of their composition showed higher CO₂ absorption rates, larger CO₂ solubilities, and lower absolute enthalpies of CO₂ absorption compared to those of single ILs. NMR spectroscopy of the IL mixture after exposure to ¹³CO₂ allowed elucidation of the chemisorbed species, wherein [AEEA][X] reacts with CO₂ to form CO₂-[AEEA]⁺ complexes stabilized by hydrogen bonding with acetate anions. Supported IL membranes composed of [AEEA][X]/[emim][AcO] mixtures were then fabricated, and the membrane with a suitable mixing ratio showed a CO₂ permeability of 25,983 Barrer and a CO₂/N₂ selectivity of 10,059 at 313.2 K and an applied CO₂ partial pressure of 40 Pa without water vapor. These values are higher than those reported for known facilitated transport membranes.

INTRODUCTION

The urgent need for strategies to reduce the global atmospheric concentrations of greenhouse gases has prompted action from governments and industries worldwide.¹⁻² Post-combustion capture is typically considered for large point sources, such as coal- or gas-fired power plants, and industrial sources that produce large volumes of CO₂. However, these point sources account for only one-third to one-half of anthropogenic CO₂ emissions. Various recent scenarios have therefore demonstrated a requirement for the large-scale deployment of negative emission technologies,³⁻⁴ which result in the net removal of greenhouse gases from the atmosphere. Among the various negative emission technologies reported to date, the development of a technology that can capture CO₂ from ambient air, referred to as “direct air capture” (DAC), is a challenge owing to the very low concentration of CO₂ in the atmosphere (i.e., ~400 ppm).²⁻⁷

Membrane separation technologies are envisioned as one of the energy-efficient CO₂ separation technologies including DAC applications.⁸⁻¹⁰ Facilitated transport membranes, in which mobile and/or fixed carriers are impregnated into the membrane matrices, are one of the options for DAC.¹¹ The facilitated transport of CO₂ through such membranes is accomplished as follows: the reactive carriers in the membranes react with CO₂ to produce CO₂-carrier complexes, which are then transported across the membranes. On the permeate side, the back reaction reversibly occurs at the low partial pressure of CO₂; eventually, CO₂ is released and the carrier is regenerated. The main challenge for such facilitated transport membranes for DAC applications is achieving a further improvement in the CO₂ permeability while maintaining, or even increasing, the CO₂/N₂ selectivity. Various properties of membrane materials influence the CO₂ permeability (i.e., the CO₂ solubility, the CO₂ absorption and desorption rate, the diffusivity (viscosity), and the enthalpy of solution of CO₂). One strategy to improve CO₂ permeability from the thermodynamic viewpoint is therefore to design carriers with high CO₂ solubilities and low absolute enthalpies of solution of CO₂, which should efficiently increase the mass of CO₂ transported through the membrane and readily desorb CO₂ at the permeate side owing to low absolute enthalpy.¹² However, it is difficult to accomplish both properties in a single material because a trade-off between the CO₂ solubility and enthalpy of solution is generally observed in such CO₂-sorptive materials.

The use of ionic liquids (ILs) as matrices for CO₂ separation membranes is regarded as a promising green technology because ILs have favorable properties, including negligibly low

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vapor pressure, high thermal/chemical stability, and low flammability.\textsuperscript{13,14} Moreover, the structural design of the component ions of ILs allows precise control of their affinities toward CO\textsubscript{2}. IL-based facilitated transport membranes, in which CO\textsubscript{2}-reactive ILs are covalently tethered and/or physically impregnated in various membrane materials, have widely been investigated.\textsuperscript{15,16} The CO\textsubscript{2}-reactive ILs include cation-functionalized ILs with amino group on the cation,\textsuperscript{17} amino acid ILs,\textsuperscript{18−22} 2-cyanopyrrolidyl-type IL,\textsuperscript{22,23} and carboxylate-type ILs.\textsuperscript{22,23} Matsuyama and co-workers investigated various facilitated transport membranes using CO\textsubscript{2}-reactive ILs (e.g., tetra-n-butylphosphonium-based amino acid ILs with L-glycine, L-alanine, L-serine, and L-proline as anions), and some of these exhibited CO\textsubscript{2} permeability and CO\textsubscript{2}/N\textsubscript{2} selectivity above the Robeson upper bounds.\textsuperscript{19}

Previously, we measured the CO\textsubscript{2} solubility and the corresponding thermodynamic parameters for a series of carboxylate-type ILs with ether groups on the anions.\textsuperscript{24} These ILs were revealed to possess lower absolute enthalpy of solution of CO\textsubscript{2} compared to well-known aqueous monoethanolamine solutions and thus are capable of desorbing CO\textsubscript{2} under mild temperature conditions below 100 °C. Although the structural design of the abovementioned “pure” ILs for specific applications is effective, the incorporation of functional groups into the ions tends to result in inferior liquid properties (e.g., higher viscosities and lower thermal stabilities). Instead, the mixing of multiple ILs can be a more practical means to fine-tune their properties than the structural design of pure ILs.\textsuperscript{25} When considering the fine control of the affinity of IL mixtures toward CO\textsubscript{2}, the suitable mixing of ILs (e.g., CO\textsubscript{2}-reactive ILs and other ILs) should result in the discovery of unprecedented and superior liquid materials. However, the effect of mixing ILs on CO\textsubscript{2} separation performance has not been fully explored, presumably because of the complexity of the mixed systems compared to single IL systems.

We herein report the production of a new type of liquid material for DAC applications by mixing two ILs, namely N-\((\text{2-aminoethyl})\)ethanolamine-based IL ([AEEA][X]) and 1-ethyl-3-methylimidazolium acetate ([emim][AcO]). [AEEA]-[X] is expected to act as a CO\textsubscript{2} carrier, whereas the Lewis basic [emim][AcO] should stabilize zwitterion/carbamic acid species that exhibit relatively low absolute enthalpy of solution as compared to carbamate species (Scheme 1). Supported IL membranes (SILMs) are then fabricated and their CO\textsubscript{2}/N\textsubscript{2} permselectivities are investigated in comparison with those of previously reported membrane materials.

### EXPERIMENTAL SECTION

**Synthesis of the ILs.** The [AEEA]+-based ILs used in this study ([AEEA][X]) were prepared by the neutralization of AEEA with equimolar amounts of the corresponding acids, as reported previously.\textsuperscript{26} For example, in the preparation of [AEEA][Tf\textsubscript{2}N] ([Tf\textsubscript{2}N]: bis(trifluoromethanesulfonyl)imide), AEEA and H[Tf\textsubscript{2}N] were mixed in water at a molar ratio of 1.0:1.0 while cooling the solution in an ice bath, and subsequently, the solution was allowed to stir for ≥2 h. After this time, the water was evaporated with a rotary evaporator, and the sample was dried in vacuo to obtain [AEEA][Tf\textsubscript{2}N].

**Measurement of the CO\textsubscript{2} Solubility and Initial CO\textsubscript{2} Absorption Rate.** The experimental apparatus used was the same as reported in the previous study except for the pressure transducer (Druck, IDOS UPM, USA).\textsuperscript{27} The uncertainties of the pressure and the temperature were 10 Pa and 0.02 K, respectively. The high-pressure cell containing the desired amount of IL was attached to the experimental apparatus, and the apparatus was evacuated to remove volatile compounds. Subsequently, the apparatus was immersed in the thermostat bath equipped with a chiller to maintain the temperature. The procedure was divided into two steps. The first step involved the determination of the quantity of the gas component. Thus, the molar amount of CO\textsubscript{2} loaded (\(n_{\text{CO}_2}\)) was calculated from the molar volume of CO\textsubscript{2} at equilibrium and the inner volume of the gas reservoir, which was preliminarily calibrated at each temperature. The liquid phase was then agitated using a stirrer bar. When the pressure change became <1 Pa h\textsuperscript{-1}, it was assumed that the components were present as a two-phase equilibrium. The concentration of the IL in the CO\textsubscript{2} phase was negligibly small. The molar amount of CO\textsubscript{2} dissolved in the IL (\(n_{\text{CO}_2}^L\)) was calculated according to the following equation

\[
n_{\text{CO}_2}^L = n_{\text{CO}_2} - V_{\text{cell}} - V_{m}^G
\]

where \(V_{m}^G\) represents the volume of the IL phase and the molar volume of the CO\textsubscript{2} phase under certain conditions, respectively. \(V_{m}^G\) was obtained from NIST REFPROP Ver. 10.0. It was assumed that the volume of the liquid phase (\(V_{m}^L\)) did not change after the CO\textsubscript{2} absorption under the present conditions. The solubility in molarity scale (\(e_{\text{CO}_2}\)), in which the uncertainty of \(e_{\text{CO}_2}\), was estimated as 0.001 mol dm\textsuperscript{-3} was obtained as follows

\[
e_{\text{CO}_2} = \frac{n_{\text{CO}_2}^L}{V_{m}^L}
\]

The same apparatus was used to measure the CO\textsubscript{2} absorption rate. More specifically, the desired amount of IL was introduced into the stainless-steel cell, and the IL was subjected to vacuum to remove any volatile components. Subsequently, CO\textsubscript{2} (≤1 kPa) was introduced into the cylinder;
the IL was present in a large excess (≥2800 times, molar equivalents) compared to CO$_2$. After reaching a constant pressure and temperature (313.15 K), the valve was opened to begin the CO$_2$ absorption experiment. The initial CO$_2$ absorption rate at the beginning of CO$_2$ absorption, $J_0$ (mmol m$^{-2}$ s$^{-1}$), was obtained from the pressure change ($\Delta p$) per unit time

$$J_0 = \frac{\Delta p V^G}{ART}$$

where $A$ is the area of the gas–liquid interface (8.04 cm$^2$), $V^G$ is the volume of the gas phase, $R$ is the gas constant, and $T$ is the temperature. $V^G$ was obtained by subtracting the volume of the IL, $V_i$, from the volume of the cell, $V_{cell}$. During the measurement, the volume of the IL was assumed to be constant.

**Analysis of the CO$_2$ Saturated IL Solution.** The experimental apparatus and procedure to prepare the CO$_2$ saturated IL solution were as described elsewhere.$^{24}$ A desired amount of IL was weighed into a glass cell using an electrical balance (Mettler Toledo, XPS0035S, USA). Then, the glass cell was immersed in a water bath, where the temperature was kept at 313.15 K. A pair of stainless-steel needles attached to a silicon cap was used for the inlet and outlet of gas. Pre-heated CO$_2$ standard gas (CO$_2$ concentration was 391 ppm) was very slowly blown through the needle under the pressure of 101 kPa. The standard gas was supplied for ~96 h until the IL was saturated with CO$_2$. After that, the saturated solution was transferred to the viscometer (Anton Paar, Stabinger SVM 3000, Austria) by using an airtight syringe to avoid air exposure. The viscosity was measured at 313.15 K. In the same manner, we prepared the IL solution saturated with a 13CO$_2$ standard (13CO$_2$ concentration was 398 ppm) or 13CO$_2$ gases to analyze the CO$_2$−IL complexes. The saturated solution was analyzed by NMR (JEOL Resonance, ECA-600, Japan, for the 13C NMR with the inverse-gated decoupling sequence and Bruker Avance 400, USA, for the 2D NMR with the C−H COSY sequence).

An FTIR spectrometer (Thermo Fisher Scientific, Nicolet iS50, USA) equipped with an ATR unit (PIKE Technologies, GladiATR, USA) was used to analyze CO$_2$ saturated solutions under atmospheric pressure (~101 kPa). ~0.1 mL of the IL was placed in a stainless-steel cell attached to the ATR unit. The ATR unit was kept at 313 K during the measurement. N$_2$ was then supplied to the cell and the IR spectrum of the neat IL was obtained. After that, the CO$_2$ standard gases (CO$_2$ concentrations: 391 ppm and 1.049%) were flowed to obtain the IR spectrum of the CO$_2$ saturated ILs.

Enthalpy of solution of CO$_2$ ($\Delta H$) was measured according to our previous study.$^{24}$ The weight of IL (w$_2$) transferred into a stainless-steel cell was determined using an electrical balance (Mettler Toledo, AL-204, USA). Then, the cell was attached to the calorimeter, and N$_2$ was supplied immediately through a pre-heating line using a mass flow controller. We measured a heat flow at regular intervals using a Calvet-type calorimeter (Setaram, µDSC7, France) at 313.15 K. The sample temperature was kept within ±0.01 K during the measurements. We assumed that the IL was thermally equilibrated when the change of heat flow was less than 0.01 mW h$^{-1}$. After that, we started the measurement of the enthalpy of solution of CO$_2$ by switching from N$_2$ to CO$_2$. An exothermic peak was observed when CO$_2$ was absorbed in the IL. The heat flow became almost constant after the IL was saturated with CO$_2$. The criterion for the saturation was the same as that for the thermal equilibration. The enthalpy of solution of CO$_2$ ($\Delta H$) was calculated as

$$\Delta H = \frac{f S}{\alpha_i (w_2/M_2)}$$

where $S$ is the integral of the exothermic peak, $\alpha_i$ is the molar ratio of dissolved CO$_2$ to IL, $M_2$ is the molecular weight of IL, and $f$ is the instrumental factor determined preliminarily. The uncertainty of $\Delta H$ is estimated to be less than 4% under the present conditions.

**Measurement of the CO$_2$/N$_2$ Gas Permeability.** The SILMs were prepared as follows. A hydrophilic PTFE membrane (Merck Millipore, JVWP04700, USA) was dipped into the IL under vacuum at 25 °C for 24 h. The PTFE filter had a pore size of 0.1 μm, a porosity of 80%, and a thickness of 30 μm. The excess IL on the filter surface was wiped up immediately before the measurement. The filling rate of each IL in the PTFE filter was calculated to be 98–99%, which is determined as a volume of IL loaded in a void of PTFE filter. The membrane thickness before and after loading the ILs was unchanged. The experimental apparatus employed for the gas separation measurements was as described in our previous report.$^{28}$ The SILM (47 mm in diameter) was placed on a stainless-steel cell with a porous hydrophobic PTFE filter (Advantec Co., T010A047A, Japan) as the support. The PTFE filter had a pore size of 0.1 μm, a porosity of 68%, and a thickness of 70 μm. The effective surface area was 13.2 cm$^2$ and the thickness of the membrane was measured using a micrometer. The feed gas was a CO$_2$/N$_2$ mixture with a CO$_2$ partial pressure of 40 Pa, while helium was used as the sweep gas. The atmospheric pressure was measured using a barometer (Druck, DP1150, USA). The flow rates of the feed and sweep gases were 400 and 20−150 cm$^3$ min$^{-1}$, respectively, and they were regulated using mass flow controllers (HORIBA STEC Inc., SEC-E40, Japan). In the present study, the feed and sweep gases did not contain water. The temperature was controlled within ±1 K during the measurement. The permeabilities of CO$_2$ and N$_2$ were evaluated based on the flow rates and the compositions. The flow rate was measured using a film flow meter (HORIBA STEC Inc., SF-1U). The composition was determined using a TCD gas chromatograph (Shimadzu Co., GC-8A, Japan).

### Table 1. CO$_2$ Absorption Rate ($J_0$), Absorption Amount ($\alpha$), Enthalpy of Solution of CO$_2$ ($\Delta H$), and Viscosity after CO$_2$ Absorption ($\eta_{CO_2}$) of [AEEA][Tf$_2$N]/[emim][AcO] (10/90 by mol %), as Well as Those of the Individual ILs

| ILs                  | $J_0$ (mmol m$^{-2}$ s$^{-1}$) | $\alpha_{CO_2}$/mol dm$^{-3}$ | $\Delta H$/kJ (mol-CO$_2$)$^{-1}$ | $\eta_{CO_2}$/mPa s |
|----------------------|-------------------------------|-------------------------------|----------------------------------|-------------------|
| [AEEA][Tf$_2$N]/[emim][AcO] (10/90 by mol) | 0.39                          | 0.157                         | −54                              | 85.5              |
| [emim][AcO]          | 3.4 × 10$^{-3}$               | 0.048                         | −61                              | 65.9              |
| [AEEA][Tf$_2$N]      | 2.3 × 10$^{-3}$               | 0.001                         | −73$^a$                         | 521               |

$^a$ $p_{CO_2} = 40$ Pa. $^b$ $p_{CO_2} = 100$ Pa. $^c$ $p_{CO_2} = 1$ kPa. $^d$ $p_{CO_2} = 101$ kPa.
RESULTS AND DISCUSSION

To investigate the effectiveness of mixing different ILs, [AEEA][Tf$_2$N] was mixed with [emim][AcO] in a molar composition of 10/90. The equilibrium and kinetic parameters for CO$_2$ absorption in the IL mixture were analyzed; more specifically, the initial CO$_2$ absorption rate ($j_0$), the CO$_2$ solubility ($c_{CO_2}$), the enthalpy of solution of CO$_2$ ($\Delta H$), and the viscosity after CO$_2$ absorption ($\eta_{CO_2}$) for the IL mixture were measured, as were the corresponding values for each IL at 313.2 K (Table 1). The $j_0$ value, defined as the number of moles of CO$_2$ absorbed per unit area and time, was measured by tracing the pressure decay caused by CO$_2$ absorption, and the initial absorption rate was plotted against the CO$_2$ pressure. A typical pressure profile is presented in Figure S1. Immediately after the valve was opened, a pressure drop was observed owing to the expansion of the gas phase. This pressure drop was completed within approximately 1 s. In this measurement, the subsequent pressure drop was assumed to be the change associated with CO$_2$ absorption into the IL. This measurement was performed for different CO$_2$ partial pressure (Figure 1a). The initial CO$_2$ absorption rate at the beginning of CO$_2$ absorption, $j_0$ (mmol m$^{-2}$ s$^{-1}$), was then calculated, and the $j_0$ at 40 Pa was obtained by extrapolation. It was found that the $j_0$ value of the IL mixture was 116 times higher than that of [emim][AcO] and 370 times higher than that of [AEEA][Tf$_2$N]. Subsequently, the $c_{CO_2}$ value was determined from the pressure difference after reaching equilibrium using the same apparatus employed to measure the $j_0$ values. The $c_{CO_2}$ was plotted as a function of the CO$_2$ partial pressure, as shown in Figure 1b. The values given in Table 1 were calculated by interpolation. Because the $c_{CO_2}$ value of [AEEA][Tf$_2$N] at CO$_2$ pressure of 40 Pa was below the detection limit of our system, the values at a CO$_2$ pressure of 100 Pa were compared in this study. A higher $c_{CO_2}$ was observed in the IL mixture than in the individual ILs, and the value increased upon increasing the CO$_2$ pressure. Next, the $\Delta H$ values for each sample were measured at the CO$_2$ pressure of 1 kPa. It was revealed that the IL mixture displayed a smaller $\Delta H$ value than the individual ILs. On the other hand, the $\eta_{CO_2}$ value for the IL mixture after the absorption of CO$_2$ was slightly higher than that of [emim][AcO] and significantly lower than that of [AEEA][Tf$_2$N]. Because the higher viscosity results in a slower diffusivity of the components, the diffusion of the CO$_2$-carrier complexes in the IL mixture should not be faster than that of [emim][AcO].

To elucidate the chemical structures of the CO$_2$-carrier complexes in the IL mixtures, the $^{13}$CO$_2$-absorbed [AEEA]-[Tf$_2$N]/[emim][AcO] mixtures (CO$_2$ partial pressure = 40 Pa) were analyzed by NMR spectroscopy. Figure 2a shows the $^{13}$C inverse-gated NMR spectra of the mixtures with different [AEEA][Tf$_2$N] compositions after $^{13}$CO$_2$ absorption. As a reference, the NMR spectra before $^{13}$CO$_2$ absorption are provided in Supporting Information (Figure S2). In the case of [emim][AcO] alone, the chemisorbed product was observed at 155 ppm. We previously analyzed the CO$_2$-chemisorbed products in various carboxylate-type ILs by $^1$H and $^{13}$C NMR spectroscopy. The peak observed at 155 ppm was originated from the reaction between CO$_2$ and the 2-H position of the imidazolium cation. The C2 hydrogen released from [emim][AcO] was transferred to [AcO]$^-$ to form carboxylic acids. Such a reaction mechanism was also supported by single-crystal X-ray structures of solid-state products.

Upon mixing 10 mol % [AEEA][Tf$_2$N] in [emim][AcO], two CO$_2$-chemisorbed products were newly observed at 161 and 162 ppm, whereas the peak corresponding to the product with [emim][AcO] at 155 ppm reduced in intensity. Increasing the mixing ratio of [AEEA][Tf$_2$N] to 70 mol % resulted in a decrease in the amount of these products, and the spectrum for $^{13}$CO$_2$-absorbed [AEEA][Tf$_2$N] showed product peaks at ~164 ppm. The integrated intensities for these CO$_2$-chemisorbed products in the IL mixtures were then ordered according to the mixing ratios of [AEEA][Tf$_2$N] giving: 10 mol % (3.4) > 0 mol % (1.9) > 70 mol % (1.9) > 100 mol % (0.15). This order is consistent with the equilibria of CO$_2$ absorption amounts of these mixtures. For the mixture containing 10 mol % [AEEA][Tf$_2$N], the ratio of the integral intensities for the different CO$_2$-chemisorbed products was 13:29:1 (i.e., at 162, 161, and 155 ppm).

To determine the molecular structures of these products, 2D NMR spectroscopy was performed. Figure 2b shows the C–H COSY spectrum of the $^{13}$CO$_2$-absorbed [AEEA][Tf$_2$N]/
[emim][AcO] mixture (10/90 mol %, CO\textsubscript{2} partial pressure = 40 Pa), in which three correlations were observed in the spectrum [i.e., 1.8−175 (A), 3.2−161 (B), and 3.3−162 ppm (C)]; the correlation (A) was assigned to the C−CH\textsubscript{3} moiety of [AcO]\textsuperscript{−} (Figure 2b, inset A), and the correlations (B) and (C) were assigned to the CO\textsubscript{2}-carrier complexes. More specifically, the correlation (B) was assigned to the CO\textsubscript{2}−NH−CH\textsubscript{2} moiety of the CO\textsubscript{2}-carrier complex, which originated from the reaction between CO\textsubscript{2} and the primary amino group of [AEEA]\textsuperscript{+} (Figure 2b, inset B). In addition, the correlation (C) was as attributed to the CO\textsubscript{2}−N−CH\textsubscript{2} moiety of the CO\textsubscript{2}-carrier complex, which originated from the reaction between CO\textsubscript{2} and the secondary amino group of [AEEA]\textsuperscript{+} (Figure 2b, inset C). It should be noted here that Kortunov et al. reported the NMR spectroscopic analyses of some CO\textsubscript{2}-sorptive amines in [emim][AcO] and suggested that [emim]-[AcO] acted as a medium for these amines to form carbamic acid/zwitterionic species after reacting with CO\textsubscript{2}.\textsuperscript{30,31} Such CO\textsubscript{2}-carrier complexes are more beneficial than carbamate species in terms of the CO\textsubscript{2} sorption amount per mol of amine (i.e., 1:1 CO\textsubscript{2}/amine stoichiometry for carbamic acid/zwitterionic species and 1:2 CO\textsubscript{2}/amine stoichiometry for carbamates).

In addition to NMR spectroscopy, IR spectroscopy\textsuperscript{32} was employed to evaluate the [AEEA][Tf\textsubscript{2}N]/[emim][AcO] mixture (10/90 mol %) and the individual ILs (Figure 3). Upon the exposure of [emim][AcO] to CO\textsubscript{2}, the asymmetric vibration of the carboxylate group (\nu\textsubscript{s}(COO\textsuperscript{−})) was observed at 1666 cm\textsuperscript{−1}, and also the stretching vibration of the carboxylic acid group (\nu\textsubscript{s}(COOH)) was observed as a shoulder peak upon increasing the CO\textsubscript{2} partial pressure (Figure 3a). In the case of the [AEEA][Tf\textsubscript{2}N]/[emim][AcO] mixture, a broad peak corresponding to both \nu\textsubscript{s}(COOH) and \nu\textsubscript{s}(COO\textsuperscript{−}) was observed at \sim1620 to 1720 cm\textsuperscript{−1} (Figure 3b, red-highlighted region) at a CO\textsubscript{2} partial pressure of 40 Pa; the intensity of this peak increased as the CO\textsubscript{2} partial pressure was increased to 1

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**Figure 2.** (a) \textsuperscript{13}C inverse-gated NMR spectra of [AEEA][Tf\textsubscript{2}N]/[emim][AcO] with different molar compositions of [AEEA][Tf\textsubscript{2}N] after dissolving \textsuperscript{13}CO\textsubscript{2}. Black dots represent carbon from \textsuperscript{13}CO\textsubscript{2}. (b) C−H COSY spectrum of \textsuperscript{13}CO\textsubscript{2}-absorbed [AEEA][Tf\textsubscript{2}N]/[emim][AcO] (10/90 mol %) with elucidated structures.
kPa. For [AEEA][Tf2N] only, no obvious change was observed in the spectra (Figure 3c). A possible interpretation of this result seen in the [AEEA][Tf2N]/[emim][AcO] mixture is the presence of multiple structures derived from [AcO]−/acetic acid species (e.g., the carboxylic acid structure of CO2−[AEEA]−, and the acetic acid structure formed by proton transfer from CO2−[AEEA]− to [AcO]− in [AEEA][Tf2N]/[emim][AcO] with a low partial pressure of CO2). Upon considering that the molar ratio of the CO2−[AcN]+ complex was much less than the CO2−[AEEA]− complexes, which was proved by 13C NMR spectroscopy as mentioned above, the dominant proton source for acetic acid formation should be the CO2−[AEEA]− complexes. The NMR and IR spectroscopy results therefore strongly suggest that the mechanistic pathway for chemisorption in [AEEA][Tf2N]/[emim][AcO] is the reaction between CO2 and the amino groups of [AEEA][Tf2N], which is stabilized by [AcO]− via hydrogen bonding. Furthermore, the previous report showed that the formation of carbamate species and protonated amines resulted in a high absolute enthalpy of the solution of CO2−. Based on this report, the carbamic acid/zwitterionic structure of the CO2−[AEEA]− complexes in [AEEA][Tf2N]/[emim][AcO] was assumed to lower the absolute enthalpy by suppressing both carbamate formation and proton transfer to amines.

Finally, the abovementioned IL mixtures were impregnated in a porous Teflon film to prepare SILMs, and the gas permeability from a mixed feed gas containing CO2/N2 (CO2 partial pressure: 40 Pa) was analyzed. Figure 4a shows the CO2 permeability values, pCO2, for the prepared SILMs with different [AEEA][Tf2N] compositions. The pCO2 value for [emim][AcO] alone was 1760 Barrer, although this value increased steeply to 20902 Barrer upon mixing with [AEEA][Tf2N] in a molar composition of 10 mol %. A further increase in the molar composition of 70 mol % lowered the pCO2 value (2332 Barrer), with [AEEA][Tf2N] itself giving the lowest pCO2 value among the various mixtures investigated (206 Barrer). In addition, the pN2 value was almost constant over the investigated composition range. Figure 4b shows the CO2/N2 permeability selectivity (S_{CO2/N2}) as a function of pCO2 (i.e., Robeson plots) for the [AEEA][X]/[emim][AcO] mixtures (10/90 mol %), where X− corresponds to chloride (Cl−), methanesulfonate (CH3SO3−), [AcO]−, nitrate (NO3−), triflate ([TfO]−), and [Tf2N]−. As indicated, the [AEEA][X]/[emim][AcO] mixtures displayed exceptionally high pCO2 and S_{CO2/N2} values. Furthermore, the maximum values were observed for [AEEA][AcO]/[emim][AcO] at a molar ratio of 15:85 (p_{CO2} = 25983 Barrer, S_{CO2/N2} = 10059). These values were higher than those previously reported for SILMs and other facilitated transported membranes under dry condition. As a typical reference, [P1444][Pro], a benchmark IL exhibiting high CO2 permeability, was prepared in our laboratory and analyzed using the same experimental procedure to give a p_{CO2} value of 22095 Barrer and a S_{CO2/N2} value of 4013, both of which were lower than those of [AEEA][AcO]/[emim][AcO].

Given the structural diversity of ILs, the abovementioned strategy (i.e., designing membrane materials by mixing plural ILs) would offer a new avenue for energy-efficient CO2 separation processes. Currently, our group is investigating the structure–property relationships of IL mixtures with various structures. Future work will also collect a range of engineering data for applications in various DAC processes.
It was found that IL mixtures comprising [AEEA][Tf$_2$N]/[emim][AcO] exhibit high CO$_2$ permeabilities and CO$_2$/N$_2$ permeability selectivity values even at a CO$_2$ feed partial pressure of 40 Pa without water vapor. The amount of CO$_2$ absorption and the CO$_2$ absorption rate by the IL mixtures was higher than those of the individual ILs, and the mixtures also exhibited the lowest absolute enthalpies of solution. The mechanistic pathway for chemisorption in the mixture was spectroscopically analyzed, and the dominant species were found to be the CO$_2$−[AEEA]$^+$ complexes, in which the zwitterion/carbamic acid species were assumed to be stabilized by [AcO]$^-$ via hydrogen bonding. These results therefore indicate that IL mixtures are promising new liquid membrane materials for DAC applications.

**CONCLUSIONS**

(e.g., gas permeability properties under humid conditions, resistance to oxidative degradation).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04756.

Materials and NMR characterization of ILs (PDF)

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**Notes**

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