High pressure CO₂ solubility and physical properties of tetrabutylphosphonium *L*-prolinate

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Abstract

This paper reports the CO₂ solubility, density, viscosity, and electrical conductivity for a kind of amino acid ionic liquids (AAILs), tetrabutylphosphonium *L*-prolinate ([P₄₄₄₄][Pro]). The physical properties of [P₄₄₄₄][Pro] showed the ordinary temperature dependency, i.e. the density and viscosity decreased and the electrical conductivity increased with a temperature rising. One mole of [P₄₄₄₄][Pro] absorbed a 0.970 mole of CO₂ at atmospheric pressure of CO₂ and 333.2 K, and desorbed only ~17 % of the absorbed CO₂ at 393.2 K. NMR spectra revealed that a CO₂ molecule formed a complex with [Pro]⁻, and [P₄₄₄₄]⁺ had a little effect on the CO₂ absorption. The CO₂ solubility increased steeply at lower pressures of CO₂ < 0.1 MPa and very gradually in the higher pressure range from 0.1 to 6 MPa at 333.15 K. Other tetrabutylphosphonium AAILs with (*S*)-2-methylprolinate ([P₄₄₄₄][MePro]) and glycinate ([P₄₄₄₄][Gly]) showed the similar pressure dependencies. The contributions of physical and chemical absorptions to the total CO₂ solubility were analyzed to discuss the effect of anion on the high-pressure CO₂ solubility. [P₄₄₄₄][Pro] and [P₄₄₄₄][Gly] showed the higher physical and chemical CO₂ absorptions (in molarity scale) in the present AAILs, respectively.

Keywords

amino acid ionic liquid, CO₂ solubility, physical property

1. Introduction

Ionic liquids (ILs) are salts, of which the melting temperatures are at or below ambient temperatures. ILs are liquid over an extended temperature range and have unique features such as negligible vapor pressure, non-flammability, high electrical conductance, and favorable miscibility with various chemicals. Because of these features, ILs have drawn attention as solvents for batteries, separations, chemical reactions, functional materials, and so on. Their physicochemical properties and solvent characteristics can be optimized by chemical modifications and combination of cations and anions for individual applications. A number of studies have been performed to understand how the chemical structures of ILs affect their characteristics.

One of the promising applications is gas sweetening, in particular, CO₂ separation. Absorption, adsorption, and membrane separation processes using ILs have been proposed depending on throughput, composition, pressure, and temperature for gas mixture sources [1-2]. Absorption and adsorption processes require not only high CO₂ capacity but also its large pressure and/or temperature variations for ILs, since the ILs have to be recycled, in general, by depressurization and/or heating. On the other hand, membrane separation process demands high CO₂ solubility and its small temperature dependency for ILs over a wide temperature range, because the gas permeation rate depends strongly on the gradient of gas concentration in the membrane. High kinetic properties are essential for each process to absorb, desorb, and transport CO₂ rapidly.

The knowledge how the chemical structure influences these properties is of importance to develop and optimize ILs. We have reported the CO₂ solubilities, densities, viscosities, and electrical conductivities for the imidazolium, ammonium, and pyrrolidinium salts with fluorinated, cyano, and acetate anions [3-12]. The ether group on the ammonium and pyrrolidinium cations improves both the CO₂ solubility (in molarity scale) and the transport

properties (lower viscosity and higher electrical conductivity) [4,9]. We have also revealed that 1-ethyl-3-methylimidazolium tetracyanoborate ([emim][TCB]) absorbs ~30 % larger amount of CO₂ and has ~45 % lower viscosity than the corresponding IL with bis(trifluoromethanesulfonyl)amide ([emim][Tf₂N]) at 298.15 K [11]. The mixture of 1-butyl-3-methylimidazolium acetate ([bmim][AcO]) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([bmim][Tf₂N]) shows a sharp viscosity decrement at the low [bmim][Tf₂N] composition, and [bmim][AcO] absorbs CO₂ stoichiometrically in the mixture with [bmim][Tf₂N] [12].

Earlier studies have reported several kinds of ionic liquids work as CO₂ absorbents. An amino acid IL (AAIL) is one of the well-known chemical absorbents, which absorb CO₂ reversibly through the chemical reaction. One of the advantages of AAILs is high CO₂ solubility; one mole of AAILs absorbs an equimolar amount of CO₂ through a 1:1 stoichiometric reaction. In the conventional amine solutions and other amine functionalized ILs, two moles of amines are consumed for one mole of CO₂ through a 2:1 reaction. First, Zhang et al. reported that the chemisorption in tetrabutylphosphonium glycinate ([P₄₄₄₄][Gly]) containing 1 wt% of water takes place *via* approximately 1:1 reaction [13]. After that, Gurkan et al. demonstrated the 1:1 absorption without water (water content was less than 800 ppm) for trihexyltetradecylphosphonium methionate ([P_{666,14}][Met]) and trihexyltetradecylphosphonium *L*-prolinate ([P_{666,14}][Pro]) [14]. CO₂ reacts with the amino group on the amino acid anion and forms a carbamate. The same research group mentioned that there is a little difference in the CO₂ solubility among the AAILs with a common trihexyltetradecylphosphonium cation [15]. Because of the excellent CO₂ solubility, the AAILs were applied not only to absorbents but also as components for adsorbents and separation membranes [16-19]. For example, the supported ionic liquid membranes (SILMs) with 1-ethyl-3-methylimidazolium glycinate ([emim][Gly]) and tetrabutylphosphonium

L-prolinate ([P₄₄₄₄][Pro]) showed much higher CO₂ permeabilities and CO₂/N₂ selectivities than the conventional polymer membranes [16,19].

Almost all the literatures reported the molar ratio based CO₂ solubility (i.e. moles of absorbed CO₂ per mole of AAIL). Such data exclude the effect of molecular volume of IL. Therefore, ~~the CO₂ capacity, that is,~~ the molarity- or molality-scaled solubilities of CO₂ are more important and direct information for engineering design in the CO₂ separation. Furthermore, earlier studies have reported the CO₂ absorption behaviors of AAILs at the limited pressures up to ~0.2 MPa so far. However, some gas-sweetening processes are operated at much higher pressures of CO₂. In order to understand whether AAILs are applied to high-CO₂ pressure sources or not, pressure-volume-temperature-composition (*pVTx*) relations for AAIL + CO₂ systems under high pressures are necessary. In the present study, we investigated *pVTx* relations for CO₂ + [P₄₄₄₄][Pro] binary system over the pressure range up to 6 MPa at 333.15 K. Phosphonium ILs generally have higher thermal stability than other ILs with imidazolium and ammonium cations. The smaller cation (i.e. [P₄₄₄₄]⁺) shows the higher volumetric CO₂ capacity compared with the larger cation (i.e. [P_{666,14}]⁺), if the CO₂ absorption of [Pro]⁻ are not strongly affected by the cation species. The *pVTx* measurements were also performed for CO₂ + tetrabutylphosphonium (*S*)-2-methylprolinate ([P₄₄₄₄][MePro]) and + tetrabutylphosphonium glycinate ([P₄₄₄₄][Gly]) systems to discuss the effect of anion species on the high-pressure CO₂ solubility. The molecular structures of the present AAILs are presented in Fig. 1. [MePro]⁻ is an analogue of [Pro]⁻, with the methyl group on the α-carbon. Note that [P_{666,14}][Gly] absorbs the larger amount of CO₂ (on molar ratio base) than [P_{666,14}][Pro] [15]. In addition, we measured the density, viscosity, and electrical conductivity of [P₄₄₄₄][Pro] over the temperature range of 298.15-363.15 K. The CO₂ solubilities in [P₄₄₄₄][Pro] at atmospheric pressure of CO₂ were also determined as a function of temperature up to 393.2 K. NMR spectroscopic analysis was performed for the CO₂ saturated [P₄₄₄₄][Pro]

to identify the product with CO₂.

2. Experimental

2.1. Materials

Tetrabutylphosphonium hydroxide ([P₄₄₄₄][OH]) aqueous solution (purity >39.4 wt%) was obtained from Sigma-Aldrich. *L*-proline (purity >99.0 %), (*S*)-2-methylproline (purity >96.0 %), and glycine (purity >99 %) were purchased from Tokyo Chemical Industry Co., Ltd. CO₂ (purity 99.99 %) was obtained from Showa Tansan Co., Ltd. Table 1 lists the chemicals with the purities and purification methods employed in the present study, and they were used without further purification.

2.2. Synthesis

[P₄₄₄₄][Pro] was synthesized by neutralization as follows: [P₄₄₄₄][OH] solution was added dropwise with stirring to the aqueous solution of *L*-proline. Then, the mixture was stirred for 24 h at room temperature. Subsequently, an appropriate amount of acetonitrile/ethanol mixture was added to recrystallize and remove the unreacted amino acid. The filtrate was dried under reduced pressure, and yellowish viscous liquid was obtained. The synthetic methods for [P₄₄₄₄][MePro] and [P₄₄₄₄][Gly] were similar to that for [P₄₄₄₄][Pro]. The AAILs were identified by ¹H NMR (Brucker Advance 500, Brucker BioSpin). The purities of AAILs were estimated >98 % for [P₄₄₄₄][Pro], >98 % for [P₄₄₄₄][MePro], and >98 % for [P₄₄₄₄][Gly]. Any excess water in the ILs was further removed under vacuum at 313 K for one week. Dried ILs were transferred to a closed cell or other instruments by an airtight syringe under dry nitrogen or argon atmosphere, of which the dew points were less than -15 °C. The water content was determined by Karl Fischer coulometric titration (KEM, MKC-510). [P₄₄₄₄][Pro], [P₄₄₄₄][MePro], and [P₄₄₄₄][Gly] contained 423, 131, and 182 ppm

(w/w) of water, respectively. The purity and purification methods are also summarized in Table 1.

2.3. Density, viscosity, electrical conductivity, and CO₂ solubility at atmospheric pressure

The instruments, experimental procedures, and calibration methods were the same as our previous reports [3,4]. The density, viscosity, and electrical conductivity were measured using the vibrating tube densimeter (Anton Paar, DMA 5000M), the rotating cylinder viscometer (Anton Paar, Stabinger SVM 3000), and the impedance analyzer (Bio Logic, SP-150), respectively. The sample temperatures were maintained within ± 0.01 K at most. The expanded uncertainties for the densities, viscosities, and electrical conductivities were ± 0.1 kg·m⁻³, ± 2 %, and ± 2 %, respectively.

The experimental equipment and method for the CO₂ solubility measurement at atmospheric pressure was described in detail elsewhere [12]. An desired amount of AAIL was introduced in a cell under dry N₂ (99.9999 %). A weight of AAIL w_{IL} was measured using an electrical balance (Mettler Toledo, XP5003S). The weights of AAIL and cell after saturated with N₂ and CO₂ were defined as w_1 and w_2 , respectively. The amount of CO₂ absorbed in [P₄₄₄₄][Pro] w_{CO_2} was obtained from the difference between w_1 and w_2 by assuming that N₂ solubility at atmospheric pressure is negligibly small. The CO₂ solubility per mole of AAIL α was presented as $\alpha_{CO_2} = (w_{CO_2}/M_{CO_2})/(w_{IL}/M_{IL})$. M_{CO_2} and M_{IL} stand for the molar masses of CO₂ and IL, respectively. The measurement was performed at $p_{CO_2} = 0.10$ MPa and the temperature was kept within ± 0.1 K. The uncertainty of α is estimated to be less than 0.01. After the measurements, [P₄₄₄₄][Pro] saturated with CO₂ at 333.2 K was transferred to a NMR tube and then quickly sealed under dry nitrogen for NMR spectroscopic analyses. ¹H and ¹³C NMR spectra were obtained using a JEOL Resonance ECA-600 with benzene-*d*₆ in a capillary as an external standard at 333 K. The NMR peaks were assigned in combination

with ab initio calculation results for isolated ions using a Gaussian 09 with B3LYP/6-311G+(2d,p) basis set [20].

2.4. $pVTx$ for AAIL + CO_2 binary systems

We used the same experimental apparatuses and procedures as reported in the previous work [5]. First, the volume expansion of AAIL phase $\Delta V_L(T, p_{CO_2})$ was determined as a function of pressure p_{CO_2} at 333.15 K. $\Delta V_L(T, p_{CO_2})$ was defined as the following equation (1).

$$\Delta V^L(T, p_{CO_2}) = \frac{V^L(T, p_{CO_2}) - V^L(T, p^0)}{V^L(T, p^0)} \quad (1)$$

$V^L(T, p_{CO_2})$ is the volume of AAIL phase saturated with CO_2 at a temperature T and a CO_2 pressure p_{CO_2} . $V_L(T, p^0)$ stands for the volume of AAIL phase under Ar atmosphere (purity, 99.9999 mol%; 0.101 MPa) at T . The height of AAIL phase in the sapphire tube cell was measured visually with a cathetometer to obtain the volume of AAIL phase. Similar measurements were performed at different CO_2 pressures, and a polynomial of $\Delta V_L(T, p_{CO_2})$ was obtained.

Next, the molar amount of CO_2 absorbed in the AAIL $n_1^L(T, p_{CO_2})$ was obtained by measuring the pressure change. $n_1^L(T, p_{CO_2})$ was calculated by the equation (2) on the assumption that the concentration of AAIL in the CO_2 phase was negligibly small.

$$n_1^L(T, p_{CO_2}) = n_1^i - \frac{V_{\text{cell}} - V^L(T, p_{CO_2})}{V_m^G(T, p_{CO_2})} \quad (2)$$

The symbols are as follows: n_1^i , the molar amount of CO_2 in the cell; V_{cell} , the inner volume of the cell; $V^L(T, p_{CO_2})$, the volume of AAIL phase calculated from eq. (1); $V_m^G(T, p_{CO_2})$, the molar volume of CO_2 in gas phase calculated using NIST REFPROP Ver. 9.0 [21]. n_1^L , the amount of IL in the cell n_2 , and $V^L(T, p_{CO_2})$ give the mole fraction of CO_2 in AAIL phase x_1 , the molarity of CO_2 in AAIL phase c_1 , and the molar volume of AAIL phase V_m^L (see the literature [5] to find the equations for calculating x_1 , c_1 , and V_m^L). The uncertainties of T , p_{CO_2} ,

x_1 , c_1 , and V_m^L are estimated as 0.02 K, 0.002 MPa, ± 0.002 , ± 0.8 , and ± 0.7 %, respectively.

3. Results and Discussion

3.1. Density, viscosity, and electrical conductivity of $[P_{4444}][Pro]$

The experimental values are summarized in Table 2. The density ρ of $[P_{4444}][Pro]$ is presented in Fig. 2. The present data were fitted to the quadratic function (3) with the standard error of the fit less than 0.005 %.

$$\rho/\text{kg}\cdot\text{m}^{-3} = 1144.50 - 5.75330\cdot 10^{-1}\cdot(T/\text{K}) - 1.98590\cdot 10^{-5}\cdot(T/\text{K})^2 \quad (3)$$

The standard errors of the coefficients are 3.75, $0.22792\cdot 10^{-1}$, and $3.45320\cdot 10^{-5}$, respectively. The literature values [22] are ~ 2 % higher than the present data as shown in Fig. 2. This deviation is larger than the uncertainties estimated in the present study and the literature. Fig. 2 presents the density of another *L*-prolinate, $[P_{666,14}][Pro]$ [23]. The density of *L*-prolinates decreased monotonically with an increase of temperature. $[P_{4444}][Pro]$ has the larger density than $[P_{666,14}][Pro]$ at certain temperatures, due to the difference of cation size, $[P_{666,14}]^+ > [P_{4444}]^+$. The thermal expansivities $\beta (\equiv (1/V)(\partial V/\partial T)_p)$ are $5.8046\cdot 10^{-4} \text{ K}^{-1}$ for $[P_{4444}][Pro]$ and $6.3796\cdot 10^{-4} \text{ K}^{-1}$ for $[P_{666,14}][Pro]$ at 298 K. The density of $[P_{4444}][Pro]$ is less sensitive to temperature than that of $[P_{666,14}][Pro]$.

Fig. 3 is the temperature T - viscosity η and molar conductivity Λ relations. Each property shows the ordinary temperature dependency. The viscosity decreased and the molar conductivity increased with temperature. These transport properties were fitted to the Vogel-Fulcher-Tammann (VFT) equation.

$$\eta/\text{mPa}\cdot\text{s} = (-3.434\pm 0.047)\cdot\exp((1314\pm 15)/(T/\text{K}-(171.4\pm 0.8))) \quad (4)$$

$$\kappa/\text{S}\cdot\text{m}^{-1} = (4.793\pm 0.020)\cdot\exp((-1247\pm 6)/(T/\text{K}-(169.8\pm 0.4))) \quad (5)$$

$$\Lambda/\mu\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1} = (10.9_6\pm 0.01_7)\cdot\exp((-1292\pm 5)/(T/\text{K}-(168.0\pm 0.3))) \quad (6)$$

The standard errors of the fits are 0.21 % for η , 0.06 % for κ , and 0.05 % for A , respectively. The viscosities reported in another work [22] are slightly higher than those measured in the present study at low temperatures as shown in Fig. 3. One possible explanation for the deviations in density and viscosity is impurities. The water contents in the present and reported [P₄₄₄₄][Pro] were sufficiently small, 423 and 51 ppm, respectively. Therefore, other impurities would influence the physical properties. Unfortunately, since the literature did not report the estimated purity, the effect of impurities on the physical properties cannot be elucidated.

3.2. CO₂ solubility in [P₄₄₄₄][Pro] at atmospheric pressure

Table 3 lists the CO₂ solubilities α (moles of CO₂ per mole of AAIL) in [P₄₄₄₄][Pro] and [P_{666,14}][Pro] [23]. [P₄₄₄₄][Pro] was solidified at 313.2 K and $p_{\text{CO}_2} = 0.10$ MPa, and we could not measure the CO₂ solubility at lower temperatures. One mole of [P₄₄₄₄][Pro] absorbed 0.97 moles of CO₂ at 333.2 K. This reveals that CO₂ reacts with [P₄₄₄₄][Pro] in the 1:1 stoichiometry. The temperature dependency of the CO₂ solubility is very small, and [P₄₄₄₄][Pro] desorbed 0.16 moles of CO₂ by heating from 333.2 K to 393.2 K. [P_{666,14}][Pro] shows the similar CO₂ absorption behavior to [P₄₄₄₄][Pro]. The length of the alkyl chain on the phosphonium has only a marginal effect on the CO₂ solubility, which suggests that CO₂ reacts with [Pro]⁻ without a significant influence of the tetraalkylphosphonium cations in the AAILs.

Fig. 4 presents the ¹H and ¹³C NMR spectra for the neat [P₄₄₄₄][Pro] and CO₂-saturated [P₄₄₄₄][Pro]. Calculated chemical shifts are summarized in Table S1 (ESI). The peaks of benzene-*d*₆ were detected at 7.1 ppm (¹H) and around 128 ppm (¹³C). Some proton peaks derived from [Pro]⁻ (e.g. 2-3 ppm) shifted to higher and a new peak at 17.5 ppm appeared after CO₂ absorption. The new peak is attributed to the protons on the carboxylic acid groups,

which were partially produced in the reaction with CO₂. This peak is a convolution of ~~There~~ ~~are~~ two possible chemical species, and the one is [Pro-CO₂]⁻, which is generated from the intramolecular proton transfer from the adducted CO₂ (-N-CO₂H) to the carboxylate group (-COO⁻). The other is ~~the generation of~~ L-proline ([ProH]), which is produced through the formation of dianion (i.e. [Pro-CO₂]⁻ + [Pro]⁻ → [Pro-CO₂]²⁻ + [ProH]). The latter was demonstrated with the theoretical method in the literature [15]. Two moles of [P₄₄₄₄][Pro] are required to absorb one mole of CO₂ in the latter case (the 1:2 stoichiometry). Therefore, the former is dominant in the present system, because [P₄₄₄₄][Pro] absorbed CO₂ in the 1:1 stoichiometry. This is also supported by the calculated chemical shifts, that is, the ¹H peak of carboxylate group on [Pro-CO₂]⁻ (17.9 ppm) is much closer to the experimental result compared to that on [ProH] (10.7 ppm) (Table S2). On the other hand, the proton peaks for [P₄₄₄₄]⁺ (0.9, 1.3-1.5, and 2.5 ppm) did not show significant changes. A similar behavior was observed in ¹³C NMR spectra. The peaks for [Pro]⁻ shifted to the higher field other than δ-carbon after the reaction with CO₂, which is consistent with the calculated chemical shifts. The new peak at 160 ppm is assigned to the carbon of carbamate. These results indicate that [Pro]⁻ plays an important role in the CO₂ absorption, while [P₄₄₄₄]⁺ does not. This results in the small impact of the alkyl chain length on the CO₂ solubility.

3.3. *pVTx for CO₂ + AAIL binary systems*

Experimental values of *pVTx* relations are summarized in Table 4. Fig. 5 presents the CO₂ solubility in molarity scale *c*₁ as a function of pressure *p*_{CO₂}. *c*₁ increased steeply at pressures up to ~0.15 MPa and gradually increased at higher pressures. [P₄₄₄₄][Pro] showed the largest *c*₁ at ~~the pressures of~~ *p*_{CO₂} < 0.15 MPa and *p*_{CO₂} > 3.5 MPa in the present study. In the pressure range of 0.15 < *p*_{CO₂} < 3.5 MPa, [P₄₄₄₄][Gly] absorbed the largest amount of CO₂ in molarity scale. *c*₁ in [P₄₄₄₄][MePro] was the smallest in the present AAILs under the

investigated conditions. Fig. 5 also shows the literature values of CO₂ solubility in [emim][TCB], which is the highest in molarity scale among the IL physical absorbents [11]. c_1 in all the present AAILs are higher than that in [emim][TCB] at the pressures investigated, though [emim][TCB] seems to absorb CO₂ more than the AAILs at the higher pressures of $p_{\text{CO}_2} > 6$ MPa.

In order to understand how the anion species influences high-pressure CO₂ solubility, c_1 is deconvoluted into the contributions of physical and chemical absorptions. According to the literature [15], we assumed three equilibria for the AAIL + CO₂ systems as follows.

[AA]⁻, [AA-CO₂]⁻, [AAH] stand for the amino acid anion, the amino acid anion-CO₂ complex, and the amino acid, respectively. The above schemes present the equilibria between the physical (scheme (I)) and chemical (schemes (II) and (III)) absorptions. The reaction in the scheme (II) is the 1:1 stoichiometry, while that in the scheme (III) is the 1:2 stoichiometry.

Our previous studies [5,7,9-11] revealed that the molarity scaled solubility in IL physical absorbent $c_{1,\text{P}}$ is approximately correlated with a linear function of pressure p_1 with a coefficient A as eq. (7).

$$c_{1,\text{P}} = Ap_1 \quad (7)$$

The equilibrium constant of scheme (II) K_1 is obtained from the molar concentrations of physically dissolved CO₂ $c_{1,\text{P}}$, un-reacted [AA]⁻ c_{AA} , and complex of [AA]⁻ and CO₂ (i.e. [AA-CO₂]⁻) $c_{1,\text{C1}}$.

$$K_1 = \frac{c_{1,\text{C1}}}{c_{1,\text{P}}c_{\text{AA}}} \quad (8)$$

Similarly, the equilibrium constant of scheme (III) K_2 is estimated by

$$K_2 = \frac{c_{1,C2}c_{AAH}}{c_{1,C1}c_{AA}} \quad (9)$$

$c_{1,C2}$ and c_{AAH} stand for the molar concentrations of $[AA-CO_2]^{2-}$ and $[AAH]$. The total amounts of CO_2 c_1 and AAIL c_2 are given by

$$c_1 = c_{1,P} + c_{1,C1} + c_{1,C2} \quad (10)$$

$$c_2 = c_{AA} + c_{1,C1} + c_{1,C2} + c_{AAH} \quad (11)$$

Finally, we obtain the following equation from eqs. (7) to (11).

$$c_1 = Ap_1 + \alpha(c_2 - 2c_2 \frac{2\alpha K_2(1-\alpha) - \sqrt{\alpha K_2(1-\alpha)}}{4\alpha K_2(1-\alpha) - 1}) + c_2 \frac{2\alpha K_2(1-\alpha) - \sqrt{\alpha K_2(1-\alpha)}}{4\alpha K_2(1-\alpha) - 1} \quad (12)$$

where

$$\alpha = \frac{Ap_1 K_1}{1 + Ap_1 K_1} \quad (13)$$

Table 5 summarizes A , K_1 , K_2 , and the standard deviations for the present CO_2 + AAIL binary systems. As shown in **Table S2**, the experimental results were **better** reproduced by taking ~~the scheme (III)~~ into consideration **the three equilibria model compared with the two equilibria model without the scheme (III)**, in particular, for the $[P_{4444}][Gly]$ + CO_2 system. A for $[P_{4444}][Pro]$ is slightly greater than those for $[P_{4444}][MePro]$ and $[P_{4444}][Gly]$, which means the physically dissolved CO_2 in $[P_{4444}][Pro]$ is a little bit larger. These values are about a half for the physical absorbent, $[emim][TCB]$ ($0.689 \text{ mol dm}^{-3} \text{ MPa}^{-1}$ at 333.2 K) [11]. K_1 for $[P_{4444}][Gly]$, $[P_{4444}][MePro]$, and $[P_{4444}][Pro]$ increases in this order, whereas K_2 shows the opposite behavior. This suggests that the 1:1 reaction (one mole of CO_2 reacts with one mole of AAIL) is promoted in $[P_{4444}][Pro]$ and $[P_{4444}][MePro]$ compared with $[P_{4444}][Gly]$. Fig. 6 shows the molarities of physically absorbed CO_2 $c_{1,P}$, and chemically absorbed CO_2 $c_{1,C}$ ($= c_{1,C1} + c_{1,C2}$) as a function of pressure. $c_{1,P}$ increases monotonically. On the other hand, $c_{1,C}$ shows steep increment at low pressures up to around 0.1 MPa and gradual decrement at

higher pressures due to the slight volume expansion of AAIL phase. [P₄₄₄₄][Pro] has the largest $c_{1,P}$, and the $c_{1,P}$ values for the others are similar to each other at the investigated pressures. $c_{1,C}$ for [P₄₄₄₄][Gly] is the largest followed by [P₄₄₄₄][Pro] and [P₄₄₄₄][MePro]. Therefore, the highest molarity c_1 in [P₄₄₄₄][Gly] at $p_1 = 0.15 - 3.5$ MPa is derived from the highest chemical absorption $c_{1,C}$, whereas the higher physical absorption $c_{1,P}$ in [P₄₄₄₄][Pro] inversely causes the highest molarity c_1 at $p_1 > 3.5$ MPa. [P₄₄₄₄][MePro] shows the lowest physical and chemical absorptions, resulting in the smallest CO₂ molarity c_1 under the present conditions.

The mole fractions of physically absorbed CO₂ $x_{1,P}$ and chemically absorbed CO₂ $x_{1,C}$ were calculated from the following equations.

$$x_{1,P} = \frac{c_{1,P}}{c_{1,P} + c_{1,C} + c_{AA} + c_{AAH}} \quad (14)$$

$$x_{1,C} = \frac{c_{1,C}}{c_{1,P} + c_{1,C} + c_{AA} + c_{AAH}} \quad (15)$$

Fig. 7 is the pressure-mole fraction plots for the present binary systems. $x_{1,P}$ increases with pressure. [P₄₄₄₄][Pro] and [P₄₄₄₄][MePro] show similar $x_{1,P}$, and $x_{1,P}$ in [P₄₄₄₄][Gly] is the smallest. This trend is different from that observed for the molarity scaled solubility (Fig. 6) because the molar volumes of AAILs ([P₄₄₄₄][Gly] < [P₄₄₄₄][Pro] < [P₄₄₄₄][MePro]) make some contributions to the molarity. We estimated the proportional constant of CO₂ physically dissolved in the AAILs k_H^∞ , like the Henry constant in dilution condition, from the eq. 14.

$$k_H^\infty = \lim_{p \rightarrow 0} \left[\frac{f_1}{x_{1,P}} \right] \quad (16)$$

f_1 stands for the fugacity of CO₂. k_H^∞ for [P₄₄₄₄][Pro], [P₄₄₄₄][MePro], and [P₄₄₄₄][Gly] are 6.8 MPa, 7.0 MPa, and 8.1 MPa, respectively. These values are between the typical fluorinated ILs, [bmim][Tf₂N] (6.0 MPa [11]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆], 8.1 MPa at 323 K [24]). Since the amino acid anions are less effective to

improve the physical absorption of CO₂ like the fluorinated anions, [P₄₄₄₄]⁺ decreases the present Henry constants presumably due to the large molar volume. The mole fractions of chemically absorbed CO₂ drastically rise at low pressures up to ~0.1 MPa, and decrease monotonically with pressure because of the increment of physically absorbed CO₂. [P₄₄₄₄][Pro] and [P₄₄₄₄][MePro] absorb larger amounts of CO₂ chemically than [P₄₄₄₄][Gly]. This is opposite to the order observed for the AAILs with [P_{666,14}]⁺ in the literature at 295 K [15]. The present results were obtained at higher temperature of 333 K, which suggests that the reaction of [Gly]⁻ with CO₂ is more sensitive to temperature than that of [Pro]⁻. Furthermore, α -methylation on [Pro]⁻ does not significantly influence the CO₂ chemical absorption.

4. Conclusion

The volumetric and transport properties of [P₄₄₄₄][Pro] were measured at atmospheric pressure. The density and viscosity decreased and the molar conductivity increased with temperature. The density and the transport properties were well correlated to the second polynomial and the VFT equations within the experimental errors, respectively. [P₄₄₄₄][Pro] absorbed CO₂ in the 1:1 stoichiometry, and desorbed only ~17 % of CO₂ by heating from 333.2 K to 393.2 K. The formation of carbamate was confirmed by NMR, and the cation had a little effect on the CO₂ solubility. The $pVTx$ relations for the CO₂ + AAIL systems were also determined at 333.2 K and pressures up to 6 MPa. [P₄₄₄₄][Pro] and [P₄₄₄₄][MePro] showed the higher physical and chemical absorptions (on mole fraction base) than [P₄₄₄₄][Gly] at the present conditions, while in the molarity scaled solubility [P₄₄₄₄][Gly] and [P₄₄₄₄][Pro] had the largest chemisorption and physisorption of CO₂, respectively, in the present AAILs.

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References

- [1] J. E. Bara, D. E. Camper, D. L. Gin, R. D. Noble, *Acc. Chem. Res.*, 43 (2010) 152-159.
- [2] M. Ramdin, T. W. de Loos, and Thijs J. H. Vlugt, *Ind. Eng. Chem. Res.* 51 (2012) 8149-8177.
- [3] T. Makino, M. Kanakubo, T. Umecky, A. Suzuki, T. Nishida, J. Takano, *J. Chem. Eng. Data* 57 (2012) 751-755.
- [4] T. Makino, M. Kanakubo, T. Umecky, A. Suzuki, *J. Chem. Eng. Data* 58 (2013) 370-376.
- [5] T. Makino, M. Kanakubo, T. Umecky, A. Suzuki, *Fluid Phase Equilib.* 357 (2013) 64-70.
- [6] T. Umecky, M. Kanakubo, T. Makino, T. Aizawa, A. Suzuki, *Fluid Phase Equilib.* 357 (2013) 76-79.
- [7] T. Makino, M. Kanakubo, T. Umecky, A. Suzuki, T. Nishida, J. Takano, *Fluid Phase Equilib.* 360 (2013) 253-259.
- [8] K. R. Harris, T. Makino, M. Kanakubo, *Phys. Chem. Chem. Phys.* 16 (2014) 9161-9170.
- [9] T. Makino, M. Kanakubo, T. Umecky, *J. Chem. Eng. Data* 59 (2014) 1435-1440.
- [10] T. Makino, M. Kanakubo, Y. Masuda, T. Umecky, A. Suzuki, *Fluid Phase Equilib.* 362 (2014) 300-306.
- [11] T. Makino, M. Kanakubo, Y. Masuda, H. Mukaiyama, *J. Solution Chem.* 43 (2014) 1601-1613.
- [12] M. Kanakubo, T. Makino, T. Umecky, *J. Mol. Liq.* *submitted*.
- [13] J. Zhang, S. Zhang, K. Dong, Y. Zhang, Y. Shen, X. Lv, *Chem. Eur. J.* 12 (2006)

4021-4026.

[14] B. E. Gurkan, J. C. de la Fuente, E. M. Mindrup, L. E. Ficke, B. F. Goodrich, E. A. Price, W. F. Schneider, J. F. Brennecke, *J. Am. Chem. Soc.* 132 (2010) 2116-2117.

[15] B. F. Goodrich, J. C. de la Fuente, B. E. Gurkan, D. J. Zadigian, E. A. Price, Y. Huang, J. F. Brennecke, *Ind. Eng. Chem. Res.*, 50 (2011) 111-118.

[16] S. Kasahara, E. Kamio, T. Ishigami, H. Matsuyama, *Chem. Commun.* 46 (2012) 6903-6905.

[17] X. Wang, N. G. Akhmedov, Y. Duan, D. Luebke, D. Hopkinson, B. Li, *Alp. Mater. Interfaces* 5 (2013) 8670-8677.

[18] X. Wang, N. G. Akhmedov, Y. Duan, D. Luebke, B. Li, *J. Mater. Chem. A*, 1 (2013) 2978-2982.

[19] S. Kasahara, E. Kamio, A. Yoshizumi, H. Matsuyama, *Chem. Commun.* 50 (2014) 2996-2999.

[20] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, 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, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

- [21] E. W. Lemmon, M. L. Huber, M. O. McLinden, NIST Standard reference database 23: reference fluid thermodynamic and transport properties-REFPROP, version 9.0. National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg (2010)
- [22] R. L. Gardas, R. Ge, P. Goodrich, C. Hardacre, A. Hussain, D. W. Rooney, J. Chem. Eng. Data 55 (2010) 1505-1515.
- [23] B. F. Goodrich, J. C. de la Fuente, B. E. Gurkan, Z. K. Lopez, E. A. Price, Y. Huang, J. F. Brennecke, J. Phys. Chem. B 115 (2011) 9140-9150.
- [24] J. L. Anthony, J. L. Anderson, E. J. Maginn, J. F. Brennecke, J. Phys. Chem. B 109 (2005) 6366-6374.

Table 1. Chemicals used in the present study.

Chemical	Source	Purification method	Purity	Analysis method
[P ₄₄₄₄][OH] ^{a)}	Sigma-Aldrich	-	>39.4 wt% ^{e)}	Titration (HCl)
<i>L</i> -proline	Tokyo Chemical Industry Co., Ltd.	-	>99.0 mol%	HPLC, Titration
(<i>S</i>)-2-methylproline	Tokyo Chemical Industry Co., Ltd.	-	>96.0 mol%	Titration
glycine	Tokyo Chemical Industry Co., Ltd.	-	>99 mol%	Titration
CO ₂	Showa Tansan Co., Ltd.	-	99.99 mol%	Gas chromatograph
[P ₄₄₄₄][Pro] ^{b)}	synthesized	Dried under vacuum	>98 mol%	NMR
[P ₄₄₄₄][MePro] ^{c)}	synthesized	Dried under vacuum	>98 mol%	NMR
[P ₄₄₄₄][Gly] ^{d)}	synthesized	Dried under vacuum	>98 mol%	NMR

a) tetrabutylphosphonium hydroxide, b) tetrabutylphosphonium *L*-prolinate, c) tetrabutylphosphonium (*S*)-2-methylprolinate, d) tetrabutylphosphonium glycinate, e) aqueous solution.

Table 2. Density ρ , viscosity η , and electrical conductivity κ of [P₄₄₄₄][Pro] at atmospheric pressure.

T/K	$\rho/\text{kg m}^{-3}$	$\eta/\text{mPa s}$	$\kappa/\text{S m}^{-1}$
298.15	971.1 ₀	1025	0.00727 ₃
303.15	968.2 ₀	692. ₈	0.0104 ₇
313.15	962.3 ₈	343. ₆	0.0201 ₀
323.15	956.4 ₆	186. ₁	0.0354 ₄
333.15	950.5 ₄	108. ₇	0.0583 ₈
343.15	944.6 ₃	67.7 ₄	0.0907 ₀
353.15	938.7 ₅	44.5 ₀	0.134 ₁
363.15	932.9 ₀	30.6 ₁	

$u(T)=0.02$ K, $u(\rho)=0.1$ kg m⁻³, $u_{\text{r}}(\eta)=0.02$, $u_{\text{r}}(\kappa)=0.02$

Table 3. CO₂ solubilities in the AAILs α at $p_{\text{CO}_2} = 0.10$ MPa.

[P ₄₄₄₄][Pro]		[P _{666,14}][Pro] [23] ^{a)}	
T / K	α	T / K	α
313.4	(0.97 ₀) ^{b)}	313	0.920
333.2	0.97 ₀	333	0.930
352.7	0.94 ₈	353	0.870
372.6	0.89 ₉	373	0.820
393.2	0.80 ₅	-	-

^{a)} The solubility was estimated from the interpolation of the literature values.

^{b)} The solution might not completely saturated with CO₂ because of solidification.

Table 4. $pVTx$ relations for the CO₂ (1) + AAIL (2) binary systems at 333.2 K.

CO ₂ (1) + [P ₄₄₄₄][Pro] (2)			
p/MPa	x_1	$c_1/\text{mol dm}^{-3}$	$V_{\text{m}}/\text{cm}^3 \text{ mol}^{-1}$
0.017 ₇	0.483	2.36 ₃	204. ₅
0.101 ₃	0.492	2.38 ₄	206. ₃
0.328 ₁	0.502	2.43 ₆	206. ₂
0.851 ₈	0.522	2.61 ₀	199. ₉
1.424 ₈	0.541	2.79 ₁	193. ₇
1.884 ₃	0.555	2.93 ₆	189. ₀
2.293 ₃	0.568	3.07 ₂	184. ₈
2.792 ₅	0.582	3.23 ₆	179. ₉
3.282 ₁	0.596	3.39 ₄	175. ₅
3.790 ₀	0.609	3.55 ₇	171. ₂
4.297 ₉	0.622	3.73 ₅	166. ₇

4.862 ₈	0.635	3.90 ₇	162. ₆
5.353 ₆	0.646	4.05 ₄	159. ₂

CO₂ (1) + [P₄₄₄₄][MePro] (2)

p/MPa	x_1	$c_1/\text{mol dm}^{-3}$	$V_{\text{m}}/\text{cm}^3 \text{ mol}^{-1}$
0.010 ₆	0.467	2.11 ₉	220. ₅
0.135 ₇	0.488	2.27 ₆	214. ₃
0.407 ₈	0.499	2.34 ₈	212. ₆
0.454 ₆	0.502	2.37 ₆	211. ₄
0.908 ₉	0.517	2.50 ₃	206. ₅
1.558 ₅	0.542	2.73 ₇	197. ₉
1.928 ₂	0.552	2.84 ₀	194. ₄
2.331 ₉	0.565	2.97 ₂	190. ₁
2.782 ₃	0.578	3.11 ₂	185. ₇
3.041 ₇	0.586	3.20 ₅	182. ₉
3.272 ₅	0.591	3.25 ₈	181. ₄
3.797 ₄	0.604	3.41 ₂	177. ₀
4.319 ₅	0.616	3.56 ₂	173. ₀
4.887 ₃	0.628	3.71 ₃	169. ₂
5.350 ₉	0.638	3.84 ₅	166. ₀

CO₂ (1) + [P₄₄₄₄][Gly] (2)

p/MPa	x_1	$c_1/\text{mol dm}^{-3}$	$V_{\text{m}}/\text{cm}^3 \text{ mol}^{-1}$
0.016 ₃	0.421	2.00 ₅	209. ₈
0.061 ₁	0.443	2.18 ₆	202. ₆
0.097 ₃	0.448	2.22 ₉	201. ₂
0.159 ₀	0.462	2.33 ₈	197. ₄

0.252 ₀	0.469	2.39 ₅	195.9
0.405 ₅	0.485	2.53 ₂	191.4
0.798 ₈	0.504	2.72 ₂	185.2
1.601 ₀	0.531	3.00 ₂	176.9
2.561 ₄	0.555	3.26 ₄	170.0
3.645 ₄	0.578	3.53 ₀	163.6
4.990 ₆	0.600	3.80 ₂	157.8

$u(p) = 0.002 \text{ MPa}$, $u(x_1) = 0.002$, $u_r(c_1) = 0.01$, $u_r(V_m^L) = 0.01$

Table 5. Coefficients of eq. 8 for the present AAIL + CO₂ binary systems.

	[P ₄₄₄₄][Pro]	[P ₄₄₄₄][MePro]	[P ₄₄₄₄][Gly]
$A/\text{mol dm}^{-3} \text{ MPa}^{-1}$	0.360±0.001	0.338±0.003	0.336±0.02
$K_1/\text{dm}^3 \text{ mol}^{-1}$	4719±473	3069±399	529±132
$K_2/-$	(1.50±0.11)·10 ⁻³	(2.70±0.44)·10 ⁻³	(1.33±0.47)·10 ⁻²
std. dev./%	0.18	0.66	2.4

Fig. 1 Molecular structures of AAILs used in the present study.

Fig. 2. The density ρ as a function of temperature T . ●, $[P_{4444}][Pro]$; ○, $[P_{4444}][Pro]$ [22]; □, $[P_{666,14}][Pro]$ [23].

Fig. 3. The viscosity η and molar conductivity Λ as a function of temperature T . ●, η for $[P_{4444}][Pro]$; ○, η for $[P_{4444}][Pro]$ [22]; □, η for $[P_{666,14}][Pro]$ [23]; ▲, Λ for $[P_{4444}][Pro]$.

Fig. 4. 1H and ^{13}C NMR spectra of $[P_{4444}][Pro]$ before and after CO_2 absorption at 333.2 K.

Fig. 5. The molarity scaled solubility of CO₂ c_1 as a function of CO₂ pressure p_1 at 333.15 K. ●, [P₄₄₄₄][Pro]; ○, [P₄₄₄₄][MePro]; ■, [P₄₄₄₄][Gly]; ◆, [emim][TCB] [11].

Fig. 6. The molarity scaled solubility of CO₂ c as a function of CO₂ pressure p_1 at 333.15 K. Black, physically absorbed CO₂; white, chemically absorbed CO₂; circle, [P₄₄₄₄][Pro]; diamond, [P₄₄₄₄][MePro]; square, [P₄₄₄₄][Gly].

Fig. 7. The mole fraction scaled solubility of CO₂ x as a function of CO₂ pressure p_1 at 333.15 K. Black, physically absorbed CO₂; white, chemically absorbed CO₂; circle, [P₄₄₄₄][Pro]; diamond, [P₄₄₄₄][MePro]; square, [P₄₄₄₄][Gly].