

CO₂ Absorption Performance of “Dry Matter” Prepared with Amino Acid-Based Ionic Liquids

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Abstract

Dry Matter (DM) is a powdery substance which is composed of micro droplets and surrounding hydrophobic silica nanoparticles. Because of the much larger surface area than that of the corresponding bulk liquid, DM, which contains amino-functionalized ionic liquids (ILs), is a promising CO₂ absorption material provided with quick absorption speed. In the present study, we successfully prepared powdery DMs by utilizing aqueous solutions of amino acid-based ILs (tetraethylammonium glycine [N₂₂₂₂][Gly], and tetraethylammonium alanine [N₂₂₂₂][Ala]). Although a DM with lysine-based IL (N₂₂₂₂)[Lys] was also prepared, only a soufflé-like material was obtained. We measured CO₂ absorption performance for the DMs to find that the mass-base absorption ability (mass-base A.A.) (CO₂ mol/DM kg) and the mol-base one (CO₂ mol/IL mol) of [N₂₂₂₂][Lys] were ca. two times of [N₂₂₂₂][Gly] and [N₂₂₂₂][Ala], while the absorption speed of the former was inferior to the latter two, *i.e.*, ca.15 min vs. 5 min for 90% absorption. In order to improve the mass-base A.A. of [N₂₂₂₂][Gly], we used 10% of aqueous poly(allylamine) (PALAm) solution instead of water. The resultant mass-base A.A. proved to be significantly larger (1.9) than either of those of the respective single component systems (1.1 and 0.75 for the bulk IL and aq. PALAm, respectively), and comparable to the A.A. (1.6 - 2.5) of 20% - 30% monoethanolamine solution which is commonly used in industrial application.

Keywords

Dry Matter, Ionic Liquid, CO₂ Absorption, Amino Acid, Polyallylamine

1. Introduction

CO₂ capture from flue gases is now vital to reduce the green-house effect. As a main process to remove CO₂ from the industrially emitted gases, the chemical absorption to aqueous solutions of low molecular weight amines, such as mo-

noethanolamine (MEA) and N-methyldiethanolamine (MDEA), has been traditionally utilized. However, this conventional procedure has some serious drawbacks, e.g., inevitable loss and emission of those corrosive amines and thermal degradation during the energy-demanding regeneration process of the absorbents [1]. As a promising candidate for CO₂-absorbing materials, amine-functionalized ionic liquids have recently attracted much attention [1]-[10]. Since ionic liquids (ILs) have favorable properties such as negligible volatility and excellent thermal stability, they are free from some of the above drawbacks. A prominent example for the application of ILs for the CO₂ absorption has been reported by Romanos *et al.* [11] who employed the “inverse supported ionic liquid phase materials” (inverse SILPs). SILP is a material in which ILs are supported or adsorbed on the surface of porous substrate. In the “inverse” SILP, which is a powder-like substance, the phases are inverted and the IL is surrounded by solid materials. For example, the inverted SILP was prepared by a two-step method; in the first step an amino acid-derived IL such as N, N, N-trimethyl-N-ethyl ammonium propionate was mixed with fumed silica nanoparticles. Then the mixture was slurried with ethanol and the suspension thus obtained was dried to obtain the final powdery substance. This substance may be called Dry Ionic Liquid (D-IL) according to our original naming [12]. However, the D-IL can be prepared, in principle, with a much easier procedure, *i.e.*, by simply mechanically mixing an appropriate IL with a hydrophobized fumed silica.

D-IL is a member of Dry Matter (DM), which is a collective name of powdery materials that are composed of micro droplets as an inner core phase and surrounding hydrophobic silica nanoparticles. According to the inner phase, DM may be called Dry Water, Dry Polymer Solution (D-PS), Dry gel and Dry Ionic Liquid (D-IL), etc. In our previous studies [12] [13], we first reported the successful preparation of powdery D-ILs. Since the liquid droplet diameter of the D-IL particles is as small as 10 μm [12], the large surface area enabled quick absorption [13]. Due to the relatively low surface tension of ILs, however, it proved to be rather difficult to obtain powdery D-ILs by employing pure ILs. As an expedient procedure we added water to ILs to increase their surface tensions and found that this method was usable to prepare powdery DMs containing ILs (aqueous IL-type of DM or aqIL-DM) for most ILs tested. For example, 1-butyl-3-methylimidazolium acetate ([bmim][ace]), which is an excellent CO₂-absorbing IL [14], provided only a paste-like substance when the bulk liquid was used, while a powdery DM could be obtained by adding 60 wt% of water. Then we examined the aqIL-DM on its CO₂ absorption ability and only found a much less absorption than that of the bulk IL. The failure of CO₂ absorption in the presence of water was interpreted in terms of the unique CO₂ absorption mechanism of [bmim][ace] [15]; C2 proton of the imidazolium ring is abstracted by an acetic acid counter anion to form a site where CO₂ reacts. Namely, stable hydration of the carboxyl anions may interfere with the proton abstraction.

In the present study we prepared aqIL-DMs by using some amino acid-based ILs, because their CO₂ absorption abilities may be rather enhanced in the presence of water [16]. The performance as CO₂-absorption materials was checked in

terms of the absorption speed and the capacity. Since water absorbs CO₂ only slightly, the addition of water to ILs would reduce the total mass-base CO₂ absorption ability even if the mol-base ability of IL employed were enhanced by the presence of water. Thus, we also tested an aqIL-DM in which water was replaced by aqueous solution of poly(allyl amine) (PALAm) because the polyamine should have a substantial CO₂ absorption ability [13] [17]. The resultant total CO₂ absorption ability, in fact, proved to become higher than either of the respective bulk absorptions.

2. Materials and Methods

2.1. Materials

Tetraethyl ammonium hydroxide ([N₂₂₂₂][OH]) and three kinds of amino acids, *i.e.*, glycine [Gly], L-alanine [Ala] and L-lysine [Lys], were purchased from Sigma Aldrich as 35 wt% aqueous solution and powder samples, respectively, and used as received. Poly(allyl amine)hydrochloride (PALAm-HCl) (MW:15000, Sigma Aldrich) was neutralized by NaOH and then filtrated through an Ultrafilter UP-10 (Advantec) for several times with pure water to remove inorganic ions and low molecular weight polymers. Concentration of PALAm thus purified was estimated by conductometric titration to be ca. 24 wt%.

Hydrophobic fumed silica particle (HDK-H18, primary particle size: 5 - 30 nm), the surface OH groups of which are methylated with poly(dimethyl siloxane) by 75%, was purchased from Wacker Asahikasei Silicone Co. and used as received.

2.2. Methods

2.2.1. Preparation of Amino Acid-Based AqILs

[N₂₂₂₂][Gly], [N₂₂₂₂][Ala], and [N₂₂₂₂][Lys] ILs were prepared by neutralizing the respective amino acids with the equimolar [N₂₂₂₂][OH]. For example, in the case of [N₂₂₂₂][Gly] 1.0 g of glycine was neutralized with 5.6 g of the 35 wt% of [N₂₂₂₂][OH] solution to obtain 6.6 g of [N₂₂₂₂][Gly] containing 55.2 wt% of water (*i.e.*, 45 wt% aqueous [N₂₂₂₂][Gly] solution). In a similar way we prepared [N₂₂₂₂][Ala] and [N₂₂₂₂][Lys] ILs containing 54 wt% and 48 wt% of water, respectively.

2.2.2. Preparation of D-IL

AqIL-DMs were prepared with a blender machine (Waring J-SPEC blender, container volume: 50 mL) by mixing 6.0 g of an aqueous IL solution and 1.05 g of the silica at a fixed speed (22,500 rpm) for 90 s (30 s × 3 with an interval of 10 s each) at a room temperature. Partial remove of water from the prepared DM samples was performed with an infrared humidity meter (FD-720, Kett Co. Ltd.) at 40 °C or 80 °C. AqIL-DM containing PALAm was also prepared with the same preparation procedure except for using mixed solutions of aq. ILs and aq. PALAm solution (9.9 wt%).

2.2.3. CO₂ Absorption Measurements

Absorption performance of aqIL-DM and bulk liquids (aq. solution of IL, aq. solu-

tion of PALAm and their mixture) for CO₂ was estimated by measuring pressure depression within connected glass cylinders (Hyper Glass Cylinder HPG-96-3 (90 mL), Taiatsu Garasu Kogyo Co. Ltd.) due to the absorption of CO₂ into 2 g of DM or bulk sample. The experimental set up which was assembled within a thermostat incubator (FMU-133I, Fukushima Kogyo Co. Ltd.) and the detailed description on the measurements were given in our previous report [13]. The absorption ability (A.A.) was measured or expressed by three kinds of ways; mol-base A.A. calculated by (mol of absorbed CO₂)/(mol of IL), mass-base A.A. (CO₂ mol/absorbent kg), and pressure-reduced A.A. (mol/mol/final partial pressure (bar) of CO₂). In order to evaluate the recyclability of the aqIL-DM ([N₂₂₂₂][Gly] + PALAm), the sample was regenerated by heating in the infrared humidity meter at 50°C, 80°C or 100°C for 1 hour. The reduced water content was almost recovered by keeping the sample under 100% humidity for 6 hrs.

3. Results and Discussion

3.1. Preparation of DMs

AqIL-DMs were prepared by mixing aqueous solutions of [N₂₂₂₂][Gly] (water content: 55%), [N₂₂₂₂][Ala] (54%) and [N₂₂₂₂][Lys] (48%), with the hydrophobic silica nano particles. The first two ILs provided powdery DMs, while the last one resulted in only a soufflé-like substance. This failure was first ascribed to the lesser amount of water than those of the others. Thus, another [N₂₂₂₂][Lys] sample containing 57% of water was tested but the result was the same; a soufflé-like substance was obtained. Since one lysine molecule has two amino groups, it was expected that the surface of the aqueous [N₂₂₂₂][Lys] solution may be more polar than those of the other two. In fact, however, the long side chain, *i.e.*, four methylene groups, seemed to lower the surface tension of the aqIL.

Aqueous [N₂₂₂₂][Gly] containing 10 wt% of PALAm (1.8 g of [N₂₂₂₂][Gly], 0.6 g of PALAm, 3.6 g of water) proved to provide a powdery DM, while only a paste-like D-PS was obtained with the 10 wt% polymer solution. The CO₂ absorption performance of the former DM was investigated.

3.2. CO₂ Absorption Performance

3.2.1. Comparison among the ILs

CO₂ absorption behaviors for the three kinds of aqIL-DMs are shown in **Figure 1** as the time course of the partial pressure. The figure also shows the result for the bulk aq. [N₂₂₂₂][Gly] to see how the absorption speed was enhanced by using the aq.IL in the DM form. In the case of the DM, it took ca.5 min to reach 90% of the final absorption level, which was much shorter than that of the bulk; ca.270 min. This absorption acceleration more than 50 times is comparable to that reported in our previous study on DMs prepared with [bmim][ace] [13]. As for [N₂₂₂₂][Lys], it took ca.15 min. This slower absorption than those of DMs prepared from [N₂₂₂₂][Gly] and [N₂₂₂₂][Ala] may be because the [N₂₂₂₂][Lys] DM was not powdery but soufflé-like.

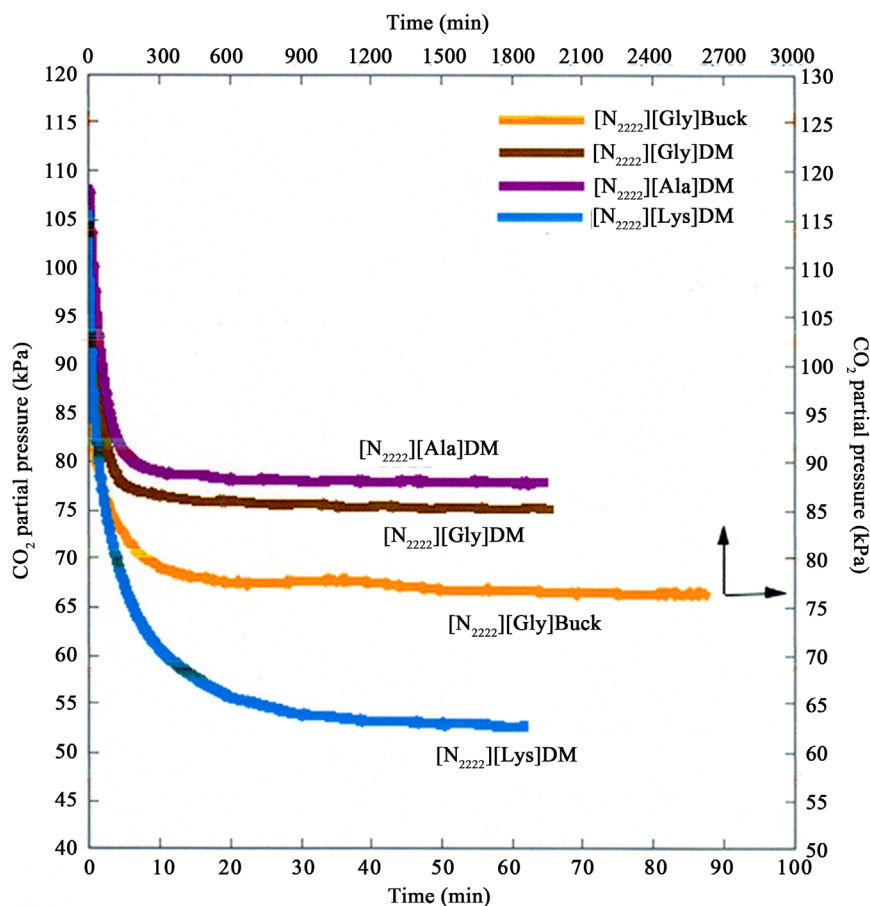


Figure 1. CO₂ absorption profiles of the amino acid-based ILs.

The experimental results on the absorption abilities are summarized on **Table 1**. As for the absorption ability measured by (mol of absorbed CO₂)/(mol of IL) (A.A. (mol/mol)) given in the 6th column, it was highest for the [N₂₂₂₂][Lys]DM, ca. two times of those of the other DMs. This means that either of the two amino groups of lysine worked as an equivalent reaction site to accommodate one CO₂ molecule. The A.A. (mol/kg), which was given in the 7th column, is a measure of CO₂ absorption ability which was calculated by (mol of absorbed CO₂)/(kg of DM or bulk liquid). Since the aqILs contained water of more than 50%, the mass-base A.A. would be useful when one compares CO₂ absorption materials for actual application in industry. In the case of 20% - 30% monoethanolamine (MEA) solution, which is often used to remove CO₂ from natural gas in the industrial scale, the A.A. (mol/kg) is ca. 1.6 - 2.5 [9]. Although the A.A. values obtained for the aqIL-DMs were lower than or at most comparable to the MEA system, the former values may be improved by reducing the water content, as shown in the following section. The A.A. (mol/mol/bar) in the last column is a measure of CO₂ absorption at the same equilibrium partial pressure. Since the present CO₂ absorption mechanism is not physisorption but via the chemical reaction with the amino group, the mol-base A.A. may not be simply proportional to the CO₂ partial pressure at equilibrium. However, the pressure-reduced

Table 1. Experimental condition and three kinds of absorption abilities for CO₂ absorption by aqIL-DMs.

IL	IL amount (mol)	P_{initial} (kPa)	P_{final} (kPa)	CO ₂ absorbed (mol)	A.A. (mol/mol)	A.A. (mol/kg)	A.A. (mol/mol/bar)
[N ₂₂₂₂][Gly]DM	3.4×10^{-3}	100.4	75.2	1.9×10^{-3}	0.56	0.95	0.75
[N ₂₂₂₂][Gly]bulk	3.4×10^{-3}	106.0	76.4	2.2×10^{-3}	0.63	1.1	0.82
[N ₂₂₂₂][Ala]DM	3.3×10^{-3}	108.1	78.0	2.3×10^{-3}	0.69	1.2	0.89
[N ₂₂₂₂][Lys]DM*	3.0×10^{-3}	105.6	52.7	4.0×10^{-3}	1.3	2.0	2.5

*Soufflé-like material.

A.A. may be utilized as a qualitative measure for CO₂ absorption material that is efficient even at a low pressure <1 bar. With this measure, the lysine-based aqIL-DM proved to be more efficient than the others.

3.2.2. Effects of Water Content

It has been known that A.A. (mol/mol) of the amino acid-based ILs may be improved by addition of substantial amount of water. For example, Zhang *et al.* [16] reported that the mol-base absorption ability of [N₁₁₁₁][Gly] (0.97 bar, 298 K) increased by adding water; from ca.0.17 for pure IL to 0.60 at 70% water. Further, according to Anderson *et al.* [10], several amino acid-based ILs containing tetrabutylphosphonium cation ([P₄₄₄₄]) showed maximum CO₂ absorption when the water/IL mol ratio was around 1.5 (water content: ca. 6% - 8%) while the A.A. (mol/mol) of [P₄₄₄₄][Ala] decreased with increasing water content up to water/IL ratio = 2.06, at least. These two studies, which were performed under different water content conditions, suggest that the A.A. of amino acid-based ILs may largely depend on the water content. In fact, the present [N₂₂₂₂][amino acid] IL systems (aqIL-DMs) also showed similar water-dependency. **Figure 2** shows the results for [N₂₂₂₂][Gly] of three different water contents as the time course of the partial pressure of CO₂. The most significant mol-base CO₂ absorption was obtained with the aqIL containing 55% of water (the same plot as that in **Figure 1**), while the second one and the least one were observed for systems containing 16% and 30% of water, respectively. Similar non-monotonic water content dependencies were also observed for [N₂₂₂₂][Ala] and [N₂₂₂₂][Lys] systems. The results are shown on **Table 2**. In the alanine-IL systems, the highest A.A. (mol/mol) was obtained in the absence of water, which is contrastive to the other two systems which showed significant CO₂ absorption in the presence of large amounts of water. As for the alanine system, some literature data are available in addition to that by Anderson *et al.* [10]; according to Jiang *et al.* [3], the mol-base A.A. of the bulk [N₂₂₂₂][Ala] was ca. 0.43°C at 40°C and ambient pressure. Although the constituting cation was different, aq. [P₄₄₄₄][Ala] solutions containing 1% or less of water have been reported to absorb almost equimolar CO₂ [2] [10]. The latter results may be compared with the present one for [N₂₂₂₂][Ala] in the absence of water. Since the DMs were treated in air, the

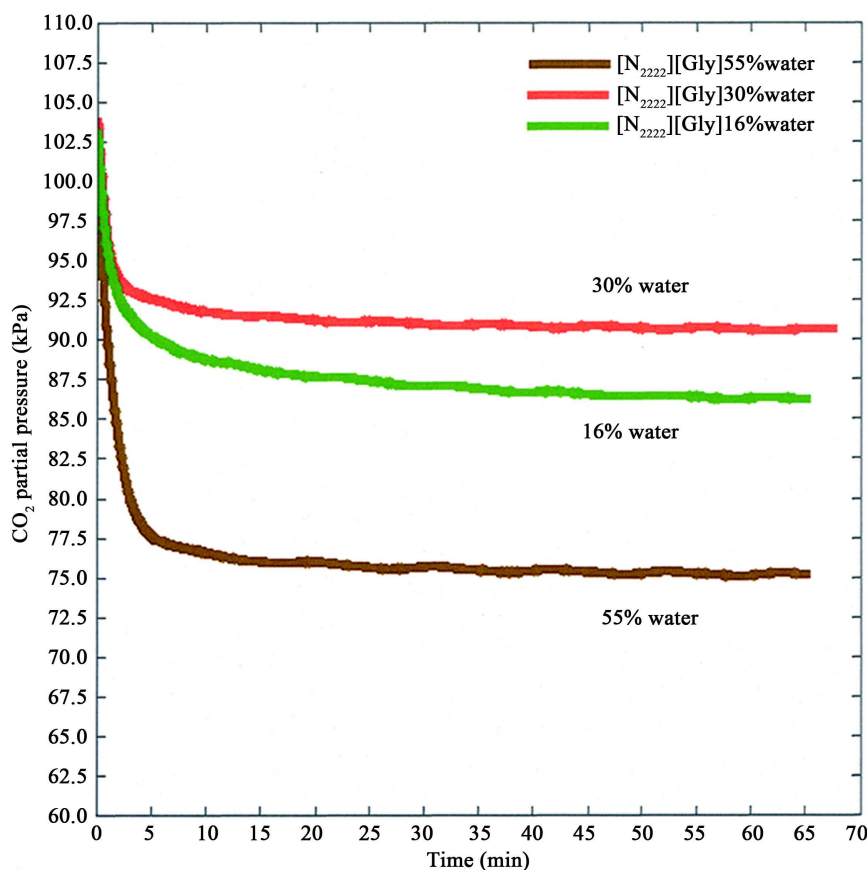


Figure 2. Effect of water content on the CO₂ absorption by aqIL-DMs prepared with [N₂₂₂₂][Gly].

Table 2. Experimental condition and the water content dependencies for CO₂ absorption by aqIL-DMs.

Amino Acid type	Water Content (%)	IL amount (mol)	P_{initial} (kPa)	P_{final} (kPa)	CO ₂ absorbed (mol)	A.A. (mol/mol)	A.A. (mol/kg)	A.A. (mol/mol/bar)
Gly	55*	3.4×10^{-3}	100.4	75.2	1.9×10^{-3}	0.56	0.95	0.75
	30	3.4×10^{-3}	103.7	90.7	1.0×10^{-3}	0.29	0.85	0.32
	16	3.4×10^{-3}	103.0	86.3	1.3×10^{-3}	0.38	1.4	0.44
Ala	54*	3.3×10^{-3}	108.1	78.0	2.3×10^{-3}	0.69	1.2	0.89
	29	3.3×10^{-3}	106.5	89.3	1.3×10^{-3}	0.40	1.1	0.45
	0	3.3×10^{-3}	103.9	62.9	3.2×10^{-3}	0.95	2.0	1.5
Lys	57*	3.0×10^{-3}	105.6	52.7	4.0×10^{-3}	1.3	2.0	2.5
	35	3.0×10^{-3}	106.6	78.3	2.1×10^{-3}	0.70	1.1	0.9
	13	3.0×10^{-3}	106.3	79.1	2.1×10^{-3}	0.70	2.0	0.9

*These row data are the same as those given on **Table 1**.

0% water sample possibly contained small amount of water after the heating at 80°C. Although some CO₂ absorption mechanisms of amine-functionalized absorbents in the presence and absence of water have been proposed by different researchers [2] [6] [16], the detailed examination is out of scope of the present

study. We just note here that the CO₂ absorption performance on the mass base, which must be important from an application point of view, was most significant for [N₂₂₂₂][Ala] in the absence of water and [N₂₂₂₂][Lys] in the presence of both large and small amount of water.

3.2.3. PALAm-Containing AqIL-DM

CO₂ absorption for the powdery aqIL([N₂₂₂₂][Gly])-DM was measured three times. As shown later, each measurement was carried out as a first absorption measurement before the CO₂ desorption by the heat treatment which was done to evaluate the recyclability of the DM. **Figure 3** and **Table 3** show only a typical

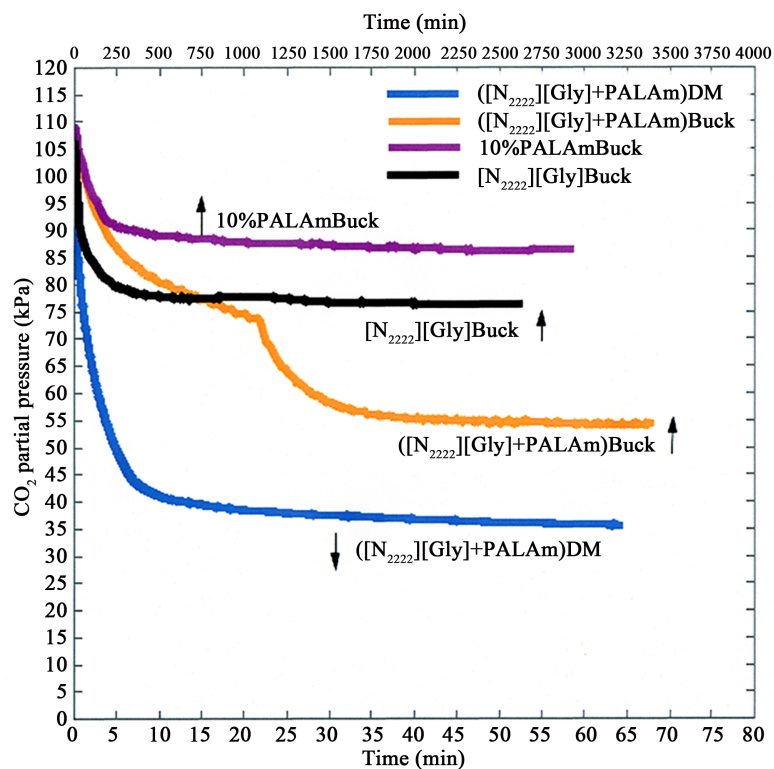


Figure 3. Comparison of CO₂ absorption profile of the PALAm-containing aqIL-DM with those of related systems.

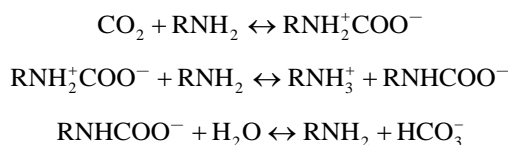
Table 3. Experimental condition and absorption abilities for CO₂ absorption by [N₂₂₂₂][Gly] and PALAm.

Systems	IL + PALAm amount (mol)	P_{initial} (kPa)	P_{final} (kPa)	CO ₂ absorbed (10 ⁻³ mol)	A.A. (mol/mol)	A.A. (mol/kg)	A.A. (mol/mol/bar)
DM (IL + PALAm)	$(3.4 + 4.1) \times 10^{-3}$	105.4	35.6	5.2	0.70 (0.65)*	1.9	2.0
Bulk (IL + PALAm)	$(3.4 + 4.1) \times 10^{-3}$	108.0	54.2	4.2	0.56	1.8	1.1
Bulk** (IL)	$(3.4 + 0) \times 10^{-3}$	106.0	76.4	2.2	0.63	1.1	0.82
Bulk (10% PALAm)	$(0 + 3.5) \times 10^{-3}$	106.8	86.4	1.5	0.43	0.75	0.50

*Average of three measurements (0.70, 0.65 and 0.61).

result among the three measurements together with those of other related bulk systems. As easily seen from the table, the aqIL-DM which contained 10 wt% of PALAm showed the best performance among the related systems by either of the three measures for the CO₂ absorption. It should be noted here that the mol-base A.A. values of the aqIL-DM (0.70 and the average value 0.65), which were calculated by (mol of absorbed CO₂)/(mol of amino groups of IL + PALAm), were superior to either of the single component bulk systems. If the respective components, *i.e.*, [N₂₂₂][Gly] and PALAm, independently absorbed CO₂, the resultant mol-base A.A. should be 0.52, *i.e.*, average of 0.63 and 0.43, which was obtained by taking the molar constitutions into account. In fact, the mol-base A.A. of the bulk IL + PALAm system, 0.56, was close to the average value. Thus, this comparison strongly suggests that the powdery state of the DM contributed to the higher A.A. value.

In order to figure out what caused the higher performance, we first examine the A.A. values of the respective bulk systems. As for the bulk PALAm solution, Nagai *et al.* [17] reported that the A.A. (mol/kg) for the 10 wt% solution reached a saturated value, 0.86, after ca.120 min of CO₂ flow through the sample at 25°C and under the ambient pressure. The A.A. value and the absorption time are both superior to those obtained in the present study; 0.75 mol/kg and ca.500 min. However, the present A.A. value, 0.75, may be comparable to the literature value if the lower pressure condition ($p_{\text{final}} = 0.864$ bar) was taken into account. Further, the several times longer absorption time may be ascribed to the difference in the CO₂ absorption method. On the other hand, the 0.43 as the mol-base A.A. is significantly less than ca. 0.65 of a typical CO₂ absorbent, monoethanolamine (MEA) obtained at 40°C under the corresponding pressure (~0.85 bar) [18] [19]. According the proposed mechanism for the CO₂ absorption into aqueous MEA solution,



CO₂ may be absorbed via the zwitterion formation, the carbamate formation and the recovering free amino group via the dissociation of the protonated MEA. Although the above three reactions comprise just a part of the complicated reaction mechanism [18], they suggest that MEA may absorb CO₂ in a molar ratio larger than 0.5, which is in fact consistent with their experimental observations. Thus, the 0.43 as the mole-base A.A. value obtained for the present aqueous PALAm solution was an unexpected result because the polymer also contains primary amino groups as MEA does. As a possible cause for the poor result, we note the phase separation and/or the gel formation due to the electrostatic cross linking formation among the carbamate anions and the protonated amino groups, which has been reported by several authors [13] [17] [19] [20]. In fact, the much slower absorption into the bulk polymer solution compared with the bulk aqIL, which is easily seen from the respective time courses of

the CO_2 pressure shown in **Figure 3**, may be ascribed to the gel formation or phase separation due to CO_2 absorption in the former system. Thus, the lower A.A. performance of the PAIAm compared with that of the small amines may be because the gel formation or phase separation partially secluded amino groups in the separated phase, keeping them intact.

This crosslinking reaction of PAIAm via CO_2 absorption should also occur in the bulk IL + PAIAm system, and in fact quite a distinguishing absorption behavior, apparently two-step absorption, was observed. Comparing the first and the second absorption “width” (decrements in the CO_2 partial pressure) with those of the respective bulk systems (the bulk aqIL and the bulk aq. PAIAm), the first one seems to be almost corresponding to the absorption by the IL and followed by the second one, *i.e.*, absorption by the polymer. Needless to say, since both absorption modes should occur simultaneously, the existence of such a marked kink in the CO_2 absorption suggests that the absorption by the polymer was largely retarded in the IL + PAIAm system. As a possible mechanism to effect such retardation, a “preferential reaction” with the IL rather than that with the polymer may be considered. As illustrated in a schema for the CO_2 diffusion through the IL + PAIAm system (**Figure 4**), most CO_2 molecules may be “trapped” with the IL amino groups before the reaction with the polymer amino groups. Further, CO_2 molecules in the polymer coil, which was depicted as a circle in the figure, would take a much longer time to diffuse through than that through the IL region, because of the crosslinking produced due to the reaction with CO_2 . Thus, it seems that in the first step ($t < \text{ca.}1000 \text{ min}$), PAIAm, which was near the surface of the bulk IL + PAIAm solution, could only react with CO_2 , while most IL molecules reacted with CO_2 rather freely, and after the first step period, free access of CO_2 to the other polymer amino groups became substantial.

Are the above speculations on the bulk systems consistent with the absorption behavior of the DM consisting of the IL and PAIAm? First of all, one must note that the time course profile of the CO_2 partial pressure was smooth and no kink was observed. This may be because the maximum diffusion length of CO_2 in the

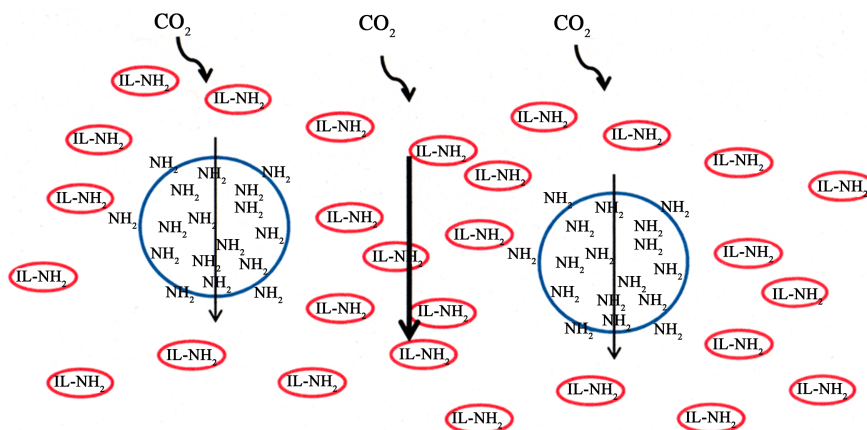


Figure 4. CO_2 diffusion schema for the bulk aqIL containing PAIAm.

liquid phase to reach the innermost amino groups from the surface was much shorter than those in the respective bulk systems; order of 100 μm for the former [12] and ~ 1 cm for the latter. Thus, the reaction of CO_2 with the respective amino groups, *i.e.*, IL and PALAm, could almost simultaneously proceed in the DM system. In fact, the higher performance of the DM compared with both bulk systems may also be explained by the same reasoning. Namely, the small size (~ 100 μm) of the DM droplets enabled quick access of CO_2 to all the amino groups before the gel formation effectively retarded the CO_2 diffusion. Then, the total A.A. in molar base should become higher than that of the bulk system, in which the polymer amino groups were partially inaccessible to CO_2 due to the gel formation. Thus, the present experimental results strongly suggest that the shortcoming involved in the bulk (IL + PALAm) system may be overcome by employing the same system in the DM form.

As for the mass-base A.A., **Table 3** tells us the DM was much superior to either of the bulk systems. This comes from the efficient use of water; although water was necessary to improve the CO_2 absorption ability of $[\text{N}_{2222}][\text{Gly}]$, water itself only scarcely absorbs the gas. Thus, the large amount of water in the DM just reduced the mass-base A.A. However, the incorporation of the PALAm into the DM could significantly improve the mass-base A.A. (1.9 vs. 0.95) because the water phase including PALAm could also work as a substantial CO_2 absorbent.

3.3. Recyclability of the DM

Recyclability is one of the prerequisites that should be met by CO_2 absorbents for industrial application. In the case of CO_2 capture by aq. MEA [10] [21], the regeneration of the absorbent has been performed by stripping with water vapor at 100°C - 120°C . In the present study, CO_2 removal was carried out simply by heating CO_2 -saturated aqIL ($[\text{N}_{2222}][\text{Gly}]$)-DM samples, which contained 10% PALA maq. solution, at 50°C , 80°C or 100°C . Then, the regenerated materials were subject to the second CO_2 absorption, and the ratio of the resultant A.A. in the molar base to that of the original one obtained before the first heat treatment was used as a measure for the recyclability. The results are summarized on **Table 4**. Unfortunately all the trials to recycle the DM material proved to be unsuccessful; although the recovery of water content was satisfying to some extent, the A.A. recovery was far less from ca. 82% of aq. MEA solution which was regenerated at 120°C [10]. As for the reason for the miserably bad results, it may be appropriate to refer to the study by Nagai *et al.* again [17]. The authors successfully prepared PALAm hydrogel by crosslinking the polymer amino groups via urea bond under high pressure of CO_2 (3.5 MPa) at 170°C . The same reaction might occur in the DM particles by the heat treatment. Namely, many free amino groups of the polymer were consumed by the irreversible urea bond formation and the resultant gel formation also made the free IL inaccessible to CO_2 . In fact, a heat treatment at 50°C for 10 wt% PALAm solution resulted in a glassy substance as shown in **Figure 5** and the solid was swollen but insoluble in water. This observation strongly suggested that some irreversible crosslinking via cova-

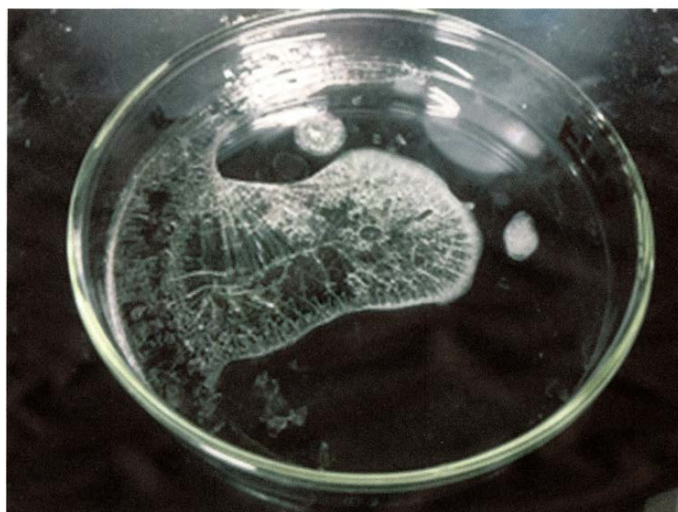


Figure 5. Glassy PALAm after a heat treatment at 50°C for 1 h.

Table 4. Experimental conditions, absorption abilities, and recoveries after heat treatment at 50°C, 80°C and 100°C for CO₂ absorption by PALAm-containing [N₂₂₂₂][Gly] systems.

Heat treatment temperature (°C)	Water content (%)	P_{initial} (kPa)	P_{final} (kPa)	CO ₂ absorbed (10 ⁻³ mol)	A.A. (mol/mol)	Recovery (%)
-	60*	105.4*	35.6*	5.2*	0.70*	-
50	51	108.5	94.8	1.0	0.13	19
	50	109.8	97.4	0.92	0.12	17
80	60	106.8	40.9	4.9	0.65	-
	55	107.3	92.6	1.1	0.15	23
100	53	109.8	95.5	1.1	0.15	23
	60	104.9	40.4	4.6	0.61	-
	53	107.5	94.9	1.0	0.13	21

*Same data as those given on **Table 3**.

lent bond formation occurred between the polymer chains. Thus, in order to apply the PALAm-containing aqIL-DM for industrial use, the irreversible urea group formation due to the heat treatment must be inhibited.

4. Conclusions

In the present study we examined the CO₂ absorption performance of several kinds of DMs to find the following results:

1) Powdery DMs were successfully prepared with amino acid-based IL/water mixtures, *i.e.*, [N₂₂₂₂][Gly], [N₂₂₂₂][Ala] as aqueous solutions of ca. 50%, while only soufflé type of DM was obtained for [N₂₂₂₂][Lys] even when the water content was as high as ca.60%;

2) The mol-base CO₂ absorption ability was largely dependent on the water content and the IL species;

3) Whereas only a paste-like D-PS was obtained with the 10 wt% PALAm solution, powdery DM was successfully prepared with [N₂₂₂₂][Gly] containing 10 wt% of the polymer and 60 wt% of water;

4) The aqIL-DM ([N₂₂₂₂][Gly] + PALAm) showed higher CO₂ absorption abilities (especially the mass-base A.A.) than those of DM containing only the IL;

5) The recyclability of the PALAm-containing aqIL-DM proved to be rather poor, probably because the heat treatment, which was necessary to remove the absorbed CO₂ from the absorbent, irreversibly crosslinked the polymer, leading to gelation of the inner phase of the DM particles.

Thus, the present study demonstrated that the amino acid-based aqIL-DM containing PALAm is a promising absorbent material for CO₂. In order to overcome the shortcoming found for the recyclability, it may be effective to use a Dry Gel system in which PALAm constitutes the gel phase [17] swollen with the aqIL. The results will be soon reported in a forthcoming paper.

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Compliance with Ethical Standards

Conflict of interest the authors declare that they have no conflict of interest.

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