

# CO<sub>2</sub> Absorption by “Dry Ionic Liquids”

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## Abstract

Dry Ionic Liquid (D-IL) never means some “water-free” ionic liquid but is a member of “Dry Matter (DM)”. DM is a collective name for powdery substances that are composed of micro droplets as an inner core phase and surrounding hydrophobic silica nano particles as the shell part. When the core part is water, it is called Dry Water (DW), which is the first member of DM, while D-IL is the newest one. Because of the much larger surface area of DM compared with that of the inner phase in bulk state, this novel substances are expected to show excellent performance for any mass transfer through the gas-liquid interface. In the present study, we investigated CO<sub>2</sub> absorption by some D-ILs and a DM containing a polyamine in terms of the speed to the equilibrium and a mol-based absorption efficiency. Compared with the respective bulk systems, the D-IL and DM systems proved to be accelerated by ca.50 times without impairing the absorption efficiency.

## Keywords

Dry Matter, CO<sub>2</sub> Absorption, Ionic Liquids, Silica Nanoparticles

## 1. Introduction

Dry water (DW) has been known since the mid-1960 s when a German patent reported its properties and manufacturing procedure with its name [1]. DW may be taken as a kind of Pickering emulsion [2], where air serves as the nonpolar continuous phase in place of common organic solvents. DW can be easily prepared by simply mixing water and hydrophobic fumed silica particles even in a home-use blending machine with a relatively high speed (typically >10<sup>4</sup> rpm) for several tens of seconds. The physico-chemical properties of DW, however, has never been studied until two groups rediscovered DW; Binks and Murakami reported that the phase inversion of air-in-water type Pickering emulsion (foam) to water-in-air type one (DW) occurs by changing the particles' hydrophilicity (hydrophobicity) and/or the volume ratio of water to air [3]. Cooper *et al.* first reported DW as a promising material for methane storage in a form

of gas hydrate [4].

Preparation conditions for DW have been rather extensively studied so far; Pezron and her coworkers investigated in their series of papers [5]-[7] successful conditions for DW and concluded that balance of the mechanical energy input and the interaction energy of water and the solid particles at the interface is the most critical factor. Namely, when vigorously mixed, only strongly hydrophobic particles produce DW, while with less hydrophobic particles one must charge a weaker mechanical power into the system, otherwise only a paste-like substance will be obtained.

The latter conclusion should also be valid for other members of “Dry Matter” (DM), which was first proposed by one of the present authors [8] as a collective name for a family of the powder like substances, e.g., DW, Dry polymer solution [9], Dry Gel [10] and Dry Ionic Liquid (D-IL) [8]. Thus, when a highly hydrophobic particle is used, the more the hydrophobicity of the liquid (or the liquid is apt to wet the particles), the less mechanical energy should be applied. This in fact seems to be consistent with the much easier formation of so-called Liquid Marble (LM) [11] compared with that of DW. LM is typically prepared by simply rolling mm-size droplets on a solid particle bed [12]. Thus, the mechanical energy input during the preparation is negligibly small and the available range of the liquid properties such as the hydrophobicity or the surface tension for LM is rather large compared with that of DM, if those properties allow the particles wet but not immersion into the liquid [13] [14]. Thus, LM may be categorized as a sub-group of DM because of its similarity in the geometrical formation, while the preparation procedure is completely different from that of DM. And the very suitability of the latter’s preparation procedure to mass production together with the much larger surface area than LM make DM much more promising functional materials than LM [15].

On the other hand, most members of DM have an inherent weak point; water easily evaporates through the rather porous shell made of silica particles. Although the evaporation may be virtually suppressed in a closed plastic (e.g., polypropylene) bottle, DW would gradually lose the inner water in an open air. In order to reduce this defect to some extent, Dry Gel (DG) has been tested by Cooper *et al.* as a potential material for the methane hydrate container. However, studies on DG are scarcely available in literatures except for that prepared with gellan gum [10].

Dry Ionic Liquid (D-IL) is in principle free from the above disadvantage which originates from the escape of the inner liquid phase of DMs because IL has virtually no vapor pressure. Further, IL’s stability at higher temperature may also extend its availability in versatile fields of application. With these unique properties, in fact, D-IL can be a promising material for CO<sub>2</sub> absorption; many ILs show high affinity to the gas and some specifically designed ILs to form a complex with CO<sub>2</sub> have also been reported [16]. Further, recovery of CO<sub>2</sub> and the absorption material may be easily performed by evacuation and/or moderate heating at high efficiency [17]. As a matter of fact, similar “high-efficiency” materials in which those outstanding properties of IL are utilized have been reported [18] [19] and especially some kinds of “supported ionic liquid phase

(SILP) CO<sub>2</sub> absorbers have been devised. For example, Kolding *et al.* used an IL-loaded hydrophobic silica gel to confirm its high performance as an SILP CO<sub>2</sub> absorber [20]. However, many kinds of drawbacks (e.g., existence of open pores, low diffusivity or high tortuosity of gases in the pore, high cost for preparation of optimum SILPs, and so on) have been pointed out for SILPs as gas (e.g., CO<sub>2</sub>) absorber or separator by G.E. Romanos *et al.* [17]. The authors have invented novel supported ionic liquid phase systems, which were named “inverse SILPs” and successfully avoided those limitations on the gas absorption and separation performance by utilizing the “inverse SLIPs”. Structure of the inverse SLIPs is inherently the same as that of D-IL; powder like substance which is composed of ionic liquid micro droplets covered with silica nano particles. However, the former is largely different from the latter in some points. In the first place, the preparation process of the inverse SLIPs is much more complicated than the original D-IL preparation method; in the former case, an IL and silica nano particles are first mixed with ethanol for ca.2 hours to make a Pickering emulsion (the inner phase is IL and the continuum medium is ethanol) and then the ethanol must be removed in vacuum to obtain the final powder like substance, while in the latter it is enough to mix both materials (IL + silica) with air in a blender machine just for 90 s! Furthermore, the mixing ratio of the inverse SILPs was fixed at  $g(\text{silica})/g(\text{IL}) = 1.5$  (IL: 40 wt.%) [17], while the original D-IL was prepared with a mixing ratio of ca.0.18 ([bmim] [I]: 85 wt.%) [8]. Silica nano particles used were also different; The inverse SLIPs were prepared with hydrophilic and less hydrophobic types of fumed silica, *i.e.*, HDK-T-30 and H 20. Free silanol group fractions on the surface are 100% and 50%, respectively, according to the manufacturer (Wacker), and the rest of the latter is methylated as Si-CH<sub>3</sub>. The usage of such “hydrophilic” silica should be due to the hydrophilicity of ethanol which was used as a continuum medium of the Pickering emulsion. This means in turn that the inverse SLIPs thus prepared may be unstable in usual usage because air is most hydrophobic. On the other hand, the original D-IL is prepared with a more hydrophobic silica (HDK-H18 with 75% of silanol methylated) in air, which is the same environment as that for its practical applications. Thus, those cited examples for the differences between the inverse SLIPs and the original D-IL would suggest that the latter is more favorable for applications as gas absorber and separator materials.

In the present study, we attempted to prepare a D-IL with a CO<sub>2</sub>-absorbing IL (1-butyl-3-methylimidazolium acetate ([bmim] [ace])) and checked the performance as a CO<sub>2</sub>-absorption material in terms of speed and capacity. We selected this IL among so many candidates including amino-functionalized ILs [16] because it has already been reported by M. B. Shiflett and his coworkers that [bmim] [ace] is superior, even when used as a bulk liquid, to the traditional amine-based processes for CO<sub>2</sub> absorption or separation from the post combustion flue gas in economic terms [21]. Thus, if it is possible to prepare powder like D-IL with the relevant IL, the total performance for the CO<sub>2</sub> absorption should be more improved due to the enhanced gas absorption speed. Of course, the excellent performance of D-IL-like materials for the gas absorption has already been demonstrated, at least qualitatively, in the distinguished study by Roma-

nos *et al.* [17]. Therefore we confined our primary goal to preparation of a powder like D-IL with [bmim] [ace] and confirmation of its feasibility as the gas absorption material. Further we also tested a potentiality of an IL + polyamine mixed system in a form of DM as CO<sub>2</sub> absorption material. Needless to say, one of the most distinguished and favorable properties of ILs must be their non-volatility. Polymers are also non-volatile and those containing amino groups in the monomer unit may be able to absorb more CO<sub>2</sub> than IL if the ability was compared per mass of the absorbents. Thus, if a polyamine could be incorporated into a D-IL, the resultant DM may be promising as a CO<sub>2</sub> absorption material even though compared with monoethanolamine that is now utilized in the industrial process [22]. In the present study, we for the first time explored these possibilities.

## 2. Materials and Methods

### 2.1. Materials

1-butyl-3-methylimidazolium acetate ([bmim] [ace]) and 1-butyl-3-methylimidazolium iodide ([bmim] [I]) were purchased from Sigma Aldrich and used as received. Poly (allyl amine) hydrochloride (PALAm-HCl) (MW: 15,000, Sigma Aldrich) was neutralized by NaOH and then filtrated through a 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.9.9%.

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.

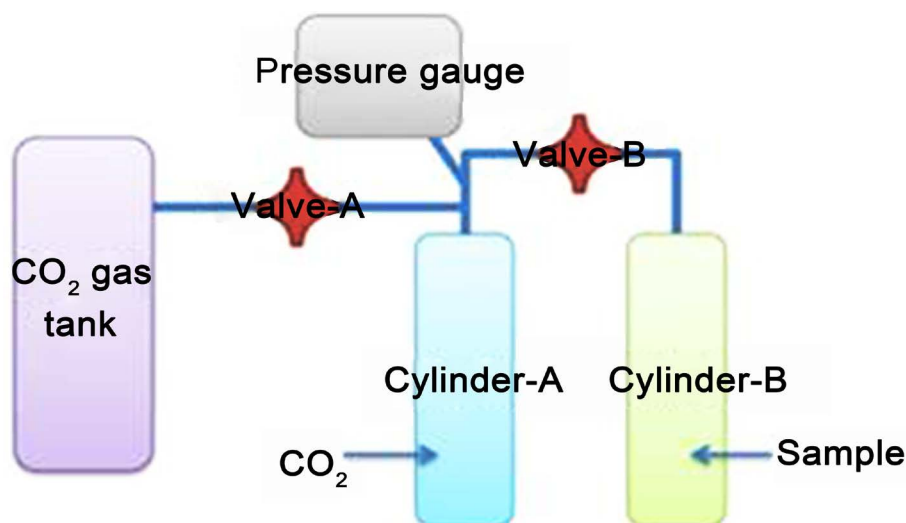
### 2.2. Methods

#### 2.2.1. Preparation of D-IL

D-IL of [bmim] [ace] was prepared with a blender machine (Waring J-SPEC blender, container volume: 50 mL) by mixing 6.0 g of the IL or its aqueous solution and 1.05 g of the silica at a fixed speed (22500 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 D-IL samples was performed with an infrared humidity meter (FD-720, Kett Co. Ltd.) at certain temperatures. D-IL containing PALAm was also prepared with the same preparation procedure except for using a mixed solution of the IL and aq. PALAm solution (9.9 wt.%) instead of the pure IL or the aq. solution.

#### 2.2.2. CO<sub>2</sub> Absorption Measurements

Absorption performance of D-ILs or bulk liquids (IL, aq. solution of IL, aq. solution of PALAm) for CO<sub>2</sub> was estimated by measuring pressure depression within connected glass cylinders due to the absorption of CO<sub>2</sub>. The experimental set up which was assembled within a thermostat incubator (FMU-133I, Fukushima Kogyo Co. Ltd.) is schematically illustrated in **Figure 1**. First, CO<sub>2</sub> gas was introduced to Cylinder A (Hy-



**Figure 1.** Diagrammatic illustration of the set up to measure the CO<sub>2</sub> partial pressure.

per Glass Cylinder HPG-96-3 (90 mL, Taiatsu Garasu Kogyo Co. Ltd.) via Valve A at a partial pressure of ca.2 bar with Valve B closed. Then, a sample D-IL or a sample bulk liquid was set in Cylinder B with Valve B closed. After 30 min of incubation time, Valve B was opened and the pressure was recorded with a pressure gauge (KDM 30, Krone Co.). Since the pressure begins to decrease at the same time as the opening of Valve B, pressure at time 0 can't be directly measured. Thus, the initial partial pressure in Cylinder A + B ( $p_{0(A+B)}$ ) was theoretically estimated by the following equation.

$$p_{0(A+B)} = p_{i(A)} V_A / (V_{A+B} - V_{\text{sample}})$$








where  $p_{i(A)}$  is the initial partial pressure of CO<sub>2</sub> introduced into Cylinder A,  $V$  is the inner volume of the cylinders including the valve parts or the sample volume.  $p_{i(A)}$  was set around at 2 bar.  $V_A$  and  $V_{A+B}$  were 95.8 cm<sup>3</sup> and 191.7 cm<sup>3</sup>, respectively. Since  $V_{\text{sample}}$  (~2 cm<sup>3</sup>) was rather small compared with  $V_{A+B}$ , the absorption experiments were carried out under an initial partial pressure of CO<sub>2</sub> ~1 bar. CO<sub>2</sub> absorption efficiency of a sample was estimated by a ratio of mol of absorbed CO<sub>2</sub> to mol of IL or PALAm (mol/mol efficiency) or by mol/(mol × bar (equilibrium CO<sub>2</sub> pressure)) (mol/(mol bar efficiency)). According to a preliminary experiment, the efficiency turned out to be estimated within ±10% error.

### 3. Results and Discussion

#### 3.1. Preparation of D-IL

D-IL preparation was attempted by using [bmim] [ace] and the silica nanoparticles. Using the bulk liquid without added water, only a creamy or paste-like substance was obtained (Table 1). This failure in preparation of a powdery D-IL may be ascribed to relatively low surface tension ( $\gamma$ ) of the pertinent IL; although  $\gamma$  of the IL is not available in literatures,  $\gamma$  of 1-ethyl-3-methylimidazolium acetate was reported to be ca.46 mN/m [23]. Thus,  $\gamma$  of [bmim] [ace] may be lower than that of [emim] [ace] because

**Table 1.** Preparation results of D-IL with [bmim] [ace].

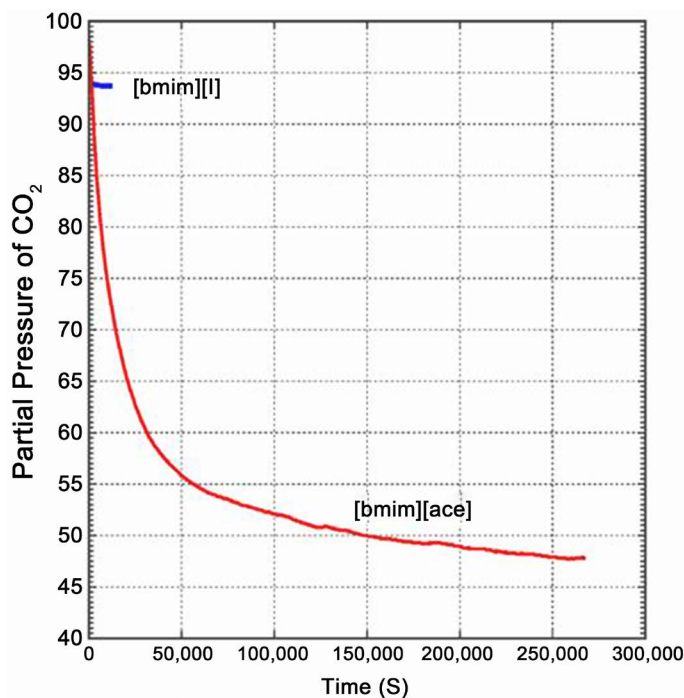
Water content	0 wt%	10 wt%	20 wt%
Appearance of Product			
Water content	30 wt%	40 wt%	
Appearance of Product			
Water content	50 wt%	60 wt%	
Appearance of Product			

the former alkyl group is larger and more hydrophobic than the latter. So far, only one successful preparation of powdery D-IL. Only with large amounts of water, it was successful; although the product prepared with the IL containing 50 wt% water was “soufflé-like” to some extent, one with 60 wt% water was wholly powdery. Effects of the water addition and the resultant changes in the appearance of D-IL on the CO<sub>2</sub> absorption performance were examined as shown below.

### 3.2. CO<sub>2</sub> Absorption by D-IL Prepared with [bmim] [ace]

CO<sub>2</sub> absorption was monitored by measuring CO<sub>2</sub> partial pressure as a function of time for two kinds of bulk ILs; [bmim] [ace] and [bmim] [I]. The latter was used because it is the only IL that provides powdery D-IL without water addition [8]. If it were also a CO<sub>2</sub>-absorbing IL, the D-IL would be promising from a view point of the expected high absorption speed. The experimental results are shown in **Figure 2** and the experimental





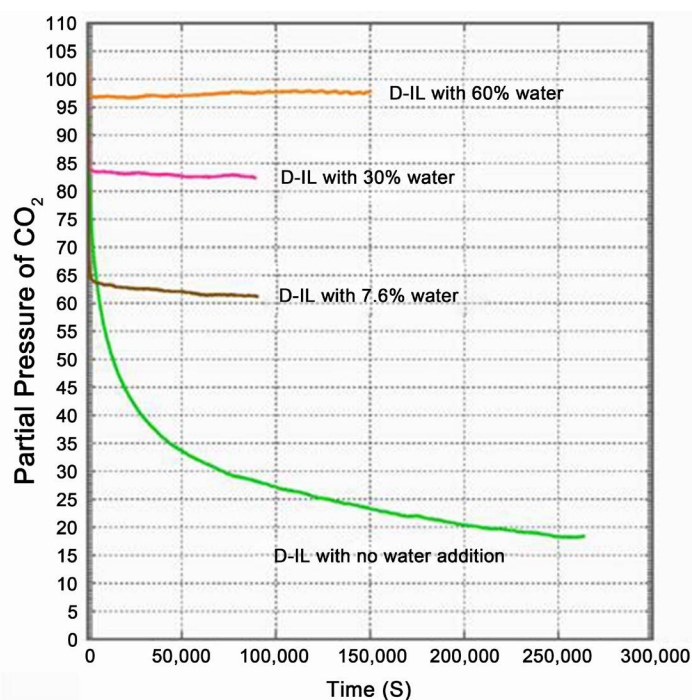
**Figure 2.** CO<sub>2</sub> absorption performance of [bmim] [I] and [bmim] [ace] observed as pressure profile.

conditions and the respective CO<sub>2</sub> absorption abilities are given on **Table 2**. In the case of [bmim] [I], the decrement in the partial pressure was only slight and the absorption soon reached at the saturation.

On the other hand, CO<sub>2</sub> absorption by bulk [bmim] [ace] was significant even at low pressures as expected from literature data [24] [25] while it took so long time (ca.72 h) to reach the saturation. The respective performance on the basis of mol of CO<sub>2</sub> absorbed by mol of IL were 0.014 at the partial pressure  $p \sim 0.94$  bar for [bmim] [I] and 0.32 at  $p \sim 0.48$  bar for [bmim] [ace]. The latter value was comparable with the literature data by Yokozeki *et al.* [24] [25]; 0.336 at  $p = 0.502$  bar and  $t = 298.1$  K. The smaller absorption (**Figure 2**), it may be due to the larger amount of IL contained in the D-IL compared with the bulk system (cf. **Table 3**). In fact, except for the initial stage of the absorption, those two profiles showed a similar tendency of pressure decrement. efficiency obtained in the present study may be safely ascribed to the lower pressure.

As a next step, CO<sub>2</sub> absorption performance by D-IL of [bmim] [ace] and those prepared by adding water to the IL was investigated in a similar way as the bulk IL cases. First of all, the creamy substance prepared without water addition was tested. The result was given in **Figure 3** and on **Table 3** together with the other ones. The creamy D-IL showed a similar performance with the bulk IL; although the initial speed of the CO<sub>2</sub> absorption, *i.e.*, the initial decrement in the partial pressure was more significant than that of the bulk.

For example, at  $t = 50,000$  s ( $\sim 14$  h), ca.83% of the initial amount of CO<sub>2</sub> was absorbed to the respective samples. The equilibrium states of CO<sub>2</sub> absorption seem to be



**Figure 3.** Effects of water addition on CO<sub>2</sub> absorption performance of [bmim] [ace]-based D-ILs.

**Table 2.** Experimental conditions and the results for CO<sub>2</sub> absorption by bulk [bmim] [I] and [bmim] [ace].

IL	IL amount (mol)	$p_{\text{initial}}$ (kPa)	$p_{\text{final}}$ (kPa)	CO <sub>2</sub> absorbed (mol)	Absorption efficiency (mol/mol)
[bmim] [I]	0.013	95.8	93.7	$1.6 \times 10^{-4}$	0.014
[bmim] [ace]	0.012	98.2	47.8	$3.8 \times 10^{-3}$	0.32

**Table 3.** Experimental conditions and the results for CO<sub>2</sub> absorption by D-ILs with and without water addition.

Water content (%)	Sample appearance	IL amount (mol)	$p_{\text{initial}}$ (kPa)	$p_{\text{final}}$ (kPa)	CO <sub>2</sub> absorbed (mol)	Absorption efficiency (mol/mol)
0	Creamy	0.025	104.9	18.4	$6.5 \times 10^{-3}$	0.25
60	Powdery	0.012	103.8	96.7	$5.3 \times 10^{-4}$	0.044
30	Powdery	0.011	99.6	82.4	$1.3 \times 10^{-3}$	0.12
7.6	Soufflé-like	0.011	98.8	61.2	$2.9 \times 10^{-3}$	0.27

fter  $2.5 - 2.6 \times 10^5$  s (69 - 72 h) for both systems. Thus, CO<sub>2</sub> absorption speed of the creamy D-IL proved to be no superior to that of the bulk IL sample. These results suggest that the IL in the creamy D-IL formed a continuous phase without increasing the effective surface area. As for the absorption ability, the molar ratio of CO<sub>2</sub> absorbed to the IL was estimated to be 0.25. This value, which was obtained at  $p = 0.18$  bar, is comparable to literature values of the bulk IL at  $p = 0.1$  bar; 0.19 - 0.23 [24] [25], as a matter of course.

Next we tested powdery samples to confirm the expected enhancement in the absorption speed. The results are shown in **Figure 3**. As described in the previous section,



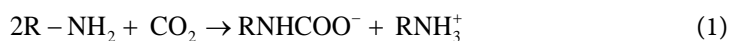
a powdery D-IL of [bmim] [ace] was successfully prepared only when substantial amount of water was added as much as 60%. As seen from the figure and **Table 3** the CO<sub>2</sub> absorption speed was so rapid that the equilibrium was established just within several minutes. The slight increase in the pressure after 5000 s may be due to evaporation of water. On the contrary to the advantage in the absorption speed, the 60% water containing D-IL showed a much lower CO<sub>2</sub> solubility than the bulk IL, just one eighth [26]. This deterioration in the absorption ability may be caused from the existence of water. According to a proposed mechanism for the chemical absorption of CO<sub>2</sub> to the relevant IL [26] [27], C2 proton of the imidazolium ring is abstracted by an acetic acid counter anion to form a site reacting with CO<sub>2</sub>. This mechanism has in fact been supported by some researches [28] [29], one of which also suggested that water may inhibit the C2 proton abstraction reaction [28]. Thus, in order to obtain a D-IL material combining a high CO<sub>2</sub> solubility and an excellent absorption speed, it should be necessary to reduce the amount of water in the inner phase of the relevant D-IL samples as much as possible with a powdery state retained. Since preparations of D-IL with [bmim] [ace] containing 50% or less of water provide only creamy substances (**Table 1**), we attempted to remove water from the D-IL containing 60% of water with an IR humidity meter at 40°C and 80°C. With this treatment, water content of the D-IL sample was reduced to 30% and 7.6% at the respective temperatures. The absorption performance of these modified samples is given on **Table 3** and **Figure 3**. With decreasing the water content, the CO<sub>2</sub> solubility into the samples increased as can be judged from the almost flat level of CO<sub>2</sub> pressure. The mol-based absorption efficiency of the 7.6% water sample was 0.27, which is still lower than 0.32. Since the equilibrium pressure at which the former value was obtained (61.2 kPa) was higher than the latter (47.8 kPa) by ca.30%, actual difference of the solubility should be more significant. This means that only a small amount of water may affect the CO<sub>2</sub> absorption to [bmim] [ace]. However, the absorption efficiency value, 0.27, is never low in light of such a relatively low equilibrium pressure (0.61 bar). Further, the absorption speed was also excellent; 90% of the saturation level was absorbed within ca.20 min. Although the 7.6% water sample was not powdery but Souffle-like, the speedy absorption suggests that the aqueous IL did not form a continuous phase but was finely divided by the silica particles with the surface wetted to some extent by the liquid. Thus, the “post-dehydration” procedure seems to be effective to prepare D-ILs as a high performance material for CO<sub>2</sub> absorption.

### 3.3. CO<sub>2</sub> Absorption by DM Containing [bmim] [ace] and PAIAm

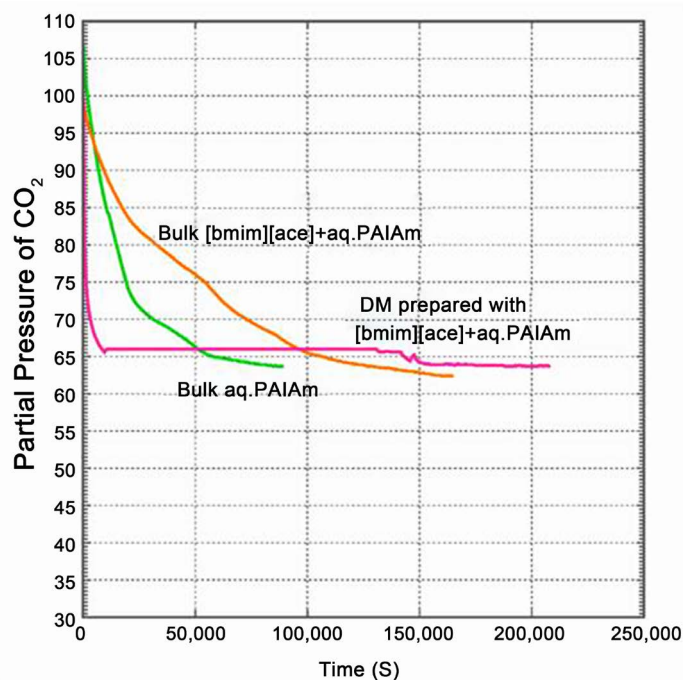
Nonvolatile CO<sub>2</sub> absorption substances are not limited to ILs; polymers containing amino groups may also be utilized for such purpose. For a polyamine to be incorporated into a DM, the polymer must be solubilized in any liquid, ideally pure ILs. Thus, we attempted to dissolve PAIAm into [bmim] [ace] or [bmim] [I], while it proved to be in vain. Many neutral polymers are known to be soluble in ILs, while polyelectrolytes seem to be mostly insoluble in them [30]. Then, an aqueous solution of PAIAm was used to prepare a DM containing [bmim] [ace] and the polyamine. By setting the water

content of the DM at 60 wt%, a Souffle-like DM was obtained.

**Figure 4** and **Table 4** show results of CO<sub>2</sub> absorption by the DM prepared above, together with those by the bulk aqueous PAIAm solution and the bulk IL + aq. PAIAm mixed solution (water content = 60 wt%). First of all, one should note the significant absorption ability of the bulk aq. solution of PAIAm as large as 0.39, a mol-based value, which is comparable with 0.32 of bulk [bmim] [ace]; if those values are converted to the mol bar-based efficiency, the former becomes 0.61 and the latter 0.67. This relatively high CO<sub>2</sub> absorption ability of the pertinent polymer is still lower than the theoretical or ideal value, 0.5; in principle, two free amino groups of PAIAm may react with one CO<sub>2</sub> molecule to form an ion-pair as the case of low molecular weight amines [31].



In the case of polyamines like PAIAm however the above ion-pair formation serves as a physical crosslinking of the polymer chains, leading to a gel formation [32]. In fact, in the above aqueous solution of PAIAm a phase separation was observed after CO<sub>2</sub>



**Figure 4.** CO<sub>2</sub> absorption performance of samples containing aqueous PAIAm solution.

**Table 4.** Experimental conditions and the results for CO<sub>2</sub> absorption by samples containing aq. PAIAm.

Sample	Sample appearance	Amount of IL or amino group (mol)	$p_{initial}$ (kPa)	$p_{final}$ (kPa)	CO <sub>2</sub> absorbed (mol)	Absorption efficiency (mol/mol)
Bulk aqueous PAIAm (9.9%)	Clear solution	$8.4 \times 10^{-3}$	106.8	63.7	$3.3 \times 10^{-3}$	0.39
Bulk [bmim] [ace] + aq. PAIAm	Clear solution	$8.8 \times 10^{-3} + 7.6 \times 10^{-3}$	100.0	62.4	$2.8 \times 10^{-3}$	0.37*
DM with [bmim] [ace] + aq. PAIAm	Soufflé-like	$6.8 \times 10^{-3} + 5.0 \times 10^{-3}$	102.7	63.7	$2.9 \times 10^{-3}$	0.58*

\*Values estimated on the basis of PAIAm mol.

absorption measurements. The post-measurement sample consisted of a turbid lower layer and a clear upper layer, which was separated by a white thin layer. By shaking the sample tube, the white layer was easily destroyed and a totally turbid liquid was obtained. If the white layer was a gel-like phase, it would retard the CO<sub>2</sub> absorption to some extent. In fact, after leaving the sample tube for two days, the whole lower layer became a soft gel.

A similar phase separation was also confirmed for the bulk [bmim] [ace] + aq. PAIAm system. In this case, however, the lower layer was already gel-like. Although the difference in the gel formation behavior between these two systems is not known at present, the slower CO<sub>2</sub> absorption of the bulk IL + PAIAm system may be ascribed to the more significant gel formation. As for the absorption efficiency, it became slightly worse than that of the bulk aq. PAIAm; if [bmim] [ace] in the mixed solution sample absorbed CO<sub>2</sub> to the same extent as the 60% water-containing sample (**Table 3**) in the mol bar-based absorption efficiency ( $0.044/0.967 = 0.046$ ), the mol-based efficiency of the IL in the mixed solution sample may be estimated as  $0.046 \times 0.624 = 0.029$ . Then, a contribution from the IL to the total amount of CO<sub>2</sub> absorbed is estimated with this efficiency to be  $2.6 \times 10^{-4}$  mol. This means in turn that the contribution from PAIAm in the total absorption amount is  $\sim 2.5 \times 10^{-3}$  mol of CO<sub>2</sub> and the efficiency becomes ca. 0.33 mol/mol. This slightly lower efficiency, compared with 0.39 of the bulk PAIAm solution, may be ascribed to the more significant gel formation. Namely, the gel network might obstruct CO<sub>2</sub> to access to free amino groups. Thus, for the pertinent pressure profile given in **Figure 4** to reach the true equilibrium, much more time would be necessary.

In the case of DM prepared with the IL + aq. PAIAm mixed solution, the CO<sub>2</sub> absorption speed was distinctly higher than those bulk systems. For example, it took ca. 90 min to absorb 90% of the saturation, while it was ca. 1600 min for the bulk mixed solution. The former elapsed time is, however, still much longer than that of the bulk IL system containing only 7.6% of water but no PAIAm, *i.e.*, ca. 20 min (**Figure 3**). This slowing down in the absorption speed, which may be due to the presence of PAIAm, may also be attributed to the gel formation as compared in the bulk systems. As for the absorption efficiency, however, the gel formation in the DM does not seem obstruct the CO<sub>2</sub> absorption; the mol-based absorption efficiency, 0.58, though it was estimated as a value per amino group of PAIAm, is higher than 0.5, the limiting value for the CO<sub>2</sub> absorption by PAIAm. This means that the IL also contributed to the significant CO<sub>2</sub> absorption to a substantial degree, although the respective contributions may not be separately estimated in the present study. Here we should note why [bmim] [ace] could absorb CO<sub>2</sub> to a significant degree irrespective of the coexistence of water. As discussed previously, the abstraction of the C2 proton of the IL cation by the counter anion (CH<sub>3</sub>COO<sup>-</sup>) should be interfered by water. The observed high level of CO<sub>2</sub> absorption suggests that this interference mechanism by water is not well working. As a probable mechanism for that, we postulate that amino groups of PAIAm are involved in the C2 proton abstraction. In fact, basicity of a primary amine is much stronger than that of

-COO<sup>-</sup>; basicity measured by  $pK_b$  values of ethyl amine is larger than that of acetate anion by a factor of  $\text{ca.}10^6$ . Then, a next question is why the abstraction by the polymer in the bulk mixed solution system did not appear to contribute to an appreciable degree. This may be safely ascribed to the observed macroscopic phase separation. Because the polymer was mostly confined to the lower layer of the sample, the amino groups would be hardly available for the IL left in the upper layer. On the other hand, in the case of the DM system each DM particle contains only a tiny amount of liquid and has a relatively large surface area. For a typical DM having a diameter of 100  $\mu\text{m}$  [8], the surface/volume ratio is as large as  $\text{ca.}10^6$  times of the bulk. Thus, it may be reasonable to assume that the gelation in the DM system prevailed through the tiny sample without leaving a separate PAIAm layer. A non-monotonic change in the CO<sub>2</sub> pressure observed for the DM sample around at  $t = 10^4$  s may be corresponding to this rather rapid development of gelation through each droplet. A “transition” to a second “stationary” state found around at  $t = 1.3 \times 10^5$  s (36 h) indicates that the CO<sub>2</sub> absorption process was not completed but just temporarily stopped by the gel formation. As stated above, PAIAm gel formed by ionic crosslinking according to Equation (1), where Rs should be replaced by polymer chains, seemed to be never robust. Thus, the gel layer, which must be much thinner than that formed for the bulk system, would be easily, at least partly, broken under a certain CO<sub>2</sub> pressure.

#### 4. Conclusions

In the present study, we have shown a promising potential of [bmim] [ace] in a form of D-IL as CO<sub>2</sub> absorption material. By the “post-dehydration” of the D-IL, the mol-based efficiency for the CO<sub>2</sub> absorption was greatly improved without impairing the absorption speed. Further, addition of PAIAm to the D-IL as another CO<sub>2</sub> absorption component proved to be effective; the amino group seemed to improve the CO<sub>2</sub> absorption by the IL in the presence of water.

A main problem to be overcome for the D-IL to be employed as a competitive CO<sub>2</sub> absorption material was also evident; water, which impairs the CO<sub>2</sub> absorption of [bmim] [ace], was necessary to prepare a powdery or Souffle-like D-IL. One solution would be to employ an amine-containing IL. For example, a group of ILs consisting of a tetraalkylammonium cation and an amino acid anion seems to be promising [17] [33]. In fact, we have plenty of choice for ILs having high CO<sub>2</sub> absorption ability [34]. Attempts have just started to endow such ILs with excellent absorption speed by forming them into D-ILs.

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#### Compliance with Ethical Standards

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

## References

- [1] Br  nner, H., Shutte, D. and Schmitz, F.-T. (1964) German Patent DE1467023.
- [2] Pickering, S.U. (1907) Emulsions. *Journal of the Chemical Society*, **91**, 2001-2021. <http://dx.doi.org/10.1039/CT9079102001>
- [3] Binks, B.P. and Murakami, R. (2006) Phase Inversion of Particle-Stabilized Materials from Foams to Dry Water. *Nature Materials*, **5**, 865-869. <http://dx.doi.org/10.1038/nmat1757>
- [4] Wang, W., Bray, C.L., Adams, D.J. and Cooper, A.I. (2008) Methane Storage in Dry Water Gas Hydrates. *Journal of the American Chemical Society*, **130**, 11608-11609. <http://dx.doi.org/10.1021/ja8048173>
- [5] Forn  , L., Perzon, I., Saleh, K., Guigon, P. and Komunjer, L. (2007) Storing Water in Powder Form by Self-Assembling Hydrophobic Silica Nanoparticles. *Powder Technologies*, **171**, 15-24. <http://dx.doi.org/10.1016/j.powtec.2006.09.006>
- [6] Forn  , L., Saleh, K., Pezron, I., Komunjer, L. and Guigon, P. (2009) Influence of Mixing Characteristics for Water Encapsulation by Self-Assembling Hydrophobic Silica Nanoparticles. *Powder Technologies*, **189**, 263-269. <http://dx.doi.org/10.1016/j.powtec.2008.04.030>
- [7] Saleh, K., Forn  , L., Guigon, P. and Pezron, I. (2011) Dry Water: From Physic-Chemical Aspects to Process-Related Parameters. *Chemical Engineering Research and Design*, **89**, 537-544. <http://dx.doi.org/10.1016/j.cherd.2010.06.005>
- [8] Shirato, K. and Satoh, M. (2011) "Dry Ionic Liquid" as a New Comer to "Dry Matter". *Soft Matter*, **7**, 7191-7193. <http://dx.doi.org/10.1039/c1sm05999h>
- [9] Miyake, M. and Satoh, M. (2015) Preparation Conditions of Dry Matter. *Kobunshi Ronbunshu*, **72**, 617-623. <http://dx.doi.org/10.1295/koron.2015-0026>
- [10] Carter, B.O., Wang, W., Adams, D.J. and Cooper, A.I. (2010) Gas Storage in "Dry Water" and "Dry Gel" Clathrates. *Langmuir*, **26**, 3186-3193. <http://dx.doi.org/10.1021/la903120p>
- [11] Aussillous, P. and Qu  r  , D. (2001) Liquid Marbles. *Nature*, **411**, 924-927. <http://dx.doi.org/10.1038/35082026>
- [12] McEleney, P., Walker, G.M., Larmour, I.A. and Bell, S.E.J. (2009) Liquid Marble Formation Using Hydrophobic Powders. *Chemical Engineering Journal*, **147**, 373-382. <http://dx.doi.org/10.1016/j.cej.2008.11.026>
- [13] Binks, B.P. and Tyowua, A.T. (2013) Influence of the Degree of Fluorination on the Behaviour of Silica Particles at Air-Oil Surfaces. *Soft Matter*, **9**, 834-845. <http://dx.doi.org/10.1039/C2SM27395K>
- [14] Tan, T.T.Y., Ahsan, A., Reithofer, M.R., Tay, S.W., Tan, S.Y., Hor, T.S.A., Chin, J.M., Chew, B.K.J. and Wang, X. (2014) Photoresponsive Liquid Marbles and Dry Water. *Langmuir*, **30**, 3448-3454. <http://dx.doi.org/10.1021/la500646r>
- [15] Carter, B.O., Adams, D.J. and Cooper, A.I. (2010) Pausing a Stir: Heterogeneous Catalysis in "Dry Water". *Green Chemistry*, **12**, 783-785. <http://dx.doi.org/10.1039/b922508k>
- [16] Yang, Z.-Z., Zhao, Y.-N. and He, L.-N. (2011) CO<sub>2</sub> Chemistry: Task-Specific Ionic Liquids for CO<sub>2</sub> Capture/Activation and Subsequent Conversion. *RSC Advances*, **1**, 545-567. <http://dx.doi.org/10.1039/c1ra00307k>
- [17] Romanos, G.E., Shulz, P.S., Bahlmann, M., Wasserscheid, P., Sapalidis, A., Katsaros, F.K., Athanasekou, C.P., Beltsios, K. and Kanellopoulos, N.K. (2014) CO<sub>2</sub> Capture by Novel Supported Ionic Liquid Phase Systems Consisting of Silica Nanoparticles Encapsulating Amine-Functionalized Ionic Liquids. *Journal of Physical Chemistry C*, **118**, 24437-24451. <http://dx.doi.org/10.1021/jp5062946>
- [18] Thomassen, P.L., Kunov-Kruse, A.J., Mossin, S.L., Kolding, H., Kegn  s, S., Riisager, A. and

- Fehrmann, R. (2013) Separation of Flue Gas Components by SILP (Supported Ionic Liquid-Phase) Absorbers. *ECS Transactions*, **50**, 433-442. <http://dx.doi.org/10.1149/05011.0433ecst>
- [19] Nurul, S.M., Bustam, M.A., Yunus, N.M. and Man, Z. (2014) Solid Supported [hmim][Tf2N] for CO<sub>2</sub> Adsorption. *Advanced Materials Research*, **879**, 149-154. <http://dx.doi.org/10.4028/www.scientific.net/AMR.879.149>
- [20] Kolding, H., Fehrmann, R. and Riisager, A. (2012) CO<sub>2</sub> Capture Technologies: Current Status and New Directions Using Supported Ionic Liquid Phase (SILP) Absorbers. *Science China Chemistry*, **55**, 1648-1656. <http://dx.doi.org/10.1007/s11426-012-4683-x>
- [21] Shiflett, M.B., Drew, D.W., Cantini, R.A. and Yokozeki, A. (2010) Carbon Dioxide Capture Using Ionic Liquid 1-Butyl-3-Methylimidazolium Acetate. *Energy and Fuels*, **24**, 5781-5789. <http://dx.doi.org/10.1021/ef100868a>
- [22] Rochelle, G.T. (2009) Amine Scrubbing for CO<sub>2</sub> Capture. *Science*, **325**, 1652-1654. <http://dx.doi.org/10.1126/science.1176731>
- [23] Schuermann, J., Huber, T., LeCorre, D., Mortha, G., Sellier, M., Duchemin, B. and Staiger, M.O. (2016) Surface Tension of Concentrated Cellulose Solutions In 1-Ethyl-3-Methylimidazolium Acetate. *Cellulose*, **23**, 1043-1050. <http://dx.doi.org/10.1007/s10570-015-0850-5>
- [24] Shiflett, M.B., Kasprzak, D.J., Junk, C.P. and Yokozeki, A. (2008) Phase Behavior of {Carbon Dioxide + [bmim][Ac]} Mixtures. *Journal of Chemical Thermodynamics*, **40**, 25-31. <http://dx.doi.org/10.1016/j.jct.2007.06.003>
- [25] Yokozeki, A., Shiflett, M.B., Junk, C.P., Grieco, L.M. and Foo, T. (2008) Physical and Chemical Absorption of Carbon Dioxide in Room-Temperature Ionic Liquids. *Journal of Physical Chemistry B*, **112**, 16654-16663. <http://dx.doi.org/10.1021/jp805784u>
- [26] Maginn, E.J. (2005) Design and Evaluation of Ionic Liquids as Novel CO<sub>2</sub> Absorbents. Quarterly Technical Reports to DOE, 1-12.
- [27] Cadena, C., Anthony, J.L., Shah, J.K., Morrow, T.I., Brennecke, J.F. and Maginn, E.J. (2004) Why Is CO<sub>2</sub> So Soluble in Imidazolium-Based Ionic Liquids? *Journal of the American Chemical Society*, **126**, 5300-5308. <http://dx.doi.org/10.1021/ja039615x>
- [28] Gurau, G., Rodriguez, H., Kelly, S.P., Janiczek, P., Kalb, R.S. and Rogers, R.D. (2011) Demonstration of Chemisorption of Carbon Dioxide in 1,3-Dialkylimidazolium Acetate Ionic Liquids. *Angewandte Chemie*, **123**, 12230-12232. <http://dx.doi.org/10.1002/ange.201105198>
- [29] Cabaço, M.I., Besnard, M., Danten, Y. and Coutinho, J.A.P. (2012) Carbon Dioxide in 1-Butyl-3-Methyl Imidazolium Acetate. I. Unusual Solubility Investigated by Raman Spectroscopy and DFT Calculations. *Journal of Physical Chemistry A*, **116**, 1605-1620. <http://dx.doi.org/10.1021/jp211211n>
- [30] Chen, Y., Zhang, Y., Ke, F., Zhou, J., Wang, H. and Liang, D. (2011) Solubility of Neutral and Charged Polymers in Ionic Liquids Studied by Laser Light Scattering. *Polymer*, **52**, 481-488. <http://dx.doi.org/10.1016/j.polymer.2010.11.034>
- [31] Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Meuleman, E. and Feron P. (2012) Towards Commercial Scale Postcombustion Capture of CO<sub>2</sub> with Monoethanolamine Solvent: Key Considerations for Solvent Management and Environmental Impacts. *Environmental Science & Technology*, **46**, 3643-3654. <http://dx.doi.org/10.1021/es204051s>
- [32] Carretti, E., Dei, L., Baglioni, P. and Weiss, R.G. (2003) Synthesis and Characterization of Gels from Polyallylamine and Carbon Dioxide as Gallant. *Journal of the American Chemical Society*, **125**, 5121-5129. <http://dx.doi.org/10.1021/ja034399d>
- [33] Yu, H., Wu, Y.T., Jiang, Y.-Y., Zhou, Z.Z. and Zhang, Z.-B. (2009) Low Viscosity Amino Acid Liquids with Asymmetric Tetraalkylammonium Cations for Fast Absorption of CO<sub>2</sub>.



*New Journal of Chemistry*, **33**, 2385-2390. <http://dx.doi.org/10.1039/b9nj00330d>

- [34] Zhang, X., Zhang, X., Dong, H., Zhao, Z., Zhang, S. and Huang, Y. (2012) Carbon Capture with Ionic Liquids: Overview and Progress. *Energy & Environmental Science*, **5**, 6668-6681. <http://dx.doi.org/10.1039/c2ee21152a>



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