

## CO<sub>2</sub> Solubilities in Amide-based Brønsted Acidic Ionic Liquids

Jelliarko Palgunadi, Jinkyu Im, Je Eun Kang, Hoon Sik Kim,\* and Minserk Cheong\*

*Department of Chemistry and Research Institute of Basic Sciences, Kyung Hee University, Seoul 130-701, Korea*

\*E-mail: khs2004@khu.ac.kr (HSK); mcheong@khu.ac.kr (MC)

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A distinguished class of hydrophobic ionic liquids bearing a Brønsted acidic character derived from amide-like compounds were prepared by a neutralization reaction of *N,N*-diethylformamide, *N,N*-dibutylformamide, 1-formylpiperidine, and  $\epsilon$ -caprolactam with trifluoroacetic acid and physical absorptions of CO<sub>2</sub> in these ionic liquids were demonstrated and evaluated. CO<sub>2</sub> solubilities in these ionic liquids were influenced by the molecular structure of the cation and were apparently increased with the molar volume. Comparison based on a volume unit reveals that CO<sub>2</sub> solubilities in these liquids are relatively higher than those in imidazolium-based ionic liquids. Henry's coefficients calculated from low-pressure solubility tests at 313 to 333 K were used to derive the thermodynamics quantities. Enthalpy and entropy of solvation may share equal contributions in solubility.

**Key Words:** Brønsted acidic ionic liquids, Amide-based ionic liquids, Carbon dioxide, Solubility

### Introduction

Ionic liquids (ILs) are a class of organic salts that are liquid over a wide range of temperatures near or at room temperature. ILs are known as novel designer solvents due to their unique properties such as, no measurable vapor pressure, tunable physical and chemical properties, and high thermal stability and they may potentially replace many conventional volatile organic solvents in reaction and separation processes.<sup>1</sup>

Sheng Dai *et al.* reported the simple preparations of a unique class of ILs with acidic character. They synthesized Brønsted acidic ILs (BAILs) by simply neutralizing amides for example *N,N*-dimethylformamide with a Brønsted acid such as nitric acid in water medium to produce an IL consisting of amide-based cation and nitrate anion. Later, this liquid salt was subject to an anion exchange step *via* a metathesis reaction with an alkali salt of bis(trifluoromethylsulfonyl)imide (M<sup>+</sup>Tf<sub>2</sub>N<sup>-</sup>) to give a low viscosity, hydrophobic room temperature ionic liquid.<sup>2</sup> The inherent acidic character of these ILs stems from a direct transfer of the acidic proton on the acid to the amide resulting in a protic IL.<sup>2,3</sup> Another group also reported the synthesis of various lactam-based BAILs and characterized their physical properties.<sup>4</sup> Those BAILs are particularly interesting because of the straightforward preparations (versatile starting materials, one-pot preparation, and solvent-free reaction) and no requirement for a complex work-up. Moreover, this type of ILs has potential applications for reactive reaction or multiphase-separation media.<sup>5</sup>

Recently, ionic liquids (ILs) combined with a supercritical CO<sub>2</sub> was proposed as a novel reaction media and a green separation technique.<sup>6</sup> ILs also have been suggested as alternative liquid absorbents for CO<sub>2</sub> capture in natural gas sweetening or in greenhouse gas control processes.<sup>7</sup> In those circumstances, the solubility of CO<sub>2</sub> in ILs are critically required. To date, numerous works reported the solubility of CO<sub>2</sub> in neutral ILs derived from various cations, such as dialkylimidazolium, quaternary ammonium, and phosphonium combined with various anions<sup>8</sup> but the CO<sub>2</sub> solubility in acidic ILs has not been studied. To

study the CO<sub>2</sub> solubility in the Brønsted acidic ILs, solubility tests at pressure close to atmosphere were conducted on the BAILs derived from selected amides (1-formylpiperidine,  $\epsilon$ -caprolactam, *N,N*-diethylformamide, and *N,N*-dibutylformamide) neutralized with an equimolar of trifluoroacetic acid.

### Experimental

**General Procedure.** Chemical reagents with purity no less than 99% were purchased from Aldrich Chemicals Co. and were used as received. CO<sub>2</sub> gas with purity 99.9% was purchased from Sin Yang Gas, Korea. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400 and 100 MHz Bruker NMR spectrometer, respectively. Densities of pure RTILs at ambient pressure were carefully estimated at 313.15, 323.15, and 333.15 K using a 5.573 ± 0.004 mL pycnometer (previously calibrated using distilled water at 298.15 K) immersed in an ethylene glycol bath. The weight of RTIL was measured using Mettler AJ180 balance with an accuracy of 10<sup>-4</sup> g.

**Synthesis of Ionic Liquids.** The ILs for CO<sub>2</sub> solubility tests were prepared according to the literature procedure with little modification.<sup>2</sup> In a typical synthesis, a 100 mL round bottom flask equipped with a magnetic stirrer was charged with an amide diluted in methanol. A dropping funnel attached to the flask was charged with a slightly excess amount of diluted trifluoroacetic acid. The flask was immersed in an ice bath and the neutralization reaction was done by slowly dropping the acid under stirring. Subsequently, the liquid product was purified and dried by evaporation under a reduced pressure (<1 mbar) at 70 °C for several hours. Equivalent product quality was obtained with the same procedure under a solvent-free condition. Purities of the ILs were no less than 99% as deduced from the NMR results.

[DEformH][TFA]: <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO, 298 K, TMS, [ppm])  $\delta$  1.17-1.28 (m, 6H), 3.37-3.47 (m, 4H), 8.15 (s, 1H), 15.41 (s, 1H). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO, 298 K, [ppm])  $\delta$  12.02, 14.07, 37.93, 43.35, 115.13 (q, *J* = 284.4 Hz,

-CF<sub>3</sub>), 159.36 (q,  $J = 39.9$  Hz, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>), 163.99.

**[DBformH][TFA]:** <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO, 298 K, TMS, [ppm]) δ 0.92-0.98 (m, 6H), 1.30-1.38 (m, 4H), 1.52-1.63 (m, 4H), 3.28-3.38 (m, 4H), 8.14 (s, 1H), 15.43 (s, 1H). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO, 298 K, [ppm]) δ 13.27, 13.40, 19.44, 19.90, 43.02, 48.53, 115.15 (q,  $J = 284.7$  Hz, -CF<sub>3</sub>), 159.45 (q,  $J = 40.0$  Hz, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>), 164.45.

**[FppdnH][TFA]:** <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO, 298 K, TMS, [ppm]) δ 1.66-1.87 (m, 6H), 3.43 (t,  $J = 5.6$  Hz, 2H), 3.55 (t,  $J = 6.0$  Hz, 2H), 8.10 (s, 1H), 15.87 (s, 1H). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO, 298 K, [ppm]) δ 23.93, 24.79, 26.13, 41.64, 48.07, 115.13 (q,  $J = 284.9$  Hz, -CF<sub>3</sub>), 159.32 (q,  $J = 40.0$  Hz, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>), 162.34.

**[CaprolH][TFA]:** <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO, 298 K, TMS, [ppm]) δ 1.63-1.77 (m, 6H), 2.50 (t,  $J = 5.6$  Hz, 2H), 3.26 (q,  $J = 4.8$  Hz, 2H), 8.53 (s, 1H). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO, 298 K, [ppm]) δ 22.43, 28.16, 30.02, 34.98, 43.22, 115.09 (q,  $J = 285.2$  Hz, -CF<sub>3</sub>), 161.17 (q,  $J = 39.6$  Hz, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>), 182.63.

**CO<sub>2</sub> Solubility Measurement.** Low-pressure solubility measurements at 313 to 333 K were carried out based on the isochoric saturation method.<sup>9</sup> Details of the measurement apparatus, technique, and data reductions are available in the Supporting Information. CO<sub>2</sub> concentrations were calculated using the gas virial equation of state truncated after the second term employing the second virial coefficients taken from the compilation by Dymond and Smith.<sup>10</sup>

## Results and Discussion

The measured densities and the calculated molar volumes of Brønsted acidic ILs at atmospheric pressure are listed in Table 1. All of the ILs under investigation were obtained as colorless and transparent liquids by reacting amides with corresponding acids in the absence of a solvent. These low-viscous liquids were found to be hydrophobic and stable under air or in water. Among ionic liquids studied, [CaprolH][TFA] was visually found to have the highest viscosity and is as viscous as ethylene glycol. The densities of all ILs are steadily decreased as temperature increases. As shown in Table 1, the molar volume of [DBformH][TFA] is greater than those of other three ILs sug-

gesting a more free volume within the molecular packing.

The CO<sub>2</sub> solubility based on mole fraction and the CO<sub>2</sub> equilibrium pressure above the liquid absorbent are listed in Table S-1 (available in the Supporting Information). The isotherm solubility at 313 K displayed in Fig. 1 shows that the CO<sub>2</sub> solubility increases linearly with the pressure rise for all ILs tested and indicates a positive deviation from Raoult's law.<sup>11</sup> Such a solubility behavior may suggest that CO<sub>2</sub> is physically absorbed, as also can be observed in other non-task-specific ILs.<sup>12</sup>

The solubility of a solute in a liquid absorbent can be expressed in terms of Henry's coefficient. In our experiments, Henry's coefficients were estimated from the slope of a linear fit of the variation of CO<sub>2</sub> solubility in mole fraction versus fugacity. Henry's coefficients at various temperatures and the standard error of the isotherm slopes are given in Table 2. As shown in Table 2 and also in Table 1, the solubility of CO<sub>2</sub> in this ILs series is little affected by the structural distinction of the cation and is increased with the molar volume following the sequence of [CaprolH][TFA] < [FppdnH][TFA] < [DEformH][TFA] < [DBformH][TFA]. Indeed, the solubility-molar volume relationship as similarly found in the imidazolium-based homologs exists but more amide-based BAILs containing various anions should be tested to give a clearer picture. Fig. 2 displays the effect of temperature on Henry's coefficient. As expected, all amide-based BAILs show negative slopes of the correlation, indicating that the CO<sub>2</sub> solubility decreases with the increase of absorption temperature.

The dependence of Henry's law coefficients with temperature was correlated as a function of temperature using an empirical equation (1) as proposed by Krause and Benson.<sup>13</sup>

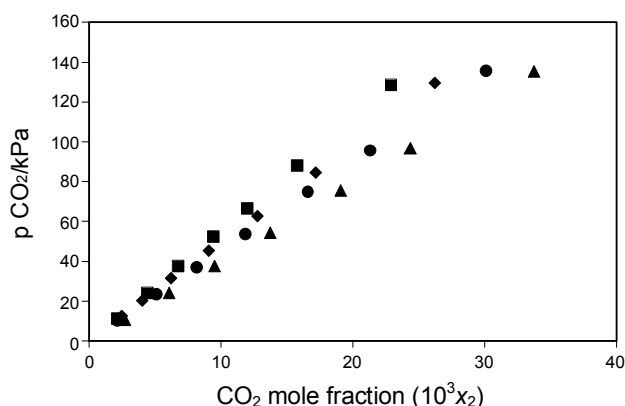
$$\ln[H_{2,1}(T) / 10^5 \text{ Pa}] = \sum_{i=0}^n B_i (T / \text{K})^{-i} \quad (1)$$

The optimized coefficients,  $B_i$ , obtained using a linear regression of multiple-variables calculation, are listed in Table S-2 in the Supporting Information along with the average absolute deviation (AAD) for each compound which is considered as the precision of the experimental data. The Henry's coefficients for [DEformH][TFA], [DBformH][TFA], [FppdnH][TFA], and

**Table 1.** Densities ( $\rho$ ) and molar volumes ( $V_m$ ) of Brønsted acidic ILs at various temperatures

$T = 313.15 \text{ K}$		$T = 323.15 \text{ K}$		$T = 333.15 \text{ K}$	
$\rho/\text{g}\cdot\text{cm}^{-3a}$	$V_m/\text{mL}\cdot\text{mol}^{-1}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V_m/\text{mL}\cdot\text{mol}^{-1}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V_m/\text{mL}\cdot\text{mol}^{-1}$
<i>N,N</i> -Diethylformamide + CF <sub>3</sub> CO <sub>2</sub> H → [DEformH][TFA] (FW 215.17)					
1.1414	188.5	1.1293	190.5	1.1169	192.6
<i>N,N</i> -Dibutylformamide + CF <sub>3</sub> CO <sub>2</sub> H → [DBformH][TFA] (FW 271.28)					
1.0510	258.1	1.0412	260.5	1.0321	262.9
1-Formylpiperidine + CF <sub>3</sub> CO <sub>2</sub> H → [FppdnH][TFA] (FW 227.18)					
1.2124	187.4	1.2009	189.2	1.1891	191.0
$\epsilon$ -Caprolactam + CF <sub>3</sub> CO <sub>2</sub> H → [CaprolH][TFA] (FW 227.18)					
1.2487	181.9	1.2379	183.5	1.2265	185.2

<sup>a</sup> $\Delta\rho = \pm 0.0001$



**Figure 1.** Isotherm CO<sub>2</sub> solubility in amide-based BAILs at 313 K: (▲), [DBformH][TFA]; (●), [DEformH][TFA]; (◆), [FppdnH][TFA]; (■), [CaprolH][TFA].

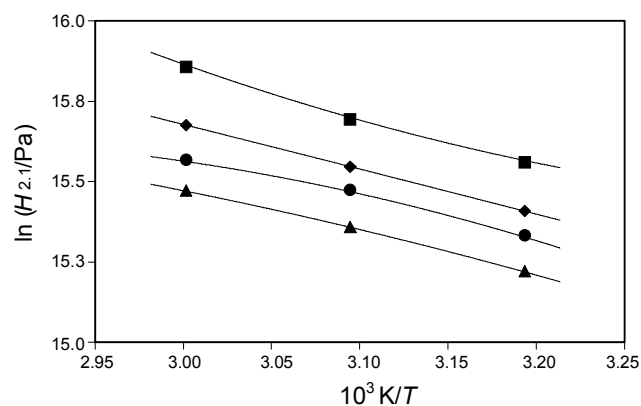
**Table 2.** Variation of Henry's-law coefficient with temperature

<i>T</i> /K	<i>H</i> <sub>2,1</sub> /MPa	Error <sup>a</sup>
[DEformH][TFA] + CO <sub>2</sub>		
313.15	4.56	0.04
323.15	5.25	0.06
333.15	5.77	0.01
[DBformH][TFA] + CO <sub>2</sub>		
313.15	4.08	0.05
323.15	4.69	0.05
333.15	5.24	0.07
[FppdnH][TFA] + CO <sub>2</sub>		
313.15	4.92	0.01
323.15	5.65	0.02
333.15	6.42	0.01
[CaprolH][TFA] + CO <sub>2</sub>		
313.15	5.72	0.06
323.15	6.54	0.01
333.15	7.70	0.10

<sup>a</sup>Standard errors of the isotherm slopes

[CaprolH][TFA] at 313.15 K obtained from Eq. (1) are 4.56, 4.08, 4.92, and 5.72, respectively. All Henry's coefficients of these ILs show positive deviations from the Raoult's law in that they are greater than the ideal value of  $0.5f_2^{liq}$  or 2.44 MPa at 313.15 K.<sup>14</sup> The positive deviation from the ideal value may indicate that the CO<sub>2</sub> solubility in the IL is not exclusively dependent on the physical interaction between CO<sub>2</sub> and the IL, but chemical interactions, such as a Lewis acid-base interaction,<sup>15</sup> should not be ruled out.

Table 3 listed CO<sub>2</sub> solubilities at room temperature in several common imidazolium-based ILs and in organic solvents obtained from the literature and compared with this work. Based on Henry's coefficient, it appears that CO<sub>2</sub> solubilities in amide-based BAILs are lower than that in [P<sub>5</sub>MIM][bFAP] (one example of IL containing highly fluorinated anion) but they are rela-



**Figure 2.** Variation of Henry's law coefficient at different temperature of absorption: (▲), [DBFormH][TFA]; (●), [DEFormH][TFA]; (◆), [FppdnH][TFA]; (■), [CaprolH][TFA]. Lines represent the smoothed data correlation using the parameters in Eq. 1 and Table S-2 in the Supporting Information.

**Table 3.** Solubilities of CO<sub>2</sub> in BAILs, in imidazolium-based ILs, and in common organics at 298 K and at atmospheric pressure

Solvent	<i>H</i> <sub>2,1</sub> /MPa	<i>S</i> <sub>CO<sub>2</sub></sub> /cm <sup>3</sup> (STP)cm <sup>-3</sup>	Ref.
[DEformH][TFA]	3.29	3.8	this work
[DBformH][TFA]	3.11	3.2	this work
[FppdnH][TFA]	3.91	3.5	this work
[CaprolH][TFA]	5.05	2.8	this work
[EMIM][Tf <sub>2</sub> N]	3.70	2.4	16
[BMIM][Tf <sub>2</sub> N]	3.30	2.4	16
[BMIM][BF <sub>4</sub> ]	5.60	2.2	16
[BMIM][Bu <sub>2</sub> PO <sub>4</sub> ]	4.24	1.8	17
[P <sub>5</sub> MIM][bFAP]	2.02	2.4	18
[[BMIM][OctSO <sub>4</sub> ]	5.58	1.4	19
[EMIM][TFA]	5.20	2.8	20
[BMIM][TFA]	4.94	2.5	20
CH <sub>3</sub> CN	6.04	7.1	16
Acetone	4.63	6.6	16
DMF	7.06	4.1	16
PC	6.70	3.9	16
MeOH	15.40	3.6	16
DMSO	10.90	2.9	16

tively comparable to those in [RMIM][Tf<sub>2</sub>N], [RMIM][TFA] ILs or acetone and are significantly greater than those in methanol, acetonitrile, or DMSO. While Henry's coefficient is more useful to express the solubility in the molecular perspective, direct comparisons based on this constant could be misleading because for an equivalent amount of CO<sub>2</sub> uptake per mass unit, an ionic liquid with relatively larger molecular formula than molecular organics will produce a smaller Henry's coefficient (means a higher solubility). It was suggested that cm<sup>3</sup>(STP)cm<sup>-3</sup> unit should be used for practical applications to compare the bulk absorption capacity of various types of solvent. Based on this solubility unit, it can be seen that CO<sub>2</sub> solubilities in tested

**Table 4.** Gibbs free energy, enthalpy, and entropy of CO<sub>2</sub> solvation in amide-based BAILs at several temperatures

T/K	$\Delta_{\text{solv}}G/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{solv}}H/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{solv}}S/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$
[DEformH][TFA] + CO <sub>2</sub>			
298.15	8.63	-19.57	-94.59
313.15	9.90	-13.70	-75.36
323.15	10.59	-10.09	-64.01
333.15	11.18	-6.70	-53.66
[DBformH][TFA] + CO <sub>2</sub>			
298.15	8.49	-15.32	-79.87
313.15	9.62	-12.54	-70.76
323.15	10.30	-10.83	-65.38
333.15	10.93	-9.22	-60.48
[FppdnH][TFA] + CO <sub>2</sub>			
298.15	9.06	-11.97	-70.51
313.15	10.11	-11.74	-69.77
323.15	10.80	-11.60	-69.33
333.15	11.50	-11.47	-68.93
[CaprolH][TFA] + CO <sub>2</sub>			
298.15	9.69	-4.09	-46.20
313.15	10.52	-9.59	-64.21
323.15	11.22	-12.97	-74.86
333.15	12.01	-16.16	-84.56

BAILs are comparable with the values by [EMIM] [TFA], DMF and propylene carbonate (PC) and are notably higher than those in several imidazolium ILs with anions containing many fluorine atoms but they are still much lower than that in acetonitrile or acetone.

The thermodynamic properties of solvation were calculated using Eq. (2) - (4) by incorporating Eq. (1) and coefficients in Table S-2.

$$\Delta_{\text{solv}}G = RT \ln \left( \frac{H_{2,1}(T, p)}{p^{\circ}} \right) \quad (2)$$

$$\Delta_{\text{solv}}H = R \left( \frac{\partial \ln(H_{2,1}(T, p)/p^{\circ})}{\partial(1/T)} \right)_p \quad (3)$$

$$\Delta_{\text{solv}}S = \left( \frac{\Delta_{\text{sol}}H - \Delta_{\text{sol}}G}{T} \right) \quad (4)$$

Table 4 lists the thermodynamic properties of CO<sub>2</sub> solvation in the amide-based BAILs at various temperatures and at standard pressure ( $p^{\circ} = 101325 \text{ Pa}$ ).

It is well known that the enthalpy of solvation is largely associated with the molecular interaction between CO<sub>2</sub> and an IL, and the entropy of solvation is related to the solvent organization surrounding the solute.<sup>16</sup> Similar to other IL-CO<sub>2</sub> systems, the solvation of CO<sub>2</sub> in BAILs under study is exothermic indicated by the negative values of enthalpy of solvation. From the table

it is obvious that the enthalpy of solvation becomes more negative as going from [CaprolH][TFA] to [DEformH][TFA] indicating stronger molecular interactions may be present. However, the entropy values in the sequence also become more negative. The more negative entropy indicates a higher degree of ordering when CO<sub>2</sub> dissolves in these ILs meaning that the dissolution of CO<sub>2</sub> is not favorable. Recalling the fact that Henry's coefficient of [DBformH][TFA] is slightly smaller than that of [DEformH][TFA] and the fact that all amide-based BAILs under study except for [CaprolH][TFA] have nearly similar Henry's values, it might be suggested that both magnitudes, enthalpy and entropy play important role in controlling the CO<sub>2</sub> solubility in this class of liquid salts.

### Conclusion

A series of amide-based Brønsted acidic ionic liquids were prepared and the solubility of CO<sub>2</sub> in these liquids were evaluated. Based on a molecular (mole fraction) and a volume unit (cm<sup>3</sup>(STP)cm<sup>-3</sup>) of absorbents, solubilities of CO<sub>2</sub> in these liquid salts are relatively higher than those in common non-task-specific imidazolium-based ILs. In term of volume unit basis, their CO<sub>2</sub> capacities are comparable to DMSO or propylene carbonate but are still much lower than those in CH<sub>3</sub>CN or acetone. The solubility of CO<sub>2</sub> in these ILs sharing the same anion exhibits molar volume-dependent behavior and thermodynamically controlled by the sum contributions of enthalpy and entropy. Reasonably high solubility of CO<sub>2</sub> combined with potential reaction processes in these amide-based BAILs may provide a fruitful green process.

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**Supporting Information Available.** Experimental details, Tables S-1 and S-2 are available on request from the corresponding author (fax: +82-2-966-3701; e-mail: mcheong@khu.ac.kr).

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