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Solubilities of CO$_2$ and Helium in an Ionic Liquid Containing Poly(amidoamine) Dendrimer Gen 0

John Chau, Gordana Obuskovic, Xingming Jie, Tripura Mulukutla, and Kamalesh K. Sirkar*

Otto H. York Department of Chemical, Biological and Pharmaceutical Engineering Center for Membrane Technologies, New Jersey Institute of Technology, Newark, New Jersey 07102, United States

Ⓢ *Supporting Information*

ABSTRACT: In this study, measurements of the solubilities of pure carbon dioxide, pure helium, and a feed mixture of 40% CO$_2$−He balance were carried out in the ionic liquid, 1-butyl-3-methyl-imidazoliumdicyanamide ([bmim][DCA]). Measurements were also made in its solution containing 20 wt % and 30 wt % poly(amidoamine) (PAMAM) dendrimer Gen 0 with and without moisture. A pressure-decay dual-transducer apparatus was employed at temperatures of 323, 353, 363, and 373 K and at pressures up to 1.38 MPa (∼200 psig). Henry's law constants of pure CO$_2$ and pure helium were determined at different temperatures for the ionic liquid. Pseudo-Henry's law constants for each of CO$_2$ and helium in a 40%−60% feed gas mixture were also determined. Solubility selectivities of carbon dioxide to helium for all liquid absorbents were also calculated at each temperature. Carbon dioxide was absorbed much more in these studied liquids, compared to helium. In addition, carbon dioxide absorption increased considerably when the amine was added to the ionic liquid and then increased several-fold when moisture was present in the amine−ionic liquid solution, compared to the CO$_2$ absorption by the ionic liquid.

1. INTRODUCTION

Greenhouse gases are believed to be the main cause for global warming, which has received a lot of attention in recent years.[1] In addition, carbon dioxide is the main contributor among the greenhouse gases, accounting for 80% of greenhouse emissions.[2] Carbon dioxide capture and storage (CCS) is considered the most important technique to curtail global climate change at the present time.[3,4] Carbon dioxide produced from Integrated Gasification Combined Cycle (IGCC) for coal has a much higher partial pressure than CO$_2$ produced in the burning of fossil fuel. As a result, precombustion CO$_2$ capture from post-shift-reactor syngas produced from IGCC is of significant interest. We are developing a pressure swing membrane absorption (PSMAB) process to simultaneously obtain purified hydrogen and CO$_2$[5] from low-temperature (L-T) post-shift-reactor synthesis gas, which will be available at ∼150 °C and pressures in the range of 200−300 psig. Our current temperature range of operation is 100−125 °C.

In this process, a porous hydrophobic membrane is used primarily as a membrane contactor to facilitate nondispersive contacting of the gas phase and the absorbent liquid phase at the membrane pore mouths via a rapid pressure swing absorption technique developed earlier by us.[6] A highly CO$_2$-selective solvent is of great interest in such a process. The composition of the syngas from a low-temperature (L-T) post-shift reactor consists of 38% H$_2$, 29% CO$_2$, 33% H$_2$O, and 0.15% CO.[7] Since hydrogen is extremely flammable, helium was used as its surrogate for our research. Solvent absorption-based method is a desired and widely used method for CO$_2$ removal. Since carbon dioxide produced from the L-T water-gas-shift reactor is at a high temperature and high pressure, the CO$_2$ liquid absorbent chosen must be thermally stable and nonvolatile. Furthermore, the chosen absorbent liquid must have a high solubility selectivity of CO$_2$ over H$_2$ and CO. Since

post L-T water-gas-shift reactor produces gases with considerable moisture, absorbents having high selectivity of carbon dioxide in the presence of water are also of interest.

Room-temperature ionic liquids (RTILs) have been considered green solvents for carbon dioxide capture, because of their unique characteristics. RTILs are bulky organic compounds whose cations are organic and anions are either organic or inorganic.[8] RTILs are in liquid form at room temperature and are chemically, thermally stable, and non-volatile. Therefore, they can be used to replace volatile organic solvents as absorbents for carbon dioxide separation.[9] Yokozeki et al. reported that carbon dioxide absorption in 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF6] is 30−300 times over that of hydrogen at hydrogen partial pressure of 0.5−3 MPa at room temperature and at lower temperatures.[10] Myers et al. succeeded in synthesizing task-specific ionic liquids (TSILs) that have functional groups which can form complexes with carbon dioxide, and they used them as a facilitated supported liquid membrane (FSLM).[11] A FSLM has been used in the separation of carbon dioxide from hydrogen at high temperature; the selectivity of CO$_2$ over H$_2$ in a FSLM has been reported to be 10−20 at ∼85 °C.[11] Yegani et al. reported that CO$_2$/H$_2$ solubility selectivity of polymeric membranes containing amine moieties dropped sharply as the feed gas moisture content decreased.[12] Meindersma et al. reviewed the application of task-specific ionic liquids for CO$_2$ separation and suggested that 1-butyl-3-methylimidazolium dicyanamide

([bmim][DCA]) could be a good choice as the CO_2 liquid absorbent.[13]

Primary and tertiary amines or compounds containing those amines can be used as carbon dioxide absorbents. However, effective CO_2 absorption requires a significant amount of moisture in systems containing tertiary amines. Previous studies have shown that a pure liquid membrane of PAMAM dendrimer Gen 0 with humidified gas streams had a very high selectivity of CO_2 over N_2/O_2 (in the range of 15 000−18 000).[14,15] This amine molecule, with a molecular weight of 517, contains four primary amines and two tertiary amines. Additional supported liquid membrane studies using pure PAMAM dendrimer Gen 0 for CO_2 separation have been carried out.[16−18] This dendrimer Gen 0 has also been used as a reactive absorbent in an aqueous solution in a hollow fiber membrane contactor at room temperature.[19] In addition, Rolker and co-workers have succeeded in achieving high CO_2/N_2 solubility selectivity in nonvolatile hyper-branched oligomeric liquid absorbents.[20]

The cost of purified analytical-grade PAMAM dendrimer Gen 0, per the Aldrich Chemical Co. catalog, etc., is quite high (on the order of $3000/kg). However, the manufacturer of this chemical proposes to supply an industrial-grade version of this compound in large scale at ~$10−20/lb.[21] This price is quite reasonable when we compare it with other specialized amines being studied (e.g., piperazine, whose bulk price is ~$9/lb). The industrial-grade dendrimer may have small amounts of impurities, all of which are going to be amines highly capable of CO_2 absorption. Furthermore, reactions of this dendrimer amine with CO_2 are completely reversible, as we have observed with runs of thousands of cycles of absorption and desorption every day in our research.[5]

Solubilities of many gases in ionic liquids have been studied and published by utilizing many different techniques, including a gravimetric method,[22−26] a pressure decay method (equilibrium pressure and volume techniques),[27,28] a quartz crystal microbalance method,[29] and gas uptake into a thin ionic liquid film technique.[30−32] This study utilizes the pressure decay method to find solubilities of pure carbon dioxide and pure helium in [bmim][DCA]. We have already indicated that this ionic liquid is a good absorbent for CO_2; more importantly, we have found that it has a very good solubility for PAMAM dendrimer Gen 0, unlike some others. Solutions of PAMAM dendrimer Gen 0 in [bmim][DCA] having 20 wt % dendrimer and 30 wt % dendrimer with and without moisture have also been investigated at different feed gas pressures up to 1.38 MPa (200 psig) and at 323, 353, 363, and 373 K. Solubilities from a CO_2−He feed gas mixture (40% CO_2, He balance) have also been obtained.

The apparent reaction equilibrium constants for reactions with primary amine functional groups in the dendrimer have been determined for dry gas systems, subject to particular assumptions. The range of reaction possibilities include only one primary amine consumed to all primary amines consumed, since PAMAM contains a total of four primary amines. Most studies of CO_2 absorption with amines in a liquid absorbent employ an amine or two having a single amine functionality: primary, secondary, or tertiary. The dendrimer of this study has multiple amine functionalities: four primary and two tertiary amines. Therefore, the analysis of the data to determine the reaction equilibrium constant is complicated with a considerable uncertainty.

2. EXPERIMENTAL PROCEDURE

2.1. Materials. The ionic liquid [bmim][DCA] was purchased from EMD Chemicals (Philadelphia, PA). Poly-(amidoamine) (PAMAM) dendrimer Gen 0 in methanol was purchased from Dendritech, Inc. (Midland, MI). Ultrahigh-purity-grade carbon dioxide, helium, and simulated precombustion syngas containing 40.67% CO_2, helium balance were obtained from Air Gas (Piscataway, NJ).

2.2. Apparatus and Measurements. The gas solubility measurements were made using a pressure decay method. The schematic of the apparatus is shown in Figure 1. The gas
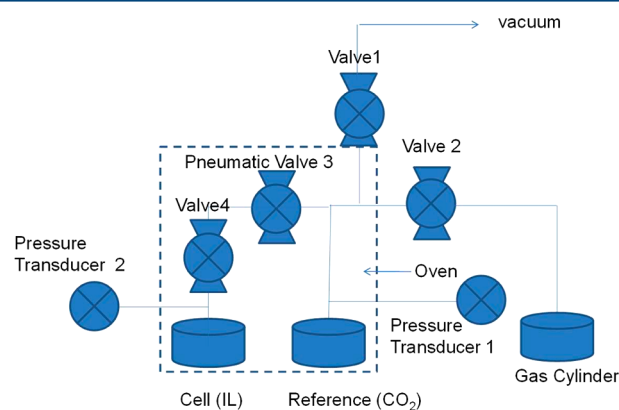

Figure 1. Apparatus for measuring gas solubility.

solubility measurement system mainly contains a cell volume, a reference volume, a programmable temperature oven (Model PH-202, ESPEC North America, Inc., Hudsonville, MI), and a gas cylinder. A volume of 10 mL of liquid absorbent was measured, weighed, and added to the cell. The entire system was then degassed for ~5 h using a vacuum pump (Model UN 726.3 FTP, KNF, Trenton, NJ) with all valves (Product No. SS-2P4T-BK, R.S. Crum & Company, Mountainside, NJ) opened. For the solubility measurement involving moisture, a predetermined amount of water was weighed and added, along with the absorbent liquids, to make up to 10 mL in a graduated cylinder. The solution is then transferred into the cell (a stainless steel cylinder). After the connection to the cell cylinder was closed with an open/closed valve (valve 4 in Figure 1), the system was degassed for 3 h without the cell cylinder to prevent water being evacuated during the degassing process. Then, the cell cylinder was attached to the system and was degassed for 15 min. The same process was repeated for the case of gas mixtures.

After the degassing process, the desired gas (CO_2, helium, or a mixture of both) was loaded into the reference stainless steel cell cylinder (Product No. 304L-05SF4-150, R.S. Crum & Company, Mountainside, NJ) with valves 1, 3, and 4 closed to a predetermined pressure while valve 2 was opened. The oven was turned on to allow the temperature of the gas to reach a desired temperature in the reference volume after opening valve 4. Then, valve 3 was opened and controlled by a pneumatic controlling unit (PneuMagnetic, Quakertown, PA) while valves 1 and 2 were closed. The pneumatic controlling unit allows any user to open and close valve 3 with a toggle switch that is easily accessible and positioned outside the oven. Valve 3 can be opened for up to 99 h, which is long enough to ensure that equilibrium is fully established between both cylinders. The

final pressure difference was used to calculate the number of moles of gas absorbed by the absorbent liquid.

Changes in pressure versus time were also read and recorded by pressure transducer units in both cell and reference cylinders. The rate of change of the pressure indicates the rate of absorption of CO_2; from such data, one can calculate the diffusion coefficient using the assumption that the depth of the liquid in the test cell is infinite.[31,32] Such calculations are not reported here; they are part of a transport modeling and separation manuscript for the PSMAB process being prepared. The pressure transducer units include two pressure transducers (Model PX32B1-250GV), two assembly cables (Model CA-6TE24-010-PX32), and two universal input ethernets (Model DP41-B-EI) purchased from Omegadyne, Inc. (Sunbury, OH). The pressure in the transducers ranges from 0 to 1.72 MPa (~250 psig) with 0.25% linearity accuracy. The transducers can withstand a temperature of up to 115 °C (388 K). This provided an upper limit to the measurements.

For a CO_2/helium gas mixture, the equilibrium gas mixture composition was determined by a gas chromatograph (Model GC-2014, Shimadzu Scientific Instruments, Inc., Somerset, NJ). A Carboxen-1010 PLOT Capillary (Product No. 25467, Sigma–Aldrich, Inc., St. Louis, MO) was used in the analysis of the gas mixture at equilibrium. Nitrogen was used as the carrier gas; column and TCD temperatures were kept at 180 and 230 °C respectively. The temperature of the split injector was kept at 200 °C with a linear velocity flow control and a split ratio of 5. The run time for the analysis was set at 10 min.

3. RESULTS AND DISCUSSIONS

3.1. Data Analysis for Pure Ionic Liquid. Solubilities of pure carbon dioxide and pure helium, as well as their mixtures, were determined in various absorbents at different temperatures and pressures up to 1.38 MPa. The gas mole fractions in absorbent liquids were calculated from the differences in the values of the initial and final pressures. The general equation of state based on the compressibility factor was used to calculate the number of moles of gas. The total number of initial moles of the desired gas at pressure P_1 is given by

$$n_T = \frac{P_1 V_{ref}}{Z_i RT} \tag{1}$$

The number of moles in the cell and reference volumes after equilibrium is reached at a pressure P_2 is given by

$$n_1 = \frac{P_2(V_{ref} + V_{cell} - V_{IL})}{Z_f RT} \tag{2}$$

The moles of gas absorbed (n_2) is

$$n_2 = n_T - n_1 \tag{3}$$

Here, P_1 is the initial feed pressure of the desired gas in the reference cylinder; P_2 is the final equilibrium pressure; V_{ref} and V_{cell} are the volumes of reference and cell cylinders, respectively; V_{IL} is the volume of absorbent added in cell cylinder; Z_i and Z_f are compressibility factors at pressures P_1 and P_2. The compressibility factor value at a temperature and a pressure point can be found in an IUPAC handbook.[33,34]

Henry's law constants for pure CO_2 and pure helium were calculated by extrapolating the solubility data of each pure gas to zero pressure and are shown in Table 1 for the ionic liquid [bmim][DCA] at 50, 80, 90, and 100 °C. The value of the pseudo-Henry's law constant for each gas was also determined

Table 1. Henry's Law Constants of Pure CO_2 and Pure Helium in [bmim][DCA] at Different Temperatures

	Henry's law constant (bar)		
temperature (K)	H_{CO_2}	H_{He}	reference H_{CO_2}[36] (bar)
323	74.4 ± 0.5	751.8 ± 5.1	60.3 ± 1.6 @303 K
353	104.2 ± 2.5	521.1 ± 7.2	94.4 ± 3.5@333 K
363	114.3 ± 3.0	440.8 ± 6.4	111.4 ± 4.8 @344 K
373	129.8 ± 1.1	365.1 ± 3.0	

for the case where we had a gas mixture: since Henry's law constant is defined for a pure component only, the result so determined is being called the pseudo-Henry's law constant when a gas mixture is used. Table 2 lists these values; we will deliberate on these later.

Table 2. Pseudo-Henry's Law Constants of CO_2 and Helium Mixture in [bmim][DCA] at Different Temperatures

	Pseudo-Henry's Law Constant (bar)	
temperature (K)	H_{CO_2}	H_{He}
323	78.2 ± 1.7	761.5 ± 3.9
353	116.9 ± 2.0	537.4 ± 3.1
363	120.5 ± 3.1	450.3 ± 3.4
373	135.3 ± 3.3	368.9 ± 3.1

3.2. Solubilities of Pure Gases at Various Temperatures. Table 1 shows that, as the temperature was increased, the solubility of CO_2 decreased in the pure ionic liquid, which is represented by an increase in the Henry's law constant. The temperature-solubility trend observed agrees with literature results for CO_2.[35] Henry's law constants of CO_2 in [bmim]-[DCA] at 30, 60, and 71 °C, as reported by Sanchez, are 60.3, 94.4, and 111.4 bar, respectively.[36] Although the measurement conditions in our study are somewhat different from these conditions, the literature values are in the expected range of the values obtained in this study. The solubility of helium in the studied absorbent, on the other hand, increased with increasing temperature. This trend can be explained based on thermodynamic relationships. For helium, increasing temperature corresponds to a positive change in the enthalpy of absorption and the entropy of absorption leading to higher solubility in liquid absorbents.[37] For CO_2, increasing temperature results in a negative change in the enthalpy of absorption and the entropy of absorption which leads to lower solubility.[37] In other words, for low-solubility gases (N_2, He, H_2, etc.), the solubility increases when the temperature increases. The reverse trend is observed for the high-solubility gases such as CO_2.[37] The same temperature-solubility trends, in terms of mole fractions, for carbon dioxide and helium in the ionic liquid [bmim][DCA] are shown in Figure 2 for a variety of pressures and four temperatures.

3.3. Solubilities of Pure Gases as a Function of Pressure. The solubilities of carbon dioxide and helium in [bmim][DCA] at the same temperatures increased with increasing pressure, as shown in Figures 3–6 (for two temperatures: 50 and 100 °C). Table 3 shows the mole fraction values of carbon dioxide in [bmim][DCA] at 30 °C for various pressures reported by Sanchez.[36] In this study, solubility measurement was carried out at the lowest temperature of 50 °C. For general comparison purpose, the mole fraction values of CO_2 in the same ionic liquid at 50 °C for similar pressures,
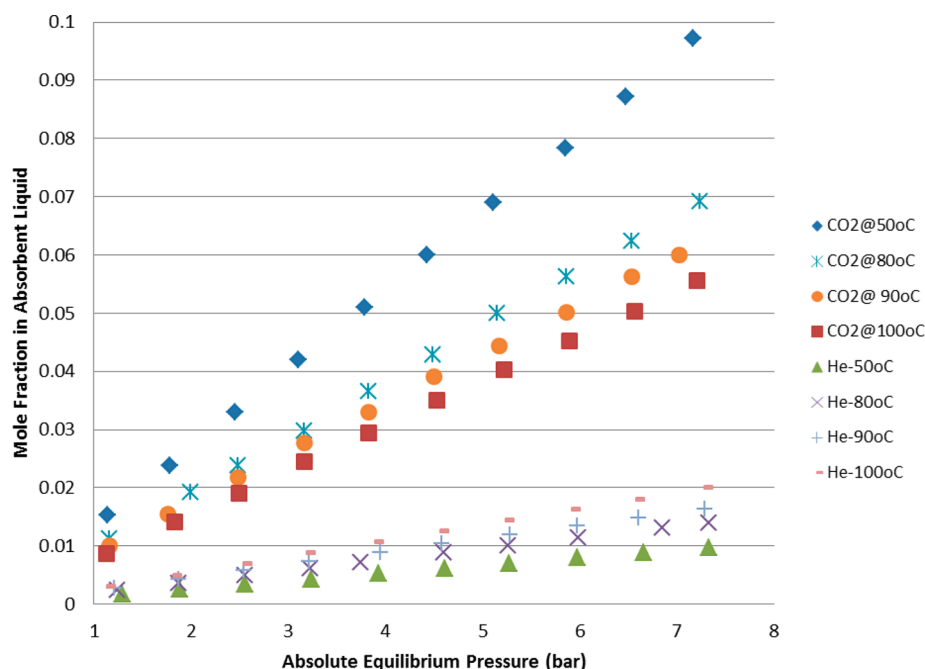
Figure 2. Influence of temperature on solubilities of pure CO_2 and helium in [bmim][DCA].
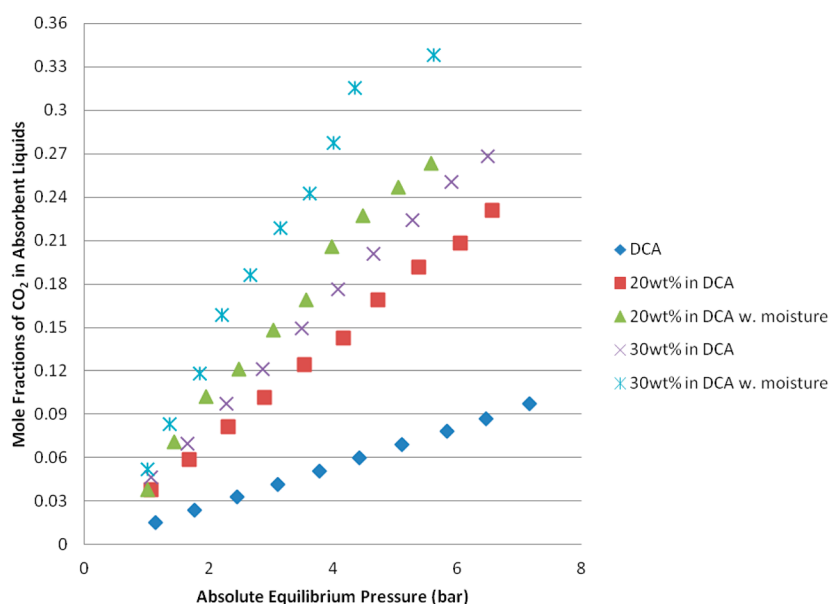

Figure 3. Solubilities of pure CO_2 in different absorbent liquids at 50 °C.

also shown in Table 3, show trends similar to those of Sanchez's at 30 °C, namely, the solubility increased with increasing pressure and, furthermore, the values are in the same range.

Table 4a shows the values of CO_2 mole fraction in [bmim][DCA] at various feed pressures and temperatures. (Table 4b, given in the Supporting Information, provides a complete dataset.) The data show that carbon dioxide mole fraction values are directly proportional to the feed pressures. In addition, for the same feed pressure, the mole fraction ratio at different temperatures is the same. [Note: mole fraction ratio = the ratio of CO_2 mole fractions at the two pressures.] The same trend could be observed for other liquid absorbents in this study (Figures 3−6).

3.4. Solubilities of Pure Gases in Different Liquid Absorbents. Solubilities of carbon dioxide in various absorbents at 50 and 100 °C are shown in Figures 3 and 4, respectively. Among those different liquid absorbents, CO_2 was least absorbed in pure [bmim][DCA]. CO_2 solubility in the absorbent increased with increasing dendrimer concentration in the absorbent solutions since a PAMAM dendrimer (generation 0) molecule contains four primary amine groups and two tertiary amine groups (Figure 7), which helps increase the CO_2 absorption. Only primary and secondary amine groups can react with CO_2 without any water present. The reaction between primary amine groups in a dendrimer molecule with CO_2 has been shown in eq 4:
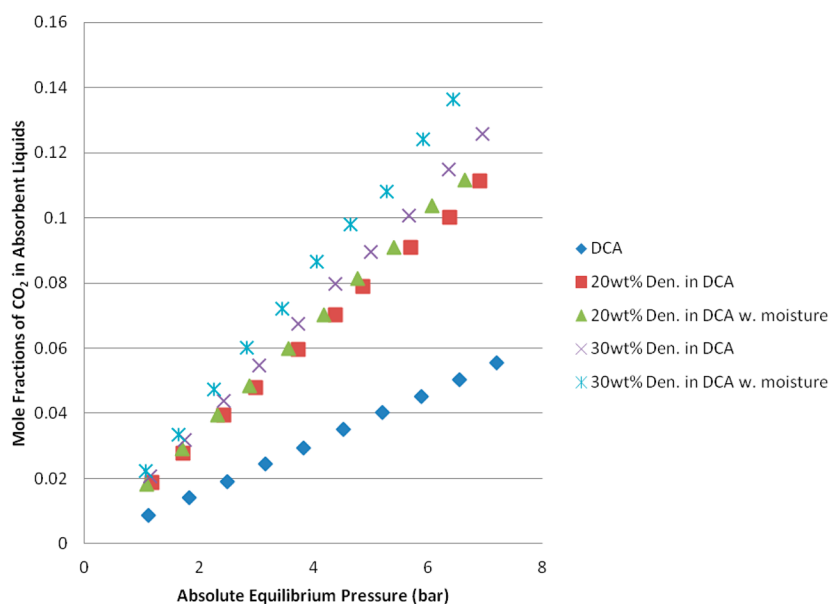
$$2R(NH_2)_4 + 4CO_2 \leftrightarrow R(NHCOO^-)_4 + R(NH_3^+)_4 \quad (4)$$

Figure 4. Solubilities of pure CO_2 in different absorbent liquids at 100 °C.
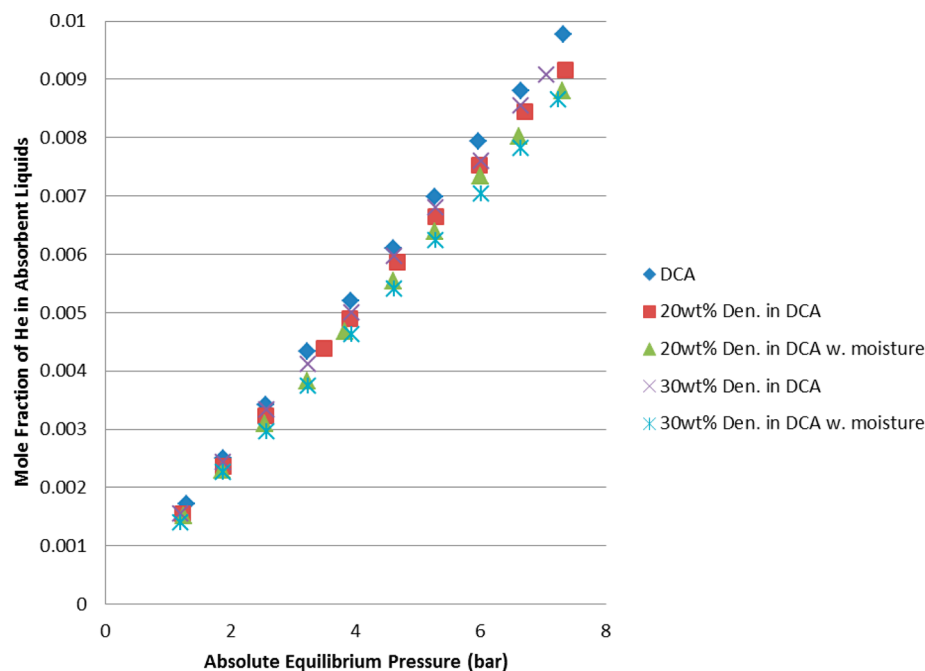

Figure 5. Solubilities of pure helium in different absorbent liquids at 50 °C.

There is spectroscopic evidence (infrared, IR) shown in Figure 8 indicating the presence of carbamate species in the dendrimer Gen 0 system with ionic liquid exposed to CO_2. Figure 9 shows that pure [bmim][DCA] did not have any band at $\sim$1655 cm^{-1} on the IR spectra, whereas 20 wt % dendrimer Gen 0 in [bmim][DCA] without any exposure to CO_2 had a band at 1655 cm^{-1}, because of the presence of the amines in the solution. Figure 8 shows that the band at the wavenumber of 1651 cm^{-1} decreased in intensity while the bands at 1567 and 1170 cm^{-1} increased in intensity after CO_2 was introduced to the 20 wt % dendrimer Gen 0 in [bmim][DCA]. This indicates that CO_2 reacted with the primary amine groups to form carbamate species. The bands at $\sim$1550 and 1100 cm^{-1} correspond to the C=O asymmetric and symmetric stretching bands of NH_2COO^-.[39,40]

In addition, CO_2 solubility increased significantly when moisture was added to the dendrimer−ionic liquid solution, because of the contribution of the tertiary amine groups contained in the dendrimer, besides the primary amine groups. Equation 5 shows the reaction of tertiary amine groups in the presence of water with CO_2:[15,38]

$$2CO_2 + R_2 - N - R - N - R_2 + 2H_2O$$
$$\leftrightarrow 2HCO_3^- + R_2 - NH^+ - R - NH^+ - R_2 \quad (5)$$
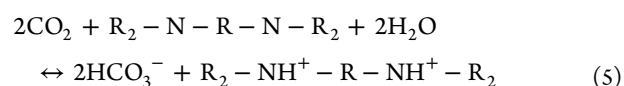
The effect of water in [bmim][DCA]-containing dendrimers on CO_2 solubility was largest at T = 50 °C, as shown in Figure 3. Some water evaporated at the higher temperature; as a result, the presence of water in [bmim][DCA]-containing dendrimer
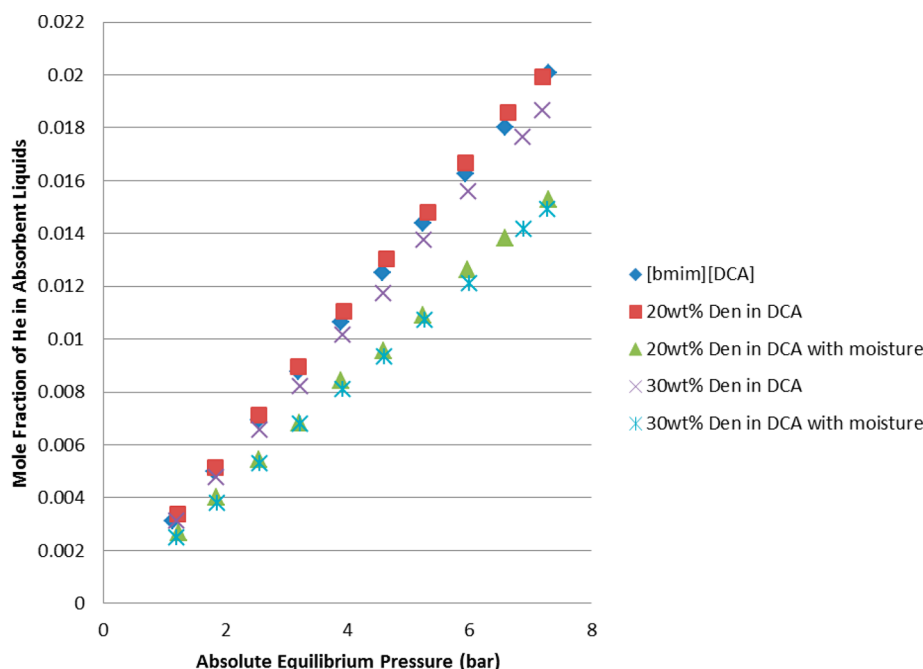
Figure 6. Solubilities of pure helium in different absorbent liquids at 100 °C.

Table 3. CO₂ Mole Fractions in [bmim][DCA] for Different Pressures at 30 and 50 °C

pressure (bar)	CO₂ mole fraction
Sanchez[36] *at 30 °C*	
2	0.035
4	0.068
5	0.08
7	0.11
9	0.13
Experimental Data at 50 °C (This Work)	
1.14	0.015
1.78	0.024
2.45	0.033
3.11	0.042
3.78	0.051
4.42	0.060
5.11	0.069
5.85	0.078
6.48	0.087
7.17	0.097

Table 4a. CO₂ Mole Fractions in [bmim][DCA] at Various Feed Pressures and Temperatures

pressure (bar)	CO₂ mole fraction	pressure ratio	mole fraction ratio
	T = 50 °C		
2.43	0.015	1.00	1.00
7.92	0.051	3.26	3.33
14.77	0.097	6.08	6.35
	T = 80 °C		
2.43	0.015	1.00	1.00
7.92	0.051	3.24	3.28
14.77	0.097	6.07	6.21
	T = 90 °C		
2.43	0.015	1.00	1.00
7.92	0.051	3.28	3.26
14.77	0.097	6.15	5.92
	T = 100 °C		
2.43	0.015	1.00	1.00
7.92	0.051	3.39	3.39
14.77	0.097	6.32	6.42
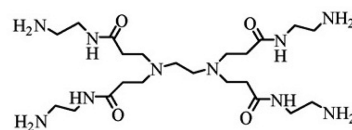
Figure 7. PAMAM dendrimer of generation 0.[15]

solutions was less effective, corresponding to a smaller increase in CO₂ solubility.

In aqueous systems, the physical solubility of CO₂ is affected by the presence of various ions. When the reactive absorption of CO₂ takes place, it is difficult to know what the concentration of free CO₂ is. A method followed in the literature[39,40] involves determining the change in solubility of an inert gas due to the presence of various ions. The ratio of this change in solubility of this inert gas due to various ions is used to correct the free CO₂ concentration by the same factor. Normally, N₂O is used to this end;[41,42] here, we have used the solubility ratio of inert helium to correct the concentration of free CO₂ in the reactive absorbent liquid:

$$H_{CO_2T} = H_{CO_2} \frac{H_{HeT}}{H_{He}} = \frac{P_f}{x} \qquad (6)$$

where H_{CO_2T} is the Henry's law constant of CO₂ that is due to physical absorption in the IL-containing dendrimer, H_{CO_2} the Henry's law constant of CO₂ in pure IL, H_{HeT} the Henry's law constant of helium in the IL-containing dendrimer, H_{He} the Henry's law constant of helium in pure IL, and x the mole fraction of free CO₂.

Because of the radically different charge climate in an ionic liquid as opposed to water (for example), the effect is expected to be minor. We find this correction to be ~5%–8%.
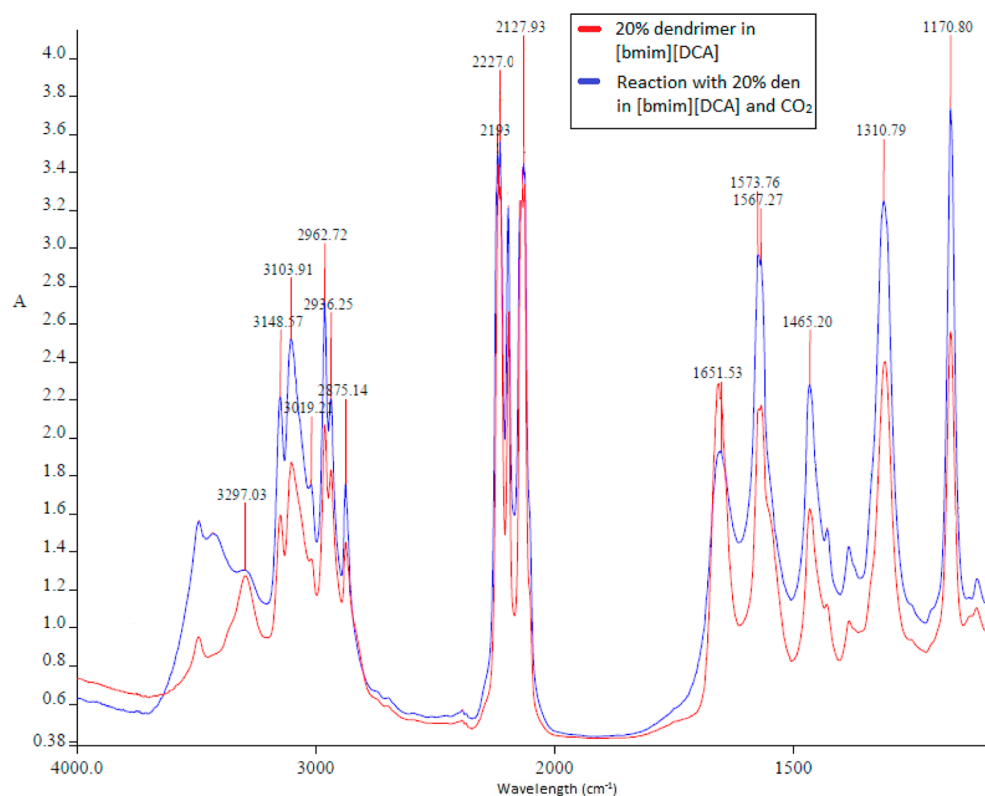
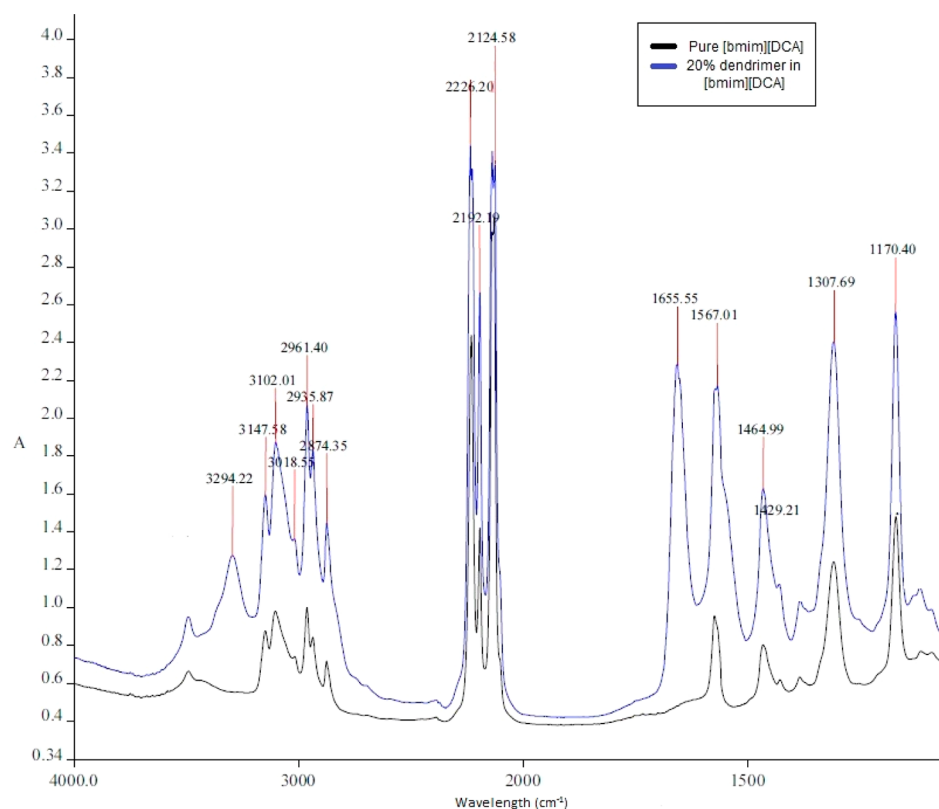**Figure 8.** IR spectra of 20 wt % dendrimer in [bmim][DCA] and other species in the solution exposed to CO_2.

Figure 9. IR spectra of pure [bmim][DCA] and 20 wt % of dendrimer Gen 0 in [bmim][DCA] not exposed to CO_2.

3.5. Solubilities of Gases in a Mixture. Table 2 summarizes the pseudo-Henry's law constants for an initial feed gas mixture containing 40% CO_2 (with the balance being

helium) for [bmim][DCA] at different temperatures. Here, we define the pseudo-Henry's law constant as the value of the slope of the curve of the gas partial pressure versus the mole
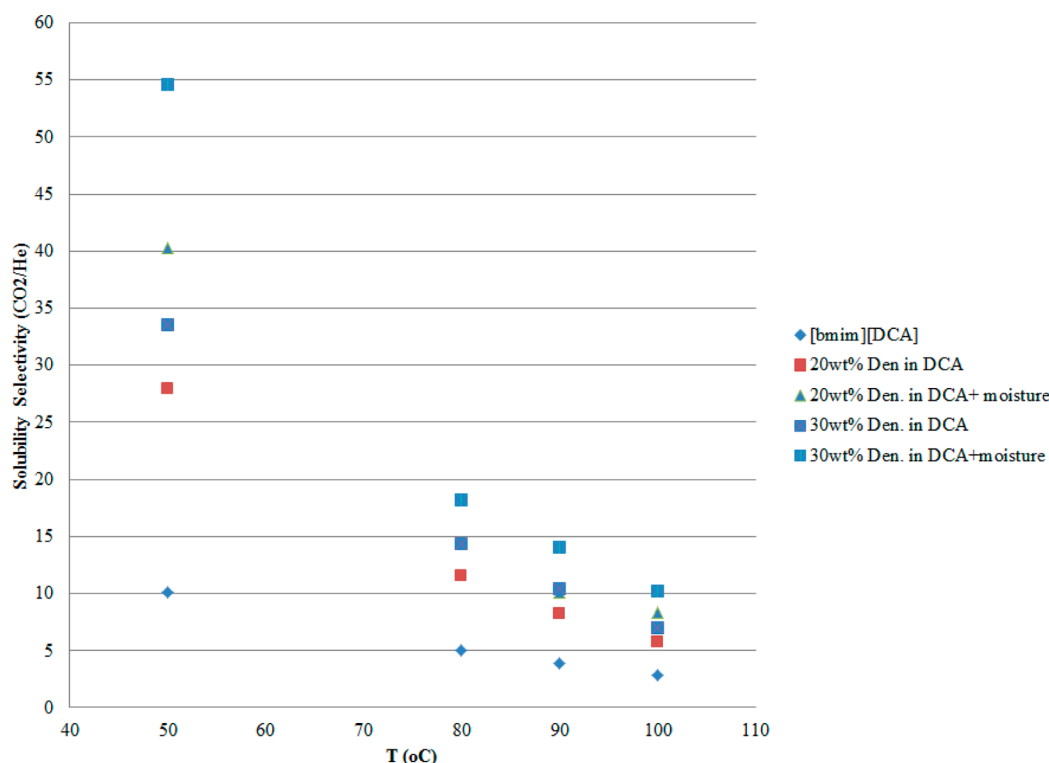
Figure 10. Solubility selectivity of CO_2/He in absorbent liquids at different temperatures.

fraction of species in liquid as this mole fraction tends to zero. The pseudo-Henry's law constants for each of CO_2 and helium in the gas mixture were slightly higher than Henry's law constants of pure CO_2 and helium. The Henry's law constants for pure CO_2 and helium in pure [bmim][DCA] at 50 °C are 74.4 and 751.8 bar, respectively, whereas the pseudo-Henry's law constants for CO_2 and helium in the gas mixture at 50 °C are, respectively, 78.2 and 761.5 bar. The differences between those values are within 5%. In addition, all the solubility trends with temperature, pressure, and different absorbent liquids observed with the pure gases were also observed here. This was also a way to verify that the results are consistent and reproducible.

3.6. CO_2–Helium Solubility Selectivity. Solubility selectivity of CO_2 over helium is defined in this study as the ratio of Henry's law constant of pure helium to that of pure carbon dioxide at a given temperature for [bmim][DCA]. For other reactive absorbents, the solubility selectivity is defined as the ratio

$$\text{Solubility selectivity (CO}_2/\text{He)}$$
$$= \frac{\text{pseudo-Henry's law constant for helium}}{\text{pseudo-Henry's law constant for CO}_2} \quad (7)$$

Here, as done previously, we define the pseudo-Henry's law constant as the value of the slope of the curve of the gas partial pressure versus the mole fraction of species in liquid as this mole fraction tends to zero. When we have a reactive absorbent, the Henry's law constant defined for physical absorption in the limit of zero mole fraction in the liquid phase is misleading. However, in all four dendrimer-containing absorbents studied (Figures 3−6), there is essentially a linear behavior over almost the entire range of pressures and certainly as the pressure is lowered.

Figure 10 shows the solubility selectivity of CO_2 over helium in several liquid absorbents at four temperatures. The solubility selectivity decreased with increasing temperature for all liquid absorbents. The highest selectivities were observed at 50 °C. Solubility selectivity of carbon dioxide over helium in pure [bmim][DCA] decreased from ~10 at 50 °C to ~2.8 at 100 °C. Furthermore, a solution of 30 wt % dendrimer in [bmim][DCA] with moisture gave the highest CO_2/He solubility selectivity among the three studied absorbents and five systems: a value of 55 was observed at 50 °C and a value of 10 was observed at 100 °C. (See Tables 7−10, given in the Supporting Information, which provide the solubility data in the dendrimer-containing ionic liquid with or without moisture for different temperatures.)

3.7. Apparent Equilibrium Constant for the Reaction in Reactive Absorption. The PAMAM Gen 0 molecule has four primary amines and two tertiary amines (see Figure 7). For a dry system, we need to focus only on primary amines. The reaction scenario is complicated by the fact that, under conditions of excess CO_2, all four primary amines in a molecule can be consumed. However, if we have a limited amount of CO_2, we can envisage a scenario where only one primary amine in a molecule has been consumed. (In reality, there will be a variety of intermediate conditions.) Here, we will develop appropriate equations for these two extreme cases, so that we can extract values of the corresponding apparent equilibrium constants. First, we focus on the situation where all four primary amines in a PAMAM Gen 0 have been consumed:

$$2R(NH_2)_4 + 4CO_2 \leftrightarrow R(NHCOO^-)_4 + R(NH_3^+)_4 \quad (8)$$

The approach for determining the equilibrium constant from the measured data is as follows. For 20 wt % dendrimer in [bmim][DCA] with a known mass (m) and volume of 0.01 L

(V_{IL}), the number of moles of dendrimer and $[bmim][DCA]$ (n_{den} and n_{IL}, respectively) are

$$n_{den} = \frac{0.2m}{517.0} \quad (9)$$

$$n_{IL} = \frac{0.8m}{205.26} \quad (10)$$

The number of moles of CO_2 absorbed in the IL-containing dendrimer, n_2, was calculated from the experimental data via eq 3. The Henry's law constants for CO_2 due to physical absorption in the IL containing dendrimer are calculated via eq 6.

This approach is adopted since the physical solubility of CO_2 in the IL will be influenced by the presence of other electrolytes/compounds such as dendrimer. The effect of these compounds on the solubility of helium will provide some guidance on the correction needed for CO_2 solubility. If N_2O was used instead of helium, the correction may have been more accurate.[41,42] However, as mentioned earlier, because of the radically different charge climate in an IL, as opposed to water (for example), the effect is expected to be minor. The mole fraction of free CO_2 in the liquid (x) is given as

$$x = \frac{n}{n + n_{IL} + n_{den}} = \frac{P_f}{H_{CO_2 T}} \quad (11)$$

Therefore,

$$n = \frac{x(n_{IL} + n_{den})}{1 - x} = \text{moles of free } CO_2 \text{ in solution} \quad (12)$$

Now, $n_{CO_2,r}$, which represents the number of moles of CO_2 reacted with primary amines present in the dendrimer, is equal to

$$n_{CO_2,r} = n_2 - n \quad (13)$$

From eq 4, the apparent reaction equilibrium constant (K_C) may be written as

$$K_C = \frac{\left(\frac{n_{R(NHCOO^-)_4}}{V_{IL}}\right)\left(\frac{n_{R(NH_3^+)_4}}{V_{IL}}\right)}{\left(\frac{n_{CO_2 free}}{V_{IL}}\right)^4 \left(\frac{n_{R(NH_2)_4}}{V_{IL}}\right)^2} \quad (14)$$

where we have assumed that any dendrimer molecule has all four primary amine groups reacting with CO_2, per eq 4. Obviously,

$$n_{R(NHCOO^-)_4} = \frac{n_{CO_2,r}}{4} = n_{R(NH_3^+)_4} \quad (15)$$

Also, the unreacted dendrimer molecules, $n_{R(NH_2)_4}$ are related to

$$n_{R(NH_2)_4} = n_{den} - \frac{n_{CO_2,r}}{4} - \frac{n_{CO_2,r}}{4}$$
$$= n_{den} - \frac{n_{CO_2,r}}{2} \quad (16)$$

Substituting relations 12, 15, and 16 into eq 14, we get

$$K_C = \frac{\left(\frac{n_{CO_2,r}}{4}\right)^2}{n^4 \left(n_{den} - \frac{n_{CO_2,r}}{2}\right)^2} V_{IL}{}^4 \quad (17)$$

Since all of the quantities on the right-hand side are known, K_C can be determined.

In the other limit, we may have only one primary amine of each dendrimer molecule reacting with CO_2. In reality, we have a variety of scenarios. However, one can calculate the K_C value in the limit where only one primary amine of each dendrimer reacts with CO_2:

$$CO_2 + 2R(NH_2)_4$$
$$\leftrightarrow R(NH_2)_3HNCOO^- + R(NH_2)_3NH_3^+ \quad (18)$$
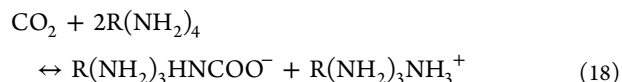
The apparent reaction equilibrium constant, K_C, in this case could be expressed as

$$K_C = \frac{(n_{CO_2,r})^2}{n(n_{den} - 2n_{CO_2,r})^2} V_{IL} \quad (19)$$

(a detailed derivation is provided in the Supporting Information).

One can calculate the theoretical capacity of CO_2 absorption by PAMAM dendrimer molecules under dry conditions, as well as under wet conditions. We have calculated this value, for example, for dry conditions for a certain concentration of PAMAM in the IL. By taking into account the total CO_2 absorbed minus the amount due to CO_2 solubility in the IL under the selected condition, one can then find out what fraction of this theoretical absorption capacity has been consumed under this particular condition. If we are very close to the theoretical capacity, we can argue that eq 8 describes the situation. On the other hand, if we are very far away from the theoretical capacity, the case for reaction 18 improves.

In Table 5a, we have provided the percent theoretical capacity consumed for a few pressures for a given temperature

Table 5a. Percent Theoretical Capacity[a] of Primary Amines Consumed under Different Pressures and Its Corresponding Apparent Equilibrium Constant of Primary Amine Reaction with CO_2 for 20 wt % Dendrimer in $[bmim][DCA]$ at Different Temperatures[b]

temperature, T (°C)	P_{feed} (bar)	% saturation (%)	K_C
50	2.43	10.56	6100 L/mol
50	14.66	97.69	29972 L^4/mol^4
80	2.39	5.51	2804 L/mol
90	2.41	4.13	2227 L/mol
100	2.47	3.84	1790 L/mol

[a]Theoretical capacity is the theoretical moles of carbon dioxide absorbed due to reacting with primary amines in the dendrimer, based on eq 4. [b]Dry system.

for 20 wt % dendrimer in the IL. (For a complete table that includes many pressures at any temperature, refer to Table 5b in the Supporting Information.) At 14.66 bar, we find that the absorption amount is 97.69% of the theoretical capacity at 50 °C. Therefore, eq 17 may be used to estimate the apparent equilibrium constant (K_C); the value is 29972 L^4/mol^4. At 2.41 bar, the absorption amount is 10.56% of the theoretical capacity at 50 °C. We may therefore use eq 19 to estimate K_C; the value is 6100 L/mol. In addition, at 80, 90, and 100 °C, eq 19 is used

to calculate the apparent equilibrium constants, because of the small percent amine saturation. The K_C values for 20 wt % dendrimer in [bmim][DCA] at 80, 90, and 100 °C are 2804, 2227, and 1790 L/mol, respectively.

We can carry out similar calculations for the 30 wt % dendrimer in the IL at different temperatures and pressures; the results are shown in Table 6a. (For a complete table, refer to

Table 6a. Percent Theoretical Capacity[a] of Primary Amines Consumed under Different Pressures and Its Corresponding Apparent Equilibrium Constant of Primary Amine Reaction with CO_2 for 30 wt % Dendrimer in [bmim][DCA] at Different Temperatures[a]

temperature, T (°C)	P_{feed} (bar)	% saturation (%)	K_C
50	2.41	9.29	6659 L/mol
50	14.66	69.58	10329 L^4/mol^4
80	2.43	4.49	3061 L/mol
90	2.43	3.93	2431 L/mol
100	2.43	2.98	1954 L/mol

[a]Theoretical capacity is the theoretical moles of carbon dioxide absorbed due to reacting with primary amines in the dendrimer, based on eq 4. [b]Dry system.

Table 6b in the Supporting Information.) Since the percent amine saturation, for most cases, at all the temperatures studied, is small, eq 19 is used to calculate the apparent equilibrium constants at different temperatures. The K_C values for 30 wt % dendrimer in [bmim][DCA] at 50, 80, 90, and 100 °C are 6659, 3061, 2431, and 1954 L/mol, respectively. At 50 °C and 14.66 bar, the percentage saturation is 69.58%. Therefore, eq 17 may be used to calculate K_C: the value is 10329 L^4/mol^4. Because of the lower percentage saturation, this value is quite different from 29972 L^4/mol^4 calculated for the 20 wt % case, with 97.69% saturation at 50 °C.

What we observe is as follows: the apparent reaction equilibrium constants decreased as the temperature was increased. Furthermore, the value of K_C for the case of only one primary amine being consumed is likely to be independent of the dendrimer concentration at all four temperatures.

4. CONCLUDING REMARKS

This study focused on determining the CO_2 absorption characteristics and CO_2–helium selectivity of an ionic liquid (IL) with or without a nonvolatile PAMAM dendrimer Gen 0 CO_2 for use in the pressure swing membrane absorption process.[5] A gas solubility apparatus was successfully setup to measure the solubility of pure CO_2, pure helium, and a CO_2–helium mixture at temperatures of 323, 353, 363, and 373 K and at pressures up to 1.38 MPa (~200 psig). Gas solubility measurements were made using a pressure decay method. Here, CO_2 solubility decreased as the temperature increased, whereas the helium solubility increased with an increase in temperature. The CO_2 and helium solubilities increased with an increase in pressure. An increase in the PAMAM dendrimer concentration led to a substantial increase in CO_2 solubility in a liquid absorbent due to reactions with the primary amine groups in the dendrimer molecule. An increase in dendrimer concentration led to a decrease in helium solubility in the liquid absorbent. The presence of water in the IL-containing dendrimer led to a considerable increase in CO_2 absorption in the liquid absorbent, because of the reactivity of the tertiary amine groups. Among the studied absorbent liquids, 30 wt %

dendrimer in [bmim][DCA] with moisture gave the highest CO_2 solubility at all temperatures studied. Higher CO_2/He solubility selectivity was observed as temperature decreased. A solution of 30 wt % dendrimer in [bmim][DCA] with moisture gave the highest CO_2/helium solubility selectivity: values of 55 at 50 °C and 10 at 100 °C. The solubilities of gases in a mixture are consistent with those of pure gases.

Estimates of apparent reaction equilibrium constant (K_C) for a dry environment were also developed for two cases: all primary amines consumed and only one primary amine consumed. The K_C values for the case of only one primary amine consumed were almost independent of dendrimer concentration at all four temperatures.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The derivation of the expression for the equilibrium constant for the case where only one primary amine in the dendrimer molecule is reacting with CO_2 has been provided in the Supporting Information. Tables showing the percent consumption of the theoretical absorption capacity of the dendrimer amine under different conditions have been included. Detailed tables for CO_2 and helium solubilities in various absorbents are also provided in the Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: 973-596-8447. Fax: 973-642-7854. E-mail: sirkar@njit.edu.

Notes

The authors declare no competing financial interest.

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