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Experimental Investigation on the Solubility and Initial Rate of Absorption of CO_2 in Aqueous Mixtures of Methyldiethanolamine with the Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate

Afshin Ahmady, Mohd Ali Hashim, and Mohamed Kheireddine Aroua*

Chemical Engineering Department, University of Malaya, 50603 Kuala Lumpur, Malaysia

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In this paper we present the results of the initial absorption rate and solubility of CO_2 in aqueous 4 M methyldiethanolamine (MDEA) mixed with various concentrations of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) at (303, 313, 323, and 333) K. All experiments were carried out at low partial pressures of CO_2, below 110 kPa. The results of this research suggested that the presence of a low concentration of [bmim][BF_4] in aqueous 4 $mol \cdot L^{-1}$ MDEA has no significant effect on the mixture loading capacity, but increased the initial absorption rate. The amine CO_2 loading capacity showed a significant decrease in the presence of high concentrations of ionic liquid in the mixture.

Introduction

The separation of acid gas impurities such as CO_2 and H_2S from gas mixtures is an important operation in the natural gas processing, petroleum refining, coal gasification, and ammonia manufacturing industries. Since CO_2 is widely regarded as a major greenhouse gas, potentially contributing to global warming, there has been considerable interest in developing technologies for capturing and sequestering large quantities of CO_2 produced from industrial sources such as fossil fuel electric power generation facilities.[1] Various technologies have been developed for CO_2 and H_2S removal from gas streams including absorption by chemical and physical solvents, cryogenic separation, and membrane separation. Among these methods, gas absorption using chemical solvents such as aqueous solutions of alkanolamines is one of the most popular and effective technologies.[2,3]

Methyldiethanolamine (MDEA) is an alkanolamine widely used in industry for CO_2 removal. It has a higher loading capacity and a lower heat of reaction in comparison to secondary alkanolamines such as DEA, but the CO_2 absorption rate in MDEA is very low. Thus, there is a growing interest in the use of activated aqueous MDEA for gas-treating processes.[3]

Recent research[4−10] on the application of room-temperature ionic liquids (RTILs) as nonvolatile solvents suggested the possibility of utilizing them as CO_2 capture solvents. Imidazolium-based RTILs possess good solubility and selectivity for CO_2 relative to N_2 and CH_4.[4] These properties make RTILs interesting media for gas separation and capture. Gas dissolution in RTILs is primarily a physical phenomenon with no chemical reaction.[4]

CO_2 solubility in pure ionic liquids (ILs) depends strongly on the type of anion rather then the type of cation. For example, Cadena et al.[5] showed that bis((trifluoromethyl)sulfonyl)imide anion has the greatest affinity for CO_2, while there is a small difference between the CO_2 solubility of ionic liquids having the tetrafluoroborate and hexafluorophosphate anions.[12] High solubility of CO_2 in ionic liquids with a fluorinated anion was also reported.[6] All tested RTILs showed a lower CO_2 loading capacity as compared to amine-based solvents.[9] The performance of the ionic liquid in absorbing CO_2 is dramatically improved by incorporating an amine function in the structure of the ionic liquid. The synthesis of these amine-functionalized imidazolium salts requires several synthetic and purification steps and is not cost-competitive with commodity chemicals such as monoethanolamine (MEA).[7]

Another strategy to improve the performance of the ionic liquids is to use their mixtures with amines. Such mixtures retain the desired properties of task-specific ionic liquids (TSILs) for CO_2 capture,[4] but without many of their inherent drawbacks such as high viscosity in their unreacted states and intractable tars due to their corresponding CO_2 adducts. Mixtures of ionic liquids, 1-butyl-3-methylimidazolium acetate ([bmim][acetate]), in an aqueous solution of MDEA and MEA were studied for CO_2 absorption in a gaseous stream.[8] The published literature regarding CO_2 absorption in ionic liquids blended with tertiary amines such as MDEA are very limited; hence, the interaction among ionic liquids, MDEA, and water is still unknown. The main objective of this study is to measure experimentally the CO_2 initial absorption rate as well as CO_2 solubility in an aqueous mixture of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4])−MDEA at different temperatures, IL concentrations, and CO_2 partial pressures. Such data are very important for the design of absorption columns and the evaluation of such solvents. To the best of our knowledge data on the rate of CO_2 absorption in such mixtures are not reported in the open literature.

Experimental Section

Chemicals. The chemicals used in the investigation were 98.5 % assay MDEA and [bmim][BF_4] (98 %) purchased from Merck as well as commercially available CO_2 ((10, 20, 30, 40, 50, and 99.99) % mixed with N_2) and N_2 (99.999 %) purchased from Mox-Linde. Distilled water was used as the solvent throughout the experiment.

Experimental Setup and Mode of Operation for the Initial Absorption Rate. The experiments were carried out in a 6.96 cm internal diameter double-jacketed stirred cell reactor

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* Corresponding author. E-mail: mk_aroua@um.edu.my. Phone: +603-7967-5206. Fax: +603-7967-5319.

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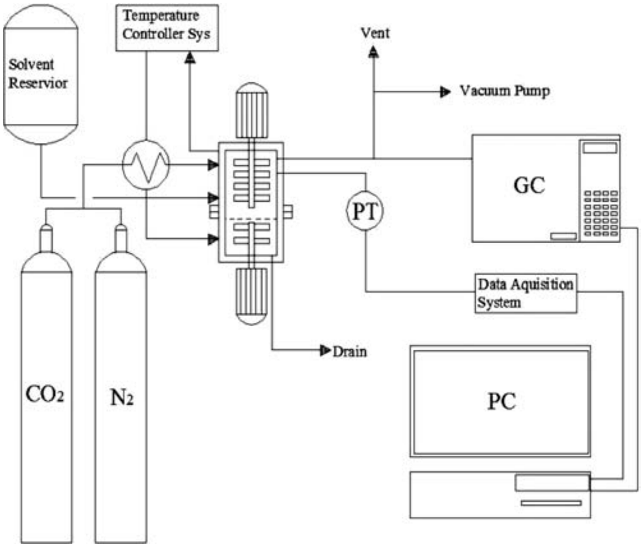

Figure 1. Schematic diagram of the experimental setup for the kinetics study.

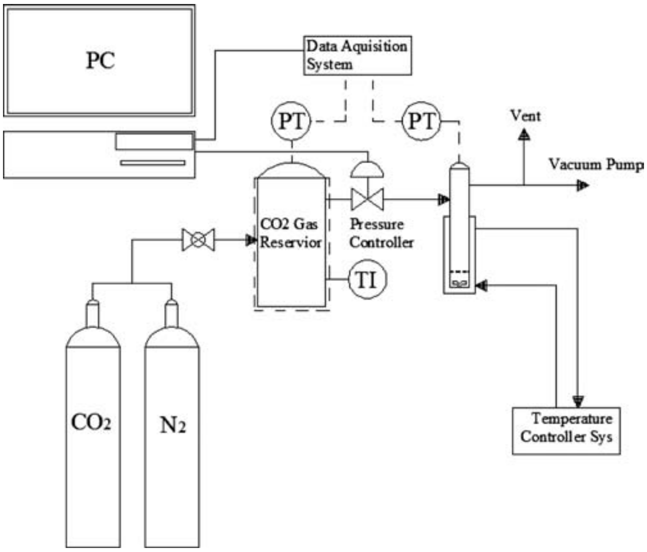

Figure 2. Schematic diagram of the experimental setup for the solubility study.

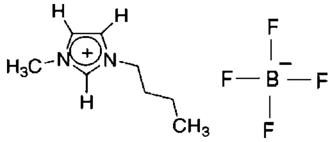

Figure 3. Molecular structure of 1-butyl-3-methylimidazolium tetrafluoroborate.

with a total volume of 850 cm^3 (Figure 1) constructed from stainless steel. The reacting gas and liquid were stirred separately using individual stirrers controlled by variable-speed electromotors. The stirrers were rotated in opposite directions to decrease rippling on the gas−liquid interface, and the stirrers can be adjusted electronically to the desired speed, with an accuracy of ± 1 rpm. Four baffles inside the reactor and specially designed impeller blades were used to prevent rippling of the liquid surface and to prevent vortex formation during stirring, thus ensuring a good mixing in the liquid phase and a flat horizontal gas−liquid interface. Water is circulated through a jacket to provide isothermal conditions. The liquid stirrer speed was maintained at 100 rpm during all experiments, while that of the gas was set at about 1200 rpm. The temperature in the reactor was measured with a J-type thermocouple and was controlled by an RC20 LAUDA water circulator. Two pressure transducers with a data acquisition system were used to record the total pressure in the reactor at 0.1 s time intervals. The reactor was operated batchwise throughout the experiments. At the beginning of every experimental run, a sufficient volume of liquid solution was prepared. This liquid was stored in the dark in sealed containers.

At the start of each experimental run, the reactor was purged with nitrogen gas, and then the liquid was fed into the reactor. Then the reactor was evacuated using a vacuum pump, so that the liquid existed under its own vapor pressure and was allowed to reach the desired temperature. In the next step CO_2 with a known partial pressure was sent to the reactor through a coil immersed in a water bath set at the same temperature as the liquid. Then the stirrers were started, and the pressure drop was recorded as a function of the absorption time. The gas and liquid temperatures and pressure inside the reactor were recorded continuously.

Experimental Setup and Mode of Operation for the Solubility Study. The experimental setup used for the measurement of the CO_2 solubility is shown in Figure 2. The setup included a jacketed stainless steel equilibrium cell equipped with a temperature controller and a pressure transducer with a data acquisition system. The preparation and loading of the gas and the liquid into the cell followed the same procedure as the absorption rate measurement. At the start of every experimental run, the stirrer was switched on and a gas was fed from the gas supply vessel to the cell through a pressure controller valve (PCV). This operation was repeated several times to reach equilibrium conditions when the pressure in the gas reservoir remained constant at a specific CO_2 partial pressure. Since the pressure in the cell was controlled at a specific value using the PCV, the pressure drop in the gas supply vessel was recorded during all steps to calculate the CO_2 solubility.

Results and Discussion

The BASF Corp. has commercialized activated MDEA solvents with up to 0.8 mol·L^{-1} piperazine in MDEA, (1.5 to 4.5) mol·L^{-1}.[11] The MDEA concentration in this work was kept constant at 4 mol·L^{-1}, a value near the typical concentration in industrial solvents. The ionic liquid [bmim][BF$_4$] (Figure 3) was selected, and its effect on the initial CO_2 absorption rate was evaluated. The selection was based on the miscibility in water and good potential of imidazolium-based ionic liquids to absorb CO_2.[5]

Initial CO_2 Absorption Rate. Initial absorption rates are determined from the slope of the pressure vs time curves covering a pressure range down to 10 % from the initial pressure of CO_2. In all experiments this portion of the pressure profile curve was linear. Measurements were carried out at four temperatures, (303, 313, 323, and 343) K, for seven [bmim][BF$_4$] concentrations under constant MDEA concentration of 4 kmol·m^{-3}. Using the ideal gas law, the following equation has been derived to compute the initial CO_2 absorption rate:

$$-r_{CO_2} = -\frac{dn_{CO_2,G}}{dt\cdot A} = -\frac{V_G}{R\cdot T\cdot A}\frac{dP_G}{dt} \qquad (1)$$

where A is the interfacial surface, m^2, R is the gas constant, 8.3143 kJ·K^{-1}·kmol^{-1}, T is the absolute temperature, and V_G

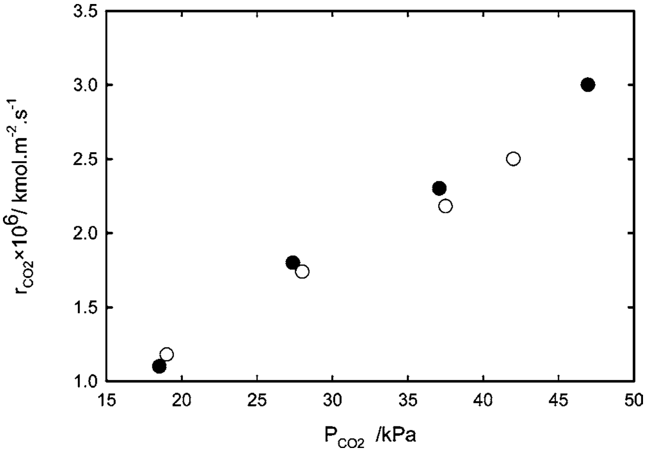

Figure 4. CO_2 absorption rate in 4.0 mol·L^{-1} aqueous MDEA at 323 K: ○, Benamor et al.;[13] ●, this work.

is the volume of gas. The gas phase was assumed ideal, and the concentration of CO_2 in the bulk liquid was assumed negligible compared to its concentration in the gas phase. P_G was obtained from the measured pressures, and all rate data were collected under reaction control conditions.

To evaluate the reliability of the data, the obtained results were compared with data from the literature. As shown in Figure 4, good concordance is observed. All experiments were repeated at least three times, and the average values are reported. To know how widely these values were dispersed from the average value, the repeatability standard deviation was calculated, and the values are given in Table 1.

Using mixtures of ionic liquids and organic amines is initially a new approach to design a solvent having the desired properties of TSILs for CO_2 capture, but without many of their inherent drawbacks,[4] as well as decreased energy required to process CO_2.[4]

As shown in Table 1 and Figure 5, the effect of the concentration of the ionic liquid on the CO_2 absorption rate is different at low temperature as compared to high temperature. For example, in the case of the gas mixture containing 30 % CO_2 (Figure 5), the presence of an ionic liquid in solution increased the CO_2 absorption rate to 2 mol·L^{-1} [bmim][BF$_4$] at 303 K. However, at 333 K, the CO_2 absorption rate increased first, and then a decrease was observed at [bmim][BF$_4$] concentrations above 1.5 mol·L^{-1}. The decrease in the CO_2 absorption rate at a high concentration of ionic liquid and a high temperature can be attributed to the physical nature of CO_2 absorption in ionic liquids as well as to a decrease of the number of water molecules as the concentration of the ionic liquid is increased. It is well established that water molecules are important species for CO_2 absorption in MDEA, since tertiary amines such as MDEA cannot react directly with CO_2. MDEA is known to be initially associated with H_2O molecules and thus weakens the H−O bond.[13]

Solubility. Since the experiments were carried out batchwise, the partial pressure of CO_2 was the equilibrium partial pressure at that loading that was directly calculated from the total equilibrium pressure in the reactor corrected for the solution vapor pressure. The total amount of absorbed CO_2 in the solution was calculated from the initial and final pressures in the gas supply vessel, according to the following equations:

$$n_{CO_2} = \frac{V_G \cdot \Delta P_G}{R \cdot T_G} \qquad (2)$$

$$m_{CO_2} = \frac{1}{m_L}\left(n_{CO_2} - \frac{V_R \cdot P_R}{R \cdot T_R}\right) \qquad (3)$$

where m_{CO_2} is the gas loading in the specific mass of the solvent at a particular respective CO_2 partial pressure, m_L is the mass of the solvent in the equilibrium cell, T_G is the absolute temperature of gas in the gas supply vessel, and V_R, P_R, and T_R are the volume, pressure, and temperature of the gas in the equilibrium cell, respectively. The ideal gas law was assumed applicable since the maximum pressure in the gas supply vessel and the cell never was more than 2 bar.

As shown in Figure 6, good agreement is obtained between the data generated in this work and those found in the open literature.

The CO_2 loading capacities at temperatures ranging from (303 to 333) K and at different concentrations of ILs for two CO_2 partial pressures, (40 and 100) kPa are presented in Table 2, and the effect of the [bmim][BF$_4$] concentration is shown in Figure 7.

It is evident that the solubility of CO_2 decreases with an increase of the [bmim][BF$_4$] concentration. The fact that CO_2 cannot react directly with tertiary amines such as MDEA, and water is the main part of the CO_2 absorption reaction associated with MDEA,[13] can explain the lower capacity of blends when water is replaced by [bmim][BF$_4$] in the solutions. This negative effect of an ionic liquid on the solubility at low concentration is negligible, but the solubility dramatically decreases at higher concentrations of [bmim][BF$_4$]. The reaction of CO_2 with aqueous MDEA is a base-catalyzed hydration of CO_2 according to the reaction[13]

$$CO_2 + MMEA + H_2O \overset{K}{\leftrightarrow} MDEA^+ + HCO_3^- \qquad (4)$$

The CO_2 solubility data in MDEA + [bmim][BF$_4$] solvents at different CO_2 partial pressures are presented in Table 3. As expected, the solubility for a given MDEA + [bmim][BF$_4$] concentration increased with increasing CO_2 partial pressure.

Conclusion

In the present study the initial absorption rate and solubility of CO_2 in the mixture of 4 mol·L^{-1} MDEA + [bmim][BF$_4$] was investigated. The experimental data show that the CO_2 absorption rate can be enhanced by adding a limited amount of [bmim][BF$_4$] in aqueous MDEA in the studied range of temperature. Furthermore, using the high concentration of ionic liquid caused a reduction in the CO_2 absorption rate in the studied mixtures.

The solubility of CO_2 in aqueous solutions of 2 mol·L^{-1} [bmim][BF$_4$] + 4 mol·L^{-1} MDEA was measured for various CO_2 partial pressure from (10 to 50) kPa. Furthermore, the effect of [bmim][BF$_4$] on the CO_2 solubility in aqueous solutions of MDEA + ILs was evaluated for two CO_2 partial pressures, (40 and 100) kPa. According to the solubility results, the CO_2 loading decreased with increasing [bmim][BF$_4$] concentration in the mixture due to a lack of water at high concentrations of [bmim][BF$_4$]. The same fact can justify the decreasing CO_2 absorption rate in the mixture at high concentrations of ILs.

Tuning of the IL concentration in aqueous MDEA + [bmim][BF$_4$] enables these combinations to be an attractive option for CO_2 capture in absorption systems. However, the

Table 1. Initial CO_2 Absorption Rate in an Aqueous Mixture of [bmim][BF_4] (1) + MDEA (2) with the Repeatability Standard Deviation (S_T) ($C_2 = 4$ kmol·m^{-3})

T / K	P_{CO_2} / kPa	C_1 / kmol·m^{-3}	$r_{CO_2} \times 10^6$ / kmol·m^{-2}·s^{-1}	$S_T \times 10^6$ / kmol·m^{-2}·s^{-1}	T / K	P_{CO_2} / kPa	C_1 / kmol·m^{-3}	$r_{CO_2} \times 10^6$ / kmol·m^{-2}·s^{-1}	$S_T \times 10^6$ / kmol·m^{-2}·s^{-1}
303	9.6	0.00	0.51	0.01	303	39.0	0.00	1.58	0.00
	9.9	0.21	0.60	0.03		38.9	0.20	1.74	0.04
	9.6	0.52	0.61	0.01		38.8	0.51	1.67	0.03
	9.6	0.98	0.61	0.01		38.8	0.99	1.84	0.02
	9.5	1.51	0.58	0.01		38.7	1.50	1.86	0.06
	9.5	2.01	0.61	0.01		38.5	2.01	2.00	0.02
313	9.2	0.00	0.68	0.03	313	38.7	0.00	2.01	0.03
	9.7	0.20	0.62	0.05		38.5	0.21	1.92	0.03
	9.7	0.51	0.61	0.03		38.4	0.50	2.00	0.04
	9.6	0.99	0.68	0.04		38.8	1.01	2.23	0.03
	9.4	1.50	0.60	0.02		38.8	1.50	2.08	0.04
	9.5	2.02	0.81	0.02		38.7	2.01	2.38	0.05
323	9.6	0.00	0.75	0.01	323	38.5	0.00	2.18	0.02
	9.9	0.20	0.63	0.04		38.8	0.20	2.13	0.06
	9.7	0.50	0.64	0.03		38.7	0.51	2.25	0.03
	9.6	1.01	0.74	0.02		38.7	1.00	2.52	0.05
	9.6	1.52	0.72	0.01		38.8	1.51	2.45	0.05
	9.8	2.01	0.85	0.01		38.4	2.02	2.40	0.06
333	9.7	0.00	0.85	0.00	333	38.6	0.00	2.25	0.08
	9.6	0.20	0.77	0.03		38.5	0.20	2.30	0.02
	9.7	0.51	0.76	0.02		38.7	0.50	2.40	0.05
	9.6	0.98	0.68	0.03		38.5	0.99	2.70	0.03
	9.5	1.49	0.93	0.08		38.4	1.51	2.74	0.06
	9.8	2.00	0.92	0.05		38.6	2.01	2.68	0.10
303	18.6	0.00	0.84	0.01	303	48.5	0.00	1.83	0.01
	18.4	0.21	0.93	0.01		48.5	0.20	1.93	0.03
	18.3	0.52	0.94	0.02		48.8	0.50	2.00	0.02
	18.6	0.98	1.00	0.02		48.7	1.01	2.11	0.05
	17.9	1.51	0.88	0.02		48.9	1.51	2.44	0.03
	18.4	2.01	0.99	0.03		48.6	1.99	2.35	0.03
313	18.4	0.00	1.10	0.02	313	48.4	0.00	2.33	0.02
	18.1	0.20	1.02	0.02		48.5	0.20	2.21	0.01
	18.3	0.51	1.00	0.02		48.3	0.50	2.20	0.01
	18.3	0.99	1.13	0.02		48.7	1.00	2.49	0.02
	18.5	1.50	1.03	0.02		48.2	1.52	2.71	0.02
	18.2	2.02	1.21	0.02		48.4	2.01	2.68	0.01
323	18.5	0.00	1.18	0.03	323	48.1	0.00	2.50	0.06
	18.6	0.20	1.04	0.01		48.5	0.21	2.37	0.02
	18.6	0.50	1.15	0.05		48.4	0.50	2.52	0.04
	18.5	1.01	1.16	0.00		48.5	1.00	2.76	0.05
	18. 3	1.52	1.28	0.01		48.3	1.52	2.80	0.06
	18.6	2.01	1.19	0.07		48.6	2.00	2.81	0.08
333	18.7	0.00	1.33	0.07	333	48.5	0.00	2.53	0.05
	18.3	0.20	1.40	0.08		48.8	0.20	2.49	0.06
	18.4	0.51	1.46	0.09		48.5	0.50	2.82	0.03
	18.5	0.98	1.28	0.10		48.6	1.01	3.04	0.01
	18.9	1.49	1.62	0.03		48.5	1.50	3.20	0.17
	18.6	2.00	1.51	0.08		48.4	2.02	3.11	0.07
303	28.9	0.00	1.19	0.01					
	28.8	0.20	1.40	0.02					
	28.3	0.50	1.47	0.02					
	28.7	0.99	1.58	0.01					
	28.7	1.50	1.71	0.01					
	28.6	2.00	1.75	0.03					
313	28.6	0.00	1.45	0.01					
	28.5	0.20	1.56	0.04					
	28.5	0.50	1.60	0.00					
	28.9	0.99	1.74	0.01					
	28.3	1.51	1.86	0.03					
	28.5	2.02	1.91	0.02					
323	28.8	0.00	1.74	0.04					
	28.3	0.20	1.68	0.04					
	28.7	0.51	1.78	0.03					
	28.8	1.01	1.96	0.04					
	28.4	1.51	1.96	0.03					
	28.5	2.00	1.91	0.03					
333	28.4	0.00	1.91	0.10					
	28.9	0.21	1.98	0.11					
	28.5	0.52	2.00	0.10					
	28.8	1.00	2.10	0.09					
	28.7	1.50	2.25	0.04					
	28.7	2.01	2.00	0.06					

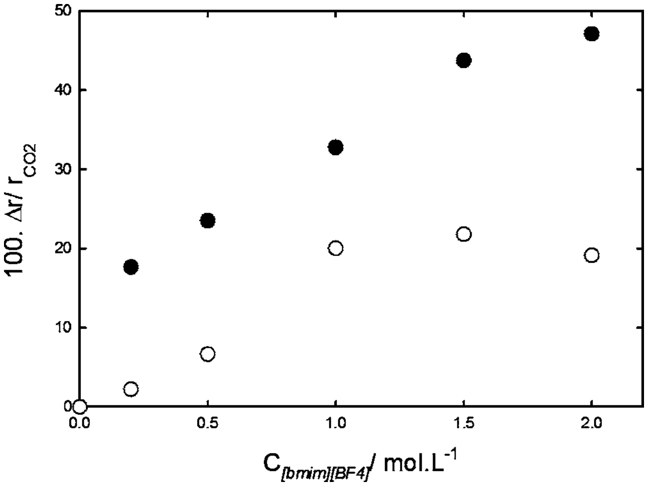

Figure 5. CO_2 absorption rate enhancement percentage as a function of the [bmim][BF_4] concentration for $P_{CO_2} = 30$ kPa: ●, 303 K; ○, 333 K.

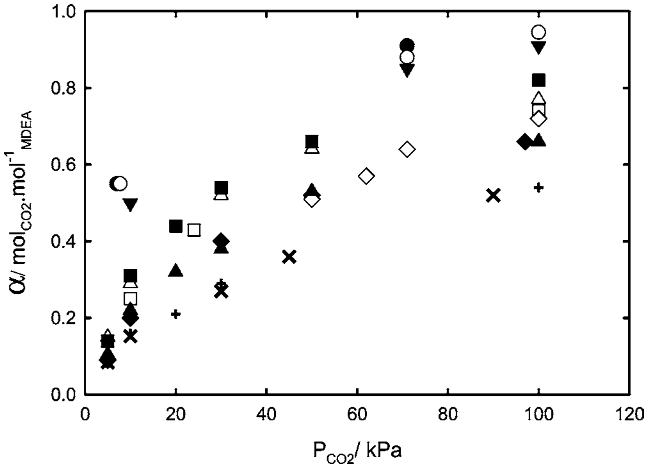

Figure 6. Solubility of CO_2 in 4 mol·L^{-1} MDEA solution: ○, Jou et al. (298.15 K);[16] ●, Chunxi et al. (298.15 K);[17] ▼, this work (298.15 K); Δ, Haji-Sulaiman et al. (303 K);[15] ■, this work (303 K); □, Jou et al. (313 K);[16] ◆, Haji-Sulaiman et al. (313 K);[15] ◇, Ermatchkov et al. (313 K);[17] ▲, this work (313 K); ×, Haji-Sulaiman et al. (323 K);[15] +, this work (323 K).

Table 2. Solubility of CO_2 in 4 mol·L^{-1} MDEA (1) + [bmim][BF_4] (2)

		m_{CO_2}			
P_{CO_2}	C_2	mol·kg^{-1}			
kPa	mol·kg^{-1}	$T = 30$ °C	$T = 40$ °C	$T = 50$ °C	$T = 60$ °C
40	0.0	2.28 ± 0.04	1.50 ± 0.08	1.16 ± 0.05	0.42 ± 0.04
	0.5	2.10 ± 0.07	1.55 ± 0.06	0.94 ± 0.09	0.37 ± 0.07
	1.0	1.77 ± 0.06	1.20 ± 0.07	0.69 ± 0.07	0.27 ± 0.05
	1.5	1.44 ± 0.09	0.86 ± 0.05	0.47 ± 0.06	0.24 ± 0.01
	2.0	1.15 ± 0.06	0.60 ± 0.05	0.38 ± 0.06	0.19 ± 0.04
100	0.0	3.27 ± 0.01	2.61 ± 0.05	2.17 ± 0.03	1.33 ± 0.04
	0.1	3.20 ± 0.10	2.85 ± 0.04	1.98 ± 0.02	1.17 ± 0.06
	0.2	3.23 ± 0.08	2.72 ± 0.06	1.78 ± 0.07	1.34 ± 0.05
	0.5	3.09 ± 0.04	2.60 ± 0.05	1.82 ± 0.05	1.98 ± 0.03
	1.0	2.88 ± 0.08	2.33 ± 0.04	1.49 ± 0.08	0.91 ± 0.06
	1.5	2.48 ± 0.08	1.78 ± 0.03	1.30 ± 0.05	0.69 ± 0.01
	2.0	1.98 ± 0.05	1.26 ± 0.02	1.00 ± 0.03	0.60 ± 0.03

mechanism of CO_2 absorption into aqueous MDEA + ILs solutions needs to be further investigated.

Acknowledgment

This work was carried out at the University of Malaya Centre of Ionic Liquid (UMCiL).

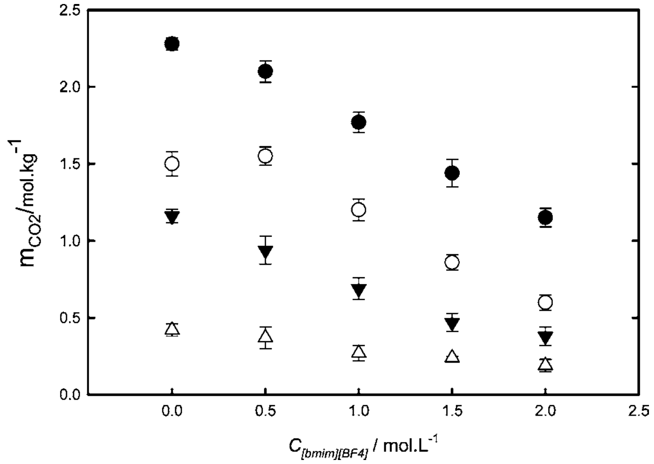

Figure 7. CO_2 loading as a function of the [bmim][BF_4] concentration in 4 mol·L^{-1} aqueous MDEA at $P_{CO_2} = 40$ kPa and various temperatures: ●, $T = 303$ K; ○, $T = 313$ K; ▼, $T = 323$ K; △, $T = 333$ K.

Table 3. Solubility of CO_2 in 4 mol·L^{-1} MDEA + 2 mol·L^{-1} [bmim][BF_4]

	m_{CO_2}			
P_{CO_2}	mol·kg^{-1}			
kPa	$T = 30$ °C	$T = 40$ °C	$T = 50$ °C	$T = 60$ °C
12	0.45 ± 0.01	0.25 ± 0.02	0.16 ± 0.02	0.08 ± 0.02
23	1.01 ± 0.01	0.45 ± 0.01	0.22 ± 0.03	0.11 ± 0.03
36	1.10 ± 0.02	0.57 ± 0.02	0.35 ± 0.05	0.17 ± 0.04
51	1.35 ± 0.02	0.73 ± 0.03	0.43 ± 0.02	0.22 ± 0.01
63	1.44 ± 0.03	0.82 ± 0.02	0.51 ± 0.03	0.27 ± 0.01

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