Synthesis, characterization and application of 1-(2-cyanoethyl)-3-(3-methoxypropane)imidazolium bromide for CO_2 capture

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Abstract. Amine scrubbing is dominating in carbon dioxide (CO_2) capturing technology because of its high affinity towards CO_2. However, the drawbacks of amine solvents are its high corrosivity and volatility. Ionic liquids (ILs) have gained a lot of attention in recent years for CO_2 capturing and have been proposed to be one of the promising alternative to the conventional solvents. The objective of this research is to design a new imidazolium based ether-nitrile functionalized ionic liquid of low viscosity to improve CO_2 capturing. The molecular structure of the ionic liquid were confirmed by ^1H NMR, ^{13}C NMR and FTIR. The thermal properties; glass transition temperature, thermal decomposition temperature, and their physical properties; water content and density were determined. The solubility of CO_2 in the synthesized ionic liquid was measured using pressure drop method. They showed high thermal stability above 200°C and the glass transition temperature was -49.80°C. The CO_2 sorption in the newly synthesized IL was 0.08, 0.12, 0.29, 1.01, 2.30 mol of CO_2/mol of IL at pressures 1, 5, 10, 15 and 20 bar respectively.

1 Introduction

Carbon dioxide has become abundant in the atmosphere due to the extensive burning of fossil fuels. The CO_2 capturing technology is now being the main focus among researchers battling against the dramatic climate change. At present, amine-based solvents are widely used in power plants to capture CO_2 [1]. However, the limitation of amine solvents is that they are highly corrosive and volatile, which is unfriendly to the environment [2]. Besides, they acquire large enthalpy of reaction and amine solvents are also sensitive to degradation in the presence of oxygen [3].

Ionic liquids (ILs) are organic salts which melts below 100ºC and are liquid form at room temperature [4]. In light of these factors, ILs have been studied intensively as a potential replacement for amine solvents. This is due to the distinctive characteristics of ILs, i.e. low volatility, high chemical and thermal stability. Furthermore, the added characteristic of ILs is the ability of designing the IL according to the specified task of application.

Imidazolium-based ILs are mostly used in CO_2 solubility due to the presence of acidic hydrogen in its ring structure. CO_2 can act as both Lewis acid and Lewis base. The CO_2 solvation is initiated by some carboxylation reaction at the C2 position of the imidazolium ring [5]. Besides, the ether functionality helps in CO_2 capture whereby the lone pair of electrons present on the oxygen atom takes part in nucleophilic attack with the carbon atom on CO_2 [4]. In a recent article, ILs with ether functionality has the ability to decrease the viscosity of ILs whereby the alkoxy chain is related to the high rotational flexibility and increases the total free volume [6, 7]. Anions play a vital role in CO_2 dissolution [8]. The common anions of interest are bromide [Br^-], tetrafluoroborate [BF_4^-], bis(trifluoromethylsulfonyl)imide [Tf_2N^-], hexafluoroposphate [PF_6^-] and methide. Carbon dioxide solubility is increased as the quantity of fluoroalkyl groups present in anions increased [9].

In the present research, ether-nitrile functionalized imidazolium-based 1-(2-cyanoethyl)-3-(3-methoxypropane)imidazolium bromide, [MOP-imC_2CN][Br] was synthesized, characterized and tested for the possible application on CO_2 capturing.

2 Methodology

2.1 Materials

Chemicals such as imidazole and 1-bromo-3-methoxypropane and solvents, i.e. methanol and acetonitrile, were purchased from Merck, Malaysia. Acrylonitrile was of Sigma Aldrich, Malaysia. All chemicals were used without any further purification.

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2.2 Synthesis

2.2.1 Synthesis of 1-(2-cyanoethyl)imidazole

The starting material; 1-(2-cyanoethyl)imidazole was synthesized by reacting imidazole with acrylonitrile and methanol as a solvent [10]. The reaction conditions were 50-55ºC, under reflux and N_2 atmosphere for 10 h and cooled to room temperature. The impurities were removed by heating at 70ºC under vacuum.

2.2.2 Synthesis of 1-(2-cyanoethyl)-3-(3-methoxypropane] imidazolium bromide, [MOP-imC_2CN][Br]

[MOP-imC_2CN][Br] was prepared by the reaction of 1-(2-cyanoethyl)imidazole with 1-bromo-3-methoxy propane at 70-80º, under reflux and N_2 atmosphere for 48 h. Then, the product was cooled to room temperature resulting [MOP-imC_2CN][Br].

2.2.3 Characterization of ILs

The synthesized IL was characterized using ^{1}H NMR, ^{13}C NMR (Bruker Avance 500 MHz) and FTIR (Perkin Elmer Spectrum One). Water content in the ionic liquid was measured using Karl Fischer titrator model Mettler Toledo DL39. Density was measured using density meter (Anton-Paar, DMA 5000 M). The thermal properties and decomposition temperature (T_d) were measured using thermogravimetric analysis (TGA) and glass transition temperature (T_g) was measured with differential scanning calorimetry (DSC) (Mettler Toledo model DSC 1).

2.2.4 CO_2 sorption study

The possible application of the IL for CO_2 capture was investigated. A custom-made instrument was used for the CO_2 sorption studies (**Fig. 1**).

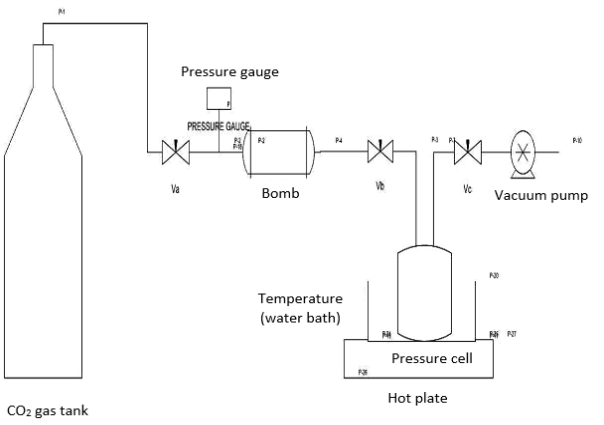

Fig. 1. Schematic diagram for CO_2 gas sorption cell

The measurement technique used was the pressure drop method. Using this method, temperature was held constant and the pressure difference was recorded during gas sorption into the sample. The initial pressure was set at a range of 1 bar to 20 bar. The amount of gas sorbed was calculated from the initial measurement of temperature, volume and pressure and the final measurement of the variables at equilibrium. The calculation was done by converting all three variables into moles of gas using Peng-Robinson equation of state [11].

The mole of CO_2 captured was calculated using equation (1).

$$n = \frac{P_{\text{ini}} \cdot V_{\text{tot}}}{Z_{\text{ini}} \cdot R \cdot T_{\text{ini}}} - \frac{P_{eq}(V_{\text{tot}} - V_{\text{sample}})}{Z_{eq} \cdot R \cdot T_{eq}} \qquad (1)$$

where n = mol of CO_2 captured, P_{ini} = initial pressure obtained in the absence of sample after expansion of the gas sample from the bomb into the whole system, V_{tot} = total volume of system, Z_{ini} = compressibility factor ($P_{ini} \times T_{ini}$), Z_{eq} = compressibility factor ($P_{eq} \times T_{eq}$), P_{eq} = pressure at equilibrium, V_{sample} = volume of sample, R is the ideal gas constant, T_{ini} = initial temperature and T_{eq} = temperature at equilibrium. Compressibility factor for CO_2 modifies the ideal gas to account for real gas behaviour [11].

3 Results and discussion

3.1 NMR analysis

The ^{1}H-NMR data for the synthesized IL is as shown in **Fig. 2** and ^{13}C-NMR data shown in **Fig. 3** respectively. The solvent used during NMR analysis was deuterated acetonitrile.

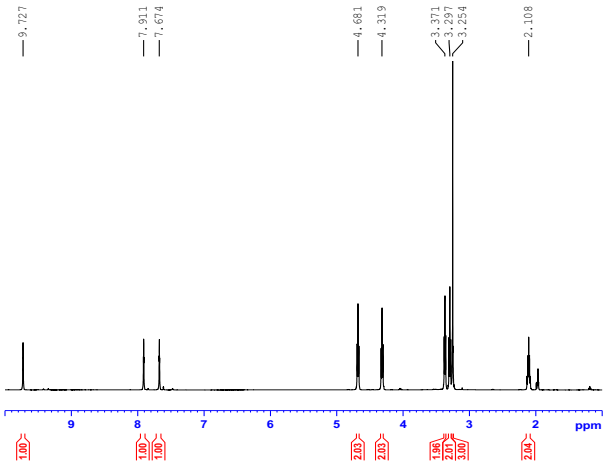

Fig. 2. ^{1}H-NMR spectra of [MOP-imC_2CN][Br]

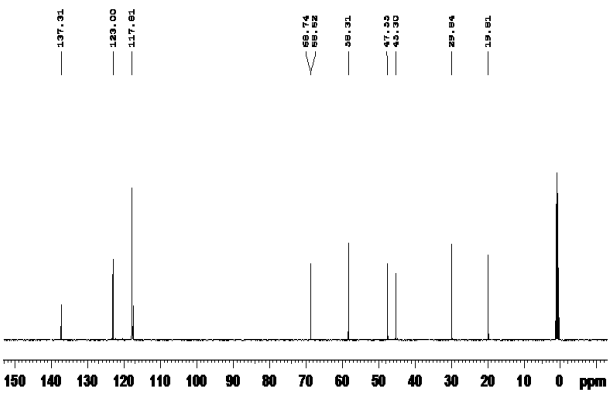

Fig. 3. ^{13}C-NMR spectra of [MOP-imC$_2$CN][Br]

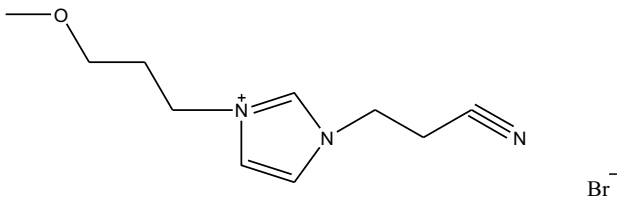

Fig. 4. Structure of [MOP-imC$_2$CN][Br]

^{1}H-NMR (500MHz, CD_3CN): δ (ppm) 9.73 (s, 1H, NCHN), 7.91 (d, 1H, CHN), 7.67 (d, 1H, CHN), 4.68 (t, 2H, CH_2CH_2N), 4.31 (t, 2H, CH_2CH_2N), 3.32 (t, 2H, CH_2CH_2CN), 3.30 (t, 2H, CH_3OCH_2), 3.25 (s, 3H, CH_3O), 2.11 (m, 2H, $CH_2CH_2CH_2$); ^{13}C-NMR (125.77MHz, CD_3CN): δ (ppm) 137.31, 123.00, 117.81, 68.74, 58.31, 47.55, 45.30, 29.84, 19.81.

Spectroscopic data for this ionic liquid were consistent with the literature data [12].

3.2 FTIR analysis

The structure of [MOP-imC$_2$CN][Br] was analysed using Fourier transform infrared (FTIR) and the FTIR spectra obtained is shown in **Fig. 5**. The peaks of wavenumbers 660, 750 and 825 cm^{-1} are the C-H stretching. A broad peak at about 3400 cm^{-1} is the O-H stretch which could be due to the presence of water. Peak at wavenumber 2250 cm^{-1} is due to C≡N stretching. Wave numbers 3050-3100 cm^{-1} and 1400-1600 cm^{-1} represents =C-H stretch and C=C of the aromatic heterocyclic ring respectively. The ether functionality (C-O-C) shows a strong stretching at about wavenumber 1160 cm^{-1}. Based on the FTIR analysis, it was observed that the IL synthesized is [MOP-imC$_2$CN][Br].

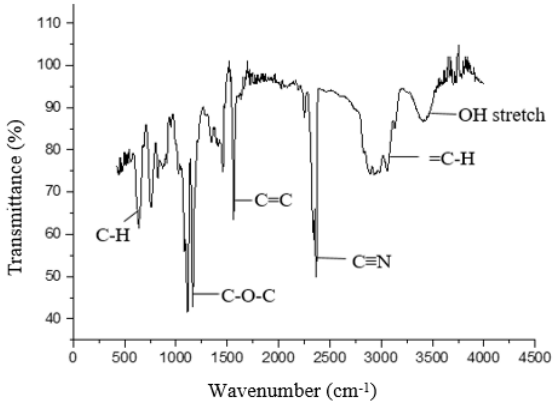

Fig. 5. FTIR spectra of [MOP-imC$_2$CN][Br]

3.3 Physical properties of [MOP-imC$_2$CN][Br]

The physical properties of [MOP-imC$_2$CN][Br] such as the water content, physical appearance and colour at room temperature are shown in **Table 1** below.

Table 1. Physical properties of [MOP-imC$_2$CN][Br]

IL	Water content (%)	Colour	Form
[MOP-imC$_2$CN][Br]	0.04	Yellowish	Liquid

3.3.1 Density of [MOP-imC$_2$CN][Br]

The density of [MOP-imC$_2$CN][Br] at different temperatures is shown in **Fig. 6** below. The plot shows that the density of the synthesized IL decreased linearly with increasing temperature. As shown in Fig. 4, the density of the IL is below 1.36 g/cm^3 at 293.15 K. Generally, ILs are much denser as compared to water [13].

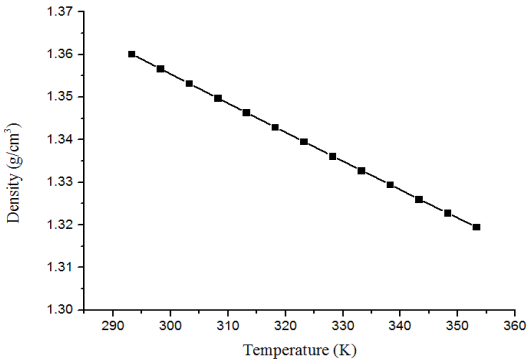

Fig. 6. Density of [MOP-imC$_2$CN][Br] as a function of temperature (K)

The density data could be correlated with equation (2).

$$\rho = A + BT \quad (2)$$

where ρ represents the density of [MOP-imC$_2$CN][Br] in g/cm^3, T is the temperature in Kelvin (K) whereas A and B are the model parameters.

Fitting results are shown in Fig. 4 and the related model parameters are listed in **Table 2** below.

Table 2. Fitting result of the experimental density of [MOP-imC$_2$CN][Br]

Parameters	[MOP-imC$_2$CN][Br]
A	1.5586
$B \times 10^4$	-6.774
R^2	0.9999

3.4 Derived thermodynamic property

3.4.1 Thermal expansion coefficient

The thermal expansion coefficient was calculated for the synthesized IL using equation 3 below since the temperature-density relationship was linear.

$$\alpha_P = -\left(\frac{1}{\rho}\right)\left(\frac{\partial \rho}{\partial T}\right)_P = -(B)/(A+BT) \quad (3)$$

where α_P represents the thermal expansion coefficient in K^{-1}, ρ is the density, A and B are the fitting parameters of equation (2).

The calculated thermal expansion coefficient is presented in **Table 3**. The thermal expansion coefficient of [MOP-imC$_2$CN][Br] obtained in the present work do not change significantly in the temperature range from 293.15 to 353.15 K. Besides, dual functionalized IL has low thermal expansion coefficient [10].

Table 3. Density and thermal expansion coefficients, α_p for [MOP-imC$_2$CN][Br]

Temperature (K)	Density (g/cm^3)	$\alpha_p \times 10^{-4}$ (K^{-1})
293.15	1.360	4.98
298.15	1.357	4.99
303.15	1.353	5.01
308.15	1.350	5.02
313.15	1.346	5.03
318.15	1.343	5.04
323.15	1.340	5.06
328.15	1.336	5.07
333.15	1.333	5.08
338.15	1.330	5.10
343.15	1.326	5.11
348.15	1.323	5.12
353.15	1.320	5.13

3.5 Thermal analysis

The IL was heated over a temperature range of 45-600°C at a heating rate of 10°C/min. The synthesized ionic liquid, [MOP-imC$_2$CN][Br], has a good thermal stability whereby the onset thermal decomposition started at 246°C with a weight loss of 7.65% and the decompositions ends around 313°C with a weight loss of 97.39%. The T_g of [MOP-imC$_2$CN][Br] was -49.80°C. The TGA profile of [MOP-imC$_2$CN][Br] is as illustrated in **Fig. 7**.

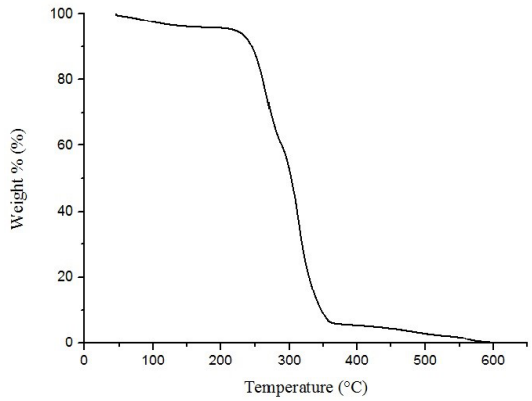

Fig. 7. TGA profile of [MOP-imC$_2$CN][Br]

A high thermal decomposition temperature of ILs gives a long-term stability of the ILs. Mostly ionic liquids are highly viscous, however, they exhibit a high thermal stability. Therefore, this property enables ILs to be used for a specified application under high temperature which significantly reduces their viscosity [10].

3.6 CO_2 solubility

The CO_2 sorption using [MOP-imC_2CN][Br] was investigated at 25°C using the custom-made gas sorption cell under different pressure condition 1, 5, 10, 15 and 20 bar.

Fig. 8 shows that CO_2 solubility in [MOP-imC_2CN][Br] increases with increasing pressure. At equilibrium pressure, P_{eq}= 0.73 bar (at 1 bar), the CO_2 absorbed was 0.08 mol of CO_2/mol of IL whereas at P_{eq}=15.82 bar (at 20 bar) the CO_2 shows an absorption of 2.30 mol of CO_2/mol of IL at 25°C. Ziyada, (2011) has reported that 1-butyl-3-propanenitrile imidazolium dioctylsulfosuccinate [C_2CN Bim][DOSS] has CO_2 absorption capacity about 2.47 mol of CO_2/mol of IL at 20 bar [10].

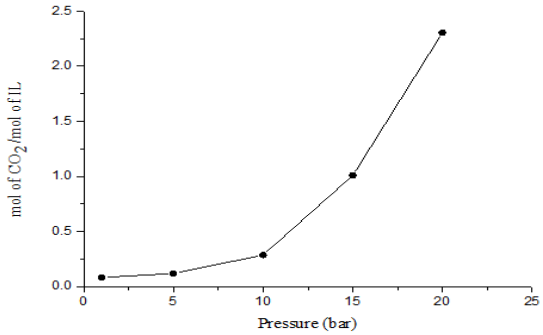

Fig. 8. Effect of pressure on CO_2 solubility in [MOP-imC_2CN][Br] at 25°C

Table 4 below shows the comparison of experimental solubility data for CO_2 in [C_2CN Bim][DOSS] and [MOP-imC_2CN][Br] at 25°C respectively.

Table 4. Experimental solubility data for CO_2 in [C_2CN Bim][DOSS] and [MOP-imC_2CN][Br] at 25°C

Pressure (bar)	CO_2 solubility (mol of CO_2/mol of IL)	
	[C_2CN Bim][DOSS]	[MOP-imC_2CN][Br]
1	0.06	0.08
5	0.30	0.12
10	0.70	0.29
15	1.28	1.01
20	2.47	2.30

At 5, 10, 15 and 20 bar, [C_2CN Bim][DOSS] has a higher CO_2 sorption than [MOP-imC_2CN][Br]. This might be due to the significant role of the DOSS anion present which has a higher affinity towards CO_2 [10]. However, [MOP-imC_2CN][Br] showed equally good CO_2 sorption whereby the imidazolium ring of the cation is tethered to the ether and nitrile functionality. In addition, at 1 bar, [MOP-imC_2CN][Br] has slightly higher CO_2 sorption compared to [C_2CN Bim][DOSS]. The presence of ether functionality enables dipole-quadrupole interactions between the oxygen atoms present and CO_2 [14]. Besides, high CO_2 solubility can also be correlated with the nitrile group that weakens the cation-anion interaction [7].

Literature shows that CO_2 sorption capacity increases with pressure because at high pressure, physical sorption becomes more significant [15]. From the trend shown in Fig. 8, it is expected that when the pressure is increased to >20 bar, the CO_2 sorption will gradually increase.

4 Conclusion

The imidazolium based ether-nitrile functionalized ionic liquid, [MOP-imC_2CN][Br] has been successfully synthesized, characterized and evaluated for CO_2 sorption. The NMR and FTIR confirmed the structure of the synthesized ionic liquid. The technique used for CO_2 sorption was the pressure-drop method. The results obtained from this study implies that [MOP-imC_2CN][Br] has a good sorption of CO_2 which is 0.08 mol of CO_2/mol of IL at P_{eq}= 0.73 bar (at 1 bar), and 2.30 mol of CO_2/mol of IL at P_{eq}=15.82 bar (at 20 bar), at 25°C. Besides, the CO_2 sorption can be further enhanced by anion exchange using selective anions which is CO_2-philic.

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