



Solubility of carbon dioxide in amine-functionalized ionic liquids: Role of the anions

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ABSTRACT

A series of amine-functionalized imidazolium cation-based ionic liquids (ILs) with different anions were synthesized and characterized by ¹H NMR, ¹³C NMR, MS-ESI, FTIR, and EA. The ILs were investigated as potential absorbents for CO₂ capture. The effects of replacing the anion with a corresponding cation were studied. The absorption capacities of the ILs for CO₂ were investigated at 30 °C and 50 °C at ambient pressures (0–1.6 bar). Amine-functionalized ILs displayed high absorption capacities toward CO₂. The CO₂ absorption capacities of the ILs increased with increasing pressure and decreased with increasing temperature. The results showed that the absorption capacities reached 0.45 mol CO₂ per mol of IL at 30 °C. The most probable mechanism underlying the interactions between CO₂ and the ILs was investigated using FTIR and ¹³C NMR, and the results showed that the absorption of CO₂ in the amine-functionalized ILs could be described as a chemical process. The CO₂ absorption results and detailed study indicated the predominance of a 1:2 mechanism, whereby the CO₂ reacted with two IL molecules to form a carbamate group. The CO₂ absorption capacity of the ILs toward each anion followed the trend: BF₄⁻ < DCA⁻ < PF₆⁻ < TfO⁻ < Tf₂N⁻. The as-synthesized ILs were selective, thermally stable, provided long-lived operational stability, could be recycled at 70 °C or under vacuum conditions, and could be used repeatedly.

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1. Introduction

Carbon dioxide (CO₂) is the main greenhouse gas, and its presence in the atmosphere has an impact on global climate change. Clean, environmentally benign, and sustainable industrial processes require that CO₂ emissions be controlled. The capture of CO₂ and subsequent geological storage (CCS) may provide a promising method for reducing greenhouse gas emissions at their sources. The development of economically viable CO₂ capture and separation processes is a key step toward reducing CO₂.

Several CO₂ capture technologies, including chemical absorption, physical absorption, and membrane separation, have been studied [1–14]. Although these amine-based methods are highly efficient with respect to CO₂ capture, several concerns remain, such as the uptake of water by the gas stream, the loss and degradation of the amines, and the economic inefficiencies of the process [15–17]. There is a pressing need for solvents that can absorb CO₂, display non-volatile and non-corrosive properties, and improve the economic efficiency of processes. The drawbacks of amine- and ammonia-based solutions in chemical absorption

processes have pushed researchers to consider ionic liquids (ILs) as promising alternatives.

ILs, also called liquid electrolytes, ionic melts, ionic fluids, liquid salts, or ionic glasses, generally include salts that form stable liquids. These materials consist of large organic bulky asymmetric cations, such as quaternary ammonium, imidazolium, pyridinium, and phosphonium ions, and small symmetric inorganic anions, including Cl⁻, Br⁻, I⁻, [BF₄]⁻, [PF₆]⁻, [Tf₂N]⁻, or organic anions, including [RCO₂]⁻ [18]. Any organic salt that displays liquid properties below 100 °C falls into this category. The physical and chemical properties of the ILs are determined by the nature of the cation and anion [19]. It is possible, therefore, to achieve specific chemical properties by tuning the combinations of cations and anions. The class of imidazolium ILs is used in a wide variety of applications to take advantage of their air and moisture stability, low flammability, thermal stability, negligible vapor pressure, liquid state that is stable over a wide range of temperatures, wide electrochemical windows, high conductivities, high ionic mobilities, easy recyclability, tunable miscibility with water and organic solvents, and good solvent properties toward a variety of organic and inorganic compounds [20–22]. As a result, the class of imidazolium-based ILs has developed into a fascinating area of research. Importantly, imidazolium-based ILs have a strong affinity toward CO₂ [23].

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The remarkable properties of ILs are primarily determined by the natures of the cations, anions, and factors associated with structural modifications introduced into either charged species. Anions appear to play the largest role in solubilizing CO₂, as supported by recent X-ray diffraction studies by Kanakubo et al. [24]. Anions that contain fluoroalkyl groups provide some of the highest CO₂ solubilities, and as the quantity of fluoroalkyl groups increases, the CO₂ solubility also increases [25]. Two properties of the cations can be used to control CO₂ solubility in ILs. First, the alkyl chain length on the cations strongly affects CO₂ stability [25]. Second, the presence of functional groups on the cation can increase CO₂ capture: the presence of ether can increase the cation free volume or the incorporation of CO₂-philic carbonyl functional moieties can stabilize CO₂. Other functional moieties, such as amines, alcohols, carboxylic groups, or nitriles, have also been reported. The ability to fine-tune the properties of cations by combining cations, anions, and functional moieties in ILs permits “solvent design. These promising strategies enable the synthesis and development of task-specific ionic liquids (TSILs) for fulfilling specific functional requirements. The design of ILs containing long alkyl chains or with functional groups that increase the free volume, thereby providing a high affinity for CO₂, provides a promising approach in this direction. Although, some studies have investigated the solubility of CO₂ in both imidazolium ILs and amine-functionalized ILs [26–34], and high CO₂ absorption capacities have been reported (0.9–1.1 mol CO₂ per mol ILs), systematic studies of the anionic effects have been limited. The present work is focused on the synthesis of amine-functionalized ILs containing one of five different anions in an effort to study the effects of the anions, for a given cation, in relation to the CO₂ absorption capacity.

We report the synthesis of a series of ILs [2-aemim][X], based on an imidazolium cation containing additional functional groups, amines, present on the alkyl R group. This new series of RTILs was synthesized and characterized, and their applications to the CO₂ capture were studied.

2. Experimental

2.1. Reagents and materials

2-Bromoethylamine hydrobromide, 1-methylimidazole, acetonitrile, ethanol, sodium tetrafluoroborate (NaBF₄), magnesium sulfate (MgSO₄), potassium hexafluorophosphate (KPF₆), Lithium bis[(trifluoromethyl)sulfonyl] amide Li(Tf₂N), sodium trifluoromethylsulfonate Na(TfO), sodium dicyanamide (Na(DCA)) were supplied from Sigma–Aldrich and were used without further purification.

2.2. Apparatus and procedures

2.2.1. Synthesis of the ionic liquids

A previously reported methodology [26] was used for the synthesis of these ILs. Alkylation of 1-methylimidazole with an alkyl amine halide was followed by halogen (Cl or Br) exchange in the presence of a slight excess (1.1 equiv) of NaBF₄, KPF₆, Li(Tf₂N), Na(TfO), or Na(DCA) in an effort to reduce the amount of halogen remaining.

2.2.1.1. Synthesis of [2-aemim][Br]. A mixture of 1-methylimidazole (8.20 g, 0.10 mol) and 2-bromoethylamine hydrobromide (20.50 g, 0.10 mol) in 50 mL acetonitrile was heated with stirring at 80 °C for 4 h. Upon completion, the solvent was removed by distillation, and the residue was recrystallized with ethanol to obtain the product (71% yield) as a white solid. ¹H NMR (500 MHz), D₂O, 25 °C:

δ = 3.25–3.29 (m, 2H, NH₂–CH₂), 4.12 (s, 3H, CH₃), 4.49 (t, J = 5.9 Hz, 1H, N–CH₂), 4.52 (t, J = 6.1 Hz, 2H, N–CH₂), 7.68 (s, 1H, NCH), 7.75 (s, 1H, NCH), 8.63 (s, 2H, NH₂), 8.99 (s, 1H, N(H)CN); ¹³C NMR (500 MHz, D₂O, 25 °C): δ = 27.42, 36.10, 36.49, 46.45, 122.13, 122.89, 136.18; MS-ESI: m/z (%): 206 (100) [2-aemim]⁺, 80 (100) [Br][–]; FTIR (neat): 3430, 3150, 3096, 2970, 2880, 1638, 1574, 1462, 1173, 1011, 970.3, 835.5, 761.2, 651.2 cm^{–1}; elemental analysis calcd (%) for C₆H₁₂N₃Br (206): C 34.95, H 5.82, N 20.38; found: C 33.63 H 5.21, N 19.2.

2.2.1.2. Synthesis of [2-aemim][BF₄]. [2-aemim][Br] (21.00 g, 0.10 mol) was transferred to an Erlenmeyer flask (250 mL). A 50 mL volume of CH₃CN/H₂O (1:1, v/v) was added, followed by NaBF₄ (12.00 g, 0.11 mol). The mixture was stirred at room temperature for 24 h, then NaOH (4.00 g, 0.10 mol) was added to neutralize the solution. The solvent was evaporated under vacuum. Solvent removal was followed by the addition of methanol (20 mL) and CHCl₃ (2 mL). The precipitated salts were filtered off, and the solvents were evaporated. The obtained yellow liquid was washed successively with chloroform (10 mL × 3) and ether (10 mL × 3). After drying for 12 h under vacuum, the product was obtained as a yellow liquid (72% yield); the water content was 2.53 μg (H₂O) mL^{–1} (RTIL). ¹H NMR (500 MHz), D₂O, 25 °C): δ = 3.25–3.29 (m, 2H, NH₂–CH₂), 4.10 (s, 3H, CH₃), 4.40 (t, J = 5.9 Hz, 1H, N-CH₂), 4.42 (t, J = 6.1 Hz, 2H, N-CH₂), 7.61 (s, 1H, NCH), 7.72 (s, 1H, NCH), 8.60 (s, 2H, NH₂), 8.88 (s, 1H, N(H)CN); ¹³C NMR (500 MHz, D₂O, 25 °C): δ = 27.38, 36.16, 36.51, 46.41, 122.11, 122.79, 135.28; MS-ESI: m/z (%): 206 (100) [2-aemim]⁺, 86 (100) [BF₄][–]; FTIR (neat): 3435, 3145, 3078, 2974, 2880, 1640, 1572, 1469, 1174, 1055, 1010, 972, 835.1, 758 cm^{–1}; elemental analysis calcd (%) for C₆H₁₂N₃BF₄ (212): C 33.96, H 5.66, N 19.8; found: C 33.12, H 5.1, N 19.7.

2.2.1.3. Synthesis of [2-aemim][PF₆]. [2-aemim][Br] (21.00 g, 0.10 mol) was transferred to an Erlenmeyer flask (250 mL). A 50 mL volume of CH₃CN/H₂O (1:1, v/v) was added, followed by KPF₆ (19.00 g, 0.11 mol). The mixture was stirred at room temperature for 24 h, and then NaOH (4.00 g, 0.10 mol) was added to neutralize the solution. The solvent was evaporated under vacuum. After solvent evaporation methanol (20 mL) and CHCl₃ (2 mL) were added. The precipitated salts were filtered off, and the solvents were evaporated. The obtained yellow liquid was washed successively with chloroform (10 mL × 3) and ether (10 mL × 3). After drying for 12 h under vacuum, the product was obtained as a yellow liquid (71% yield); the water content was 1.98 μg (H₂O) mL^{–1} (RTIL); ¹H NMR (500 MHz), D₂O, 25 °C): δ = 3.25–3.29 (m, 2H, NH₂–CH₂), 4.08 (s, 3H, CH₃), 4.42 (t, J = 5.9 Hz, 1H, N–CH₂), 4.50 (t, J = 6.1 Hz, 2H, N–CH₂), 7.61 (s, 1H, NCH), 7.75 (s, 1H, NCH), 8.59 (s, 2H, NH₂), 8.91 (s, 1H, N(H)CN); ¹³C NMR (500 MHz, D₂O, 25 °C): δ = 27.42, 36.10, 36.49, 46.45, 122.13, 122.89, 136.18; MS-ESI: m/z (%): 206 (100) [2-aemim]⁺, 144 (100) [PF₆][–]; FTIR (neat): 3430, 3148, 3101, 2976, 2881, 1641, 1575, 1460, 1170, 1017, 967, 836, 833, 761, 558 cm^{–1}; elemental analysis calcd (%) for C₆H₁₂N₃PF₆ (270): C 26.6, H 4.4, N 15.5; found: C 25.82, H 3.99, N 15.1.

2.2.1.4. Synthesis of [2-aemim][Tf₂N]. [2-aemim][Br] (21.00 g, 0.10 mol) was transferred to an Erlenmeyer flask (250 mL). A 50 mL volume of CH₃CN/H₂O (1:1, v/v) was added, followed by Li(Tf₂N) (30.00 g, 0.11 mol). The mixture was stirred at room temperature for 24 h, and then NaOH (4.00 g, 0.10 mol) was added to neutralize the solution. The solvent was evaporated under vacuum. Solvent evaporation was followed by the addition of methanol (20 mL) and CHCl₃ (2 mL). The precipitated salts were filtered off, and the solvents were evaporated. The obtained yellow liquid was washed successively with chloroform (10 mL × 3) and ether (10 mL × 3). After drying for 12 h under vacuum, the product was obtained as a yellow liquid (69% yield); the water content was 1.92 μg (H₂O) mL^{–1} (RTIL). ¹H NMR (500 MHz),

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