



Carbonation and decarbonation of non-aqueous solutions with different compositions of ethylene glycol and various amidines



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ABSTRACT

A mixture of equivalent amounts of amidine, alcohol, and carbon dioxide forms alkylcarbonate amidinium salts. Here we studied the effect of the composition of solutions consisting of ethylene glycol (EG) as the alcohol and one of various amidines on their ability to absorb and desorb carbon dioxide. Compounds containing single or multiple formamidine groups were synthesized and dissolved in EG. The ability of these solutions to absorb carbon dioxide was studied for various ratios of EG to amidine and at various temperatures. An excess of at least ten equivalents of EG relative to the amidine was required for rapid and complete reaction of the base with carbon dioxide. Excess EG also reduced the viscosity of the solution, and in this way increased the absorption rate. However, the excess EG appeared to have stabilized the formed alkyl carbonate salts via hydrogen bonding, resulting in a relatively low degree of decarbonation of the solution at elevated temperatures. This effect would cause the working capacity to be decreased were this type of material be used for carbon dioxide capture applications. Our results suggest that, in general, the compositions of the alcoholic solutions of superbases need to be optimized to achieve high-efficiency absorption and desorption of carbon dioxide.

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1. Introduction

Carbon dioxide emitted from the combustion of fossil fuels has been considered to cause global warming and ocean acidification (Taub, 2010). To counter these threats, a material that has a large capacity to capture CO₂ and that can be regenerated using little energy has been sought. The most established CO₂-capture technology is based on aqueous amine solutions (Rochelle, 2009); however, the water-based systems have several drawbacks including poor energy efficiency (Yu et al., 2009). Numerous absorbents have been introduced in recent years. Non-aqueous CO₂-capture liquids have recently been suggested as a potential alternative to aqueous amine solutions due to their low heat capacities. Examples of these liquids are anhydrous amines (Im et al., 2011), ionic liquids (Bates et al., 2002; Cadena et al., 2004; Jessop et al., 2005), task-specific ionic liquids (Wang et al., 2010) and superbases (Kim and Park, 2010). A variety of solid-state absorbents or adsorbents have also been introduced in recent decades (Kim and Park, 2010; Gray et al., 2008; Hicks et al., 2008; Yang et al., 2012; Lee et al., 2014).

Among these new materials, the mixtures consisting of superbases (amidines or guanidines) and aliphatic alcohols that can bind CO₂ reversibly to form alkylcarbonate salts have been studied as potential CO₂ absorbents due to their efficient CO₂ absorption at low temperatures as well as the low heat capacity of the non-aqueous solutions. In the mixtures of a superbase and an alcohol, the carbonation transforms the initially non-ionic solutions into polar ionic liquids, which upon heating are transformed back into the non-ionic form (Jessop et al., 2005; Liu et al., 2006). The ion pairs made up of protonated superbase cations and alkylcarbonate anions are stabilized by the strong hydrogen bonding between the cations and anions. Such carbonate salts are stable even at elevated temperatures. Our recent study has shown the stability of the carbonated ionic species in the organic solution to be highly dependent on the composition of hydrogen-bonding components in the solution (Rajamanickam et al., 2015). Such dependence on composition may apply to other organic CO₂ absorbents containing little or no water.

The product of the reaction of the superbase/alcohol mixture with CO₂ is an adduct of the superbase, alcohol, and CO₂ in a 1:1:1 molar ratio (Jessop et al., 2005; Heldebrant et al., 2005). The composition of the absorbent solution, for example, the amidine-to-alcohol molar ratio, may greatly affect the capture performance. While use of alcohols in amounts as small as possible would

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help to increase the gravimetric capture capacity of absorbents (Heldebrant et al., 2008), a sufficient amount of the alcohol component is needed to optimize the absorption rate, equilibrium CO₂ loading and viscosity.

Here we present a systematic study of the carbonation and decarbonation chemistries of mixtures of an alcohol, specifically ethylene glycol (EG), and compounds containing formamidine groups. We synthesized several amidine derivatives containing one to three amidine groups per molecule and mixed them with the EG to produce various solutions. We studied the effect of the EG-to-amidine ratio on the degree of carbonation and decarbonation of the solutions at different temperatures. The best carbonation and decarbonation conditions were sought to achieve the maximum absorption performance and reaction rate while minimizing the difference between the optimal temperatures for absorption and regeneration. We also studied the effect of the chemical structure of the amidines and the composition of their solutions in EG on the viscosity of the resultant solutions to achieve lower solution viscosities that are essential for higher absorption efficiency and reaction rate as well as for their applicability for CO₂ capture process.

2. Experimental

2.1. Materials and characterization

All reagents, unless otherwise noted, were obtained from a commercial supplier (Sigma Aldrich, TCI) and were used without further purification. THF was distilled over sodium benzophenone ketyl in a nitrogen atmosphere. Liquid amines were dried over CaH₂ overnight and distilled under reduced pressure. CO₂ was dried by passing it through a CaSO₄ column for capture experiments. ¹H and ¹³C NMR spectra were recorded on a JEOL-DELTA2 (400 MHz) spectrometer in CDCl₃ (reference 7.26 ppm for ¹H and 77.16 ppm for ¹³C NMR) or DMSO-*d*₆ (reference 2.50 ppm for ¹H and 39.52 ppm for ¹³C NMR). Viscosity was measured using a Brookfield DV-II+ Pro viscometer at the desired temperature with a cone and plate geometry (cone radius 24 mm, 0.8° cone angle). The formulation was taken into the cup of the viscometer and measured using spindle CP-40. The stabilization energy of amidinium alkylcarbonate salts (BBF/EG) resulting from the addition of excess EG was measured using a Thermal Hazard Technology (THT) micro reaction calorimeter (μRC) with μW sensitivity at 40 °C. The BBF/EG carbonate salts with 1 eq. EG was prepared from BBF/EG 2 eq. mixture after full CO₂ absorption for 24 h at 60 °C. Heat energy was produced upon addition of excess EG.

2.2. General procedure for the preparation of amidine derivatives

An amine (1 eq.) and *N,N*-dimethylformamide dimethyl acetal (3 eq.) were refluxed with stirring in THF (30 mL/g amine) under nitrogen for 3 h. The reaction was monitored by ¹H NMR analysis. After completion of the reaction, the solution was cooled to room temperature and the excess solvent was evaporated by using a rotary evaporator. Then, the amidine was subjected to reduced pressure overnight at room temperature. The obtained amidine was used to capture CO₂ without further purification.

2.2.1. *N*'-(4-Methylphenyl)-*N,N*-dimethyl formamidine (mPF)

¹H NMR (400 MHz, DMSO): 7.65 (s, 1H), 6.98 (m, 2H), 6.79 (m, 2H), 2.88–2.96 (d, 6H), 2.22 (s, 3H). ¹³C NMR (DMSO): 153.2, 149.5, 130.2, 129.3, 120.5, 39.1, 20.4. FT-IR (KBr): 3024, 2916, 2806, 1635, 1605, 1510, 1102. Yield: >98%.

2.2.2. *N*'-Benzyl-*N,N*-dimethylformamidine (BF)

Transparent yellow liquid; ¹H NMR (400 MHz, DMSO): 7.49 (s, 1H), 7.15–7.29 (m, 5H), 4.33 (s, 2H), 2.79 (s, 6H). ¹³C NMR (DMSO): 155.7, 142.7, 128.1, 127.4, 126.1, 62.9, 58.6. FT-IR (KBr): 3029, 2921, 1652, 1605, 1510, 1104. Yield (%): >99%.

2.2.3. *N,N*'-(1,4-Phenylenebis(methylene))bis(*N,N*-dimethylformimidamide) (PBMBF)

¹H NMR (400 MHz, DMSO): 7.47 (s, 2H), 7.12 (s, 4H), 4.29 (s, 4H), 2.77 (s, 12H). ¹³C NMR (CDCl₃): 155.9, 140.4, 127.5, 59.4, 37.3. FT-IR (KBr): 3048, 2916, 2816, 1642, 1488, 1092. Yield: >99%.

2.2.4. *N,N*'-(Ethane-1,2-diyl)bis(*N,N*-dimethylformimidamide) (EBF)

¹H NMR (400 MHz, CDCl₃): 7.24 (s, 2H), 3.34 (s, 4H), 2.80 (s, 12H). ¹³C NMR (CDCl₃): 156.1, 58.3, 37.3. FT-IR (KBr): 2914, 2845, 1646, 1110. Yield: >92%.

2.2.5. *N,N*'-(Butane-1,4-diyl)bis(*N,N*-dimethylformimidamide) (BBF)

Transparent yellow liquid; ¹H NMR (400 MHz, CDCl₃): 7.25 (s, 2H), 3.22 (m, 4H), 2.81 (s, 12H), 1.49 (m, 4H). ¹³C NMR (CDCl₃): 154.6, 55.2, 36.9, 30.1. FT-IR (KBr): 2922, 1651, 1106. Yield: >99%.

2.2.6. *N,N,N,N*'-(Nitrilotris(ethane-2,1-diyl))tris(*N,N*-dimethylformamidine) (NETF)

¹H NMR (400 MHz, CDCl₃): 7.33 (s, 3H), 3.30 (t, 6H), 2.81 (s, 18H), 2.62 (t, 6H). ¹³C NMR (CDCl₃): 155.8, 58.0, 54.6, 37.2. FT-IR (KBr): 2916, 2845, 1648, 1109. Yield: >99%.

2.3. General procedure for CO₂ absorption/regeneration

The amidine derivative and EG were degassed overnight prior to use. The CO₂ at atmospheric pressure was bubbled through about 15.0 g of an amidine/EG solution in a customized glass flask under a CO₂ flow of 100 and 10 mL/min for absorption and regeneration, respectively. The flask was immersed in an oil bath pre-heated at the desired temperature. The solution was stirred to produce a homogeneous solution prior to starting the absorption process. The amount of CO₂ absorbed was determined by measuring the difference between the mass of the total glassware without the water condenser before and after CO₂ absorption after cooling the reaction solution to room temperature. The molar CO₂ loading and capacity of the mixtures were also determined by measuring the weight at regular time interval. The mass of CO₂ absorbed was determined to within ±0.1 mg by using an analytical balance.

3. Results and discussion

3.1. Synthesis of amidines

A series of organic compounds containing one to three amidine groups per molecule (Scheme 1). Amidines have been synthesized by several methods using organometallic catalysts (Benati et al., 2006; Garigipati, 1990), acidic catalysts (Weintraub et al., 1968; Schnur, 1979), and other methods (Dräger et al., 2002; Sychała, 1999; Zhu and Lu, 2010; Kumagai et al., 2004). In the present study, condensation of aromatic or aliphatic primary amines with *N,N*-dimethylformamide dimethyl acetal (1:3 eq.) in dry THF gave the amidine derivatives in high yield. The synthetic conditions were modified slightly from the known method according to the chemical structures of the reactant amines (Porcheddu et al., 2009). The transformations of the aromatic amines to the corresponding

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