

Kinetics of carbon dioxide binding by 1,1,3,3-tetramethylguanidine in 1-hexanol



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ABSTRACT

Switchable solvents, also known as the carbon dioxide-binding organic liquids (CO₂BOLs), are novel solvents featuring the ability to switch between polar and non-polar states, opening a wide range of applications, such as combined synthesis and product separation. In addition, these solvents have very suitable properties for carbon dioxide capture, such as low heat capacities, high boiling points, higher physical and chemical absorption capacities and reversible fixation of carbon dioxide. In this study, kinetic analysis of one of these solvent systems, 1,1,3,3-tetramethylguanidine (TMG) in 1-hexanol, was performed so as to enable the design of experiments and absorber models. The reaction mechanism was determined to comply with termolecular reaction mechanism and pseudo-first order behavior was observed in excess TMG and 1-hexanol. The activation energy of the reaction was also reported.

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1. Introduction

There has been a steady increase in carbon dioxide capture and storage (CCS) studies over the past two decades, as a result of the emerging problem of global warming. According to Herzog (2011), all components of CCS industry are available at present; however those are not yet utilized in an integral CCS concept. An indirect reason behind that disintegrity is the cost of operation of the absorption/desorption processes and hence the infeasibility of the scale-up of the capacities (David and Herzog, 2000; Herzog, 2001). Usually, the capture and subsequent separation of carbon dioxide require intense amounts of energy, owing to the reboiler duty of conventional desorption processes (Abu-Zahra et al., 2007a,b). The intense energy requirements of these processes have led researchers to study alternative solvent systems which would capture carbon dioxide at much lower pressures and release it at temperatures below the boiling point of the solvent. Targeting chemical and power industries, capture of carbon dioxide by solvent scrubbing constitutes a major part of carbon capture studies, whereas several alternatives have been proposed for other carbon dioxide separation problems.

Among these efforts, carbon dioxide-binding organic liquids (CO₂BOLs) have gathered considerable attention from the CCS community. CO₂BOLs are liquid solutions comprised of an alcohol as the solvent, and a strong amidine or guanidine base that chemically fixes carbon dioxide. When CO₂ is captured by CO₂BOLs, the reaction product is an amidinium or guanidinium alkylcarbonate, depending on the base. As reported by Heldebrant et al. (2009), this provides an important advantage over conventional aqueous alkanolamine solutions in terms of CO₂-binding enthalpy. Carbamate and bicarbonate salts, which form upon the reaction of aqueous alkanolamine solutions with CO₂, have more hydrogen bonding compared to alkylcarbonate salts (Heldebrant et al., 2009; Peeters et al., 2007). This implies that the regeneration of CO₂BOLs upon CO₂ capture may require less energy compared to aqueous alkanolamine solutions. In fact, there have been preliminary studies on the desorption of CO₂BOLs, which show that the desorption process can be carried out at temperatures as low as 50 °C (Heldebrant et al., 2009, 2010; Jessop et al., 2005; Ozturk, 2011).

CO₂BOLs promise important improvements over the conventional amine-scrubbing agents, such as the widely used aqueous monoethanolamine (MEA) system. Namely, CO₂BOLs have high boiling points and low vapor pressures, good physical and chemical absorption capacities, lower heat capacities (compared to water) and a non-corrosive nature (Heldebrant et al., 2009).

Before they were proposed for carbon dioxide capture, however, these solvents were classified as “reversible ionic liquids” and it was

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shown that their polarity can be switched by the use of carbon dioxide (Heldebrant et al., 2010, 2011; Jessop et al., 2005). It is possible to switch the non-ionic lean solvents into ionic solvents by simply bubbling carbon dioxide through the solution, and revert back to non-ionic state by thermal stripping of carbon dioxide at temperatures well below the boiling point of the solvent (Heldebrant et al., 2010, 2011). These “switchable solvents”, also known as switchable polarity solvents (SPS), therefore brought new possibilities for various chemical applications even before their potential use for carbon dioxide capture.

The versatility and novel features of CO₂BOLs/SPSs allow their utilization for various chemical synthesis/separation processes. In fact, several examples of switchable solvent applications have started to emerge in the literature in the recent years (Cao et al., 2012; Jessop et al., 2012; Zhang et al., 2013). While there have been a limited number of studies incorporating TMG, there are recent efforts for utilizing TMG in gas absorbers (Lail and Coleman, 2011).

Reaction kinetics and mechanisms are essential either to create rate-based carbon dioxide absorber models, or to design experiments/processes for the utilization of switchable solvents. In the light of all the promising features of switchable solvents (or CO₂BOLs), here we attempt to make a comprehensive analysis of the reaction mechanism and kinetics of the reaction between 1,1,3,3-tetramethylguanidine (TMG) and carbon dioxide in 1-hexanol.

As reported by Heldebrant et al. (2009), use of different alkanol components in CO₂BOLs has little effect on the reaction enthalpy. It was also shown that the choice of linear alkanol has a limited contribution to rate constants (up to ±30%) of the CO₂BOLs (Ozturk, 2011; Ozturk et al., 2012). Therefore, we believe the results of this paper can also provide insight for applications with different alcohols.

In the following sections, we first introduce applicable reaction mechanisms briefly. Next, we explain the stopped-flow method and other experimental details used in our analysis. In Section 3, we discuss the results of our analysis and determine reaction rate constants and activation energies. Finally, we conclude with the implications of our findings regarding the TMG/1-hexanol system.

2. Experimental

2.1. Reaction mechanism

Amine solutions are currently highly preferred post-combustion carbon dioxide capturing agents in the industry (Tontiwachwuthikul and Idem, 2013). As a result of their popularity, a number of reaction mechanisms were eventually introduced, and later enhanced, to explain the kinetics of the reaction with carbon dioxide. However, there is no specific mechanism proposed for the reaction of TMG/1-hexanol solution with carbon dioxide. Therefore, a good first step can be to draw an analogy between reactions of amines and TMG with carbon dioxide. Based on this analogy, one can attempt to apply the principles of the relevant reaction mechanism to the novel solvent system at hand, and evaluate the compatibility. At this point, it should be noted that as with many reactions including those pertaining to amines, detailed and rigorous analyses are a must to pinpoint a reaction mechanism (Vaidya and Kenig, 2007). On the other hand, authors believe that the data made available in this study would be open to further analyses, since it is always possible to fit a different reaction mechanism, should a new one be proposed.

There have been several reports in the past suggesting that the ultimate product of the reaction between carbon dioxide and alcoholic solutions of TMG is a guanidinium alkyl carbonate salt (Heldebrant et al., 2005, 2008; Pereira et al., 2008). Similarly, bicarbonate salts form along with carbamates when aqueous solutions of

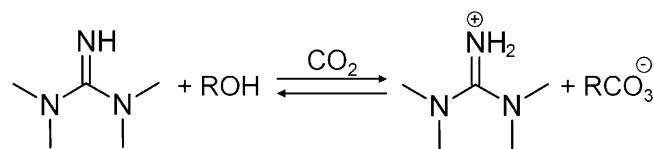


Fig. 1. Proposed overall reaction of TMG/alcohol solution with carbon dioxide (Heldebrant et al., 2008).

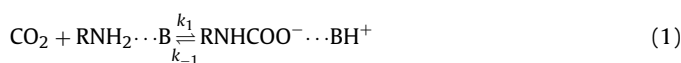
amines react with carbon dioxide, and alkyl carbonates arise when the solvent is an alcohol instead (Barzagli et al., 2013; Donaldson and Nguyen, 1980; Versteeg and van Swaaij, 1988).

Although not classified as an amine, a similar reaction pathway can be anticipated for TMG, considering the presence of an N–H bond (similar to a secondary amine), the same constituents in the reaction except for the amine (a linear alcohol and carbon dioxide), and the same products of the reaction (an alkyl carbonate salt). In fact, Heldebrant et al. (2008) proposed an overall reaction, which can be seen in Fig. 1. Pereira et al. (2008) also made an extensive study on the reaction of TMG and carbon dioxide using rigorous NMR and TGA-FTIR analyses along with quantum mechanical calculations and confirmed this reaction. In their study, they proposed formation of a carbamate, a zwitterionic carbamate and a bicarbonate and experimentally confirmed the presence of the bicarbonate structure in the reaction products, while pointing to an uncertainty for the formation of a carbamate or a zwitterionic carbamate structure. They also note the instability of the carbamates, leading to release of carbon dioxide from the complex; which is known to happen with sterically hindered or tertiary amines. This study is also important in our analysis as it provides a proof that the N–H bond on TMG can be deprotonated. With all these similarities stated, the reaction of TMG/1-hexanol solution with carbon dioxide is worth inspection from an amine kinetics perspective.

Usually, mechanisms are classified according to primary, secondary and tertiary amines. In the case of tertiary amines, Donaldson and Nguyen (1980) proposed a base catalyzed mechanism for the amine-carbon dioxide reactions. Since TMG has one N–H bond, this mechanism may not be suitable for our analysis.

For primary and secondary amines, both zwitterion (Caplow, 1968; Danckwerts, 1979) and termolecular (Crooks and Donnellan, 1989; Da Silva and Svendsen, 2004) reaction mechanisms were shown to describe amine-carbon dioxide reactions satisfactorily (Vaidya and Kenig, 2007, 2010). In the zwitterion mechanism, the overall reaction is assumed to take place in two steps. A zwitterion is produced in the first step, which reacts further in the second step to give the ultimate products of the amine-carbon dioxide reaction. Since the use of zwitterion mechanism is more tedious due to the number of parameters involved, and considering the equivalent applicability of both mechanisms (Vaidya and Kenig, 2010), we opt to use the termolecular reaction mechanism in this study.

According to the termolecular reaction mechanism, a molecule of amine (TMG, in this case) simultaneously reacts with a molecule of carbon dioxide and a molecule of a base to form a loosely-bound encounter complex, as shown in Eq. (1). Here B denotes the base and RNH₂ is the amine. Apart from the amine itself, the dominating base B can be water or a hydroxide ion in aqueous solutions, or in this study an alcohol (Citra, 1999). In the aqueous case, the contribution from hydroxide ion can be neglected, as negligible amounts exist freely in the solution (Laddha and Danckwerts, 1981).



While a fraction of the resulting intermediate breaks up to form carbon dioxide and amine, a smaller fraction reacts further with an additional molecule of base (in this case TMG or 1-hexanol) to

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