



A study of species formation of aqueous tertiary and hindered amines using quantitative ^{13}C NMR spectroscopy

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ABSTRACT

Tertiary and sterically hindered amines have been chosen as potential candidate absorbents, recommended for their high carbon dioxide (CO_2) loading capacity and easy regeneration. In this study, the CO_2 absorption characteristics of these amines were studied using ^1H nuclear magnetic resonance (NMR) and quantitative ^{13}C NMR. The equilibrium experiments were conducted in the vapor–liquid equilibrium (VLE) apparatus, which was used to measure the CO_2 absorption capacities and relative absorption rates of aqueous solutions of methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP). The CO_2 loaded absorbents were used for NMR measurement to determine the distribution of species formed in the absorbents. This process confirmed the reaction mechanisms of the individual absorbents in relation to CO_2 absorption capacities.

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1. Introduction

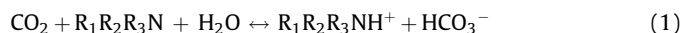
Tertiary and sterically hindered amines react with carbon dioxide (CO_2) to form bicarbonate species and they are advantageous as CO_2 absorbents as (because) they are thermally regenerated at low temperatures and have high absorption capacity [1]. However, their reactivity with CO_2 is low and thus their reaction rates are low. Therefore, improvement of their reaction rates and absorption capacity is desirable and a number of studies have investigated blending for this purpose [2–5]. In blending or synthesis experiments, understanding the chemical characteristics and mechanisms of the species in solution is a key to the prediction of their chemical equilibrium, which determines their overall effectiveness as absorbents. For this reason, the absorption mechanisms of tertiary and sterically hindered amines have been intensively studied by many researchers.

Several researchers proposed the absorption mechanisms for these two types of amines. Versteeg and Van Swaaij [6] suggested that tertiary amines underwent physical absorption, and Bosch et al. [7] and Xu et al. [8] explained absorption by sterically hindered amines as being a result of the deprotonation of zwitterions. Sharma [9] and Alper [10] suggested that first order reactions occurred between sterically hindered amines. At present, the most reliable mechanisms are recognized as those based on the

quantum mechanical calculations for sterically hindered amines by da Silva and Svendsen [11] and the base catalyst effect of tertiary amines suggested by Donaldson and Nguyen [12]. However, since most mechanism studies conducted thus far have relied on modeling, actual experiments that analyze the reactivity and speciation of the molecules in solutions are still needed. In the present study, we examined a tertiary amine, methyldiethanolamine (MDEA), and a sterically hindered amine, 2-amino-2-methyl-1-propanol (AMP), using ^1H NMR and quantitative ^{13}C NMR with the aim of determining the absorption characteristics and speciation of each amine.

2. Reaction mechanism

In addition to acting as bases, through deprotonation reactions of their zwitterions, tertiary amines also are able to undergo direct reactions with CO_2 . Donaldson and Nguyen [12] suggested Eq. (1), which can be viewed as a form of base catalyst hydrolysis, as the underlying mechanism of the reaction of CO_2 with tertiary amines:



Similarly, sterically hindered amines also preferentially undergo bicarbonate combination rather than carbamate formation. Singh et al. [13] suggested that the initial reaction rate of a sterically hindered amine was slow because of the steric hindrance due to amine group substituents. da Silva and Svendsen [11] caution that the name “sterically hindered” conveys an overly simple physical interpretation of carbamate stability add that the effect of a

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Notation

$P_{\text{CO}_2}^*$	equilibrium partial pressure of CO_2 (kPa)
T	absolute temperature (K)
R	universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
n	mole (g mol^{-1})

Greek letters

δ	chemical shift (ppm)
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Subscripts

Si	before absorbing in reservoir
St	after absorbing in reservoir
Ri	before absorbing in reactor
Rt	after absorbing in reactor
R	reactor
S	reservoir

substituent group on the stability of a species can take many forms. Substituent groups can affect donating or withdrawal of electrons through bonds. There can be energetically favourable or unfavourable interactions with groups to which the substituent is not directly bonded (this is steric hindrance). Using AMP as a representative sterically hindered amine, the major reactions between AMP solutions and CO_2 will be the formation of carbamate and bicarbonate, as suggested in Eqs. (2) and (3)

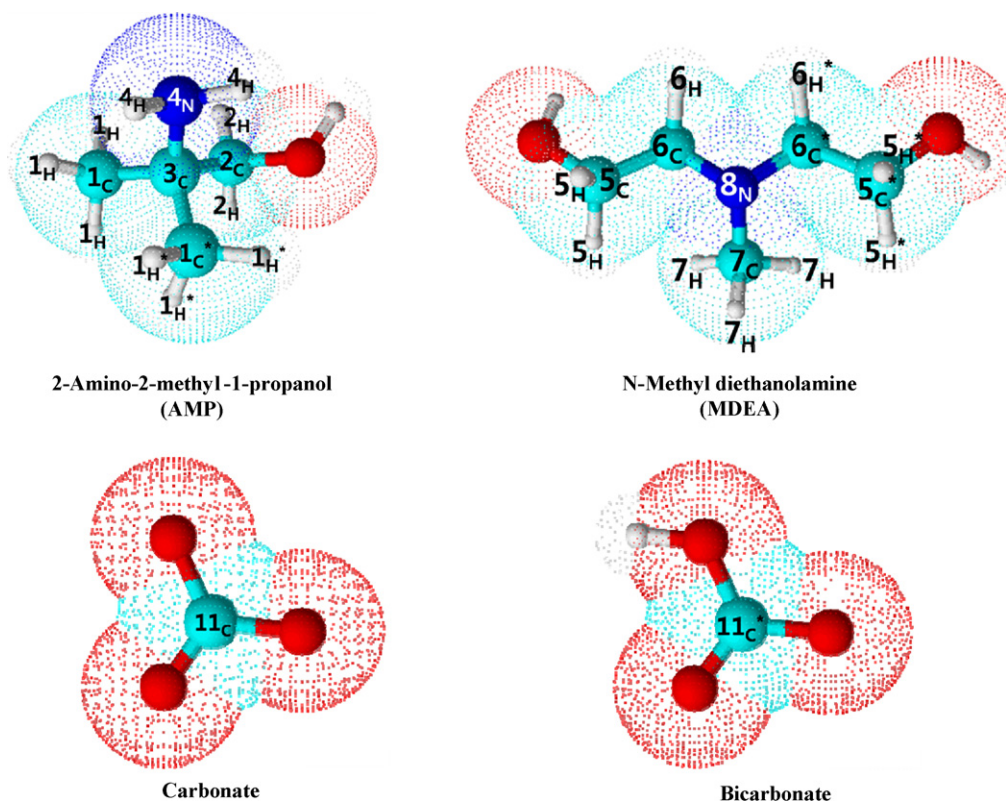
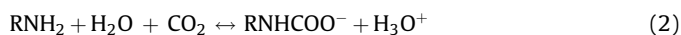


Fig. 1. Molecular structure of species in MDEA and AMP aqueous solution.

Based on these mechanisms, the present study considered that tertiary and sterically hindered amines would undergo selective formation of bicarbonate species, as shown in Fig. 1, under CO_2 loading.

3. Experimental

As reagents, AMP (99%) from ACROS Co. and MDEA (98.5%) from FLUKA Co. were used in the experiment without any separate purification. Deionized water at room temperature was used to prepare the reagents at 30 wt%. An AVANCE 500 MHz from Bruker Co. was used for NMR analysis with D_2O (99.99%) from Sigma-Aldrich and 1,4-dioxane as an internal and external standard reference, respectively.

Fig. 2 shows a schematic diagram of the vapor–liquid equilibrium apparatus used in the experiment. The device consisted of a gas reservoir, a reactor, a temperature and pressure indicator, and a recorder that stored records in real time. The gas reservoir (internal volume; 300.29 cm^3) and the reactor (internal volume; 322.56 cm^3) were made of stainless steel and the reactor was equipped with a magnetic stirrer in order to maximize the contact area with CO_2 . The CO_2 gas was put into the reservoir and preheated to 40°C by a constant-temperature water bath before being injected into the reactor. The reactor was maintained at 60°C in order to measure absorption capacities in relation to temperatures. Before injecting CO_2 , residual gases in the reactor were removed using a vacuum pump. The reactor was designed so that its internal pressure measured during absorption reactions can be stored in real time.

After opening the connected valve between the reservoir and reactor injecting carbon dioxide at a constant pressure, and then the absorption test was performed. Pressure of reactor decreased as a function of the absorption of CO_2 with the proceeding of the reaction, and then it was determined that it reached to absorption

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