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Carbamate stability measurements in amine/CO_2/water systems with Nuclear Magnetic Resonance (NMR) spectroscopy

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Abstract

NMR experiments were carried out for 30 mass % aqueous solutions of monoethanolmine (MEA), ethylenediamine (EDA) and piperazine (PZ) at 25 °C. To distinguish between the amine/protonated amine and bicarbonate/carbonate pairs, an earlier method developed for primary amine (2-amino-2-methyl-1-propanol) was implemented. The amine protonation constant, the dissociation constant of carbonic acid from literature, and pH measurements for different ionic strengths, were all employed and the data were correlated with ionic strength.

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Keywords: diamine, NMR, carbamate, CO_2 capture

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1. Introduction

CO_2 capture is based on the removal of carbon dioxide from power plants and large stationary industrial sources as these represent the best targets for emissions reduction. Various carbon capture and storage (CCS) technologies are available worldwide. Chemical absorption using amine base solvents is at present the most viable technology for CO_2 capture and has the potential to remain the most important process also in the future.

Amines are usually employed as absorbents for CO_2 capture and monoethanolamine (MEA), diisopropanolamine (DIPA), N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) are commonly used. However, due to problems associated with alkanolamines, such as their degradation in oxygen rich atmospheres,

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considerable energy need for solvent regeneration, environmental issues and recycling efficiency, the quest to find alternative candidates is very important [1, 2].

Carbamate stability is a very important parameter for determining the absorption capacity and regeneration energy requirement. The carbamate formation constant can be expressed as a product of carbamate formation ($AmCO_2^-$) in the system divided by the free amine (Am) and carbonate (HCO_3^-) species at a certain loading. The reported experimental data is very limited and scarce. Nuclear Magnetic Resonance (NMR) can certainly measure the species produced in the amine/CO_2/water system. However all species cannot be observed directly due to fast exchanging protons in the system [3-5]. To distinguish amine (Am) from protonated amine (AmH^+) and carbonate (CO_3^{2-}) from bicarbonate (HCO_3^-), different techniques were suggested, i.e. pH shift calibration and chemical shift calibration in NMR for the specific species [6-8]. Holmes, et al., (1998) [9] suggested an empirical correlation based on chemical shift of the carbonate and bicarbonate peaks in the NH_3/CO_2/water system. Jakobsen, et al., (2008) [10] suggested an empirical calibration correlation based on a changing of the chemical shift in amine/protonated amine and carbonate/bicarbonate by adding an acid. Very recently, Ciftja, et al., (2014) [11] proposed a method to separate amine/protonated amine and carbonate/bicarbonate by using a mass balance and electroneutrality. This method provides full liquid speciation by separating the carbonate/bicarbonate and amine/protonated amine based on pH measurements, ionic strength (I) and the pK_a of the different systems.

^{13}C-NMR was employed to study the carbamate formation and to estimate an apparent carbamate stability constant in aqueous solutions of CO_2 and monoethanolamine (MEA), ethylenediamine (EDA) and piperazine (PZ) at 25°C. The direct liquid-phase speciation method is published in literature [4, 12] The activity coefficient model together with mass balance/electro neutrality are introduced to estimate the individual species, hence the carbamate formation constant can be derived.

The main objective of the paper is to verify the method implemented by Ciftja, et al., [11] with a known system such as monoethanolamine/CO_2/water as well as for diamine systems such as piperazine/CO_2/water and ethylenediamine/CO_2/water.

2. Methods and Materials

2.1. Chemicals

The chemicals with purity ≥ 99% used in this study, monoethanolamine (MEA), ethylenediamine (EDA), piperazine (PZ) and deuterium oxide (D_2O), all supplied from Aldrich and 1,4-dioxane (D8) from Fulka were used without any further purification. The amine solutions were prepared from distilled water by weight. The resulting solutions were loaded with CO_2 (grade 5.0) by bubbling of gas. The initial loading was estimated from the weight change of the solution after CO_2 bubbling and the final loading of the prepared solutions were analyzed for CO_2 and amine content. Their concentrations were determined by a titration/precipitation method and compared with the NMR results. The pH of each sample was measured using a Metrohm 827 pH Lab Meter. The pH - electrode was calibrated using pH buffers of 12 (± 0.02), 9 (± 0.02), and 4 (± 0.02), supplied by Mettler Toledo.

2.2. Sample preparation

Loaded and unloaded solutions of 30 mass % amine in water with volume about 0.4 mL were filled into 5 mm Norrel 507-HP tubes and weighed in a Mettler AE163 digital analytical balance with accuracy of ±0.0001g. A small amount of D_2O (5-10 mass % of solution) was added to obtain a signal lock. A GVLab fixed-speed vortex mixer was used to mix all the contents in the NMR tubes.

A standard of 1,4-dioxane (5% of the total mass of solution) was added to provide a sharp peak with a known chemical shift in the NMR spectrum and positioned in a region distant from the sample peaks. All the spectra analyzed were calibrated based on the chemical shift of 3.75 ppm for proton NMR and of 67.19 ppm for carbon NMR [13]. All the NMR spectra were recorded on a Bruker Avance 400 DPX spectrometer at 25 °C.