

Absorption of carbon dioxide in alkanolamine and vegetable oil mixture and isolation of 2-amino-2-methyl-1-propanol carbamate



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ARTICLE INFO

Article history:

Received 17 October 2013

Received in revised form 18 March 2014

Accepted 19 March 2014

Available online 24 April 2014

Keywords:

Alkanolamines

Vegetable oil

CO₂ absorption

AMP-carbamate

ABSTRACT

The carbon dioxide emission has to be efficiently controlled due to environmental, economic and social demands. Among the various technologies, gas absorption technology is of great importance for the capture of CO₂ and to prevent global warming. In the present work, the absorption of carbon dioxide in alkanolamines in aqueous and vegetable oil medium was assessed and it was found that the absorption in organic medium is higher than in aqueous medium. Among the alkanolamines in various vegetable oil media, 2-amino-2-methyl-1-propanol (AMP) in the coconut oil medium was found to exhibit the highest absorption capacity for CO₂ gas. The precipitate resulting after passing CO₂ through AMP in the vegetable oil medium was analyzed by FT-IR, ¹H NMR and ¹³C NMR spectroscopic techniques and identified as AMP-carbamate. The influence of various operating conditions such as amine concentration, reaction time, temperature and pressure of CO₂ gas on the AMP-carbamate yield was analyzed. Under optimized conditions, the maximum yield of 52% of AMP-carbamate was obtained. Thus the AMP in vegetable oil medium emerges to be a promising candidate for capturing CO₂ and for isolation of value added product (AMP-carbamate).

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Introduction

The control of anthropogenic carbon dioxide emission is one of the most challenging environmental issues faced by industrialized countries, as CO₂ is the largest contributor accounting for 60% of the global warming effect. [1]. International Panel on Climate Change (IPCC) predicts that by the year 2100, the atmosphere may contain up to 570 ppm_v CO₂ causing a rise of mean global temperature of around 1.9 °C and an increase in mean sea level of 3.8 m. Hence, it is very important from both the environmental and economical point of views to find an efficient way for separating carbon dioxide from flue gases to minimize its emission into the atmosphere and convert it into value added products.

Utilization of carbon dioxide as a resource is the strategic idea in the mitigation of carbon dioxide. Carbon dioxide can be converted into an assortment of value added products such as bicarbonates, carbonates and carbamates [2]. Among them, carbamate is one of the most substantial value added product obtained by reaction of CO₂ with amines. It is being used as an insecticide, human medicine and as a preservative [3].

Among the different separation techniques developed for the removal of CO₂ gas, solvent absorption is the most widely employed method and aqueous alkanolamines are the most commonly used chemical absorbents for the removal of acidic gases for over 60 years [4]. By the addition of a primary or secondary amine to a purely physical solvent such as water, the CO₂ absorption capacity and rate are enhanced many fold. Several studies have been reported [5–9] for the measurement of absorption of CO₂ in alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-amino-2-methyl-1-propanol (AMP) and 2-methylaminoethanol (MAE) in aqueous medium.

Recently, special attention has been paid [10–13] over the use of alkanolamines in non aqueous solvents for the removal of

Abbreviations: AMP, 2-amino-2-methyl-1-propanol; DEA, diethanolamine; MAE, 2-methyl aminoethanol; MDEA, methyl diethanolamine; MEA, monoethanolamine; TEA, triethanolamine.

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acidic gases because of their high absorption capacity and low corrosiveness. The most important advantage is their low energy consumption during the regeneration of used liquor. In conventional aqueous amine scrubbing methods, relatively low temperatures (less than 50 °C) are required for CO₂ uptake and high temperatures in the range of 120–140 °C are required for the desorption. The heat required to maintain the thermal differential in aqueous amine system is the major factor which increases the total cost and energy consumption of the process. But in the case of non-aqueous amine sorbents, both the absorption and desorption process can be carried out at relatively low temperatures (not more than 30 °C). Several authors [14–16,10,17] have measured the absorption of carbon dioxide into aqueous and non-aqueous solutions of triethanolamine, methyl diethanolamine (MDEA) and 2-amino-2-methyl-1-propanol, and reported that the disadvantages witnessed in the case of aqueous absorbents could be circumvented by the use of non-aqueous absorbents.

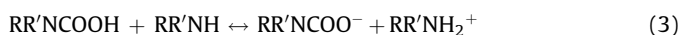
Wedlake et al. [18] measured the absorption of CO₂ in silicone oil. Bobbo et al. [19] estimated the absorption of CO₂ in commercial oil, linear chained pentaerythritol esters (PECs) and in branched pentaerythritol esters (PECs). Yeh et al. [20] measured the absorption of CO₂ in olive oil, dog fat, human fat and rat-pooled fat. However, the absorption of CO₂ in alkanolamines in vegetable oil medium has never been reported in the literature. Vegetable oil [21] is a complex mixture of chemically distinct components, with di- and triglycerides as major components and free fatty acids, phosphatides, sterols, fatty alcohols and fat-soluble vitamins as minor components. Vegetable oil is considered to be a non-hazardous and affordable chemical which could be used as a novel and greener non-aqueous medium.

In the present work, an attempt has been made to measure the absorption of CO₂ in alkanolamines in aqueous and organic (non-toxic and natural vegetable oil) medium. In addition to that, AMP-carbamate has been isolated and characterized by FT-IR, ¹H NMR and ¹³C NMR spectroscopic studies. The various operating parameters such as amine concentration, reaction time, temperature and pressure of CO₂ gas have been optimized to get the maximum yield. To our knowledge this is the first study which reports the isolation of the value added product AMP-carbamate from AMP and vegetable oil mixture for carbon dioxide capture and utilization.

Reaction fundamentals

Alkanolamines in aqueous medium

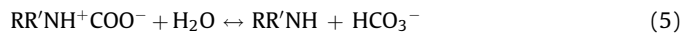
Zwitterion mechanism is the well-established mechanism for the description of the reaction between carbon dioxide and primary or secondary amines. It was originally proposed by Caplow [22] and then reintroduced by Danckwerts [23]. The electrophilic nature of the carbon atom of CO₂ making it susceptible to nucleophilic attack. The nucleophilic addition of primary or secondary amine with carbon dioxide can create a zwitterionic transition state, which can undergo an intramolecular proton transfer to form a neutral carbamic acid. The subsequent reaction of this carbamic acid with a Bronsted base amine can lead to a formation of an ammonium carbamate (0.5:1 CO₂: amine ratio) [24]. So, primary and secondary amines can exhibit both Lewis and Bronsted basicity in an aqueous medium.



The overall reaction is:



In the case of sterically hindered amine, since the carbamate formed is unstable, further reaction of the carbamate with water may lead to a final bicarbonate product with a 1:1 CO₂: amine ratio,



In tertiary amines the reaction pathway depends upon the nucleophilicity of water rather than amine, leading to the formation of carbonic acid, which on further reaction with a Bronsted base amine produces ammonium bicarbonate (1:1 amine: CO₂). Due to the lack of proton they cannot undergo an intramolecular proton transfer to form a neutral carbamic acid; therefore they act as a chemical sink for CO₂ in aqueous solution simply by providing only Bronsted basicity.



Alkanolamines in non-aqueous medium

In the case of primary and secondary alkanolamines in non-aqueous system, the zwitterions formed by the nucleophilic addition of CO₂ with amine are unstable and can rapidly rearrange via proton transfer to the corresponding carbamic acid. Both the zwitterions and the carbamic acids can generally be unstable, and it is not known which equilibrium form undergoes further reaction, although it is posited that the carbamic acid may be deprotonated by a second equivalent of free amine to produce an ammonium carbamate salt [24,25] with the overall stoichiometric requirement of two moles of amine per one mole of carbon dioxide absorbed (0.5:1 CO₂:non-tertiary amine). These reactions are possible in the aqueous system also, but in non-aqueous system the possibility for further reaction of carbamate with water is less. Thus, the ammonium carbamate formation is more favorable [26,27] than bicarbonate formation and the loading capacity can exceed the predicted theoretical value due to the equilibrium established between zwitterions and carbamic acid.

In the case of tertiary amines, they are unable to form the carbamic acid/carbamate species [28] and the reaction of tertiary amines with CO₂ in non-aqueous system is less pronounced due to the absence of water nucleophile.

Materials and methods

Chemicals

Various alkanolamines employed in this study are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-methylaminoethanol (MAE), 2-amino-2-methyl-1-propanol (AMP). All the chemicals were purchased from the Merck Company in 96–98% purity. The chemicals were used without further purification. CO₂ gas of two different concentrations (99% CO₂ gas and 15% CO₂ gas in N₂ gas) of Research Grade was purchased from Supreme Engineering Services, India. Alkanolamines in aqueous medium were prepared using distilled water. Alkanolamines in organic media were prepared using various commercially available vegetable oils such as coconut oil, sunflower oil, groundnut oil, palm oil and gingelly oil.

Apparatus and procedure

A schematic diagram of the experimental setup is shown in Fig. 1. The reactor consists of 1 L capacity stainless steel cylindrical tank equipped with a stainless steel diffuser to generate fine bubbles and endure intense mixing. The tank was kept on the

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