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Kinetics of carbon dioxide absorption by nonaqueous solutions of promoted sterically hindered amines

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Abstract

The mechanism and kinetics of CO_2 capture using piperazine (PZ) promoted nonaqueous solutions of 2-amino-2-methyl-1,3-propanediol (AMPD) and 2-amino-2-ethyl-1,3-propanediol (AEPD) were investigated by stopped-flow technique. The termolecular mechanism was used to model the kinetics of the reactions. AMPD or AEPD like other sterically hindered amines absorbs CO_2 in an equimolar ratio that is significantly higher than that of monoethanolamine (MEA). However, the steric hinderance results in decreased reaction rate as in the case of AMPD and AEPD. The reaction can be promoted by addition of small amounts of cyclic polyamines, such as PZ or its derivatives. Our results show clearly that nonaqueous solutions of AMPD and AEPD can achieve reaction rates comparable to commercial systems by the addition of small amounts of PZ.

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Keywords: Amines; carbon dioxide; ethanol; nonaqueous solution; piperazine; reaction kinetics; sterically hindered amines; stopped-flow; termolecular mechanism

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1. Introduction

The increase in greenhouse gas emissions from fossil fuel combustion over the past century is known to be part of the cause of global warming [1]. Among greenhouse gases, CO_2 is the primary contributor to the problem due to its high abundance, and thus it is a major target for reduction. The conventional technology to capture CO_2 on large scale is the absorption/desorption process, in which aqueous solutions of alkanolamines (specifically, 30 wt. percent monoethanolamine (MEA)) are frequently used as solvents [2]. This process is energy-intensive and costly with other side effects, hence alternative and affordable solvents or technologies for CO_2 capture are desired. In principle, an optimized CO_2 absorber/desorber system should have high CO_2 loading to decrease the solvent circulation and high reaction rate to enhance CO_2 absorption rate so that the unit is compact. However, aqueous alkanolamine solutions have low CO_2 loadings (much less than theoretical maximum of 0.5 mol CO_2/mole amine) due to stable carbamate formation [3]. In order to combat this deficiency, sterically hindered amines have been introduced which can have loadings as much as 1 due to unstable carbamate ion [4]. However, steric hinderance -while increasing the loading capacity- often decreases the rate of reaction with CO_2 [5-8]. In fact, it is rare to find a sterically hindered amine with sufficiently fast reaction and 2-amino-2-methyl-1-propanol (AMP) could be considered as the only exception. Another approach is to use highly active amine promoters such as cyclic diamines especially piperazine (PZ) to compensate the rate loss due to steric hinderance. Compared to MEA, PZ has a faster reaction rate, higher absorption capacity and higher resistance to thermal and oxidative degradation [9-11]. In addition, compared to aqueous systems, the use of nonaqueous systems (i.e., ethanol system or methanol system) is considered to be a promising alternative method for CO_2 capture, due to high solubility and capacity, low corrosiveness and low energy consumption for the regeneration of used solvents [12-15]. To that effect, solution of two sterically hindered amines namely, 2-amino-2-methyl-1,3-propanediol (AMPD) and 2-amino-2-ethyl-1,3-propanediol (AEPD) in ethanol (or 1-hexanol) was investigated and piperazine (PZ) was used as a promoter. Interest in AMPD and AEPD comes from the fact that both of them can be produced from renewable sources, that is from 1,2 propanediol which is abundant as a side product of biodiesel process. Recently, it was reported that biodiesel derived glycerol could be utilised as a renewable feedstock for replacing fossil-derived chemicals. Catalytic conversion of glycerol to value-added chemicals such as propanediols (1,2-PDO, 1,3-PDO) are of great importance [16,17]. As for the promoter, PZ and PZ derivatives are good candidates for promoting the reaction rate both in aqueous and nonaqueous systems when sterically hindered amines are employed for carbon dioxide capture [10].

Reaction kinetics is a critical parameter to predict the efficiency of the CO_2 absorption. There are several techniques for the investigation of reaction kinetics such as stirred cell, laminar jet absorber, wetted sphere and stopped-flow. Among these techniques, stopped-flow, a direct method, has been widely used due to its characteristics, such as the large coverage of reaction rates and reproduceable experiment data [18]. Therefore, in this work, the mechanism and kinetics of CO_2 capture using PZ as an activator to AMPD and AEPD in ethanol were investigated by stopped-flow technique. Termolecular mechanism was used to model the kinetics of the system as will be described within the following text.

2. Experimental Methods

2.1. Reagents

PZ of purity ≥ 99.0% was supplied by Sigma-Aldrich (St. Louis, MO). Sterically hindered amines, AMPD and AEPD of purities ≥ 99.8%, and ethanol of purity ≥ 99.9% were supplied by Merck (Darmstadt, Germany) and J.T. Baker, respectively. These reagents were used without further purification. Carbon dioxide with a purity of 99.9% was supplied by Linde (Munich, Germany). The experiments were carried out in ethanol using amines of concentrations 0.50 kmol/m^3 of AMPD and AEPD promoted by 0.05–0.25 kmol/m^3 of PZ, at 298 K.