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Kinetics of carbon dioxide (CO_2) with ethylenediamine, 3-amino-1-propanol in methanol and ethanol, and with 1-dimethylamino-2-propanol and 3-dimethylamino-1-propanol in water using stopped-flow technique

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ABSTRACT

Pseudo first order rate constants of homogeneous reactions of carbon dioxide (CO_2) with primary amines, ethylenediamine (EDA) and 3-amino-1-propanol (3AP), in methanol and ethanol in the concentration range of 20–120 mol m^{-3}; and with tertiary amines, 3-dimethyl-amino-1-propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P), in water in the concentration range of 20–120 mol m^{-3} were measured using a stopped-flow apparatus in a temperature range of 293–313 K. Dissociation constants for aqueous 3DMA1P and 1DMA2P systems at different temperatures were also measured. Both tertiary amines were found to react faster with CO_2 than N-methyldiethanolamine (MDEA). The orders of the reaction were determined and the constants were regressed using the mechanism that fitted best the experimental data for each system. Second order reaction rate constants of ethylenediamine (EDA) in methanol and ethanol were higher than those of 2-((2-aminoethyl)amino) ethanol (AEEA), a fast reacting amine, whereas the rates of reaction of 3AP were found to be less than those of monoethanolamine (MEA) in methanol and ethanol. As expected, for both EDA and 3AP, the second order reaction rate constants were found to be lower in non-aqueous media than in water.

1. Introduction

Acid gases such as carbon dioxide, hydrogen sulphide, carbonyl sulphide, etc. are absorbed by aqueous and non-aqueous solutions of pure or blended alkanolamines. The kinetics of reaction between alkanolamines in different reaction media and acid gas have a very prominent effect on the overall acid gas absorption rate and the design of absorption column that determines the cost-effectiveness of the CO_2 capture system. Therefore, a thorough knowledge of reaction mechanisms in different media and their corresponding rate constants are required.

Kinetic data of various primary, secondary and tertiary amines with acid gases, such as CO_2 and H_2S, have been published in the literature since 1960, and were reviewed by Blauwhoff et al. [1], and later by Versteeg et al. [2] and recently by Vaidya et al. [3].

Littel et al. [4] studied aqueous solutions of triethanolamine (TEA), dimethyl-monoethanolamine (DMMEA) and diethylmonoethanolamine (DEMEA) and found the reaction order for each amine to be one in agreement with the base catalyst mechanism. Versteeg et al. [2] reviewed data published on tertiary amines (MDEA and TEA) and concluded that no discrepancies exist with regard to the overall reaction order, which is equal to two.

Non-aqueous media, such as methanol or ethanol, reduce the regeneration cost in amine plants [5], and are therefore of interest as alternative reaction media for CO_2 absorption. Sada et al. [6] studied aqueous and non-aqueous (methanol, ethanol, 2-propanol) solutions of TEA, and found the reaction order to be unity with respect to the amine, in accordance with the conclusion drawn by Versteeg et al. [2]. Benitez-Garcia et al. [7] studied the effect of basicity of four tertiary amines (TEA, MDEA, DEMEA and triethylamine) on CO_2 absorption rates and found that the second order kinetic rate constant increased with increasing basicity. The same phenomena were observed by Sada et al. [6] for MEA and DEA. The reaction order was found to change gradually for MEA from 1 to 1.9 for water to methanol, ethanol and 2-propanol. Alvarez-Fuster et al. [8] found that the reaction order with respect to cyclohexamine in ethanediol (a more polar solvent than ethanol) to be 1 as compared to 1.8 in ethanol. Sada et al. [6] and Versteeg et al. [9] observed the order of reaction with respect to amine to vary inversely with solvent polarity. Some of the literature data available [10–17] for various alkanolamines in non-aqueous systems are listed in Table 1. Previous studies by Li et al. [18,19] of the kinetic rate for CO_2 absorption in an aqueous system of ethylenediamine (EDA) and 3-amino-1-propanol (3AP) showed a higher rate constant than conventional aqueous MEA solution within similar

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Table 1
Kinetic studies of CO_2-alkanolamines in non-aqueous media.

Technique/method	Author	System studied
Stirred cell	Sada et al. [6,11,12]	1. Non-aq. EDA in (methanol, ethanol, ethyleneglycol) 2. Non-aq. MEA, DEA & TEA (methanol, ethanol, 2-propanol) 3. Non aq. monoisopropanol amine, cyclohexylamine
	Versteeg et al. [9]	4. Non-aq. DEA & DIPA (ethanol and n-butanol)
	Henni [13]	5. Non-aq. MDEA (sulfolane)
Condumetric	Ali et al. [14]	Non-aq. aniline, cyclohexamine, hexamine in (ethanol)
	Crooks and Donnellan [15]	DEA in ethanol
	Li [16]	Non-aq. AEEA in (ethanol and methanol)
Stirred semi-batch tank	Park et al. [17]	Non-aq. TEA in (methanol, ethanol, n-propanol, n-butanol, ethylene glycol, propylene glycol and propylene carbonate)
Wetted sphere	Davis and Sandall [10]	DEA, DIPA in (polyethylene glycol)

temperature and concentration ranges. In the present work, we further study the kinetics of these two primary amines in two polar solvents: methanol and ethanol. The chemical structures of the studied amines used for non-aqueous media are shown in Fig. 1.

Tertiary amines are often blended with faster reacting primary and/or secondary amines to take advantage of their high loading capacity, low solvent degradation rate and low regeneration cost. But due to the low reaction rate, the operation requires a large number of theoretical stages in the absorption column for a given loading, which in turn increases the capital cost of gas sweetening plants. Hence, tertiary amines having high loading capacity as well as a competitive reaction rate are of great interest.

The present work investigates the kinetics of tertiary amines: 3-dimethylamino-1-propanol and 1-dimethylamino-2-propanol in aqueous media that have high CO_2 capacity loading [20,21]. The chemical structures of the studied tertiaryamines are shown in Fig. 2.

2. Experimental

In this work, the stopped-flow technique is used for the direct measurement of pseudo first-order kinetics for different aqueous and non-aqueous diamines, as well as primary, secondary and tertiary alkanolamines. The experimental setup is a standard SF-51 stopped flow unit from Hi-Tech Scientific Ltd., UK. It is an assembly of four major units; a sample-handling unit, a conductivity-detection cell, an A/D converter and a microprocessor. The sample-handling unit is comprised of a stainless steel case which provides support and an enclosure for the sample flow circuit. Schematics of this flow circuit are shown in Fig. 3.The entire flow circuit, with the exception of the stop/waste syringe, is enclosed in a thermostat and maintained at a constant temperature by an external water bath within ±0.1 K. The front panel of the sample handling unit displays a temperature indicator with a resolution of 0.1 K and an air pressure indicator. A pneumatic air supply

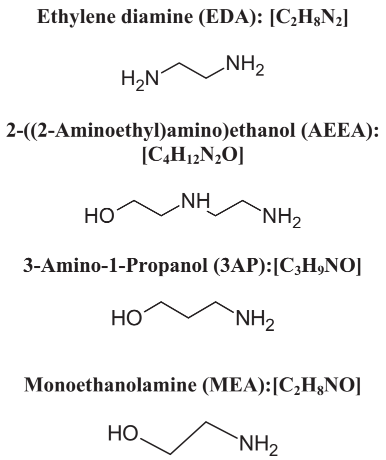

Fig. 1. Molecular structure of amines studied in non-aqueous medium (EDA, 3AP).

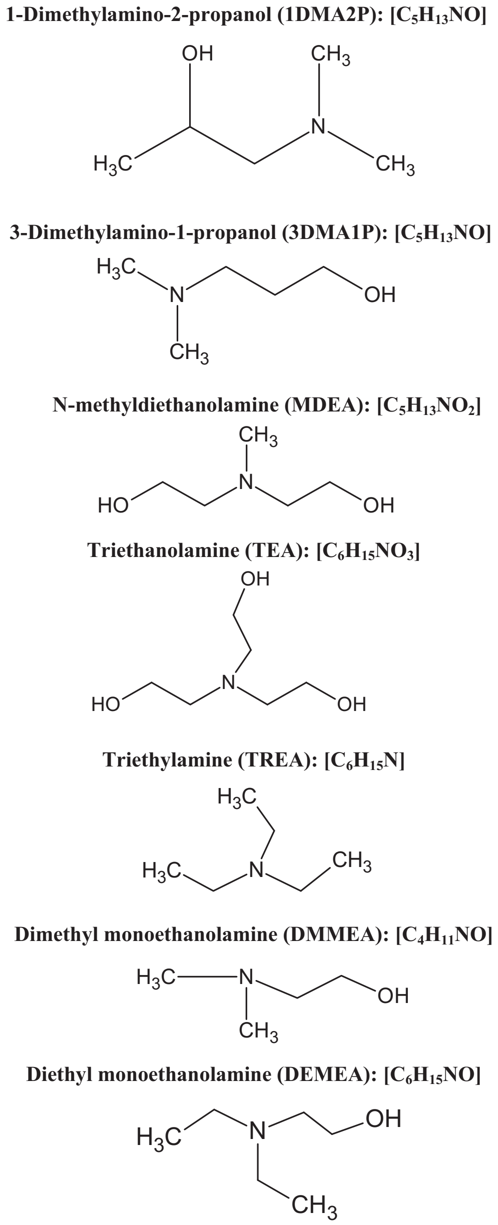

Fig. 2. Molecular structures of studied tertiary alkanolamines (1DMA2P, 3DMA1P).