



Kinetics of absorption of carbon dioxide in 2-amino-2-methyl-1-propanol + N-methyldiethanolamine + water

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ABSTRACT

The rate at which CO₂ is absorbed in the solvent system 2-amino-2-methyl-1-propanol (AMP) + N-methyldiethanolamine (MDEA) + H₂O was determined at 30, 35, and 40 °C in a wetted-wall column. Ten different concentrations of the solvent system were used in which MDEA concentration was varied as 1.0 and 1.5 kmol m⁻³; that of AMP, as 0.1, 0.2, 0.3, 0.4, and 0.5 kmol m⁻³. The overall pseudo-first order reaction rate constants for the CO₂ absorption estimated from the kinetics data are presented. Data suggest that a small increase in AMP concentration at fixed MDEA concentration in the solvent system will result in significant increase on the rate of CO₂ absorption. The absorption was described in terms of a hybrid reaction rate model, which assumed a second-order reaction (CO₂ + MDEA) and a zwitterion mechanism for the reaction between CO₂ and AMP. The apparent rate constants estimated from the measurements were compared to the corresponding values predicted from the model; the result was satisfactory, with an overall AAD of 4.0%.

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1. Introduction

MDEA, despite its slow reaction rate with CO₂, has been found attractive as solvent, in aqueous form, for CO₂ removal from gas stream due its high solution concentration, high CO₂ loading, lower heat of reaction (with CO₂), low corrosive property, slow degradation rate, and low evaporation loss (*i.e.*, low vapor pressure). Its slow rate of reaction with CO₂, however, can be overcome by blending MDEA with another alkanolamine (a tertiary or sterically-hindered alkanolamine) or an activator in an aqueous solution, resulting in a solvent system with high absorption capacity, low energy requirement (during solvent recovery), and outstanding stability. Reports on kinetic studies on rate of CO₂ absorption into different alkanolamine-based solvents systems: alkanolamine + water (Alper, 1990; Barth *et al.*, 1984; Blauwhoff *et al.*, 1984; Bosch *et al.*, 1990; Bougie and Iliuta, 2009; Chakraborty *et al.*, 1986; Hartono *et al.*, 2009; Jamal and Lim, 2006; Jamal *et al.*, 2006; Ko and Li, 2000; Rinker *et al.*, 1995; Saha *et al.*, 1995; Xu *et al.*, 1996), alkanolamine + activator + water (Paul *et al.*, 2009; Seo and Hong, 1999, 2000; Sun *et al.*, 2005; Xu *et al.*, 1992), and primary (or secondary) amine + tertiary (or sterically-hindered) amine + water (Glasscock *et al.*, 1991; Horng and Li,

2002; Liao and Li, 2002; Lin *et al.*, 2009; Mandal and Bandyopadhyay, 2006a,b; Rangwala *et al.*, 1992; Sakwattanapong *et al.*, 2009; Vaidya and Kenig, 2007; Wang and Li, 2004; Xiao *et al.*, 2000; Zhang *et al.*, 2001, 2002) have been made available in literature. In practically all cases, CO₂ absorption has been generally found better in the two latter solvent systems, on the bases of the combined performance of the solvent as to loading, absorption/reaction rate, and energy requirement during solvent regeneration.

In this paper, kinetics data for the absorption/reaction in the system CO₂ + AMP + MDEA + H₂O at different amine concentrations and temperatures were determined. AMP, a sterically-hindered alkanolamine, was added to the widely used MDEA + water solvent system to improve the solvent's absorption capacity and lower its regeneration economics. The way in which the considered amine, *i.e.*, AMP and MDEA, capture CO₂ could be describe via the so-called shuttle mechanism theory. In this mechanism, the fast reacting property of AMP is utilize to quickly absorb CO₂ and the products formed will then react to MDEA and the free AMP will continue reacting with CO₂ and the process goes on, thus, allowing more CO₂ molecules to be captured. The other physical and transport properties necessary to evaluate such (kinetics) data, *i.e.*, density, viscosity, solubility, and diffusivity, were also measured. The N₂O analogy was used to estimate the solubilities and diffusivities of the CO₂ in the aqueous alkanolamine solvent systems under study.

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Nomenclature

d	outside diameter of the wetted-wall column, m
D	diffusivity of a gas in liquid, $\text{m}^2 \text{s}^{-1}$
E_∞	value of enhancement factor in instantaneous reaction region
g	gravitational constant
h	height of wetted-wall column, m
H	Henry law constant, $\text{kPa m}^3 \text{ kmol}^{-1}$
Ha	Hatta number, defined in Eq. (14)
k_{app}	apparent reaction rate constant, s^{-1}
k_L	liquid phase mass transfer coefficient
$k_{\text{OH}^-}^*$	reaction rate constant for CO_2 hydration, i.e., Eq. (4)
k_{ov}	overall pseudo-first order reaction rate constant, s^{-1}
$K_{\text{p,MDEA}}$	MDEA protonation constant ($=[\text{R}_3\text{N}][\text{H}^+]/[\text{R}_3\text{NH}^+]$), kmol m^{-6}
K_w	dissociation constant for water ($=[\text{H}^+][\text{OH}^-]$), $\text{kmol}^2 \text{ m}^{-6}$
L	liquid flow rate, $\text{m}^3 \text{ s}^{-1}$
N_A	specific absorption rate, $\text{kmol m}^{-2} \text{ s}^{-1}$
p_A	partial pressure of CO_2 , kPa
r	reaction rate
t	temperature, $^\circ\text{C}$
t_c	contact time, s
T	temperature, K

Greek symbols

α	loading of CO_2 in amine, $\text{kmol of CO}_2/\text{kmol of amine}$
η	viscosity, mPa s
ρ	density, g cm^{-3}
ϕ	absorption rate, kmol s^{-1}

2. Theory

2.1. Reactions of CO_2 in aqueous solution

The first reaction, hydration of CO_2 ,



is so slow ($k_{\text{H}_2\text{O}} = 0.026 \text{ s}^{-1}$ at 25°C) (Pinsent *et al.*, 1956) that it may practically be neglected (Blauwhoff *et al.*, 1984).

The second reaction, the bicarbonate formation:



is fast and can enhance mass transfer even at low OH^- concentrations. Thus, absorption experiments to determine the kinetics of the reaction of CO_2 with MDEA + H_2O should be interpreted very carefully as the reaction of CO_2 with OH^- may have a significant contribution to the observed reaction rate. The forward reaction of the reversible reaction between CO_2 and OH^- (Pinsent *et al.*, 1956) is

$$r_{\text{CO}_2-\text{OH}^-} = k_{\text{OH}^-}^* [\text{CO}_2][\text{OH}^-] \quad (3)$$

and

$$\log_{10}(k_{\text{OH}^-}^*/(\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1})) = 13.635 - \frac{2895}{(T/K)} \quad (4)$$

2.2. Dependence of reaction rate on MDEA

For the reaction of CO_2 with tertiary alkanolamines (R_3N), the following mechanism was proposed (Donaldson and Nguyen, 1980):



This reaction mechanism is essentially a base-catalyzed hydration of CO_2 , and the mechanism implies that tertiary amines cannot react directly with CO_2 . Versteeg and van Swaaij (1988a), in a study on the absorption of CO_2 into nonaqueous (ethanol) solutions of MDEA, found that only physical absorption occurs in nonaqueous tertiary alkanolamine systems. Such finding upholds the validity of the mechanism in Eq. (5).

Most literature on CO_2 kinetics with tertiary amines in aqueous solutions assumed that the reaction of CO_2 with MDEA is a pseudo-first order reaction (Blauwhoff *et al.*, 1984; Tomcej and Otto, 1989; Versteeg and van Swaaij, 1988a), i.e.,

$$r_{\text{CO}_2-\text{MDEA}} = k_{2,\text{MDEA}}[\text{CO}_2][\text{MDEA}] \quad (6)$$

2.3. Reaction rate dependence on AMP

The kinetics of the reaction associated with the absorption of CO_2 into aqueous solutions of AMP have been reported in some literature (Alper, 1990; Chakraborty *et al.*, 1986; Saha *et al.*, 1995; Sartori *et al.*, 1987; Yih and Shen, 1988; Zioudas and Dadach, 1986). Second-order rate constants for the reaction between CO_2 and AMP have been reported (Alper, 1990; Chakraborty *et al.*, 1986; Saha *et al.*, 1995; Sartori *et al.*, 1987; Yih and Shen, 1988). The zwitterion mechanism proposed by Caplow (1968) and Danckwerts (1979) is a generally accepted reaction mechanism for the carbamate formation of the reaction of CO_2 with primary or secondary alkanolamines. It has been used successfully to describe such reactions in aqueous alkanolamine solutions (Blauwhoff *et al.*, 1984) and in some organic and viscous solutions (Sada *et al.*, 1985; Versteeg and van Swaaij, 1988a). For the absorption of CO_2 into aqueous mixtures of AMP + MDEA, a zwitterion mechanism has also been applied for the reaction of CO_2 with AMP (Seo and Hong, 2000). In this study, the zwitterion mechanism is applied to the reaction between CO_2 and AMP for the CO_2 absorption into $\text{PZ} + \text{AMP} + \text{H}_2\text{O}$. The base which removes the proton of the zwitterions could be AMP, MDEA, OH^- , or H_2O . Thus, the reaction rate for CO_2 -AMP can be expressed as,

$$r_{\text{CO}_2-\text{AMP}} = \frac{[\text{CO}_2][\text{AMP}]}{\frac{(1/k_{2,\text{AMP}}) + 1/((k_{2,\text{AMP}}k_{\text{H}_2\text{O}}/k_{-1})[\text{H}_2\text{O}])}{+(k_{2,\text{AMP}}k_{\text{OH}^-}/k_{-1})[\text{OH}^-] + (k_{2,\text{AMP}}k_{\text{MDEA}}/k_{-1})[\text{MDEA}] + (k_{2,\text{AMP}}k_{\text{AMP}}/k_{-1})[\text{AMP}]}} \quad (7)$$

where $k_{2,\text{AMP}}$ is the reaction rate constant for the formation of a zwitterion from CO_2 and AMP, k_{-1} is the reaction rate constant for the reverse reaction of the zwitterion, $k_{\text{H}_2\text{O}}$, k_{OH^-} , k_{AMP} , k_{MDEA} are the reaction rate constants for subsequent removal proton reaction from a zwitterion by bases: H_2O , OH^- , AMP, and MDEA, respectively.

2.4. Reaction rate for CO_2 absorption into AMP + MDEA + H_2O

For the absorption of CO_2 into AMP + MDEA + H_2O , the overall CO_2 reaction rate can then be expressed as follows,

$$r_{\text{ov}} = r_{\text{CO}_2-\text{AMP}} + r_{\text{CO}_2-\text{MDEA}} + r_{\text{CO}_2-\text{OH}^-} \quad (8)$$

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