

Thermodynamic and mass transfer modeling of carbon dioxide absorption into aqueous 2-piperidineethanol



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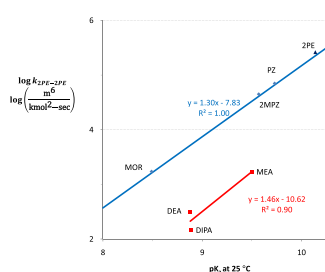
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HIGHLIGHTS

- Liquid film mass transfer coefficient is most sensitive to the carbamate reaction.
- Carbamate reaction rate follows same trend as unhindered amines.
- 2PE forms a more stable carbamate than AMP.
- Bicarbonate reaction rate is ten times faster than for an analogous tertiary amine.
- The PFO assumption applies at low temperature, lean loading conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 December 2015

Received in revised form

6 July 2016

Accepted 13 July 2016

Available online 15 July 2016

Keywords:

Separations

CO₂ capture

eNRTL

Wetted-wall column

Hindered amine

Carbamate stability

ABSTRACT

Amine scrubbing is a necessary technology to offset CO₂ emissions from fossil-fuel power plants. Of the many solvents studied, hindered amines are of particular interest for their marriage of the capacity of tertiary amines with rates a hundredfold greater than tertiary amines. The relatively rapid rates of hindered amines have not been adequately explained, despite their extensive use in commercial solvents. This work seeks to explain the rapid rate of mass transfer of 2-piperidineethanol (2PE) and uses this rationale to draw general conclusions on hindered amines.

Quantitative ¹³C NMR data were collected to determine the equilibrium of carbamate in 30 wt% 2PE. Using these data along with VLE and pK_a data, a rigorous thermodynamic model of 8 molal 2PE was built with electrolyte-NRTL and activity-based kinetics. Wetted-wall column flux data were fit to create the activity-based mass transfer model. Using this comprehensive model, the mass transfer rate was examined through sensitivity studies and Brønsted correlations.

This work shows that 2PE forms a more stable carbamate than 2-amino-2-methyl-1-propanol. The carbamate reaction is the most significant component of mass transfer at 40 °C. The Brønsted correlation for carbamate reactions of unhindered amines predicts the rate of carbamate reaction of 2PE, but the Brønsted correlation for bicarbonate underpredicts the regressed rate. The CO₂ solubility is fit with five parameters with an ARD of 0.84%. The kinetics are fit with a carbamate- and a bicarbonate-forming reaction with an ARD of 7.03%.

The chief conclusions are (1) that the rapid mass transfer of hindered amines is due to the formation of carbamate and the high pK_a of the amine, (2) the carbamate formation rate appears unimpeded by steric hindrance and is predicted by a Brønsted correlation, suggesting that hindered amines react in the same manner as unhindered amines.

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Nomenclature

2D NMR	2-dimensional NMR experiment (dimensionless)
2MPZ	2-methylpiperazine (dimensionless)
2PE	2-piperidineethanol (dimensionless)
A	wetted area (m ²)
AMP	2-amino-2-methylpropanol (dimensionless)
ARD	average relative deviation (%)
a_i	activity of i (dimensionless)
C_p	heat capacity at constant pressure (kJ/kg K)
$[CO_2]_T$	concentration of total CO ₂ (mol/m ³)
COSY	correlation spectroscopy (dimensionless)
D_{CO_2}	diffusion of CO ₂ (m ² /s)
D_{Am}	diffusion of amine and products (m ² /s)
DEA	diethanolamine (dimensionless)
DIPA	diisopropanolamine (dimensionless)
E	enhancement factor (dimensionless)
E_A	activation energy (kJ/mol)
E_D	diffusion activation energy (kJ/mol)
eNRTL	electrolyte non-random two liquid (dimensionless)
ESRK	Redlich-Kwong equation of state (dimensionless)
f_{CO_2}	fugacity of CO ₂ (Pa)
H_{CO_2}	Henry's constant for CO ₂ in solution (Pa m ³ /mol)
$H_{CO_2-H_2O}$	Henry's constant for CO ₂ in water (Pa)
HMBC	heteronuclear multiple bond correlations (dimensionless)
HSQC	hetero single quantum coherence (dimensionless)
k_{2PE}	reaction rate constant for the formation of bicarbonate (kmol/m ³ s)
$k_{2PE-2PE}$	reaction rate constant for the formation of carbamate (kmol/m ³ s)
K_g	overall mass transfer coefficient (mol/m ² s Pa)
k_g	gas film mass transfer coefficient (mol/m ² s Pa)
k'_g	liquid film mass transfer coefficient (mol/m ² s Pa)
$k'_{g,PFO}$	PFO liquid film mass transfer coefficient (mol/m ² s Pa)
k^0_l	physical liquid film mass transfer coefficient (m/s)
$k^0_{l,prod}$	the physical mass transfer of the products (m/s)
k_c	concentration-based reaction rate constant
k_{corr}	corrected value of reaction rate constant (kmol/m ³ s)
k_a	activity-based reaction rate constant (kmol/m ³ s)
k_D	reaction pre-exponential (kmol/m ³ s)
K_c	mole fraction, concentration-based carbamate stability constant (dimensionless)

K_{EQ}	reaction equilibrium constant (dimensionless)
k_f	forward rate of reaction (kmol/m ³ s)
k_r	reverse rate of reaction (kmol/m ³ s)
$k_{regressed}$	regressed value of reaction rate constant (kmol/m ³ s)
m	molality (mol solute/kg solvent)
MOR	morpholine (dimensionless)
n	overall reaction order
$\dot{n}_{CO_2,in}$	molar flow of inlet gas (mol/s)
$\dot{n}_{CO_2,out}$	molar flow of outlet gas (mol/s)
NRTL	non-random two liquid (dimensionless)
\hat{N}_i	predicted value (dimensionless)
N_i	experimental value (dimensionless)
\hat{N}_{CO_2}	predicted CO ₂ flux (mol/s m ²)
N_{CO_2}	experimental CO ₂ flux (mol/s m ²)
PCEs	property constant estimation system (dimensionless)
$P_{CO_2}^*$	equilibrium partial pressure of CO ₂ (Pa or kPa)
PFO	pseudo first-order (dimensionless)
PZ	piperazine (dimensionless)
R	gas constant (J/mol K)
r_{CO_2}	rate of reaction of CO ₂ (kmol/m ³ s)
T	temperature (K or °C)
VLE	vapor-liquid equilibrium (dimensionless)
V_m	molar volume (m ³ /kmol)
WWC	wetted-wall column (dimensionless)
x_i	mole fraction of i (dimensionless)
w_i	mass fraction of i (dimensionless)

Greek symbols

α	CO ₂ loading (mol CO ₂ /mol alk)
δ	chemical shift, dimensionless distance through liquid boundary layer (ppm)
ΔG	Gibbs free energy (J/mol)
$\gamma_{CO_2}^*$	asymmetric activity coefficient of CO ₂ (dimensionless)
γ_i	activity coefficient (dimensionless)
μ_i	viscosity of i (cP)
ρ_i	density of i , correlation coefficient (kg/m ³ , dimensionless)
\bar{v}	molar volume (m ³ /kmol)
σ	standard deviation (dimensionless)
$\tau_{i,j}$	eNRTL binary interaction parameter (dimensionless)

1. Introduction

Amine scrubbing has been proposed as a way to reduce carbon dioxide emitted from fossil-fuel power plants (Rochelle, 2009). One of the most important choices in designing an amine scrubber is what solvent to use. Initial research in this field focused on amines used for natural gas sweetening: monoethanolamine and piperazine-promoted methyldiethanolamine. Sterically hindered amines have been proposed both on their own (Bougie and Iliuta, 2012; Endo et al., 2011; Sartori and Savage, 1983) or in a blend (Li et al., 2013). Sterically hindered amines provide CO₂ capacity comparable to tertiary amines with kinetic rates a hundred times faster (Sartori and Savage, 1983).

However, the reason for fast kinetics has not been fully explained. Sartori and Savage (1983) hypothesized that low carbamate stability leads to more free amine, but this does not explain the intrinsic rate of reaction. Bosch et al. (1990) created a numerical model to fit 2-amino-2-methylpropanol (AMP) kinetic data at 25 °C, and showed that the termolecular

mechanism, AMP + H₂O + CO₂ ↔ AMPH⁺ + HCO₃⁻, proposed by Chakraborty et al. (1986) is insufficient to explain the rates. However, Bosch et al. (1990) were unable to explain the reaction rate trend with pK_a.

This paper shows that the hindered amine 2-piperidineethanol (2PE) forms carbamate and that this reaction explains mass transfer performance. 2PE is a hindered, secondary amine that is more thermally and oxidatively stable than MEA (Freeman, 2011; Voice, 2013). Compared to AMP, 2PE shows similar capacity with 1.5-times-faster mass transfer, despite its five-times-greater viscosity (Li, 2015). Also compared to AMP, 2PE is less thermally stable, but as oxidatively stable (Voice, 2013). As a secondary amine, 2PE can form nitrosamines, which are carcinogenic (Fine et al., 2014). A study of piperidine showed low ecotoxicity and ready biodegradability, but no work on 2PE was available (Eide-Haugmo et al., 2012).

Prior NMR studies reported no 2PE carbamate (Fernandes et al., 2012; Paul et al., 2009), but in this work 2PE carbamate has been quantified using a technique that previously quantified carbamate

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