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Thermodynamic and Mass Transfer Model of Carbon Dioxide Absorption into Aqueous 2-piperidineethanol

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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.

Keywords: separations; CO₂ capture; eNRTL ; wetted-wall column; hindered amine; carbamate stability

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, $\text{AMP} + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{AMPH}^+ + \text{HCO}_3^-$, 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-piperidinethanol (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 formation in AMP (Ciftja et al., 2014). These speciation data were used to build a thermodynamic and mass transfer model of concentrated, aqueous 8 molal 2PE. A variety of regression cases and sensitivity studies explain the contributions of kinetics and diffusivity to the observed mass transfer performance.

A greater understanding of 2PE contributes to a broader understanding of sterically hindered amines. The importance of hindered amines is recognized in two patents covering 2PE (Sartori and Leder, 1978a, 1978b), and furthermore, one commercial solvent, KS-1, is a hindered amine (Mimura et al., 1997).

2 Methods

2.1 Experimental Methods

2.1.1 Sample preparation

Amine solutions were prepared from 2-piperidineethanol (with purity ≥96%) supplied by TCI Europe and were used as received without further purification. Amine solutions were prepared with distilled water, and the resulting solution was 30 wt.% amine. The solutions were loaded with CO₂ (grade 5.0) supplied by AGA Gas (AGA Gas GmbH, Hamburg, Germany). The amine concentration was determined by acid-

base titration with 0.1M H₂SO₄ (Kim et al., 2008). Total CO₂ in the loaded samples was measured with BaCl₂ method (Ma'mun et al., 2005).

About 0.25 mL of loaded/unloaded solution was filled into 5 mm Wilmad® 527-PP-7 NMR tubes and a Coaxial Insert WGS-5BL was inserted with known 1,4-dioxane and deuterium oxide (D₂O). The tubes were weighed in a Mettler Toledo ME204 digital analytical balance with accuracy of ±0.0001g. About 10 mass % deuterium oxide (D₂O) was added to provide a field-frequency lock and the chemical shifts were referenced to 1,4-dioxane.

In order to identify the species formed in loaded and unloaded aqueous solutions, different techniques described by Ciftja et al. (2013) were used. First, qualitative analyses (¹H, ¹³C, COSY, HSQC and HMBC) were carried out to identify the species, and then quantitative ¹³C analyses were conducted to obtain the exact amount of each species formed in the systems. These experiments used special capillary tubes provided by Wilmad-Labglass for the mixture of 1,4 dioxane (99.9% purity) and deuterium oxide (99.8% purity) to avoid any dilution of the solvent.

The NMR spectra were recorded on a Bruker Avance DPX 400 MHz NMR spectrometer operating at a frequency of 100.62 MHz for ¹³C and 400.13 MHz for ¹H with a 5 mm DUAL ¹H/¹³C probe head. Experimental details on quantitative ¹³C NMR experiments and the estimated parameters are given by Ciftja et al. (2013). All spectra were measured at 25 °C with processing and integration done using MestReNova software V10.0.2.

The carbamate stability constant K_c was reported on a non-activity, mole fraction basis using Equation 1 to allow for comparison to other work (Perinu et al., 2014).

$$K_c = \frac{[2PECOO^-]}{[2PE][HCO_3^-]} \quad (1)$$

The reported value is the average of the lean and rich loading K_c values at 25 °C.

2.2 2PE Thermodynamic Model

The model was constructed in Aspen Plus® V8.4 using the asymmetric electrolyte non-random two-liquid (eNRTL) model for the liquid phase and ESRK for the vapor phase. The eNRTL model is an activity coefficient excess Gibbs free energy model with demonstrated capability to model highly non-ideal aqueous amine systems (Zhang et al., 2011). The following APV84 databanks were used in this order: PCD, Aqueous, Solids, Inorganic, and Pure28. The 2PE components were defined using AMP analogs based on the model of Li et al. (2014). AMP was chosen as it has similar carbamate stability. The aqueous Gibbs free energy of formation ΔG_{aq}° and the aqueous enthalpy of formation ΔH_{aq}° for the ions, 2PECOO⁻ and 2PEH⁺, and the Gibbs free energy of formation ΔG° and the enthalpy of formation ΔH° for the molecule 2PE were initialized at the values of AMP⁻, AMPH⁺, and AMP as listed in Table S1. 2PE was treated as a Henry's component with an ideal gas reference state. The reference state for water was pure (i.e., symmetric), while for the other species it was infinite dilution (i.e., asymmetric).

Equations 2 through 7 were the model chemistry. Equations 2 through 4 were used throughout the model, except for the pK_a regression. To regress pK_a , Equations 5 through 7 were used. Proton and hydroxide ions were not used throughout the model, as the magnitude of either mole fraction was less than 10^{-12} . Inclusion would have hindered convergence by creating a poorly scaled component matrix.

For each reaction, the mole-fraction, activity-coefficient-based equilibrium constant K_i was calculated using Equation 8.

$$K_i = \exp\left(-\frac{\Delta G_i}{RT}\right) \quad (8)$$

The available thermodynamic data are summarized in Table 1. The heat capacity data of Chiu et al. (2010) were not regressed as the measured 2PE concentration is significantly greater than 8 molal.

Table 1: 2PE Thermodynamic data

System	Type	# of data	T (°C)	Loading ($\frac{\text{mol CO}_2}{\text{mol alk}}$)	C_{Am}	Source
2PE	C_p	11	30–80	unloaded	100 wt. %	(Chiu et al., 2010)
		44			0.2–0.8 mol frac.	
2PE+H ₂ O	pK_a	5	15–60	unloaded	<0.1 M	(Xu et al., 1992)
2PE+H ₂ O+CO ₂	NMR	7	25	0–0.814	3.3 m	this work
	VLE	14	40–100	0.205–0.635	8 m	(Chen, 2011)

The ΔG_{aq}° and ΔH_{aq}° for 2PEH^+ were manually adjusted to fit the pK_a data (Xu et al., 1992). $\Delta G_{aq,2\text{PEH}^+}^\circ$ was set to fit the pK_a at 25 °C, and $\Delta H_{aq,2\text{PEH}^+}^\circ$ was set to fit the temperature dependence.

For the NMR data, ΔG_{aq}° and ΔH_{aq}° for 2PECOO^- were manually adjusted to minimize the absolute relative deviation (ARD) as defined by Equation 27. $\Delta G_{aq,2\text{PECOO}^-}^\circ$ was set to fit the measured

concentration at 25 °C. $\Delta H_{aq,2PECOO}^\circ$ was adjusted until the amount of carbamate decreased with increasing temperature. This decrease was expected as carbamate formation is an exothermic reaction. Attempts to estimate a value of $\Delta H_{aq,2PECOO}^\circ$ using AMP NMR data failed due to the narrow temperature range measured (Ciftja et al., 2014).

The activity coefficients γ_i of the species were correlated to fourteen VLE data (Chen, 2011) using the Aspen Plus® Data Regression System (DRS). The eNRTL model computes γ_i from the excess Gibbs energy which is comprised of long-range and short-range interactions along with a Born correction for the infinite dilution reference state (Chen and Song, 2004). Only the short-range interactions of molecule–salt (m,ca) and salt–molecule (ca,m) were regressed using the binary interaction term τ_{ij} of Equation 9.

$$\tau_{i,j} = C_{i,j} + \frac{D_{i,j}}{T} + E_{i,j} \left[\frac{T_{ref} - T}{T} + \ln \left(\frac{T}{T_{ref}} \right) \right] \quad (9)$$

Five parameters were used to fit the data: three $C_{ca,m}$ parameters ($2PEH^+, CO_3^{2-}$)/ H_2O , ($2PEH^+, CO_3^{2-}$)/ $2PE$, ($2PEH^+, HCO_3^-$)/ $2PE$, $D_{H_2O/(2PEH^+, HCO_3^-)}$, and $D_{(2PEH^+, HCO_3^-)/H_2O}$. The default for interactions for $m \neq H_2O$ was $C_{m,ca} = 10$ and $C_{ca,m} = -2$, while for $m = H_2O$ was $C_{m,ca} = 8$ and $C_{ca,m} = -4$. Regardless of the molecule, $D_{m,ca} = D_{ca,m} = 0$ was the default. These defaults are set by Aspen Plus® on the basis of the typical eNRTL values (Zhang and Chen, 2011).

2.3 2PE Mass Transfer Model

2.3.1 2PE Hydraulics

Table 2: 2PE hydraulic data

System	Type	# of data	T (°C)	Loading ($\frac{\text{mol CO}_2}{\text{mol alk}}$)	C_{Am} (wt.%)	Source
2PE+H ₂ O	ρ	60	15–60	unloaded	5–30	(Paul et al., 2006)
	μ	60			5–30	
	ρ	30	25–84.2		10–100	(Xu et al., 1992)
	μ	35	25–85.2		10–100	
2PE+H ₂ O+CO ₂	μ	4	40	0.205–0.684	45–49	(Chen, 2011)

Table 2 lists the available hydraulic data. The unloaded data are not applicable to the loaded solvent used in CO₂ capture. Only the loaded viscosity μ data were fit by regressing parameters $a-g$ of Equation 10.

$$\frac{\mu_{2PE}}{\mu_{H_2O}} = \exp \left\{ [(aw_{2PE} + b)T + cw_{2PE} + d] * [(ew_{2PE} + fT + g)\alpha + 1] * \frac{w_{2PE}}{T^2} \right\} \quad (10)$$

Fitting the change in viscosity with respect to loading is important for diffusion rates, which are shown later to be most significant at high loading and high temperature. As the four data points were at constant temperature and amine concentration, the parameters most correlated to loading, e and g , were regressed in MATLAB using `nlinfit`. All other parameters were left at the values of piperazine (PZ) (Frailie, 2014). As no loaded density data were available for 2PE, PZ parameters were used for Equation 11 (Frailie, 2014).

$$\rho_{2PE} = x_{H_2O}\rho_{H_2O} + x_{2PE}(aT + b) + x_{CO_2}(cT + d) + x_{CO_2}x_{2PE}(eT + f) \quad (11)$$

The use of PZ as a hydraulic basis is effective because of the wide range of data incorporated into the PZ correlations. Density is not a critical property for kinetic modeling or steady state operation, with the usage of density limited to the conversion of volumetric flow rates to mass flow rates. The impact on contact time in the WWC is negligible. Approximating the density of 2PE by that of PZ is expected to have a negligible impact on the results.

2.3.2 Diffusivity

The diffusion of CO_2 in solvent (m^2/sec) was assumed to follow Versteeg and van Swaaij (1988) (Equation 12).

$$D_{CO_2} = [2.35 \times 10^{-6} \exp(-2119/T)] \left(\frac{\mu_{water}}{\mu_{soln}} \right)^{0.8} \quad (12)$$

In the absence of loaded diffusion data, the diffusion of amine and products D_{Am} was estimated as one-half the value of D_{CO_2} . This expression gives very similar performance to the expression used by Chen and Rochelle (2013). A direct comparison of the two using the fourteen different temperature and loading WWC conditions of 8 m 2PE regressed yielded an ARD of 4.9%.

2.3.3 Flowsheet

Figure 1: WWC flowsheet

The Aspen Plus® Ratesep model shown in Figure 1 replicated the wetted wall column (WWC) used to collect the mass transfer data (Chen and Rochelle, 2011). During operation of the experimental apparatus, six flux points, three desorption and three absorption, were collected at each loading and temperature; details of the method are in Chen and Rochelle (2011). The model flowsheet used two absorber RADFRAC columns to simulate the greatest absorption and desorption fluxes of the six points. As these two points gave the greatest fluxes, there was less experimental error than for the lower flux points nearer equilibrium. Experimental fluxes ranged from -2.1×10^{-2} to -1.0×10^{-2} mol/m²-sec (Chen, 2011). The model flux is calculated by Equation 13.

$$\hat{N}_{CO_2} = \frac{\dot{n}_{CO_2,in} - \dot{n}_{CO_2,out}}{A} \quad (13)$$

Two flash blocks were used to calculate $P_{CO_2}^*$ of the rich and lean streams. The reproducibility of the WWC was estimated as 8.5% for the liquid-side mass transfer coefficient k'_g , and this value was applied to the flux as an estimate of experimental error (Li, 2015).

1 Bishnoi and Rochelle (2000) characterized the gas film resistance k_g , and Pacheco (1998) characterized
 2 the physical liquid film resistance k_l^0 . These resistances were used to interpret the experimental data
 3 and were also used in the model.

4 **2.3.4 Reaction Set**

5 The reactions were modeled with activities a_i and the termolecular mechanism (Crooks and Donnellan,
 6 1989), as exemplified by Equation 14.

$$-r_{CO_2} = k a_{CO_2} a_{Am} a_B \quad (14)$$

7 Only the most significant reactions were regressed; hence, H_2O and OH^- were neglected as bases. At
 8 50 wt.% 2PE, H_2O was outcompeted by 2PE (Li, 2015), and the concentration of OH^- was negligibly
 9 small. The reaction set comprised two elementary kinetic reactions, Equations 15 and 16, and one
 10 equilibrium reaction, Equation 17.

11 The equilibrium reaction was an instantaneous proton exchange and therefore calculated by Equation 8.
 12 Aspen Plus® calculated the mass transfer rates using Maxwell-Stefan equations (Krishna and Standart,
 13 1976). The kinetic reactions were each modeled as a pair of forward and reverse reactions, with the
 14 reverse reaction calculated from Equation 18 through a Fortran calculator block.

$$k_r = \frac{k_f}{K_{EQ}} \quad (18)$$

15 The rates were modeled by the Arrhenius power law of Equation 19 with $T_{ref}=313.15$ K.

$$k = k_0 \exp \left[-\frac{E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (19)$$

16 **2.3.5 Brønsted Correlation**

17 The rates of the kinetic reactions were estimated using a Brønsted correlation (Versteeg and van Swaaij,
 18 1988), which correlates the rate constant with the pK_a of the amine. k_0 of k_{2PE} was estimated by
 19 assuming that the bicarbonate-forming reaction for 2PE follows $\ln(k_{2PE}) = pK_a - 14.24 [=] \frac{m^3}{mol \cdot sec}$,
 20 which is the tertiary amine correlation by Versteeg and van Swaaij (1988). First the concentration-based
 21 k_2 ($m^3/mol \cdot sec$) was found using the pK_a at 20 °C and then converted to an activity-basis at 40 °C and a
 22 loading of 0.537 mol CO_2/mol alkalinity using Equation 20 with $n=2$. (A derivation of Equation 20 is
 23 included in the supplementary materials.)

$$k_a = \frac{k_c \bar{\rho}^n}{\gamma_{2PE}^{n-1} \gamma_{CO_2}^*} \quad (20)$$

E_A was assumed to be the same as that of MDEA as measured by Ko and Li (2000). Following a similar procedure for the carbamate-forming reaction but using the termolecular ($n = 3$) Brønsted correlation at 25 °C $\log(k_{2PE-2PE}) = 1.3pK_a - 7.83 [=] \frac{m^6}{kmol^2 \cdot sec}$ (Chen and Rochelle, 2013), the k_0 of $k_{2PE-2PE}$ was estimated.

An alternate correlation was developed using the regressed value for the analogous carbamate reaction in the PZ model developed by Frailie (2014). The same slope of 1.3 was assumed and a new intercept was found using the activity-based k_0 at 40 °C yielding $\log(k_0) = 1.3pK_a - 2.34$. By using a 40 °C value in a 25 °C correlation, equivalent activation energies were assumed for each amine. For both cases, E_A was set to 35 kJ/mol based on literature (Bishnoi and Rochelle, 2000; Cullinane, 2005). The predicted values are summarized in Table 3.

Table 3: Predicted activity-based kinetic parameters ($T_{ref} = 313.15$ K)

k_i	Equation	k_0 (kmol/sec-m ³)	E_A (kJ/mol)	k_0 Basis
$k_{2PE-2PE}$	15	1.31E+10	35.0	Brønsted (Chen and Rochelle, 2013)
		6.95E+10		PZ-Brønsted (Frailie, 2014)
k_{2PE}	16	4.23E+04	44.9	Brønsted (Versteeg and Swaaij, 1988)

2.3.6 Kinetic Parameter Regression

In order to determine the effect of carbamate on mass transfer, nine different ways of fitting the data were explored as listed in Table 4, where $k_{2PE-2PE}$ is the forward rate constant of Equation 15, k_{2PE} is the forward rate constant of Equation 16, K_c is the carbamate stability constant, Brønsted means the rate was set to the value predicted by the Brønsted correlation, and PZ-Brønsted means it was set to the value predicted from the Brønsted correlation with the intercept calculated from PZ. For cases where K_c was set, it was set at the experimentally determined value as presented in the Thermodynamic Results section. For cases where K_c was regressed, the amount of carbamate was forced to decrease with increasing temperature at a similar rate to cases where K_c was not regressed.

1

Table 4: Mass transfer test matrix

Case	K_c	k_{2PE}	$k_{2PE-2PE}$	% ARD
1	regress	Brønsted	Brønsted	13.4
2			PZ-Brønsted	24.1
3			regress	12.1
4			instantaneous	49.6
5	—	regress	—	11.3
6	set	Brønsted	regress	18.0
7		regress	regress	7.03
8			Brønsted	7.36
9			PZ-Brønsted	18.2

2 For each case, the twenty-four strongest absorption and desorption fluxes spanning 40 to 100 °C and
3 0.20 to 0.70 mol CO₂/mol alkalinity were fit (Chen, 2011).

4 **2.3.6.1 Film Discretization**

5 Ratesep uses film theory to describe the mass transfer, wherein the liquid close to the gas-liquid
6 interface is divided into many discrete slices with heat and mass transfer calculations done in each slice.
7 32 discretization points were used as given in Table S2.

8 **2.3.6.2 Loading Adjustment**

9 For each loading and temperature, the loading was adjusted to ensure zero flux at zero driving force per
10 Frailie (2014). This adjustment accounts for both experimental error as well as error in the
11 thermodynamic model. This adjustment was run simultaneously with the kinetic parameter regression.

12 **2.3.7 Kinetic Analysis**

13 To examine how the model performs under process-scale absorber conditions, the relative gas film
14 resistance k_g was calculated across loading and temperature. The effect of k_l^0 on k_g' at a fixed loading
15 and at various temperatures was also calculated. The overall gas-side mass transfer K_g is represented by
16 Equation 21.

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{1}{k_g'} \quad (21)$$

17 k_g' comprises reaction and diffusion resistances as defined by Equation 22 (Sachde, 2016).

$$\frac{1}{k'_g} = \frac{H_{CO_2}}{Ek_l^0} + \frac{1}{k_{l,prod}^0} \left(\frac{\partial P_{CO_2}^*}{\partial [CO_2]_T} \right) \quad (22)$$

1 The reaction resistance is represented by the first term. As shown later, this resistance dominates at low
 2 temperature and low loading, where the concentration of species in the liquid boundary layer is nearly
 3 equal to the concentration in the bulk liquid. Under these conditions, the system is in the pseudo first-
 4 order (PFO) regime. In the PFO regime, k'_g is represented by Equation 23 (Chen and Rochelle, 2013).

$$k'_{g,PFO} = \frac{\sqrt{D_{CO_2} k [Am]^2 \gamma_{Am}^2}}{\gamma_{CO_2}^{0.5} H_{CO_2-H_2O}} \quad (23)$$

5 Converting Equation 23 from a concentration basis to a mole-fraction basis yields Equation 24,

$$k'_{g,PFO} = \frac{\sqrt{D_{CO_2} (k_{2PE-2PE} a_{2PE}^2 + k_{2PE} a_{2PE} a_{H_2O}) / V_m}}{\gamma_{CO_2}^{0.5} H_{CO_2-H_2O}} \quad (24)$$

6 This expression was compared to the expression of Equation 22 to determine whether or not the WWC
 7 operates in PFO .

8 The sensitivity of k'_g to the reaction rate constants, D_{CO_2} , D_{Am} , μ , and $k_{l,0}$ for all species was quantified by
 9 using a central difference to approximate the derivative. Each variable was changed $\pm 5\%$ for each point.

10 The rate constant of the carbamate reaction was compared to other cyclic secondary amines to
 11 determine if 2PE obeyed the Brønsted correlation. In order to do so, the rate constant was corrected
 12 using Equation 25 to account for an artificial dependence of k'_g on the diffusion of the amine (Chen and
 13 Rochelle, 2013).

$$k_{corr} = \sqrt{\left(\frac{D_{Am}}{D_{CO_2}} \right)} k_{regressed} \quad (25)$$

14 D_{Am} of 2PE was compared to other solvents to determine if the diffusivity was correlated with viscosity.
 15 To determine how strong a function of temperature diffusivity was, the diffusion activation energy E_D of
 16 2PE was calculated using an Arrhenius plot and Equation 26.

$$E_D = -R \frac{\ln D_{Am}}{1/T} \quad (26)$$

17 3 Results

18 3.1 NMR Experimental Results

The reaction between CO₂ and aqueous 2-piperidineethanol (2PE) at two different CO₂ loadings (mol CO₂/mol alkalinity) was studied at 25 °C. The potential species formed in CO₂ loaded 2PE solution are 2PE, 2PEH⁺, and 2PECOO⁻. The molecular structure of the main species are shown in Figure 2. In addition, the following species are present: H₂O, H₃O⁺, OH⁻, CO₂, HCO₃⁻, and CO₃²⁻. Amine/protonated amine and bicarbonate/carbonate, both of which involve proton transfer have very rapid reaction rates with very small relaxation times. Therefore the ¹³C NMR will average the peaks for these species (Ciftja et al., 2013).

Figure 2: Speciation in loaded aqueous solution of 2-piperidineethanol (2PE).

NMR spectra were acquired to identify any new species in the system. Figure 3 shows a quantitative ¹³C NMR spectra for unloaded aqueous solution (red spectra) and CO₂ loaded aqueous solution of 2PE (blue and green spectra) at 25 °C. The chemical shift for the system is in the range $\delta = 10$ -170 ppm. Seven signals that belong to the 2PE/2PEH⁺ peaks are in the unloaded solution (red spectra, Figure 3).

2PE forms carbamate when CO₂ is introduced into the solution. At 0.138 mol CO₂/mol alkalinity new peaks (labeled with primed numbers, Figure 3) were observed and assigned to carbamate and confirmed from 2D NMR experiments. Prior NMR studies reported no carbamate as they used dilute 2PE (Fernandes et al., 2012; Paul et al., 2009).

The carbonate/bicarbonate peak appears at $\delta = 163.93$ ppm and, with increased loading, shifts to lower frequencies ($\delta = 162.99$ ppm) due to the increased acidity of the system. The chemical shifts in ppm for all the species in the unloaded/loaded aqueous 2PE systems at 25 °C are given in Table S3 in the Supporting Information.

Figure 3: Quantitative ^{13}C NMR spectra for 30 wt. % 2PE- CO_2 - H_2O system at 25 °C.

Table 5 gives the liquid phase speciation for aqueous 2PE calculated directly from the species concentrations obtained by NMR. The reaction products are predominately the bicarbonate species. Thus, the bicarbonate/carbonate levels increase with CO_2 loading whereas the amine/protonated amine levels remain more or less constant (Table 5).

Table 5: NMR speciation (mole fraction) for 30 wt.% 2-PE/ CO_2 / H_2O system at 25 °C.

Loading (mol CO_2 /mol alk)	$x_{2\text{PE}/2\text{PEH}^+}$	$x_{2\text{PECO}_2^-}$	$x_{\text{HCO}_3^-/\text{CO}_3^{2-}}$
0.00	6.22E-04	0.00E+00	0.00E+00
0.138	6.42E-04	1.29E-05	3.89E-05
0.814	6.13E-04	2.73E-05	2.47E-04

3.2 2PE Thermodynamic Results

Table 6 lists the thermodynamic data incorporated, which are pK_a , NMR, and VLE.

The average relative deviation (ARD) as defined by Equation 27 is used to quantify the goodness of fit.

$$\text{ARD} (\%) = \frac{100}{N} \sum_N \frac{|\hat{N}_i - N_i|}{N_i} \quad (27)$$

Table 6: Thermodynamic data and fit

Data	[2PE]	T	Loading	Data	ARD	Source
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type		(°C)	(mol CO ₂ /mol alk)	points	(%)	
pK _a	<0.1 M	15– 60	—	5	0.26	(Xu et al., 1992)
NMR	3.3 m	25	0– 0.814	7	2.39	this work
VLE	8 m	40– 100	0.199– 0.695	14	0.84	(Chen, 2011)

To fit the five pK_a data points (Xu et al., 1992), the two parameters of 2PEH⁺ were found to be: $\Delta G_{aq}^{\circ} = -1.77 \times 10^8$ J/kmol and $\Delta H_{aq}^{\circ} = -4.02 \times 10^8$ J/kmol. To fit the NMR data points, the two parameters of 2PECOO⁻ were found to be: $\Delta G_{aq}^{\circ} = -4.66 \times 10^8$ J/kmol and $\Delta H_{aq}^{\circ} = -7.64 \times 10^8$ J/kmol. As the measurements were done at 3.3 m and the mass transfer regression was done at 8 m, there is an assumption that the activity coefficients are well behaved across this concentration range. To check this assumption, log K_c was computed at both concentrations at 40 °C and 0.51 mol CO₂/mol alk. At 3.3 m, log K_c is 1.0 while at 8 m log K_c is 0.90. While there is a discrepancy, this does not impact the conclusions from the model. The parameters of 2PE were left at the initial AMP-derived values of $\Delta G^{\circ} = -0.847 \times 10^8$ J/kmol and $\Delta H^{\circ} = -2.70 \times 10^8$ J/kmol.

This fit resulted in a K_c that changed from 0.90 at 40 °C to 0.42 at 100 °C. Examining other eNRTL thermodynamic models at 20 °C and 100 °C showed a relative molality-based decrease in the maximum concentration of carbamate of 10% and 12% for models of MEA and 2MPZ (Chen, 2011; Plaza, 2011). For AMP, this decrease is 39% from a model incorporating NMR data (Ciftja et al., 2014) based on the AMP model of Li et al. (2014). For 2PE, this decrease is 51%.

To check the model sensitivity to the chosen value of $\Delta H_{aq,2PECOO^-}^{\circ}$, case 7 of Table 4 was repeated with the same relative decrease as AMP. The resulting reaction parameter values were within 2%, except for a 12% decrease in k_0 of k_{2PE} .

The VLE data were fit by the parameters shown in Table 7.

Table 7: VLE parameters

Parameter	Species	Value	σ
$C_{ca,m}$	(2PEH ⁺ , CO ₃ ²⁻)/H ₂ O	- 5.27	0.03
$C_{ca,m}$	(2PEH ⁺ , CO ₃ ²⁻)/2PE	- 4.75	0.11
$C_{ca,m}$	(2PEH ⁺ , HCO ₃ ⁻)/2PE	- 3.45	0.05
$D_{m,ca}$	H ₂ O/(2PEH ⁺ , HCO ₃ ⁻)	- 1096	60
$D_{ca,m}$	(2PEH ⁺ , HCO ₃ ⁻)/H ₂ O	648	32

Non-regressed binary interaction parameters were left at default or set to analogous values from an AMP model (Li et al., 2014).

Figure 4 shows the thermodynamic model, the experimentally measured data, and the loading adjusted data. The loading range for coal conditions is approximately $P_{CO_2}^* = 0.5$ to 5 kPa at 40 °C, which is 0.37–

1 0.68 mol CO₂/mol alk (Chen and Rochelle, 2011; Frailie, 2014). The VLE fit between these bounds is most
2 important for predicting mass transfer performance in the full-scale process.

3
4 **Figure 4: VLE of 8 m 2PE; lines are predictions at 20 °C intervals, solid points are WWC VLE**
5 **from Chen (2011); open points are loading adjusted VLE.**

6 The differential heat of absorption is predicted from the VLE using the thermodynamic relationship of
7 Equation 28, a modification of the Gibbs-Helmholtz equation (Li et al., 2014; Mathias and O'Connell,
8 2012).

$$\Delta H_{abs} = RT^2 \left(\frac{\partial \ln f_{CO_2}}{\partial T} \right)_{P,x} \quad (28)$$

9 The predictions of Figure 5 are generated by applying Equation 28 to the VLE. As expected, no
10 temperature inflection is observed, indicating the thermodynamic dominance of one reaction across the
11 whole loading range. The good behavior of the predicted curves indicates that the model behavior in
12 general is trustworthy. The rapid drop in ΔH_{abs} at 120 °C is due to the high partial pressure of CO₂,
13 resulting in the CO₂ being physically absorbed as free CO₂. Across typical absorber loading and
14 temperature conditions, ΔH_{abs} of both AMP (Li et al., 2014) and 2PE show little loading dependence,
15 with ΔH_{abs} of 2PE being less than 5 kJ/mol.

Figure 5: 8 m 2PE predicted $-\Delta H_{\text{abs}}$ at 20 °C increments using Equation 28

The speciation predicted by the model at 40 °C is shown in Figure 6 and compared to data in Figure 7. Using the model predictions for loadings corresponding to 0.5 and 5 kPa CO₂ at 25 °C, the concentration-based mole fraction $\log K_c$ was calculated from Equation 1. For 2PE, this is 1.08, which is greater than AMP, whose value is 0.56 (Ciftja et al., 2014). Thus, the carbamate of 2PE is more stable than that of AMP. This difference may be attributable to the greater pK_a of 2PE than AMP (Li, 2015; McCann et al., 2011).

Figure 6: 8 m 2PE speciation prediction at 40 °C

Figure 7: Model predictions (lines) at 30 wt.% 2PE and 25 °C compared to data (points)

The species activity coefficients are shown in Figure 8.

Figure 8: 8 m 2PE activity coefficient prediction at 40 °C

3.3 2PE Mass Transfer Results

3.3.1 Hydraulics

Figure 9 shows that the viscosity correlation using the parameters of Table 8 fit the viscosity data (ARD = 0.36%) and give reasonable temperature behavior. As expected, the two regressed parameters are tightly correlated ($\rho = -99.9$). The unregressed parameters were fixed at the PZ value as this ensures a well behaved correlation due to the extensive data fit by the PZ correlation (Frailie, 2014). The temperature dependence predicted for 2PE is similar to that observed in 40 wt.% MEA and 44 wt.% 2MPZ (Chen, 2011; Plaza, 2011). As will be shown later, the mass transfer becomes more dependent on diffusion than reaction rate at higher temperatures and loadings, and as the liquid species diffusion depends on viscosity to the 0.8 power, the temperature behavior of viscosity impacts the mass transfer regressions at these conditions.

1

Table 8: 2PE viscosity parameters for Equation 10

Parameter	2PE (PZ)	95% CI
a	912	—
b	1890	—
c	968	—
d	1.39E-05	—
e	-1.13 (9.46)	[-2.20,-0.053]
f	5.40	—
g	2.81 (- 0.158)	[2.31, 3.31]

2

Figure 9: 8 m 2PE viscosity predictions at 20 °C intervals; points are data from Chen (2011).

With no CO₂ loaded density data available for 2PE, the parameters were equated to those of PZ as listed in Table 9 (Frailie, 2014). This gives very similar performance to PZ. The density correlation is shown in Figure 10.

7

Table 9: 8 m 2PE density parameters of Equation 11

Parameter	Value
a	-0.002
b	1.99
c	0.002
d	1.98
e	-0.010
f	0.303

8

Figure 10: Density prediction of 8 m 2PE at 20 °C intervals

3.3.2 Kinetic Parameter Regression

The cases of Table 4 were run until the best fit was achieved. These cases can be interpreted by considering how the dominant mass transfer phenomena change with loading and temperature.

As cases 1 through 4 regressed parameters related to carbamate, these cases only fit where carbamate is significant. As the fit of case 3 is representative of these four cases, it is shown in Figure 11. All of these cases underpredict N_{CO_2} at high loading or high temperature, indicating that carbamate is not significant at these conditions. Case 4 with the instantaneous carbamate reaction overpredicted the flux for all 40 and 60 °C points (average ratio of predicted to experimental flux is 1.68) and underpredicted the flux for 80 and 100 °C points (average ratio of predicted to experimental flux is 0.78), illustrating the change from kinetic-controlled to diffusion-controlled mass transfer. In all cases, increasing K_c increased flux as more CO₂ would form carbamate before reaching equilibrium.

Without carbamate in the model, Figure 12 shows that case 5 has a bias in the fit of the 40 and 60 °C, meaning case 5 cannot fit the full loading range. As Figure 12 overpredicts at high loading, the bicarbonate is more significant there.

Cases 7 and 8 are able to fit the data across the full temperature and loading range as shown by Figure 13 and Figure 14. They are able to fit the full range because the reactions are significant at different loading and temperature ranges. Cases 1 through 4 illustrated that carbamate is significant at 40 and 60 °C for all loading, while case 5 showed that bicarbonate was significant at 40 and 60 °C at high loading and for all of the 80 and 100 °C conditions. That case 7 is a marginal improvement over case 8 shows that 2PE obeys the Brønsted prediction for the carbamate reaction.

Case 9, as with case 4, overpredicts where the carbamate reaction is significant, indicating that the carbamate rate is overpredicted by the PZ-Brønsted correlation. Case 9 fits better than case 4 by adjusting the bicarbonate reaction rate and better fitting the 80 and 100 °C data.

1 Figures 11–14 show no difference between the desorption and absorption points due to the loading
 2 adjustment.

3
 4 **Figure 11: 8 m 2PE predicted flux ratioed to experimental flux (Chen, 2011) for case 3; ■ 40 °C,**
 5 **● 60 °C, ▲ 80 °C, ◆ 100 °C; shaded region indicates experimental error.**

6
 7 **Figure 12: 8 m 2PE predicted flux ratioed to experimental flux (Chen, 2011) for case 5; ■ 40 °C,**
 8 **● 60 °C, ▲ 80 °C, ◆ 100 °C; shaded region indicates experimental error.**

1

2

3 Figure 13: 8 m 2PE predicted flux ratioed to experimental flux (Chen, 2011) for case 7; ■ 40 °C,
 4 ● 60 °C, ▲ 80 °C, ◆ 100 °C; shaded region indicates experimental error.

5

6 Figure 14: 8 m 2PE predicted flux ratioed to experimental flux (Chen, 2011) for case 8; ■ 40 °C,
 7 ● 60 °C, ▲ 80 °C, ◆ 100 °C; shaded region indicates experimental error.

At low loading with plentiful free amine, the carbamate reaction is most important; whereas at high loading the free amine has been depleted, and the bicarbonate reaction becomes more important than the carbamate reaction.

The adjusted loading for case 7 is shown in Table 10 and Figure 4, where the most significant adjustments occur at lean 40 °C points. The low loading, low temperature data have less flux for both desorption and absorption, and so are more susceptible to experimental error. The higher loading, higher temperature data have more flux, and so experimental error decreases. Additionally, error in loading will also have greater impact at low loading due to the greater slope of the equilibrium curve, as seen in Figure 4.

Table 10: Loading adjustment for case 7 compared to data (Chen, 2011)

T (°C)	Loading		Relative loading adjustment (%)
	exp. (mol CO ₂ /mol alk)	adjusted	
40	0.205	0.146	-21
60	0.202	0.211	4.2
80	0.215	0.222	3.1
100	0.199	0.208	3.8
40	0.36	0.296	-9.1
60	0.367	0.391	6.3
80	0.375	0.363	-3.9
100	0.36	0.358	-0.80
60	0.524	0.532	1.0
80	0.525	0.487	-8.5
40	0.684	0.679	2.5
60	0.695	0.685	-2.5

The estimated rate constants and the results of the four best fitting cases from Table 4 are presented in Table 11 and shown in Figures 11–14. For case 7, E_A of $k_{2PE-2PE}$ could not be fit with statistical significance, and so it was fixed. Comparing the regressed values to those predicted from Brønsted correlations shows that the bicarbonate rate constant is underpredicted by the correlation, whereas the carbamate rate constant was predicted well.

The bicarbonate rate is surprisingly greater than the correlation, as this suggests that 2PE does not form bicarbonate using the same mechanism as a tertiary amine, which is the base-catalyzed hydration of

- 1 CO₂. Speculatively, this could be due to primary and secondary amines catalyzing the hydration of CO₂
- 2 faster than tertiary amines.

1

2

Table 11: 8 m 2PE kinetic parameters;* mole-fraction, concentration-based at 0.51 mol CO₂/mol alk 40 °C

Case	$k_{2PE-2PE}$				k_{2PE}				ARD	
	k_0 (kmol/sec-m ³)		E_A (kJ/mol)		k_0 (kmol/sec-m ³)		E_A (kJ/mol)		log K_c^*	(%)
	Value	σ	Value	σ	Value	σ	Value	σ		
Brønsted	1.31E+10	—	35.0	—	4.23E+04	—	44.9	—		—
PZ- Brønsted	6.95E+10	—	35.0	—	4.23E+04	—	44.9	—		—
7	1.10E+10	1.72E+08	35.0	at bound	8.48E+05	8.78E+04	50.1	2.43	0.90	7.03
8	1.31E+10	—	35.0	—	3.83E+05	3.76E+04	64.4	2.34	0.90	7.36
5	—	—	—	—	3.07E+08	4.05E+06	35.0	0.63	—	11.3
3	5.04E+09	2.69E+03	90.0	0.850	4.23E+04	—	44.9	—	1.6	12.1

Figure 15 shows the fit of k'_g for case 7. There are two effects of temperature on k'_g . The primary effect is a decrease in k'_g as temperature increases due to the change in the slope of the equilibrium curve in term two of Equation 22. This change in slope is why the decrease in k'_g is more severe when moving from 80 °C to 100 °C rather than the other 20 °C increments shown. The secondary effect is the non-monotonic temperature trend of k'_g , wherein there is an increase moving from 40 °C to 60 °C, but above that temperature k'_g decreases. This effect makes physical sense as moving from 40 °C to 60 °C the reaction rate increases, and above 60 °C, while the reaction rate continues to increase, diffusion becomes controlling and limits mass transfer above 60 °C.

The experimental data do not show this secondary effect. This is because the difference between 40 °C and 60 °C is within the estimated experimental error of 8.5% for all but the leanest loading, which has a higher experimental error (Chen and Rochelle, 2013). This non-monotonic trend is seen in other hindered amines. For 2MPZ, the model predicts a non-monotonic trend that is not seen in the data (Chen and Rochelle, 2013), while the trend is seen in the data of AMP (Chen, 2011).

As for the two non-regressed points of Figure 15, the second-highest loading 40 °C point does not follow the trend of the other three 40 °C points. The reported desorption flux for this point does not follow the expected order as it is greater than the highest loaded 40 °C desorption flux (Chen, 2011). The highest loading 80 °C point was excluded because the WWC was not operated in the absorption mode, making the loading adjustment calculation impossible. That this point is predicted by the model further validates the model.

Figure 15: 8 m 2PE k'_g predictions for case 7 (lines) at $P_{CO_2} = 0.5P_{CO_2}^*$ and data (points); open points not regressed (Chen, 2011).

3.3.3 Kinetic Analysis

Figure 16 and Figure 17 show the sensitivity of k'_g for case 7. These two figures allow for a comparison of the mass transfer variables at 40 °C and 100 °C. At 40 °C the single most significant variable is $k_{2PE-2PE}$,

indicating that kinetics are the most important mass transfer resistance (term one of Equation 22). While at 100 °C, the single most significant variable is k_l^0 , which as all species k_l^0 was varied includes $k_{l,prod}^0$. This significance indicates that the diffusion resistance is most important, term two of Equation 22. k_l^0 in the first term is less significant as CO₂ is less sensitive to k_l^0 than the products. The high sensitivity to $k_{2PE-2PE}$ at 40 °C demonstrates the necessity of modeling the carbamate reaction and not just the bicarbonate reaction. In fact, a reasonable fit at 40 °C could be obtained ignoring the bicarbonate reaction. The increasing sensitivity to k_l^0 shows that the PFO assumption breaks down at high loadings, as is corroborated by Figure 18.

Figure 16 and Figure 17 confirm what was seen by the different regression cases. Cases 1 through 4 corroborate the dominance of the carbamate reaction as seen in Figure 16. Case 5 corroborates that the bicarbonate reaction is more important than the carbamate reaction as seen in Figure 17. As D_{Am} was not regressed, the cases could not show that at high temperature and high loading, D_{Am} is the most important contribution to mass transfer.

The observed sensitivity to D_{Am} at 40 °C is not predicted by two-film theory. The equal dependence on D_{Am} and D_{CO_2} is a result of how Aspen Plus® handles the forcing of the half-order dependence of k'_g on D_{CO_2} per penetration theory as shown in Equation 24.

Figure 16: Sensitivity of k'_g at 40 °C for case 7 at $P_{CO_2} = 1.1 P_{CO_2}^*$

Figure 17: Sensitivity of k'_g at 100 °C for case 7 at $P_{CO_2} = 0.5P_{CO_2}^*$

Figure 18 expands on the PFO assumption of Equation 24 by showing how closely it matches the model predictions at 40 and 100 °C. The mass transfer is not in the PFO regime at 100 °C; at this temperature, diffusion cannot keep pace with the rate of reaction. At 40 °C, $k'_g \approx k'_{g,PFO}$. At 100 °C, the rate of reaction is nearly instantaneous, but, as Figure 17 shows, k'_g is still sensitive to the kinetics, indicating that the rate of reaction is not instantaneous.

Figure 18: Mechanisms of CO₂ absorption for case 7 at $P_{CO_2} = 1.1P_{CO_2}^*$, k'_g by model (solid), $k'_{g,PFO}$ by Equation 24 (dashed), and k'_g at instantaneous conditions (dotted)

Figure 19 shows that the carbamate reaction rate for 2PE obeys the Brønsted correlation. The regressed rate was corrected using Equation 25. While Figure 19 shows that the reaction rate of 2PE is faster than PZ, the overall rate of mass transfer in 8 m PZ as measured using the same apparatus is faster by a factor of 2.5 at 40 °C (Chen and Rochelle, 2011). Possibly this could be due to the accumulation of 2PE carbamate at the interface leading to a decrease in the net forward rate. This accumulation explains why the 40 °C curve of Figure 18 is not completely in the PFO regime. Due to the low K_c of 2PE compared to PZ, this accumulation of carbamate would be more problematic in 2PE than in PZ. Figure 19 compares the formation of the monocarbamate only, while PZ can also form a dicarbamate. A comparison of the rate of PZ dicarbamate formation and PZ carbamate formation shows that the dicarbamate formation rate is less than 5% that of the carbamate formation rate (Frailie, 2014).

Figure 19: Brønsted plot at 25 °C for the concentration-based carbamate reaction of amines (Chen and Rochelle, 2013) for case 7

The diffusion activation energy E_D for solvents at zero and rich loading are compared in Table 12. There is a moderate linear correlation ($R^2 = 0.74$) between activation energy and viscosity, $E_D = 0.78\mu + 20$, as suggested by Chen and Rochelle (2013). As previously discussed, D_{Am} is significant at rich loading at low temperature and at all loadings at high temperatures. For this reason, further research into loaded D_{Am} is suggested.

Table 12: Diffusion activation energy as calculated by Equation 26

Amine	Molarity	Loading	μ at 60 °C	E_D	Source
	(M)	$\left(\frac{\text{mol CO}_2}{\text{mol alk}}\right)$	(cP)	(kJ/mol)	
2PE	3.93	0	5.07	22.9	this work
	3.52	0.68	11.88	29.6	
2MPZ	4.5	0	4.1	25.6	(Chen & Rochelle, 2013)
	4.4	0.35	12.6	27.9	
MDEA	1	0	0.6	17.8	(Snijder et al, 1993)
	4	0	2.3	23.1	
PZ	4.74	0	3.01	20.97	(Frailie, 2014)
	4.07	0.39	6.26	27.62	

The contribution of gas film resistance in the WWC to the overall mass transfer in partial pressure units is shown in Figure 20. As the temperature increases, the contribution of k_g decreases, with the sharpest drop between 80 and 100 °C. In the operational loading range of 0.37–0.68 mol CO₂/mol alkalinity at process-scale absorber conditions, the contribution of k_g drops from 25% to 7%. At stripper conditions, k_g does not contribute significantly.

Figure 20: Relative gas film resistance in 8 m 2PE at $P_{CO_2} = 1.1P_{CO_2}^*$ for case 7

In Figure 21, the WWC is in PFO when the curve is a flat line. As temperature increases, the applicability of PFO starts at greater values of k_l^0 and holds for a smaller range of k_l^0 . Typical k_l^0 values for 2PE in the WWC fall between 4×10^{-6} and 8×10^{-5} m/sec. Contactors can span a wide range of k_l^0 , with structured packing in a process-scale absorber having similar values to the WWC and laminar jet having much greater values. The significance of k_l^0 on k_g' increases at higher loading and temperature, as seen in Figure 16 and Figure 17.

Figure 21: k'_g vs k_l^0 in 8 m 2PE at 0.53 mol CO_2 /mol alkalinity and $P_{CO_2} = 1.1P_{CO_2}^*$ for case 7

4 Conclusions

1. k'_g is most sensitive to the carbamate reaction and nearly insensitive to the bicarbonate reaction, proving the need to model the carbamate reaction to fit the performance data for the sterically hindered amine.
2. The carbamate reaction rate constant is in line with the carbamate reaction rate constants of three unhindered cyclic secondary amines from the Brønsted correlation.
3. 2PE forms a more stable carbamate ($\log K_c=1.08$) than AMP ($\log K_c=0.56$).
4. The bicarbonate reaction rate surprisingly is an order of magnitude greater than predicted by the Brønsted correlation for tertiary amines.
5. The PFO assumption applies to the WWC for increasingly higher k'_l 's and for less of a range as temperature increases.
6. The PFO assumption applies at 40 °C up to a loading of 0.60 mol CO₂/mol alk but not at greater temperature or loading.
7. The activation energy of the diffusion of amine-products is moderately correlated ($R^2=0.74$) with viscosity.

This work demonstrates the importance of accounting for the carbamate reaction in 2PE and more broadly for all hindered amines. Thus, for solvents blending a hindered amine with a rate promoter, modeling the hindered amine carbamate reaction is necessary to model the mass transfer performance. The model created by this work can be used for process modeling and design of a full-scale absorber and stripper. Fruitful research opportunities presented by this work include more loaded viscosity measurements as well as temperature-variable NMR measurements. The viscosity measurements would allow for more accurate diffusion coefficients, while the NMR measurements would validate the temperature dependence of K_c .

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4.2 Nomenclature

Term	Definition	Units
2D NMR	2-Dimensional NMR experiment	—
2MPZ	2-methylpiperazine	—
2PE	2-piperidineethanol	—
A	wetted area	m ²
AMP	2-amino-2-methylpropanol	—

ARD	average relative deviation	%
a_i	activity of i	—
C_p	heat capacity at constant pressure	kJ/kg-K
$[CO_2]_T$	concentration of total CO_2	mol/m ³
COSY	correlation spectroscopy	—
D_{CO_2}	diffusion of CO_2	m ² /sec
D_{Am}	diffusion of amine and products	m ² /sec
DEA	diethanolamine	—
DIPA	diisopropanolamine	—
E	enhancement factor	—
E_A	activation energy	kJ/mol
E_D	diffusion activation energy	kJ/mol
eNRTL	electrolyte non-random two liquid	—
ESRK	Redlich-Kwong equation of state	—
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	—
HSQC	hetero single quantum coherence	—
k_{2PE}	reaction rate constant for the formation of bicarbonate	kmol/m ³ - sec
$k_{2PE-2PE}$	reaction rate constant for the formation of carbamate	kmol/m ³ - sec
K_g	overall mass transfer coefficient	mol/m ² -sec-Pa
k_g	gas film mass transfer coefficient	mol/m ² -sec-Pa
k'_g	liquid film mass transfer coefficient	mol/m ² -sec-Pa
$k'_{g,PFO}$	PFO liquid film mass transfer coefficient	mol/m ² -sec-Pa
k_l^0	physical liquid film mass transfer coefficient	m/sec
$k_{l,prod}^0$	the physical mass transfer of the products	m/sec
k_c	concentration-based reaction rate	
k_{corr}	corrected value of reaction rate constant	kmol/m ³ -sec
k_a	activity-based reaction rate	kmol/m ³ -sec
k_0	reaction pre-exponential	kmol/m ³ -sec

K_c	mole fraction, concentration-based carbamate stability constant	—
K_{EQ}	reaction equilibrium constant	—
k_f	forward rate of reaction	kmol/m ³ -sec
k_r	reverse rate of reaction	kmol/m ³ -sec
$k_{regressed}$	regressed value of reaction rate constant	kmol/m ³ -sec
m	molality	mol solute/kg solvent
MOR	morpholine	—
n	overall reaction order	
$\dot{n}_{CO_2,in}$	molar flow of inlet gas	mol/sec
$\hat{n}_{CO_2,out}$	molar flow of outlet gas	mol/sec
NRTL	non-random two liquid	—
$\hat{N}_i$	predicted value	—
N_i	experimental value	—
$\hat{N}_{CO_2}$	predicted CO ₂ flux	mol/sec-m ²
N_{CO_2}	experimental CO ₂ flux	mol/sec-m ²
PCES	property constant estimation system	—
$P_{CO_2}^*$	equilibrium partial pressure of CO ₂	Pa or kPa
PFO	pseudo first-order	—
PZ	piperazine	—
R	gas constant	J/mol-K
r_{CO_2}	rate of reaction of CO ₂	kmol/m ³ -sec
T	temperature	K or °C
VLE	vapor-liquid equilibrium	—
V_m	molar volume	m ³ /kmol
WWC	wetted-wall column	—
x_i	mole fraction of i	—
w_i	mass fraction of i	—
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	—
γ_i	activity coefficient	—
μ_i	viscosity of <i>i</i>	cP
ρ_i	density of <i>i</i> , correlation coefficient	kg/m ³ , —
$\bar{\rho}$	molar volume	m ³ /kmol
σ	standard deviation	—
$\tau_{i,j}$	eNRTL binary interaction parameter	—

4.3 References

- Bishnoi, S., Rochelle, G.T., 2000. Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chem. Eng. Sci.* 55, 5531–5543. doi:10.1016/S0009-2509(00)00182-2
- Bosch, H., Versteeg, G.F., Swaaij, W.P.M. van, 1990. Kinetics of the Reaction of CO₂ with the Sterically Hindered Amine 2-Amino-2-Methylpropanol at 298 K. *Chem. Eng. Sci.* 45, 1167–1173.
- Bougie, F., Iliuta, M.C., 2012. Sterically Hindered Amine-Based Absorbents for the Removal of CO₂ from Gas Streams. *J. Chem. Eng. Data* 57, 635–669. doi:10.1021/je200731v
- Chakraborty, A., Astarita, G., Bischoff, K., 1986. CO₂ Absorption in Aqueous Solutions of Hindred Amines. *Chem. Eng. Sci.* 41, 997–1003.
- Chen, C.-C., Song, Y., 2004. Generalized electrolyte-NRTL model for mixed-solvent electrolyte systems. *AIChE J.* 50, 1928–1941. doi:10.1002/aic.10151
- Chen, X., 2011. Carbon Dioxide Thermodynamics, Kinetics, and Mass Transfer in Aqueous Piperazine Derivatives and Other Amines. The University of Texas at Austin.
- Chen, X., Rochelle, G.T., 2013. Modeling of CO₂ Absorption Kinetics in Aqueous 2-Methylpiperazine. *Ind. Eng. Chem. Res.* 52, 4239–4248.
- Chen, X., Rochelle, G.T., 2011. Aqueous piperazine derivatives for CO₂ capture: Accurate screening by a wetted wall column. *Chem. Eng. Res. Des.* 89, 1693–1710. doi:10.1016/j.cherd.2011.04.002
- Chiu, L., Liu, H., Li, M., 2010. Heat Capacity of Alkanolamines by Differential Scanning. *J. Chem. Eng. Data* 631–636.
- Ciftja, A.F., Hartono, A., Svendsen, H.F., 2014. Experimental study on carbamate formation in the AMP–CO₂–H₂O system at different temperatures. *Chem. Eng. Sci.* 107, 317–327. doi:10.1016/j.ces.2013.12.028
- Ciftja, A.F., Hartono, A., Svendsen, H.F., 2013. ¹³C NMR as a method species determination in CO₂ absorbent systems. *Int. J. Greenh. Gas Control* 16, 224–232. doi:10.1016/j.ijggc.2013.04.006
- Crooks, J.E., Donnellan, J.P., 1989. Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution. *J. Chem. Soc. Perkin Trans. 2* 2, 331. doi:10.1039/p29890000331
- Cullinane, J.T., 2005. Thermodynamics and Kinetics of Aqueous Piperazine with Potassium Carbonate for Carbon Dioxide Absorption. The University of Texas at Austin.
- Eide-Haugmo, I., Brakstad, O.G., Hoff, K.A., da Silva, E.F., Svendsen, H.F., 2012. Marine biodegradability and ecotoxicity of solvents for CO₂-capture of natural gas. *Int. J. Greenh. Gas Control* 9, 184–192.

doi:10.1016/j.ijggc.2012.03.006

Endo, T., Kajiya, Y., Nagayasu, H., Iijima, M., Ohishi, T., Tanaka, H., Mitchell, R., 2011. Current status of MHI CO₂ capture plant technology, large scale demonstration project and road map to commercialization for coal fired flue gas application. *Energy Procedia* 4, 1513–1519. doi:10.1016/j.egypro.2011.02.019

Fernandes, D., Conway, W., Burns, R., Lawrance, G., Maeder, M., Puxty, G., 2012. Investigations of primary and secondary amine carbamate stability by ¹H NMR spectroscopy for post combustion capture of carbon dioxide. *J. Chem. Thermodyn.* 54, 183–191. doi:10.1016/j.jct.2012.03.030

Fine, N.A., Nielsen, P.T., Rochelle, G.T., 2014. Decomposition of nitrosamines in CO₂ capture by aqueous piperazine or monoethanolamine. *Environ. Sci. Technol.* 48, 5996–6002. doi:10.1021/es404949v

Frailie, P., 2011. Modeling Energy Performance of Methyldiethanolamine / Piperazine in CO₂ Capture.

Frailie, P.T., 2014. Modeling of Carbon Dioxide Absorption/Stripping by Aqueous Methyldiethanolamine/Piperazine. The University of Texas at Austin.

Freeman, S.A., 2011. Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture. The University of Texas at Austin.

Kim, I., Svendsen, H.F., Børresen, E., 2008. Ebulliometric Determination of Vapor - Liquid Equilibria for Pure Water , Monoethanolamine, N -Methyldiethanolamine, 3-(Methylamino)-propylamine, and Their Binary and Ternary Solutions. *J. Chem. Eng. Data* 53, 2521–2531.

Ko, J.-J., Li, M., 2000. Kinetics of absorption of carbon dioxide into solutions of N-methyldiethanolamine+ water. *Chem. Eng. Sci.* 55, 4139–4147.

Krishna, R., Standart, G.L., 1976. A Multicomponent Film Model Incorporating a General Matrix Method of Solution to the Maxwell-Stefan Equations. *AIChE J.* 22, 383–389.

Li, H., Frailie, P.T., Rochelle, G.T., Chen, J., 2014. Thermodynamic modeling of piperazine/2-aminomethylpropanol/CO₂/water. *Chem. Eng. Sci.* 117, 331–341. doi:10.1016/j.ces.2014.06.026

Li, L., 2015. Carbon Dioxide Solubility and Mass Transfer in Aqueous Amines for Carbon Capture. The University of Texas at Austin.

Li, L., Voice, A.K., Li, H., Namjoshi, O., Nguyen, T., Du, Y., Rochelle, G.T., 2013. Amine blends using concentrated piperazine. *Energy Procedia* 37, 353–369. doi:10.1016/j.egypro.2013.05.121

Ma'mun, S., Nilsen, R., Svendsen, H.F., Juliussen, O., 2005. Solubility of Carbon Dioxide in 30 mass % Monoethanolamine and 50 mass % Methyldiethanolamine Solutions. *J. Chem. Eng. Data* 50, 630–634. doi:10.1021/je0496490

Mathias, P.M., O'Connell, J.P., 2012. The Gibbs–Helmholtz Equation and the Thermodynamic Consistency of Chemical Absorption Data. *Ind. Eng. Chem. Res.* 51, 5090–5097. doi:10.1021/ie202668k

McCann, N., Phan, D., Fernandes, D., Maeder, M., 2011. A systematic investigation of carbamate stability constants by ¹H NMR. *Int. J. Greenh. Gas Control* 5, 396–400. doi:10.1016/j.ijggc.2010.01.008

Mimura, T., Simayoshi, H., Suda, T., Iijima, M., Mituoka, S., 1997. Development of energy saving technology for flue gas carbon dioxide recovery in power plant by chemical absorption method and steam system. *Energy Convers. Manag.* 38, S57–S62. doi:10.1016/S0196-8904(96)00246-4

Pacheco, M., 1998. Mass Transfer, Kinetics and Rate-based Modeling of Reactive Absorption. The

University of Texas at Austin.

Paul, S., Ghoshal, A.K., Mandal, B., 2009. Absorption of Carbon Dioxide into Aqueous Solutions of 2-Piperidineethanol: Kinetics Analysis. *Ind. Eng. Chem. Res.* 48, 1414–1419. doi:10.1021/ie800723b

Paul, S., Mandal, B., 2006. Density and viscosity of aqueous solutions of 2-piperidineethanol,(2-piperidineethanol+ monoethanolamine), and (2-piperidineethanol+ diethanolamine) from (288 to 333) K. *J. Chem. Eng. Data* 51, 1406–1410.

Perinu, C., Arstad, B., Jens, K.-J., 2014. NMR spectroscopy applied to amine–CO₂–H₂O systems relevant for post-combustion CO₂ capture: A review. *Int. J. Greenh. Gas Control* 20, 230–243. doi:10.1016/j.ijggc.2013.10.029

Plaza, J.M., 2011. Modeling of Carbon Dioxide Absorption using Aqueous Monoethanolamine, Piperazine and Promoted Potassium Carbonate. The University of Texas at Austin.

Rochelle, G.T., 2009. Amine scrubbing for CO₂ capture. *Science* (80-.). 325, 1652–4. doi:10.1126/science.1176731

Sachde, D.J., 2016. Absorber Performance and Configurations for CO₂ Capture using Aqueous Piperazine. The University of Texas at Austin.

Sartori, G., Leder, F., 1978a. Process and amine-solvent absorbent for removing acidic gases from gaseous mixtures US 4240923 A.

Sartori, G., Leder, F., 1978b. Process for Removing Carbon Dioxide Containing Acidic Gases from Gaseous Mixtures using a Basic Salt Activated with a Hindered Amine. 4112050.

Sartori, G., Savage, D.W., 1983. Sterically Hindered Amines for CO₂ Removal from Gases. *Ind. Eng. Chem. Fundam.* 22, 239–249.

Snijder, E.D., te Riele, M.J.M., Versteeg, G.F., van Swaaij, W.P.M., 1993. Diffusion coefficients of several aqueous alkanolamine solutions. *J. Chem. Eng. Data* 38, 475–480. doi:10.1021/je00011a037

Versteeg, G.F., Swaaij, W.P.M. Van, 1988. Solubility and Diffusivity of Acid Gases (CO₂, N₂O) in Aqueous Alkanolamine Solutions. *J. Chem. Eng. Data* 33, 29–34.

Versteeg, G.F., Swaaij, W.P.M. van, 1988. On the kinetics between CO₂ and alkanolamines both in aqueous and non-aqueous solutions—II. Tertiary amines. *Chem. Eng. Sci.* 43, 587–591.

Versteeg, G.F., van Swaaij, W.P.M., 1988. On the Kinetics Between CO₂ and Alkanolamines both in Aqueous and Non-Aqueous Solutions I. Primary and Secondary Amines. *Chem. Eng. Sci.* 43, 573–585.

Voice, A.K., 2013. Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing. The University of Texas at Austin.

Xu, S., Wang, Y., Otto, F.D., Mather, A.E., 1992. Physicochemical properties of 2-piperidineethanol and its aqueous solutions. *J. Chem. Eng. Data* 37, 407–411. doi:10.1021/je00008a008

Zhang, Y., Chen, C., 2011. Thermodynamic Modeling for CO₂ Absorption in Aqueous MDEA Solution with Electrolyte NRTL Model. *Ind. Eng. Chem. Res.* 50, 163–175. doi:10.1021/ie1006855

Zhang, Y., Que, H., Chen, C.-C., 2011. Thermodynamic modeling for CO₂ absorption in aqueous MEA solution with electrolyte NRTL model. *Fluid Phase Equilib.* 311, 67–75. doi:10.1016/j.fluid.2011.08.025

1 4.4 Supporting Information

2 4.4.1 Derivation of Equation 20

3 This equation converts from the concentration, ideal based k_c to the mole-fraction, activity-coefficient
4 based k_a . It is derived by equating the two different bases and converting as demonstrated for the
5 carbamate reaction.

$$-r_{CO_2} = k_c [Am]^2 [CO_2] = k_a a_{Am}^2 a_{CO_2}$$

$$\frac{k_c [Am]^2 [CO_2]}{a_{Am}^2 a_{CO_2}} = k_a$$

6 By definition, $a_i = x_i \gamma_i$. Substituting and canceling the concentration terms yields

$$\frac{k_c}{\gamma_{Am}^2 \gamma_{CO_2}^*} = k_a$$

7 The conversion to an activity basis is complete, but unit analysis shows that an additional factor is
8 needed for the concentration to mole-fraction conversion

$$\frac{\text{m}^6}{\text{kmol}^2 \cdot \text{sec}} [=] \frac{\text{kmol}}{\text{m}^3 \cdot \text{sec}}$$

9 This factor is the molar volume $\bar{\rho}^3$. Repeating the unit analysis with this factor shows the units are now
10 correct, and the conversion is complete.

$$\left(\frac{\text{m}^6}{\text{kmol}^2 \cdot \text{sec}} \right) \left(\frac{\text{kmol}^3}{\text{m}^9} \right) [=] \frac{\text{kmol}}{\text{m}^3 \cdot \text{sec}} \blacksquare$$

Table S1: Initial species definition

Species	ΔG° or ΔG_{aq}° (J/kmol) $\times 10^8$	ΔH° or ΔH_{aq}° (J/kmol) $\times 10^8$
2PE	- 0.847	- 2.70
2PECOO ⁻	- 4.58	- 7.50
2PEH ⁺	- 1.69	- 3.99

Table S2: Liquid film discretization; $\delta=0$ at the gas-liquid interface, $\delta=1$ at the bulk liquid

Point	δ	Point	δ	Point	δ
1	6.40E-05	12	1.87E-03	23	3.15E-02
2	7.68E-05	13	2.70E-03	24	3.78E-02
3	1.59E-04	14	3.89E-03	25	4.54E-02
4	2.29E-04	15	5.60E-03	26	5.90E-02
5	3.30E-04	16	8.06E-03	27	8.26E-02
6	4.76E-04	17	1.06E-02	28	1.24E-01
7	5.71E-04	18	1.27E-02	29	1.98E-01
8	7.00E-04	19	1.52E-02	30	3.17E-01
9	9.86E-04	20	1.82E-02	31	5.07E-01
10	1.18E-03	21	2.19E-02	32	8.62E-01
11	1.42E-03	22	2.63E-02		

**Table S3: Chemical shift (δ) for loaded and unloaded 30 wt.% aqueous 2-PE solution at 25 °C
(loading = mol CO₂/mol alk)**

Loading	0	0.138	0.814
Peak	chemical shift (δ) in ppm		
1	59.4	58.3	58.4
2	39.4	36.4	36.7
3	54.3	54.9	54.7
4	32.6	29.3	29.6
5	25.0	22.7	22.9
6	26.1	23.0	23.4
7	46.7	45.4	45.5
1'	—	62.4	62.5
2'	—	39.6	39.6
3'	—	59.4	59.4
4'	—	32.2	32.2
5'	—	19.6	19.6
6'	—	26.3	26.3
7'	—	47.6	47.6
8'	—	163.4	163.4

$\text{HCO}_3^-/\text{CO}_3^{2-}$	—	163.9	163.0
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Table S4: Scalar pure component properties

	Units	2PE	Source
DGFORM	J/KMOL	-8.5E+07	AMP (Li et al., 2014)
DHFORM	J/KMOL	-2.7E+08	AMP (Li et al., 2014)
OMEGA	J/KMOL	0.41376	PZ (Frailie, 2014)
PC	N/SQM	795654.3	PCES
RKTZRA		0.308959	equated to ZC
TC	K	659.4686	PCES
VC	CUM/KMOL	0.4165	PCES
ZC		0.308959	PCES

Table S5: Pure component T-dependent parameters of 2PE as estimated by PCES

	CPIG	PLXANT
Temperature units	K	K
Property units	J/KMOL-K	N/SQM
Element 1	-38427.6	1.08E+02
Element 2	896.8209	-12041.6
Element 3	-0.51826	0
Element 4	7.68E-05	0
Element 5	0	-11.4922
Element 6	0	6.17E-18
Element 7	280	6
Element 8	1100	4.77E+02
Element 9	36029.2	659.4686
Element 10	29.39165	
Element 11	1.5	

Table S6: NRTL parameters with MDEA as analog (Frailie, 2011)

Component i	H ₂ O	CO ₂
Component j	2PE	2PE
Temperature units	K	K
Element 1	0	-5
Element 2	-0.29076	-5
Element 3	0	2000
Element 4	-92.3338	2000
Element 5	0.2	0.2

Element 6	0	0
Element 7	0	0
Element 8	-0.05084	0
Element 9	0	0
Element 10	0.007005	0
Element 11	546.3	546.3
Element 12	1546.3	1546.3

Table S7: Henry parameter values with PZ as analog (Frailie, 2011)

Component i	2PE
Component j	H ₂ O
Property units	N/SQM
Element 1	40.91662
Element 2	-10550.3
Element 3	0
Element 4	-0.01308
Element 5	0
Element 6	2000
Element 7	0

4.5 Figure Captions

Figure 1: WWC flowsheet

Figure 2: Speciation in loaded aqueous solution of 2-piperidineethanol (2PE).

Figure 3: Quantitative ¹³C NMR spectra for 30 wt. % 2PE-CO₂-H₂O system at 25 °C.

Figure 4: VLE of 8 m 2PE; lines are predictions at 20 °C intervals, solid points are WWC VLE from Chen (2011); open points are loading adjusted VLE.

Figure 5: 8 m 2PE predicted $-\Delta H_{\text{abs}}$ at 20 °C increments using Equation 28

Figure 6: 8 m 2PE speciation prediction at 40 °C

Figure 7: Model predictions (lines) at 30 wt.% 2PE and 25 °C compared to data (points)

Figure 8: 8 m 2PE activity coefficient prediction at 40 °C

Figure 9: 8 m 2PE viscosity predictions at 20 °C intervals; points are data from Chen (2011).

Figure 10: Density prediction of 8 m 2PE at 20 °C intervals

Figure 11: 8 m 2PE predicted flux ratioed to experimental flux (Chen, 2011) for case 3; ■ 40 °C, ● 60 °C, ▲ 80 °C, ◆ 100 °C; shaded region indicates experimental error.

Figure 12: 8 m 2PE predicted flux ratioed to experimental flux (Chen, 2011) for case 5; ■ 40 °C, ● 60 °C, ▲ 80 °C, ◆ 100 °C; shaded region indicates experimental error.

Figure 13: 8 m 2PE predicted flux ratioed to experimental flux (Chen, 2011) for case 7; ■ 40 °C, ● 60 °C, ▲ 80 °C, ◆ 100 °C; shaded region indicates experimental error.

Figure 14: 8 m 2PE predicted flux ratioed to experimental flux (Chen, 2011) for case 8; ■ 40 °C, ● 60 °C, ▲ 80 °C, ◆ 100 °C; shaded region indicates experimental error.

Figure 15: 8 m 2PE kg' predictions for case 7 (lines) at $PCO_2 = 0.5PCO_2^*$ and data (points); open points not regressed (Chen, 2011).

Figure 16: Sensitivity of kg' at 40 °C for case 7 at $PCO_2 = 1.1PCO_2^*$

Figure 17: Sensitivity of kg' at 100 °C for case 7 at $PCO_2 = 0.5PCO_2^*$

Figure 18: Mechanisms of CO₂ absorption for case 7 at $PCO_2 = 1.1PCO_2^*$, kg' by model (solid), kg , PFO' by Equation 24 (dashed), and kg' at instantaneous conditions (dotted)

Figure 19: Brønsted plot at 25 °C for the concentration-based carbamate reaction of amines (Chen and Rochelle, 2013) for case 7

Figure 20: Relative gas film resistance in 8 m 2PE at $PCO_2 = 1.1PCO_2^*$ for case 7

Figure 21: kg' vs kl_0 in 8 m 2PE at 0.53 mol CO₂/mol alkalinity and $PCO_2 = 1.1PCO_2^*$ for case 7

4.6 Table Captions

Table 1: 2PE Thermodynamic data

Table 2: 2PE hydraulic data

Table 3: Predicted activity-based kinetic parameters ($T_{ref} = 313.15$ K)

Table 4: Mass transfer test matrix

Table 5: NMR speciation (mole fraction) for 30 wt.% 2-PE/CO₂/H₂O system at 25 °C.

Table 6: Thermodynamic data and fit

Table 7: VLE parameters

Table 8: 2PE viscosity parameters for Equation 10

Table 9: 8 m 2PE density parameters of Equation 11

Table 10: Loading adjustment for case 7 compared to data (Chen, 2011)

Table 11: 8 m 2PE kinetic parameters; * mole-fraction, concentration-based at 0.51 mol CO₂/mol alk 40 °C

Table 12: Diffusion activation energy as calculated by Equation 26

Table S1: Initial species definition

Table S2: Liquid film discretization; $\delta=0$ at the gas-liquid interface, $\delta=1$ at the bulk liquid

Table S3: Chemical shift (δ) for loaded and unloaded 30 wt.% aqueous 2-PE solution at 25 °C (loading = mol CO₂/mol alk)

Table S4: Scalar pure component properties

Table S5: Pure component T-dependent parameters of 2PE as estimated by PCES

Table S6: NRTL parameters with MDEA as analog (Frailie, 2011)

Table S7: Henry parameter values with PZ as analog (Frailie, 2011)

Graphical Abstract

$$\log \left(\frac{k_{2PE-2PE}}{\text{kmol}^2\text{-sec}} \right)$$