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Enhancements in Mass Transfer for Carbon Capture Solvents Part I: Homogeneous Catalyst

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1 challenges not often addressed when designing a chemical or catalytic additive for industrial CCS
2 systems, where consideration of solvent chemistry is typically the primary goal.

3 **Keywords:** Post-combustion; CO₂ capture; Mass transfer; Amine; Catalyst; Additives.

4 **1. Introduction**

5 Increasing concern over global CO₂ emissions has led to new regulations from the US
6 Environmental Protection Agency (EPA) for coal-fired power generation, which is responsible for
7 the emission of billions of tons annually. As of January 2014, new coal burning units require
8 carbon capture and storage (CCS) processes to reduce CO₂ emissions to 1100 lb/MW.¹ Amine-
9 based carbon capture is the most widely studied, and most likely to be implemented commercially,
10 method for CO₂ purification from flue gas.² However, the cost of these systems is still prohibitive,
11 and reduction in both capital and operational costs, relative to the Department of Energy (DOE)
12 reference case 12, 30 wt.% monoethanolamine (MEA), is necessary.³ In general, capital costs arise
13 on the absorption side of the process, while operational costs arise on the CO₂ stripping/solvent
14 regeneration side. Construction of the absorption tower (absorber) alone accounts for
15 approximately 20% of the initial capital investment for construction of a carbon capture system;
16 therefore significant effort has focused on understanding and increasing absorption kinetics of the
17 amine solvent in the absorption tower.^{2, 4-7}

18 Research toward increasing CO₂ absorption in solvent-based CCS processes has focused on three
19 main strategies: (1) solvent development/amine blends,⁸⁻¹⁴ (2) modification of the packing material
20 to increase wetted surface area,¹⁵⁻¹⁶ and (3) the addition of catalysts, such as small-molecule
21 carbonic anhydrase (CA) mimics,¹⁷⁻²⁰ to increase the chemical kinetics of absorption and
22 desorption²¹ reactions. The development of new amines and solvent blends has been delivering

1 incremental gains, as there is always a tradeoff between reactivity and stability, where increased
2 absorption kinetics is generally associated with higher regeneration energy and reboiler duty.²²⁻²³
3 In addition, the emission of amine degradation products,²⁴⁻²⁵ particularly carcinogenic
4 nitrosamines from secondary amine solvents,²⁶ rises concerns over the use of some potentially
5 effective absorption solvents. Absorption catalyst development has also been plagued with process
6 difficulties, and the most widely studied (1) carbonic anhydrase (CA), and (2) the CA mimic,
7 $[\text{Zn}(\text{cyclen})(\text{H}_2\text{O})](\text{ClO}_4)_2$, are ineffective under CCS conditions.^{27, 22}

8 Recent work has led to the first reported examples of homogenous CO_2 hydration catalysts that
9 allowed for mass transfer enhancement in kinetically-fast primary amine solvents.²⁷⁻²⁹ These
10 catalysts incorporate electron donating ligand environments and ionic secondary coordination
11 sphere groups to increase solubility in aqueous solutions, promote CO_2 hydration, and facilitate
12 bicarbonate dissociation away from the metal center. Previous reports have detailed the synthesis,
13 characterization, and preliminary laboratory testing of these catalysts under conditions conducive
14 to carbon capture processes, i.e. low CO_2 concentration (0.14 atm), and high amine concentration
15 (5 M). These previously reported complexes were shown to be stable toward the high temperatures
16 (up to 145 °C) and oxidizing flue gas contaminants (SO_x and NO_x) associated with industrial CCS
17 processes. Herein we report the testing and analysis of the novel catalyst $[\text{Co}^{\text{III}}(\text{Salphen-COO}^-$
18 $)\text{Cl}]\text{HNEt}_3$ (**1**), and describe the difficulties associated with integrating the new additive into a
19 bench scale, heat-integrated absorber-stripper process.

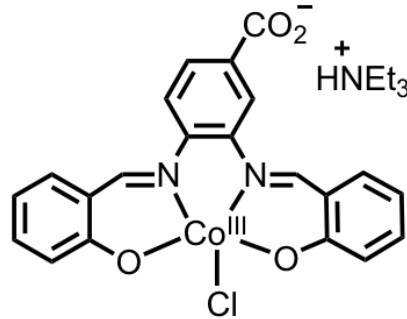
20 **2. Experimental**

21 **2.1. General.** Reagents for solvent mixtures, catalyst synthesis, and kinetics studies were
22 purchased from Sigma Aldrich, monoethanolamine was purchased from Univar. Solutions of
23 monoethanolamine (MEA, 5 M) and the A2P/AMP blended solvent (0 – 30 wt. % of each

1 component) were prepared by weight % and adjusted to an alkalinity of 5.0 mol N/Kg.
2 Experimental methods for pH drop,^{27, 30} total inorganic carbon loading,³¹ and alkalinity³¹
3 measurements were conducted according to reported procedures. The surface tension and the
4 surface elasticity data were acquired at 22 °C on a Biolin Scientific Optical Tensiometer, using
5 Oneattension software. The viscosity of the solutions were determined by using the Brookfield
6 DVI viscometer. Catalyst loading of 2.3 g/L is used based on previously reported studies.²⁸⁻²⁹
7 Foaming volume measurements were conducted in a 100 mL graduated cylinder, with 10 mL of
8 solvent, under study. Simulated flue gas (14% CO₂ with balance N₂) gas was purged through a gas
9 impinger at a constant flow rate (0.6 L/min). The volume of the foam formed with continuous
10 purging of CO₂ was then recorded as a function of time.

11 **2.2. Synthesis of [Co^{III}(Salphen-COO⁻)Cl]HNEt₃ (1).** N,N'-disalicylidene-4-carboxy-1,2-
12 phenylenediamine (Salphen-COOH)³² was synthesized by stirring salicylaldehyde (1.80 mL, 16.9
13 mmol) and 3,4-diamino benzoic acid (1.01 g, 6.5 mmol) in ethanol (40 mL) overnight, then
14 collecting the orange solid (2.05 g, 86% yield) by filtration and washing with ethanol and diethyl
15 ether. The Salphen-COOH ligand was suspended in ethanol (30 mL), followed by addition of
16 triethylamine (2.80 mL, 20.1 mmol). An ethanolic (30 mL) solution of CoCl₂•6H₂O (1.49 g, 6.2
17 mmol) was added to the reaction mixture drop wise over 15 min to give dark brown solution, and
18 the reaction mixture was stirred overnight at room temperature. Diethyl ether (50 mL) was added,
19 and the resulting brown precipitate was collected by vacuum filtration. The solid product was
20 washed with methanol (30 mL), diethyl ether (30 mL), and allowed to air dry, giving **1** (3.07 g,
21 93%) as a brown powder. FTIR-ATR (cm⁻¹): 3369 (s), 2979 (m), 1601 (vs, C=N), 1539 (s), 1442
22 (s), 1369(s), 1304(s), 1151(s). ESI-ToF (m/z): 417.02777 [**1** – Et₃N – Cl]⁺. Elemental analysis [**1**

1 • 2H₂O]. Anal. Calc. for C₂₇H₃₃ClCoN₃O₆: C, 54.97; H, 5.64; N, 7.12. Found: C, 55.43; H, 5.64;
2 N, 6.82.



3
4 **Figure 1.** Proposed structure of **1**.

5 **2.3. Breakthrough Solvent Evaluation Apparatus:** Breakthrough experiments were conducted
6 as previously reported.^{27, 29} In a representative procedure, the breakthrough solvent evaluation
7 apparatus (**Figure 2**) consists of a 30 ml gas saturator, a 30 ml bubbler, a condenser, and a CO₂
8 analyzer. Both the saturator and the bubbler are made of Pyrex®, and are immersed in a water bath
9 maintained at 40 °C. A CO₂ feed gas stream (12%-14%) balanced with N₂ is saturated with water
10 in the saturator and bubbled through a 30 wt% MEA solution in the bubbler (1L/min). The gas
11 effluent is dried over drierite and analyzed for CO₂ concentration (vol%) using a CO₂ analyzer
12 (VIA-510, HORIBA, 0.5% precision). Data of CO₂ outlet concentration with respect to time is
13 continuously recorded with 1 second interval using an in-house Labview program.

14 The difference of inlet and outlet CO₂ concentration represents the absorbed amount of CO₂ at a
15 particular time. The integration of the concentration difference represents the CO₂ loading, as
16 expressed in equation (1),

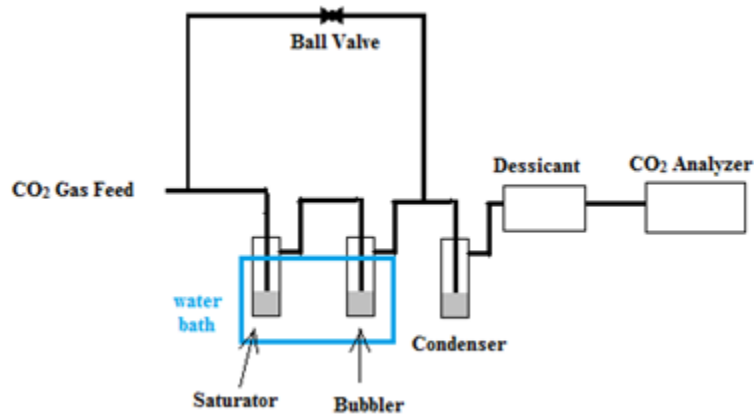
17

$$\text{CO}_2 \text{ Loading (mol CO}_2\text{/kg solution)} = \frac{\int_0^t (C_{in} - C_{out}(t)) dt}{m_{sol}} \quad (1)$$

1 where C_{in} is the CO₂ feed gas rate in mol/s, C_{out} is the CO₂ effluent rate in mol/s, t is time in second,
2 and m_{sol} is the mass of solution in kg.

3 In addition, the absorption rate can be described by the derivate of CO₂ loading with respect to
4 time is given by equation (2),

5
$$\text{Absorption rate (mol CO}_2\text{/kg solution/s)} = \frac{d \text{CO}_2 \text{ Loading}}{dt} \quad (2)$$



6

7 **Figure 2.** Schematic of breakthrough apparatus

8 **2.4. Determination of Mass Transfer Coefficient by Wetted Wall Column (WWC):** Wetted

9 wall column experiments were conducted as previously reported.³¹ A schematic of the WWC used
10 in this test is shown in **Figure 3**. In a representative procedure, 30 wt% aqueous MEA is loaded to
11 a mol CO₂/mol MEA level of approximately 0.1 with CO₂ by sparging the solution reservoir with
12 a concentrated 30 vol% CO₂/N₂ mixture for 6-12 min. Catalyst was added to the solution (1, 2.3
13 g/L) to give a clear, yellow solution. The solution is then heated to 40 °C by circulating through a
14 heat exchanger bath at 180 ml/min. Once the solution is thermally stable, a CO₂ gas feed mixed
15 with N₂ at 6.6 L/min (3-14.7 vol%), pre-heated and water saturated by a direct contact heat
16 exchanger, is allowed to contact with the liquid countercurrent on the surface of the column.

1 Absorption or desorption of CO₂ occurs across the contacting area, which gives a CO₂
2 concentration difference in the gas stream between the inlet and outlet of the column. Flux and
3 driving force can be obtained from the concentration difference. Four different CO₂ concentrations
4 in the gas stream were tested at the same carbon loading. Liquid samples downstream of the WWC
5 were collected during the process for carbon loading, viscosity, density, and pH measurements.
6 The above procedure was repeated for different carbon loadings.

7 The overall mass transfer coefficient at the operating condition can be calculated from equation
8 (3),

$$K_G = \frac{N_{CO_2}}{A \Delta P_{CO_2}} \quad (3)$$

9 in which N_{CO_2} is the flux of CO₂, K_G is the overall mass transfer coefficient, ΔP_{CO_2} is the log mean
10 of CO₂ partial pressure, and A is the contacting surface area. Diffusivity of CO₂, which is not
11 directly measured in this work, can be calculated from a modified Stokes-Einstein equation in
12 equation (4),

$$(D_{CO_2})_{\text{amine soln}} = (D_{CO_2})_{\text{water}} \left(\frac{\eta_{\text{water}}}{\eta_{\text{amine soln}}} \right)^{0.8} \quad (4)$$

13 in which D_{CO_2} is the diffusivity of CO₂ in amine solution or water, and η is the viscosity of amine
14 solution or water.

15 The flux is calculated by the CO₂ concentration difference at the inlet and outlet of the wetted wall
16 column as shown equation 5,

$$N_{CO_2} = N_{CO_2}^{in} - N_{CO_2}^{out} = y_{CO_2}^{in} N_t^{in} - y_{N_2}^{in} N_t^{in} \frac{y_{CO_2}^{out}}{y_{N_2}^{out}} \quad (5)$$

- 1 in which the molar flow rates N_t were calculated from total volume flue rate at standard condition,
 2 y_i is the molar fraction of component i .
 3 Since the CO₂ dynamically transfers from gas phase to liquid phase, the partial pressure of CO₂
 4 decreases along the wetted wall column. To better represent the true average partial pressure of
 5 CO₂ in the column, log mean of the driving forces was taken at the inlet and the outlet of the
 6 column, as given by equation (6),

$$\Delta P_{CO_2} = \frac{P_{CO_2}^{in} - P_{CO_2}^{out}}{\ln\left(\frac{P_{CO_2}^{in} - P_{CO_2}^*}{P_{CO_2}^{out} - P_{CO_2}^*}\right)} \quad (6)$$

- 7 in which $P_{CO_2}^i$ is the partial pressure of CO₂, as shown in equation (7).

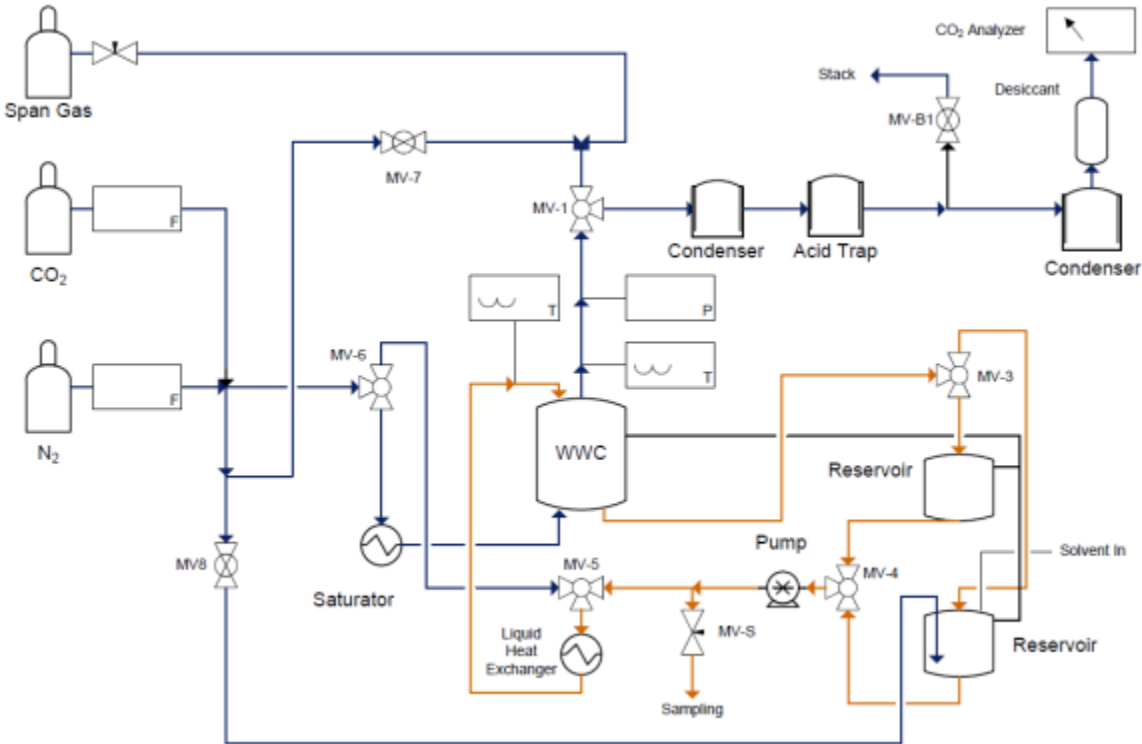
$$P_{CO_2}^i = y_{CO_2}^i (P_{total} - P_{water}) \quad (7)$$

- 8 As the feed gas is saturated with water in the saturator, the partial pressure of water can be written
 9 as its saturation pressure at the temperature T from equation (8).

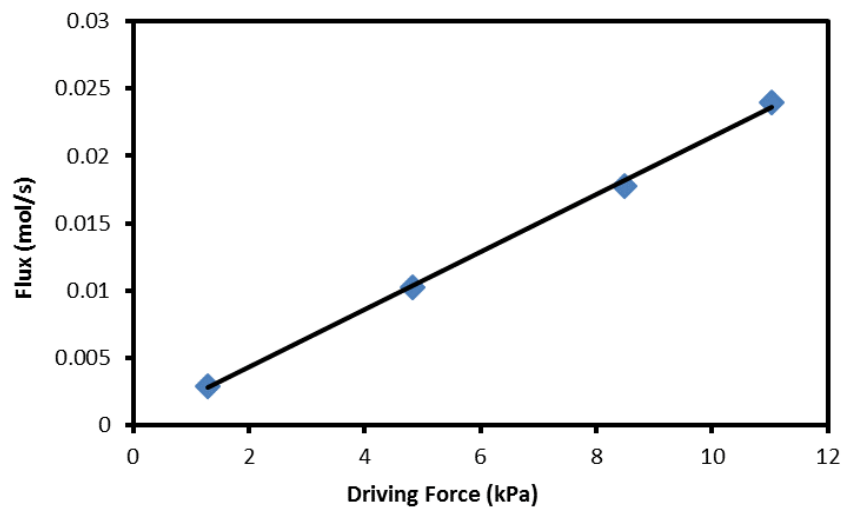
$$P_{water} = \exp\left(7255 - \frac{7207}{T} - 7.139 \ln(T) + 4.046 \times 10^{-6} T^2\right) \quad (8)$$

- 10 The equilibrium partial pressure of CO₂, $P_{CO_2}^*$, can be calculated by making the flux N_{CO_2} to be
 11 zero at zero driving force through an iterative routine in MATLAB where the two equations are

1 simultaneously solved. A typical relationship of flux N_{CO_2} and driving force of CO_2 is shown in
 2 **Figure 4**. The linearity of the two indicates a pseudo first order approximation.



3
 4 **Figure 3**. Schematic of wetted wall column apparatus utilized for mass transfer coefficient
 5 measurements.

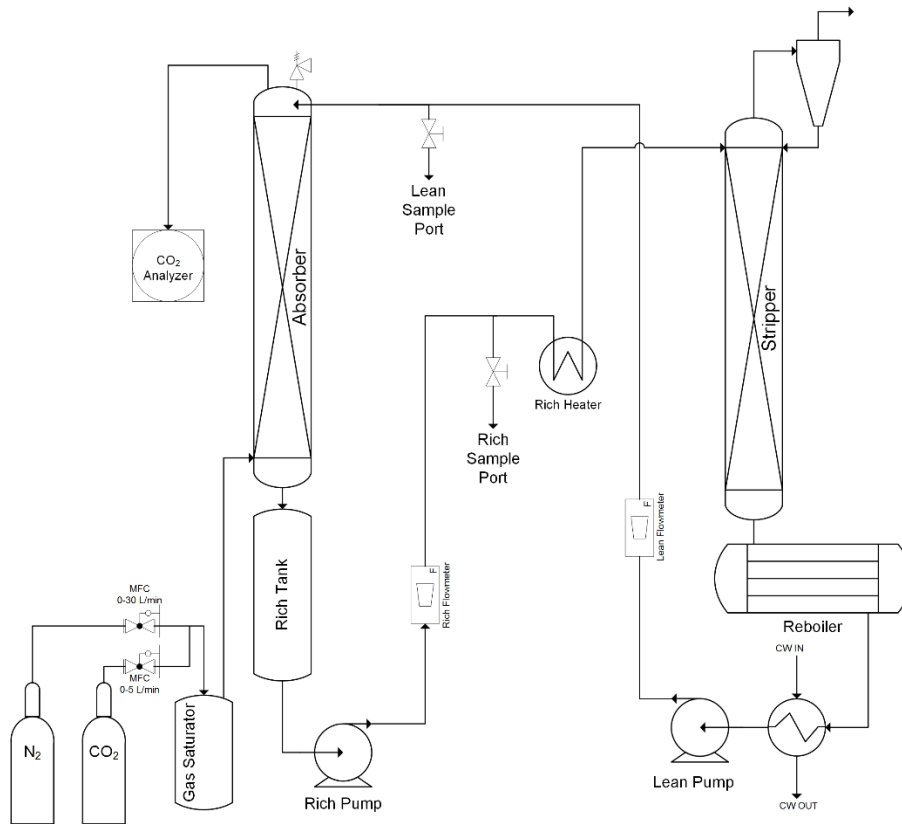


1 **Figure 4.** A typical relationship of flux N_{CO_2} and driving force of CO_2 from wetted wall column
2 experiment.

3 **2.5. Effects of Flue Gas Contaminants on Catalyst Activity.** In a representative procedure, a
4 stock solution of **1** at a loading of 2.3 g/L was prepared in 5 M aqueous MEA (250 mL). A 25 mL
5 aliquot of the stock solution was treated with 1000 ppm $NaNO_2$ (0.250 g of $NaNO_2$) for 24 hours
6 followed by evaluation in the pH-drop apparatus for the above method. This method was repeated
7 for treatments with 1000 ppm $NaNO_3$, Na_2SO_4 , and combination of the three for a total
8 concentration of 3000 ppm NO_x and SO_x derived salts. Gaseous NO_x contaminants were generated
9 in-situ and bubbled through a 25 mL aliquot of the stock solution containing **1** for 30 min prior to
10 evaluation via the pH-drop apparatus. For the generation of NO_x gas, a 100 mL two-necked round
11 bottom flask was charged with solid $NaNO_2$ (2.25 g, 33 mmol) and a magnetic stir bar. One neck
12 was sealed with a rubber septum, and the other was fitted with a glass adapter containing a hose
13 barb. Rubber tubing was attached via the hose barb adapter and a needle was fitted to the end of
14 the rubber tubing. Concentrated sulfuric acid was added drop wise through the septum with
15 constant stirring resulting in the immediate appearance of a brown fume.

16 **2.6. Thermal Stability.** In a representative procedure, a stock solution of **1** (2.3 g/L) was prepared
17 in 5 M aqueous MEA solution. A 50 mL aliquot was taken from the stock solution and 14% CO_2
18 gas with N_2 span was bubbled through the solution until a pH of 10.5 was reached. The solution
19 was transferred to an autoclave, sealed, placed in an oven, and heated at 145 °C for 92 hours. The
20 autoclave was then removed from the oven and cooled to room temperature. The activity of the
21 catalyst was assayed by taking a 25 mL aliquot and evaluating via the pH-drop method as described
22 above.

23 **2.7. Integrated Bench Scale CO_2 Capture System.**



1

2 **Figure 5.** Simplified process flow diagram of integrated bench scale CO₂ capture system.

3 **Figure 5** shows the schematic of the integrated bench-scale absorption/regeneration system which
 4 consists of a 7.6 cm ID clear PVC scrubber with a 2 m height of packing, a 7.6 cm ID stainless
 5 steel stripper with a 2 m height of packing, and a condenser for solvent recovery in the stripper
 6 exhaust. The packing inside both absorber and stripper are 6x6 mm ceramic Raschig rings. A
 7 decoupled heater and a chiller are installed to provide sensible heat for rich solvent heating and
 8 lean solvent cooling to enhance the flexibility of the experimental matrix. A hot oil system is
 9 installed to provide necessary heat for solvent regeneration. Liquid flow rate is controlled by 2
 10 centrifugal pumps. Two in-line flow meters have been installed to monitor the volumetric solvent
 11 flow rates both entering and exiting the stripper. Feed gas is supplied by two mass flow controllers
 12 (MFC) deployed to control the CO₂ and N₂ flow rates. CO₂ and N₂ are mixed to simulate flue gas
 13 conditions of 14% CO₂ at a total flow rate of 30 L/min. The gases are sent through a water saturator

1 and then injected to the bottom of the absorber. A Horiba CO₂ analyzer is used to measure the
2 online CO₂ concentration at the absorber outlet.

3 The measurements of CO₂ absorption efficiency and rich solution regeneration energy requirement
4 at various conditions were performed during the bench-scale parametric study. The CO₂ absorption
5 efficiency is related to the gas inlet and outlet CO₂ flow rates by equation (9):

$$\varphi_{CO_2} = \frac{n_{CO_2}^{in} - n_{CO_2}^{out}}{n_{CO_2}^{in}} \quad (9)$$

6 where φ_{CO_2} , CO₂ capture efficiency, %; $n_{CO_2}^{in}$, gas inlet CO₂ mole flow rate, mol/s; $n_{CO_2}^{out}$, gas outlet
7 CO₂ mole flow rate, mol/s. The inlet CO₂ flow rate, $n_{CO_2}^{in}$ was calculated directly from the CO₂
8 MFC flow rate. The outlet CO₂ flow rate was calculated by equation (10):

$$n_{CO_2}^{out} = C_{CO_2}^{out} \frac{V_{N_2}^{in}}{1 - C_{CO_2}^{out}} \quad (10)$$

9 where $C_{CO_2}^{out}$, outlet CO₂ concentration, %; $V_{N_2}^{in}$, inlet N₂ flow rate, L/min. the outlet CO₂
10 concentration, $C_{CO_2}^{out}$ was measured by an Horiba CO₂ analyzer, which was calibrated
11 before each test. The inlet N₂ flow rate, $V_{N_2}^{in}$ was obtained from the MFC.

12 The rich CO₂ solution regeneration energy is calculated from the reboiler heat duty assuming an
13 adiabatic system by equation (11):

$$Q_{CO_2}^{ov} = \frac{Q_R}{n_{CO_2}^{in} - n_{CO_2}^{out}} \quad (11)$$

14 where $Q_{CO_2}^{ov}$, overall regeneration energy per unit of CO₂ regeneration, kJ/mol CO₂; Q_R , reboiler
15 heat duty, kW. The reboiler heat was provided by hot oil recirculation, the heat duty Q_R is
16 calculated by equation (12):

$$Q_R = C_p^{oil} m_{oil} \rho_{oil} (T_R^{in} - T_R^{out}) \quad (12)$$

1 where C_p^{oil} , hot oil heat capacity, kJ/g/K; m_{oil} , hot oil flow rate, L/s; ρ_{oil} , hot oil density, g/L; T_R^{in} ,
2 reboiler inlet temperature, °C; T_R^{out} , reboiler outlet temperature, °C. Mobiltherm 603 heat transfer
3 oil was used in the reboiler system.

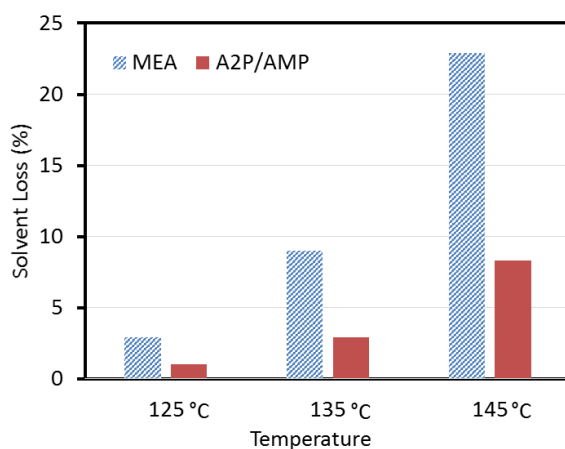
4 3. Results

5 **3.1. Solvent Properties.** The development of homogenous CO₂ hydration catalysts for industrial
6 CCS processes is a complex task, with multiple competing determinate factors. Monoethanolamine
7 (MEA) is the most widely investigated solvent due to its low cost and fast kinetics for CO₂
8 absorption. However, there are concerns over the commercial implementation due to the high
9 energy cost for solvent regeneration and thermal degradation rates associated with MEA solvents.³
10 ³³ To circumvent these disadvantages we formulated a blended solvent consisting of a thermally
11 stable primary amine and a sterically-hindered primary amine, 1-amino-2-propanol (A2P) and 2-
12 amino-2-methyl-1-propanol (AMP).³⁴ Sterically-hindered amines such as AMP tend to exhibit
13 slower kinetics of CO₂ absorption,³⁵ making them ideally suited for enhancement by the addition
14 of a catalytic additive to increase capture rate. If the absorption rate of a hindered amine solvent
15 can be brought close to that of a fast solvent such as MEA, the combination of a faster reaction
16 rate, lower degradation rate, and lower regeneration energy would give a preferable solvent
17 mixture with fast absorption, low energy requirements, and low solvent makeup.

18 The reactions of aqueous alkanolamines with CO₂ have been studied by a variety of methods, and
19 are widely discussed in the literature.^{19, 35-42} The rate of MEA-carbamate formation with CO₂ (k_2)
20 is widely debated in the literature and varies from 4000 M⁻¹s⁻¹ to 8000 M⁻¹s⁻¹, with the most
21 common values between 5000 – 6000 M⁻¹s⁻¹, depending on the method, conditions, pH, and
22 temperature.^{36-37, 39, 43-49} Additional studies have discussed the individual kinetics of A2P and AMP

1 amine solutions.^{35, 39-40, 46, 50} The reported k_2 (298 K) values for the reaction of CO₂ with A2P are
2 4400 – 5300 M⁻¹s⁻¹,^{35, 50} while the more sterically-hindered AMP is much slower with reported
3 values of 502 – 810 M⁻¹s⁻¹.^{40, 46} The blended A2P/AMP solvent is therefore expected to exhibit
4 slower kinetics than the MEA base case, however the addition of a catalyst to boost absorption
5 kinetics in combination with lower regeneration energy and decreased solvent makeup from
6 degradation (*vide infra*) would make the A2P/AMP solvent blend a competitive alternative to
7 MEA.

8 In order to have a robust solvent for commercialization, long-term thermal stability of the amines
9 is critical, as the capture solvents are often exposed to high temperatures during the CO₂ capture
10 process which is solvent- and stripper operating pressure-dependent. MEA has well-documented
11 thermal degradation at temperatures above 120 °C.⁵¹⁻⁵³ The thermal stability of the novel
12 A2P/AMP solvent blend was examined, relative to MEA, through extended and constant exposure
13 to elevated temperatures of 125 °C, 135 °C, and 145 °C for 168 hours. The A2P/AMP blend shows
14 a 70% decrease in the rate of amine loss (as percent of initial) at the high temperatures associated
15 with stripper conditions over a 168 hour period (**Figure 6**).



1 **Figure 6.** Thermal degradation (% loss) of carbon loaded MEA and A2P/AMP at stripping
2 temperatures over 168 h, $\alpha = 0.45$ mol C/mol N, for both MEA and A2P/AMP.

3 Physical solvent properties such as viscosity⁵⁴ and surface tension⁵⁵ are known to impact the
4 solution side diffusion and mass transfer resistance for reactants and products, and an increase in
5 these properties have been associated with decreasing mass flux of CO₂ into capture solutions.
6 Surface elasticity is an indication of surfactant-like behavior and is a key factor in solvent
7 foaming,⁵⁶ which can lead to detrimental process implications for industrial systems.⁵⁷ For these
8 reasons it was imperative to determine the effect of **1** on the solvent physical properties, if notable.
9 The viscosity, surface tension, and elasticity of the carbon capture solutions were measured at
10 carbon loadings across the solvent operational range ($\alpha = 0 - 0.55$) in the absence and presence of
11 **1**. Solutions of MEA and A2P/AMP solvent containing 2.3 g/L of **1** were compared to baseline
12 solutions of the solvent with no additional additive. As can be seen in **Figure 7a** and **7b**, there are
13 no observable differences in viscosity for both solvents, and a small decrease in surface tension in
14 MEA at high loadings ($\alpha > 0.3$) by the addition of **1**. The surface elasticity of A2P/AMP solutions
15 is unaffected by the addition **1**, indicating **1** is not acting as a surfactant in A2P/AMP, however
16 there is a sharp increase in elasticity upon the addition of **1** to MEA (**Figure 7c**). This increase in
17 surface elasticity is accompanied by the presence of solvent foaming when simulated flue gas is
18 bubbled into solutions of MEA + **1** (**Figure 7d**), which is also observed in pH drop and
19 breakthrough experiments, and precluded the use of this solvent mixture in packed column
20 experiments (*vide infra*).

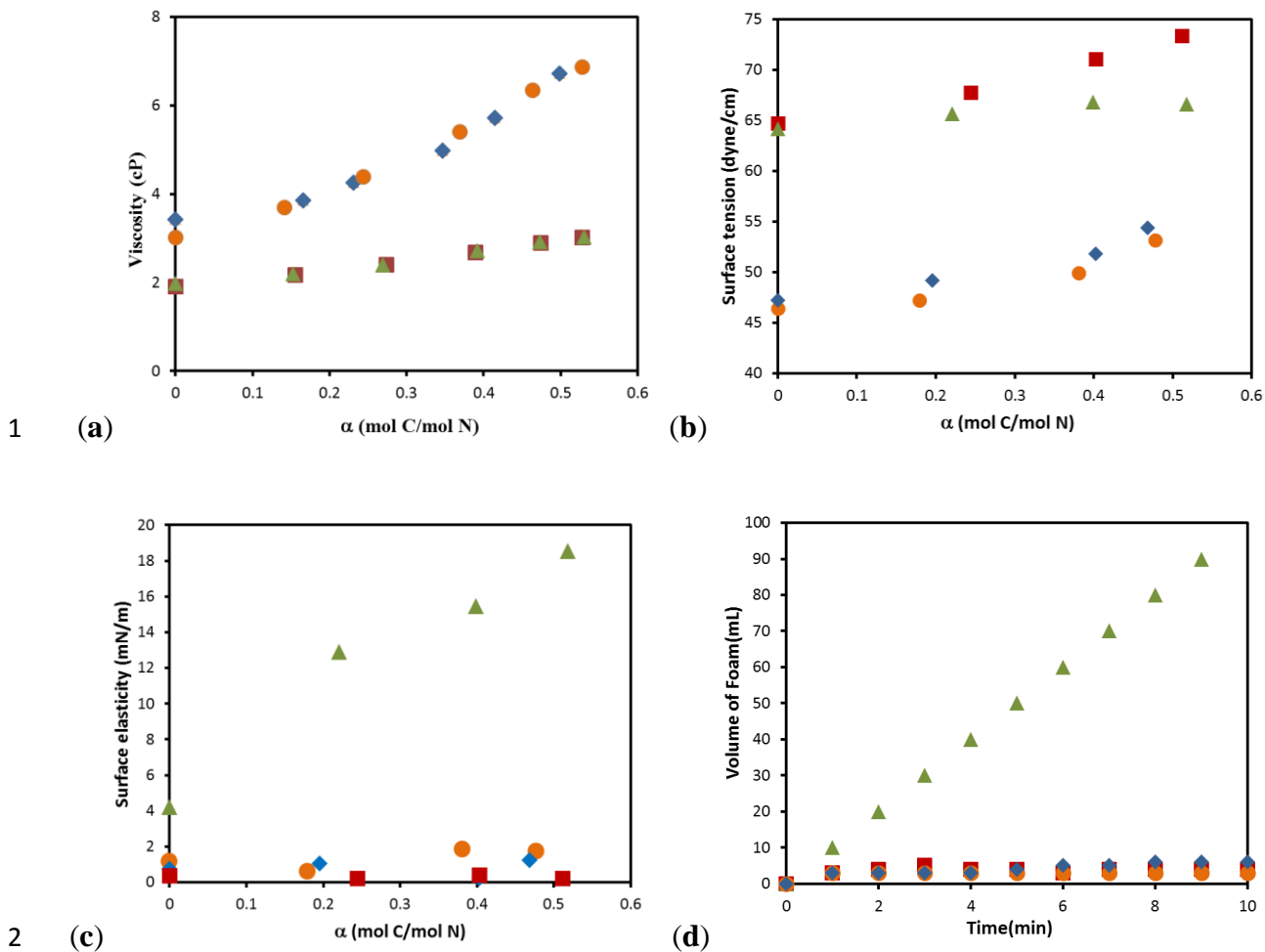
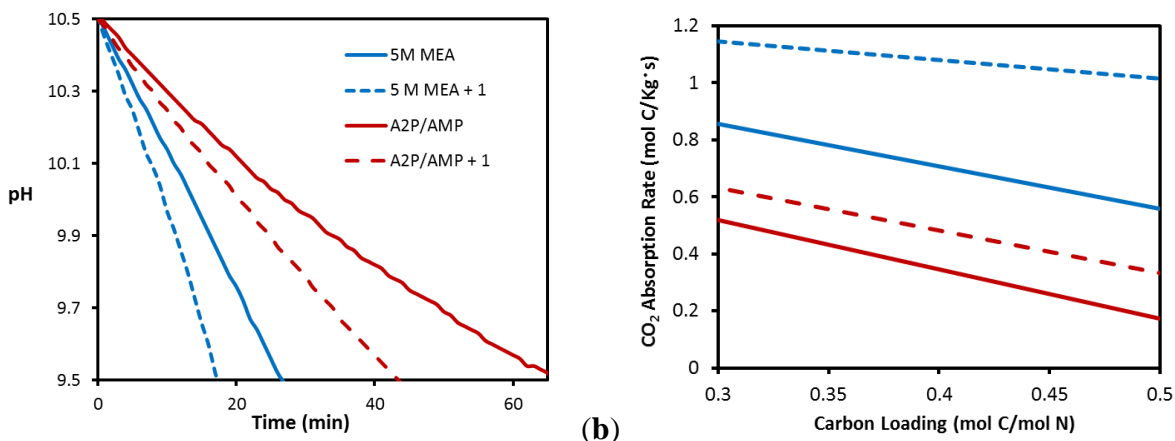


Figure 7. (a) Viscosity (b) surface tension and (c) surface elasticity versus carbon loading for carbon capture solutions with and without additive **1**. (d) Foaming versus time for carbon capture solutions with and without additive **1**. (■ = 30 wt.% MEA, ▲ = MEA + 2.3 g/L **1**, ● = A2P/AMP, ◆ = A2P/AMP + 2.3 g/L **1**).

3.2. Initial Screening.

For evaluation of the influence of **1** on reaction kinetics, a pH drop method was used as a quick screening process.²⁷ The activity of **1** and its propensity to improve overall mass transfer was evaluated by bubbling simulated flue gas (14% CO₂ / N₂ balanced) into solutions of 5 M MEA and A2P/AMP containing **1**, and compared to the reference amine solutions. As the acid gas (CO₂) is absorbed into an amine solvent, there is a decrease in the pH of the solution as protons are released to balance carbamate/bicarbonate formation. Therefore, in pH drop experiments a more negative slope is a qualitative indication of a more rapid absorption of CO₂ by

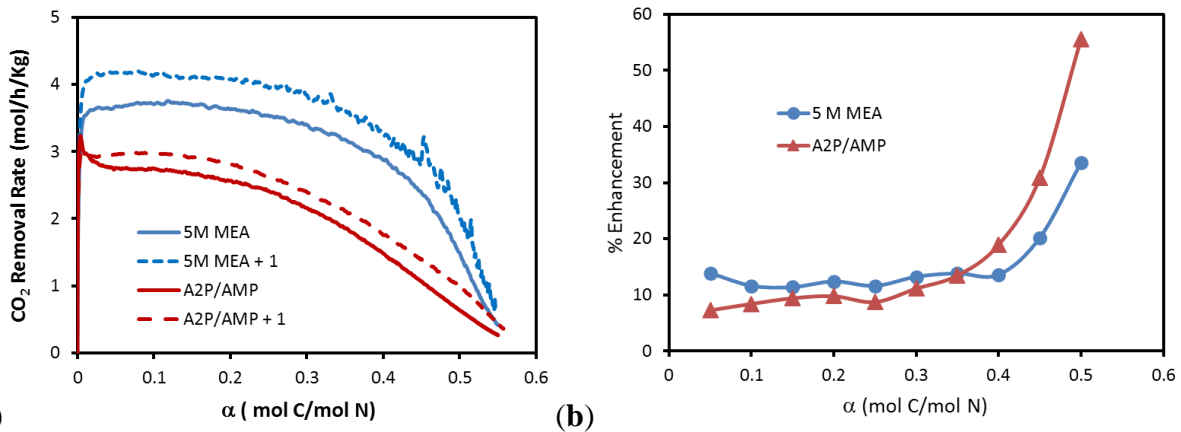
1 the solvent under the same setup and operating conditions. As shown in **Figure 8**, a significant
 2 enhancement in CO₂ absorption is observed upon the addition of **1** to both solvents, as indicated
 3 by the increased slope of the pH drop curve (**Figure 8a**) (e.g. increased rate of CO₂ absorption,
 4 **Figure 8b**), relative to additive-free baseline for both 5 M MEA and the A2P/AMP blended
 5 solvent. The large difference between the MEA and A2P/AMP baseline rates is expected, as MEA
 6 is well known to be a kinetically fast solvent, while A2P/AMP is formulated to be kinetically
 7 slower with lower solvent regeneration energy and higher thermal stability. These preliminary pH
 8 drop experiments indicate that addition of **1** results in an increased CO₂ absorption rate in both
 9 solvents, however the observation of foaming in solutions of MEA + **1** at higher loadings is
 10 concerning from a process standpoint, and the surfactant-like activity of **1** in MEA makes it
 11 difficult to determine if the observed enhancement in MEA is from catalytic activity, surfactant-
 12 like behavior, or a combination of both.



13 **(a)** pH drop kinetics testing of 5M MEA (—), 5M MEA with additive **1** (---), A2P/AMP
 14 **(—)**, and A2P/AMP with additive **1** (---), and **(b)** corresponding CO₂ removal rate.

16 **3.3. Determination of CO₂ Removal Rate.** After the success of the initial activity screening by
 17 pH drop, we sought to obtain a more quantitative determination of the enhancement in CO₂

1 removal kinetics enhancement facilitated via the addition of **1** into MEA and A2P/AMP capture
 2 solutions. In the breakthrough experiment there is extensive mixing between the gas bubbles and
 3 the liquid, and therefore diffusion resistance in the gaseous layer and bulk liquid is lowered to
 4 allow for observation of the kinetics from the reaction resistance. The breakthrough data in **Figure**
 5 **9a** shows an increase in CO₂ removal rate (relative to the solvent baseline), over the entire
 6 absorption range, upon the addition of **1** to both 5 M MEA and A2P/AMP solvents. However,
 7 foaming of the MEA + **1** solution is again observed at higher loadings ($\alpha > 0.3$).

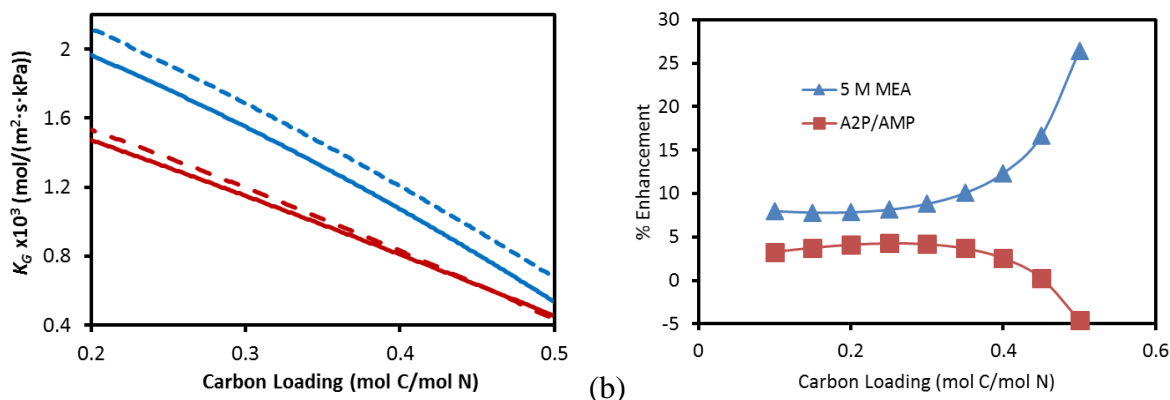


8 **(a)** Breakthrough data for carbon capture solvents with and without additive **1** in MEA
 9 **Figure 9.** **(a)** Breakthrough data for carbon capture solvents with and without additive **1** in MEA
 10 and A2P/AMP (14% CO₂ inlet). **(b)** Percent enhancement in CO₂ removal rate upon addition of **1**
 11 to MEA (blue) and A2P/AMP (red) capture solvents.

12 In a typical absorber column, absorption kinetics are faster at the top of the column where the
 13 capture solution is lean ($\alpha < 0.30$), and the rate decreases as more CO₂ is absorbed and the
 14 concentration of free amine decreases. The slowest absorption rates are observed with rich
 15 solutions ($\alpha > 0.40$) at the bottom of the column, requiring additional residence time or absorber
 16 height, for diminishing returns at higher loadings. The MEA samples show a higher removal rate
 17 than A2P/AMP as expected, but both solvents show enhancement upon addition of **1**. A greater
 18 degree of enhancement would translate to less additional absorber height required to obtain a
 19

1 similar increase in rich loading, and save on capital cost in absorber construction. As observed in
2 controlled laboratory-scale testing, additive **1** enhanced mass transfer at higher carbon loadings (α
3 > 0.40) where decreasing concentration of free amine limits the overall mass transfer rate, and
4 increasing viscosity of the capture solvent increases liquid resistance to mass transfer. The results
5 shown in **Figure 9b** demonstrate that the catalyst provides mass transfer enhancement over the
6 entire range, however the degree of enhancement is not uniform. The percent enhancement at lower
7 loadings is between 7 – 13 % upon addition of **1**, but at higher loadings ($\alpha > 0.4$ for MEA and $\alpha >$
8 0.25 for A2P/AMP) the enhancement increases significantly. Interestingly, the two curves cross at
9 $\alpha = 0.35$ and a much larger maximum enhancement is observed for the slower A2P/AMP solvent
10 (55 % at $\alpha = 0.5$), while the faster MEA solvent shows a 33% enhancement at $\alpha = 0.5$. The
11 increased enhancement at higher loadings is a good indication that **1** is performing as designed,
12 catalyzing the CO₂ hydration reaction that becomes more prevalent at higher loadings where the
13 concentration of free amine is diminished.

14 To include the liquid side diffusion resistance in the experiment, the mass transfer coefficient of
15 CO₂ transfer was measured in 5 M MEA and A2P/AMP solvents, with and without **1**, at 40 °C on
16 a wetted wall column (WWC) to approximate conditions in the absorber. The data in **Figure 10a**
17 shows the effect of carbon loading on the mass transfer coefficient, as an average of three (3)
18 replicate runs. As with the breakthrough data, addition of **1** to the 5 M MEA capture solvent
19 showed improvement in mass transfer over the entire experimental range, but at a relatively low
20 magnitude.

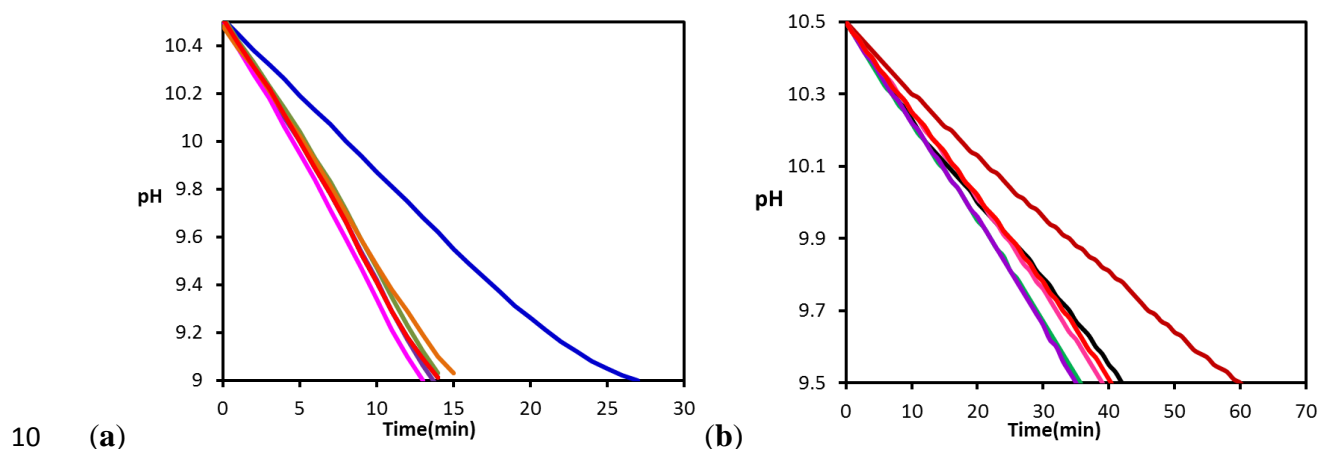


1 (a) (b)
 2 **Figure 10.** (a) Overall mass transfer coefficient (K_G) versus CO_2 loading from wetted wall
 3 column. 5 M MEA baseline (solid blue), 5 M MEA + 2.3 g/L **1** (blue dashed); A2P/AMP
 4 baseline (red solid), A2P/AMP + 2.3 g/L **1** (red dashed). (b) Percent enhancement versus carbon
 5 loading for MEA and A2P/AMP solutions containing **1** over respective baseline.

6 The effect of **1** on mass transfer was also examined for solutions of A2P/AMP (**Figure 10a**),
 7 although no significant enhancement was observed. The mass transfer of both the baseline and
 8 solutions containing **1** are equal near $\alpha = 0.5$ (**Figure 10b**). This lack of activity in A2P/AMP is
 9 inconsistent with the breakthrough data described in **Figure 9**, but represents one of the difficulties
 10 encountered in transitioning from highly controlled fundamental laboratory tests to more process
 11 relevant testing approaches. While the breakthrough experiment lowers diffusion resistance in
 12 order to isolate and analyze changes in the reaction resistance, the wetted-wall experiment
 13 maximizes diffusion resistance to allow for the identification of the mass transfer coefficients (K_g).
 14 By maximizing diffusion resistance in a kinetically slow, more viscous solvent such as the
 15 A2P/AMP blend, it is not surprising that no enhancement is observed in the WWC from a catalyst
 16 such as **1** that is designed to reduce only the reaction resistance. However, neither of these
 17 experiments are actually representative of conditions in a packed absorber column and it is
 18 important to conduct packed-column testing to determine enhancement when reaction and
 19 diffusion resistance are combined under process-relevant conditions (*vide infra*).

20 **3.4. Catalyst Integrity.** Flue gas contaminants, including NO_x and SO_x , are minor byproducts of
 21 coal combustion but are strong oxidants that have the potential to deactivate complexes such as **1**.

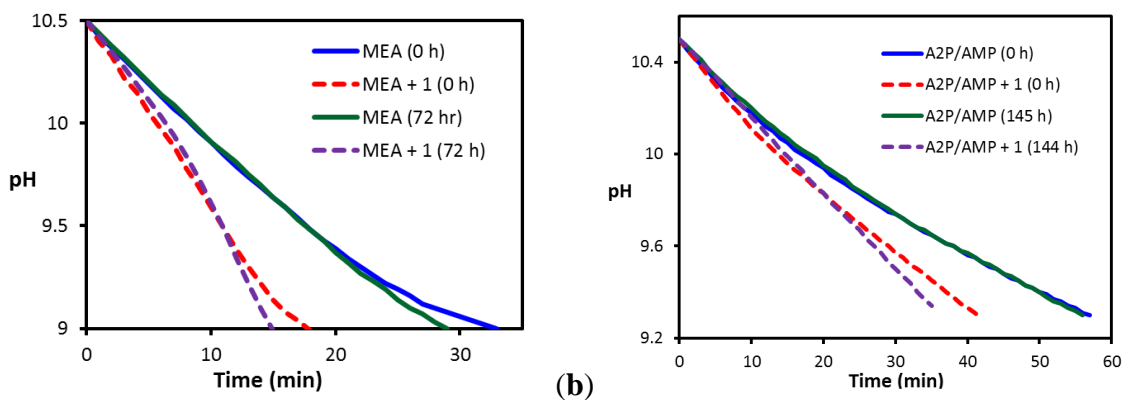
1 In order to examine the stability of **1** toward degradation by NO_x and SO_x, pH drop experiments
 2 were conducted in both capture solvents in the presence of 1000 ppm NO_x, and SO_x derived
 3 products. These concentrations are considered to be in the operational range of an amine-based
 4 capture process,⁵⁸ and no decrease in activity was observed (**Figure 11a**). Experiments were also
 5 conducted where solutions containing **1** were exposed to a large excess NO_x gas, generated from
 6 NaNO₂ and H₂SO₄ (see experimental section 2.5), as well as with all contaminants combined
 7 together. As shown in **Figure 11b**, negligible changes were observed in the pH drop testing,
 8 suggesting that NO_x and SO_x derived components do not affect the ability of **1** to increase mass
 9 transfer of the capture solutions.



11 **Figure 11.** pH drop testing of the stability of **1** toward NO_x and SO_x oxidative contaminants in
 12 MEA and A2P/AMP capture solutions. (a) blue = 5 M MEA baseline; black = MEA + **1**, green =
 13 MEA + **1** + 1000 ppm NaNO₃, purple = MEA + **1** + 1000 ppm NaNO₂, pink = MEA + **1** + 1000
 14 ppm Na₂SO₄, orange = MEA + **1** + excess NO_x, red = MEA + **1** + all NO_x/SO_x. (b) maroon =
 15 A2P/AMP baseline, black = A2P/AMP + **1**, green = A2P/AMP + **1** + 1000 ppm NaNO₃, purple =
 16 A2P/AMP + **1** + 1000 ppm NaNO₂, pink = A2P/AMP + **1** + 1000 ppm Na₂SO₄, orange =
 17 A2P/AMP + **1** + excess NO_x, red = A2P/AMP + **1** + all NO_x/SO_x.

18 Elevated temperatures in the carbon capture process are another source of chemical degradation,
 19 and an important barrier to commercial viability. It is imperative that any solvent component be
 20 stable at the temperatures observed in the stripping process for solvent regeneration. In order to

1 verify the thermal stability of **1**, activity assays via pH drop were performed after exposing
2 solutions of 5 M MEA with and without **1** to 145 °C for 72 hours and solutions of A2P/AMP with
3 and without **1** to 145 °C for 144 hours. As shown in **Figure 11**, there is no decrease in activity
4 observed upon heating for the solvent baseline, or for solutions containing **1**. Assuming 10%
5 residence time in the stripper, we estimate **1** would have a lifetime of over 1500 hours in an
6 industrial CCS process.



7 **(a)** **(b)**
8 **Figure 11.** Thermal stability of **1** in solutions of 5 M MEA **(a)** and the A2P/AMP **(b)** at 145 °C.

9 **3.5. Integrated Bench-Scale CO₂ Capture System.** The improved performance and effect on
10 overall energy penalty upon addition of **1** was determined using a bench-scale integrated CO₂
11 capture unit. The energy demand and performance of the A2P/AMP + **1** solvent blend was
12 compared to both A2P/AMP and 30% MEA. Solutions of MEA + **1** were not evaluated in the
13 bench-scale apparatus, due to foaming concerns and the possibility of damaging equipment from
14 solvent overflow. To accurately compare the different solvents tested, CO₂ capture efficiency was
15 maintained at 90% and the energy penalty was minimized through adjustment of process
16 parameters (i.e. liquid flow rate (L/G), stripper pressure, and hot oil temperature). The energy
17 penalty for the MEA and A2P/AMP baseline cases were very similar, at 234 and 236 kJ/mol CO₂,
18 respectively. Although A2P/AMP is designed to improve the overall thermodynamics with the

1 addition of AMP while maintaining faster kinetics with the addition of A2P, the blended A2P/AMP
 2 solvent has similar cyclic capacity as MEA but achieves a much lower rich loading in the absorber
 3 column (2.00 vs. 2.51 mol CO₂/kg). Upon the addition of **1** to the A2P/AMP solvent blend, the
 4 enhanced absorption kinetics increased the overall capture efficiency, and the liquid flow was
 5 decreased in order to maintain the 90% capture condition. Decreasing the liquid load increases
 6 cyclic capacity, as seen in **Table 2**, reducing the sensible heat requirement and decreasing the
 7 overall energy penalty of the A2P/AMP solvent by 21%.

8 **Table 2.** Reaction conditions and energy demand for CO₂ capture in Bench Unit for different
 9 solvents.

Solvent	Energy Demand (kJ/mol CO ₂)	Capture Efficiency (%)	Stripper Pressure (kPaa)	Cyclic Capacity (mol CO ₂ /kg)	Solvent Flowrate (mL/min)
MEA	234	92	110	0.84	150
A2P/AMP	236	92	128	0.72	150
A2P/AMP+ 1	187	89	179	1.37	60

10

Solvent	Rich Loading (mol CO ₂ /kg)	Lean Loading (mol CO ₂ /kg)	Reboiler T (°C)	Q _R (kW)	Rich Viscosity (cP)
MEA	2.51	1.67	92	0.72	3.3
A2P/AMP	2.00	1.28	91	0.72	7.2
A2P/AMP+ 1	2.08	0.707	106	0.52	7.4

11

12 **4. Discussion**

13 **4.1. Catalytic Solvent Evaluation Challenges.** Transitioning from the lab-scale testing methods,
 14 pH drop and breakthrough, to the more quantitative engineering testing methods such as the
 15 wetted-wall column introduces physical changes in the capture process. The decrease in the overall
 16 relative activity of **1** within the transition process, i.e. from breakthrough to wetted-wall, raises
 17 questions about how these physical differences affect the solvent evaluation between the solvent
 18 mixtures since the chemistry *in situ* remains unchanged. Bubbling simulated flue gas into the
 19 capture solution, as in the breakthrough experiment, minimizes the liquid side diffusion resistance

1 in equation (13), which is maximized in the wetted-wall column. However, the wetted-wall column
 2 is heavily influenced by physical properties of the solvent, such as viscosity and surface tension,
 3 due to the lack of turbulent force from counter-current gas flow and shearing force from the liquid
 4 flow through packing material. These turbulent forces destabilize the liquid film in a packed
 5 column and provide more liquid-gas contact to decrease the effect of liquid-side diffusion
 6 resistance.

$$\frac{1}{k'_g} = \underbrace{\frac{\sqrt{Dk_2[M]}}{H}}_{\text{Mass Transfer}} + \underbrace{\frac{1}{k_{l,prod}^\circ}}_{\text{Reaction Resistance}} \underbrace{\frac{\Delta P_{CO_2}^*}{\Delta \alpha \cdot [M]}}_{\text{Diffusion Resistance}}$$

(13)

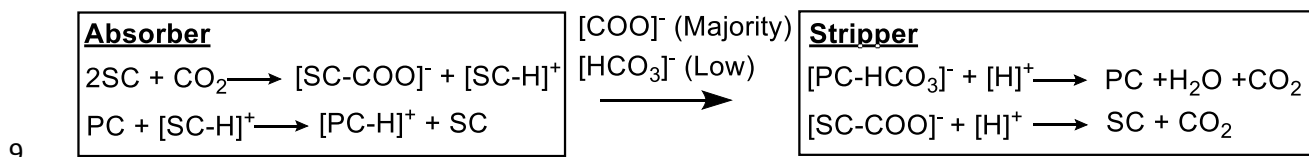
8 While the addition of **1** to the capture solutions had no effect on the solution viscosity and only
 9 minor effects on MEA surface tension, there is a dramatic increase in the elasticity of MEA upon
 10 the addition **1**. The surfactant-like activity of **1** in solutions of MEA make determining the source
 11 of any enhancement difficult to isolate, although previous studies have shown the addition of
 12 surfactants to capture solutions may cause formation of a single layer film on the surface that
 13 blocks CO₂ gas diffusion into the liquid and artificially depress the local amine concentration,
 14 decreasing overall mass transfer.⁵⁵ However, the constant surface tension and elasticity in solutions
 15 of A2P/AMP and A2P/AMP + **1** indicates there is no surfactant-like activity in this solvent blend
 16 and any enhancement is likely a result of the catalyst performing as designed. The lack of
 17 correlation between the surface properties and capture efficiency in these solutions seems counter-
 18 intuitive when compared to traditional models of mass transfer in these systems, however as other
 19 recent work has shown, caution must be taken when predicting improvements based on

1 fundamental and idealized laboratory testing methods, as counter-intuitive behavior was observed
2 upon the addition of surfactants to stirred-reactor experiments with a flat gas/liquid interface,⁵⁵
3 much like the wetted-wall experiments here. We previously concluded that although the addition
4 of surfactant lowers surface tension of the solution, it does not serve to promote bulk solvent
5 mixing on its own in these flat interface systems. The lack of bulk mixing is likely exacerbated in
6 the current wetted-wall experiments, due to the lack of mechanical mixing.

7 The lower rich loading of the A2P/AMP makes it an ideal candidate for addition of **1** and its
8 increased CO₂ absorption properties to both increase the rich loading of the solvent and thereby
9 decrease the overall energy demand of the system. Upon addition of **1** to A2P/AMP, the energy
10 demand was reduced to 187 kJ/mol CO₂, a 21% reduction. This reduced energy penalty was
11 achieved by decreasing the liquid flowrate from 150 mL/min down to 60 mL/min, while
12 maintaining 90% CO₂ capture and increasing the stripper pressure to 180 kPaa (**Table 2**). The
13 reduced liquid flowrate achieved upon addition of **1** nearly doubled the cyclic capacity of the
14 solvent (0.72 to 1.37 mol CO₂/kg). This increased cyclic capacity of the solvent reduces the
15 sensible heat required to heat the solvent and remove the CO₂ in the stripper. The increased rich
16 loadings, in addition to the increased cyclic capacity, reduces the energy demand through an
17 increased CO₂/H₂O (water vapor) ratio in the stripper. This allows for the higher stripper pressures,
18 lowering downstream compression costs, while reducing the energy consumption per unit of CO₂
19 produced.

20 **4.2. Solvent and Catalyst Behavior.** The absorption reactions for any amine based system can be
21 broken into two primary reactions as depicted in **Scheme 1**. The absorption of CO₂ is primarily
22 dictated by the reaction of the primary amine (SC) to form carbamate. The SC reaction generates
23 one mole of proton for each mol of CO₂ captured, leading to primary amines being generally

1 limited on a molar basis to 0.5 CO₂:1 N. The A2P/AMP solvent utilizes the primary amine A2P as
 2 the main component; with AMP added to principally act as a proton receiver (PC) in the solution.
 3 The PC serves to free more of the main component, enabling it to react with CO₂, and stabilizes
 4 the bicarbonate anion at higher carbon loadings. This allows a more carbon rich solution to be
 5 achieved. The pK_a of this proton receiver (AMP) is 9.8, which is higher than that of A2P (9.2)
 6 used in solvent. Therefore, the PC preferentially associates with the proton allowing more of the
 7 main component to react with CO₂. The reaction from the proton receiver to directly produce
 8 bicarbonate is prohibitively slower (100x), as is carbamate hydrolysis.



10 **Scheme 1.** Schematic for reactions occurring in the CO₂ capture cycle. In the illustration: SC -
 11 The constituents of the primary amine; PC - The constituents of the proton receiver/hindered
 12 amine.
 13 Complex **1** in this work was designed as a carbonic anhydrase (CA) mimic to catalyze CO₂
 14 hydration. Thus, it is expected to function similarly to CA's in directly catalyzing the reaction of
 15 dissolved CO₂ in solution to form bicarbonate and a proton. The proton is then trapped by the PC
 16 component (**Scheme 1**) of the solvent, thereby enhancing the overall mass transfer and capacity.
 17 Due to the nature of the solvent chemistry it can be expected that a greater benefit from the addition
 18 of **1** will be observed at higher carbon loadings where CO₂ hydration and bicarbonate formation
 19 dominates the capture regime.

20 **4.3. Catalyst Cost and Scalability.** The economic considerations are imperative when scaling-up
 21 a new technology. **1** is synthesized in a simple three-step process using all easily acquired
 22 commercial reagents, and the product from each step is isolated via filtration without the need for

1 further purification. The simplistic synthesis methodology attunes itself to already existing large-
2 scale manufacturing processes. We estimate the cost of **1** to be ~\$0.25 per liter of carbon capture
3 solvent, which roughly equates to \$100 - \$200 per megawatt of electricity generated. Cost of any
4 solvent additive is required to be low enough so that it can be treated as a disposable material as it
5 will be removed from the capture system during the thermal solvent reclamation process.
6 Additionally, **1** contains a non-toxic 3d metal and is not expected to impart any hazardous waste
7 requirements onto the solvent for disposal.

8 **5. Conclusions**

9 Herein we have demonstrated the development and transition from fundamental and idealized
10 laboratory investigations to CCS process relevant testing of catalyst, **1**, for the purpose of
11 enhancing overall mass transfer of CO₂ into carbon capture solvents for post-combustion acid gas
12 scrubbing technologies and reducing operational costs. Taken together, these studies provide
13 valuable insight into the performance of **1**, and more importantly considerations that should be
14 taken into account when testing new chemical additives for CCS processes. In laboratory
15 experiments that limit diffusion resistance, such as the pH drop and breakthrough methods, the
16 performance of **1** is as expected. Catalyzing the CO₂ hydration reaction increases max flux,
17 especially at higher loadings when the diminishing concentration of free amine and increasing
18 viscosity of the solvent slow CO₂ absorption. In the wetted-wall column, when diffusion resistance
19 is significant, the activity of **1** is greatly reduced due to the lack of bulk solvent mixing. Process
20 relevant testing of the A2P/AMP + **1** solvent was demonstrated in an integrated bench-scale
21 capture unit, and the activity of **1** decreases the capture energy of CO₂ in an integrated process by
22 21% compared to a 30 wt. % MEA base case by increasing the cyclic capacity and decreasing the
23 sensible heat required for solvent regeneration.

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6 References

- 7 1. (a) Standards of Performance for Greenhouse Gas Emissions From New Stationary Sources:
8 Electric Utility Generating Units, Environmental Protection Agency (Jan. 8, 2014). (b) Carbon Pollution -
9 Emission Guidelines for Existing Stationary Sources: Electric Utility Generating Units, Environmental
10 Protection Agency (June 2, 2014).
- 11 2. Liang, Z. W.; Rongwong, W.; Liu, H. L.; Fu, K. Y.; Gao, H. X.; Cao, F.; Zhang, R.; Sema, T.; Henni, A.;
12 Sumon, K.; Nath, D.; Gelowitz, D.; Srisang, W.; Saiwan, C.; Benamor, A.; Al-Marri, M.; Shi, H. C.; Supap, T.;
13 Chan, C.; Zhou, Q.; Abu-Zahra, M.; Wilson, M.; Olson, W.; Idem, R.; Tontiwachwuthikul, P., Recent progress
14 and new developments in post-combustion carbon-capture technology with amine based solvents. *Int. J.*
15 *Greenhouse Gas Control* **2015**, *40*, 26-54.
- 16 3. Cost and Performance Baseline for Fossil Energy Plants - Volume 1: Bituminous Coal and Natural
17 Gas to Electricity (Rev 2, November 2010).
- 18 4. Lu, Y.; Ye, X. H.; Zhang, Z. H.; Khodayari, A.; Djukadi, T., Development of a Carbonate Absorption-
19 Based Process for Post-Combustion CO₂ Capture: the Role of Biocatalyst to Promote CO₂ Absorption Rate.
20 *Energy Procedia* **2011**, *4*, 1286-1293.
- 21 5. Vinoba, M.; Bhagiyalakshmi, M.; Grace, A. N.; Kim, D. H.; Yoon, Y.; Nam, S. C.; Baek, I. H.; Jeong, S.
22 K., Carbonic Anhydrase Promotes the Absorption Rate of CO₂ in Post-Combustion Processes. *J. Phys.*
23 *Chem. B* **2013**, *117* (18), 5683-5690.
- 24 6. Penders-van Elk, N. J. M. C.; Hamborg, E. S.; Huttenhuis, P. J. G.; Fradette, S.; Carley, J. A.; Versteeg,
25 G. F., Kinetics of absorption of carbon dioxide in aqueous amine and carbonate solutions with carbonic
26 anhydrase. *Int. J. Greenhouse Gas Control* **2013**, *12*, 259-268.
- 27 7. Penders-van Elk, N. J. M. C.; Fradette, S.; Versteeg, G. F., Effect of pKa on the kinetics of carbon
28 dioxide absorption in aqueous alkanolamine solutions containing carbonic anhydrase at 298 K. *Chem. Eng.*
29 *J.* **2015**, *259*, 682-691.
- 30 8. Li, L.; Voice, A. K.; Li, H.; Namjoshi, O.; Nguyen, T.; Du, Y.; Rochelle, G. T., Amine blends using
31 concentrated piperazine. *Energy Procedia* **2013**, *37*, 353-369.
- 32 9. Voice, A. K.; Vevelstad, S. J.; Chen, X.; Nguyen, T.; Rochelle, G. T., Aqueous 3-
33 (methylamino)propylamine for CO₂ capture. *Int. J. Greenhouse Gas Control* **2013**, *15*, 70-77.
- 34 10. Sherman, B.; Chen, X.; Nguyen, T.; Xu, Q.; Rafique, H.; Freeman, S. A.; Voice, A. K.; Rochelle, G. T.,
35 Carbon Capture with 4 M Piperazine/4 M 2-Methylpiperazine. *Energy Procedia* **2013**, *37*, 436-447.
- 36 11. Lin, P. H.; Wong, D. S. H., Carbon dioxide capture and regeneration with amine/alcohol/water
37 blends. *Int. J. Greenhouse Gas Control* **2014**, *26*, 69-75.
- 38 12. Shi, H. C.; Naami, A.; Idem, R.; Tontiwachwuthikul, P., Catalytic and non catalytic solvent
39 regeneration during absorption-based CO₂ capture with single and blended reactive amine solvents. *Int.*
40 *J. Greenhouse Gas Control* **2014**, *26*, 39-50.

- 1 13. Adeosun, A.; Abu-Zahra, M. R. M., Evaluation of amine-blend solvent systems for CO₂ post-
2 combustion capture applications. *Energy Procedia* **2013**, *37*, 211-218.
- 3 14. Aroonwilas, A.; Veawab, A., Integration of CO₂ capture unit using single- and blended-amines into
4 supercritical coal-fired power plants: Implications for emission and energy management. *Int. J.*
5 *Greenhouse Gas Control* **2007**, *1* (2), 143-150.
- 6 15. Tsai, R. E.; Schultheiss, P.; Kettner, A.; Lewis, J. C.; Seibert, A. F.; Eldridge, R. B.; Rochelle, G. T.,
7 Influence of surface tension on effective packing area. *Ind. Eng. Chem. Res.* **2008**, *47* (4), 1253-1260.
- 8 16. Tsai, R. E.; Seibert, A. F.; Eldridge, R. B.; Rochelle, G. T., A Dimensionless Model for Predicting the
9 Mass-Transfer Area of Structured Packing. *AIChE J.* **2011**, *57* (5), 1173-1184.
- 10 17. Floyd, W. C., III; Baker, S. E.; Valdez, C. A.; Stolaroff, J. K.; Bearinger, J. P.; Satcher, J. H., Jr.; Aines,
11 R. D., Evaluation of a carbonic anhydrase mimic for industrial carbon capture. *Environ. Sci. Technol.* **2013**,
12 *47* (17), 10049-55.
- 13 18. Koziol, L.; Valdez, C. A.; Baker, S. E.; Lau, E. Y.; Floyd, W. C.; Wong, S. E.; Satcher, J. H.; Lightstone,
14 F. C.; Aines, R. D., Toward a Small Molecule, Biomimetic Carbonic Anhydrase Model: Theoretical and
15 Experimental Investigations of a Panel of Zinc(II) Aza-Macrocyclic Catalysts. *Inorg. Chem.* **2012**, *51* (12),
16 6803-6812.
- 17 19. Zhang, X. P.; Vaneldik, R.; Koike, T.; Kimura, E., Kinetics and Mechanism of the Hydration of CO₂
18 and Dehydration of HCO₃⁻ Catalyzed by a Zn(II) Complex of 1,5,9-Triazacyclododecane as a Model for
19 Carbonic Anhydrase. *Inorg. Chem.* **1993**, *32* (25), 5749-5755.
- 20 20. Zhang, X. P.; Vaneldik, R., A Functional Model for Carbonic Anhydrase - Thermodynamic and
21 Kinetic Study of a Tetraazacyclododecane Complex of Zinc(II). *Inorg. Chem.* **1995**, *34* (22), 5606-5614.
- 22 21. Liang, Z.; Idem, R.; Tontiwachwuthikul, P.; Yu, F.; Liu, H.; Rongwong, W., Experimental study on
23 the solvent regeneration of a CO₂-loaded MEA solution using single and hybrid solid acid catalysts. *AIChE*
24 *J.* **2016**, *62* (3), 753-765.
- 25 22. Evans, M. G.; Polanyi, M., Further considerations on the thermodynamics of chemical equilibria
26 and reaction rates. *Trans. Faraday Soc.* **1936**, *32*, 1333-1360.
- 27 23. Nwaoha, C.; Idem, R.; Supap, T.; Saiwan, C.; Tontiwachwuthikul, P.; Rongwong, W.; Al-Marri, M.
28 J.; Benamor, A., Heat duty, heat of absorption, sensible heat and heat of vaporization of 2-Amino-2-
29 Methyl-1-Propanol (AMP), Piperazine (PZ) and Monoethanolamine (MEA) tri-solvent blend for carbon
30 dioxide (CO₂) capture. *Chem. Eng. Sci.*
- 31 24. Huang, Q. Z.; Bhatnagar, S.; Remias, J. E.; Selegue, J. P.; Liu, K. L., Thermal degradation of amino
32 acid salts in CO₂ capture. *Int. J. Greenhouse Gas Control* **2013**, *19*, 243-250.
- 33 25. Wang, T. L.; Jens, K. J., Oxidative Degradation of AMP/MEA Blends for Post-combustion CO₂
34 Capture. *Energy Procedia* **2013**, *37*, 306-313.
- 35 26. Voice, A. K.; Hill, A.; Fine, N. A.; Rochelle, G. T., Nitrosamine formation and mitigation in blended
36 amines for CO₂ capture. *Int. J. Greenhouse Gas Control* **2015**, *39*, 329-334.
- 37 27. Kelsey, R. A.; Miller, D. A.; Parkin, S. R.; Liu, K.; Remias, J. E.; Yang, Y.; Lightstone, F. C.; Liu, K. L.;
38 Lippert, C. A.; Odom, S. A., Carbonic anhydrase mimics for enhanced CO₂ absorption in an amine-based
39 capture solvent. *Dalton Trans.* **2016**, *45* (1), 324-333.
- 40 28. Lippert, C. A.; Widger, L. R.; Sarma, M.; Liu, K. L., Catalyst Development for Rate Enhanced Acid
41 Gas (CO₂) Scrubbing. *Energy Procedia* **2014**, *63*, 273-278.
- 42 29. Lippert, C. A.; Liu, K.; Sarma, M.; Parkin, S. R.; Remias, J. E.; Brandewie, C. M.; Odom, S. A.; Liu, K.
43 L., Improving carbon capture from power plant emissions with zinc- and cobalt-based catalysts. *Catal. Sci.*
44 *Technol.* **2014**, *4* (10), 3620-3625.
- 45 30. Bond, G. M.; Stringer, J.; Brandvold, D. K.; Simsek, F. A.; Medina, M. G.; Egeland, G., Development
46 of integrated system for biomimetic CO₂ sequestration using the enzyme carbonic anhydrase. *Energy Fuels*
47 **2001**, *15* (2), 309-316.

- 1 31. Liu, K.; Jinka, K. M.; Remias, J. E.; Liu, K. L., Absorption of Carbon Dioxide in Aqueous Morpholine
2 Solutions. *Ind. Eng. Chem. Res.* **2013**, *52* (45), 15932-15938.
- 3 32. Delaney, M. S.; Reddy, D.; Wessling, R. A., Oxygen/nitrogen transport in glassy polymers with
4 oxygen-binding pendent groups. *Journal of Membrane Science* **1990**, *49* (1), 15-36.
- 5 33. Rao, A. B.; Rubin, E. S., A Technical, Economic, and Environmental Assessment of Amine-Based
6 CO₂ Capture Technology for Power Plant Greenhouse Gas Control. *Environ. Sci. Technol.* **2002**, *36* (20),
7 4467-4475.
- 8 34. Gouedard, C.; Picq, D.; Launay, F.; Carrette, P. L., Amine degradation in CO₂ capture. I. A review.
9 *Int. J. Greenhouse Gas Control* **2012**, *10*, 244-270.
- 10 35. Conway, W.; Wang, X.; Fernandes, D.; Burns, R.; Lawrance, G.; Puxty, G.; Maeder, M., Toward the
11 understanding of chemical absorption processes for post-combustion capture of carbon dioxide:
12 electronic and steric considerations from the kinetics of reactions of CO₂(aq) with sterically hindered
13 amines. *Environ. Sci. Technol.* **2013**, *47* (2), 1163-9.
- 14 36. Conway, W.; Wang, X.; Fernandes, D.; Burns, R.; Lawrance, G.; Puxty, G.; Maeder, M.,
15 Comprehensive kinetic and thermodynamic study of the reactions of CO₂(aq) and HCO₃⁻ with
16 monoethanolamine (MEA) in aqueous solution. *J. Phys. Chem. A* **2011**, *115* (50), 14340-9.
- 17 37. McCann, N.; Phan, D.; Wang, X.; Conway, W.; Burns, R.; Attalla, M.; Puxty, G.; Maeder, M., Kinetics
18 and mechanism of carbamate formation from CO₂(aq), carbonate species, and monoethanolamine in
19 aqueous solution. *J. Phys. Chem. A* **2009**, *113* (17), 5022-9.
- 20 38. Benamor, A.; Aroua, M. K., An Experimental Investigation on the rate of CO₂ Absorption into
21 aqueous methyldiethanolamine solutions. *Korean J. Chem. Eng.* **2007**, *24* (1), 16-23.
- 22 39. Vaidya, P. D.; Kenig, E. Y., CO₂-Alkanolamine Reaction Kinetics. *Chem. Eng. Technol.* **2007**, *30* (11),
23 1467-1474.
- 24 40. Xu, S.; Wang, Y. W.; Otto, F. D.; Mather, A. E., Kinetics of the reaction of carbon dioxide with 2-
25 amino-2-methyl-1-propanol solutions. *Chem. Eng. Sci.* **1996**, *51* (6), 841-850.
- 26 41. Sami, H. A.; Merchant, S. Q.; Fahim, M. A., Reaction kinetics of some secondary alkanolamines
27 with carbon dioxide in aqueous solutions by stopped flow technique. *Sep. Purif. Technol.* **2002**, *27*, 121-
28 136.
- 29 42. Ume, C. S.; Ozturk, M. C.; Alper, E., Kinetics of CO₂ absorption by a blended aqueous amine
30 solution. *Chem. Eng. Technol.* **2012**, *35* (3), 464-468.
- 31 43. Penny, D. E.; Ritter, T. J., Kinetic study of the reaction between carbon dioxide and primary
32 amines. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79* (9), 2103-2109.
- 33 44. Barth, D.; Tondre, C.; Delpuech, J. J., Stopped-flow investigations of the reaction kinetics of carbon
34 dioxide with some primary and secondary alkanolamines in aqueous solutions. *Int. J. Chem. Kinet.* **1986**,
35 *18* (4), 445-457.
- 36 45. Crooks, J. E.; Donnellan, J. P., Kinetics and mechanism of the reaction between carbon dioxide and
37 amines in aqueous solution. *J. Chem. Soc., Perkin Trans. 2* **1989**, (4), 331-333.
- 38 46. Alper, E., Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1-propanol
39 and carbon dioxide. *Ind. Eng. Chem. Res.* **1990**, *29* (8), 1725-1728.
- 40 47. Laddha, S. S.; Danckwerts, P. V., Reaction of CO₂ with ethanolamines: kinetics from gas-
41 absorption. *Chem. Eng. Sci.* **1981**, *36* (3), 479-482.
- 42 48. Hikita, H.; Asai, S.; Ishikawa, H.; Honda, M., The kinetics of reactions of carbon dioxide with
43 monoethanolamine, diethanolamine and triethanolamine by a rapid mixing method. *The Chemical*
44 *Engineering Journal* **1977**, *13* (1), 7-12.
- 45 49. Ali, S. H.; Merchant, S. Q.; Fahim, M. A., Reaction kinetics of some secondary alkanolamines with
46 carbon dioxide in aqueous solutions by stopped flow technique. *Sep. Purif. Technol.* **2002**, *27* (2), 121-136.

- 1 50. Henni, A.; Li, J.; Tontiwachwuthikul, P., Reaction Kinetics of CO₂ in Aqueous 1-Amino-2-Propanol,
2 3-Amino-1-Propanol, and Dimethylmonoethanolamine Solutions in the Temperature Range of 298–313 K
3 Using the Stopped-Flow Technique. *Ind. Eng. Chem. Res.* **2008**, *47* (7), 2213-2220.
- 4 51. Kohl, A.; Nielsen, R. *Gas Purification, 5th ed.*; Gulf Publishing Co.: Houston, TX, 1997.
- 5 52. Aouini, I.; Ledoux, A.; Estel, L.; Mary, S.; Grimaud, J.; Valognes, B., Study of carbon dioxide capture
6 from industrial incinerator flue gas on a laboratory scale pilot. *Energy Procedia* **2011**, *4*, 1729-1736.
- 7 53. Gunasekaran, P.; Veawab, A.; Aroonwilas, A., Corrosivity of Single and Blended Amines in CO₂
8 Capture Process. *Energy Procedia* **2013**, *37*, 2094-2099.
- 9 54. Song, D.; Seibert, A. F.; Rochelle, G. T., Effect of Liquid Viscosity on the Liquid Phase Mass Transfer
10 Coefficient of Packing. *Energy Procedia* **2014**, *63*, 1268-1286.
- 11 55. Bryant, J. J.; Lippert, C.; Qi, G.; Liu, K.; Mannel, D. S.; Liu, K., Enhanced Carbon Capture through
12 Incorporation of Surfactant Additives. *Ind. Eng. Chem. Res.* **2016**, *55* (27), 7456-7461.
- 13 56. Georgieva, D.; Cagna, A.; Langevin, D., Link between surface elasticity and foam stability. *Soft*
14 *Matter* **2009**, *5* (10), 2063-2071.
- 15 57. Maddox, R. N. *Gas and Liquid Sweetening In Gas Conditioning and Processing*, Third Edition;
16 Campbell, J. M., Ed.; Campbell Petroleum Series: Norman, OK, **1994**.
- 17 58. Huang, Q. Z.; Thompson, J.; Bhatnagar, S.; Chandan, P.; Remias, J. E.; Selegue, J. P.; Liu, K. L., Impact
18 of Flue Gas Contaminants on Monoethanolamine Thermal Degradation. *Ind. Eng. Chem. Res.* **2014**, *53* (2),
19 553-563.