Understanding the Corrosion of CO₂-loaded 2-Amino-2-Methyl-1-Propanol Solutions Assisted by Thermodynamic Modeling

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Abstract

Corrosion of A106 carbon steel in a naturally aerated 30 wt.% 2-amino-2-methyl-1-propanol-based solution (AMP, a sterically hindered primary amine) with $0.43 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{AMP}}$ was evaluated at 80°C . Substantial decrease in corrosion rate, i.e., over two orders of magnitude, was observed over the initial 70 h, which is the result of formation of a protective FeCO_3 layer followed by passivation of the A106 surface. Mechanisms for formation of these protective layers are discussed with comparison to corrosion in a 30 wt.% monoethanolamine solution as well as with the help of thermodynamic modeling of the AMP- H_2O - CO_2 system. Experimental solubility data from literature were employed to extract a thermodynamic model for aqueous solutions of AMP with concentrations ranging from 17.8 to 36.6 wt. % at various CO_2 loadings. Liquid phase speciation was determined by employing an electrolyte-NRTL model. The AMP carbamate stability constant, molecule-ion pair, and molecule-molecule interaction parameters in the studied concentrations were obtained. The determined CO_2 equilibrium properties are in agreement with previously reported experimental data.

Keywords: sterically hindered amine; AMP; corrosion; steel; thermodynamic modeling; passivity

1. Introduction

The use of aqueous solutions of alkanolamines to remove CO₂ emissions from gas phase process streams has been proven to be reliable in many chemical industries. Primary and secondary amines generally exhibit a high CO₂ absorption rate but are limited by a high heat of regeneration and low achievable CO₂ loading (mole of dissolved CO₂/mole of amine). Tertiary amines generally show the opposite behavior with relatively lower reactivity, lower heats of regeneration, and higher CO₂ loading. The reaction between CO₂ and tertiary amines is a classical acid-base proton transfer reaction; primary and secondary amines, however, tend to combine with CO₂ forming more stable carbamate compounds, which require a larger energy penalty to release CO₂ and regenerate the amine. These different reaction pathways lead to different characteristics for primary and secondary amines to tertiary amines (Arcis et al., 2014). Sterically hindered amines, defined as either a primary amine in which the amino group is attached to a tertiary carbon or a secondary amine in which the amino group is attached to at least one secondary or tertiary carbon (Zhao and Winston Ho, 2012), present advantages in terms of a faster CO₂ absorption rate with respect to the tertiary amines, a higher solvent capacity, and a lower desorption energy when compared to their unhindered counterparts because of the instability of their carbamate but favorable bicarbonate pathway (Afkhampour and Mofarahi, 2013; Arcis et al., 2014; Ciftja et al., 2011; Ciftja et al., 2014; Dash et al., 2011; Hamborg and Versteeg, 2009; Hartono et al., 2013; Kundu and Bandyopadhyay, 2006; Li et al., 2014; Mehdizadeh et al., 2013; Pahlavanzadeh et al., 2010; Park et al., 2002; Richner and Puxty, 2012; Sartori and Savage, 1983; Seo and Hong, 1996; Silkenbäumer et al., 1998; Tong et al., 2012; Wu et al., 2013; Yih and Shen, 1988). Furthermore, sterically hindered amines generally have low volatilities and lower degradation rates as a consequence of the bicarbonate reaction pathway (Ciftja et al., 2011; Hartono et al., 2013; Yih and Shen, 1988). For example, 2-amino-2-methyl-1-propanol (AMP), a sterically hindered form of monoethanolamine (MEA), was reported to display lower carbamate stability, a better loading capacity for CO₂, and higher thermal stability when compared to MEA, which is especially the case at higher pressures (Barzagli et al., 2013; Ciftja et al., 2011; Hartono et al., 2013; Yih and Shen, 1988).

Corrosion is also an important consideration with application of alkanolamine solvents, and sterically hindered amines have demonstrated relatively lower corrosivity than their unhindered forms as a result of the formation of protective corrosion layers (Afkhamipour and Mofarahi, 2013; Campbell et al., 2016; Eustaquio-Rincón et al., 2008; Gunasekaran et al., 2013; Mimura et al., 1995; Veawab et al., 1996; Veawab et al., 1997; Veawab et al., 1999a, b). The abovementioned properties make AMP potentially viable for CO₂ capture as a component in blended solvents or as a single amine if its CO₂ absorption rate can be promoted, e.g., by use of a catalyst. Solution speciation has been reported to be important evaluating the corrosivity of CO₂ loaded aqueous solutions of alkanolamines and to understand the corrosion mechanism in the system (Zheng et al., 2016a; Zheng et al., 2016b, c). For example, the bicarbonate concentration in these alkanolamines can have a significant impact on the resulting corrosion of process units as well as the formation of corrosion products (Zheng et al., 2016a; Zheng et al., 2016b, c). Thus, a reliable thermodynamic model for the CO₂:AMP:H₂O system is crucial in estimating the solution speciation for understanding the corrosion mechanism. Some work has been done on solubility measurements and thermodynamic modeling of CO₂ in aqueous solutions of various alkanolamine systems including AMP (Arcis et al., 2014; Ciftja et al., 2014; Hamborg and Versteeg, 2009; Hartono et al., 2013; Kundu and Bandyopadhyay, 2006; Li et al., 2014; Liang et al., 2015; Mehdizadeh et al., 2013; Pahlavanzadeh et al., 2010; Park et al., 2002; Rebolledo-Morales et al., 2011; Richner and Puxty, 2012; Silkenbäumer et al., 1998; Tong et al., 2012; Wu et al., 2013). The Kent-Eisenberg thermodynamics model (Pahlavanzadeh et al., 2010; Park et al., 2002; Rebolledo-Morales et al., 2011) or various equations for Gibbs energy and activity coefficients, such as NRTL (Hartono et al., 2013), Pitzer (Arcis et al., 2014; Silkenbäumer et al., 1998), e-UNIQUAC (Mehdizadeh et al., 2013), and extended Debye–Hückel equation (Ciftja et al., 2014; Richner and Puxty, 2012; Tong et al., 2012), have been applied to AMP-based solutions. However, in order to evaluate the corrosivity of these solutions at specific conditions (e.g. amine concentrations and system temperatures), a detailed thermodynamic model is necessary to closely approximate solution speciation at relative conditions.

In this work, a thermodynamic model based on electrolyte-NRTL equations was developed by employing the experimental solubility data of CO₂ in aqueous solutions of AMP from the literature (Silkenbäumer et al., 1998). The solution speciation can be produced from this model for AMP concentrations ranging from 17.8 to 36.6 wt.% and at various temperatures. Corrosion behavior of 1018 carbon steel (CS) and AISI 420 stainless steel in AMP solutions has been reported previously by Veawab et al (Gunasekaran et al., 2013; Veawab et al., 1996; Veawab et al., 1997; Veawab et al., 1999a, b) and Campbell et al. (Campbell et al., 2016), and Palmero et al. (Palmero et al., 2013), respectively. However, an understanding of the corrosion behavior of steels at different stages and especially formation of protective corrosion layers such as FeCO₃ and passive film on the steel surface in AMP solutions is still lacking. Therefore, corrosion of CS in an example solution of naturally aerated 30 wt.% AMP with 0.43 mol_{CO2}/mol_{AMP} was evaluated over an extended time period by electrochemical corrosion measurements such as linear polarization resistance (LPR) testing and corrosion potential (E_{corr}) measurements, and surface characterization such as SEM and XRD in addition to thermodynamic modelling.

2. Methods and Materials

2.1 Corrosivity Evaluation

Considering the intrinsically corrosive characteristics of the operating conditions in a real post-combustion CO₂ capture process, stainless steels are normally used for process units. However, the price of stainless steel is substantially higher than carbon steel (about 3-4 times). To lower the total capital cost for a post-combustion CO₂ capture process, the evaluation of carbon steel was performed. Furthermore, A106 grade B carbon steel is usually designed to be used as seamless pipe at high temperatures and pressures, which is suitable for typical operating conditions for CO₂ capture plants (e.g., around 120 °C and 75 psi in the stripper). Therefore, to evaluate corrosivity of the CO₂:AMP:H₂O system, A106 Grade B carbon steel cylinders (with a diameter of 9.5 mm and a height of 13 mm) were chosen to perform corrosion studies. All of the samples

were ground with SiC sand paper to a final 800 grit, and then ultrasonically cleaned with deionized water and acetone. MEA (99%, technical grade), AMP (99%, Acros Organicstm), and CO₂ (99.5%, chemically pure grade) were purchased from Univar, Fisher, and SCOTT-GROSS company, respectively.

Corrosion studies were carried out in a static system of 30 wt.% AMP with a CO₂ loading of 0.43 mol_{CO2}/mol_{AMP}. To simulate the operating condition of the cross-over heat exchanger between the stripper and the absorber, a temperature of 80°C was chosen for this study. For comparison, a corrosion study in a benchmark solvent of 30 wt.% MEA, with all other conditions held constant between the MEA and AMP systems, is also shown in this work. Both solutions were exposed to air during the preparation, storage, and experimental testing process as this non-pressurized vessel was open to air. No deaeration method was used in this work, i.e., the solutions were naturally aerated.

A corrosion cell with a standard three-electrode setup was used for electrochemical testing with a saturated calomel electrode (SCE) as the reference electrode and a graphite rod as the counter electrode. The LPR method was employed to study corrosion behavior over an extended time period, and the details of this method can be found elsewhere (Zheng et al., 2015; Zheng et al., 2014a; Zheng et al., 2014b). The corrosion current density (i_{corr} , $\mu\text{A cm}^{-2}$) was calculated using standard Tafel slopes of 100 mV/decade for both the anodic (β_a) and cathodic (β_c) reactions with equation 1. Subsequently, the corrosion rate (V , $\text{g m}^{-2} \text{d}^{-1}$) was calculated using equation 2.

$$i_{\text{corr}} = \frac{\beta_a \beta_c}{2.3 R_p (\beta_a + \beta_c)} \quad (1)$$

$$V = i_{\text{corr}} K W_{\text{eq}} \quad (2)$$

where R_p is the polarization resistance (ohms), K is a constant of $8.954 \times 10^{-3} \text{ g cm}^2 \mu\text{A}^{-1} \text{m}^{-2} \text{d}^{-1}$, and W_{eq} is the equivalent weight (g/equivalent). To verify reproducibility of this work, all tests were repeated, and these results are also presented (Figure 1). Moreover, E_{corr} was measured over an extended duration.

To further understand the corrosion as well as formation of corrosion products, surface characterization by scanning electron microscopy (SEM) and X-ray diffraction (XRD), and solution analysis such as solution alkalinity, CO₂ loading, and pH were carried out. The details of these methods are described elsewhere (Zheng et al., 2014b; Zheng et al., 2016b). Moreover, to better identify the formed corrosion layers on the surface during different steps, the cross-section of corroded samples was prepared and characterized by FEI Helios Nanolab 660 (including focused ion beam (FIB) techniques and SEM characterization, FIB/SEM). A liquid metal ion source of gallium was used for cross section milling. An ion beam voltage of 30 kV was used for all cross-section milling steps, and the beam current was reduced to 80 pA for the final polishing step. In addition to these experimental techniques, thermodynamic modeling of the aqueous solutions of AMP was carried out.

2.2 Solution Chemistry and Thermodynamic Modeling

The following independent reactions are considered in CO₂ loaded aqueous alkanolamine solutions.

Ionization of water,

Dissociation of dissolved CO₂ through carbonic acid,

Dissociation of bicarbonate,

Carbamate reversion to bicarbonate (hydrolysis reaction),

Dissociation of protonated amines,

To account for the non-ideality of the electrolyte solutions, the liquid phase chemical reaction equilibria, K_i , can be approximated as the product of individual species activities,

$$K_i = \prod_j a_j^{\nu_j} \quad (8)$$

where a_j and ν_j are the activity and stoichiometric coefficients of species j , respectively. Equation 8 can be written in terms of activity coefficients, in mole fraction scale,

$$K_i = \prod_j (x_j \gamma_j)^{\nu_j} \quad (9)$$

where, x_j and γ_j are the mole fraction and activity coefficient of species j , respectively. The dissociation constant for the protonated AMP was extracted from experimental data reported in the literature (Hamborg and Versteeg, 2009). The carbamate reversion to bicarbonate constant for equation 6 was adjusted during regression analysis.

For the Henry's law component, the phase equilibrium equation can be written as follows,

$$y_i \varphi_i P = x_i \gamma_i H_i \exp \left(\frac{v_i^\infty (P - P^0)}{RT} \right) \quad (10)$$

For the solvent (water and alkanolamine), vapor-liquid equilibrium is given by,

$$y_s \varphi_s P = x_s \gamma_s P_s^0 \varphi_s^0 \exp \left(\frac{v_s (P - P_s^0)}{RT} \right) \quad (11)$$

where, P , φ_i , H_i , and v_i are the total pressure, fugacity coefficient, Henry's constant, and partial molar volume at infinite dilution for molecular species i , in the mixed solvent of water and alkanolamine at the system temperature, T , and at vapor pressure of the mixed solvent, P , respectively. P^0 , P_s^0 , and v_s are the saturation vapor pressure of the mixed solvent, saturation vapor pressure of pure solvent (water or alkanolamine), and molar volume of the pure solvent, all at the system temperature, T , respectively. The temperature dependent Henry's law constant of CO_2 in AMP was selected from literature (Dash et al., 2011). The employed and estimated parameters for the temperature dependence of the Henry's law constant (Pa/mole fraction) of CO_2 in AMP and water and

for the mole fraction based equilibrium constants of reactions 3 through 7 are listed in Tables 1 and 2 (Al-Juaied and Rochelle, 2006; Austgen et al., 1989; Dash et al., 2011). The parameters for the temperature dependent equilibrium constant for dissociation of protonated AMP, reaction 7, were selected from the default values in the Aspen Plus[®] version 8.0 data bank without any alteration.

Table 1. The parameters required to calculate the Henry's law constant* (Pa/mole fraction).

	A_{ij}	B_{ij}	C_{ij}	D_{ij}
CO ₂ -AMP ^a	3.2864	-820.8630	1.6973	-0.0020
CO ₂ -H ₂ O ^b	170.7126	-8477.7110	-21.9574	0.0058

$$^* \ln(H_{ij}) = A_{ij} + \frac{B_{ij}}{T} + C_{ij} \ln(T) + D_{ij}T, T \text{ is the temperature in Kelvin.}$$

^a Henry's constant is in kPa (Dash et al., 2011)

^b (Austgen et al., 1989)

Table 2. Temperature dependent equilibria constant parameters* (mole fraction).

reaction no.	A	B	C	D	Reference
1	132.899	-13445.900	-22.477	0.000	a
2	231.000	-12092.100	-36.782	0.000	a
3	216.050	-12431.700	-35.482	0.000	a
4	-74.475(±0.443)	2.028(±0.073)	14.911(±0.022)	-0.022(±0.061)	this work
5	-3.687	-6754.686	0.000	0.000	a

$$^* \ln(K_{eq}) = A + \frac{B}{T} + C \ln(T) + DT, T \text{ is temperature in Kelvin.}$$

^a (Al-Juaied and Rochelle, 2006)

In this study, the activity coefficient model based on electrolyte nonrandom two-liquid (electrolyte-NRTL) theory for aqueous electrolyte systems is used to represent liquid-phase activity coefficients (Austgen et al., 1989; Chen et al., 1982; Chen and Evans, 1986; Mock et al., 1986).

The model parameters, including pair and binary interaction parameters, and coefficients for temperature dependent functions of chemical reaction equilibria were obtained through the Aspen Plus[®] data regression system (Matin et al., 2013). Unless reported otherwise, all molecule-ion pair interaction parameters, which include the water

molecule with at least one of the non-dominant ions in solution (i.e. OH^- , H_3O^+ , CO_3^{2-} , AMPCOO^-), were held constant (8, -4) and for AMP with the same ions were held constant to (15, -8). The non-randomness factor for the water-salt pair and the salt-water pair was held constant at 0.2, and for all molecules (other than water)-salt pair and all salt-molecules (other than water)-pair was held constant at 0.1 (Matin et al., 2013).

The calculated NRTL molecule-molecule binary interaction parameters and molecule-ion pair interaction parameters for the different species in the solution are given in Tables S1 and S2 (supporting information).

3. Results and Discussion

3.1 Corrosion Behavior of Carbon Steel in 30 wt.% AMP

Figure 1. Corrosion rates versus time for A106 in 30 wt.% AMP and 30 wt.% MEA solutions with a CO_2 loading of 0.43 C/N at 80°C. The corrosion rates for A106 in MEA solution are from our previous work (Zheng et al., 2015; Zheng et al., 2014a; Zheng et al., 2016a).

Figure 1 shows the corrosion rates for A106 carbon steel in a naturally aerated 30 wt.% AMP with a CO₂ loading of 0.43 mol_{CO2}/mol_{AMP} at 80°C as a function of exposure time. The corrosion rate decreased sharply from about 2 mm/y to less than 0.01 mm/y after 70 h, indicative of protective layer formation. The initial corrosion rate (2 mm/y) is comparable to that (approximately 3 mm/y) reported by Veawab's group in both 27 wt.% and 36 wt.% AMP solutions at 80°C with saturated CO₂ loading (Gunasekaran et al., 2013; Veawab et al., 1999a). Also, the initial corrosion rate for A106 is about 4 times higher than that of AISI 420 stainless steel in 18 wt.% AMP solution with continuous CO₂ purging during that experiment (Palmero et al., 2013). The corrosion rate after approximately 70 h, 0.01 mm/y, is much lower than that of 1018 CS (0.26 mm/y and 0.09 mm/y with and without dissolved O₂, respectively) reported by Veawab et al. in 22 wt.% AMP solution saturated with CO₂ after 120 h under boiling conditions (Veawab et al., 1996). The higher corrosion rates from their work might be due to erosion and convection effects from the continuous purging process and/or a higher testing temperature.

For comparison, the corrosion rates for A106 in naturally aerated 30 wt.% MEA solution with a CO₂ loading of 0.43 mol_{CO2}/mol_{MEA} at 80°C, from our previous work (Zheng et al., 2015; Zheng et al., 2014a; Zheng et al., 2016a), are also presented in Figure 1. With increases in time to approximately 100 h, the corrosion rate increased from 1.55 to 2.88 mm/y for A106 in the MEA solution with CO₂ loading and subsequently stabilized up to a testing duration of approximately 200 h. Eventually, the corrosion rate in the AMP solution with CO₂ loading (0.01 mm/y) is over two orders of magnitude lower than that in the MEA solution (~3 mm/y) even though the initial corrosion rate was slightly higher in the AMP solution. In addition, the results showed that the trends in corrosion with time are opposite and reproducible in both solutions (Figure 1).

To understand the differences in corrosion behavior of carbon steel in AMP and MEA solutions with CO₂ loading, SEM and XRD were used to characterize the corroded samples after electrochemical testing (Figures 2 and 3). An approximately 5 µm-thick and dense layer of FeCO₃ (a known protective corrosion layer), with a typical morphology of cubic clusters (Zheng et al., 2014a; Zheng et al., 2014b), was formed on the A106 surface in the AMP solution at 80°C after approximately 115 h. This is

consistent with the observation of FeCO_3 on the surface of 1018 CS after 144 h in a deaerated 45 wt.% AMP solution with a continuous flow of CO_2 at 80°C (Campbell et al., 2016). In addition, the formation of a dense layer of FeCO_3 is similar to that in piperazine (a secondary amine, PZ) and methyl diethanolamine (a tertiary amine, MDEA) solutions (Xiang et al., 2014; Zheng et al., 2014a; Zheng et al., 2014b). However, no dense layer of FeCO_3 was observed in the corresponding MEA solution at 80°C after 200 h but mainly residual Fe_3C (Zheng et al., 2015; Zheng et al., 2014a). Residual Fe_3C was reported to be the result of preferential dissolution of the ferrite phase in MEA solution (Zheng et al., 2015; Zheng et al., 2014a), the exposure of which resulted in galvanic corrosion of A106, as evidenced by the increase in the corrosion rate with increases in time before up to 100 h (Figure 1).

Figure 2. SEM surface morphologies (a and b) and cross-sectional image (c) of A106 in 30 wt.% AMP solution with a CO_2 loading of 0.43 C/N at 80°C after approximately 115 h.

Figure 3. XRD spectra of A106 in 30 wt.% AMP solution with a CO₂ loading of 0.43 C/N at 80°C after approximately 115 h.

The formation of a protective layer of FeCO₃ on CS in CO₂:amine:H₂O systems is mainly dependent on the concentrations of Fe²⁺ and HCO₃⁻ (and/or CO₃²⁻), ionic strength, temperature, and partial pressure of CO₂ (Zheng et al., 2016b, c). Briefly, the saturation degree of FeCO₃ (δ_{SD}) is proportional to the Fe²⁺ concentration ($c_{Fe^{2+}}$) and the square of HCO₃⁻ concentration ($c_{HCO_3^-}$) but inversely proportional to the partial pressure of CO₂ (P_{CO_2}) and solubility constant of FeCO₃ (K_{sp}) in the system (equation 12).

$$\delta_{SD} \propto \frac{c_{Fe^{2+}} c_{HCO_3^-}^2}{K_{sp} P_{CO_2}} \quad (12)$$

Thus, to better understand FeCO₃ formation behavior in AMP and MEA solutions with CO₂ loading, the solution speciation and HCO₃⁻ concentration were estimated by Aspen Plus[®].

3.2 Thermodynamic modeling

Figure 4. Modelled (this work) and experimental (Silkenbäumer et al., 1998) CO_2 partial pressure as a function of solution CO_2 loading at various temperatures and AMP concentrations for the CO_2 :AMP: H_2O system.

For thermodynamic modeling, experimental VLE data for a ternary system of CO_2 :AMP:H $_2\text{O}$ at AMP concentrations of 17.8, 17.9, 35.4, 35.8, and 36.6 wt. % ($2.4 - 6.5 \text{ mol.kg}^{-1}$) from the literature were used for data regression (Silkenbäumer et al., 1998). In order to obtain consistent parameters and thermodynamic quantities, the regression was conducted in multiple stages (Matin et al., 2013). At each step, the model was validated with experimental VLE data reported for a ternary system of CO_2 :AMP:H $_2\text{O}$ at various temperatures and solution CO_2 loadings. The binary interaction parameters, which contribute to the excess Gibbs energy, are characteristic of pair interactions of species of the solution and theoretically are independent of solution composition (Austgen et al., 1989; Chen et al., 1982). Figure 4 shows our model-estimated CO_2 partial pressure compared with experimental data from the literature as a function of solution CO_2 loading. As can be seen, at both the low and high ends of the concentration range studied (~ 18 and ~ 37 wt% AMP in Fig. 4 (a) and (b), respectively), the estimation from the model matches the experimental data.

Figure 5. Liquid phase speciation data predicted by our model compared to experimental values reported by Ciftja et al. as a function of carbon loading in 30 wt% AMP solution at 25°C (Ciftja et al., 2011).

The experimental data for solution speciation and pH available for CO₂ loaded aqueous solutions of 30 wt.% AMP were used to evaluate the model performance (Figures 5 and 6). Figure 5 shows experimental and predicted liquid phase component speciation as a function of CO₂ loading (Ciftja et al., 2011). Although the speciation data were not used for model parameter regression, the model results show similar trends with the experimental data for various species in the solution. The figure provides a qualitative and also quantitative indication for the low stability of AMP carbamate (AMPCOO⁻). As can be expected for AMP, a sterically hindered amine, the carbamate concentration is negligible through the entire range of CO₂ loadings investigated here, and bicarbonate formation is favored. This is consistent with higher CO₂ absorption capacity of aqueous solutions of AMP compared to that of MEA.

Figure 6. Solution pH and ionic strength predicted by our model compared to experimental data reported by Ciftja et al. as a function of carbon loading in 30 wt% AMP solution at 25°C (Ciftja et al., 2011).

Also, the ionic strength and solution pH predicted by this model are shown in Figure 6. The solution pH is consistent with the experimental data reported by Ciftja et al.

(Ciftja et al., 2011). The increase in predicted ionic strength with carbon loading reflects the formation of charged species such as AMPH^+ , HCO_3^- , and CO_3^{2-} .

Table 3. Carbamate stability constants ($1/K_6$) at different temperatures estimated in this work, compared to literature values.

T (K)	$K_{\text{carb.}}^{\text{a}}$		
	AMP ^b	AMP ^c	AMP ^d
298	1.8E-02	1.4E-02	4.9E-02
313	1.2E-02	5.4E-03	3.3E-02
333	7.4E-03	1.8E-03	2.0E-02
^a mole fraction unit; ^b this work; ^c (Arcis et al., 2014); ^d (Silkenbäumer et al.,			

Table 3 displays the carbamate stability constant values obtained in this study and by other researchers for AMP at different temperatures. As can be seen, the AMP carbamate stability constant, $1/K_6$, is about four orders of magnitude lower than that for MEA with a concentration of 28.6 (in molality scale) at 25°C, which is typical for a non-hindered primary alkanolamine.

3.3 Speciation-Dependent Formation of Protective Corrosion layers

With the thermodynamic model, solution speciation was estimated for the conditions in the corrosion study. The HCO_3^- concentration is approximately an order of magnitude higher in a 30 wt.% AMP solution than that in a 30 wt.% MEA solution at 80°C with a CO_2 loading of 0.4 $\text{mol}_{\text{CO}_2}/\text{mol}_{\text{amine}}$ (Figures 7 and S1). This corroborates that a much higher δ_{SD} can be achieved in an AMP solution (equation 12) due to the higher HCO_3^- (and/or CO_3^{2-}) concentration as well as an initially higher generation rate of Fe^{2+} (i.e., a slightly higher initial corrosion rate as evidenced in Figure 1). Subsequently, these concentrations resulted in the faster formation of a FeCO_3 layer. There is a lack of thermodynamic data for amine solutions, and thus, a quantitative calculation of δ_{SD} is challenging. However, from the results presented in this work as well as in past works, it appears that amines which preferentially form bicarbonate over carbamate upon aqueous

CO₂ absorption, such as sterically hindered primary and secondary amines (e.g., AMP) (Campbell et al., 2016), tertiary amines (e.g., MDEA) (Campbell et al., 2016; Xiang et al., 2014), and some secondary amines (e.g., PZ) (Zheng et al., 2014a; Zheng et al., 2014b), possess the ability to promote a protective FeCO₃ layer formation on carbon steel when the CO₂ loading is high enough. From a corrosion point of view, these amines or their blends should be pursued as CO₂ capture solvents.

Figure 7. Simulated speciation of HCO₃⁻ vs. carbon loading in 30 wt.% AMP (red dashed curve) and 30 wt.% MEA (black solid curve, from our previous work (Zheng et al., 2016b)) solutions at 80°C.

E_{corr} is also an important parameter when characterizing a corrosion system because it can provide information about changes in localized conditions such as the concentration of species related to the corrosion process and passivation behavior of the steel surface. Therefore, to more fully understand the corrosivity of CO₂:AMP:H₂O, E_{corr} of A106 was measured versus time in the 30 wt.% AMP solution with a CO₂ loading of 0.43 mol_{CO₂}/mol_{AMP} at 80°C (Figure 8). E_{corr} , initially stable at -0.88 V vs. SCE, sharply increased after 40 h to -0.45 V vs. SCE where it remained stable. These data are consistent with spontaneous passivation of A106 underneath the FeCO₃ layer in AMP solution (Zheng et al., 2016a).

Figure 8. Corrosion potential as a function of time for A106 in 30 wt.% AMP solution with a CO₂ loading of 0.43 C/N at 80°C.

As observed in naturally aerated PZ- and MEA-based systems (Zheng et al., 2016a; Zheng et al., 2014b), the FeCO₃ layer can further oxidize to Fe₃O₄. The possible oxidation reactions of FeCO₃ in AMP systems are listed in reactions 13-15, with the corresponding Nernst equations given in equations 16-18.

$$E_{\text{r}(\text{Fe}_3\text{O}_4/\text{FeCO}_3)} = E_{\text{r}(\text{Fe}_3\text{O}_4/\text{FeCO}_3)}^o + \frac{RT}{2F} \ln (c_{\text{H}^+}^8 c_{\text{CO}_3^{2-}}^3) \quad (16)$$

$$E_{\text{r}(\text{Fe}_3\text{O}_4/\text{FeCO}_3)}' = E_{\text{r}(\text{Fe}_3\text{O}_4/\text{FeCO}_3)}^o + \frac{RT}{2F} \ln (c_{\text{H}^+}^5 c_{\text{HCO}_3^-}^3) \quad (17)$$

$$E_{\text{r}(\text{Fe}_3\text{O}_4/\text{FeCO}_3)}'' = E_{\text{r}(\text{Fe}_3\text{O}_4/\text{FeCO}_3)}^o + \frac{RT}{2F} \ln (c_{\text{H}^+}^2 P_{\text{CO}_2}^3) \quad (18)$$

where $E_{\text{r(Fe}_3\text{O}_4/\text{FeCO}_3)}$ and $E^o_{\text{r(Fe}_3\text{O}_4/\text{FeCO}_3)}$ denote reversible potentials (vs. SHE) under experimental and standard conditions, respectively. R , T , F , c_{H^+} , and $c_{\text{CO}_3^{2-}}$ are the gas constant, temperature in Kelvin, Faraday's constant, concentration of protons, and concentration of carbonate ions. The $c_{\text{CO}_3^{2-}}$, $c_{\text{HCO}_3^-}$, and P_{CO_2} were estimated via the generated model to be 0.38 mol/L, 1.43 mol/L, and 12.2 kPa in 30 wt.% AMP solution with a CO_2 loading of 0.43 mol $_{\text{CO}_2}$ /mol $_{\text{AMP}}$ at 80°C. After substitution of these data into the equations, simplified forms for equations 16-18 were obtained and are correspondingly shown in equations 19-21.

$$E_{\text{r(Fe}_3\text{O}_4/\text{FeCO}_3)} = 2.07 - 0.28\text{pH} \quad (19)$$

$$E_{\text{r(Fe}_3\text{O}_4/\text{FeCO}_3)}' = 1.04 - 0.18\text{pH} \quad (20)$$

$$E_{\text{r(Fe}_3\text{O}_4/\text{FeCO}_3)}'' = 0.59 - 0.07\text{pH} \quad (21)$$

For the 30 wt.% AMP solution with CO_2 loading of 0.43 mol $_{\text{CO}_2}$ /mol $_{\text{AMP}}$ at 80°C, the bulk pH value was measured to be 9.18. Therefore, reversible potentials under the testing conditions for reaction 13-15 were calculated to be -0.74 V, -0.85 V, and -0.29 V vs. SCE. The E_{corr} of -0.45 V vs. SCE (Figure 8) is higher than the reversible potentials of reactions 13-14, which implies that the formation of a passive layer of Fe_3O_4 may be via one or both of these pathways. The actual dominant passivation pathway is dependent on the localized conditions such as H^+ , HCO_3^- , and CO_3^{2-} concentrations. No passivating Fe_3O_4 could be detected by XRD after 115 h although passivation occurred at that time in the 0.43 mol $_{\text{CO}_2}$ /mol $_{\text{AMP}}$ CO_2 -loaded 30 wt.% AMP solution (Figures 3 and 8). It is likely that complete transformation of the 5 μm FeCO_3 layer to Fe_3O_4 occurs over several weeks, and, after only 115 h, Fe_3O_4 is shielded by FeCO_3 and/or too thin to be detected at the resolution limit of this method (Han et al., 2009; Zheng et al., 2016a). To better identify the formed corrosion layers on the A106 surface over time, cross-section of the sample after corrosion in AMP solution for 115 h was prepared and characterized by FIB/SEM, as shown in Figure 9. A very thin corrosion layer (approximately 300 nm) was observed between the top FeCO_3 and A106 substrate. Combined with the sharp increase in corrosion potential (Figure 8) and its corresponding thermodynamic calculation, and

the XRD results show the disappearance of FeCO_3 and appearance of Fe_3O_4 in naturally aerated MEA-based solutions after a prolonged duration (over 1000 h) as presented previously (Zheng et al., 2016c). The thin layer was identified to be Fe_3O_4 , as indicated in Figure 9. Inversely, the FIB/SEM result corroborated that the transformation of FeCO_3 to Fe_3O_4 would occur in the presence of dissolved oxygen.

Figure 9. FIB/SEM surface and cross-sectional morphologies of A106 after corrosion in 30 wt.% AMP solution with a CO_2 loading of 0.43 C/N at 80°C for 115 h.

Therefore, corrosion layers of FeCO_3 and Fe_3O_4 , which inhibit further corrosion of A106, can be formed on its surface in naturally aerated CO_2 -loaded AMP solution. The corrosion benefits of AMP for A106 Grade B carbon steel have been discussed in this work, and similar results are expected for other steels (normally carbon steels), for which dissolution of Fe is preferable to other alloy elements in CO_2 -loaded amine-based solutions, and where compounds enriched in Fe are the major corrosion products.

4. Conclusions

AMP is a promising carbon capture solvent, and we have expanded the understanding of this amine through in-depth analysis of its corrosivity towards carbon steel by examining a naturally aerated 0.43 $\text{mol}_{\text{CO}_2}/\text{mol}_{\text{AMP}}$ CO_2 -loaded 30 wt.% AMP

solution at 80°C with LPR testing, corrosion potential measurements, SEM, XRD, and FIB/SEM as well as thermodynamic modeling. Main findings include:

1. The calculated AMP carbamate stability constant is very low due to steric hindrance, consistent with expected low values for this alkanolamine.
2. AMP, a sterically hindered primary amine, showed over two orders of magnitude less corrosivity than its corresponding unhindered counterpart MEA due to an order of magnitude higher HCO_3^- concentration generated in hindered amines after capturing CO_2 , resulting in the rapid formation of protective layers of FeCO_3 and Fe_3O_4 on the steel surface.
3. FeCO_3 layer was metastable in the naturally aerated AMP solution and would be further oxidized to Fe_3O_4 as a passive layer.

ACKNOWLEDGEMENTS

This work is supported by the State of Kentucky Energy and Environment Cabinet (PON2 127 1400002757 1), which includes the Carbon Management Research Group (CMRG) members of Duke Energy, Electric Power Research Institute (EPRI), Kentucky Department of Energy Development and Independence (KY-DEDI), Kentucky Power (AEP), and LG&E and KU Energy.

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