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Corrosion Study of Carbon Steel in CO₂ Loaded Amine-Amino Acid Solutions-Case of Mixtures of N-Methyldiethanolamine and L-Arginine

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Abstract. This research presents an electrochemical corrosion investigation to quantify the corrosiveness of carbon steel in blends of methyldiethanolamine (MDEA) and arginine (Arg) at two molar concentration and different solvent proportions. The selected temperatures range varied from 20 °C to 50 °C and the CO₂ partial pressure was in the range of 49-100 kPa. The obtained data showed increased corrosion rate with increased CO₂ partial pressure and increased the temperature of the solution. However, when added to MDEA, arginine was found to act as an inhibitor, the higher Arginine proportion in the mixture, the more inhibition effect was observed.

1. Introduction

The CO₂ absorption process using aqueous amine solutions is still the choice for the removal of CO₂ from natural and industrial gas streams. Common industrial applications include natural gas processing, coal gasification, and manufacturing of hydrogen and ammonia. Besides such industrial applications, the CO₂ absorption process is considered to be a highly rated potential technique for reducing greenhouse gas emission from flue gas streams [1]. CO₂ absorption process using aqueous amine solutions has long encountered corrosion problems. Corrosion seems to take place in several plant locations including the bottom portion of the absorber, the rich-lean heat exchanger, the regenerator, and the reboiler. Both uniform corrosion and localized attacks such as pitting, galvanic, erosion, stress cracking, and intergranular corrosion were commonly found. Methyldiethanolamine is widely used in combination with Piperazine for natural gas treatment, in tail gas treating and hydrogen sulfide enrichment units for selectively removing hydrogen sulfide from gas streams. The corrosion effect of MDEA on plant material had been studied by a number of investigators, they showed that metals corrosion rate in MDEA solutions [4, 5] is lower than that of secondary and primary amines.

Amino acids present potential benefits over amines in CO₂ separation. Amino acids typically have significantly lower vapor pressures, resulting in reduced solvent losses. Furthermore, they demonstrated greater resistance to oxidative degradation and lower toxicity than alkanolamines. Amino acids, such as arginine, glycine, alanine, and taurine, have been proposed as alternatives to amines in recent years [6, 7] and have been used commercially in acidic gas treating processes. Amino acids are used as green inhibitors against steel corrosion [8, 9]. In this work, electrochemical techniques were used to investigate the corrosiveness of blends of MDEA and Arginine on carbon steel at a total two molar concentration with different solvent proportions, temperatures, and different CO₂ partial pressures. The obtained results indicate that the corrosion rate increased with increased CO₂ partial pressure and increased temperature. However, when added to MDEA, arginine



was found to act as an inhibitor, the higher arginine proportion in the mixture, the more inhibition effect was observed.

2. Experimental

2.1 Materials

Reagent-grade MDEA with a mass purity of 99% from Sigma-Aldrich and arginine 99% purity from Riedel-de Haen were used. All chemicals were used without further purification. CO₂ with a purity of 99.999% was purchased from the local market. Distilled water was used for solvent preparation. The working electrode made from carbon steel (CS1018) consisted of a 7.85-mm diameter with an active area of 0.484 cm².

2.2 Experimental setup and procedure

A schematic diagram of the experimental set up is shown in Figure. 1. A 125 ml corrosion cell was used, a reference electrode made of Ag/AgCl filled with 3 M KCL solution. The counter electrode, a rod from graphite 6 mm diameter. The cell temperature was controlled using a water circulator. Gamry Ref 600 potentiostat was used for electrochemical measurements with General Purpose Electrochemical Software (GPES version 4.9.007) to control the instrument and record corrosion data. Echem Analyst™ Software was used to analyze the data. Carbonated solutions were prepared by absorbing CO₂ in solutions of MDEA and Arg. Three different CO₂ concentrations were applied, 50, 70 and 100%. The temperature was varied from 20 to 50 °C. The total solution concentration was kept at 2 M with different arginine proportions. The CO₂ loading was determined by gas chromatograph. Once the CO₂ absorption has reached equilibrium, corrosion tests were performed. The open circuit potential (OCP) of the cells were measured until they were stable (defined as OCP < 5 mV/10 min). The Tafel polarization curves were obtained over a potential range ± 250 mV versus (OCP) with a scan rate of 1 mV/ s. The EIS (AC impedance) (frequency range: 100 mHz to 100 kHz applied DC potential OCP, the amplitude of applied potential: 10 mV). The linear polarization resistance (LPR) method was applied to investigate the validity of Tafel and EIS results. LPR was at potential range ±20 mV vs. OCP, the scan rate of 0.125mV/s.

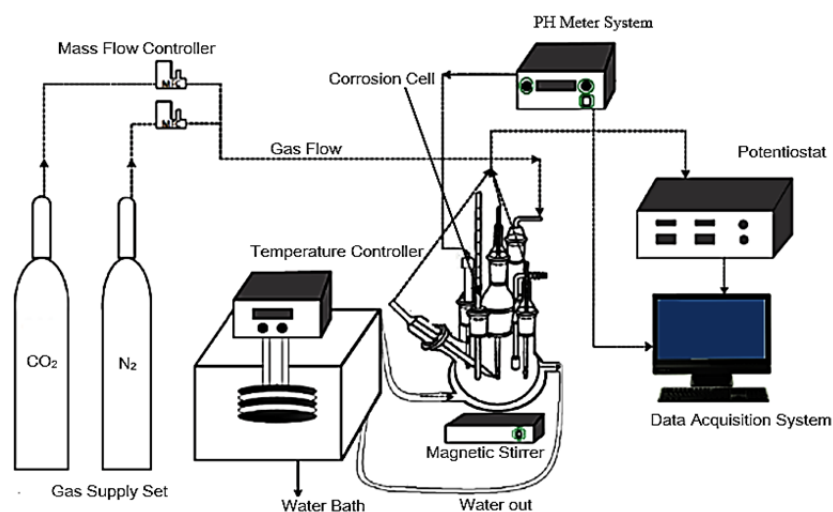


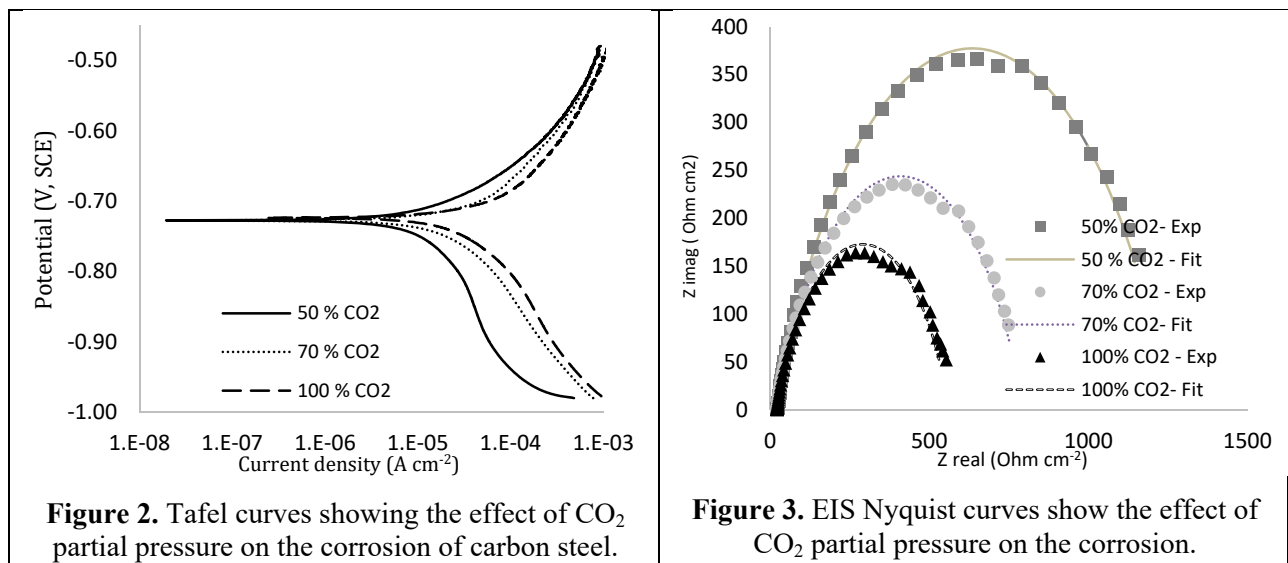
Figure 1. Schematic diagram of the experimental setup.

3. Results and discussion

3.1 Effect of CO₂ partial pressure on carbon steel corrosion

3.1.1 Polarization behavior of CO₂ partial pressure. Three typical partial pressure values of CO₂ (50, 70, and 100%) were applied at 20 °C and (1.95M / 0.05M) mixture of MDEA/Arg. Figure. 2 shows that the polarization curves (Tafel plot) have shifted to the right with increased CO₂ partial pressure. This indicates that the corrosion current density increased with increased CO₂ partial pressure [10]. Increasing CO₂ partial pressure led to increased CO₂ loading in the solution, which in turn led to an increase in the corrosion rate.

3.1.2 EIS, Nyquist behavior of CO₂ partial pressure effect on corrosion. Nyquist diagrams (Figure. 3) shows a one-time constant in the EIS curve that is the capacitive loop, which indicates that the sample surface was covered with corrosion scale.



The EIS data measured was fitted to an electrochemical equivalent circuit (Figure. 4). R_s represents the solution resistance, R_{ct} , R_p is the charge transfer resistance, and Q_{dl} is constant phase element (CPE) used as a substitute of the double layer capacitance due to the non-ideal capacitive response of the steel/electrolyte interface. Fitted curves are given in Figure 3. The features of EIS graphs measured are identical while the diameter of EIS curves decreases with increased CO₂ partial pressure. The EIS results confirm the results validity of polarization curves.

3.1.3 Linear polarization resistance (LPR) behavior of CO₂ partial pressure.

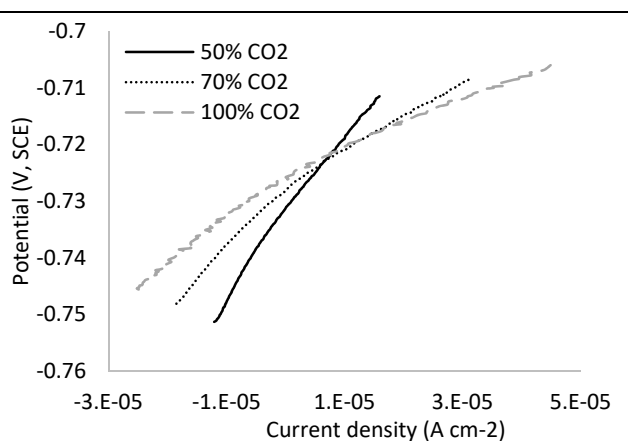
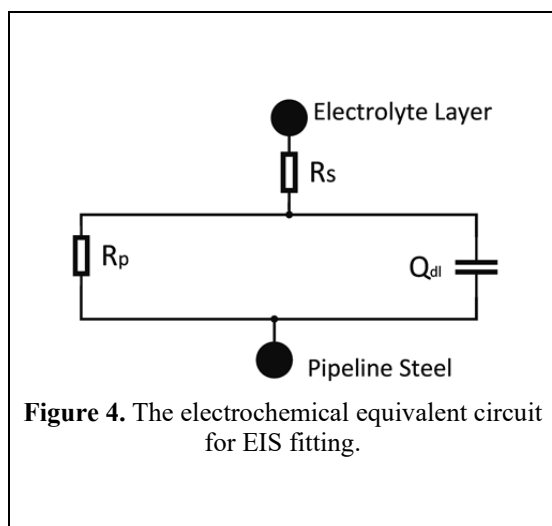
In Figure 5, polarization resistance lines for the influence of CO₂ partial pressure are shown. The slope of lines decreased with increasing CO₂ partial pressure indicating that the transition resistance (LPR) between the electrodes and the electrolyte decreased. This means that the corrosion current density increased, which in turn led to an increase in the corrosion rate of carbon steel.

3.1.4 Effect of temperature on corrosion of carbon steel

3.1.5 Polarization behavior of temperature. Tafel plots on the effect of temperature on carbon steel corrosion are shown in Figure 6. At 100% CO₂ partial pressure, four temperatures (20, 30, 40 and 50 °C) were applied to the blend MDEA/Arg solution. We observe that Tafel curves move right with increased temperature, which indicates that the corrosion current density increases when the temperature goes up [11], increasing the temperature pushes the rate of metal dissolution and hence the oxidation-reduction reaction.

3.1.6 EIS, Nyquist behavior of temperature effect on corrosion. Nyquist plots showing the temperature effect are presented in Figure 7. We observe that only one capacitive loop exists. This indicates that corrosion scale covered the sample surface. The EIS graphs have identical features with

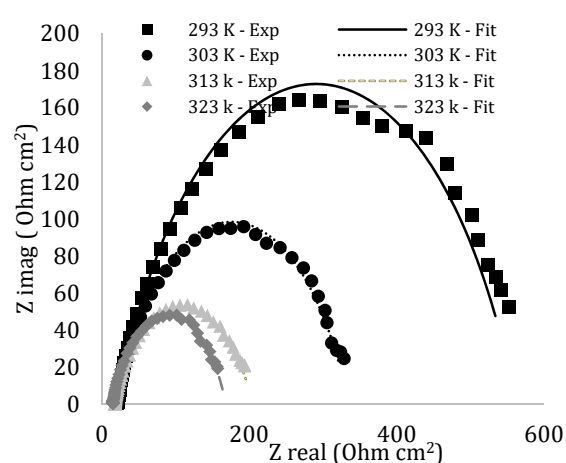
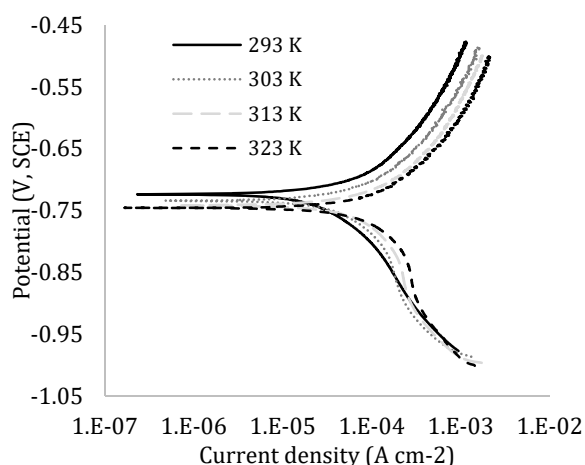
decreasing diameter of the curve as the temperature increased. The EIS data was fitted to the same electrochemical equivalent circuit. In general, R_{ct} and R_s decreased with increased temperature indicating that the corrosion rate of the steel increase with temperature.



3.1.7 LPR behavior of temperature effect on corrosion. Temperature effect on the corrosion of carbon steel was further investigated by linear polarization resistance technique (LPR) as shown in Figure 8. The slopes of the curves decreased with increased temperature indicating that the linear polarization resistance between the electrodes and the electrolyte decreased leading increased corrosion current density, which in turn led to an increase in the corrosion rate of carbon steel in the solution.

3.1.8 Effect of MDEA/Arg mixing ratio on carbon steel corrosion

Tafel plots, electrochemical impedance spectroscopy, and linear polarization resistance were used to investigate the inhibition effect of Arginine. Arginine concentration was chosen to be 0.03 M, 0.05 M and 0.1 M in a total solution concentration of 2 moles. The temperature was set at 20 °C and CO_2 concentration was fixed at 70%.



3.1.9 Tafel curves behavior of MDEA/Arginine ratio effect. From Tafel plot shown in Figure 9, we can see that the curves move left with increased Arginine concentration, which means that corrosion

rate decreases. The inhibition effect of different amino acids against steel corrosion had been investigated in different solutions such as HCl [8] and sulfamic acid [9] solution. Inhibition efficiency tends to increase by increasing the inhibitor concentration [16].

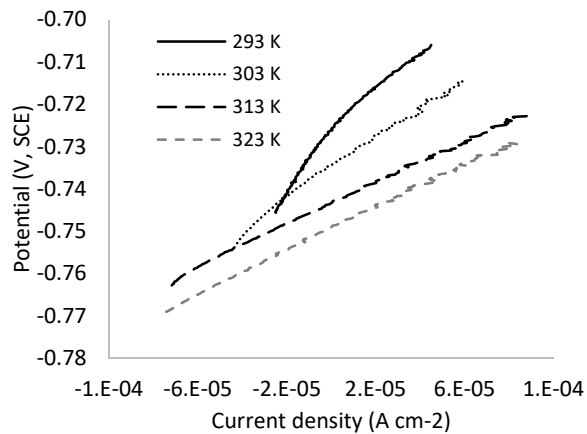


Figure 8. Temperature effect on corrosion investigated by LPR method.

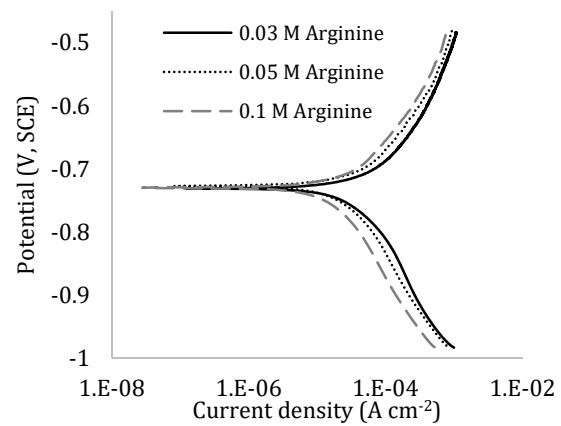


Figure 9. Tafel curves showing the effect of MDEA/Arginine mixing ratio on the corrosion.

3.1.10 EIS, Nyquist behavior of arginine concentration effect on corrosion. Nyquist plots showing Arginine effect are presented in Figure 10, only one-time constant exists in the EIS curves that is a capacitive loop which indicates that the sample surface was covered with corrosion scale. Using the same electrochemical equivalent circuit to fit the collected EIS data, fitted curves are given in Figure 10 where the diameter of EIS curve increased as the Arginine concentration increased.

3.1.11 LPR behavior of arginine concentration effect on corrosion. Linear polarization resistance as shown in Figure 11 investigated the effect of Arginine (Arg) concentration on the corrosion of carbon steel. The slope of lines increases with increasing Arginine concentration, which means that the linear polarization resistance (LPR) between the electrodes and the electrolyte also increases. This means that the corrosion current density decreased which causes a decrease in the corrosion rate of carbon steel in the solution.

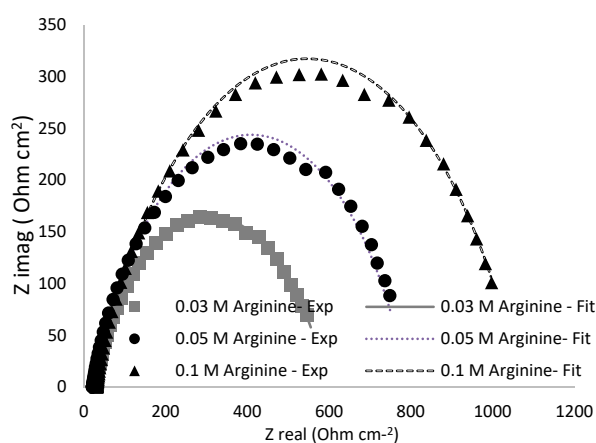


Figure 10. EIS Nyquist curves show the effect of MDEA/ARG ratio on the corrosion.

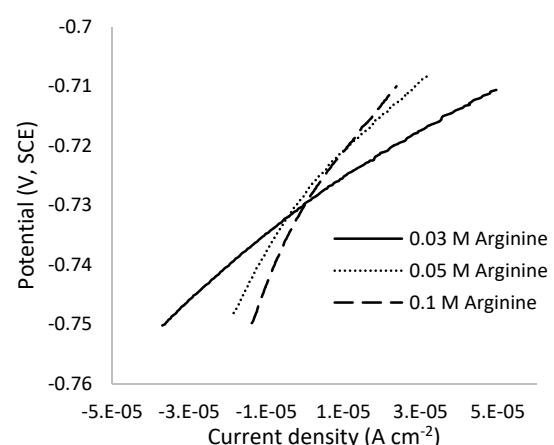


Figure 11. The corrosion effect of MDEA/ARG mixing ratio.

4. Conclusion

The corrosion of carbon steel (1018) in aqueous mixtures of MDEA and Arginine was investigated using different electrochemical techniques. Effects of CO₂ partial pressure, temperature, and

Arginine/MDEA proportions were considered. Increasing CO₂ partial pressure in the solution caused an increase in the corrosion rate of carbon steel. The carbon steel Corrosion was found to increase with increasing temperature due to the increased metal dissolution rate and hence the oxidation-reduction reaction. Arginine was found to play inhibitor role, the corrosion rate decreased with increased Arginine concentration.

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