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Effects of Ethanoic Acid and Mono-Ethylene-Glycol on Mild Steel Corrosion in Deaerated Environment

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Abstract

The Depositions of scale and wax in transporting pipeline are one of the major causes of corrosion problems in the oil and gas industry. They can lead to production and/or operational shutdown as well as revenue loss. Corrosion/scale depositions can occur in production equipment and surface facilities especially in flow line casing. In addition, deposition of scale in oilfield can plug oil and gas production lines, pumps, and tubing and reduces the flow of fluid through the pipelines. Different work had been published on the corrosion of carbon steel in CO2 environment, but not enough have been seen on the effects of HAc and MEG in CO2 saturated environment. In this paper, the combined effects of HAc on corrosion of carbon steel in CO2 saturated environment were investigated at 25oC and 80oC especially when different concentrations of MEG were added repeatedly using 3.5% wt. NaCl solution in a semi-circulated loop setup. Weight loss method and electrochemical measurements using linear polarization resistance (LPR) were used to evaluate the reactions and efficiencies of HAc and MEG on the carbon steel corrosion at different temperatures and concentrations. The results obtained show that MEG is found to be very effective in reducing the corrosion rate of carbon steel in the presence of HAc at different conditions tested. The corrosion rate reduced drastically on addition of 20% and 80% MEG concentration to the solution, compared to when only HAc was presence. A more satisfactory results were obtained with the 80% MEG at both temperatures where the corrosion rates decreases from 0.70 mm/yr to 0.32 mm/yr and from 0.38 mm/yr to 0.11 mm/yr respectively.

Keywords: CO2 corrosion, mild steel, acetic acid, MEG, scale deposition.

Introduction

Natural gas usually contains about 20 – 100 Ibm of water per MMSCF of gas, depending on the saturated point at the operating conditions. Pipeline failures due to corrosion could be very costly in terms of safety, cost or environmental damage [1].Carbon steel are preferably used to transport oil and gas products from the well over long distances because of cost and its availability. Apart from oil/or gas been transported in the pipeline, it is common that wells produce other products that are likely to cause corrosion, such as water (H₂O), carbon dioxide (CO₂), hydrogen sulphide (H₂S) and acetic acid (CH₃COOH). However, the processing and transportation of this gas is hindered by corrosion due to water content and formation of gas hydrates in pipelines. Water can condense along the pipeline due to temperature difference between the source and process plant which invariably can lead to more corrosion and gas hydrate formation [2].

MonoEthylene glycol (MEG) most time is injected into the pipeline to lower the freezing point as well as reducing the corrosion rate of the pipeline. Thermodynamic hydrate inhibitors are at imes applied to prevent the formation of hydrates that can block the pipelines in most gas production system. More importantly, MEG has an advantage of inhibitor prevention because it is less toxic when compare to methanol and has low density [3-6]. Besides, MEG has corrosion inhibition properties, but the corrosion inhibition of MEG is normally not enough to protect the carbon steel used in the construction of oil and gas pipeline

Many studies had been devoted on corrosion of carbon steel in CO₂ environment, but none emphasizing on the conditions when acetic acid and MEG are present. Gulbrandsen et al [5] in their work reported that MEG altered the anodic half reaction of the corrosion process or dissolution of iron. They related the results to the possible adsorption of MEG on the steel surface. The corrosion rate of steel in the presence of MEG can be lower compared to that without MEG [5, 8]. De Waard and Milliams [8] demonstrated that addition of glycol to wet gas pipeline influenced CO₂ corrosion by lowering the dew point of water and consequently could reduce the severity of Top-of-the-line corrosion. He further explained that the corrosion rate at the bottom of the line decreases when glycol mixes with the water phase [2, 5, 6, 8, 9]. The influence of other parameters such as O₂, H₂S in continuation with MEG had been studied, but the effects of acetic acid are yet to be understood [5, 6, 9, 10]. Similarly, the use of pH stabilization in MEG-containing system has successfully been implemented in the multiphase transportation of natural gas [2, 3, 6]. The pH stabilization reduces the cathodic reaction of the corrosion of steel while encouraging the formation of protective iron carbonate on the surface of the carbon steel pipeline. Meanwhile, when formation water is produced from the well, pH stabilization become undesirable method for preventing corrosion as other unwanted scale may form along the pipeline [8, 11].

CO₂ corrosion in the presence of acetic acid (HAc) is known as major causes for premature failures in oil and gas pipelines that usually made of carbon steel [12]. Also, acetic acid (HAc) is often the most abundant volatile organic acids in formation water. In oilfield pipelines at low partial pressure of CO₂ (pCO₂), the corrosion issues are easily managed, but when small amounts of acetic acids are present, the corrosivity of the brine can change dramatically [13]. It has been experimentally shown that the total quantity of organic acids in produced water in oil and gas system is approximately between 500-3000 ppm of which HAc contributes about 50-90% of organic acids [14]. However, a systematic investigation of field data showed that undissociated HAc concentration higher than 0.1-1 mM was a critical factor for CO₂ corrosion [13]. Garsany et al. [15] proposed that the role of acetic acid is to act as a reactant in the cathodic process which could have a significantly higher rate than the reduction of protons or carbonic acid in oilfield conditions. The three main cathodic reactions involving acetic acid are given below [15]:

$$2HAc + 2e^- \rightarrow 2Ac^- + H_2 \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_2$$
 (2)

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^-$$
 (3)

From equation (3), the reaction mechanism and kinetics of the iron dissolution with the overall reaction are affected by acetic acid, CO₂ partial pressure and pH [16]. Dugstad [17] and Gunaltun et al. [18] in their results from field observations/laboratory investigations that the presence of HAc may induce a detrimental effect on the overall corrosion rate

and the pitting morphology in sweet systems. Field experienced has also shown that HAc is a key factor in the localized topof-line corrosion attacks in gas-condensate to pipeline [19]. Moreover, the presence of HAc also tend to solubilize the dissolving iron ions and suppress FeCO₃ formation, which can passivate the steel surface [20].

However, from the published work reviewed so far, there appeared to be many unanswered questions on how MEG affect the CO₂ corrosion mechanism during film formation in the presence of HAc. This paper looks at the corrosion rate of carbon steel under the influence of acetic acid and monoethylene glycol during film formation and dissociation.

Experimental Procedure

The experiments were performed in a mini circulation flow loop. A peripheral pump circulates the test solution from the reservoir to the test cell. A small diameter pipe maintained a constant liquid volume flow in the cell. The reservoir tank and the test cell were continuously purged with CO₂ to removed oxygen completely from the test solution. Once de-oxygenation has been achieved, the required amount of HAc, MEG and inhibitors were added at the start of every experiment. The temperatures were controlled by means of a heating plate with a temperature sensor in the cell. The pH of the solution was adjusted to the desired value throughout the experiments by adding sodium bicarbonate (NaHCO₃) or hydrochloric acid (HCl) as required.

Experimental Set-Up

The test specimens used entirely for this study are mild steel with a surface area of 8.11cm^2 and a circular hole toward the top end. A copper wire of 0.02 mm diameter was spot welded and used on the test coupons to ensure electrical contact between the electrode and electrolyte. The test coupons were suspended in the test solution by passing a plastic wire through the coupon and the wire was hung to a plastic rod held in place of the glass cell top holes. Prior to introduction into the test cell, the test coupons were successively ground with 240, 600 and 800 SiC grit paper and polished with 1200 SiC paper.it was then cleaned with acetone, rinsed with distilled water and dried. The general composition of the carbon steel samples used in this work is given in Table 1.

Four test solutions were prepared. The first test solution was prepared with 3.5% wt. sodium chloride (NaCl) as the blank solution without HAc and MEG. The second test solution was prepared using 3.5% NaCl solution and 500ppm, 1000ppm and 2000ppm of HAc without MEG. The third test solution was prepared using 3.5% NaCl solution, 500ppm, 1000ppm and 2000ppm of HAc and 20% MEG, while the fourth test solution was prepared using 3.5% NaCl, 500ppm, 1000ppm and 2000ppm of HAc and 80% MEG respectively. Table 3 summarizes the composition of test matrix used for this study.

Measurement Techniques

The weight loss and linear polarization resistance measurement methods were performed on the carbon steel samples in all the test solutions at temperatures of 25°C and 80°C respectively. The weight loss is measured, determined and the corrosion rate calculated by applying Equation 1:

$$= \frac{WL(g)}{\rho \times t \times A} \times K\left(\frac{mm}{yr}\right) \tag{1}$$

Where:

CR = corrosion rate, mm/yr,

 $\rho = \frac{\text{density of the material, 7.86 g/cm}^3}{\text{density of the material}}$

WL = weight loss, grams, t = the exposed time, hr

A = the exposed coupon surface area, cm²,

 $K = conversion factor, 8.76 \times 10^4$

However, the electrochemical measurements were carried out using a commercial potentiostat. A three-electrode configuration was used in all the measurements. The carbon steel sample was used as the working electrode, while the

Ag/AgCl wire was used as reference electrode. The linear polarization curves were obtained in the potential range of -10 to +10 mV (vs. E_{corr}) with a scan rate of 0.1 mV/s.

Results and Discussion

Weight loss

The weight loss results for the first set of experiments (3.5% wt. NaCl without HAc, and MEG), the second test solution(3.5% wt. NaCl with 500ppm, 1000ppm, 1000ppm, and 2000ppm HAc and without MEG), the third test solution(3.5% wt. NaCl with 500ppm, 1000ppm, 2000ppm HAc and 20% MEG), the fourth test solution(3.5% wt. NaCl with 500ppm, 1000ppm, 2000ppm HAc and 80% MEG) evaluated at 25°C and 80°C are presented in Figures 1 to 6 and are summarized in Table 3 to Table 8 respectively.

Solution with HAc

Figure 1 and Figure 2 shows the relationship between the average corrosion rate of carbon steel pipeline against time in a solution containing 3.5% wt. NaCl and at different concentrations of HAc at 25°C and 80°C respectively.

At 25°C (Figure 1), the corrosion rate increased drastically over time as the concentrations of HAc increases. As can be seen, the corrosion rate for the blank solution (solution without HAc) is approximately 0.35 mm/yr. On addition of 500ppm HAc, the corrosion rate increases drastically from 1.30 mm/yr to 1.76 mm/yr for period of two hours in the solution. Further addition of 1000 ppm and 2000 ppm of HAc to the solution raises the corrosion rate to approximately 1.65 mm/yr and 1.80 mm/yr after 14 hours duration in the solution.

Similarly, at 80°C (Figure 2), the corrosion rate also increases over time as different concentrations of HAc were added to the solution. As can be seen from Figure 2, the corrosion rate increased from about 1.05 mm/yr to approximately 2.80 mm/yr on addition of different concentration of HAc to the system. Though, the corrosion increases rapidly at both temperatures, it is however higher at 80°C than at 25°C. This higher increased in corrosion rate in high temperature is caused as a result of fast reaction rate that usually occurs at higher temperatures. Similarly, it is also assumed that a protective Iron carbonate (FeCO₃) scale are formed and however remain protective in the presence of HAc provided the supersaturation is at maximum to sustain the protective films formed. Tables 3 and 4 presents the summary of the average weight loss per unit area fot the carbon steel used for the experiments at 25°C and 80°C respectively.

Solution with HAc and MEG

Figure 3 to Figure 6 shows the corrosion rate of carbon steel pipeline against time in a solution containing 3.5% wt. NaCl with HAc and 20%/80% MEG at 25°C and 80°C. As observed from the results (Figure 3 – Figure 6), the introduction of MEG (20% and 80%) had significant influenced in reducing the corrosion of carbon steel materials. At 25°C and 20% MEG (Figure 3), the corrosion rate reduces drastically from 1.92 mm/yr to 0.78 mm/yr for the 14 hours duration of the test. Similarly, at 25°C and 80% MEG (Figure 4), the corrosion rate also decreases with time from about 3.5 mm/yr to approximately 0.65 mm/yr for the same period of time in the solution.

At 80°C and 20% MEG (Figure 5), the average corrosion rate after 14 hours in solution decreases from 3.05 mm/yr to about 0.76 mm/yr and from 2.0 mm/yr to 0.98 mm/yr at 80°C and 80% MEG (Figure 6. The continues decreased in corrosion rate on addition of different concentrations of MEG to the solution is caused by the reduction in pH of the solution. Tables 7 and 8 shows the summary of the average corrosion rate with time for the carbon steel samples in the presence of different concentrations of HAc and MEG respectively.

Linear Polarization Resistance (LPR) Results

The performance of different concentrations of HAc and MEG on the corrosion rate of carbon steel pipeline in CO₂ saturated environment at temperatures of 25°C and 80°C were also evaluated using the electrochemical measurement technique (LPR).

At 25°C, (Figure 7), the corrosion rate increases with increase in time as was expected. At 0ppm of HAc, the corrosion increases rapidly from about 0.34 mm/yr to 0.92 mm/yr after 10hours test duration. The addition of 500ppm, 1000ppm and 2000ppm of HAc raised the corrosion from 0.65 mm/yr to 1.20 mm/yr, 0.61 mm/yr to 1.45 mm/yr and from 0.75 mm/yr to 1.62 mm/yr respectively. At 80°C (Figure 8), the corrosion rate also increases with increased in concentrations of HAc compared to the blank solution. At 0 ppm of HAc, the corrosion rate moved from 0.4mm/yr to 1.2 mm/yr. Addition of 500ppm, 1000ppm and 2000ppm of HAc increases the corrosion rate from 0.85mm/yr to 1.4 mm/yr, 0.8 mm/yr to 1.65 mm/yr and from 0.85 mm/yr to 1.83 mm/yr respectively.

However, the introduction of 20% MEG and 80% MEG drastically decreases the corrosion rate to a minimum level. At 25°C (Figure 7), the corrosion rate decreases from 0.60 mm/yr to 0.35 mm/yr on addition of 20% MEG and from 0.40 mm/yr to 0.15 mm/yr on addition of 80% MEG to the solution. Similarly, at 80°C (Figure 8), the corrosion decreases from 0.70 mm/yr to 0.32 mm/yr on addition of 20% MEG to the system and from 0.38 mm/yr to 0.11 mm/yr on after adding 80% MEG to the solution. However, this reduction in corrosion rate prove that corrosion reaction is inhibited by addition of 20% MEG and 80% MEG to the solutions. As it is observed, the corrosion rate for the inhibited samples reduces drastically to less than 0.4 mm/yr compared to the uninhibited samples with HAc only.

Conclusions

In this work, the combined effect of various concentrations of HAc and MEG on corrosion rate of carbon steel in CO₂ saturated environment were evaluated at 25°C and 80°C, pH of 6.6, and CO₂ partial pressure of 0.54 bar. The results obtained so far showed changes in mechanism of corrosion rate with time at different concentrations of HAc and MEG studied. The weight loss method gives a more reliable results of the corrosion rate as a function of time for the carbon steel tested. It is seen that the presence of HAc in the solution of 3.5% wt. NaCl increases the corrosion rate at both temperatures for the entire duration of the test but, addition of 20% and 80% MEG concentrations decreased the corrosion rate rapidly to a minimum level of about 0.15 and 0.35 mm/yr respectively.

The application of electrochemical measurements also showed similar results to that of the weight loss method. It can be observed that the corrosion rate on addition of 20% and 80% MEG reduces the corrosion rate for all the conditions tested. A more satisfactory results were obtained with the 80% MEG at both temperatures where the corrosion rates decreases from 0.70 mm/yr to 0.32 mm/yr and fom 0.38 mm/yr to 0.11 mm/yr respectively.

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Table 1: Chemical composition of mild steel (wt. %)

Com	С	Si	M	S	P	Sn	Cr	Ni	M	Cu	Al
p.			n						0		
Val.	0.	0.	1.	0.0	0.0	0.0	0.	0.	0.	0.	0.0
%	08	25	54	01	19	08	04	03	01	12	38

Table 2: Composition of the test matrix used for the experimental set used

Parameters	Values
Test solution	3.5% wt. NaCl
Test material	Carbon steel
Partial pressure of CO ₂ (bar)	0.54
MEG concentrations	[20%, 80%]
рН	6.6
Temperature (°C)	[25, 80]
C _{HAc} (ppm)	[0, 1000, 2000, 3000]
Surface area (cm ²)	8.11
Test method	[WL, and LPR]

Table 3: Average corrosion rate as a function of time for mild steel corrosion in the presence of HAc at 25oC and 80oC respectively

8	T=2	25°C			T= 80°C					
	HAc C	onc, ppm								
T(hrs.)	0	500	1000	2000	T(hrs.)	0	500	1000	2000	
2	0.38	0.46	1.05	1.04	2	0.48	1.25	1.72	1.71	
4	0.44	0.63	1.2	1.26	4	0.59	1.43	1.86	1.88	
6	0.54	0.77	1.24	1.32	6	0.65	1.58	2.01	2.12	
8	0.69	0.95	1.46	1.46	8	0.9	1.66	2.32	2.35	
10	0.72	1.22	1.58	1.5	10	1.26	1.74	2.55	2.62	
12	0.82	1.38	1.64	1.59	12	1.25	1.81	2.6	2.8	
14	1.08	1.47	1.82	1.73	14	1.5	2.04	2.71	2.89	

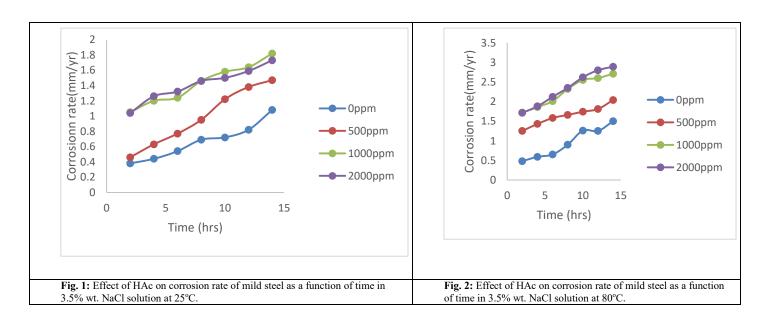
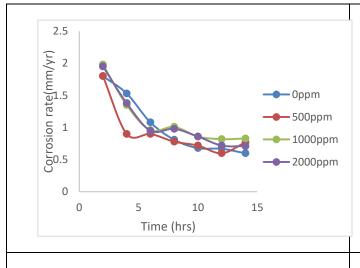


Table 4: Average corrosion rate as a function of time for mild steel corrosion in the presence of HAc and different concentrations of MEG at 25oC.

	$\Gamma = 25^{\circ} \text{C}, 20^{\circ}$				T= 25°C, 80% MEG					
	HAc+	MEG			HAc + MEG					
T(hrs.)	0	500	1000	2000	T(hrs.)	0	500	1000	2000	
2	1.80	1.80	1.98	1.95	2	3.17	3.55	3.58	3.4	
4	1.53	0.90	1.35	1.38	4	3.17	1.82	2.58	2.24	
6	1.08	0.90	0.96	0.95	6	3.1	1.42	1.79	2.1	
8	0.81	0.78	1.01	0.98	8	2.64	1.12	1.34	1.88	
10	0.68	0.720	0.86	0.86	10	2.74	0.99	1.19	0.97	
12	0.67	0.60	0.82	0.72	12	2.50	0.94	1.02	0.66	
14	0.60	0.77	0.83	0.71	14	2.26	0.81	0.93	0.67	



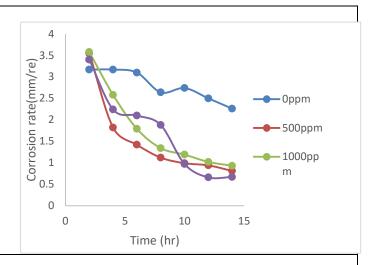
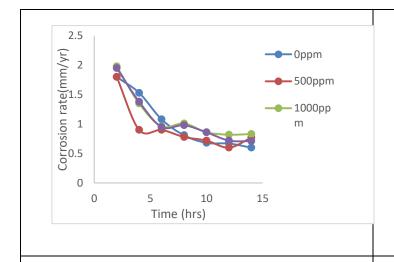


Figure 3: Combined effect of HAc and 20% MEG on corrosion rate of carbon steel as a function of time in 3.5% wt. NaCl solution at 25°C.

Figure 4: Combined effect of HAc and 80% MEG on corrosion rate of carbon steel as a function of time in 3.5% wt. NaCl solution at 25°C.

Table 5: Average corrosion rate as a function of time for mild steel corrosion in the presence of HAc and different concentrations of MEG at 80oC.

7	Γ= 80°C, 20 HAc +								
T(hrs.)	0	500	1000	2000	T(hrs.)	0	500	1000	2000
2	1.80	1.80	1.98	1.95	2	3.17	3.55	3.58	3.4
4	1.53	0.90	1.35	1.38	4	3.17	1.82	2.58	2.24
6	1.08	0.90	0.96	0.95	6	3.17	1.42	1.79	2.1
8	0.81	0.78	1.01	0.98	8	2.64	1.12	1.34	1.88
10	0.68	0.72	0.86	0.86	10	2.74	0.99	1.19	0.97
12	0.67	0.60	0.82	0.72	12	2.50	0.94	1.02	0.66
14	0.60	0.77	0.83	0.71	14	2.26	0.81	0.93	0.67



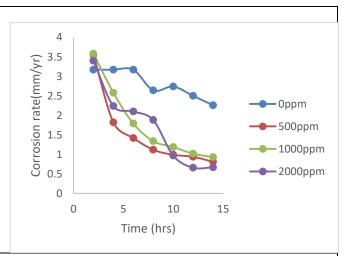
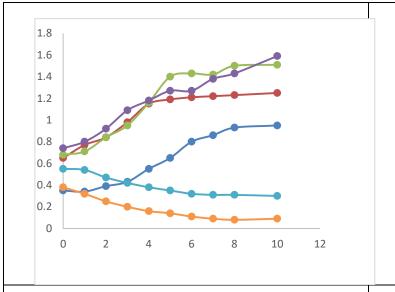


Figure 5: Combined effect of HAc and 20% MEG on corrosion rate of carbon steel as a function of time in 3.5% wt. NaCl solution at 80°C.

Figure 6: Combined effect of HAc and 80% MEG on corrosion rate of carbon steel as a function of time in 3.5% wt. NaCl solution at 80°C.



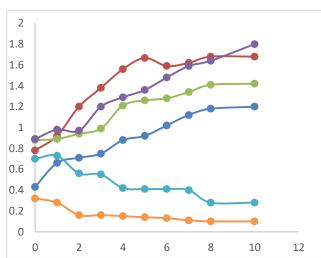


Figure 7: Performance of HAc and 20% MEG on corrosion rate of carbon steel sample as a function of time in 3.5% wt. NaCl solution at 25° C.

Figure 8: Performance of HAc and 20% MEG on corrosion rate of carbon steel sample as a function of time in 3.5% wt. NaCl solution at 80° C

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