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ORIGINAL PAPER

CO_2 corrosion of carbon steel in the presence of acetic acid at higher temperatures

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Abstract The corrosion behaviour of X 65 carbon steel in the presence of acetic acid in N_2- and CO_2-saturated systems has been investigated using electrochemical techniques. The presence of acetic acid does not influence the anodic reaction but strongly accelerates the cathodic reaction. The cathodic reaction and consequently the corrosion rate of mild steel in the CO_2-saturated system increase with increase in acetic acid concentration and temperature. From the values of the apparent activation energies, the corrosion reaction in the absence of acetic acid was found to be under mixed interfacial reaction/diffusion control while interfacial reaction control dominates in the presence of acetic acid. The reduction of adsorbed undissociated acetic acid on the metal surface is proposed as the key species primarily responsible for accelerated corrosion rate at all temperatures.

Keywords CO_2 corrosion · Acetic acid · Electrochemical techniques · Mild steel

1 Introduction

The term “organic acid” as used in the oil and gas industries applies to a broad range of organic compounds which contain the organic acid radical –COOH. The hydrocarbon part of the compounds can be aliphatic acids: R–COOH (where R is a straight or branched chain), aromatic acids: Ar–COOH (where Ar is a benzene ring or substituted benzene rings) or naphthenic acids: X–COOH (where X is a cycloparafinic ring) [1]. Most of the organic acids in petroleum systems have been shown to be formed from degradative alterations of lipid components of sediments [2]. These compounds are reported to be present in crude oils from many parts of the world [3]. Their effects on CO_2 corrosion of carbon steel and low-alloy steel are not a new problem. In 1944, the effects of organic acids and CO_2 on the corrosivity of produce water were shown by Menaul [4]. Few years later, Shock and Sudburry [5] in an attempt to correlate the corrosivity of production with organic acids concluded that severe corrosion attack will occur in wells producing greater than one atmospheric partial pressure of CO_2 or produce water in the pH range 4.0–4.5 if organic acids are present, and that no corrosion will occur at pCO_2 less than 0.2 atmosphere in the absence of organic acids. In 1973, Obukhora [6] reported that organic acids and CO_2 in gas condensate wells are contributing factors to high corrosion rates. A notable organic acid, and the most prevalent low molecular weight organic acid found in oil and gas environment, is acetic acid [7]. It contributes 50–90% of the organic acids [8] and its presence in process water has been confirmed as a potential factor in CO_2 corrosion [9]. Its effects manifest in both top- and bottom-of-line of oil and gas pipelines [8, 10].

Several researchers have reported an increase in the rate of CO_2 corrosion of carbon steel in the presence of acetic acid [9–17] and variable trends with respect to corrosion rate versus time and concentration of acetic acid were reported. These have been reviewed by George and Nesic [7]. The later also concluded that the undissociated form of acetic acid, present at lower pH, is responsible for the increases observed in the corrosion rate. However, attention was focused at lower temperature (22 °C).

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In an attempt to fully comprehend the basic mechanism of acetic acid in CO_2 corrosion, potentiodynamic polarization and linear polarization resistance measurements were carried out at 40–80 °C. This paper extends the investigation of George and Nesic [7] to higher temperatures in an attempt to answer a part of the second principal question raised: Does the mechanism of CO_2 corrosion of mild steel in the presence of acetic acid change at high pressure and temperature?

2 Experimental

The experimental setup and procedures are as previously described [7]. The glass cell was filled with 2 dm^3 of the test solution, made up of de-ionized water +1% by mass NaCl, de-aerated and saturated with required gas (carbon dioxide or nitrogen gas). The pH and oxygen concentration were used to determine when the solution was in equilibrium. The appropriate amount of acetic acid was then added to the cell and further de-oxygenation was carried out for another 10 min. The pH was monitored before and after the acetic acid was added to ensure a constant solution composition. When needed hydrochloric acid (HCl) or sodium hydrogen carbonate ($NaHCO_3$) was added to adjust the pH. The temperature was maintained within ±1 °C in all experiments.

Prior to each experiment, the working electrode surface was polished with silicon carbide paper up to 600-grit, rinsed with 2-propanol, placed in an ultrasonic acetone bath for about 5 min to remove possible residue of polishing and air dried. The dried sample was mounted on the specimen holder, immersed into the test solution and the electrode's rotation velocity was set and allowed to rotate for 10 min before any electrochemical measurements were carried out.

The free corrosion potential was measured until the potential stabilized within ±1 mV and the polarization resistance (R_p) measurements were conducted by polarizing the working electrode ±5 mV from the free corrosion potential and scanning at 0.1 mV s^{-1}. The solution resistance was measured using electrochemical impedance spectroscopy (EIS) and the measured R_p was corrected. The potentiodynamic polarization sweeps were conducted at a constant pH and sweep rate of 0.2 mV s^{-1}.

3 Results and discussion

3.1 Effects of acetic acid concentration

The anodic and cathodic potentiodynamic curves for X 65 mild steel in 1% NaCl solutions saturated with N_2 and CO_2 in the absence (blank) and presence of 1,000 ppm total acetic acid at 80 °C, pH 5 and 1,000 rpm are shown in Fig. 1. N_2 gas, being an inert gas, was used to remove any interference from the carbonic species, so that the effects of the acetic acid would be clearly appreciated. In both the N_2- and CO_2-saturated solutions active dissolution characteristics appeared in the anodic curves, while the cathodic curves for the N_2- and CO_2-saturated solutions are different. A Tafel-type curve, in which the potential is linear with respect to log current, indicates that the reaction is under activation control, whereas a limiting current region, in which the curve moves vertically upward, shows diffusion control. A closer look at the curves in Fig. 1 shows that the profile of the cathodic curve in the absence of acetic acid (in the N_2-saturated solution) reveals more of an activated controlled cathodic process. Comparing this curve with that of the CO_2-saturated system in the absence of acetic acid (blank), a limiting current is clearly seen to develop and the cathodic shoulder becomes more pronounced indicating a situation in which diffusion control is present and dominant. This behaviour has been ascribed to the non-homogeneous reaction of CO_2 hydration on the electrode surface [18]. Comparing the curves generated in the N_2- and CO_2-saturated solutions it was observed that CO_2 accelerated the anodic, as well as the cathodic, reactions. This effect is associated with the difference in mechanism of corrosion in these media and indicates that CO_2 is involved in both the anodic and cathodic reactions at pH ≥ 5 [19, 20]. The obvious limiting current observed in the CO_2-saturated solutions is due to diffusion of hydrogen ions.

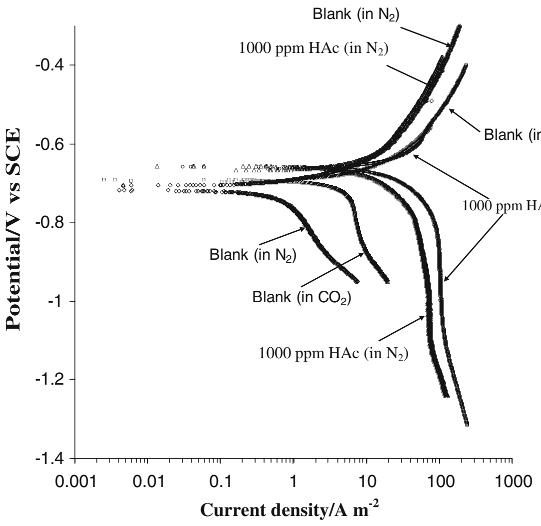

Fig. 1 Effect of acetic acid concentration on the polarization curves for X 65 carbon steel in N_2- and CO_2-saturated 1% NaCl solution at pH 5, 80 °C and 1,000 rpm

Addition of acetic acid was observed not to have any influence on the active dissolution characteristics of the

Table 1 Polarization parameters for X 65 carbon steel in N_2- and CO_2-saturated 1% NaCl solutions containing acetic acid at pH 5

Temp. (°C)	Total acetic acid concentration (ppm)	$-E_{corr}$ (mV)	I_{corr} (A m^{-2})
N_2-saturated solutions			
80	Blank	713	41
	1,000	661	2,483
CO_2-saturated solutions			
40	Blank	721	96
	1,000	658	370
60	Blank	707	188
	1,000	667	855
80	Blank	692	486
	500	665	1,050
	1,000	660	2,800
	5,000	656	3,675

anodic curve but significantly affected the cathodic reaction in both N_2- and CO_2-saturated solutions. The cathodic diffusion shoulders were increased as well as the cathodic limiting and corrosion current densities (Table 1). Similar observations have been previously reported [7, 18]. It should be stressed here that at a fixed pH the effects on the cathodic limiting current density are due principally to the presence of acetic acid in the solutions either in its undissociated form or as acetate ions. Comparing the cathodic curves generated in the two media with acetic acid, the cathodic reaction was accelerated more in the CO_2-saturated system than in the N_2-saturated system. This is most probably due to the additional contribution of the carbonic species to the cathodic reaction.

The results obtained from varying the concentration of acetic acid from 0 to 5,000 ppm total (added) acetic acid in a CO_2-saturated system are shown in Fig. 2. An increase in concentration of total (and consequently undissociated) acetic acid shifts the cathodic curve to higher values of current density. A similar observation was previously reported [7]. It is also observed, from Fig. 2, that the anodic reaction was unaffected by the presence of acetic acid at all concentrations. It may thus be concluded that the previously reported retardation in the anodic reaction in the presence of acetic acid [7, 12] may be due to the large changes of the corrosion potentials at lower temperatures, as pointed out by George and Nesic [7].

A positive shift in the corrosion potentials in the presence of acetic acid, which increases with acetic acid concentration, is also observed in both Figs. 1 and 2 and in Table 1. This positive shift in E_{corr} coupled with an increase in the cathodic reaction is an indication of an electro-catalytic effect of the acetic acid or its reaction product on the corrosion process [21]. This effect is usually due to the change in the average activation energy barriers of the anodic and cathodic reactions of the corrosion process [21].

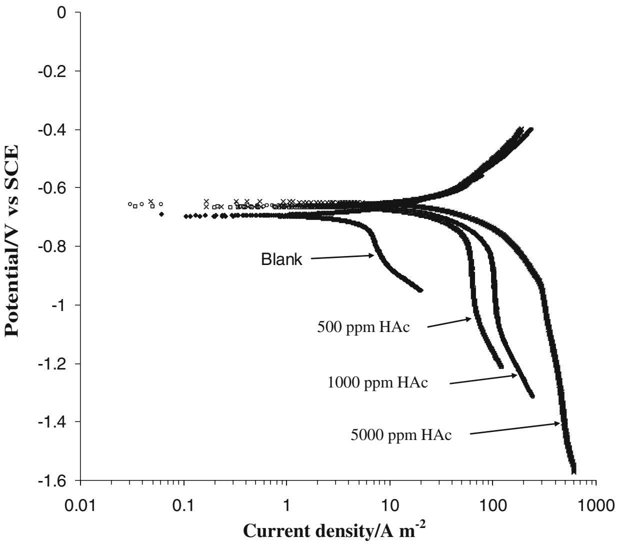

Fig. 2 Effect of acetic acid concentration on the polarization curves for X 65 carbon steel in CO_2-saturated 1% NaCl solution at pH 5, 80 °C and 1,000 rpm

From the linear polarization resistance (LPR) measurements carried out within 10 min of immersion of the metal in the test solutions, it is also observed (Fig. 3) that an increase in acetic acid concentration increased the corrosion rate. The LPR and estimated Tafel extrapolation corrosion rates (Fig. 3) are in agreement.

3.2 Effects of temperature

The effect of temperature on the polarization curves in the presence of 1,000 ppm total acetic acid is as shown in Fig. 4. Increase in temperature is observed to accelerate

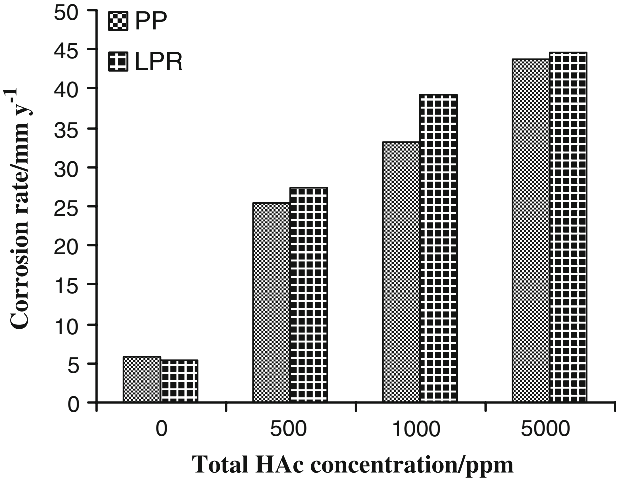

Fig. 3 Corrosion rate versus total acetic acid concentration at 80 °C, pH 5, 1,000 rpm, as measured by the LPR and polarization (PP) methods

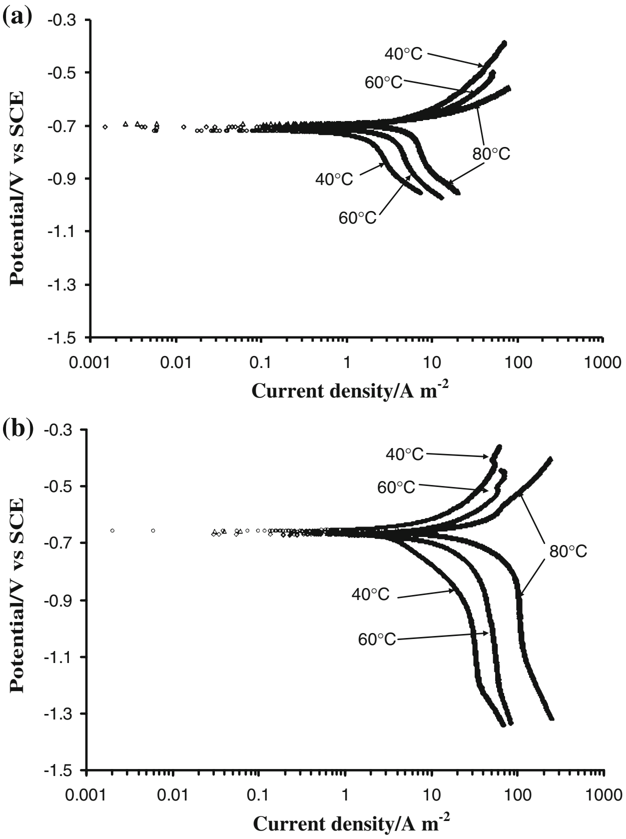

Fig. 4 Effect of temperature on the polarization curves for X 65 carbon steel in CO_2-saturated 1% NaCl solutions in the **a** absence and **b** presence of 1,000 ppm acetic acid at pH 5 and 1,000 rpm

both the anodic and cathodic reactions in the absence and presence of acetic acid. This is due to the acceleration of all the processes involved in corrosion: electrochemical, chemical, transport, etc. with increase in temperature [20]. The apparent activation energies (E_a) for the corrosion process were calculated from the condensed Arrhenius equation as follows:

$$\log \frac{i_{corr(2)}}{i_{corr(1)}} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (1)$$

where $i_{corr(1)}$ and $i_{corr(2)}$ are the corrosion current densities at temperatures T_1 (40 °C) and T_2 (80 °C), respectively. The calculated activation energy values in the absence and presence of the acetic acid are 31.26 and 73.29 kJ mol^{-1}, respectively. The increase in activation energy in the presence of acetic acid is an indication of a change in the reaction mechanism. In the absence of acetic acid, the activation energy is slightly higher than that of aqueous diffusion coefficient (5–20 kJ mol^{-1}) [22] and indicates a mixed interfacial reaction/diffusion control but in the presence of acetic acid, the activation energy of 73.29 kJ mol^{-1} is consistent with a control by an interfacial reaction [23, 24]. This is in agreement with the findings from Tafel analysis at pH 4 and 22 °C [7]. It therefore follows that the increase in corrosion rate in the presence of acetic acid at higher temperature is due to the ease in overcoming the activation energy barrier with increase in temperature.

3.3 Mechanism of acetic acid in CO_2 corrosion

Since acetic acid does not influence the anodic reaction, it would appear that the mechanism of attack of carbon steel in N_2- and CO_2-saturated solutions by acetic acid involves its participation in the cathodic reaction. In CO_2-saturated solutions containing acetic acid, the compounds most likely to be involved in the cathodic reactions during the corrosion process are carbonic acid, hydrogen carbonate ions and acetic acid and the possible cathodic reactions are [7, 25–27].

$$2H^+ + 2e^- \Leftrightarrow H_2 \qquad (2)$$

$$2H_2CO_3 + 2e^- \Leftrightarrow H_2 + 2HCO_3{}^- \qquad (3)$$

$$2HCO_3{}^- + 2e^- \Leftrightarrow H_2 + 2CO_3{}^{2-} \qquad (4)$$

$$HAc + e^- \Leftrightarrow Ac^- + {}^1\!/\!_2H_2 \qquad (5)$$

Acetic acid ($pK_A = 4.75$) [28] is a significantly stronger acid than carbonic acid ($pKA = 6.35$) [29] and $HCO_3{}^-$, ($pKA = 10.32$) being the weakest. Also, the equilibrium:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \qquad (6)$$

lies strongly to the left so that the equilibrium concentration of carbonic acid is low and the rate of the hydration is very slow [13, 29, 30], whereas the dissociation of acetic acid is inherently fast (with a rate constant of $\sim 10^6$ s^{-1}), although a suitable concentration may render it rate-determining [13, 31]. It therefore follows that Eq. 5 is the dominant cathodic reaction and responsible for the increase in the cathodic reaction rate. The reaction steps for the direct reduction of acetic acid may be formulated as:

$$M + HAc \Leftrightarrow MHAc_{ads} \tag{7}$$

$$MHAc_{ads} \xrightarrow{k} MH_{ads} + Ac^{-} \tag{8}$$

$$MH_{ads} + e^{-} \Leftrightarrow M + {}^{1}\!/_{2}H_2 \tag{9}$$

In this mechanism, the metal serves as an active site for binding of the acetic acid and for electron transfer reactions that lead to the release of the adsorbed hydrogen ion.

From Fig. 1, it was observed that carbonic acid species also contribute to the cathodic reaction. In addition to the possible contributions of Eqs. 3 and 4 to the cathodic reaction, a regeneration of the undissociated acetic acid in the presence of carbonic acid according to Eq. 10:

$$H_2CO_3 + Ac^{-} \Leftrightarrow HAc + HCO_3{}^{-} \tag{10}$$

may also contribute to the accelerated cathodic reaction compared to the N_2-saturated solution.

4 Conclusions

- The presence of acetic acid in N_2- and CO_2-saturated systems does not affect the anodic reaction, but strongly affects the cathodic limiting and corrosion current densities. The cathodic reaction and consequently the corrosion rate of mild steel in a CO_2-saturated system increases with increase in acetic acid concentration under the experimental conditions studied.
- Increase in temperature increases the rate of CO_2 corrosion. The increase in corrosion rate in the presence of acetic acid at higher temperature is due principally to the ease in overcoming the activation barrier with increasing temperature. From the values of the apparent activation energies, the corrosion reaction in the absence of acetic acid is under mixed interfacial reaction/diffusion control while interfacial reaction control dominates in the presence of acetic acid.
- The reduction of adsorbed undissociated acetic acid on the metal surface is probably the key species primarily responsible for accelerated corrosion rate at all temperatures.

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