

Article

Effect of Monoethanolamine on Corrosion of A283 Carbon Steel in Propionic Acid Solution

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Abstract. This research studied the effect of monoethanolamine or MEA on corrosion of A283 carbon steels both in water and 5 vol.% propionic acid solution at boiling point temperature of solution. MEA concentrations ranging from 30 to 90 wt.% in water was used. The 5 vol.% propionic acid containing around 45 and 75 wt.% MEA additions (100:1 and 100:5) by volume in the test solution was studied. The carbon steel coupons were tested in a liquid phase, liquid and vapor phase and vapor phase. The weight losses of coupons were evaluated to calculate corrosion rate. A scanning electron microscope and X-ray diffraction were used to characterize the corrosion surface of coupons. The results showed that the corrosion rate order was in the liquid phase > in the liquid and vapor phase > in the vapor phase. MEA decreased the corrosion rate of A283 carbon steel both in water and 5 vol.% propionic acid solution containing around 45 and 75 wt.% MEA additions (100:1 and 100:5) by volume. MEA can be considered as corrosion inhibitor of carbon steel both in water and propionic acid solution. The formed layers of FeO(OH), Fe₂O₃ and Fe₃O₄ on the surface were detected to prevent a corrosion attack. The formed layer of Fe₃C was also found and discussed. The more severe corrosion was in ferrite.

Keywords: Monoethanolamine, propionic acid, carbon steel, corrosion.

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1. Introduction

In an A283 carbon steel steam system of a company, it was contaminated with acetic and propionic acids. These acids can be involved in corrosion of the carbon steel steam system [1]. Corrosion of this steam system has been controlled using a corrosion inhibitor containing monoethanolamine (MEA), having a $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ formula. MEA is an organic corrosion inhibitor, which normally can decrease the rates of cathodic and anodic reactions. Chemisorption of MEA on the metal surface may involve in decreasing corrosion of carbon steel. The chemisorption process is influenced by the chemical bond between the metal and inhibitor, and the charge transfer from the inhibitor molecule to the metal, resulting in a protective film on the metal surface [2, 3].

Alkanolamines are normally corrosion inhibitors in CO_2 absorption systems. Examples of alkanolamines are monoethanolamine, diethanolamine, methyldiethanolamine, diisopropylamine and diglycolamine. Monoethanolamine is susceptible to oxidation to amino acetic acid and has been widely used in separating CO_2 from other gas systems. Copper, iodine and zinc ions were used to treat alkanolamine solution for separating CO_2 . They enhanced protection of metal corrosion [4-7].

Corrosions of A106 carbon steel in anoxic CO_2 based solution with 30 wt.% MEA were studied at 80°C and 120°C . The corrosion rate decreased with an increase in immersion duration and temperature. The formed layers of $\text{Fe}_2(\text{OH})_2\text{CO}_3$ or FeCO_3 on the surface were detected to prevent a corrosion attack [8].

On the other hand, corrosion of AISI 1018 carbon steel in the CO_2 absorption process using MEA solution was evaluated at 80°C . The concentration of MEA had an effect on the corrosion of carbon steel. When the MEA concentration increased from 5.0 to 7.0 and 9.0 kmol/m^3 , the corrosion rate increased from 0.55 to 0.72 and 1.06 mmpy, respectively. The increase of corrosion rates were attributed because of the increase of HCO_3^- in the solution, resulting in a greater rate of iron dissolution [9].

Nevertheless, whether or not MEA increases corrosion of carbon steel is not clear. Adding 1 and 5 vol.% MEA solutions (concentrations of about 45 and 75 wt.%) to 5 vol.% acetic acid solution, corrosions of carbon steel in liquid, liquid and vapor and vapor phases at boiling point of solution were studied for 1 day. Carbon steel was severely corroded in the liquid phase. The corrosion rates of carbon steel decreased, especially at 5 vol.% addition [10].

The effect of MEA on carbon steel corrosion in propionic acid solution has not been found very rare in the literature review. Therefore, this work studied corrosions of A283 carbon steel in liquid, liquid and vapor and vapor phases at boiling temperature of solution for 24 hours. The test solutions were MEA concentrations in the range of 30-90 wt.% and 5 vol.% propionic acid and contained around 45 and 75 wt.% MEA solutions in the ratio part (100:1 and 100:5) by volume.

2. Experiment

2.1. Sample Preparation

The nominal chemical composition (wt.%) of A283 carbon steel is shown in Table 1. All of the tested coupons with dimensions of 20 x 50 x 3 mm were prepared according to NACE TM0169-2000 [11] and ASTM G4 [12]. The coupons were ground with SiC paper down to 600 grits, ultrasonically cleaned with acetone, and kept in a silica gel 184eparation184 for 24 hours at room temperature before testing.

Table 1. Chemical composition (wt.%) of A283 carbon steel.

Element	C	Si	Mn	P	S	Cr	Mo	Ni
Amount (wt.%)	0.056	0.027	0.274	0.020	0.013	0.033	0.003	0.017
Element	Al	Cu	Ti	V	Sn			
Amount (wt.%)	0.032	0.024	0.001	0.001	0.001			

2.2. Immersion Corrosion Testing

After measurements of the dimensions and weight, coupons were hung on a rack in liquid, liquid and vapor and vapor phases in an apparatus as shown in Fig. 1 [13]. The test solutions were MEA solutions with a

concentration of 0, 30, 45, 60, 75 and 90 wt.%, 5 vol.% propionic acid solution, 5 vol.% propionic acid with around 45 and 75 wt.% MEA solution in the ratio part (100:1 and 100:5) by volume. The test conditions were at boiling temperature of solution for 24 hours. The solution pHs before and after test were measured by a pH meter.

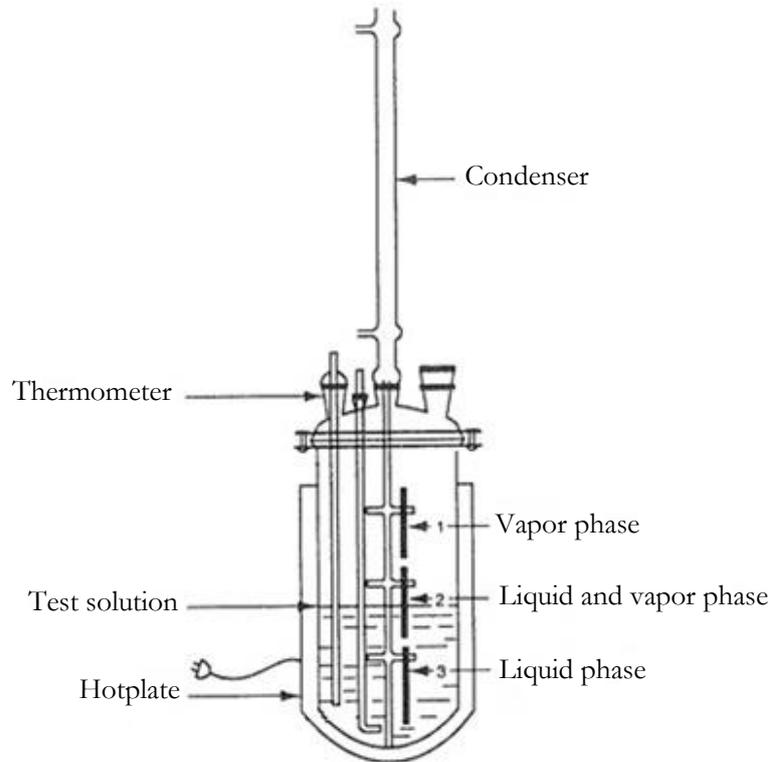


Fig. 1. Immersion corrosion testing [13].

2.3. Cleaning Coupons after Test

According to ASTM G1 [14], tested coupons were cleaned with solutions of concentrated 1000 ml hydrochloric acid (HCl) solution + 20 g antimony trioxide (Sb_2O_3) and 50 g stannous chloride (SnCl_2) at 20-25°C for 1-25 mins. After that, they were ultrasonically cleaned with acetone, and kept in a silica gel 185 separation for 24 hours.

2.4. Characterization Methods

Corrosion rates (CPR) were calculated according to ASTM G1 [14] from mass losses of at least three samples by Eq. (1).

$$\text{CPR} = \frac{KW}{\rho At} \quad (1)$$

Where: K = a constant (8.76×10^4 mm/y), W = mass loss in g, ρ = density in g/cm^3 , A = area in cm^2 , and t = time of exposure in hours

The corroded coupons were experimented for surface morphologies by a scanning electron microscope (SEM) and for surface composition by X-ray diffraction (XRD) with a $\text{Cu K}\alpha$ x-ray at the incident of 0.02 degrees.

3. Results and Discussion

Figure 2 shows the corrosion rates of A283 carbon steel in different concentrations of MEA solutions at boiling point temperature of solution. Adding MEA concentrations in the range of 30 to 90 wt.%, the corrosion rates of A283 carbon steel in liquid, liquid and vapor and vapor phases decreased from about 1.71,

0.76, 1.10 mm/y to about 0.11, 0.11 and 0.14 mm/y, respectively. This might have been due to MEA adsorption on the metal surface resulting in a protective film. Then, the rates of cathodic and anodic reactions decreased [15, 16]. From Fig. 2, MEA can be considered as a corrosion inhibitor. The results were similar to those of Wichaya Saihan and Siwakorn Suksawat [10], but not those of Immanuel Raj Soosaiprakasam and Amornvadee Veawab [9].

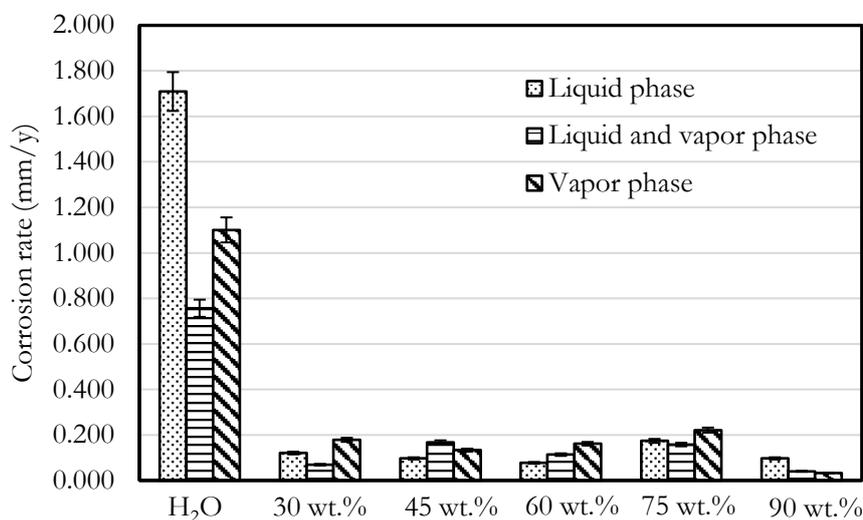


Fig. 2. Corrosion rates of A283 carbon steel in different concentration of MEA solution at boiling point temperature.

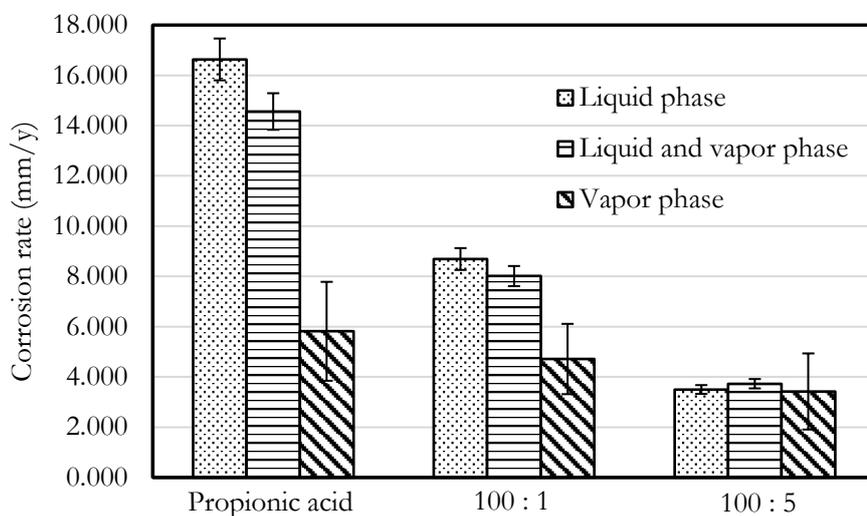


Fig. 3. Corrosion rates of A283 carbon steel in 5 vol.% propionic acid solutions with around 45 wt.% MEA solution at 100:1 and 100:5 additions by volume and boiling point temperature.

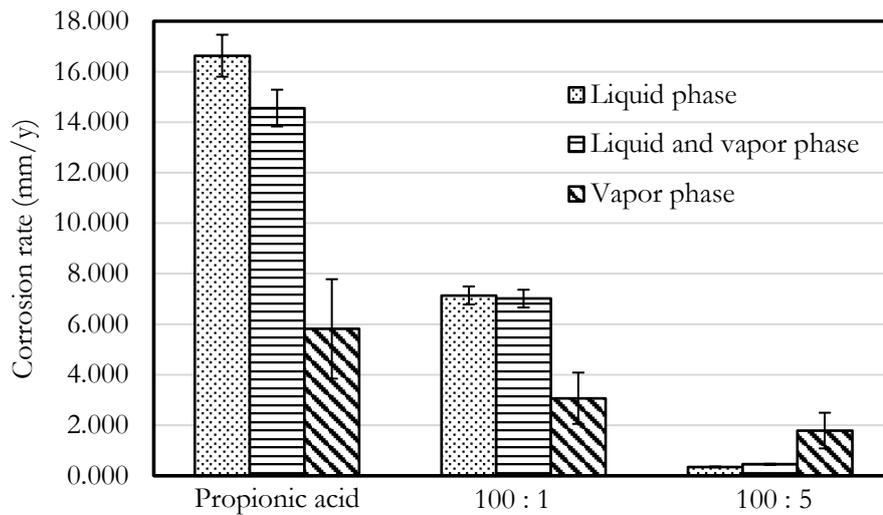


Fig. 4. Corrosion rates of A283 carbon steel in 5 vol.% propionic acid solutions with around 75 wt.% MEA solution at 100:1 and 100:5 additions by volume and boiling point temperature.

Figures 3 and 4 showed that carbon steel in 5 vol.% propionic acid solution corroded in the liquid phase higher than in the liquid and vapor phase and vapor phase, respectively, because of more homogeneous solution concentration. Increase of about 45 and 75 wt.% MEA solutions from 0 to 100:1 and 100:5 additions by volume to the test solution, corrosion rates of A283 carbon steel in liquid, liquid and vapor and vapor phases decreased. This showed that MEA could reduce the corrosion rate of carbon steel. The solution pHs before and after testes were 4-6 in all additions of MEA solutions (Figs. 3 and 4), except in 100:5 additions by volume of around 75 wt.% MEA solutions (Fig. 4). The pHs increased from 4 before test to 10 after test. The inhibition effect of MEA on decrease of A283 corrosion rate was clear by around 75 wt.% MEA solution addition of 100:5 by volume in Fig. 4, because of high base solution resulting in possibly carbon steel passivity.

Figures 5a and 6a showed XRD patterns of A283 carbon steel after in liquid phase testing of 5 vol.% propionic acid, 5 vol.% propionic acid with around 45 and 75 wt.% MEA additions of 100:1 and 100:5 by volume. They showed the sharp peak of Fe (ICDD 01-089-7194) for all conditions. However, zooming in 15 to 45 degree analysis (Fig. 5b-d and Fig. 6b-d), they showed some iron oxides and the Fe_3C were found to form on the surface. Both in 5 vol.% propionic acid (Figs. 5d and 6d) and 5 vol.% propionic acid with around 45 wt.% MEA at 100:1 addition by volume in the test solution (Fig. 5c), they showed that only Fe_3C (ICDD 00-034-0001) appeared on the surface. By additions of around 45 wt.% MEA solutions at 100:5 by volume in the test solution, (Fig. 5b), the Fe_3O_4 (ICDD 01-071-6336) and Fe_2O_3 (ICDD 01-076-4579) were observed. Due to low partial pressure of O_2 [17], it was thought that the Fe_2O_3 and Fe_3O_4 could not be formed but Fe_3C could exist (Figs. 5c and 5, 6d). The higher concentrations of MEA could result in enough O_2 for iron oxide formations (Fig. 5b). Similar results can be observed in Fig. 6b-c. The FeO(OH) (ICDD 01-081-0462), Fe_3O_4 and Fe_2O_3 were found to form on the surface, with around 75 wt.% MEA at 100:1 additions by volume in the test solution (Fig. 6c) [18, 19]. This could be enough O_2 . However, increasing MEA from 100:1 to 100:5 additions by volume in the test solution, the FeO(OH) and Fe_2O_3 disappeared on the surface (Fig. 6b). Only Fe_3O_4 was found on the surface.

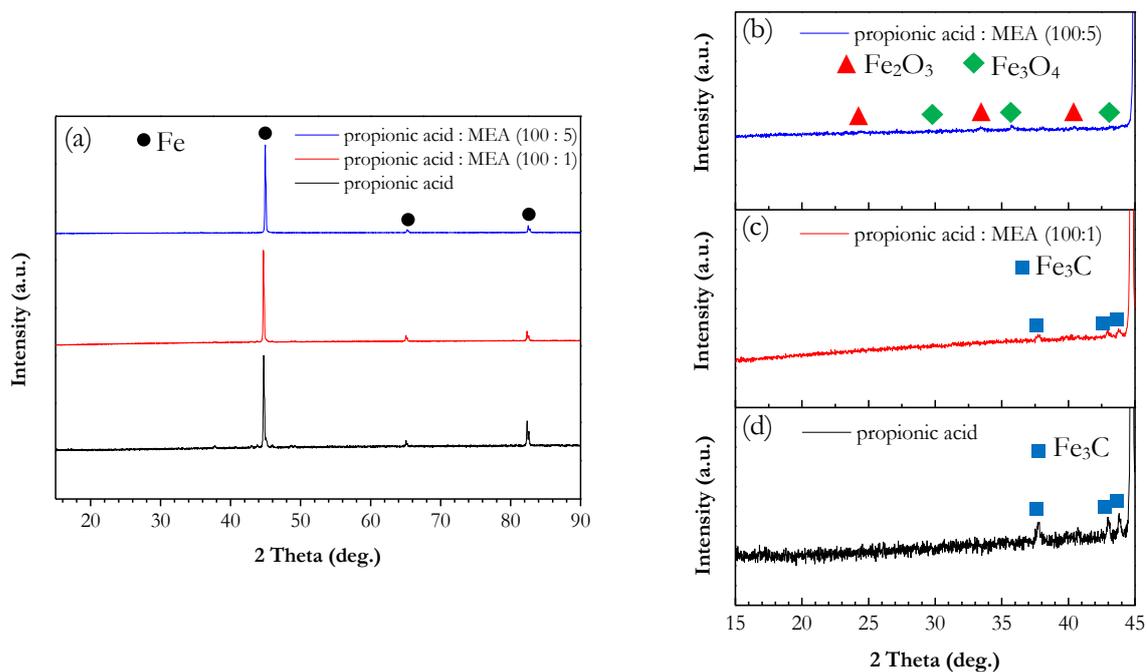


Fig. 5. XRD patterns of A283 carbon steel after in liquid phase testing of 5 vol.% propionic acid and 5 vol.% propionic acid with around 45 wt.% MEA additions.

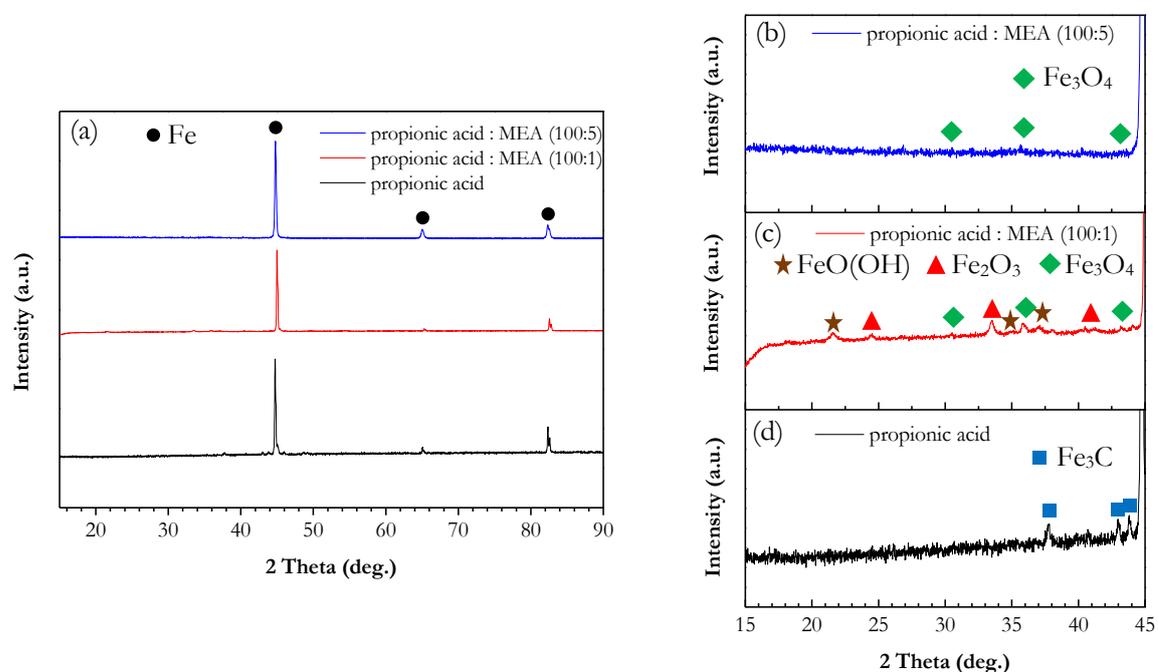
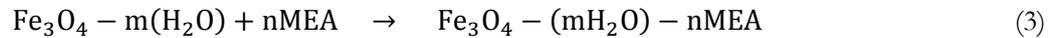
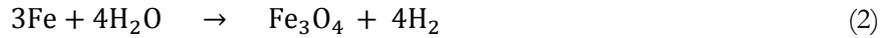


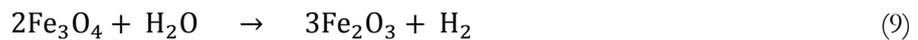
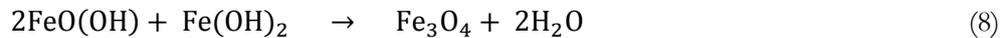
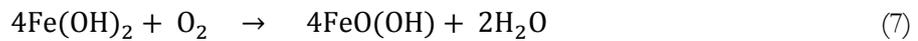
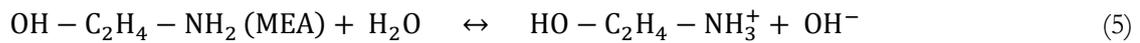
Fig. 6. XRD patterns of A283 carbon steel after in liquid phase testing of 5 vol.% propionic acid, and 5 vol.% propionic acid with around 75 wt.% MEA additions.

From literature review [16], the adsorption of MEA on the hydroxylated Cr_2O_3 surface of steel inhibited the steel corrosion. The two mechanisms of MEA effect on reduction of steel corrosion were then proposed: the adsorption of MEA and the formations of protective layers at surface of A283 carbon steel.

The adsorption of MEA on Fe_3O_4 corrosion product to inhibit Fe dissolution by water was shown as Eq. (2)-(3).



The formations of protective layers were shown as Eq. (4)-(9).



The dissolution of Fe is usually followed Eq. (4) because of oxygen reduction in water. MEA could react with water to form OH^- (Eq. (5)) [20] and then reduced dissolution of Fe to form $\text{Fe}(\text{OH})_2$ by Eq. (6). The formation of corrosion product ($\text{FeO}(\text{OH})$) (Fig. 6c) could be possible by Eq. (7) [21]. The $\text{FeO}(\text{OH})$ could be converted to Fe_3O_4 (Figs. 5b and 6b-c) followed Eq. (8) [22]. The formation of Fe_2O_3 (Figs. 5b and 6c) might be formed by the transformation of Fe_3O_4 as shown in Eq. (9) [9].

The A283 carbon steel is composed of two microstructures or phases: ferrite and pearlite (Fig. 7a). The pearlite was positioned on the grain boundary. Figure 7b-d shows the corroded phases after corrosion test in solutions of 5 vol.% propionic acid solution in liquid, vapor phases, and 5 vol.% propionic acid solution with around 45 wt.% MEA additions of 100:5 by volume in the liquid phase, respectively. The Fe_3C was more cathodic than ferrite [23-25]. Therefore, the most corroded phases were ferrite not pearlite, because it contained Fe_3C which had more corrosion resistance than ferrite. The more severe corrosion was found in ferrite, when the coupons were in liquid, as shown in Fig. 7b. By addition of MEA into solution, the corroded ferrite was decreased, as shown in Fig. 7d.

4. Conclusions

Corrosion of A283 carbon steel in MEA solutions, 5 vol.% propionic acid solution with around 45 and 75 wt.% MEA additions of 100:1 and 100:5 by volume in the test solution at boiling temperature of solution were studied for 1 day. Based on the results, the following conclusions were obtained:

- (1) MEA reduced corrosion rates of A283 carbon steel in 5 vol.% propionic acid solution.
- (2) Corrosion rates of A283 carbon steel in 5 vol.% propionic acid solution in liquid phase were higher than in liquid and vapor and in vapor phases.
- (3) In 5 vol.% propionic acid solution, by adding around 75 wt.% MEA solutions decreased the corrosion rate of A283 carbon steel greater than by adding around 45 wt.% MEA solutions at the same volume addition.
- (4) The formed layers of corrosion products were Fe_3C , $\text{FeO}(\text{OH})$, Fe_2O_3 and Fe_3O_4 .

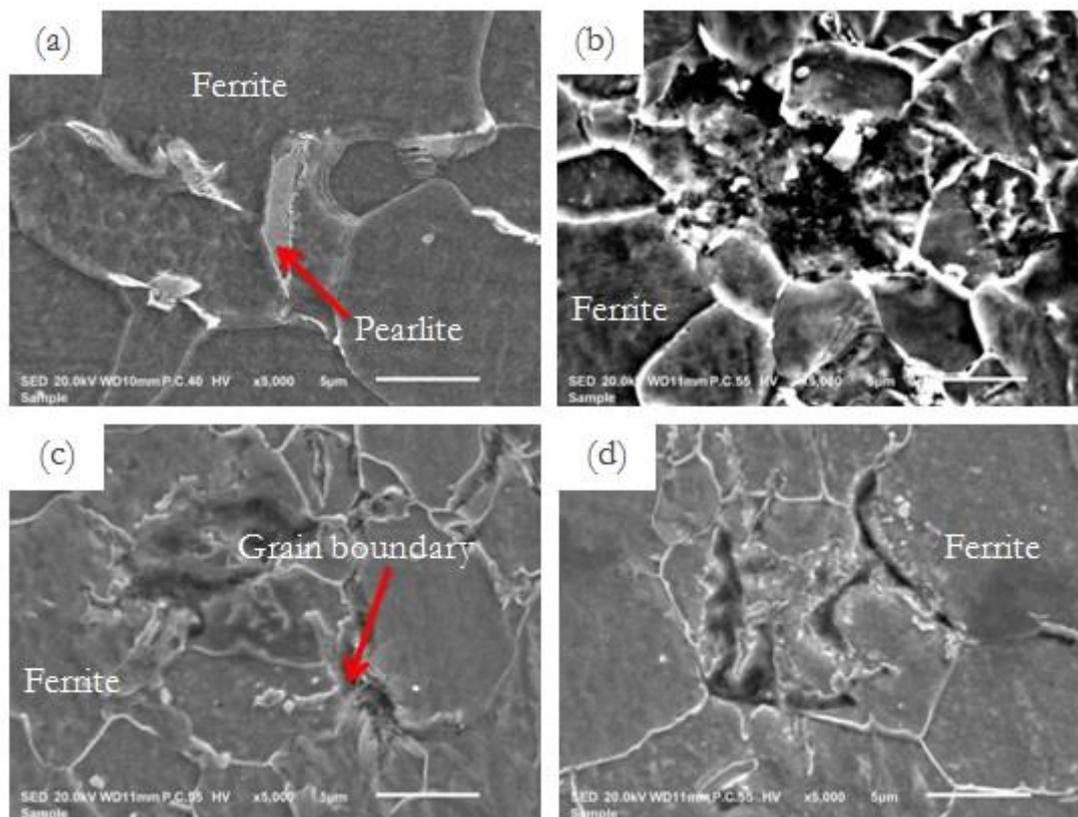


Fig. 7. SEM surface morphologies of (a) A283 carbon steel, (b) after the corrosion test of (a) in 5 vol.% propionic acid solution in liquid phase, (c) after the corrosion test of (a) in 5 vol.% propionic acid solution in vapor phase and (d) after the corrosion test of (a) 5 vol.% propionic acid solution with around 45 wt.% MEA (100:5) in the liquid phase.

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