Short Communication

Inhibitive Effect of N,N-Dimethyl Ethanolamine on Carbon Steel Bar in Chloride Contained Cement Extract

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For studying the inhibitive effect of N,N-Dimethylethanolamine (DMEA) on carbon steel bar in cement extract, the corrosion behavior of steel bar in solution contained with 0%, 0.5%, 1.0% and 2.0% (wt.%) DMEA was investigated by open circuit potential (OCP), linear polarization (LPR), potentiodynamic polarization, and AC impedance spectroscopy (EIS), respectively. The values of OCP for samples were significantly decreased after 336 h immersed in the cement extract without DMEA; while these of the samples in solutions contained DMEA were only slightly changed during the whole immersion process. The potentiodynamic polarization results suggest the DMEA is a cathodic inhibitor in the chloride contaminated cement extract. Moreover, there is only slight corrosion inhibition effect in the solutions contained DMEA in the initial stage. After immersion for 336 h, the LPR and EIS results indicated that the polarization resistance and impedance obviously increased with the concentration of DMEA. The inhibition effect of DMEA on carbon steel increased with the concentrations. Simultaneously, the further analysis of EIS results suggests that the DMEA forms an absorption layer on the surface of rebar and inhibit the the corrosion of carbon steel.

1. INTRODUCTION

The corrosion of the reinforced steel bar, as one of the main failure reasons, significantly decreases the durability of concrete structure [1]. In order to enhance the lifetime of marine structures, stainless steel bar, corrosion inhibitor, epoxy resin coated steel bar, cathodic protection, etc. are used in construction. Among them, inhibitors are used widely for its convenience, exceptional performance for

corrosion mitigation and economically profitable [2]. Initially, the inhibitors for concrete are mainly inorganic salt, such as calcium nitrite. Recently, the calcium nitrite based inhibitors are gradually forbidden for its toxicity and high corrosion risk when the dosage is insufficient [3]. The ethanolamine-based migration inhibitor attracts many scientists' attention for its eco-friendly and high inhibition effect [4-5]. Extensive studies have been done on the ethanolamine-based inhibitor since its good performance on corrosion inhibition for reinforcing steel bar [6]. Firstly, the inhibition mechanism of the ethanolamine-based inhibitor has been studied. Wombacher [7] reported that the ethanolamine-based inhibitor could form the protective film both on the anodic and cathodic regions on the surface of steel bar. Then, the authors thought that it should be classified as the composite inhibitor. Jamil [8, 9] also studied the inhibition behavior of an ethanolamine-based inhibitor and noticed that the corrosion potential do not show significantly influence, while the reactivity of the anodic reaction of rebar are obviously reduced by the inhibitor. Thus, Jamil et al. [8, 9] classified the ethanolamine-based inhibitor as anodic corrosion inhibitor. However, Gaidis [10] reported that the ethanolamine-based inhibitor is cathodic corrosion inhibitor for the ethanolamine and DMEA mainly influence the cathodic reaction of the corrosion process of steel bar. The aforementioned discrepancy on the inhibition mechanism of the ethanolamine-based inhibitor maybe closely related with the different types of alcohol amine or the concentration of the inhibitor [11]. In the present study, the inhibitor behavior of N,N-Dimethylethanolamine in the chloride contaminated cement extract were investigated and the inhibition mechanism also been discussed.

2. MATERIALS AND EXPERIMENTS

2.1 Materials

Carbon steel rods with 10 mm diameter were cut to 20 mm length and the sample was ground with emery paper up to No.600. Samples were degreased with acetone, rinsed with distilled water, and dried in hot air. Copper wires were welded on one end. After that, the side face and the welded end were coated with epoxy resin, while only the other cross-section of the rebar was exposed to electrochemical testing. Ordinary Portland cement (PO 42.5) was added into distilled water at the ratio (wt. %) of 1:5 and stirred for 30 min. After 12 h, the cement extract filtered from the mixed solutions (pH=12.5) was used as the concrete pore solution. An electrolyte consisting of 3.0% (wt.%) sodium chloride was prepared to accelerate the corrosion of rebar in the experiment. Different concentrations of DMEA, including 0%, 0.5%, 1%, and 2% (wt.%) were added in the cement solution to study the inhibitor effect of DMEA.

2.2 Experiments

The open circuit potential (OCP), linear polarization resistance (LRP), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) of carbon steel in cement extract with different concentrations of DMEA were tested after immersed for 24 h, 168 h, 336 h, and 672 h. Each

electrochemical test was performed in triplicate, using a new sample for each round. All electrochemical testing were performed by using a CS350 workstation (Corrtest Instrument, China) with a classical three-electrode cell. A saturated calomel electrode (SCE) and a platinum plate are used as reference and counter electrode, respectively. The linear polarization resistance was tested at voltages of ±10 mV, with respect to the OCP, and a scan rate of 10 mV/min. The potentiodynamic polarization were test from -0.3~1.2 V with respect to the OCP at a rate of 1 mV/s. The electrochemical impedance spectroscopy was performed at a frequency ranging from 10^5 to 10^{-2} Hz with an alternating current disturbance signal of 15 mV.

3. RESULTS AND DISCUSSION

3.1 Open circuit potential

The evolution of open circuit potential for carbon steel samples in the simulated concrete pore solution with different concentrations of DMEA is presented in figure 1. It is easy to notice that there is no obviously difference for the OCP values in the initial 336 h for carbon steel in pore solution with different concentrations of DMEA. As the immersion time prolong, the OCP of the control sample significantly decreased and even lower than -800 mV after immersion for 672 h, while that for the samples immersed in the solutions mixed with DMEA almost maintained -600 mV. This situation suggests that the DMEA in cement extract blocks the decrease of OCP after 336 h.
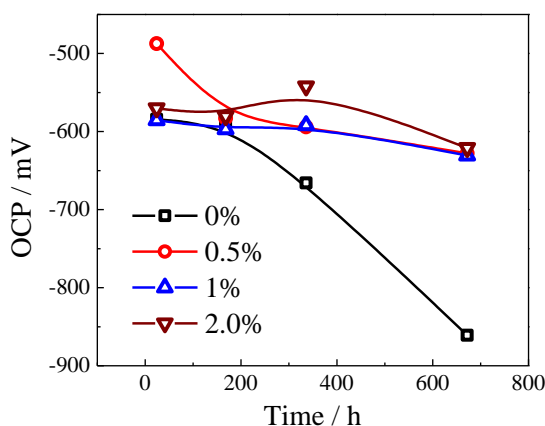

Figure 1. The values of OCP for carbon steel samples in the cement extract (pH=12.5) contaminated with 3.0% NaCl and with different concentrations of DMEA.

3.2 Potentiodynamic polarization

The potentiodynamic polarization curves of carbon steel samples in cement extract with various concentration of DMEA are presented in figure 2. As can be seen, the corrosion potential of the samples significantly decreased with the concentration of the inhibitor. Simultaneously, the corrosion current density of carbon steel also decreased with the addition of DMEA. This situation

suggests that the DMEA is a cathodic corrosion inhibitor and it is consistent with the earlier reports from Gaidis [10].
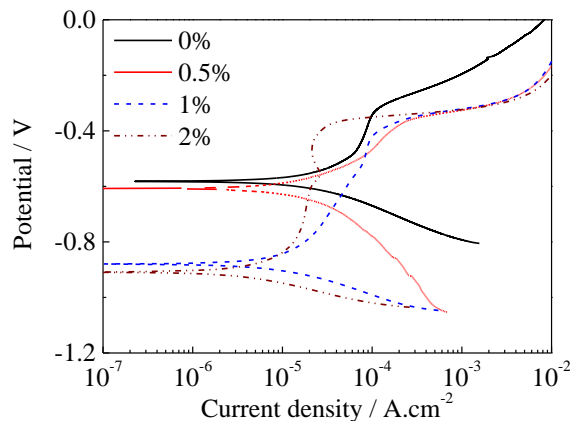

Figure 2. The potentiodynamic polarization curves of carbon steel samples at a rate of 1 mV/s in the cement extract (pH=12.5) contaminated with 3.0% NaCl and with different concentrations of DMEA.
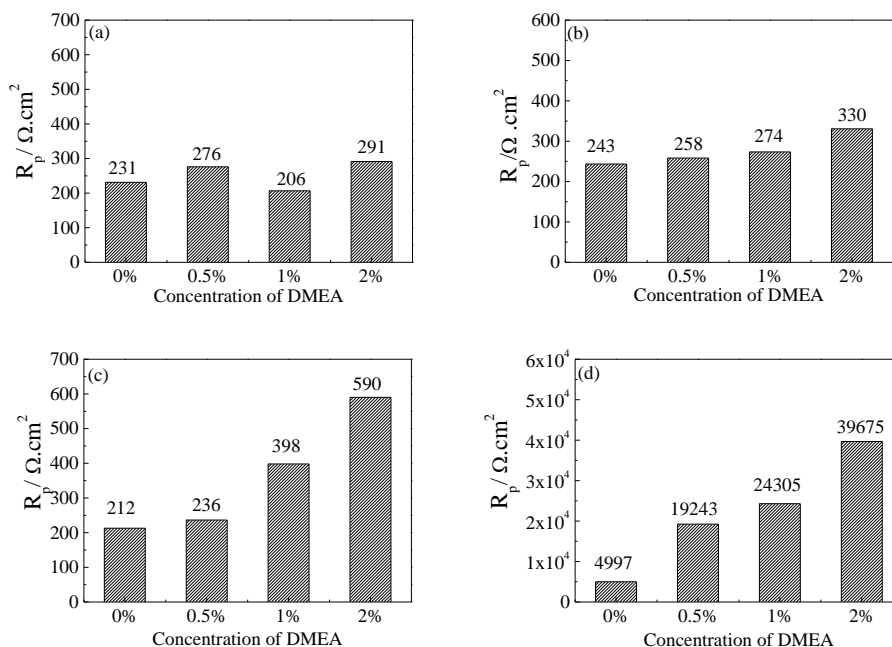
3.3 Linear polarization resistance

Figure 3. The values of R_p changes with time in cement extract (pH=12.5) contaminated with 3.0% NaCl and with different concentrations of DMEA,(a) 24 h, (b) 168 h, (c) 336 h, (d) 672 h.

The results of linear polarization resistance (R_p) for carbon steel in pore solution with various concentrations of DMEA are presented in figure 3. As the results show, the value of R_p does not show obvious difference for samples in solution with different concentration of DMEA in the first 168 h. As the immersion time prolong, the R_p gradually increased with the concentration of DMEA. After immersion for 336 h, the values of R_p for samples in solution with 2.0% DMEA exceeds 2 time of that

for the carbon steel in control solution (Fig 3(c)). As the immersion time further prolong, the increase of R_p is more significant when the DMEA concentration increased. The R_p of samples in solution with 2.0% DMEA became almost 10 time of that for the samples in the control solution.

The corrosion current density (i_{corr}) of carbon steel also can be calculated from R_p according to equation (1)~(3).

$$i_{corr} = \frac{\beta_a\beta_c}{2.303R_p(\beta_c-\beta_a)} \qquad (1)$$

$$B = \frac{\beta_a\beta_c}{2.303(\beta_c-\beta_a)} \qquad (2)$$

$$i_{corr} = \frac{B}{R_p} \qquad (3)$$

where β_a and β_c are the anodic and cathodic Tafel slopes, respectively, on a log scale [12]. Previous studies indicated that carbon steel bar in concrete has respective anodic and cathodic Tafel slopes of ~90 mV/dec and −180 mV/dec [13-15]. Therefore, the value of B = 26 mV/dec. As such, in the present study, the i_{corr} values were all determined from Eq. (3), using this B value [13-15]. As the result in figure 4 shows, the corrosion current density only slightly decreased in the initial 336 h. Then, it is obviously decreased as the immersion time increased. This situation is consistence with the OCP (figure 1) and potentiodynamic polarization results (Fig 6), which suggests that the DMEA performs inhibition effect mainly after 336 h in the chloride contaminated pore solution. On the other hand, it is easy to notice that the corrosion current density decreased with the concentration of DMEA at 672 h.
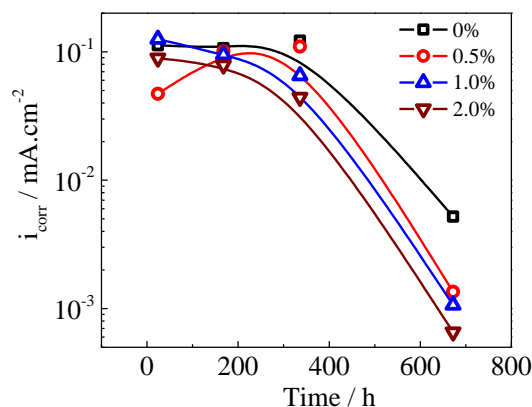

Figure 4. The values of i_{corr} changes with time in cement extract (pH=12.5) contaminated with 3.0% NaCl and with different concentrations of DMEA.

3.4 Electrochemical impedance spectroscopy

The EIS results of carbon steel samples in cement extract with different concentration of DMEA are presented in figure 5. It can be seen that there are two arcs in the Nyquist plots of carbon steel in the chloride contaminated pore solution in the initial 336 h. After that, it changed to an arc with large radius after 672 h immersed in the solution. Moreover, the radius of the Nyquist plots was evidently increased by the addition of DMEA. The results concur with the OCP, LRP results, which

indicated that the DMEA can significantly inhibit the corrosion the carbon steel after 336 h in the chloride contaminated solution.

EIS results are further fitted to an equivalent circuit (Fig. 6) by using the Zsimpwin software. In the equivalent circuit, R_s represents the solution resistance, R_{ad} and Q_{ad} are the resistance and capacitance of the adsorption DMEA layer on the surface of carbon steel, while the R_{ct} and Q_{ct} are the polarization resistance and the double layer capacitance, respectively [16, 17]. The fitted results of adsorption DMEA layer resistance (R_{ad}) and the polarization resistance (R_{ct}) are presented in figure 7. As the results show, both the values of R_{ad} and R_{ct} increased with immersion time. On the other hand, the fitted R_{ad} and R_{ct} also increased with the concentration of DMEA in the cement extract. Interestingly, the increase of the former is more significant than that of the latter. This situation concurs with the earlier study reported by Díaz-Gómez [18], in which authors also noticed that both the R_{ad} and R_{ct} increased with the concentration of inhibitor. Meanwhile, the increment of the value of R_{ad} was more obvious than that of the R_{ct}. The Fitting results of EIS suggest that the DMEA could effectively inhibit the corrosion of carbon steel in the chloride contaminated pore solution after 336 h. A protective absorbed layer form in the cement extract when DMEA were added in the cement extract, the absorbed layer significantly increased with the concentration of DMEA in pore solution.
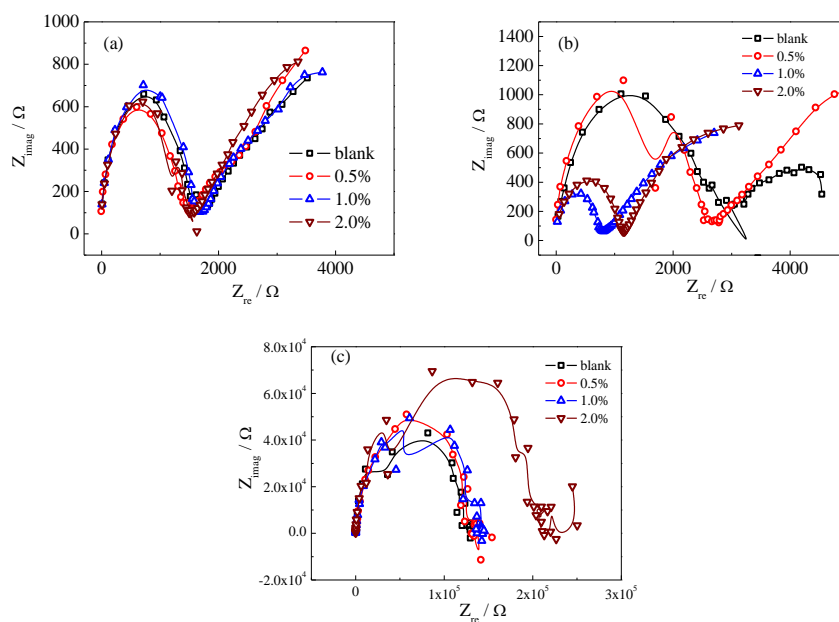

Figure 5. Nyquist plots of the reinforced steel bar in cement extract (pH=12.5) contaminated with 3.0% NaCl and with different concentrations of DMEA, (a) 24 h，(b) 336 h，(c) 672 h.
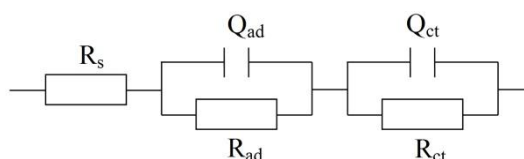

Figure 6. Equivalent electrical circuit for modeling the impedance data.
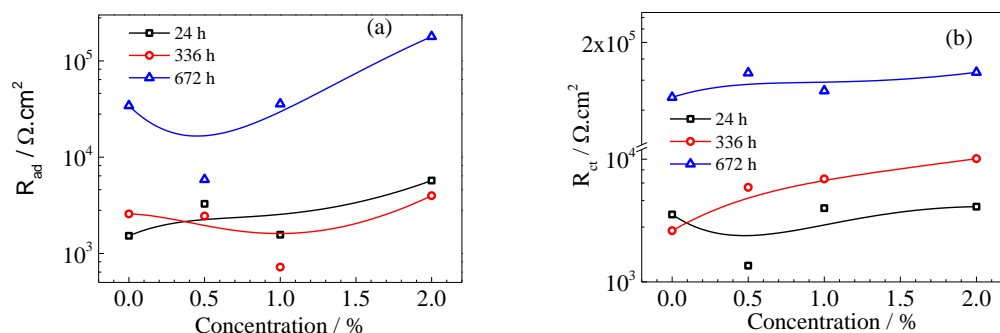
Figure 7. Fitted results of EIS test in the cement extract (pH=12.5) contaminated with 3.0% NaCl and with different concentrations of DMEA, (a) the adsorption DMEA layer resistance (R_{ad}), (b) the polarization resistance (R_{ct}).

3.5 Corrosion of rebar

After immersion for 672 h, the carbon steel in pore solution with various concentration of DMEA was examined and the results were presented in figure 8. It is easy to notice that the carbon steel in the cement pore solution without DMEA was seriously corroded after 672 h immersion (figure 8(a)). For these samples in the solution with DMEA, the addition of inhibitor obviously alleviates the corrosion of samples in the cement extract. Furthermore, the corrosion of samples was also reduced as the concentration of DMEA increased from 0.5% to 2.0%. The corrosion situation of samples is consistent with the electrochemical testing results, together confirm that the DMEA is an effective inhibitor for carbon steel in chloride contaminated cement extract.
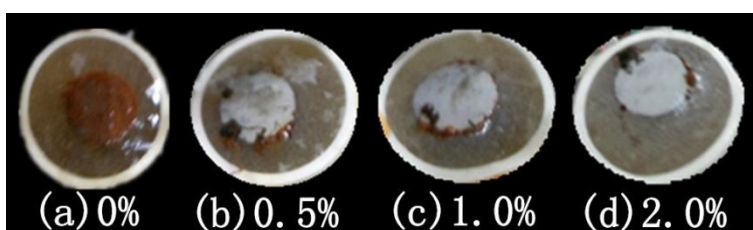

Figure. 8 Photographs taken after 672 h of immersion in the cement extract (pH=12.5) contaminated with 3.0% NaCl and with different concentration of EDMA, (a) 0%, (b) 0.5%, (c) 1.0%, (d) 2.0%.

4. CONCLUSIONS

(1) DMEA is an effective corrosion inhibitor of carbon steel in chloride contaminated cement extract. The inhibition effect significant increased with the concentration of DMEA in the pore solution.

(2) DMEA is a cathodic inhibitor in the chloride contaminated cement extract. A absorb layer forms on the surface of carbon steel and inhibits the corrosion of rebar in the simulated concrete pore solution. Moreover, the resistance of the absorb layer significantly increased with the concentration of DMEA in the solution.

(3) The addition of DMEA in pore solution only slightly inhibits the corrosion of carbon steel in the initial stage. After immersion for 336 h, the corrosion inhibition effect of DMEA obviously increased as the time further increased.

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