Inhibitive effect of N,N'-Dimethylaminoethanol on carbon steel corrosion in neutral sodium chloride solution, at different temperatures

Mohammed Hassoune[1], Abdelillah Bezzar[1], Latéfa Sail[1] and Fouad Ghomari[1]

[1]Laboratory E.O.L.E, Abou Bekr Belkaid University, Civil Engineering, Tlemcen, Algeria

Abstract. The inhibition of carbon steel corrosion in neutral sodium chloride solution by N,N'-Dimethylaminoethanol (DMEA), at different temperatures, was investigated using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results obtained confirm that DMEA is a good organic corrosion inhibitor for carbon steel in 0.5M of NaCl (concentration encountered in the Mediterranean seawater), over the whole range of temperatures studied. The inhibition efficiency (IE%) increases with increasing DMEA concentration; it reaches highest value for a concentration around 0.125 mol.L^{-1}. Potentiodynamic polarization data show that, the compound studied in this research predominantly act as anodic-type inhibitor. The EIS study reveals that the addition of DMEA decreases the corrosion rate of carbon steel in neutral sodium chloride solution, due to the fact that the inhibitor molecules are strongly adsorbed on the active sites following Langmuir isotherm, thus leading to the formation of a stable protective film on the steel surface which is able to keep the metal/solution interface in a passive state. Furthermore, the values of the activation parameters, i.e. ΔHa and Ea obtained in this study indicate that the adsorption process of DMEA is endothermic and could be mainly attributed to chemisorption, respectively.

1 Introduction

Due to low cost and excellent mechanical properties, carbon steel is extensively used in construction and widely applied as the constructional material in large number of industries. However, it gets corroded when exposed to aggressive environments like chloride-rich media, which results in terrible wastage of both resources and money. This is the reason why the corrosion and passivation behavior of carbon steel are quite general and important phenomena in our daily life. Therefore, there is a great economical incentive in developing methods and materials to mitigate the corrosion of carbon steel [1, 2].

The use of corrosion inhibitors is one of the most widely practical methods for protection of metals and alloys against corrosion, this technique has attracted increasing attention in recent years. Different classes of inorganic compounds are used as corrosion inhibitors for carbon steel in various harsh media. However, unfortunately, most of them present health hazards or are very expensive. These features certainly limit the field of their application [3]. Environmentally friendly organic inhibitors containing heteroatoms N, O, and S in the molecules were reported to be effective inhibitors for metals and al alloys in an environment containing aggressive ions [4, 5]. There are many studies deal with the corrosion inhibition effects of these organic compounds in acidic solutions, especially in the treatment of steel and ferrous alloys in hydrochloric or sulphuric acid [6-8]. However, very little literature is reported on the corrosion protection of carbon steel in neutral chloride medium, which leads to extensive general and localized pitting corrosion of carbon steel [9, 10].

The organic inhibitors are typically based on mixtures of alkanolamines and amines. Amino alcohol compounds are frequently used as organic corrosion inhibitors due to their high solubility (easy application) and their low toxicity; they can be more effective when the corrosion degree is relatively low or before the corrosion initiation phase of metal [11]. It is reported that the inhibiting action of this compounds is due to the adsorption and/or formation of physical barrier on the metal/solution interface [12, 13]. This process depends upon the nature and surface charge of the metal, the type of aggressive media, the chemical structure of the inhibitor, and the nature of its interaction with the metal surface [14, 15].

The present work aims to investigate the efficiency of N,N'-Dimethylaminoethanol (DMEA), an amino alcohol compound, used as an organic corrosion inhibitor for carbon steel in 0.5M NaCl solution, using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The effects of inhibitor concentration and temperature on the efficiency of the DMEA were examined. Moreover, the inhibition mechanism of DMEA in the test solution is studied and discussed.

2 Experimental

2.1 Materials

In order to conduct the gravimetric and electrochemical measurements, specimens of carbon steel were prepared from commercial reinforcing carbon steel (XC38). Its chemical composition is given in Table 1.

Table 1. Chemical composition of tested steel [16].

Chemical Elements	C	Si	Mn	P	S	Cr
Composi- (wt. %)	0.259	0.271	1.25	0.012	0.040	0.05
Chemical Elements	Ni	Al	Cu	V	Su	Fe
Composi- (wt. %)	0.114	0.003	0.29	0.068	0.017	97.65

The N,N'-Dimethylaminoethanol (DMEA) was used as organic corrosion inhibitor in the present study, its chemical structure is shown in Figure 1. The molecular formula of DMEA is $C_4H_{11}NO$, while its molar mass is 89.14 g.mol^{-1}.
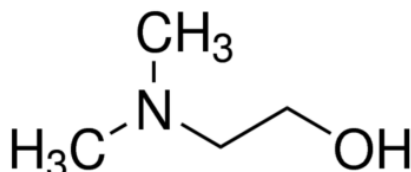

Fig. 1. Chemical structure of DMEA.

2.2 Gravimetric measurements

Prior to the tests, disc-shaped steel specimens (27 ± 2 mm diameter and 2 ± 0.2 mm thickness) were mechanically polished with emery papers (with grade from 120 to 1000), washed with distilled water, degreased with acetone, dried and weighed (m_1) by means of an analytical balance with 0.1mg readability. The clean weighed steel specimens was completely immersed, at an inclined position, in a glass vessel containing 50 ml solution of 0.5M NaCl, without and with addition of different concentrations of DMEA, for 360 hours, at various temperatures (298, 313 and 328 K). Then, the carbon steel specimens were reweighed (m_2) after washing and drying.

Based on the gravimetric measurements, the corrosion rate (CR) in (mg.cm^{-2}.h^{-1}) was calculated according to the following equation,

$$CR = \frac{m_1 - m_2}{S.t} \tag{1}$$

where, m_1 and m_2 are the average weights of specimen (mg), before and after immersion, respectively; S is the immersed surface area (cm^2) of the specimen and t is the immersion time (h). The inhibition efficiency (IE%) of the inhibitor was calculated using the relation:

$$IE(\%) = \frac{CR_0 - CR_{inhib}}{CR_0} * 100 \tag{2}$$

where CR_0 and CR_{inhib} represent the corrosion rate, respectively, without and with DMEA.

2.3 Electrochemical studies

The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), were carried out using a Potentiostat/Galvanostat (Voltalab80 Model PGZ402), driven by (Voltamaster4) software. Conventional three electrode system was used for electrochemical experiments. In this setup, polished carbon steel specimens with 1.05 cm^2 exposed surface area were used as working electrode, platinum electrode as an auxiliary electrode, and saturated calomel electrode (SCE) as a reference electrode. The three electrodes setup was immersed in glass cell, containing 200 ml of the test solution (0.5M NaCl), without and with addition of different concentrations of DMEA.

The potentiodynamic polarization measurements were started from cathodic to anodic direction, from -1000 to -300 mV with respect to the (SCE), with a scan rate of 0.5 mV.s^{-1}. The corrosion current (I_{corr}), was obtained by extrapolation of anodic and cathodic regions of the Tafel plots. From (I_{corr}), the inhibition efficiencies (IE%) were calculated using the following relation,

$$IE(\%) = \frac{I_{0corr} - I_{corr}}{I_{0corr}} * 100 \tag{3}$$

were (I_{0corr}) and (I_{corr}) denote the corrosion current densities in the absence and presence of inhibitor, respectively.

EIS measurements were carried out using a signals of amplitude perturbation of 10 mV, over a frequency range from 100 kHz to 50 mHz. The impedance parameters were obtained from the Nyquist plots. The inhibition efficiencies (IE%) were calculated according to the following equation,

$$IE(\%) = \frac{R_{ct} - R_{ct0}}{R_{ct}} * 100 \tag{4}$$

were R_{ct} and R_{ct0} refer to the charge transfer resistances obtained in the presence and absence of inhibitor, respectively.

The potentiodynamic polarization curves and Nyquist plots were recorded after 24 hours of immersion of steel specimens in the test solution, without and with addition of different concentrations of DMEA, at 298K.

3 Results and discussion

3.1 Gravimetric measurements

3.1.1 Effects of inhibitor concentration

The corrosion rate (CR) and inhibition efficiency (EI%), obtained from the gravimetric measurements for carbon

steel specimens immersed in the test solution for 360 hours, as a function of inhibitor concentration, at 298K, are shown in Figure 2.

It can be seen from Figure 2 that the DMEA inhibits the corrosion of carbon steel in the test solution, and the inhibition efficiency increases with increasing inhibitor concentration. This can be attributed to the adsorption of DMEA molecules at carbon steel/NaCl solution interface. The maximum efficiency of 88% is obtained at 0.125 mol.L^{-1} of DMEA; and for concentrations higher than 0.125 mol.L^{-1}, no appreciable change in inhibition efficiency was observed. This may be imputed to competitive adsorption between the inhibitor molecules and metal surface, which was already covered with initial layers of molecules from the initial inhibitor concentration (0.125 mol.L^{-1}).
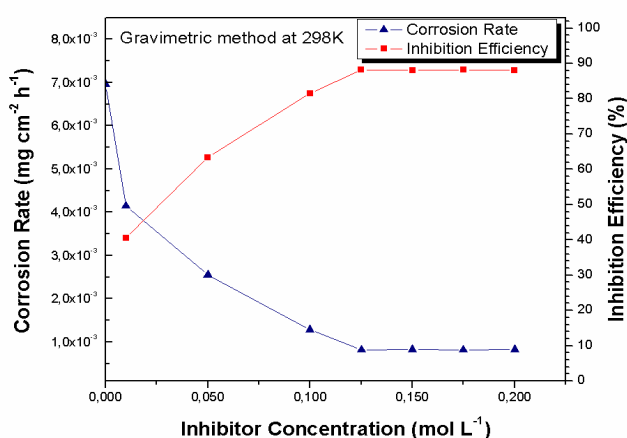

Fig. 2. Corrosion rate and inhibition efficiency of C-steel specimens in the test solution, with and without DMEA.

3.1.2 Effect of temperature

In order to investigate the inhibition mechanism and calculate the activation parameters of the corrosion process, gravimetric measurements were carried out at various temperatures, between 298 and 328 K. The corrosion rate (CR) and corresponding inhibition efficiency (IE%) obtained at studied temperatures are shown in Figures 3 and 4, respectively.

It is clear from Figure 3 that when the temperature increases, the corrosion rate (CR) of carbon steel increased, both in uninhibited and inhibited solutions. The increase in corrosion rate with temperature is more important in the absence or presence of low concentrations of DMEA. Furthermore, Figure 4 shows that the inhibition efficiency increases slightly as the temperature increases from 298 to 328 K. This can be explained by the fact that the increase in temperature leads to higher desorption of water molecules, thus leaving a larger surface area for the adsorption of inhibitor molecules [17].
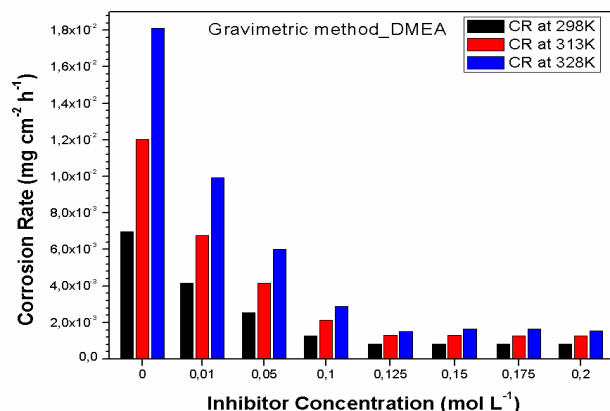

Fig. 3. Effect of temperature on the corrosion rate (CR) of C-steel in the test solution, with and without DMEA.
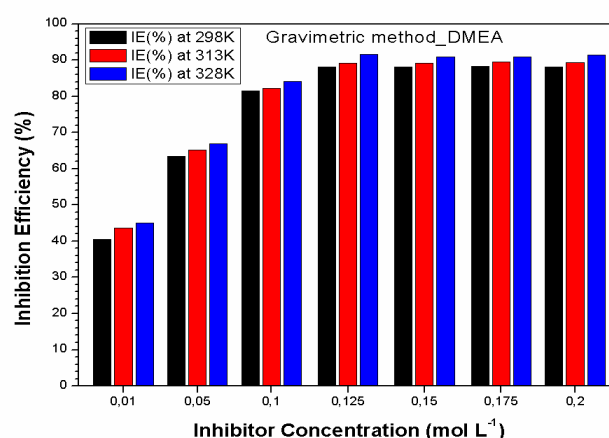

Fig. 4. Effect of temperature on the inhibition efficiency (EI%) of C-steel in the test solution, with and without DMEA.

The degree of surface coverage (θ) was calculated for different inhibitor concentrations by assuming a direct relationship between the surface coverage (θ) and inhibition efficiency (IE%), such as θ = IE/100. The C/θ versus C at the various temperatures were plotted (Figure 5). All plots give straight lines with almost unit slope. This behavior confirmed that the adsorption of DMEA molecules obeys Langmuir adsorption isotherm.
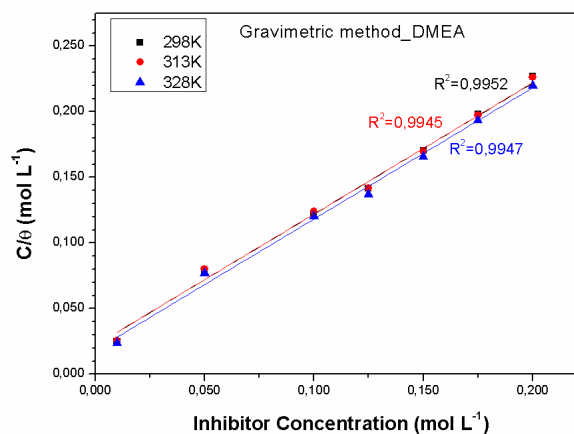

Fig. 5. Langmuir isotherm for C-steel in the test solution, with and without DMEA, at various temperatures.

The activation parameters of the corrosion process in the studied range of temperature were calculated by means of the Arrhenius equation and transition state equation, respectively [18, 19]:

$$Ln(CR) = \frac{-E_a}{RT} + Ln(A) \qquad (5)$$

$$CR = \frac{RT}{Nh} \exp\frac{\Delta S_a}{R} \exp\frac{-\Delta H_a}{RT} \qquad (6)$$

where E_a is the apparent activation energy, R the universal gas constant, T the temperature, A the Arrhenius pre-exponential factor, N Avogadro's number, h Plank's constant, ΔS_a the entropy of activation and ΔH_a the enthalpy of activation.

The results obtained of activation parameters in the studied range of temperature are shown in Table 2.

An examination of this table reveals that the addition of DMEA decreases the activation energy (E_a); this decline is more significant at concentrations equal or superior to 0.125 mol.L^{-1}. According to Bentiss et al., and Sankarapapavinasam et al. [20, 21], unchanged or lower values of activation energy (E_a) in the inhibited solutions with respect to that of the blank (without inhibitor), suggest charge sharing or transfer from the organic inhibitor molecules to the metal surface, thus forming coordinate covalent bond i.e. chemisorption. Moreover, the positive sign of enthalpy of activation (ΔH_a), as shown in Table 2, reflects the endothermic nature of the metal dissolution process, suggesting that the dissolution of carbon steel is slow in the presence of DMEA [22, 23]. The negative values of entropies of activation (ΔS_a) imply that the activated complex in the rate-determining step represents an association rather than a dissociation step, meaning that there is less disorder when moving from the reactants to the activated complex [24, 25].

Table 2. The values of activation parameters E_a, ΔH_a and ΔS_a for C-steel in the test solution, with and without DMEA.

Concentration (mol L^{-1})	E_a (KJ mol^{-1})	ΔH_a (KJ mol^{-1})	ΔS_a (J mol^{-1} K^{-1})
Blank	25.94	23.35	-207.74
0.010	23.67	21.08	-219.70
0.050	23.21	20.61	-225.27
0.100	22.06	19.46	-234.48
0.125	16.46	13.86	-257.04
0.150	18.73	16.14	-249.54
0.175	18.93	16.33	-249.00
0.200	16.97	14.38	-255.35

3.2 Electrochemical measurements

3.2.1 Potentiodynamic polarization

Potentiodynamic polarization curves for carbon steel in the test solution (0.5M NaCl), without and with addition of different concentrations of DMEA at 298K, are shown in Figure 6.
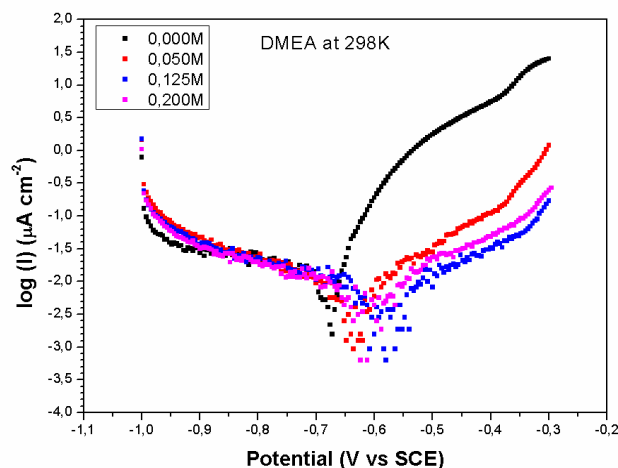

Fig. 6. Potentiodynamic polarization curves for C-steel in the test solution, with and without DMEA, at 298K

The electrochemical corrosion parameters are calculated from this graph; they listed in Table 3.

Table 3. Electrochemical parameters for C-steel in the test solution, with and without DMEA, at 298K.

C_{inhib} mol/L	E_{corr} (mV)	I_{corr} µA/cm^2	βa mV/dec	βc mV/dec	IE (%)
Blank	-693.8	18.52	121.3	581.9	/
0.050	-647.4	6.36	182.1	334.6	65.66
0.125	-591.7	3.59	236.5	456.1	80.61
0.200	-615.0	3.69	238.2	416.8	80.09

It can be seen from this Table 3 that , the value of current density (I_{corr}) for carbon steel in 0.5M NaCl blank solution equals 18,52 µA.cm^{-2}, and decreases with increasing DMEA concentration. This indicates that the investigated organic compounds acts as efficient inhibitor towards carbon steel dissolution in NaCl medium, and the degree of inhibition depends on their concentrations. When 0.125 mol L^{-1} of DMEA was added to the solution, the current density decreased to 3.59 µA cm^{-2} and results in the maximum inhibition efficiency of 80.61%. It can also be noticed from Figure 6 and Table 3 that with the addition of DMEA, both anodic and cathodic currents (βa and βc) change and the corrosion potential (E_{corr}) moves towards a more positive values. According to Ferreira et al. and Cai et al. [26, 27], if the displacement in (E_{corr}) is more than 85 mV in the positive direction with respect to the (E_{corr}) obtained in the solution without inhibitor, then the inhibitor could be considered as an anodic-type. In the present study, the maximum (E_{corr}) shift is more than 100 mV in the positive direction, indicating that DMEA acts mainly as an anodic-type corrosion inhibitor.

3.2.2 Electrochemical impedance spectroscopy(EIS)

EIS measurements were carried out, in order to get more information about the corrosion inhibition phenomenon

by DMEA. Nyquist plots obtained for frequencies ranging from 100 kHz to 50 mHz, at corrosion potentials for carbon steel without and with various concentration of DMEA, at 298K are shown in Figure 7,
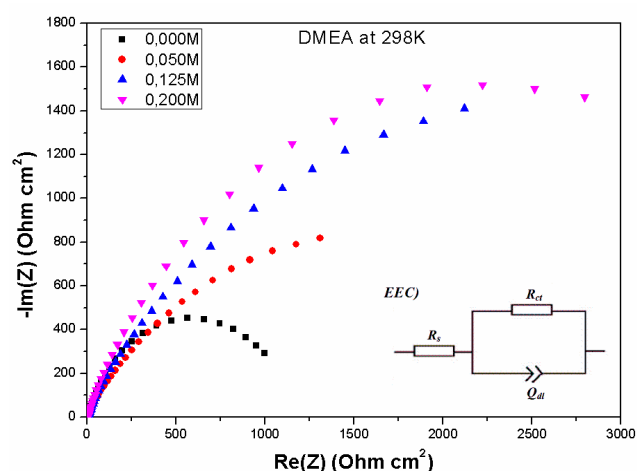

Fig. 7. Nyquist plots obtained for C-steel in the test solution containing different concentrations of DMEA, at 298K.

Nyquist representation of the impedance spectra, can be analyzed through fitting to the equivalent electric circuit (EEC) model, shown in Figure 7. In this model, (R_s) represents the resistance of the electrolyte and (R_{ct}) the charge transfer resistance. The (Q_{dl}) is associated with the double layer capacitance; their values may be obtained by using a constant phase element (CPE), which represents a non-ideal frequency dependent capacitance [28]. There is a variable value (a), associated with the CPE, which generally ranges between 1 and 0.5. It describes the distribution of the dielectric relaxation times in the frequency domain; when (a) is close to 1, the (CPE) represents a capacitor [29]. The corresponding impedance quantitative parameters, derived from Nyquist plots by using the equivalent electric circuit (EEC) shown in Figure 7, and the percentages of the inhibition efficiency (IE%) are given in Table 4.

Table 4. Electrochemical parameters for C-steel in the test solution, with and without DMEA, at 298K.

C_{inhib} (mol/L)	R_s ($\Omega.cm^2$)	Rct ($\Omega.cm^2$)	CPE_{dl}		IE (%)
			$Q_{dl}*10^{-4}$ F.cm^{-2}.s^{a-1}	a_2	
Blank	5.744	1069	8.29	0.62	/
0.050	4.576	2455	7.75	0.67	56.46
0.125	5.519	3944	4.87	0.70	72.90
0.200	5.035	4313	3.80	0.75	75.21

It can be seen from this table that, (R_s) value decreases slightly as the concentration of DMEA increased in the test solution. This may be attributed due to more involvement of ions in test solution containing inhibitor, resulting an increase in the solution conductivity [30]. On the other hand, (R_{ct}) value increases while (Q_{dl}) value decreases with increasing inhibitor concentration, and consequently leads to an increase in

the inhibition efficiency of DMEA. The increase in (R_{ct}) values may be ascribed to the gradual replacement of water molecules by the adsorbed inhibitor molecules which form an adherent film on the carbon steel surface [31]. Thus, the decrease in (Q_{dl}) values, which may have resulted from a decrease in the local dielectric constant and/or from an increase in the double layer thickness, suggests that the adsorption of the DMEA molecules took place at the metal/solution interface [32, 33]. The maximum inhibition efficiency (EI%) for DMEA measured by (EIS) is 75.21%, obtained at 0.2 mol L^{-1}.

4 CONCLUSION

The inhibition efficiencies obtained in the present study from weight loss, potentiodynamic polarization, and EIS methods are in good agreement. The following conclusions could be drawn:

The DMEA significantly reduces the corrosion rate of carbon steel in 0.5M NaCl solution. The inhibition efficiency increases with increasing DMEA concentration; it reaches highest value for a concentration around 0.125 mol.L^{-1},

The DMEA acts as an efficient organic corrosion inhibitor over the whole range of temperatures studied. The values of the activation parameters, i.e. ΔH_a and E_a obtained indicate that the adsorption process of DMEA is endothermic and could be mainly attributed to chemisorption, respectively.

The adsorption of DMEA molecules obeys Langmuir adsorption isotherm,

The potentiodynamic polarization results reveal that the studied inhibitor is predominantly anodic-type in 0.5M NaCl solution,

The EIS study reveals that the addition of DMEA decreases the corrosion rate of carbon steel in 0.5M NaCl solution, due to the adsorption of inhibitor molecules on the steel surface, thus leading to the formation of a protective film which is able to keep the metal/solution interface in a passive state.

REFERENCES

1. J. L. Yao, B. Ren, Z. F. Huang, P. G. Cao, R. A. Gu, Electrochim. Acta **48**, 1263 (2003).
2. C. A. Melendres, N. CamilloneIII, T. Tipton, Electrochim. Acta **34**, 281 (1989).
3. R. T. Loto, C. A. Loto, T. Fedotova, Int. J. Electrochem. Sci. **7**, 10763 (2012).
4. G. Bereket, A. Pinarbasi, Corros. Eng. Sci. Technol. **39**, 308 (2004).
5. Z. Grubac, R. Babic, M. H. Metikos, J. Appl. Electrochem. **32**, 431 (2002).
6. M. Lebrini, M. Lagrenée, H. Vezin, L. Gengenbre, F. Bentiss, Corros. Sci. **47**, 485 (2005).
7. A. S. Fouda, H. A. Mostafa, F. El-Taib, G. Y. Elewady, Corros. Sci **47**, 1988 (2005).
8. K. S. Jacob, G. Parameswaran, Corros. Sci. **52**, 224 (2010).
9. M. DuduKcu, B. Yazici, M. Erbil, Mater. Chem. Phys. **87**, 138 (2004).

10. E. M. Sherif, J. H. Potgieter, J. D. Comins, L. Cornish, P. A. Olubambi,C. N. Machio, Corros. Sci. **51**, 1364 (2009).

11. T. A. Söylev, C. McNally,M. Richardson, Cem. Concr. Res. **37**, 972 (2007).

12. A. K. Satpati,P. V. Ravindran, Mater. Chem. Phys. **109**, 352 (2008).

13. S. Abd El Rehim, H. Hassan,M. Amin, Mater. Chem. Phys. **78**, 337 (2003).

14. M. Abdallah, Corros. Sci. **46**, 1981 (2004).

15. R. Solmaz, G. Kardas, M. Culha, B. Yazici,M. Erbil, Electrochim. Acta **53**, 5941 (2008).

16. L. Sail, F. Ghomari, A. Khelidj,A. Bezzar, Eur. J. Environ. Civ. En. **18**, 699 (2014).

17. M. Yadav, S. Kumar,L. Gope, J. Adhes. Sci. Technol. **28**, 1072 (2014).

18. H. Zarrok, A. Zarrouk, B. Hammouti, R. Salghi, C. Jama,F. Bentiss, Corros. Sci. **64**, 243 (2012).

19. L. Messaadia, O. ID El mouden, A. Anejjar, M. Messali, i. R. Salgh, O. Benali, O. Cherkaoui,A. Lallam, J. Mater. Environ. Sci. **06**, 598 (2015).

20. F. Bentiss, M. Traisnel, N. Chaibi, B. Mernari, H. Vezin,M. Lagrenée, Corros. Sci. **44**, 2271 (2002).

21. S. Sankarapapavinasam, F. Pushpanaden,M. F. Ahmed, Corros. Sci. **32**, 193 (1991).

22. M. Lagrenée, B. Mernari, M. Bouanis, M. Traisnel,F. Bentiss, Corros. Sci. **44**, 573 (2002).

23. G. N. Mu, X. Li,F. Li, Mater. Chem. Phys. **86**, 59 (2004).

24. S. Sankarapapavinasam,M. F. Ahmed, J. Appl. Electrochem. **22**, 390 (1992).

25. V. Ramesh Saliyan,A. V. Adhikari, Bull. Mater. Sci. **31**, 699 (2008).

26. E. S. Ferreira, C. Giacomelli, F. C. Giacomelli,A. Spinelli, Mater. Chem. Phys. **83**, 129 (2004).

27. J. Cai, C. Chen,J. Liu, Corros. Eng. Sci. Techn. **49**, 66 (2014).

28. H. E. Jamil, A. Shriri, R. Boulif, M. F. Montemor,M. G. S. Ferreira, Cem. Concr. Compos. **27**, 671 (2005).

29. J. J. Shi,W. Sun, Int. J. Miner. Metall. Mater. **19**, 38 (2012).

30. H. S. Ryu, J. K. Singh, H. S. Lee, M. A. Ismail,W. J. park, Constr. Build. Mater. **133**, 387 (2017).

31. S. A. Umoren, J. Adhes. Sci. Technol. **30**, 1858 (2016).

32. E. McCafferty,N. Hackerman, J. Electrochem. Soc. **119**, 146 (1972).

33. S. Jyothi,J. Ravichandran, J. Adhes. Sci. Technol. **28**, 2347 (2014).