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Corrosion inhibition of 304 stainless steel in sodium chloride by ciprofloxacin and norfloxacin

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Heterocyclic organic compounds namely ciprofloxacin and norfloxacin were used as corrosion inhibitor for protection of 304 stainless steel in 1.5 percent NaCl solution. The inhibition effect of these compounds was investigated by using electrochemical techniques such as open circuit potential (OCP) and potentiodynamic polarization. The results obtained reveal that these compounds are very good corrosion inhibitors and show their best performance at a concentration of 1800 ppb. Potentiodynamic curves indicate that these compounds are anodic type of inhibitors.

Keywords: Corrosion inhibition, 304 Stainless steel, Ciprofloxacin, Norfloxacin, Potentiodynamic polarization

Norfloxacin and ciprofloxacin are well-known compounds of fluoroquinolone group used against bacterial growth worldwide. Generally coatings, paints and organic compounds are used for corrosion mitigation. The organic chemicals especially, heterocyclic compounds containing heteroatoms like S, N, O, Se with loosely bound lone pair of electrons and compounds with π electrons, undergo adsorption on the metal surface and protect the material from the aggressive environment. Various workers have used organic compounds for corrosion inhibition of stainless steel at different concentrations in acidic, basic and salt solutions[1-11]. Stainless steel, due to its high strength, workability and high corrosion resistance is used in various scientific and engineering applications like chemical and pharmaceutical industry[12,13], food and beverage industry[14], petrochemical industry[15-17], oil and water pipe lines[18], ship and naval structures[19,20]; architectural applications, water supply and desalination plants[13].

To protect the materials of construction of various industries, use of organic compounds as corrosion inhibitor has been recommended. The corrosion inhibition actions of the organic compounds containing heteroatoms such as undecanoic acid hydrazide, 2-mercaptobenzothiazole, and 2-hydrazinobenzothiazole on carbon steel in HCl solution[21], morpholinium caprylate, morpholinium sebacate and laurate[22,23]**,** morpholinium oleate[24] and morpholinium stearate[25] have been investigated for steel. Al-Mayouf *et al*.[26] investigated the corrosion inhibition efficiency of azoles: 2-mercaptobenzoazole (MBA), and its derivatives (2-mercaptobenzo-imidazole, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole); 2-methyl benzoazole and its derivatives (2-methyl benzoimidazole, 2-methyl benzoxazole, -methyl benzothiazole and 2-methyl benzoselenazole) against 304 stainless steel in acidic solution. Some of these compounds exhibited inhibition efficiency up to 90% at a concentration of $5x10^{-4}$ M and stated efficiency of the heteroatoms in the decreasing order as Se> S > N > O. The aim of the present investigation was to find out inhibition performance of ciprofloxacin and norfloxacin as suitable inhibitor for control of corrosion of 304 stainless steel in 1.5% sodium chloride solution.

Experimental Procedure

304 Stainless steel of commercial grade in sheet form having composition as follows: C - 0.06, Si - 0.53, Mn - 0.10, P - 0.032, S - 0.016, Ni - 8.16, Cr - 18.17%; and Iron- balance, were used in the present investigation. For electrochemical polarization, samples of 1 × 3 cm were sheared from the commercial grade sheets. The surface of these samples was successively polished by using the Emery papers of grades 1/0, 2/0, 3/0, and 4/0 obtained from Sianor, Switzerland to obtain a scratch free mirror finish surface. The polished samples were washed with detergent solution, rinsed with distilled water and

finally degreased with acetone. The specimens were dried and stored in a desiccators containing silica gel as a dehydrating agent.

Ciprofloxacin and norfloxacin were procured and their inhibition efficiency was determined with electrochemical techniques. Molecular structures of these compounds are shown in Fig. 1. Pure NaCl obtained from S.D.Fine Chemicals was used to prepare its 1.5% solution with double distilled water.

Electrochemical Measurement System, DC 105, containing software of DC corrosion techniques from M/S Gamry Instruments Inc., 734, Louis Drive, Warminster, PA-18974, USA has been used for performing corrosion potential and polarization experiments. For electrochemical polarization studies (corrosion potential, and potentiodynamic polarization) flag shaped specimens with sufficiently long tail were cut from the stainless steel sheet. These samples were polished as described above leaving a working area of 1 cm^2 on both sides of the flag and a small portion at the tip for providing electrical contact. Rest of the surface was isolated from the corroding solution by coating with enamel lacquer including side edges. The test specimen was connected to the working electrode holder with the help of a screw. About 50 mL of the corrosive medium was taken in a mini corrosion testing electrochemical cell. This volume was appropriate to permit desired immersion of electrodes. The electrochemical investigation was carried out using microprocessor based corrosion measurement system (CMS-105, Gamry Instruments Inc., USA.). The three-electrode system cell i.e. working electrode, reference electrode (Saturated Calomel Electrode), and counter electrode (graphite rod), was used throughout the electrochemical measurements. Open circuit potential measurements and potentiodynamic polarization experiments were carried out at the concentration of 300, 600, 900, 1200, 1500, 1800 and 2100 ppb of the inhibitors.

The value of inhibition efficiency in terms of corrosion current density was determined by using the following equation:

$$E = 100 \times (i_o - i) / i_o \quad \text{... (1)}$$

where i_o and i are the corrosion current density of the uninhibited and inhibited samples respectively.

Results and Discussion

Open circuit potential (OCP) measurement

Inherent reactivity of the metallic materials in a particular environment is determined from its open circuit potential (corrosion potential). The influence of

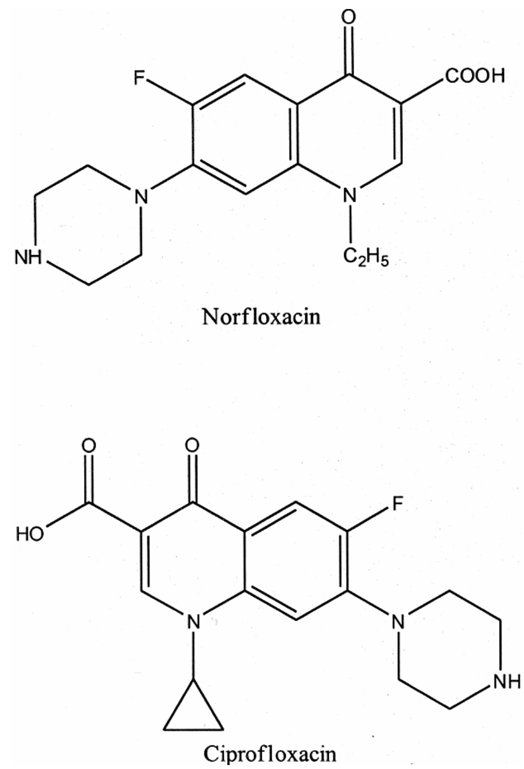

Fig. 1—Molecular structure of (a) Norfloxacin ($C_{16}H_{18}N_3O_3F$) and (b) Ciprofloxacin ($C_{17}H_{18}N_3O_3F$)

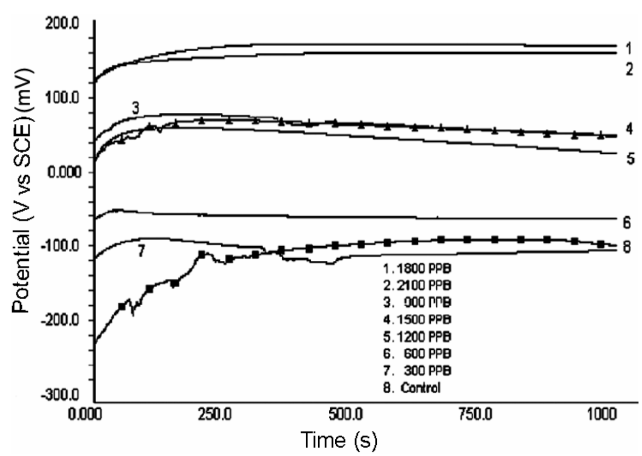

Fig. 2—Corrosion potential of 304 stainless steel exposed to 1.5% NaCl solution with different concentrations of norfloxacin.

the corrosive and inhibitive species present in the electrolyte may be predicted by analyzing the nature of the OCP curve. The variation of open circuit potential of 304 Stainless steel exposed to 1.5% NaCl solution containing inhibitors i.e., norfloxacin and ciprofloxacin are shown in Figs 2 and 3 respectively. The steady state potential is obtained after 120-300 s of the exposure period. In the presence of different concentration of

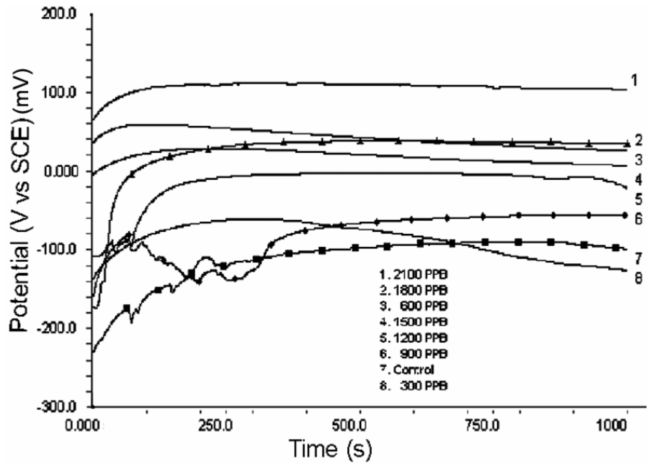

Fig. 3—Corrosion potential of 304 stainless steel exposed to 1.5% NaCl solution with different concentrations of ciprofloxacin.

inhibitors, OCP is shifted towards the positive potential direction and gets stabilized thus indicating the adsorption of the inhibitors on the metal surface. Maximum shift of the corrosion potential in the positive direction is obtained in the presence of 1800 ppb of norfloxacin as shown in Fig. 2, which indicates the optimum concentration of norfloxacin. Similarly for ciprofloxacin, maximum shift is obtained at 2100 ppb as shown in Fig. 3.

Potentiodynamic polarization

The anodic and cathodic polarization curves of 304 stainless steel exposed to 1.5% NaCl solution containing norfloxacin and ciprofloxacin in concentrations ranges from 300-2100 ppb are shown in the Figs 4 and 5 respectively, which was carried out at

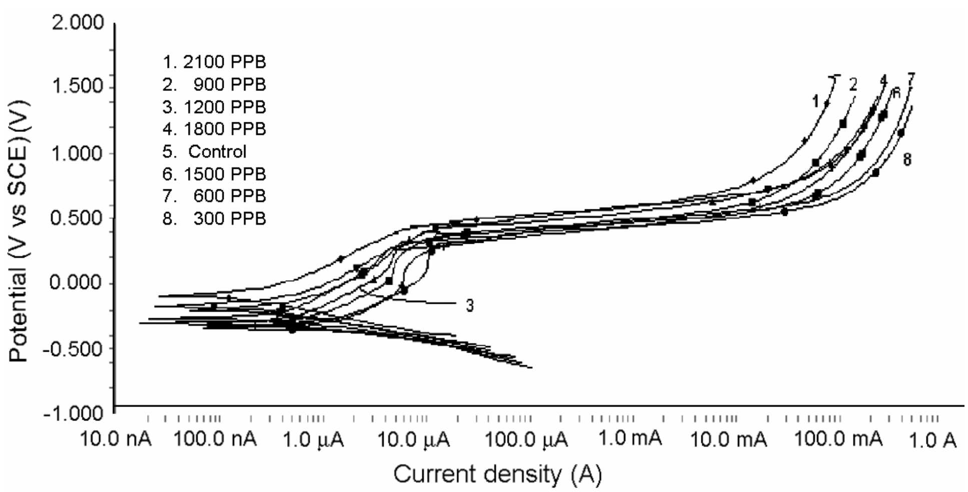

Fig. 4—Potentiodynamic polarization curve of 304 stainless steel exposed to 1.5% NaCl with different concentrations of norfloxacin.

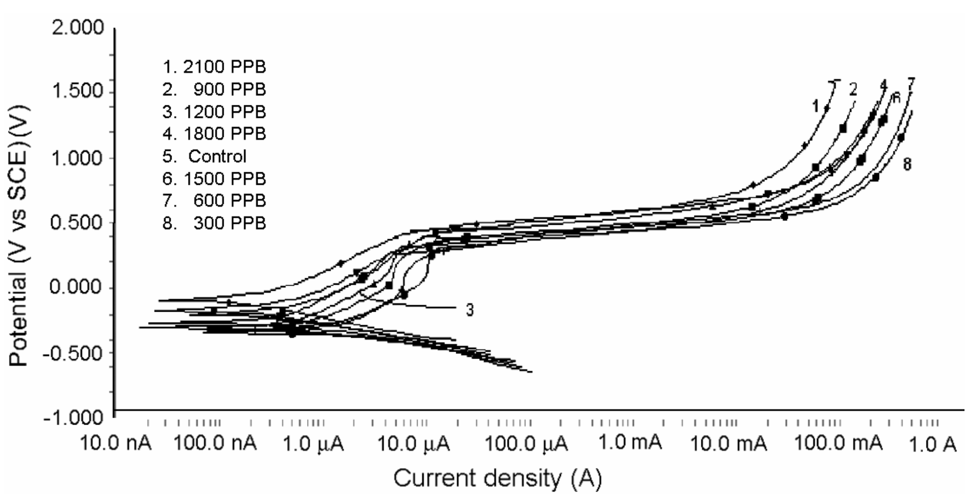

Fig. 5—Potentiodynamic polarization curves of 304 stainless steel exposed to 1.5% NaCl solution with different concentrations of ciprofloxacin.

a scan rate of 10 mV/s. The effect of different concentration of both compounds on various electrochemical parameters like corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel constant (β_a), cathodic Tafel constant (β_c), corrosion rate and % inhibition efficiency, etc. of 304 stainless steel is shown in Table 1. The maximum inhibition efficiency of norfloxacin and ciprofloxacin obtained were 94.97% and 93.99% respectively at 1800 ppb of the inhibitor. The action of an inhibitor in an aggressive chloride medium is probably due to adsorption of the inhibitor on the metal/solution interface which acts as a barrier. Corrosion inhibitors with heteroatoms having loosely bound lone pair of electrons and pie electrons undergo adsorption (chemisorptions / physisorption), or complexation on the metal / metal oxide surface thereby preventing the access of cathodic reactant (O_2, H^+ etc.), aggressive corrosive species like chloride ions and inhibits the dissolution of metal whose inhibition efficiency (E) depends on different parameters of the system (pH, temperature, exposure period, metal composition, etc.) as well as on it's structure[27-29].

$$Fe \longrightarrow Fe^{2+} + 2e \text{ (Anodic reaction)} \qquad \text{... (2)}$$

$$Fe^{2+} + O_2 + 2e^- + H_2O \longrightarrow [Fe(H_2O)_x]^{2+} / Fe(OH)_2 \text{ (Cathodic reaction)} \qquad \text{... (3)}$$

When the chloride ion approaches to the charged ionic iron / oxide surface following attracting forces[30] comes into play: coulombic forces, induction of the adsorbent by the approaching ion, electrostatic polarization of the ion and non-polar Van der Waal's forces. Corrosion pit initiation, propagation and dissolution of iron in NaCl solution accounts for adsorption of chloride ions on the oxide surface, penetration of the chloride through oxide film and localized dissolution of 304 stainless steel at the metal/oxide interface which is based on electrode kinetics model of McCafferty[31].

$$[Fe(H_2O)_x]^{2+} + (s+2)\,Cl^- \longrightarrow [Fe(H_2O)_{x-s}(Cl^-)_s]Cl_2 + sH_2O \qquad \text{... (4)}$$

Organic inhibitors are the compounds with at least one electron donor group that is usually regarded as reaction center for adsorption[32]. Norfloxacin and ciprofloxacin, both contain 3 oxygen atoms, 3 nitrogen atoms and one fluorine atom, homo- and heterocyclic rings with conjugated and isolated double bonds which may get effectively adsorbed on the surface of stainless steel and protects the surface from aggressive chloride ions. Here the organic compound having heteroatoms with lone pair of electrons acts as a Lewis base and the Fe with half-filled d-orbital acts as a Lewis acid. The affinity of the compounds towards adsorption on the Fe surface is more than that of the H_2O and aggressive chloride ions. This stability of inhibitor-Fe adsorption bond is based on the Pearson's Hard and Soft Acid and Base principle[33].

Table 1—Electrochemical parameters for inhibition of corrosion of 304 stainless steel exposed to 1.5% NaCl with different concentration of norfloxacin and ciprofloxacin.

Conc. (ppb)	βa (V/dec.)	βc (V/dec.)	I_{corr} (μA. cm^{-2})	E_{corr} (mV)	Corrosion rate (mpy)	% of inhibition efficiency
Control	738.6e-3	171.1e-3	1.930	-317.0	883.8e-3	—
Norfloxacin						
300	640.8e-3	155.3e-3	1.470	-329.0	669.5e-3	23.83
600	533.5e-3	151.0e-3	1.030	-288.0	472.8e-3	46.63
900	282.6e-3	174.1e-3	0.283	-121.0	129.5e-3	85.34
1200	278.0e-3	125.4e-3	0.248	-184.0	113.3e-3	87.15
1500	270.8e-3	164.4e-3	0.265	-120.0	121.0e-3	86.27
1800	252.7e-3	154.4e-3	0.097	-17.80	44.32e-3	94.97
2100	256.3e-3	162.5e-3	0.117	-17.50	53.37e-3	93.94
Ciprofloxacin						
300	750.2e-3	179.6e-3	2.260	-333.0	1.032	—
600	254.9e-3	118.8e-3	0.173	-192.0	78.95e-3	91.04
900	611.4e-3	138.0e-3	0.962	-305.0	439.6e-3	50.15
1200	574.3e-3	124.1e-3	0.658	-298.0	300.8e-	3 65.91
1500	470.7e-3	117.7e-3	0.419	-262.0	191.6e-3	78.29
1800	256.6e-3	124.2e-3	0.116	-162.0	53.06e-3	93.99
2100	271.2e-3	154.8e-3	0.133	-85.20	60.86e-3	93.12

$$n\ \text{Inhibitor}_{(\text{solution})} + [\text{Fe}(\text{H}_2\text{O})_x]^{2+} \xrightarrow[\text{Complexation}]{\text{Adsorption /}} [\text{Fe}(\text{Inhibitor})_y]^{2+} + x\text{H}_2\text{O solution} \quad \ldots (5)$$

(where $x > n > y$)

A single inhibitor displaces a large number of water molecules and chloride ions; and forms complex with the metal. The complex formed is stabilized on the surface assumed nonporous and insoluble in the medium whereas, the inhibitor is chemically inert and doesn't decompose during its use as inhibitor. The adsorbed layer effectively protects the steel surface from the aggressive nature of chloride ions.

Conclusions

(i) Norfloxacin and ciprofloxacin are good inhibitors for 304 stainless steel in 1% sodium chloride solution.

(ii) Norfloxacin is more efficient inhibitor than ciprofloxacin in sodium chloride medium.

(iii) Since anodic Tafel's constant decreases with increasing inhibitor concentration, both compounds act as anodic inhibitors.

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