Anodic Behaviour of Mild Steel in Carboxylic Acid Solutions Containing NO_2^-, Cl^- and NO_3^- Ions.

By

M. S. ABDEL AAL and M. H. WAHDAN

Department of Chemistry, Faculty of Science, Assiut University, Assiut-Egypt

THE anodic behaviour of mild steel in deaerated 0.05 M solutions of acetic, oxalic, tartaric, malic and citric acids was studied by the potentiostatic technique. The effect of NO_2^-, Cl^- and NO_3^- ions on such behaviour was investigated. Except for acetic acid solution containing Cl^- and NO_3^- ions, the corrosion potential of steel in all examined acids was shifted in the positive direction in the presence of the investigated anions at all examined concentrations. Anodic polarization of steel in the pure acids indicated that the passivating film in oxalic acid is Fe_2O_3. The corresponding film in tartaric acid is probably the duplex oxide Fe_3O_4/Fe_2O_3. For acetic, malic and citric acids the passivating film is probably a non-stoichiometric higher iron oxide. For acetic acid the presence of NO_2^- ion decreased both the primary passivation potential, critical and passive c.ds. For oxalic, tartaric, malic and citric acids NO_2^- ion (10^{-5} - 10^{-3}M) accelerated the anodic dissolution of steel in both active and passive regions and hindered its passivation. At 10^{-2}M NO_2^- ion, the active dissolution of steel in all examined acids was inhibited and passivation became more feasible. In the presence of 10^{-5} and 10^{-4}M Cl^- ion, the active dissolution of steel in acetic, oxalic and tartaric acids was inhibited. However, it was greatly enhanced in case of malic and citric acids. In most cases the passivating oxide film was attacked by Cl^- ions. In presence of 10^{-3}M Cl^- ion, steel did not passivate. The anodic behaviour of steel in the presence of NO_3^- ion (10^- - 10^{-3}M) was found to be approximately similar to that obtained in the presence of Cl^- ion.

Most of the studies on the effect of inorganic anions on the anodic behaviour of mild steel were carried out in solutions of the pure salts of such anions[1-7]. The effect of a number of anions on the electrode potential of mild steel (in aerated solutions) was studied by Brasher[1], The electrode potential varies with concentration according to

$$E = a - b \log C$$

where a and b are constants. Further Brasher suggested[2] that anions can contribute both to destruction of the oxide film on mild steel and to passivation process in which oxide film is stabilised. Gadiar and Balachandra[3] studied the effect of some inorganic inhibitors on the corrosion of mild steel in distilled water. Their results showed that K_2CrO_4, $K_2Cr_2O_7$, KNO_2, LiOH and $K_2Cr_2O_7 + Na_2SiO_3$ in concentration $\geq$ 200 ppm inhibit the corrosion of mild steel, while Na_2SiO_3, Na_3PO_4 and KNO_3 inhibited the corrosion only partially in concentrations $\leq$ 1000 ppm.

Evans[4] reported that a deaerated $NaNO_2$ solution is unable to protect mild steel at a concentration which is adequate for protection under aerated conditions. The anodic passivation of iron and steel in NaOH, $Na_2B_4O_7$ and Na_2HPO_4 solutions containing Cl^- ion was studied by Rajagopalan and Venu[5]. They concluded that the break-through potential is associated with the displacement of the inhibitive anion with the aggressive one. Mao and Hoare[6] studied the anodic dissolution of mild steel in solutions containing both Cl^- and NO_3^- ions. They found that Cl^- ions produce localised dissolution of the passive film formed in presence of NO_3^- ions. Engell[7] reported that for steel OH^-, NO_3^-, CH_3COO^-, SO_4^{2-} and ClO_4^- inhibited pitting by Cl^- ions and their effeciency decreasing in the order given.

The present study is on the effect of NO_2^-, and Cl^- and NO_3^- ions on the anodic behaviour of mild steel in solutions of acetic, oxalic, tartaric, malic and citric acids, some of the acids commonly present in canned foods and possibly, have an important bearing on the corrosion of the steel exposed at pores or scratches penetrating the tin coating[8], using Steady state potentiostatic technique,

EXPERIMENTAL

The mild steel (0.1 C, 0.6 Mn, 0.035 P and 0.035% S) was donated by Bohler (V E.W. Austria) in the annealed condition. Specimens were machined in cylindrical form 2 cm in length and 0.2 cm in diameter. They were inserted in Teflon so that only the flat surface was in contact with solution.

Electrolytes :

0.05 M solutions of acetic, oxalic, tartaric, malic and citric acids, were prepared from the Analar reagents and bidistllled water and were deaerated by O_2–free nitrogen for at least 6 hours before the electrode was introduced into the cell. The pH of the solutions was adjusted to a value of 4.5, by adding NaOH.

In order to determine quantitatively the effect of NO_2^-, Cl^- and NO_3^- ions on the anodic behaviour of steel in the carboxylic acid solutions, increments of a concentrated solution of both $NaNO_2$, KCl and KNO_3 were added to the cell.

Potential and polarization measurements :

Before potential measurements, the specimens were cleaned cathodically in 0.5 M Na_2SO_4 solution with vigorous H_2 evolution to remove any surface contamination and air formed oxide film, preceded by surface polishing using successive grades of emery paper. Before use, the electrode was degreased with absolute ethanol (A.R. grade) washed with double distilled water and inserted in the polarization cell described elsewhere[9]. Potentials were measured with MUIRHEAD D-972-A potentiometer, using a SCE half cell, and quoted with respect to SCE at 30°C.

Potentiostatic polarization was with a Wenking ST 72 potentiostat by manually changing the potentiometer step wise at 20 mV/2 min. At the desired potential, the steady state current was recorded 2 min. later.

RESULTS AND DISCUSSION

Open circuit corrosion potentials :

The steady state corrosion potentials, E_{corr} (attained after about 2 hours of immersion) of steel

TABLE 1

Corrosion potentials of mild steel in carboxylic acid solutions in the presence of NO_2^-, Cl^- and NO_3^- ions.

Anion Conc. (M/L)		Acetic acid E_{corr} mV (SCE)	Oxalic acid E_{corr} mV (SCE)	Tartaric acid E_{corr} mV (SCE)	Malic acid E_{corr} mV (SCE)	Citric acid E_{corr} mV (SCE)
	0	−634	−748	−680	−704	−694
	10^{-5}	−650	−715	−672	−686	−670
NO_2^-	10^{-4}	−624	−728	−662	−680	−672
	10^{-3}	−604	−730	−644	−644	−644
	10^{-2}	−576	−716	−636	−628	−636
	10^{-6}	−654	−676	−666	−670	−652
	10^{-5}	−650	−686	−670	−670	−648
Cl^-	10^{-4}	−650	−680	−670	−660	−664
	10^{-3}	−656	−684	−656	−666	−682
	10^{-5}	−642	−680	−670	−662	−644
NO_3^-	10^{-4}	−644	−728	−670	−652	−650
	10^{-3}	−646	−720	−664	−656	−718

tartaric, malic and citric acids in the absence and the presence of NO_2^-, Cl^- and NO_3^- ions in the concentration range 10^{-4}–10^{-3}M are given in Table 1. Values of E_{corr} in presence of 10^{-6}M Cl^- ion and 10^{-2}M NO_3^- ion are also tabulated. The data given in Table 1, indicate that the value of E_{corr} for steel in solutions of the pure acids (free inorganic anions) decreases in the order, acetic > tartaric > citric > malic > oxalic acid. Except for oxalic acid, the order of decrease of E_{corr} is parallel to the increase of stability of their complexes with iron ions[10]. The large negative shift in E_{corr} in oxalic acid solution (the stability of its complexes with iron ions lies between those of tartaric and citric acids) is probably attributed to the formation of a film of insoluble ferrous oxalate at the electrode surface[11].

In presence of NO_2^- ions (10^{-5}–10^{-2}M) the value of E_{corr} is shifted in the positive direction for all examined acids irrespective of the nature of the acid. The large positive shift in E_{corr} in presence of 10^{-2}M NO_2^- ion denotes passivation or inhibition of the corrosion of steel. Similar results were obtained by El Din and Khedr[12] for zinc in 10^{-2}M sodium nitrite solution.

The results obtained in the presence of Cl^- ions (10^{-6}—10^{-3}M) indicate that the value of E_{corr} in all examined acid (except acetic) is shifted in the positive direction, for one and the same acid such value does not change appreciably with Cl^- ion concentration. For acetic acid, the negative shift in E_{corr} suggests corrosion stimulation.

The effect of NO_3^- ions on the corrosion potential of steel in the examined carboxylic acids is approximately similar to that of Cl^- ions.

Anodic behaviour in acetic acids olutions :

The anodic polarization curves of steel in acetic acid solution in the absence and the presence of NO_2^-, Cl^- and NO_3^- ions are shown in Fig. 1. Anodic passivation parameters are included in Table 2.

The results obtained in the pure acid solution indicated that the primary passivation potential (E_{pp}) occurs at fairly high positive value namely +1200 mV. Passivation develops gradually and the passive region covers a relatively narrow range of potential (~ 200 mV). Similar behaviour was obtained by Nord and Bech-Nelsen[13] for iron in acetic-acetate buffer solutions.

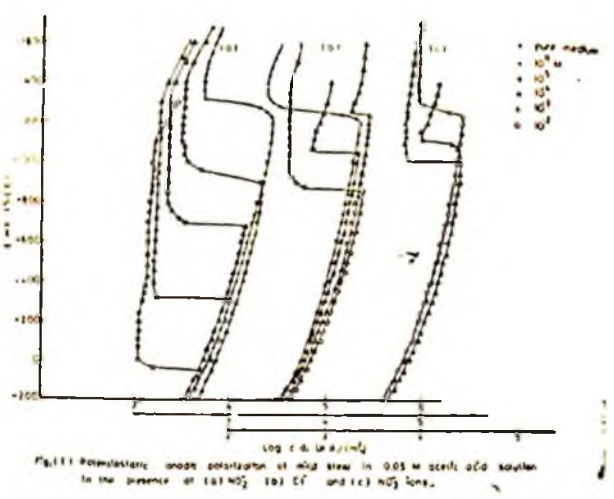


Fig. 1 : Potentiostatic anode polarization of mild steel in 0.05 M acetic acid solution in the presence of (a) NO_2^- (b) Cl^- and (c) NO_3^- ions.

The higher anodic currents in the active region suggest that the primary passivating layer (probably basic iron acetate[14]). The value of E_{pp} cannot be correlated to one of the oxide systems of iron and probably corresponds to a non-stoichiometric higher iron oxide[15,16].

The curves representing the anodic behaviour in presence of 10^{-5}–10^{-2} M NO_2^- ions (Fig. 1a) and the data included in Table 2, indicate that the presence of NO_2^- ions decreases both critical and passive c.d. (I_{cc} and I_p) and shifts the value of E_{pp} to less positive values. The potential range of the passive region increases in the direction of increasing NO_2^- ion concentration. It is suggested that NO_2^- ion inhibits anodic dissolution of steel in both active and passive regions and renders its anodic passivation more feasible. This is probably attributed to adsorption of NO_2^- ions at the electrode surface.

TABLE 2

Passivation parameters for mild steel in carboxylic acid solutions in the presence of NO_2^-, Cl^- and NO_3^- ions.

Anion Conc.		Acetic acid			Oxalic acid			Tartaric acid			Malic acid			Citric acid		
	(M/L)	E_{pp} (mV)	I_{cc} (mA/cm²)	I_p (mA/cm²)	E_{pp} (mV)	I_{cc} (mA/cm²)	I_p (mA/cm²)	E_{pp} (mV)	I_{cc} (mA/cm²)	I_p (mA/cm²)	E_{pp} (mV)	I_{cc} (mA/cm²)	I_p (mA/cm²)	E_{pp} (mV)	I_{cc} (mA/cm²)	I_p (mA/cm²)
	0	+1220	24.8	4.78	−560	3.36	0.16	−40	17.6	0.22	+120	26.4	0.32	+320	32.0	0.4
	10^{-5}	+880	19.8	3.04	−540	3.12	0.70	+240	21.8	1.20	+1140	55.2	3.36	+740	48.8	0.9
NO_2^-	10^{-4}	+680	13.4	1.09	−520	3.20	1.84	+180	23.2	0.70	+1000	43.2	2.00	+800	46.4	1.2
	10^{-3}	+300	9.6	1.56	−460	4.72	2.75	+180	24.0	0.65	+ 640	35.2	1.10	+780	33.6	1.2
	10^{-2}	−60	5.44	1.20	−520	2.32	1.20	−160	8.8	1.16	+ 140	18.8	2.88	+140	21.6	2.2
	10^{-6}	+1220	20.0	2.12	−520	3.20	0.21	+60	19.6	0.70	+1360	55.2	5.60	+920	53.6	2.4
	10^{-5}	+860	21.6	3.68	−560	2.00	0.13	+20	16.0	0.32	+1560	55.2	7.90	+840	42.4	2.7
Cl^-	10^{-4}	+1060	19.2	6.40	−560	2.40	0.12	+60	14.4	0.40	—	—	—	+780	35.2	5.0
	10^{-3}	—	—	—	−560	2.64	0.09	—	—	—	—	—	—	—	—	—
	10^{-5}	+1240	22.2	7.60	−540	3.28	0.52	+140	21.2	0.70	+1240	55.2	4.80	+960	45.6	1.6
NO_3^-	10^{-4}	+1000	22.0	5.75	−540	2.40	0.44	+240	20.8	0.92	+1300	56.0	6.24	+820	45.6	5.2
	10^{-3}	+1040	20.6	8.40	−540	2.96	0.63	+440	25.1	1.65	—	—	—	—	—	—

From the data given in Table 2, and the curves in Fig. 1b it can be observed that Cl^- ion at concentrations of 10^{-6} and 10^{-5}M decreases both I_{cc} and I_p, indicating their inhibitive action on the anodic dissolution of steel in both active and passive regions. This can be attributed to the adsorption of Cl^- ions at the electrode surface. At 10^{-5}M Cl^- ion the value of E_{pp} is appreciably decreased and the potential range of the passive region becomes more wide. El Din et al.,[17] and Abdel Aal and Osman[18] found that Cl^- ion inhibits the anodic dissolution of tin in alkaline medium upto a concentration of 10^{-4}M. Although Cl^- ion at a concentration of 10^{-4}M have inhibitive effects on the active dissolution of steel in acetic acid, the value of I_p is appreciably increased. This is also associated with a pronounced contraction of the passive region. It can be concluded that at such Cl^- ion concentration the passivating oxide layer is attacked by Cl^- ions. At 10^{-3}M Cl^- ion steel did not passivate. Tobias and Nobe[19] found that maraging steel did not passivate in H_2SO_4 solution (pH 1) containing NaCl concentration of 0.03% and above.

The results obtained in presence of NO_3^- ions ($10^{-5}-10^{-3}$M), indicate that although the anodic behaviour is similar to that obtained in the presence of Cl^- ions, the value of I_p is appreciably increased at all examined concentrations. This suggests that NO_3^- ions are efficient agents for the dissolution of the passivating oxide film.

Anodic behaviour in oxalic acid solutions :

The anodic polarization curves of steel in 0 05M solution of oxalic acid in the absence and the presence of NO_2^-, Cl^- and NO_3^- ions are shown in Fig. 2. Anodic passivation parameters are included in Table 2.

The anodic polarization curve in the pure acid solution shows that the active-passive transition occurs at a well defined potential and the value of E_{pp} amounts to -560 mV. This value agrees closely with the equilibrium potential of the system Fe/Fe_3O_4 at the same solution pH (E_{Fe/Fe_3O_4} = −589 mV vs SCE at pH 4.5). An adherent black layer was observed at the electrode surface. Evans[4] reported that inhibition of iron in aerated solutions of dibasic organic acids leads to a thick protective film of magnetite.

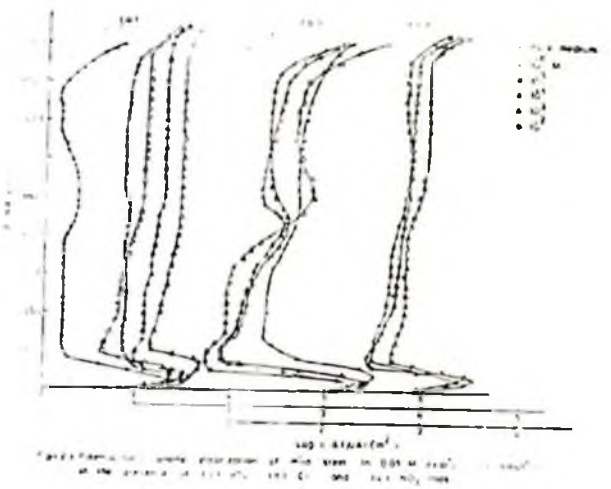


Fig. 2 : Potentiostatic anodic polarization of mild steel in 0.05 M oxalic acid solution in the presence of (a) NO_2^- (b) Cl^- and (c) NO_3^- ions.

The value of I_{cc} in oxalic acid is much lower than that obtained for steel in pure acetic acid. This suggests that the primary passivating layer formed at the electrode surface in oxalic acid (which is substantially consisting of insoluble ferrous oxalate[11]) is more protective and much less porous than the corresponding layer formed on steel in acetic acid solution.

The curves representing the anodic behaviour of steel in presence of NO_2^- ions (10^{-5}-10^{-3}M) and the data included in table 2, indicate that for solutions containing 10^{-5} and 10^{-4}M NO_2^- ion the value of I_{cc} is not appreciably affected while that of I_p is markedly increased. The value of E_{pp} is shifted by 20 and 40 mV in the positive direction, respectively. As the concentration of NO_2^- ion is increased to a value of 10^{-3}M, the value of I_{cc} is increased by about 30% of the original value and I_p is increased by about 50% of the value obtained in presence of 10^{-4}M NO_3^- ion. The primary passivation potential is shifted 100 mV in the positive direction.

It can be concluded that at the high dilutions of NO_2^- ion (10^{-5} and 10^{-4}M) the active dissolution of steel is not appreciably affected. At 10^{-3}M NO_2^- ion, the active dissolution of steel is greatly

enhanced and its anodic passivation is hindered. Although NO_2^- ion at a concentration of 10^{-2}M, inhibits the active dissolution of steel in oxalic acid the value of I_p is still much higher than that obtained in tho pure acid solution.

It may be assumed that the displacement of inhibiting oxalate ions adsorbed at the passivating oxide film and/or the oxidation of NO_2^- ions at the preanode layer increase appreciably the anodic current in the passive region. Rajagopalan and Venu[15] attributed the lower passive current of iron and steel in borax solution to the better adsorption of borate ion at the oxide film.

The results obtained for the anodic behaviour of steel in oxalic acid solution containing Cl^- ions (Fig. 2b and table 2) indicate that Cl^- ion within the concentration range $10^{-5}-10^{-3}$M, has inhibitive effects on the anodic dissolution of steel in both active and passive regions. However, the potential range of the passive region is appreciably decreased. For solutions containing 10^{-5} and 10^{-4}M Cl^- ion as the potential was made more positive than -50 mV, the value of I_p increases, attaining a maximum at a potential of about $+250$ mV, then it decreases again assuming a second steady state value which is not far removed from that of the initial passive region. This suggests that attack of the oxide film by Cl^- ions (with the consequent increase in I_p) is followed by film repair via precipitation of the insoluble ferrous oxalate at pores. At 10^{-3}M Cl^- ion, although the value of I_p is the lowest one, passivity breakdown occurs at a potential of about $+100$ mV.

Although Cl^- ion at a concentration of 10^{-6}M does not affect appreciably the active dissolution of steel, it has a dissolution action on the passivating oxide film. It has been reported[6] that Cl^- ions are efficient agents for the dissolution of anodic films on iron and iron-based materials.

From the curve shown in Fig. 2c, and the data given in Table 2, it is seen that although NO_3^- ion at concentrations of 10^{-4} and 10^{-3}M increases slightly the value of E_{pp}, it decreases appreciably the value of I_{cc}. This indicates inhibition of the active dissolution of steel. At 10^{-5}M NO_3^- ion the value of I_{cc} is not markedly influenced.

The increase in I_p at all examined concentrations of NO_3^- ion can be ascribed to the displacement of the inhibiting oxalate ions and/or the dissolution action of NO_3^- ions on the passivating oxide film.

Anodic behaviour in tartaric acid solutions :

Figure 3 shows the anodic polarization curves of steel in 0.05 M solution of tartaric acid in the absence and the presence of NO_2^-, Cl^- and NO_3^- ions. Anodic passivation parameters are included in Table 2.

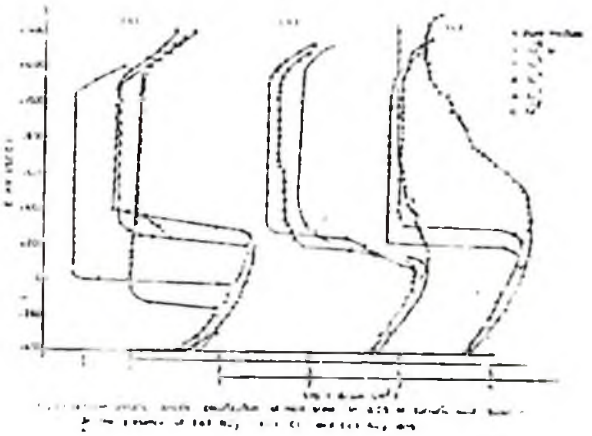


Fig. 3 : Potentiostatic anodic polarization of mild steel in 0.05 M tartaric acid solution in the presence of (a) NO_2^- (b) Cl^- and (c) NO_3^- ions.

For the pure solution of tartaric acid, the active passive transition exhibited by the anodic polarization curve occurs at relatively higher positive potential ($E_{pp} = -40$ mV vs SCE) than that obtained in oxalic acid solution. The value of E_{pp} is about 240 mV more positive than the equilibrium potential of the system Fe_3O_4/Fe_2O_3 at the same solution pH ($E_{Fe_3O_4/Fe_2O_3} = -285$ mV vs SCE at pH 4.5), It is suggested that the passivating film is probably the duplex oxide Fe_3O_4/Fe_2O_3 formed at certain overpotential. Ashworth and Boden[20] reported a value of 210 mV as an overpotential of Fe_3O_4 formation.

The curves shown in Fig. 3a show that NO_2^- ion within the concentration range 10^{-5}-10^{-3}M accelerates the anodic dissolution of steel in both active and passive regions and hinders its anodic passivation (both I_{cc} and E_{pp} are increased). At 10^{-2}M NO_2^- ion the value of E_{pp} is shifted 120mV in the negative direction and and I_{cc} is decreased to 1/2 of the original value. This indicates inhibition of the active dissolution of steel and facilitation of its anodic passivation.

Similar to the behaviour of steel in oxalic acid, the value of I_p in tartaric acid is markedly increased at all NO_2^- ion concentrations.

From the results obtained in the presence of Cl^-ions (Fig.3b and Table 2) it is seen that at 10^{-6}M Cl^- ion, the value of E_{pp} is shifted 100mV in the positive direction and both I_{cc} and I_p are increased. This indicates stimulation of the anodic dissolution of steel in both active and passive regions. For solutions containing 10^{-5} and 10^{-4}M Cl^- ion, although the value of E_{pp} is shifted in the positive direction, the value of I_{cc} is appreciably decreased denoting inhibition of the active dissolution of steel. The slight increase in the value of I_p may be ascribed to the displacement of tartarate ions adsorbed at the oxide surface.

In the presence of 10^{-3}M Cl^- ion, steel did not passivate and current oscillations occur within the potential range +340 to +460 mV, indicating pitting attack by Cl^- ions.

Inspection of the results obtained in the presence of 10^{-5}-10^{-3} M NO_3^- ion (Fig. 3c and Table 2) indicates that the anodic dissolution of steel in tartaric acid is acceerated in both active and passive regions and its anodic passivation is hindered (the value of E_{pp} is shifted to much higher positive values). The increase in I_p at all NO_3^- ion concentrations is similar to that obtained in oxalic acid, although it is greater in tartaric acid.

Anodic behaviour in malic acid solutions :

The anodic polarization curves of steel in 0.05 M solution of malic acid in the absence and presence of NO_2^-, Cl^- and NO_3^- ions are shown in Fig. 4. Anodic passivation parameters are included in Table 2.

It seen from Fig. 4a, that the active-passive transition exhibited by the anodic polarization curve in the pure acid solution occurs at a relatively higher positive potential than those obtained in both oxalic and tartaric acids. The value of E_{pp} which amounts to +120 mV (vs SCE) can not be correlated to one of the oxide systems of iron and probably corresponds to a non-stoichiometric higher iron oxide. The value of I_p relative to those of oxalic and tartaric acids indicates that the degree of passivation of steel in the latter two acids is much better than that in the former one.

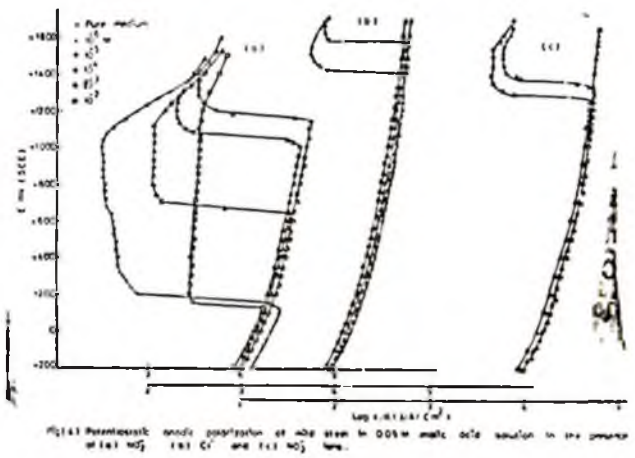


Fig. 4 : Potentiostatic anodic polarization of mild steel in 0.05 M malic acid solution in the presence of (a) NO_2^- (b) Cl^- and (c) NO_3^- ions.

The curves representing the anodic behaviour in malic acid solutions containing NO_2^- ions (Fig. 4a) and the data included in table 2, indicate that NO_2^- ion within the concentration range 10^{-5}–10^{-3}M promotes the anodic dissolution of steel in both active and passive regions. The most pronounced effect is obtained with 10^{-5}M NO_2^- ion. At such concentration the value of E_{pp} is shifted by about 1000 mV in the positive direction, I_{cc} is increased to a value more than twice the original value and I_p becomes an order of magnitude greater than that of the pure acid solution.

The anodic behaviour of steel in malic acid solution containing 10^{-2}M NO_2^- ion is similar to that obtained in oxalic acid at the same NO_2^- ion concentration. The pronounced increase in I_p in presence of NO_2^- ion at all examined concentrations is similar to those obtained in the other two dicarboxylic acids.

For solutions containing 10^{-6} and 10^{-5} M Cl^- ion the anodic polarization curves exhibit active-passive transition at fairly high positive potentials. At both Cl^- ion concentrations, the value of I_{cc} is more than twice the original value and the potential range of the passive region is very much contracted. Higher values of I_p in such solutions suggests attack by Cl^- ions.

In presence of 10^{-4} and 10^{-3}M Cl^- ion anodic passivation of steel in malic acid can not be achieved.

From the curves shown in Fig. 4c, and the data included in Table 2, it is seen that the anodic behaviour of steel in malic acid containing 10^{-5} and 10^{-4}M NO_3^- ion is similar to that obtained in presence of 10^{-6} and 10^{-5} M Cl^- ion, although values of E_{PP} and I_p are slightly lower. In malic acid solution containing 10^{-3} M NO_3^- ion, steel did not passivate.

Anodic behaviour in citric acid solutions :

The anodic polarization curve of steel in the pure citric acid solution (Fig. 5a) shows that the active-passive transition occurs at much higher more positive) potential than those obtained in (the studied dicarboxylic acids. The primary passivation potential has a value of +320 mV and the value of I_{cc} amounts to 32 mA/cm^2. As previously suggested (in case of acetic and malic acids) the high positive value of E_{PP} for steel in citric acid solution probably corresponds to a non stoichiometric higher iron oxide.

The anodic behaviour of steel in citric acid solution containing NO_2^- ions was found to be quite similar to those obtained in the studied dicarboxylic acids.

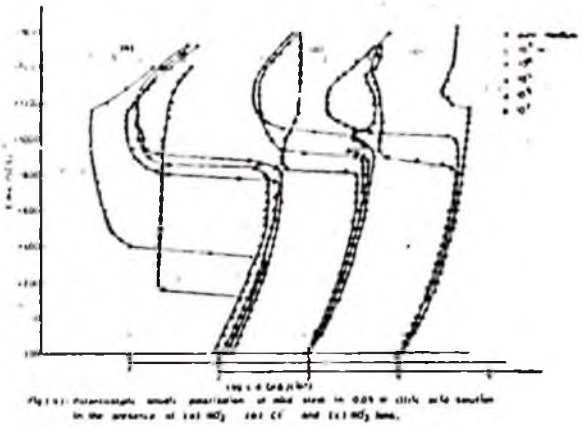


Fig. 5 : Potentiostatic anodic polarization of mild steel in 0.05 M citric acid solution in the presence of (a) NO_2^- (b) Cl^- and (c) NO_3^- ions.

The curves representing the anodic behaviour of steel in presence of Cl^- ions (Fig. 5b) and the data included in Table 2, indicate that within the concentration range 10^{-6}-10^{-4}M, values of E_{PP}, I_{cc} and I_p are markedly increased. This is also associated with an appreciable contraction in the potential range of the passive region. It is thus concluded that Cl^- ion within this concentration range promotes the anodic dissolution of steel in both active and passive regions. The sharp increase in I_p in presence of 10^{-6}-10^{-4}M Cl^- ion is similar to that obtained in malic acid in presence of 10^{-6} and 10^{-5}M concentrations. At 10^{-3}M Cl^- ion steel did not passivate and undergoes pitting attack.

The anodic polarization curves in presence of $10^{-5}-10^{-3}$ M NO_3^- ion (Fig. 5c) show that the anodic beheviour of steel in solutions containing NO_3^- ions is similar to that obtained in chloride containing solutions within the same concentration range (excluding current oscillations at 10^{-3} M Cl^- ions).

REFERENCES

1. D. M. Brasher, *Nature. Lond.* 193, (1962) 868.
2. D. M. Brasher, *Brit. Corr. J.* 4(3), (1969) 122.
3. H. S. Gadiar and J. Balachandra, *Trans. Ind. Inst. Metals* 19, (1966) 189.
4. U. R. Evans *"The corrosion and oxidation of metals" First suppl. Volume p. 68. Edward Arnold Ltd. Lond.* (1868).
5. K. S. Rajagopalan and K. Venu, *Brit. Corr. J.* 6. (1971) 216
6. K. Mao and J. P. Hoare, *Corros. Sci.* 13. (1973) 799.
7. H. J. Engell, *Electrochim. Acta,* 22, (1977) 987.
8. S. C. Britton *"Tin Versus Corrosion" p. 35, I.T R.I. Pub.* No. 510 (Sept. 1975).
9. M. S. Abdel Aal, I. M. Issa and A. Zedan *J. Appl Electrochem.* 6(6), (1976) 79.
10. I. M. Kolthoff and P. J. Elving, *"Treatise on Anal. Chem." Intersci. Pub. New York.* 1962, Part II Vol. 2 p. 258.
11. J. C. Wood, *Corrosion,* 34(2) (1978) 70.
12. A. M. Shams El Din and M. G Khedr, *Corros. Sci.* 12, (1972) 393.
13. H. Nord and G. Bech-Nielsen, *Electrochim. Acta,* 16, (1971) 849.
14. D. M. Sowarous and N. Hackerman, *J. Electrochem. Soc.,* 102(2), (1950) 297.
15. K G. Weil and K. F. Bonhoeffer, *Z. Physik. Chem. N.F.* 4175 (1955).
16. M. J. Pryor, *J. Electrochem Soc.* 106, (1959) 557.
17. A. M. Shams El Din, *I.S.E., 27th Meeting, Sept.* 6–11, 1976 *Zurich, Switzerland,* No. 164.
18. M. S. Abdel Aal and A. H. Osman, *Corrosion,* 36 (11), (1980) 173.
19. R. F. Tobias and K. Nobe, *Corrosion,* 25(4), (1969) 173.
20. V. Ashworth and P. I. Boden, *Corros. Sci.* 14. (1974) 209.