Physical Sciences Section

EFFECT OF CHROMATE, NITRITE AND BENZOATE IONS ADDITIVES ON THE CORROSION BEHAVIOUR OF LOW CARBON STEEL IN ACID MEDIUM

GAMAL K. GOMMA

Faculty of Education, Chemistry Department, Kafr El-Sheikh, Egypt

The effect of CrO_4, NO_2 and C_6H_5COO ions on the inhibitive behaviour of low carbon steel electrodes in aqueous solutions of mono-, di- and tri-chloroacetic acids at pH 1 to 4 is calculated by studying potential-time variation, weight loss measurements and galvanostatic polarisation. It has been found that the steady state potentials which obey the relationship $E = a - b \log C$, where (a) is a proportional constant and (b) is the order of the reaction which can be obtained from the linear plot of $\log C$ versus $\log$ corrosion rate which depend on the type of the acids and C is the molar concentration of the acids, is shifted towards less negative values with the increase in the concentration of additive ions and from pH 1 to 2 and then increases again at pH = 3 to 4. The decrease in the rate of corrosion with increase of anion concentration is probably due to the fact that additive ions act as anodic inhibitors. The critical current density for passivation varies with the nature and concentration of the additive anion.

Key words: Steel, Chromate, Nitrate, Benzoate, Inhibition.

Introduction

In aerated solutions of oxidizing anions such as chromate and nitrite, the protective film is mainly formed by the dissolved oxygen [1,2]. The effect of benzoates as corrosion inhibitors for iron in presence of air, was taken to demonstrate that the reduction of the inhibitor is not a prerequisite for passivation and that inhibition is mainly due to the reduction of oxygen in presence of those inhibitors [3]. The function of an anodic inhibitor is to prevent or retard the reaction at anodic areas [4]. In the present work, the effect of chromate, nitrite and benzoate on the corrosion inhibition of corrosion of low carbon steel is studied in aqueous solutions of mono-, di-and tri-chloroacetic acids. Steady state potential as a function of both time and concentration of the acid containing different anions has been studied. The corrosion rate of low carbon steel has also been evaluated using the weight-loss measurement.

Experimental

Solutions of mono-, di- and tri-chloroacetic acids (0.1 mol. dm^{-3}) containing different concentrations of the potassium salt of chromate and sodium salts of nitrite and benzoate (AR Quality) were prepared in doubly distilled water. The concentration range selected for the inhibitive anions for this investigation was 10^{-5}–10^{-2} mol. dm^{-3}. Solutions were always prepared fresh. The pH of the final solutions was adjusted by adding small amount of NaOH or perchloric acid. All reagents were of analytical grade.

Low carbon steel electrodes (1 cm length and 1 cm dia.) were welded to a hard copper wire fixed in a glass tube by means of neutral wax. The immersed area of electrode was effectively kept outside the tube. Before being used, electrodes were abraded successively with 1 and 00 grade emery papers and then degreased with acetone. The Pyrex glass electrode-vessel, without rubber connections, could accommodate 60 ml of the test solution. The variation of potential of the steel electrode under open circuit conditions in the tested solutions was followed as a function of time till steady state values were established. These measurements were followed against (SCE) by means of a manual potentiometer. The corrosion rate is determined by weight-loss techniques. Experiments were carried out at 30°. Samples (0.5 x 2 x 5 cm) were abraded with different grades of emery paper, degreased by acetone, weighed and then each sample was immersed in 100 ml Pyrex-glass beaker containing 60 ml of the test solution. The type of attack and its extent was observed and recorded at different times as well as at the end of the test period. Samples were then cleaned by brushing under running water and immersed in pickling solution (10% H_2SO_4 + 1% thiourea) to remove corrosion products. Samples rested at the angle of about 60° to the horizontal with the top edge at least 2 cm below the surface of the solution. The sample thus touched the glass at the four corners only. At least duplicate samples were used for each case. The solution lost by evaporation during the period of the test was compensated by adding distilled water.

Anodic polarisation of low carbon steel was measured galvanostatically according to Uhlig and Woodside [5]. The electrode was cathodically polarized at 1500 mV for about 15 mins. The current was discontinued to allow the potential to decay to a constant value. Anodic polarisation was conducted at different current densities and at each density the corresponding potential was recorded followed by discontinuing

the current and waiting for the attainment of the open circuit potential. The process was repeated until the potential of oxygen evolution was reached.

The cell used for polarisation measurements was composed of two compartments separated by a fritted glass disc to prevent mixing of anolyte and catholyte. Potentials were measured with reference to a saturated calomel electrode (SCE) with a fine Luggin capillary positioned close to the electrode surface in order to minimise ohmic potential drop.

Results and Discussion

Potential-time measurements. Potential-time curves for low carbon steel electrodes in 0.1 M tri-, di-, and mono-chloroacetic acid solutions containing CrO_4, NO_2, and C_6H_5COO at concentration of 10^{-5} to 10^{-2} mol. dm^{-3} obtained under open circuit conditions, showed that the steady state potential values are shifted towards a less negative direction with increasing additive concentration and with increasing pH Values from 1 to 3 and then increase at pH=4.

The positive shift in the values of steady-state potential in presence of CrO_4^-, NO_2 and C_6H_5COO is higher than that obtained for chloroacetic acid solutions free from inhibiting ions. (Table 1).

Relation between steady-state potential and acid concentration. Results given in Fig. 1 show the relationship between the molar concentration (C) of additive ions added to 0.1 mol. dm^{-3} solutions of the three acids and the values of steady-state potential of low carbon steel electrodes. In all cases, the negative potential decreases with increase in the concentration of additive ions. The straight line relationship is found to obey a relation, which follows the equation (1).

$$E = a - b \log C \quad \text{...} \quad (1)$$

where "a" is a proportional constant and "b" is the order of the reaction which can be obtained from the linear plot of log C versus log corrosion rate which depend on the nature of the electrolyte and surface preparation [6,7] and C is the molar concentration of the acids.

The slopes obtained from the linear plots (b values) given in Table 2. Similar relationships are found for tin in acid solutions [8]. The decrease in the (b) values seems to be related to the decrease in aggressiveness of the anion. It is worth mentioning that these anodic inhibitors are being widely used in industrial practice. They represent different types of anodic inhibitors. Thus sodium benzoate is a non-oxidizing salt of a

TABLE 1. STEADY-STATE POTENTIAL VALUES (SCE) FOR LOW CARBON STEEL IN PRESENCE OF CrO_4^-, NO_2^- AND $C_6H_5COO^-$ IONS IN 0.1 Mol.dm^{-3} CHLOROACETIC ACID SOLUTIONS.

Anion	ClCH₂COOH				Cl₂CHCOOH				Cl₃COOH			
mol.dm⁻³/pH	Steady-state potential (-mv) vs SCE											
	1	2	3	4	1	2	3	4	1	2	3	4
Nil	555	300	350	590	820	335	375	609	964	585	470	740
IN PRESENCE OF CrO_4^-												
1x10⁻⁵	364	280	340	568	549	300	350	575	810	450	460	655
1x10⁻⁴	254	220	235	521	545	278	335	565	775	370	425	594
1x10⁻³	237	200	230	500	525	263	320	530	675	320	400	502
1x10⁻²	199	180	300	453	509	255	311	500	620	275	350	418
IN PRESENCE OF NO_2^-												
1x10⁻⁵	414	272	280	349	450	260	325	400	471	255	400	500
1x10⁻⁴	390	150	179	249	420	200	265	340	455	243	360	489
1x10⁻³	189	100	150	211	330	170	225	300	430	220	340	475
1x10⁻²	171	28	59	100	290	150	200	250	405	200	325	450
IN PRESENCE OF $C_6H_5COO^-$												
1x10⁻⁵	361	227	300	342	263	200	225	232	499	263	400	530
1x10⁻⁴	340	169	235	315	220	150	194	212	489	255	375	509
1x10⁻³	225	81	140	200	200	100	150	195	473	240	360	489
1x10⁻²	70	18	60	85	150	85	135	170	465	232	340	470

carboxylic acid; potassium chromate is an oxidizing salt of an inorganic acid with a divalent anion yielding an insoluble reduction product that is incorporated into the growing oxide film on the metal surface. Sodium nitrite is also an oxidizing salt of an inorganic acid, but with a monovalent anion and yields no insoluble reduction product. The order of increasing inhibition is benzoate>nitrite>chromate.

Relation between steady state potential of low carbon steel and the pH value of acid solutions. Figures 2-4 represent the relationship between the steady state potential values and pH of the medium. These plots show a maximum potential at pH = 2 for tri-, di- and mono-chloroacetic acid. It is clear that the corrosion process of low carbon steel in these acid solution is not governed by [H]+. Thus we find that trichloroacetic acid would be more aggressive than monochloroacetic acid and the increase in acid concentration would lead to a noble shift of the free corrosion potential [9,10]. Thus the results suggest that the chloroacetate anion and not the [H]+ is controlling the corrosion process. This behaviour may be attributed to the formation of steel complexes with the chloroacetate as li-

gands, which in turn reduces the activity of steel in solution and results in a change in the corrosion potential of steel to the less active direction followed by a decrease in the corrosion rate. i.e. the corrosion process is anodically controlled. These results indicate that tri-chloroacetic acid is considerably more aggressive towards low carbon steel than di-, and mono-
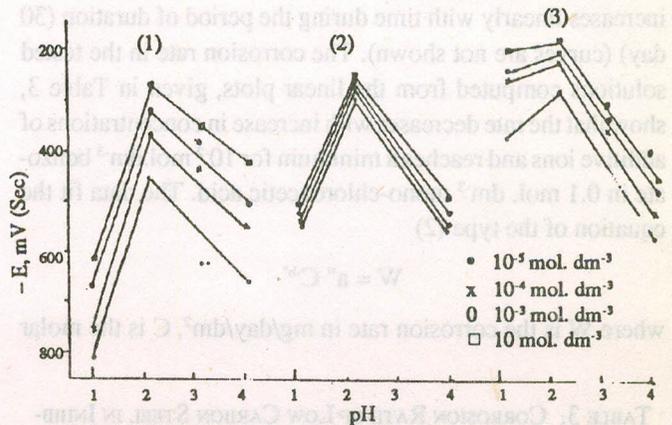
Fig.2 . Steady-state potential/pH relationship for steel electrode in CrO_4^- at different concentrations in(1) tri-, (2) di-, and (3) mono-chloroacetic acid.

TABLE 2. VALUES OF (b) OBTAINED IN 0.1 Mol.dm⁻³ SOLUTION OF TRI-, DI- AND MONO-CHLOROACETIC ACID IN PRESENCE OF CrO_4^-, NO_2^- AND $CH_6C_5OO^-$.

Chloroacetic acid	Values of (b) in presence of		
	$C_6H_5COO^-$	NO_2^-	CrO_4^-
Tri-	-70	-75	-80
Di-	-40	-50	-60
Mono-	-10	-20	-30
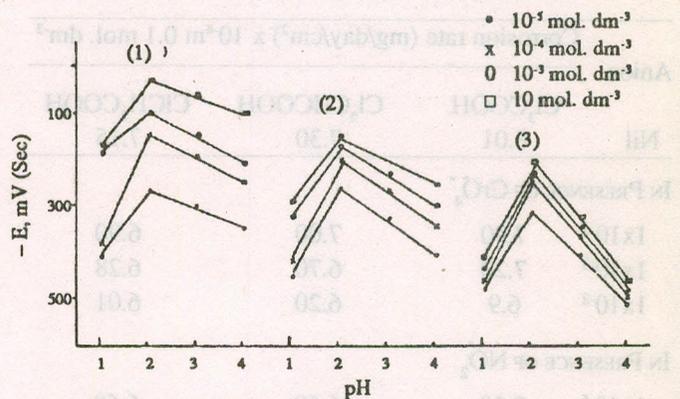
Fig.3. Steady state potential/pH relationship for steel electrode in NO_2^- at different concentrations in (1) tri-, (2) di-, and (3) mono-chloroacetic acid.

Fig.1. E, mV vs log C for low carbon steel in tri-, di- and mono-chloroacetic acid in presence of (o) CrO_4^-, (x) NO_2^- and (o) $C_6H_5COO^-$ at pH = 1.
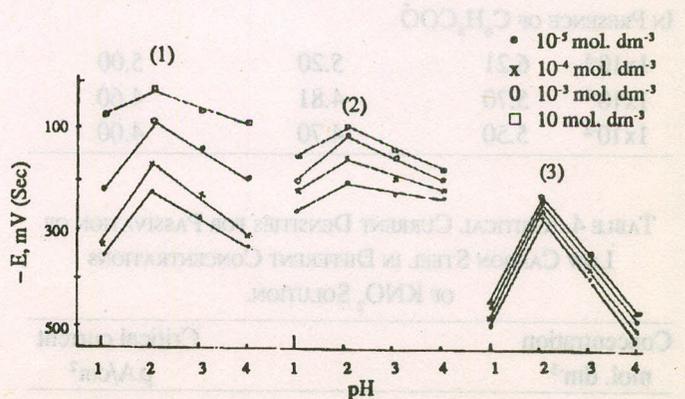
Fig.4. Steady state potential/pH relationship for steel electrode in $C_6H_5COO^-$ at different concentrations in (1) tri-, (2) di- and (3) mono-chloroacetic acid.

chloroacetic acid as follows tri- > di- > mono-, which is in parallel to the values of the dissociation constants (K) 2×10^{-1}, $3,32 \times 10^{-2}$ and 1.4×10^{-3} for tri-, di- and mono-chloroacetic acid respectively. A similar results have been obtained in previous work [11-13].

Weight-loss technique. Results show that the weight-loss increases linearly with time during the period of duration (30 day) (curves are not shown). The corrosion rate in the tested solutions computed from the linear plots, given in Table 3, show that the rate decreases with increase in concentrations of additive ions and reaches a minimum for 10^{-2} mol.dm^{-3} benzoate in 0.1 mol. dm^{-3} mono-chloroacetic acid. The data fit the equation of the type (2)

$$W = a'' \, C^{-b''}$$

where W is the corrosion rate in mg/day/dm^2, C is the molar

TABLE 3. CORROSION RATE OF LOW CARBON STEEL IN INHIB-
ITOR SOLUTION IN 0.1 Mol.dm^{-3} TRI-, DI- AND MONOCHLO-
ROACETIC ACID SOLUTION AT pH 1.

Anion	Corrosion rate (mg/day/cm^2) x 10^{-4}m 0.1 mol. dm^{-3}		
	Cl_3COOH	$Cl_2CHCOOH$	$ClCH_2COOH$
Nil	8.01	7.30	7.15
IN PRESENCE OF CrO_4^-			
1×10^{-5}	7.90	7.00	6.90
1×10^{-3}	7.20	6.70	6.28
1×10^{-2}	6.9	6.20	6.01
IN PRESENCE OF NO_2^-			
1×10^{-5}	7.30	6.50	6.60
1×10^{-3}	6.80	6.00	5.95
1×10^{-2}	6.18	5.80	5.60
IN PRESENCE OF $C_6H_5COO^-$			
1×10^{-5}	6.21	5.20	5.00
1×10^{-3}	5.70	4.81	4.60
1×10^{-2}	5.50	4.70	4.00

TABLE 4. CRITICAL CURRENT DENSITIES FOR PASSIVATION OF
LOW CARBON STEEL IN DIFFERENT CONCENTRATIONS
OF KNO_2 SOLUTION.

Concentration mol. dm^{-3}	Critical current μA/cm^2
1×10^{-5}	100
1×10^{-3}	65
1×10^{-1}	6

concentration and (a") and (b") are constants which depend on the type of anion. The decrease in the corrosion rate with increase in additive anion concentration suggests that additive ions act as inhibitors.

The inhibitive function of these anion may be associated with the formation of an insoluble reduction product which is incorporated into the growing oxide film.

Anodic polarisation. Anodic polarisation measurements of low carbon steel in NO_2 anion as an example of the inhibitive anions (Table 4). The critical current density decreases with increase in anion concentration contained 0.1 mol.dm^{-3} tri-chloroacetic acid solution. The value of i_{crit} has taken as inhibitor [14]. The function of the inhibitor is to block the pores in the oxide film. Accordingly, the passive potential is most probably due to the high resistance [15] in the pores of the oxide film (anodic areas) which leads to a very low current density at the cathodes. In this way local potential differences on the surface are eliminated and there is no longer any driving force for local corrosion cells (curves are not shown). It is known that nitrites is an oxidizing inhibitor, thus oxygen itself can exert inhibitive powers by aiding repassiovation. These results suggest that the film theory will play an important role in the corrosion inhibition as well as the adsorption theory. Thus the oxidizing inhibitor is more easily adsorbed on the surface resulting in a small cathodic sites in contact with relatively large anodic site. This leads to the decrease in corrosion rate, since small amount of oxygen is supplied to the cathodic sites thereby hindering up the cathodic reaction in response to this, the anodic reaction decreases.

References

1. U.R. Evans, *The Corrosion and Oxidation of Metal* (Arnold, London, 1960), pp. 142.
2. H.C. Gatos, Corrosion, **12**, 23 (1956).
3. G.H. Cartledge, J. Phys. Chem., **64**, 1877 (1960).
4. H.C. Gatos, European Symp. On "Inhibitors of Corrosion", Ferrara Italy (1960), Published by Univ. Ferrara, Italy (1961), pp. 257-270.
5. H.H. Uhlig and G.E. Woodside, J. Phys. Chem., **57**, 280 (1953).
6. D.M. Brasher, Nature, London, **193**, 868 (1962).
7. D.M. Brasher, J. C.R. Beryron, A.D. Mercex and J.E.R. Brouin, C.R. Lemo, Eur. Symp. on "Inhibit. Corr. "Ferrara, Italy **22**, 559 (1964).
8. S.M. Abdel Wahaab, O. Abo-Wafa, G.E. Kamel and S.M. Rashwan, J. Chem. Tech. Biotechnol., **36**, 305 (1986).
9. C. Wagner and W. Traud, J. Electrochem., **44**, 391 (1938).
10. A.C. Makrides and N.M. Huckerman, J. Electrochem. Soc., **105**, 156 (1938).
11. G.K. Gomma, R.M. Issa, H.Y. El-Baradie and H.E. Shokry,

J. Indian Chem. Soc., **70**, 31 (1993).

12. G.K. Gomma, H.Y. El-Baradie, R.M. Issa and H.E. Shokry, Indian J. Technology, **31**, 725 (1993).

13. M.H. Wahdan and G.K. Gomma, Asian J. Chem., **6**, 143 (1994).

14. E.F. Duffek and S.D. Meknney, J. Electrochem. Soc., **12**, 103 (1956).

15. M. Cohen, Corrosion, **9**, 372 (1943).