Inhibition of Corrosion of Low-Carbon Steel in Aqueous Solution of Bromide by Nitrite

GAMAL K. GOMMA

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

　　　The corrosion rates of low carbon steel in aqueous solution of potassium bromide in presence of nitrite at different temperatures and concentrations were determined. The potential ennobled as the concentration of nitrite is increased in aqueous solution of bromide. The degree of coverage of the metal surface by the adsorbed nitrite is influenced by the temperature. Nitrite remained effective at the test duration. The inhibitor shifts the corrosion potential to the anodic position and polarises both the cathodic and anodic half-reaction. The mechanism of the action of the inhibitor in aqueous solution of bromide indicates that it is an anodic inhibitor.

INTRODUCTION

According to the thermodynamic instability of metals, when a metal is immersed in water, it tends to corrode[1-3]. Many studies have been made on the corrosion of metals in halide medium[4-8]. It is an important objective to find more efficient low-cost inhibitors. Inhibition was attributed to the adsorption of the inhibitor on the metal surface. The **Film theory of protective activity** proposed by Balezin *et al.*[9] may be used to explain the inhibition efficiency. According to this theory, inhibition is due to the formation, on the metallic surface, of a layer produced by reaction between the metal, the inhibitor and the corrosive ions. The solubility of such corrosion products determines whether the additives act as corrosion inhibitor or stimulator, corresponding to low and high solubilities, respectively. Halides, sulphate and nitrate ions are aggressive anions. The function of an anodic inhibitor is to prevent or retard the reaction at the anodic area[10]. Sanyal and Grover[11] showed that sodium nitrite can be used as inhibitor for mild steel in water mains at 40°C.

EXPERIMENTAL

Stock solutions of potassium bromide and nitrite (AR Quality) were prepared in double distilled water and then diluted as required.

Low carbon steel electrodes (0.05% C) (1 cm length and 1 cm^2 diam.) were always machined after each experiment and were welded to a hard copper wire

fixed in a glass tube by means of neutral wax. The immersed area of electrode was effectively outside the tube. Before being used, the electrodes were abraded successively with 1 and 00 grade emery papers and then degreased with acetone. The corrosion rate is determined by weight-loss techniques. All experiments were conducted at room temperature (30°C) unless otherwise stated, the samples (0.5 × 2 × 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 extent of attack was recorded at different times as well as at the end of the test period. The samples were then cleaned by brushing under running water and immersed in pickling solution (10% H_2SO_4 + 1% thiourea) to remove corrosion products, the samples rested at an 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.

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

The corrosion current density was calculated by extrapolating the cathodic Tafel line to the experimentally measured free corrosion potential. The percentage inhibition[12], (P.I.) is given by

$$P.I. = 100 \times (1 - W_2/W_1)$$

where W_1 and W_2 are the corrosion rates in absence and in presence of inhibitor, respectively. In the present investigation an attempt has been made to study the corrosion of low carbon steel and influence of nitrite on it.

RESULTS AND DISCUSSION

Effect of concentration

The effect of concentration of nitrite on its inhibition efficiency in aqueous solution of constant concentration (10 M^{-1}) of potassium bromide is shown in Table 1. The loss in weight were progressively decreased with the rise in concentration of nitrite.

Table 1 shows the results of weight-loss of low carbon steel in different concentrations (10^{-4} to 10^{-1} M) of potassium bromide solution in the presence and absence of nitrite.

TABLE 1

EFFECT OF KBr CONCENTRATION ON THE CORROSION OF LOW
CARBON STEEL CONTAINING KNO$_2$

Duration = 7 days, temp. 30°C.

Concentration KBr (M)	Weight-loss (mg. dm^{-2}) × 10^{-5}		
	KBr	KBr + 0.01 mole nitrite	KBr + 0.4 mole nitrite
1×10^{-4}	0.896	0.223 (75.11)	nil (100)
1×10^{-3}	1.770	0.832 (52.99)	nil (100)
1×10^{-2}	1.790	0.864 (51.73)	nil (100)
1×10^{-1}	2.830	1.715 (39.50)	nil (100)

Values in parentheses represent per centage inhibition.

It is clear that at higher concentration of potassium bromide, low carbon steel required larger amount of nitrite.

Effect of temperature

The effect of temperature (25–80°C) on the corrosion of low carbon steel in the presence and absence of nitrite in 10^{-1} M potassium bromide is shown in Table 2. Nitrite maintained its inhibitive effect over the entire temperature range. It may be attributed to increased chemisorption[13-15] of nitrite ennobling the formation of a protective oxide film[16-19].

TABLE 2

EFFECT OF TEMPERATURE ON CORROSION OF LOW-CARBON STEEL
IN 10^{-1} M KBr CONTAINING KNO$_2$

Duration: 1 day

Temperature	Weight-loss (mg.dm^{-2}) × 10^{-5}		
	KBr	KBr +0.01M NO$_2$	KBr + 0.4 M NO$_2$
25	0.118	0.0713 (39.57)	nil (100)
50	0.225	0.0835 (62.88)	nil (100)
80	0.374	0.108 (71.12)	nil (100)

Values in paraentheses represent per centage inhibition.

Effect of time

For various times of immersion for the low carbon steel sample (7–30 days) in 10^{-1} M potassium bromide solution with and without inhibitor, shown in Table 3, nitrite was effective in long test periods giving good per centage of protection in all cases. However, the requirement of inhibitor concentration was increased in longer test duration as expected.

TABLE 3

EFFECT OF PERIOD OF IMMERSION ON CORROSION OF LOW CARBON STEEL (0.05% C) IN 0.1 M KBr CONTAINING KNO_2

Time (days)	Weight-loss $(mg.dm^{-2}) \times 10^{-5}$		
	KBr	KBr + 0.01 M KNO_2	KBr + 0.4 M KNO_2
7	2.830	2.070 (26.85)	nil (100)
15	3.5	2.290 (34.57)	nil (100)
22	3.982	2.431 (38.95)	nil (100)
30	4.425	2.625 (40.67)	nil (100)

Values in parentheses represent per centage inhibition at 30°C.

Polarisation measurements

Anodic and cathodic polarisation curves for low carbon steel in 10^{-1} M potassium bromide solution with and without inhibitor are show n in Fig. 1. It will be seen that in the absence of any inhibitor (blank) there is both cathodic and anodic polarisation but the anodic polarisation is considerably increasd in presence of inhibitor. The polarisation measurements indicate that nitrite controls the anodic process. The protective effect of nitrite is due to the formation of passive film[20,21]. The Tafel parameters and inhibitor efficiency were calculated[22], and are given in Table 4.

TABLE 4

TAFEL PARAMETERS AND INHIBITION EFFICIENCY

Solution	Tafel slope	$I_{corr.}$ mA/cm^2	Rate of corr. by linear polarisation. (mg. cm^2 day^{-1})
10^{-1} M KBr	0.046	158×10^{-2}	9×10^{-6}
10^{-1} M KBr + 0.4 M NO_2	0.040	137×10^{-2}	8×10^{-6}

With Inhibitor

(Blank)

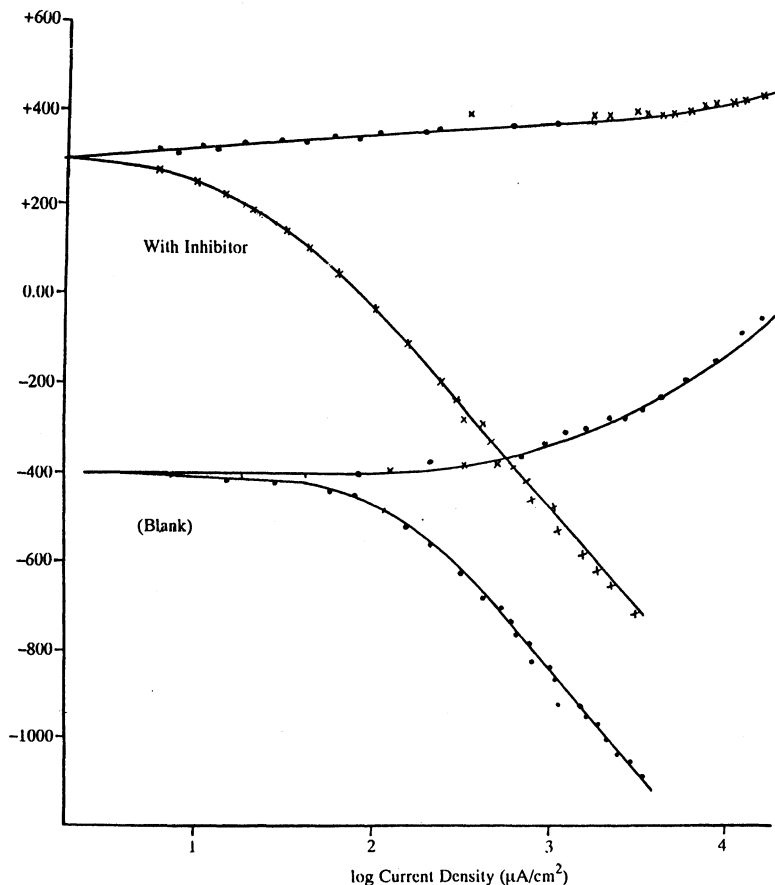log Current Density (μA/cm^2)

Fig. 1

REFERENCES

1. U.R. Evans, Metallic Ccorrosion, Passivity and Protection, Edward Arnold, London, p. 287 (1940).

2. C.W. Drane, in Corrosion, ed. L.L. Shreir, George Newnes Ltd., London, Vol. 1, p. 2, 13 (1963).

3. H.H. Uhlig, Corrosion and Corrosion Control, Wiley, New York, p. 187 (1964).

4. S.C. Antonyan, N.K. Tagmazyan, T.R. Melikyan, D.G. Rafaely, G.O. Torosyan and A.T. Babayan, Deposited Doc. Viniti, U.S.R.R. 4587, 81 (1981).

5. S. Todeosz, D. Kazimierz and B. Andrzei, *Ochr. Korros. Pol.*, **25**, 113 (1982).

6. A.V. Fokhin, M.V. Pospelov and A.N. Levichev, *Zashch. Met.*, **19**, 287 (1983).

7. K. Kobayashi and K. Ishii, *Symp. Corros. Inhibitors*, **2**, 480 (1980).

8. K. Pillai, Chandrasekhar and R. Narayan, *J. Elec. Soc.*, 125, 1898 (1898).

9. I.N. Putilova, S.A. Balezin and V.P. Brannik, Metallic Corrosion Inhibitors, Pergamon Press, Oxford, 55 (1960).

10. H.C. Gatos, *European Symp. on Inhib. of Corro.*, Ferrara (Italy) (1960) (published Univ. Ferrara 257–270) (1961).

11. B. Sanyal and T.K. Grover, *Labdev J. sci. Technol.*, **4**, 33 (1966)

12. G. Trabanalli and V. Carassiti, Advances in Corrosion Sci. and Techn., Eds. M.G. Fontana and R. Staehle, Vol. 1, Plenum Press, New York, p. 147 (1970).

13. D.M. Brasher, First Ferrara Symposium, 93 (1960).

14. H.H. Uhlig, *Chem. Eng. News*, **24**, 3154 (1964).

15. R. Powers and N.J. Hackerman, *J. Electrochem. Soc.*, **100**, 314 (1953).

16. U.R. Evans, *J. Chem. Soc.*, 1020 (1927).

17. D.M. Brasher, J.G. Beynon, A.D. Mercer and J.E.R. Brown, *Second Ferrara Symposium* 517 (1965).

18. M. Stern, *J. Electrochem. Soc.*, **105**, 638 (1958).

19. P. Hancock and J.E.O. Mayne, *J. Appl. Chem.*, **9**, 345 (1859).

20. K. Hanffek and B.Z. Ilschner, *Electrochem.*, **58**, 382 (1954).

21. N. Cabrer and N.F. Mott, *Rep. Prog. Phy.*, **12**, 163 (1948).

22. S.N. Prajapati, I.M. Bhatt and K.P. Soni, *J. Indian Chem. Soc.* 52, 65 (1975).