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Inhibition effect of sodium boro-gluconate on mild steel with and without nitrite ions in low chloride containing water

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As an alternative for the replacement of chromate containing corrosion inhibitors for mild steel in cooling water systems, sodium borogluconate (SBG) has been evaluated by gravimetric and electrochemical methods in water containing 100 p.p.m. Cl^- in an open system at ambient temperature. An inhibitor efficiency of 90% has been obtained in the presence of optimum concentration (50 p.p.m.) of SBG alone. However, the inhibition efficiency tends to decrease after 48 h of immersion due to the formation of soluble iron gluconate complexes. The formation of the complex is evident from the shift of the u.v. absorption peaks of Fe(II) and Fe(III) in the presence of gluconate ions. To stabilize the inhibitive action of SBG, NO_2^- ions were added in an equal mass ratio and their combined effect was found to be very effective in maintaining inhibition efficiency up to 100 h of immersion.

1. Introduction

Gluconates and gluconic acids are known to be effective non-toxic inhibitors for iron and mild steel in cooling water [1–6]. Further, it has been reported that their inhibitive power increases with the addition of borate ions because of their combined synergistic effect [7]. Lahodney–Sarc *et al.* [8, 9] have attempted to develop gluconate–borate mixtures in various concentrations as inhibitors for mild steel in water and have also found relatively better inhibition in comparison to the individual effects. However, most of the investigations on gluconate–borate effects have been carried out in chloride free water and further study is needed to evaluate their effect in chloride containing water.

Formation of soluble metal complexes with iron is one of the major problems with gluconate containing compounds [10] and hence their effectiveness decays within a few hours after immersion. It is not yet clear whether the dissolution of iron in the presence of sodium borogluconate (SBG) is mainly due to complex ion formation or to other reactions. In order to understand the effectiveness of SBG in chloride containing water, a study has been undertaken with mild steel in water containing 100 p.p.m. Cl^-. An attempt has also been made to maintain the inhibiting effectiveness of SBG by the addition of NO_2^- ions.

2. Experimental procedure

Experiments were carried out at ambient temperature (28 ± 2° C) and in an open system in 100 p.p.m. Cl^- solutions. Sodium borogluconate was prepared by adding equal molar amounts of sodium gluconate and boric acid in triple distilled water. All solutions were prepared using analytical grade chemicals. Steel (0.1%C) 1 mm thick was used for corrosion studies. Specimens were polished to mirror finish with 1/0 to 3/0 emery papers and degreased with trichloroethylene.

2.1. *Immersion tests*

Simple immersion tests were performed using 3.7 cm × 2.5 cm mild steel specimens. The specimens were completely immersed in 400 cm^3 solution with the help of glass hooks. Specimens were removed and de-rusted at various times up to 100 h.

2.2. *Analytical studies*

The complexation studies were conducted using a u.v. visible absorption spectrophotometer (Hitachi U.3400) in the 250 to 500 nm wavelength range using a 1 cm quartz cell at room temperature. The following solutions were used in the investigation of the complex formation characteristics of iron(II) and iron(III) with gluconate ions:

(i) 0.005 M ferrous ammonium sulphate;
(ii) 0.005 M ferrous ammonium sulphate + 0.045 M sodium gluconate;
(iii) 0.001 M ferric ammonium sulphate;
(iv) 0.001 M ferric ammonium sulphate + 0.009 M sodium gluconate.

Triple distilled water was used in the reference cell for the measurements of absorbance spectra of iron(II), solutions (i), iron(III), solutions (iii), while 0.045 M and 0.009 M sodium gluconate and triple distilled water were used in the reference cell for the measurement of absorbance spectra of iron(II), solution (ii), and iron(III), solution (iv), complexes, respectively.

2.3. *Electrochemical studies*

A conventional three electrode cell consisting of a working mild steel (1 cm^2 area), a platinum counter electrode (1 cm^2 area) and reference electrode (saturated calomel electrode) containing 200 cm^3 of test solution was adopted for electrochemical polarization experiments. Potentiodynamic polarization was carried out over a range of ±150 mV from the corrosion potential at a scan rate of 1 mV s^{-1} using a potentiostat (PAR EG&G 173) and a programmer (PAR EG&G 175).

3. Results

3.1. *Weight-loss data*

Figure 1 shows the inhibition efficiency of SBG at different concentrations (25 p.p.m., 50 p.p.m. and 100 p.p.m.) over a period of 100 h of immersion for mild steel in chloride solutions (100 p.p.m.). The percentage inhibition efficiency was determined as follows:

$$\text{Inhibition efficiency} = \frac{W_0 - W_i}{W_0} \times 100 \qquad (1)$$

where W_0 is the weight loss without inhibitor and W_i is the weight loss with the inhibitor. A maximum of 90% inhibition efficiency was obtained for 50 p.p.m. SBG up to 24 h of immersion. The inhibition efficiency decreased after 48 h of immersion in 50 p.p.m. of SBG and the colour of the solution became slightly yellow. No corrosion product accumulated on the electrode surface even after 100 h of immersion and the solution appeared dark pink. However, in the presence of 25 p.p.m. SBG, a little corrosion product was found on the surface and no coloration was noticed even up to 72 h of immersion. The rate of decrease of inhibition efficiency was relatively high in 100 p.p.m. of SBG. To maintain the inhibition efficiency of SBG, NO_2^- ions were introduced along with SBG in a 1 : 1 ratio (25 p.p.m. each). The corresponding inhibition data are shown in Fig. 2. A very high efficiency (95%) was obtained in the presence of 50 p.p.m. of NO_2^- ions alone but it decreased to 50% after 100 h of immersion. However, the same efficiency was achieved in the presence of a NO_2^-, SBG (25 p.p.m. each) mixture and the effectiveness (84%) was maintained, even up to 100 h immersion. These results indicate the beneficial effect of the combination of nitrite ions and SBG.

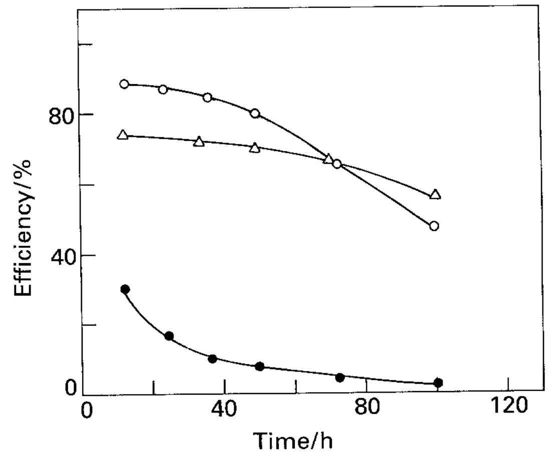

Fig. 1. Percentage corrosion inhibition efficiency in presence of various concentrations of sodium borogluconate (SBG) in sodium chloride solution up to 100 h immersion (●) 100 p.p.m. SBG, (○) 50 p.p.m. SBG, (△) 25 p.p.m. SBG.

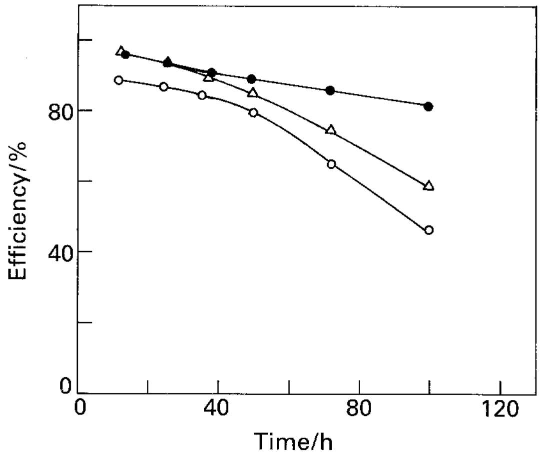

Fig. 2. Percentage corrosion inhibition efficiency in presence of nitrite, SBG and their mixture in sodium chloride solution up to 100 h immersion. (●) 25 p.p.m. SBG + 25 p.p.m. NO_2^-, (△) 50 p.p.m. NO_2^-, (○) 50 p.p.m. SBG.

3.2. *Absorption spectra*

The appearance of a pink colour during immersion tests of mild steel in the presence of SBG indicated the formation of a soluble complex of iron. To understand the cause of this coloration and the nature of film, u.v. absorption spectra were taken for iron(II) and iron(III) alone and in the presence of sodium gluconate Figs 3 and 4. An increase of the absorbance peak height and a shift of wavelength from 300 to 320 nm in comparison to iron(II) alone clearly indicated the formation of soluble iron–gluconate complex. In the presence of iron(III) and gluconate ions, a similar absorption peak and further shift of the wavelength from 297 to 336 nm were noted (Fig. 4), even at very low concentration of ferric ammonium sulphate (0.001 M). The present complexation studies indicated that both, iron(II) and iron(III) readily formed complexes with gluconate ions.

3.3. *Electrochemical studies*

The variation of open circuit potential (o.c.p.) of mild steel in the presence of SBG with time up to 24 h of immersion is given in Fig. 5. After 5 h a sudden shift of OCP in the active direction is observed in the

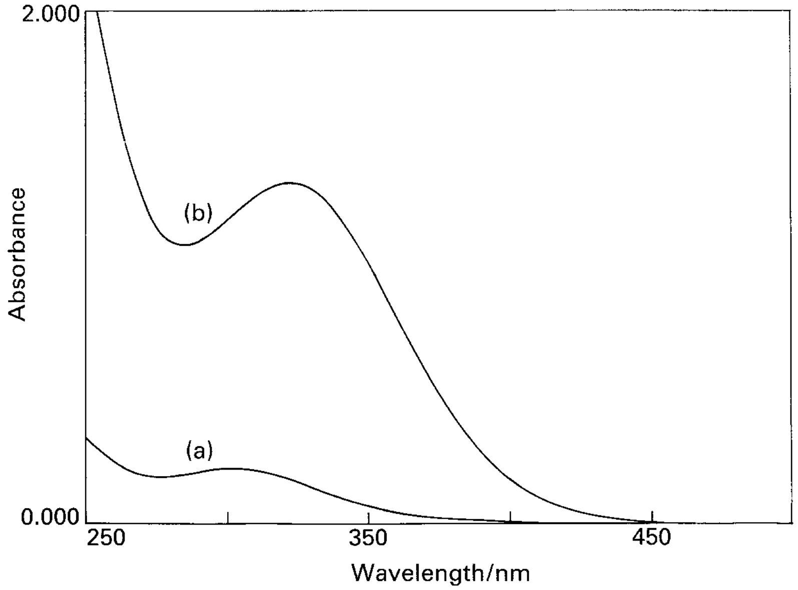

Fig. 3. U.v. absorption spectra of iron(II) and iron(II) gluconate ions (a) 0.005 M ferrous ammonium sulphate; (b) 0.005 M ferrous ammonium sulphate + 0.045 sodium gluconate.

solution containing 100 p.p.m. of SBG. This indicates the dissolution of iron through complex formation. After the complex formation has started, the o.c.p. continuously increases in the active direction. In the presence of 50 p.p.m. of SBG, the o.c.p. remains at −470 mV. In solutions of SBG and nitrite and nitrite alone, the steady o.c.p. values remains at −430 and −440 mV, respectively. However, attainment of steady state potential took longer in the presence of SBG.

Polarization curves have been recorded in all the investigated solutions and these are shown in Figs 6 and 7. Table 1 summarizes the kinetic parameters. I_{corr} values have been obtained by extrapolating the linear portion of the partial anodic and cathodic curves at $\eta > 50$ mV. The percentage inhibition efficiency was calculated by the formula

$$\text{Inhibition efficiency} = \frac{I_a - I_b}{I_a} \times 100 \qquad (2)$$

where I_a and I_b are the corrosion current density without and with inhibitors. Efficiencies obtained from the I_{corr} values (Table 1) are in good agreement with weight loss results.

The polarization results indicate that b_a values are high in the presence of NO_2^- ion while b_c is greater in the presence of SBG alone (Fig. 6). A significant increase in b_a and b_c values is obtained in the presence of NO_2^- and SBG mixture (Fig. 7). A decrease of anodic and cathodic currents in the presence of the NO_2^- and SBG mixture indicates mixed anodic and cathodic control of the inhibitor system.

4. Discussion

The results suggest that SBG is an inhibitor for mild steel in water containing small concentrations of chloride in the initial stages only. After a certain time, depending on SBG concentration, soluble iron gluconate complex is formed leading to a decrease in the inhibition efficiency. Higher concentration of SBG (100 p.p.m.) has been shown to have a detrimental effect on inhibition efficiency, even for short times of immersion. Formation of soluble iron

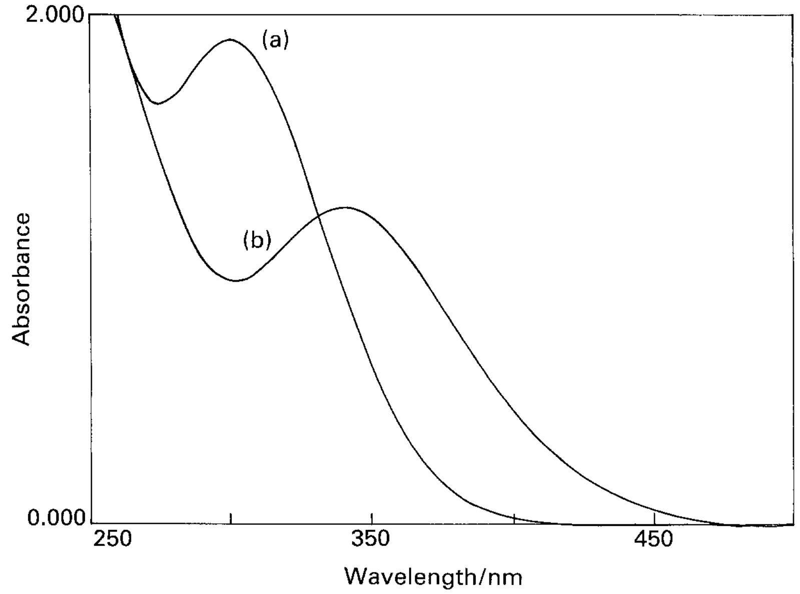

Fig. 4. U.v. absorption spectra of iron(III) and iron(III) gluconate ions. (a) 0.001 ferric ammonium sulphate; (b) 0.001 ferric ammonium sulphate + 0.009 M sodium gluconate.

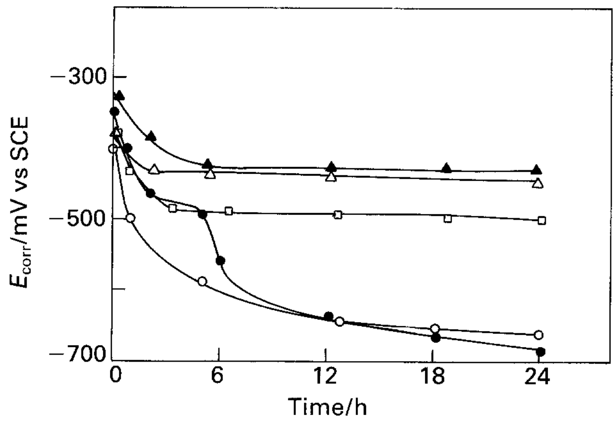

Fig. 5. Open circuit potential variation with time up to 24 h of immersion in presence of SBG, nitrite and their mixture in sodium chloride solution. (○) Blank, (●) 100 p.p.m. SBG, (□) 50 p.p.m. SBG, (△) 50 p.p.m. NO_2^-, (▲) 25 p.p.m. NO_2^- + 25 p.p.m. SBG.

complexes with gluconate ion is one of the major problems in the use of gluconate containing compounds as cooling water inhibitors for prolonged periods. For solutions of lower concentration of SBG (25 p.p.m.), the efficiency is less (75%) and the complexation reaction starts slowly after 72 h of immersion. The shift of the absorbance wave length of iron(II) from 300 to 320 nm and iron(III) from 297 to 336 nm in the presence of gluconate ion indicates the formation of complexes.

The weight loss results show that the inhibition efficiency is maintained up to 24 h in the presence of an adequate concentration of SBG (50 p.p.m.). This may be due to initial adsorption of SBG on the metal surface which covers the maximum surface area. After nearly 48 h of immersion gluconate ions may react with the film/iron oxide and form complexes with iron. The time delay between the initial adsorption of SBG on the metal surface and complex formation might be one of the reasons for the initial inhibition in the presence of optimum concentration of SBG.

Apart from adsorption phenomenon, inhibition of the oxygen reduction reaction also plays a significant role in the presence of SBG. Increase in the cathodic Tafel constant (b_c) and decrease of the cathodic current in the presence of SBG show that the rate of the oxygen reduction reaction is decreased. Similar results have been reported by Lohodney–Sarc *et al.* [9] for sodium gluconate. They have observed that the inhibition of cathodic reaction is more pronounced in dilute solution than in concentrated solution.

Nitrite ion is a well known [11–15] oxidizing type of cooling water inhibitor because of its unique role in forming and repairing the oxide film. In the present investigation, nitrite ion alone has shown 95% inhibition efficiency by controlling the anodic reaction. The SBG-NO_2 (1 : 1 ratio) mixture shows almost the same initial efficiency and about 85% efficiency up to 100 h. Therefore, the presence of nitrite ion along with SBG is effective in improving the inhibition efficiency due to the retention of the oxide film for a longer period by nitrite ion.

5. Conclusion

The presence of 50 p.p.m. of SBG shows an inhibition effect on the dissolution of mild steel in water containing 100 p.p.m. of chloride in an open system. But the inhibition efficiency tends to decrease after 48 h of immersion due to the formation of soluble iron gluconate complexes, as revealed by u.v. absorption spectroscopy. Low concentration (25 p.p.m.) of SBG is unable to give maximum efficiency while higher concentration (100 p.p.m.) enhances the rate of complexation reaction in a very short time. Nitrite and SBG mixture (25 p.p.m. each) has been found to be very effective in combination in maintaining the protective nature of oxide film up to 100 h of immersion. Kinetic data predict that NO_2^- is predominantly an anodic inhibitor while SBG is a cathodic one. One may conclude that SBG may be successfully used as a cooling water inhibitor along

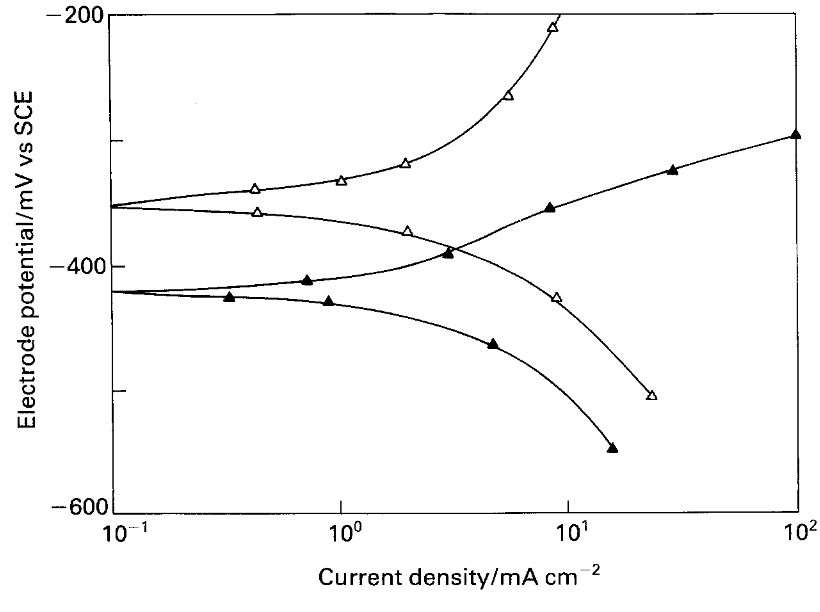

Fig. 6. Polarization curves recorded in presence of SBG and nitrite in sodium chloride solution. (△) 50 p.p.m. NO_2^-, (▲) 50 p.p.m. SBG.

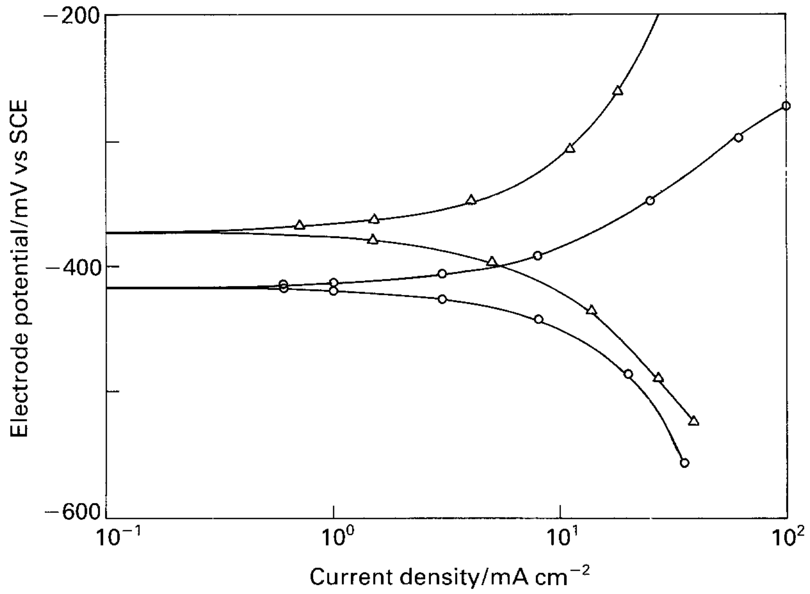

Fig. 7. Polarization curves recorded in the presence of nitrite and SBG mixture in sodium chloride solution, (○) Blank, (△) 25 p.p.m. NO_2^- + 25 p.p.m. SBG.

Table 1. Various kinetic parameters obtained from polarization curves

System	E_{corr} /mV	b_a /mV dec^{-1}	b_c /mV dec^{-1}	*Efficiency* /%
100 p.p.m. Cl^-	−415	75	110	–
100 p.p.m. Cl^- +50 p.p.m. SBG	−435	110	160	85
100 p.p.m. Cl^- +50 p.p.m. NO_2^-	−360	190	95	93
100 p.p.m. Cl^- +25 p.p.m. NO_2^- +25 p.p.m. SBG	−375	180	150	94

with nitrite ions in water containing low concentrations of chloride ions since SBG is harmless to the environment.

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