INHIBITION OF THE CORROSION OF MILD STEEL BY CARBONYL COMPOUNDS IN POTASSIUM SULPHATE MEDIUM

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Inhibition of the corrosion of mild steel in neutral potassium sulphate medium was investigated using several aldehydes and ketones. Alphatic aldehydes e.g. formaldehyde, prophionaldehyde and n-butyraldehyde provided ca. 59 percent, 69 percent and ca. 80 percent inhibition efficiency while benzaldehyde provided ca. 89 percent inhibition efficiency. p-Tolualdehyde was found to be a stimulator. Ketones were found to behave poorly as inhibitors. Electrochemical studies indicated that all the inhibitors inhibited the cathodic reaction. Detailed mechanisms regarding the structure of inhibitors and their performance have been considered.

Knowledge of the mechanism of inhibition effect contributes to a theoretical approach in the choice of inhibitors for a given medium and a corresponding metal. Adsorption mechanism has been suggested as one of the first hypotheses [1] and it was stated that under constant temperature, the curves characterising the relation of inhibition coefficient and concentration of inhibitors resemble adsorption isotherms. This supposition, however, appeared groundless for inhibitors like thiourea, thiodiglycol, aldehydes etc. Initially corrosion decreased with increase in inhibitor concentration but as the concentration increased further, the corrosion process inreased and with considerable concentration, inhibitor became a stimulator [2]. Rhodes and Kuhn [3] proposed an equation on the basis of adsorption theory showing the relationship between the protective action of the inhibitor and its molecular weight

$$Z = k M^{n} \qquad \ldots\ldots\ldots(1)$$

where M is the molecular weight of the inhibitor, k and n are constants. But, the studies of Khemkhadze and Balezin [4] indicated that among the aldehydes, formaldehyde was the most effective and the effectiveness decresed with increase in molecular weight.

Thereafter, there have been many publications on the effect of molecular structure of organic inhibitors on their corrosion inhibition properties. Trabanelli et al [5] have given a comprehensive treatment of the mechanism and phenomenology of the action of organic inhibitors while Blomgren & Bockris [6] performed electrocapillary measurements to study adsorption of aromatic amines at metal-solution interface. Evans [7] has suggested that concentration of these inhibitors are so small that they cannot form even a monolayer of adsorbed species on metal surface. Instead, the role of inhibitors is to repair the oxide films as these are ruptured at particular points. Kunitsugu [8] has attempted to put forward the idea of soft acids and bases where metal is considered to be a soft acid and the inhibiting molecule is considered to be a soft base.

Various theories of inhibition by organic inhibitors have been suggested [9-14]. Hackerman et al [9] have suggested that observations of the shift of the open circuit potential in the presence of an inhibitor permits the specification of which partial process is influenced by the inhibitor. It has been shown for nitrogen containing inhibitors that the inhibition increases with the electron density at nitrogen atom due to electron repelling effects of the substituents [10,11]. During inhibition studies on iron by aniline and aniline derivatives, Donahue et al [12-14] have proposed that transition from a nearly pure adsorption to pure chelation process is possible. The authors have reported deviation from adsorption correlation for p-toluidine as well as for m-toluidine and have attributed it to the surface chelate. Antropov, in a comprehensive treatment on the correlation between kinetics of corrosion and the mechanism of inhibition by organic compounds, has shown that adsorption (physical, specific or chemical) is an inevitable part of the process of inhibition and reduction and that is why the charge on the metal plays an important

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role in the performance of all organic inhibitors of corrosion [15].

In a system under test, the presence of oxygen too, determines a great decrease in inhibitor effectiveness. It has been proposed that this effect is due to lesser degree of surface covering owing to increased metal dissolution rate caused by a higher cathodic current density value [16].

Though, there have been exhaustive investigations regarding the inhibition mechanisms by nitrogen containing organic compound, carbonyl compounds have not been investigated in detail The function of chainlength in inhibiting the corrosion process is not well understood so also is the substituents effect. The existing liteature does not adequately cover the steric effects of the inhibitors as well as their orientation during the adsorption process. This paper attempts to understand the inhibition by carbonyl compounds in potassium sulphate solution by taking some of these factors into consideration.

EXPERIMENTAL

For direct weightloss experiments, coupons of size 25 mm x 20 mm x 1.4 mm were cut from a carbon steel sheet of composition C 0.12, Mn 0.32, P 0.03 S 0.03 and Si 0.04. The coupons were polished upto 600 girt emery paper, degreased in acetone and used for immersion in different corrosive and inhibitive media open to air. Blank weightloss data were first recorded in distilled water and distilled water containing 400 ppm potassium sulphate. The varying amounts of inhibitors were then added to distilled water containing 400 ppm K_2SO_4 and weight loss data were recorded again. Two ketones (cyclohexanone and acetophenone) and five aldehydes were selected as inhibitors. Out of the five aldehydes selected three were aliphatic viz. formaldehyde, propionaldehyde and butyraldehyde and two were aromatic viz. benzaldehyde and p-tolualdehyde. All the exposures were carried out for 7 days.

Inhibitors which gave good corrosion inhibition efficiency were selected for further investigations by electrochemical potentiostatic polarization technique. Two approaches were adopted for potential current measurements. According to first approach, the specimens were first immersed in respective solutions and the corrosion potentials were recorded with respect to SCE after reaching steady state. Potentials were increased in steps of 20 mV and the corresponding currents were recorded. Only one type of polarization studies i.e. anodic or cathodic, were done at a time so that any changes in solution composition do not affect the other type of polarization measurements. According to second approach, the specimens were kept at a potential of -1500 mV for about 45 minutes in the respective solution and then potentials were stepped up in steps of 20 mV and the coresponding currents were recorded. The steps of 20 mV were reduced to 10 mV near the corrosion potential to arrive at a true value of corrosion potential. All the polarization studies were carried out upto + 500 mV/SCE.

RESULTS

Weightloss Studies

Mild steel corroded at a rate of 17.02 mdd in distilled water and at a rate of 20.66 mdd in distilled water containing 400 pmm K_2SO_4. Table 1 shows the corrosion rates of mild steel in water containing K_2SO_4 with the addition of various amounts of two ketones viz. acetophenone and cyclohexanone. It is evident from the table that though ketones provided some protection to mild steel in corrosive medium, yet the inhibition was not significant. The degree of protection offered by ketones seemed to be independent of their structural properties (e.g. maximum of 19% inhibition efficincy observed in presence of 2000 ppm of cyclohexanone).

Table 2 represents the corrosion rates of mild steel in distilled water containig 400 ppm

TABLE 1

CORROSION RATES OF MILD STEEL WITH THE ADDITION OF DIFFERENT CONCENTRATION OF INHIBITORS (KETONES) TO DISTILLED WATER CONTAINING 400 ppm K_2SO_4

Inhibitor	Concentration ppm	Corrosion rate (mdd)	Inhibition efficiency (%)
-	-	20.66	-
Acetophenone	2,500	17.37	15.9
	3,000	17,25	16.5
	3,500	17.14	17.0
Cyclchexaone	2,000	16.74	19.0
	2,500	16.82	18.6
	3,00	16.95	18.0

K_2SO_4 with the addition of aldehydes. It can be seen that aromatic aldehyde, i.e. benzaldehyde, provided best inhibition efficiency when compared to aliphatic aldehydes (viz. formaldehyde, propionaldehyde and butyraldehyde), while p-tolualdehyde behaved as an stimulator rather than inhibitor during 7 days exposure.

Electrochemical Studies

As mentioned earlier, two approaches were adopted for potentiostaic polarization measurements. In the first approach, the specimens were first immersed seperately in 400 ppm K_2SO_4 and this solution containing 2000 ppm amounts of formaldehyde, propionaldehyde, n-butyraldehyde, benzaldehyde and p-tolualdehyde.

The corrosion potentials were allowed to attain steady state and potential-current measurements were made Fig. 1 and 2 show the anodic and cathodic polarization curves after steady state. If one considers the current density as a function of overpotential (i.e. change from corrosion potential), it can be seen that the cathodic currents in presence of aldehydes were significantly lower than those in potassium sulphate alone while anodic currents were higher. The lower values of cathodic currents in presence of inhibiting aldehydes indicate that these inhibitors interfere with the cathodic reaction (a) to provide inhibition while higher currents during anodic polarization could be attributed to the oxidation of aldehydes into acids rather than to the anodic dissolution of the mild steel.

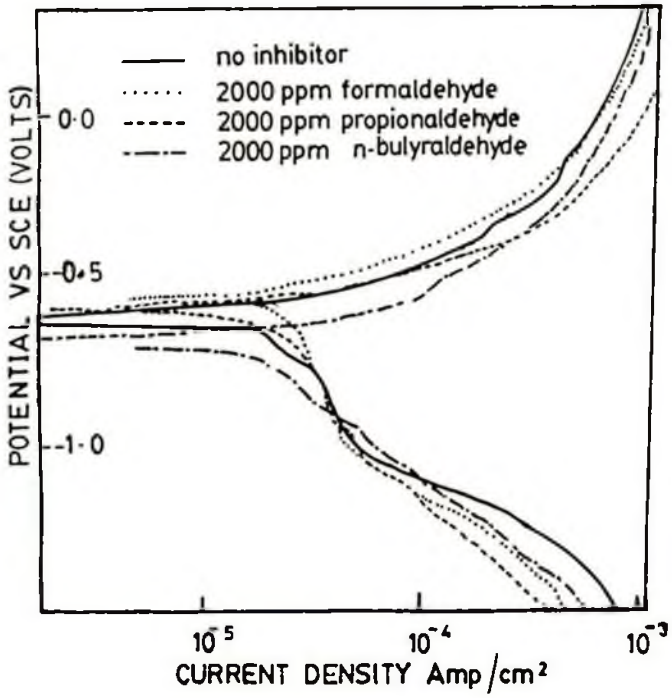


Fig. 1 Polarisation curves for carbon steel from corrosion potential in 400 ppm K_2SO_4 solution.

TABLE 2

CORROSION RATES OF MILD STEEL IN DISTILLED WATER CONTAINING 400 ppm K_2SO_4 WITH THE ADDITION OF DIFFERENT CONCENTRATION OF INHIBITORS (ALDEHYDES)

Inhibitor	Concentration ppm	Corrosion rate (mdd)	Inhibition efficiency (%)
-	-	20.66	-
Formaldehyde	1,000	17.92	13.2
	1,500	15.82	23.5
	2,000	8.39	59.4
Propionaldehyde	1,000	9.93	51.9
	1,500	8.58	58.5
	2,000	6.38	69.1
n-Butyraldehyde	1,000	5.26	74.5
	1,500	4.44	78.5
	2,000	4.05	80.4
Benzaldehyde	1,500	2.76	86.6
	2,000	2.28	89.0
	2,500	2.26	89.1
p-Tolualdehyde	1,000	25.00	-
	1,200	34.03	-
	1,400	35.80	-

Figures 3 & 4 show the polarization curves obtained using the second approach (described in experimental). It can be seen that corrosion potential in potassium sulphate solution was -530 mV/SCE and moved to ca.-655 mV/SCE with the addition of 2000 ppm formaldehyde to -650 mV/SCE with the addition of propionaldehyde, to -715 mV/SCE with the addition of butyraldehyde and to -670 mV/SCE with the addition of 2000 ppm benzaldehyde. It is evident from these figures and weightloss measurements (Table 2) that these aldehydes move the corrosion potential of caron steel in the cathodic direction,thus, acting as cathodic inhibitors.

DISCUSSION

The findings of this investigation can be

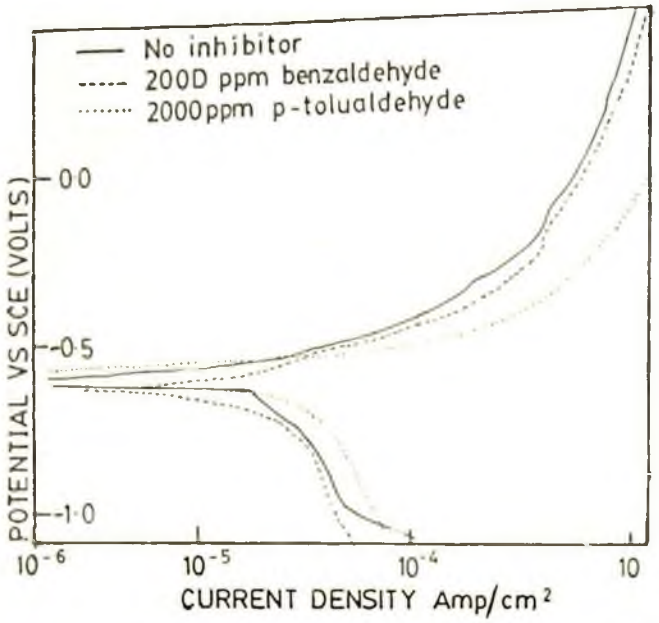


Fig. 2 Polarization curves for carbon steel from corrosion potential in 400 ppm K_2SO_4 solution

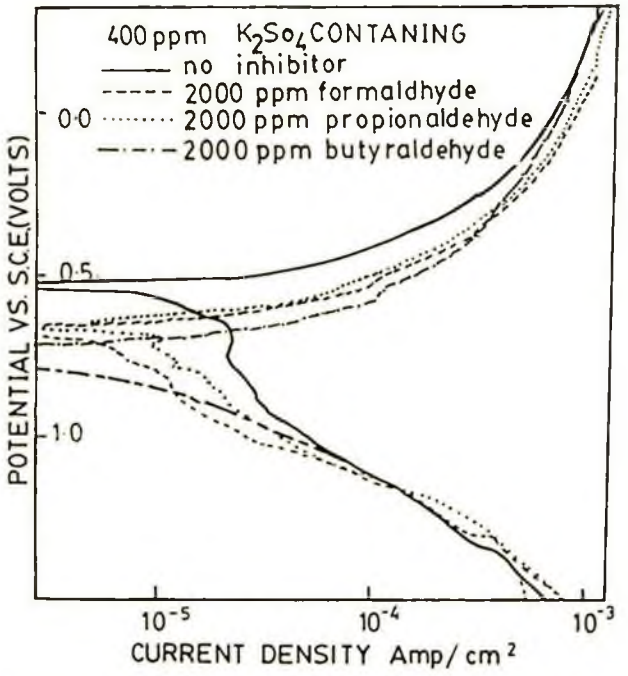


Fig. 3 Cathodic to anodic polarisation curves for carbon steel in 400 ppm K_2SO_4 solution

summarised as follows:-

1. Aliphatic aldehydes are good corrosion inhibitors for iron in neutral sulphatc medium and their inhibitive action increase as function of molecular weight.

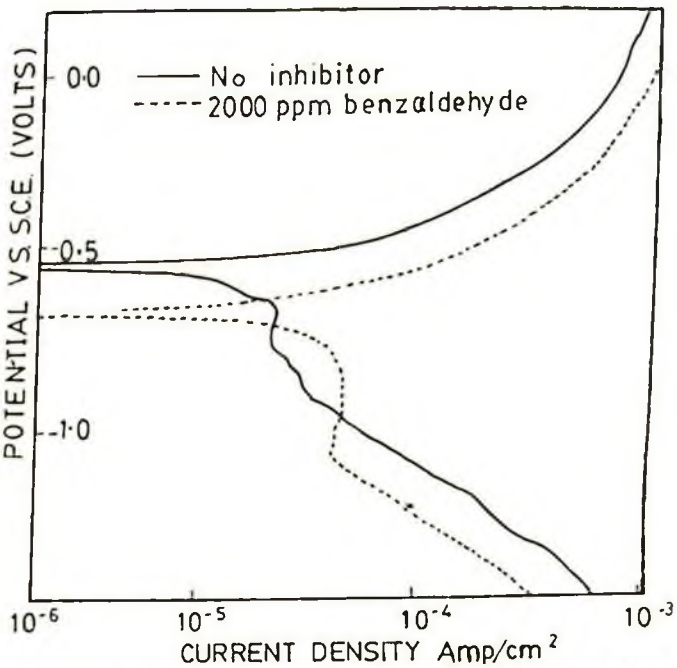


Fig.4 Cathodic and anodic polarization curves for carbon steel in 400 ppm K_2SO_4 solution

2. Benzaldehyde was found to be a better corrosion inhibitor than the aliphatic aldehydes. Substitution to the aromatic ring plays an important role in the inhibiting properties of organic aromatic inhibitors as p-tolualdehyde was found to be a stimulator.

3. Ketones are generally poor inhibitors when compared to aldehydes.

It is evident from the table 2 that the same concentration of n-butyraldehyde provided a better inhibition efficiency than formaldehyde and propionaldehyde in K_2SO_4 medium. The observations are in agreement with the model proposed by Rhodes and Kuhn [3] that the protective action of an inhibitor increases with increase in molecular weight. However, Khemkhadze et al [4] have reported contrary observation for aldehydes. As suggested by Antropov [15], adsorption (physical, specific or chemical) is an inevitable part of the processes of inhibition and the charge on the metal in a particular medium plays an important role in the performance of all organic inhibitors. In this context, point of zero charge for a metal is important for finding out the charge on a metal in a medium. Antropov et al [17] have quoted a value of 0.0 volt/SHE or -0.24 V/SCE for zero charge potential of iron calculated from electronic work function while Aizian[18] quotes a value of -0.37 volts/SHE or -0.61

V/SCE. Rostron [19] suggests two zero charge potentials for iron; one for iron covered with a layer of hydrogen atoms which is -0.37 volts/SHE and the other for bare iron metal in electrolyte containing no specifically adsorbable species; this is of the order of -0.02 V/SHE. For the interpretation of our results, we shall take the value of -0.24 V/SCE for zero charge potential of iron because the surface is unlikely to be covered by hydrogen atoms in neutral medium.

The corrosion potentials of iron in presence of various inhibitors in K_2SO_4 solution were found to be more negative than -0.24 V and hence the metal acquired a negative charge on the surface. Consequently, there is an electrostatic attraction between this metal surface and positively charged inhibitor species. An aliphatic aldehyde molecule e.g. propionaldehyde, is polarized as follows:



and the positive charge on the carbon atom bonded to oxygen will be shared by the entire chain of carbon atoms since CH_3 group is known to be electron donor. Hence, propionaldehyde molecule can be adsorbed on the iron metal through carbon atoms rather than oxygen atom. As the chain length increases from formaldehyde to butyraldehyde, the surface area covered by a single molecule will also increase and consequently inhibition efficiency shall also increase as observed by the author.

Shifts of corrosion potentials in the negative direction as well as lower currents at more negative potentials indicate that the inhibitor interferes with the cathodic reaction (s) [9]. The corrosion of iron in neutral aerated sulphate medium includes the following elect - rochemical reactions:

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad .....(2)$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad .....(3)$$

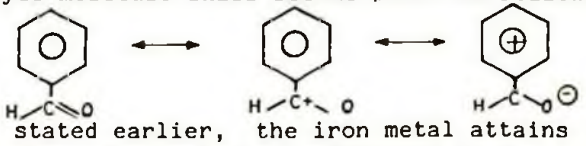
In presence of formaldehyde, propionaldehyde or n-butyraldehyde, the dissolved oxygen will partly be consumed by the aldehydes as alehydes are known to get oxidised readily into corresponding acids by contact with air [20]. Thus, the function of aliphatic aldehydes in inhibiting the corrosion process appears to be two fold:

(a) by getting adsorbed on the surface through carbon atoms and thus hindering the corrosion process physically; and

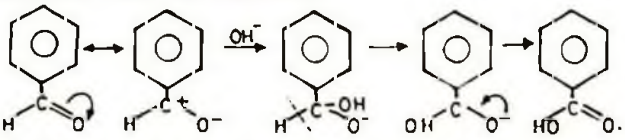
(b) by consuming part of the oxygen available for corrosion of iron and there by reducing the corrosion rate.

The higher values of anodic currents in inhibitive solutions are not because of higher anodic dissolution of iron but rather due to oxidaion of aldehydes to corresponding acids. These acids could still act as inhibitors as benzoic acid is known to be an inhibitor for iron

Benzaldehyde provided better inhibition than aliphatic aldehydes, the main reason being the presence of π-electron cloud over the aromatic ring. In the neutral sulphate medium, benzaldehyde molecule shall become polar as follows:



As stated earlier, the iron metal attains a negative charge in the medium and in presence of benzaldehyde, positive charge on the π -electron cloud shall attract the benzaldehyde molecule towards the negatively charged metal. Since the benzaldehyde is a planar molecule because of SP^2 hybridization, its adsorption on the surface will be parallel through π -electrons [6] thereby providing a good inhibition. The adsorbed aldehyde molecule on the surface shall not provide a route for oxygen to react with the metal. The higher anodic current in presence of benzaldehyde are probably due to oxidation of benzaldehyde to benzoic acid as follows:



OH^- is available by the oxygen reduction in neutral medium as explained by equation (3).

The most important observation regarding the importance of structural features in the performance of an organic inhibitor was made in case of p-tolualdehyde which was found to be a stimulator. While benzaldehyde was found to be a good inhibitor, the introduction of a CH_3 group in para position changed the inhibiting properties of benzaldehyde drastically. It appears to be an amazing observation. Donahue et al[13,14] have reported similar observation in case of p-toluidine and m-toluidine and have considered the following mechanism for iron dissolution [21]

$$Fe + OH^- \rightleftarrows (FeOH)_{ads} + e^- \quad ....(4)$$

$$(FeOH)_{ads} \rightarrow (FeOH)^+ + e^- \quad ....(5)$$

$$(FeOH)^+ \rightarrow Fe^{2+} + OH^- \quad ....(6)$$

where step (4) is in quasi equilibrium, step (5) is rate limiting and step (6) is fast. Donahue et al [13] suggest that if the effect of inhibitor is on the adsorbed intermediate say, by some sort of chelation mechanism, the evaluation is less direct. Adsorbed intermediate might interact with the n inhibitor molecules as follows:

$$(FeOH)_{ads} + nI \rightleftarrows [(FeOH).\ I_n]_{ads} \quad ...(7)$$

to form a complex which is adsorbed on the surface. If the following description reaction takes place

$$[(FeOH)_{ads}.\ I]_{nads} \rightarrow [(FeOH).\ I_n]^+ + e^- \quad ...(8)$$

then an inhibitor which was inhibiting corrosion becomes a stimulator. The desorption in case of p-tolualdebyde could be possible becuase CH_3 group attached to benzaldehyde in p-position has SP^3 hybridization and therefore p-tolualdehyde no more remains a planar molecule like benzaldehyde. Consequently, the adsorption of inhibitor on the surface through π -electron is disturbed, thus providing a way for desorption reaction as suggested by equation (8). Ketones were found to be poor inhibitors probably because of two reasons. Firstly, their oxidation into corresponding acids is not feasible under the experimental conditions and secondly because the polarity of $> C = O$ group is much less than in the case of aldehydes. As a result of this, the positive charge developed on the carbon atom of carbonyl group is much less as compared to aldehydes. Another reason for poor performance of cyclohexanone could be the absence of π-electron cloud, while that for acetophenone could be the electron donating property of CH_3 group thus resulting in to reduction of polarity of $> C = O$ group.

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