

## Research Article

## Polarization Studies on Corrosion inhibition of tin coated steel in 1.0M monochloroacetic acid

Sangita Sharma\*, Kinnari H. Parikh and Naveen Kumar

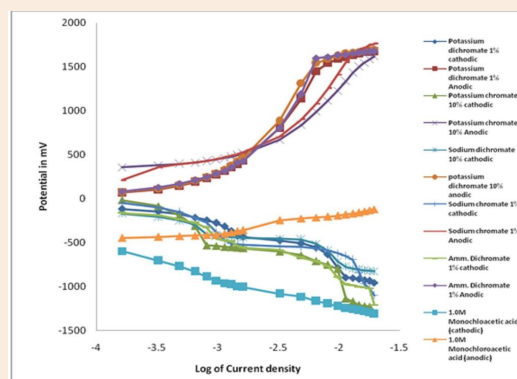
Department of chemistry, Hemchandracharya North Gujarat University, Patan – 384 265 (Gujarat) India

**Abstract**

The corrosion inhibition capacity of some chromates and dichromates were studied in 1.0M monochloroacetic acid against tin coated steel by polarization techniques and weight loss method. The corrosion behaviour is established by polarization curves like Tafel slopes, extrapolation of cathodic Tafel lines and intersection of cathodic and anodic lines at open circuit potential in presence and absence of inhibitors. Some electrochemical parameters like corrosion current are calculated from Tafel's lines. The efficiencies are reasonably well when compared with those obtained from weight loss method. All inhibitors induced the increase in positive potential for both anodic and cathodic polarization curves. The calculated values of corrosion current were  $I_{\text{corr(in)}} > I_{\text{corr(in)}}$ . All inhibitors are good inhibitors and acted by raising the anodic potential.

**Keywords:** Tin coated steel, Monochloroacetic acid, chromates, Passivation, polarization.

A mechanism is proposed for corrosion of tin coated steel in acidic medium and its inhibition in presence of chromates and dichromates.

**\*Correspondence**

Sangita Sharma,

Email: smridhee2000@yahoo.co.in

**Introduction**

The corrosion of metal occurs when they come in contact with environment and it is most common industrial problem [1-3]. Thus it has been the topic of interest for research for many researchers [4-6]. The widely used metal is iron or its alloys, out of these tin coated steel is most commonly used. Tin coated steel is used in packing material for baby food, milk powder, coffee tins, oil cans etc. Corrosion inhibitors are of great practical importance, being extensively employed in minimizing metallic waste in engineering materials. A large number of organic [7-13], inorganic inhibitors [14-20] and the extract of the various parts of the plants [21-24] have been used for having the significant inhibitors. In the present study, chromates and dichromates are used as inhibitors for tin coated steel in 1.0M monochloroacetic acid by polarization measurement method because from literature, it is found that little work is done on corrosion studies of tin coated steel.

**Experimental**

Tin coated steel used in present work is taken from Tata Tin Plate, Jamshedpur, India. Each sheet was 0.21mm in thickness, Type is Double reduced, Grade Coating is Equally Coated, Temper Designation is DR 550 (DR 08), Hardness 30RT is 73 +3/-3 and Classification is Bright finish. The chemicals used are of A.R. grade. All the solutions were prepared in conductivity water and standardized by different method [20] and their purities were checked by noting their melting points, solubility and crystallization method [25-26].

The metal coupons used were of circular design, diameter 2.8 cm with a handle 3 cm long and 0.5 cm wide. The specimen was first cleaned with distilled water followed by 1:1(v/v) alcohol-acetone mixture and dried. The handle and the back of the test coupon as well as of the auxiliary platinum electrode were covered with paraffin wax and then coated with perspex dissolved in ethyl acetate solution. In this way only one side of circular portion of tin coated steel and platinum electrode was exposed to the corrosive medium.

The three electrode system was used for potentiodynamic polarization studies. The circular coupon acted as working electrode, saturated calomel electrode as reference electrode and platinum electrode of same dimension as counter or auxiliary electrode. The electrochemical cell used is H-type pyrex glass cell containing a built in capillary to make connection to the reference saturated calomel electrode. It also has porous partition to separate the two compartments. In each compartment, the volume of corrosive media was 80 ml.

For maintaining temperature the specimen were placed in a corrosive medium taken in a closed beaker in High Precision Water Bath (Cat. No. MSW – 274) which has readability  $\pm 0.1^\circ\text{C}$ . The selected inhibitors used are potassium chromate, sodium chromate, potassium dichromate, sodium dichromate and ammonium dichromate. Different concentrations of the above inhibitors are used to find inhibition efficiencies of these inhibitors.

## Results and Discussion

The influence of current density on the cathodic and anodic polarization of tin coated steel in 1.0M monochloroacetic acid containing of inhibitor has been studied according to Evans diagram. The value of corrosion current density in presence and absence of the inhibitor were obtained from the graph while percentage efficiency was calculated using the following equation

$$\text{Inhibition Efficiency(\%)} = \left( \frac{I_{\text{corr(without inhibitor)}} - I_{\text{corr(with inhibitor)}}}{I_{\text{corr(without inhibitor)}}} \right) \quad (1)$$

Where  $I_{\text{corr(without inhibitor)}}$  is the corrosion current in absence of inhibitor and the  $I_{\text{corr(with inhibitor)}}$  is the corrosion current in presence of inhibitors. The efficiency of inhibitors under investigation have been calculated from (i) extrapolation of cathodic Tafel to open circuit potential (ii) from intersection of cathodic and anodic Tafel line at open circuit potential. Both these methods are in agreement as far efficiencies of inhibitor are concerned.

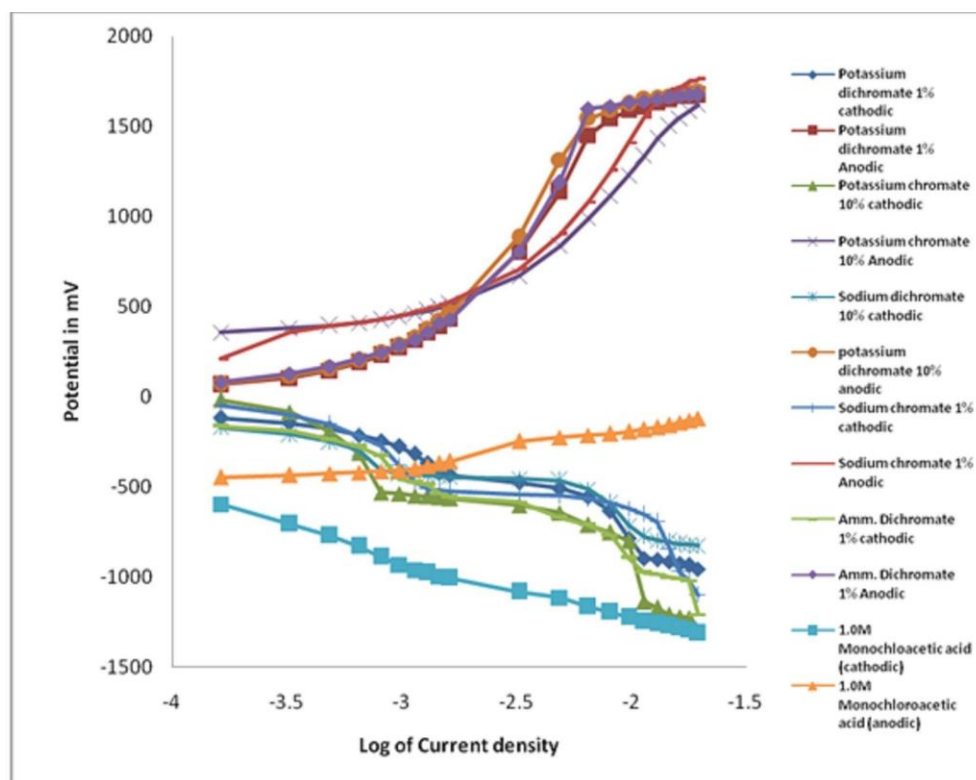
The corrosion current of tin coated steel electrode in the presence of the chromates and dichromates in 1.0 monochloroacetic acid was determined by the intersections of the extrapolated of the anodic and cathodic curves at the corrosion potential using Tafel slopes. Tafel parameters and efficiencies of inhibitors for 1.0M monochloroacetic acid are presented in **Table 1** and the polarization curves for chromate and dichromate inhibitors are shown in **Figure 1**. The electrochemical parameters like corrosion current density, cathodic current and anodic currents are presented in the table 2. It was found that the shift of the potential in both cathodic and anodic potential is markedly in the positive direction.

As seen in **figure 1**, cathode and anodic currents has increased by a factor of 10 – 100 depending on the nature inhibitor and its concentration. The corrosion potential shifts to positive values and there is decrease in negative value of cathodic current in presence of inhibitors in comparison to absence of inhibitors. The corrosion potential shifts to positive values and cathodic currents correlated well with increase in concentration of inhibitor in a wide range of 1% to 12%. Practically parallel shift of cathode curves shows that adsorption of the compound does not depend on the potential in wide range 200mV to 400mV respective to corrosion potential and that in the cathodic region, molecules are not desorbed from metal surface.

**Table 1** Tafel parameters and efficiency of Tin coated Steel in 1.0M monochloroacetic acid

Temperature: 35±0.1°C									
Name of inhibitor	Inhibitor Concentration	Tafel Slope		Energy transfer coefficient	Corrosion Current		Inhibitor efficiency from extrapolation	Inhibitor efficiency from intersection	Inhibitor Efficiency from weight loss method
		Anodic	Cathodic	$\alpha$ (Cathodic)	From extrapolation of cathodic Tafel line	From intersection of cathodic and anodic line at open circuit potential			
Nil	---	0.80	1.20	0.012	$1.78 \times 10^{-2}$	$1.78 \times 10^{-2}$	---	---	---
Potassium Chromate	10%	0.71	0.48	0.030	$2.82 \times 10^{-4}$	$5.52 \times 10^{-4}$	98	97	55
	11%	1.44	0.55	0.027	$8.61 \times 10^{-4}$	$1.43 \times 10^{-4}$	52	92	69
	11.5%	1.02	0.75	0.019	$5.52 \times 10^{-4}$	$9.28 \times 10^{-4}$	97	95	93
	12%	0.85	0.52	0.028	$4.73 \times 10^{-4}$	$7.99 \times 10^{-4}$	97	96	66
Potassium dichromate	1%	1.93	0.62	0.024	$1.00 \times 10^{-4}$	$1.41 \times 10^{-4}$	94	92	48
	2%	0.81	0.34	0.043	$3.33 \times 10^{-4}$	$5.06 \times 10^{-4}$	98	97	51
	2.5%	1.18	0.38	0.038	$4.65 \times 10^{-4}$	$6.53 \times 10^{-4}$	97	96	97
	3%	0.87	0.41	0.036	$3.6 \times 10^{-4}$	$4.27 \times 10^{-4}$	98	98	83
Sodium chromate	10%	1.06	0.49	0.030	$6.4 \times 10^{-4}$	$8.62 \times 10^{-4}$	96	52	21
	11%	0.77	0.30	0.049	$2.1 \times 10^{-4}$	$4.75 \times 10^{-4}$	99	97	61
	11.5%	1.03	0.62	0.024	$5.12 \times 10^{-4}$	$8.62 \times 10^{-4}$	97	95	93
	12%	0.94	0.41	0.036	$4.1 \times 10^{-4}$	$7.43 \times 10^{-4}$	98	96	59
Sodium dichromate	1%	1.02	0.40	0.037	$5.52 \times 10^{-4}$	$7.43 \times 10^{-4}$	97	96	45
	2%	0.80	0.41	0.036	$3.53 \times 10^{-4}$	$5.12 \times 10^{-4}$	98	97	64
	2.5%	1.03	0.29	0.050	$3.8 \times 10^{-4}$	$4.75 \times 10^{-4}$	98	97	97
	3%	1.08	0.41	0.036	$4.10 \times 10^{-4}$	$5.52 \times 10^{-4}$	98	97	86
Ammonium	1%	1.11	0.51	0.029	$4.75 \times 10^{-4}$	$6.40 \times 10^{-4}$	97	96	34

dichromate	2%	1.01	0.38	0.038	$4.09 \cdot 10^{-4}$	$5.94 \cdot 10^{-4}$	98	97	56
	2.5%	0.94	0.36	0.041	$4.10 \cdot 10^{-4}$	$6.40 \cdot 10^{-4}$	98	96	97
	3%	0.80	0.47	0.031	$5.52 \cdot 10^{-4}$	$6.89 \cdot 10^{-4}$	97	96	79



**Figure 1** Effect of current density on the cathodic and anodic potential of tin coated steel in 1.0M monochloroacetic acid in absence and presence of inhibitors

Anodic Tafel slopes increase and cathodic Tafel decrease in presence of inhibitors. However, decrease in cathodic Tafel slopes is significantly large. From polarization curves, it is clear that both anode and cathode are polarized with addition of inhibitor. However, anodic polarization is more than that of cathodic polarization. So, selected inhibitors act as anodic inhibitors.

Upon anodic polarization, the slope of the curve changes sharply with respect to blank due to significant increase of anodic currents and emergence of two Tafel regions and these slopes and potentials of transition zone changed depending upon the inhibitor concentration. At second region of the current, current increased rapidly. The slopes of the polarization curve decreased or increased (uncertain) with increasing inhibitor concentration. The current density of all investigated compounds at different concentrations when reverse scanned tended to reach the blank curves.

The shift of potential to positive values and more significant change of anode currents in comparison with cathode current show that the studied compounds function as inhibitors of mixed type with predominant influence of anodic process.

**Table 2** Effect of Corrosion current density ( $I_{\text{corr}}$ ) on Tin Coated Steel in 0.5M Monochloroacetic acid in presence of of chromate and dichromates

Name of the inhibitor	concentration	Cathodic Current	Anodic Current	Corrosion Current
Nil	-----	0.0200	0.0251	0.0111
Potassium chromate	10%	0.0028	0.0044	0.0017
	11%	0.0041	0.0064	0.0025
	11.5%	0.0033	0.0044	0.0019
	12%	0.0028	0.0044	0.0017
Potassium Dichromate	1%	0.0023	0.0003	0.0014
	2%	0.0012	0.0014	0.0006
	2.5%	0.0018	0.0028	0.0011
	3%	0.0013	0.0018	0.0008
Sodium chromate	10%	0.0028	0.0038	0.0016
	11%	0.0010	0.0019	0.0007
	11.5%	0.0026	0.0035	0.0015
	12%	0.0018	0.0026	0.0011
Sodium dichromate	1%	0.0023	0.0033	0.0013
	2%	0.0012	0.0017	0.0007
	2.5%	0.0010	0.0012	0.0006
	3%	0.0015	0.0024	0.0009
Ammonium dichromate	1%	0.0018	0.0023	0.0010
	2%	0.0013	0.0018	0.0008
	2.5%	0.0017	0.0023	0.0010
	3%	0.0014	0.0018	0.0008

Potentiodynamic studies showed that the activity of inhibitor is connected not only with the blocking of metal surface at the expense of adsorption of inhibitor molecules, but also with a significant change of mechanism of anode and cathode reactions. The change of polarization curve gives the evidence that used compounds inhibit one or more adjoining reactions on the electrode surface. The inhibitor efficiency of a compound depends on the molecular size, molecular structure and mode of interaction with metal surface.

The presence of inhibitors results in marked shift in both cathodic and anodic branches of polarization curves compared to the blank. This displacement means that the inhibitors influence both cathodic and an anodic process [27] i.e. reduces cathodic hydrogen evolution and anodic dissolution of the steel. In general, a cathodic inhibitor shifts the corrosion potential to negative direction w.r.t uninhibited condition. And an anodic inhibitor shifts corrosion potential to positive direction w.r.t uninhibited condition. Also  $I_{\text{corr(unin)}} > I_{\text{corr(in)}}$  and  $E_{\text{corr(unin)}} < E_{\text{corr(in)}}$  for electrolytes to which anodic inhibitors is added. In present study,  $I_{\text{corr(unin)}} > I_{\text{corr(in)}}$  for all the selected inhibitors and it reveals for predominance of anodic polarization and declares that all selected inhibitors are anodic inhibitors.

As reflected from Tafel curves Table 1, the inhibitors reduce both the anodic cathodic currents diversions suggest that the chromate and dichromates are mixed type of inhibitors. The inhibitors inhibit the corrosion by physical adsorption or chemisorption or film formation. All these processes involve the electrostatic interactions between the metal surface and the inhibitors. The negative ions get adsorbed on the positively charged metal surface.

The corrosion current values decreases on increasing the concentration of the inhibitor and the polarization increases with increase in the concentration of the inhibitor. The corrosion current indicate that the corrosion rate is

significantly reduced by the effect of formation of the thin oxide layer, passive layer and the thickness of the layer increases with increase in passivation.

Both cathode and anode were polarized by the addition of the chromates and dichromates but the anodic polarization was more significant. In potassium chromate, the corrosion potential shift in positive direction for both the cathode and anode curves. On increasing the concentration the anode gets significantly polarized. The anode show positive and cathode show negative value in presence of sodium chromate revealed that both the areas get affected. The dichromates of potassium show the negative polarization and dominantly affect cathodic areas whereas dichromate of sodium polarizes the anodic area more than the cathodic areas. Similar behaviour is shown by ammonium dichromates but the magnitude of the polarization is larger than the others selected inhibitors.

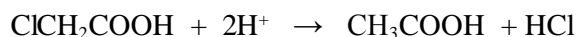
The corrosion current was obtained by the extrapolations of the linear parts of the cathodic and anodic polarization curves.  $I_{corr}$  is determined by polarization break method using the following equation

$$I_{corr} = \frac{I_p - I_q}{I_p + I_q} \quad (2)$$

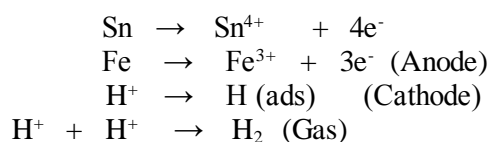
Where,  $I_p$  and  $I_q$  are cathodic and anodic intercepts respectively. If  $I_p$  is greater than  $I_q$ , the reaction is under anodic control and  $I_{corr}$  is close to value of  $I_q$ . Conversely if  $I_q$  less than  $I_p$ , the reaction is under cathodic control and  $I_{corr}$  is close to  $I_p$ . The calculated  $I_{corr}$  values are presented in table 2. As per values of  $I_{corr}$ , it is evident that corrosion reactions in present set of experimental condition are under anodic control.

### Mechanism of the corrosion

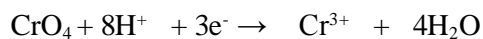
The mechanism of the corrosion and its inhibition in 1.0M monochloroacetic acid can be explained on the fact that the rate of corrosion was low and it increases with time. Dissociation of monochloroacetic acid produces hydrochloric acid and acetic acid. The acids produced react with tin coated steel and liberate hydrogen gas. The liberated gas further reduce the monochloroacetic acid auto catalytically.



The acids produced dissolve the metal and the following corrosion reactions takes place



A high rate of metal dissolution is expected if cathodic curve intersects in the anodic curve in active region. Thus addition of inorganic inhibitors in proper concentration prevent the corrosion by passivation. Passivation can take place either or due to physical or chemical adsorption. Here adsorption of negatively charged chromates or dichromates ions on positively charged metal surface in presence of positive ions takes place, it is called as synergistic adsorption. This phenomenon is caused by sharing of charges or charge transfer between inhibitor species and metal surfaces. It is basically chemisorption. The process of film formation is complex and it depends on its thickness, composition, solubility, temperature and other physical forces. Dichromates and chromates form passive films which resist corrosion and do not require oxygen for passivation. Chromates are reduced to form chromium (III) according to following reaction



A mixed potential is created by oxidation of iron and reduction of chromium and this potential lies in passivation region. So, a mixed oxide is formed due to iron oxide and chromium oxide ( $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ ) [29].

On the basis of the functioning, the inhibitors are of two types: type A which form the inhibiting layer on the metal surface and, type B those which reduces the aggressiveness of the environment or AB Type (mixed) those which is both type A and B. In the present study, the dichromates and chromates act as A type inhibitors. On addition of inhibitors, the active sites of the metals were occupied by the inhibitor molecules due to strong forces of attraction. The complex ions are formed apparently on the surface of the metal.

## Conclusion

The inhibition efficiencies increase with increase in concentration of the inhibitor. It is also found that among the dichromates used the ammonium dichromate is more efficient than the others. The pronounced shift of potential in the positive direction is indicative of predominance of anodic polarization on the addition of the inhibitors. This shows that the chemisorption of the molecules takes on the metallic surface by complexation of the molecules on metal ions which remain in a solid state and function as passivators. A synergistic type of adsorption is proposed.

Chromates and Dichromates polarize both the electrodes and change the Tafel slopes of both currents but dominantly act as anodic inhibitors. Dichromates are found better inhibitors than chromates. The efficiency of inhibitors obtained by the potentiodynamic polarization methods and weight loss method are in close agreement.

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