



Polarization Studies on Inhibitory Effect of Chromates and Dichromates on Corrosion of Tin Coated Steel in 0.5M Monochloroacetic Acid

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Abstract: Chromates and Dichromates have been tested for its inhibitory effects towards tin coated steel in 0.5M monochloroacetic acid. The corrosion behaviour of potassium chromate, sodium chromate, potassium dichromate, sodium dichromate and ammonium dichromate was studied by polarization curves, Tafel parameters like Tafel slopes, extrapolation of cathodic Tafel line and intersection of cathodic and anodic line at open circuit potential in presence of inhibitors have been tabulated along with other electrochemical parameters and corrosion current have been calculated from Tafel lines. The efficiencies are calculated and compared reasonably well with those obtained from loss in weight data. All the inhibitors induce a significant increase of potential positive and direction accounts for cathodic polarization. The I_{corr} has also been calculated and that accounts well for cathodic reactions in presence of chromates and dichromates as inhibitors.

Keywords: Polarization, Tin Coated Steel, Potassium chromate, Potassium dichromate, Sodium chromate, Sodium dichromate and Ammonium dichromate, Monochloroacetic acid.

Introduction

Corrosion of metal is a major industrial problem that has attracted a lot of investigators in recent years¹⁻³. Corrosion inhibitors are of great practical importance, being extensively employed in minimizing metallic waste in engineering materials². Electrolytic tin plate undoubtedly enjoys the pride of place as a packaging medium especially for food. It owes its unique position to its “nine layers sandwich structure”, each of which contributes to its eminence as a packing material.

Tin coated steel is used for baby food tins, milk powder tins, coffee tins, oil cans *etc.* Today TCIL, India is also capable of supplying excellent quality of thin strip DR for Instant Coffee packaging and other OTS products in the range of 0.17mm, 0.19mm and 0.21mm respectively.

Detailed review of literature has revealed that bulk of work is carried out on mild steel and a little work is available on coated steel. Only a few references are available on tin coated steel.

Experimental

Tin coated steel used in present work has procured by 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 were of A.R. grade. All the solutions were prepared in conductivity water and standardized by different methods⁴ and their purities were checked by noting their melting points, solubility and crystallization method⁵.

For polarization studies

The metal coupon was of circular design, diameter 2.8 cm with a handle 3 cm long and 0.5 cm wide. The specimen was first washed distilled with water followed by alcohol-acetone mixture and dried. The handle and the back of the test coupon as well as of the auxiliary platinum electrode were coated with first paraffin wax and then coated with perspex from ethyl acetate solution, leaving only the circular portion having an apparent surface area of tin coated steel exposed to the corrosive medium.

In present study, the metal coupon which was circular in design and prepared with perspex leaving only a circular portion of apparent surface area is a working electrode. The other electrode was platinum of the same dimension and called auxiliary electrode. For these measurements, H-type pyrex glass cell with porous partition to separate the two compartments was used. It also contained a built in capillary to make connection to the reference saturated calomel electrode. In each compartment, the volume of corrosive media was 80 ml. For maintaining temperature the specimen in a corrosive medium were placed in "High Precision Water Bath" Cat. No. MSW – 274 with readability $\pm 0.1^\circ\text{C}$.

After the tests, the specimen can be cleaned with saturated ammonium acetate solution⁶⁻⁷. But in present study only distilled water was used to remove corrosion products of tin coated steel in monochloroacetic acid.

The electrochemical cell used here for potentiodynamic polarization studies was a three electrode system with (1) working (2) reference and (3) counter. A saturated calomel electrode (SCE) has been used as reference electrode.

Results and Discussion

The influence of current density on the cathodic and anodic polarization of tin coated steel in 0.5M monochloroacetic acid containing (0.1%, 0.5%, 1%, 1.5%) of inhibitor has been studied according to Evans diagram (fig. 1). 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 reaction:

$$\eta = \left(\frac{I_{\text{corr without Inhibitor}} - I_{\text{corr with Inhibitor}}}{I_{\text{corr without Inhibitor}}} \right) * 100 \quad (1)$$

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 show a good agreement in efficiencies of inhibitor as evaluated from loss in weight data. Tafel parameters and efficiencies of inhibitors for 0.5M monochloroacetic acid are presented in Table 1 and the polarization curves are given in Figure 1-5.

Table 1. Tafel parameters and efficiency of Inhibitors of Tin Coated Steel in 0.5M Monochloroacetic acid at Temperature : 35±0.1°C

Name of Inhibitor	Inhibitor Concentration %	Tafel slope β		Energy Transfer coefficient α	Corrosion current		Inhibitor Efficiency from Extrapolation %	Inhibitor Efficiency from Intersection %	Inhibitor Efficiency from weight loss method %
		Anodic Volts	Cathodic Volts		From extrapolation of Cathodic Tafel line	From intersection of Cathodic and Anodic line at open circuit potential			
Nil		0.69	1.27	0.012	7.94×10^{-3}	8.41×10^{-3}			
	0.10	0.58	0.77	0.019	1.31×10^{-3}	2.4×10^{-3}	84	71	
Potassium chromate	0.50	1.09	0.72	0.020	7.30×10^{-4}	1.00×10^{-3}	91	88	
	1.00	2.04	1.16	0.013	1.00×10^{-3}	1.17×10^{-3}	87	86	77-85
	1.50	2.22	0.86	0.017	1.41×10^{-3}	1.92×10^{-3}	82	77	
	0.10	0.43	0.68	0.021	1.26×10^{-3}	1.24×10^{-3}	84	85	
Potassium dichromate	0.50	1.3	1.46	0.010	1.66×10^{-3}	2.29×10^{-3}	79	73	
	1.00	2.68	0.49	0.030	1.00×10^{-3}	1.38×10^{-3}	87	84	78-88
	1.50	1.79	0.76	0.019	1.38×10^{-3}	2.14×10^{-3}	83	75	
	0.10	0.29	0.56	0.026	7.20×10^{-4}	1.56×10^{-3}	91	81	
Sodium chromate	0.50	1.38	0.66	0.022	1.24×10^{-3}	1.92×10^{-3}	84	77	
	1.00	1.87	0.72	0.020	1.24×10^{-3}	1.70×10^{-3}	84	80	84-94
	1.50	3.01	0.65	0.022	1.41×10^{-3}	1.60×10^{-3}	82	81	
	0.10	0.54	0.62	0.024	7.90×10^{-4}	1.24×10^{-3}	90	85	
Sodium dichromate	0.50	1.09	0.69	0.021	1.00×10^{-3}	1.37×10^{-3}	87	84	
	1.00	1.75	0.91	0.016	1.28×10^{-3}	1.66×10^{-3}	84	80	70-81
	1.50	1.96	0.97	0.015	2.15×10^{-3}	2.78×10^{-3}	73	67	
	0.10	0.84	0.66	0.022	1.72×10^{-3}	2.88×10^{-3}	78	66	
Ammonium dichromate	0.50	2.2	0.76	0.019	1.92×10^{-3}	2.47×10^{-3}	76	71	
	1.00	1.98	0.61	0.024	1.17×10^{-3}	1.41×10^{-3}	85	83	84-94
	1.50	1.74	0.63	0.023	1.10×10^{-3}	1.41×10^{-3}	86	83	

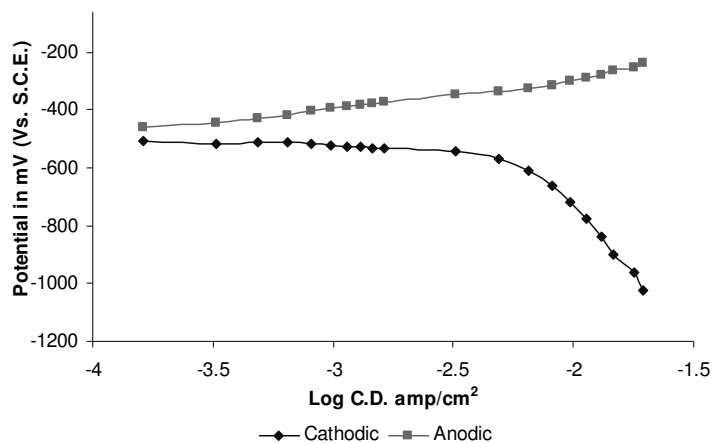


Figure 1. Effect of varying current density on the cathode and anode potential of tin coated steel in 0.5M monochloroacetic acid

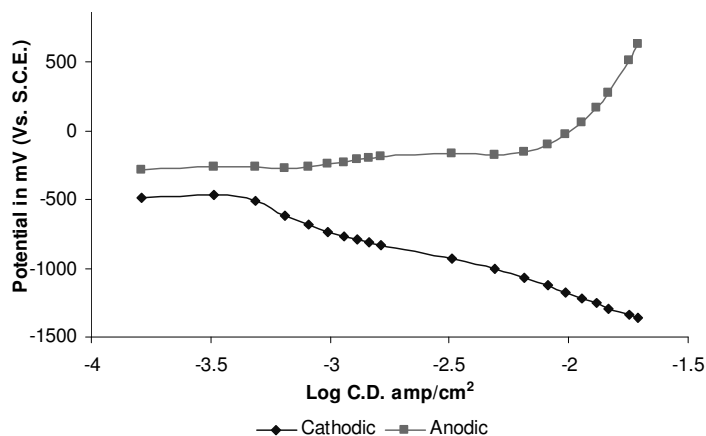


Figure 2. Effect of varying current density on the cathode and anode potential of tin coated steel in 0.5M monochloroacetic acid in the presence of 0.1% Potassium chromate

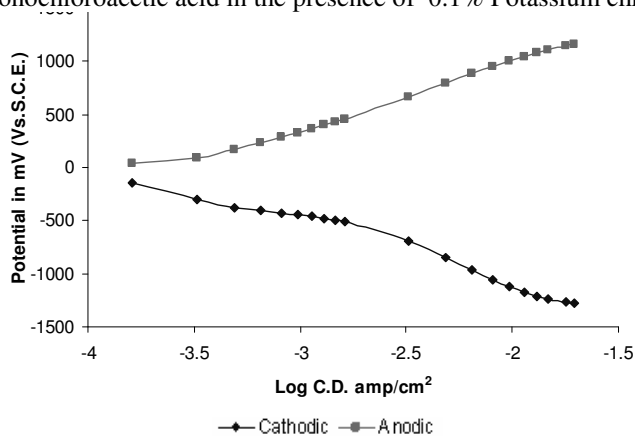


Figure 3. Effect of varying current density on the cathode and anode potential of tin coated steel in 0.5M monochloroacetic acid in the presence of 0.5% Potassium chromate.

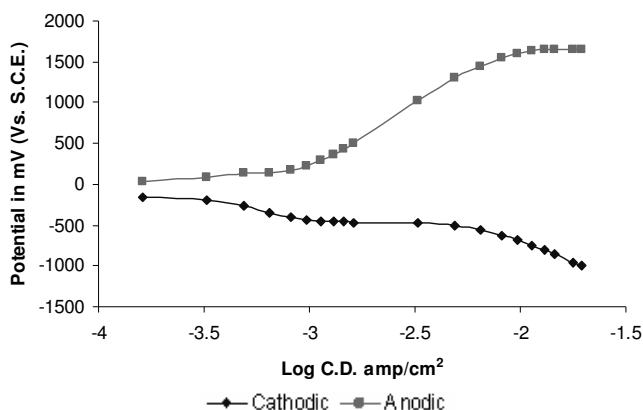


Figure 4. Effect of varying current density on the cathode and anode potential of tin coated steel in 0.5M monochloroacetic acid in the presence of 1.0% Potassium chromate

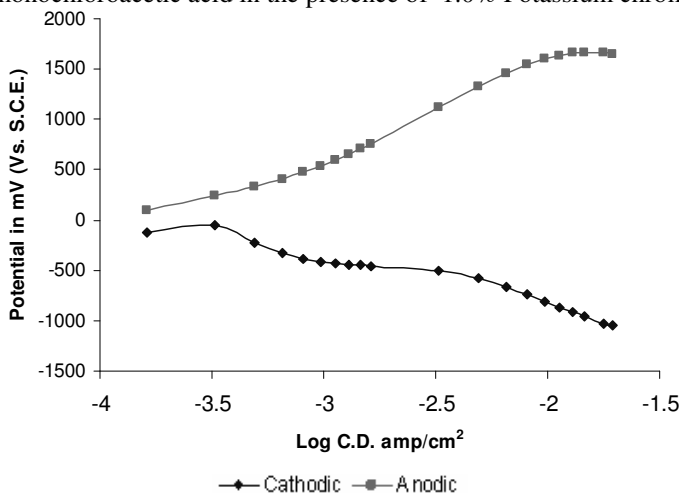


Figure 5. Effect of varying current density on the cathode and anode potential of tin coated steel in 0.5M monochloroacetic acid in the presence of 1.5% Potassium chromate

In 0.5M monochloroacetic acid, the corrosion potential of tin coated steel is -463 mV. In acidic medium, in general the shift of corrosion potential in the negative direction in presence of inhibitors give indication for the immediate effect of the inhibitor on the anodic reaction; however all the inhibitors induce a significant increase in positive direction accounts for cathodic polarization. The initial shift of the potential is the consequence of both polarization effects and of change in the ratio of anodic and cathodic areas. Thus the pronounced shift of potential in the negative direction indicative of cathode polarization by impressed currents need not be considered as inconsistent with the steady state potential shifting in the positive direction on the addition of the inhibitors. It may be that the effect of an inhibitor can be either a change in the exchange current or an increase in polarization or both.

With chromates and dichromates as inhibitors initially there is a high shift in potential a positive direction and with increase in inhibitor concentration there is an increase in the shift, which shows that cathodic action comes into play with decrease in initial value. In 0.5M monochloroacetic acid at 1% concentration of both chromates and dichromates induce a significant increase in

cathode polarization. At current density of 1.62×10^{-3} the shift of cathode potential during cathodic polarization is -327mV as compared to -532mV in uninhibited 0.5M monochloroacetic acid in presence of 1% potassium dichromate. In 0.5M monochloroacetic acid, potassium chromate, potassium dichromate, sodium chromate, sodium dichromate and ammonium dichromate act as a inhibitor by influencing cathodic reactions and this behavior increases with increase in concentration till optimum concentration is achieved. These results are in good agreement with results obtained by loss in weight method.

I_{corr} is determine by polarization break method using the following equation

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

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 greater than I_p reaction is under cathodic control and I_{corr} is close to I_p .

The I_{corr} value are calculated and presented in table 2. As per values of I_{corr} , it is evident that corrosion reactions in present set of experimental condition are under cathodic control.

Table 2. Effect of corrosion current density (I_{corr}) on tin coated steel in 0.5M monochloroacetic acid in presence of chromates and dichromates

Inhibitor name and its concentration		i_p	I_q	I_{corr}
Nil		0.011	0.02	0.00709677
Potassium chromate	0.1%	0.004875	0.006427	0.00277222
	0.5%	0.002972	0.008831	0.00222365
	1.0%	0.00537	0.008831	0.00333938
	1.5%	0.006687	0.012	0.00429411
Potassium dichromate	0.1%	0.004018	0.01	0.00286631
	0.5%	0.004325	0.007244	0.00270813
	1.0%	0.002582	0.003342	0.00145662
	1.5%	0.006368	0.014	0.00437706
Sodium chromate	0.1%	0.003162	0.011	0.00245601
	0.5%	0.003698	0.016	0.00300376
	1.0%	0.003936	0.006081	0.00238942
	1.5%	0.004457	0.005715	0.0025041
Sodium dichromate	0.1%	0.004797	0.013	0.00350402
	0.5%	0.004325	0.014	0.00330423
	1.0%	0.004055	0.01	0.00288509
	1.5%	0.008241	0.0136	0.00513152
Ammonium dichromate	0.1%	0.006945	0.01	0.00409855
	0.5%	0.01	0.011	0.0052381
	1.0%	0.006887	0.008299	0.00376368
	1.5%	0.00537	0.006471	0.00293466

Conclusion

Chromates and dichromates act as cathodic inhibitors. Tafel parameters and corrosion current density, I_{corr} values support this argument. The initial shift of the potential is the

consequence of both polarization effects and of change in the ratio of anodic and cathodic areas. Thus the pronounced shift of potential in the negative direction indicative of cathode polarization by impressed currents need not be considered as inconsistent with the steady state potential shifting in the positive direction on the addition of the inhibitors. It may be that effect of an inhibitor can lead either (i) a change in the exchange current or (ii) an increase in polarization or (iii) both.

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