

Chromates and Dichromates as corrosion inhibitors for Tin coated steel in 0.5M Monochloroacetic acid

Sangita Sharma, Kinnari H. Parikh and J.J.Vora*

*Department of Chemistry,
Hemchandracharya North Gujarat University,
Patan -384 265 (Gujarat), India.*

Email : smridhee2000@yahoo.co.in

Abstract : The corrosion behavior of Tin coated steel in monochloroacetic acid and its inhibition by chromates and dichromates were studied by using weight loss technique at 35 to 55 ± 0.1 °C. All the data reveal that chromates and dichromates acts as an inhibitor in the acid environment. The % inhibition efficiency of chromates and dichromates decrease with increase in inhibitor concentration, period of immersion and temperature. The experimental data fits into the Temkin, Freundlich and Langmuir adsorption isotherms. Thermodynamic parameters for adsorption of chromates and dichromates were calculated from the experimental data.

Keyword : Potassium chromate, Sodium chromate, Potassium dichromate, Sodium dichromate, Ammonium dichromate, corrosion inhibition, Adsorption isotherms, Tin coated steel, Monochloroacetic acid.

Introduction :

Corrosion is inevitable [1] and is a serious problem because it contribute to depletion of our natural resources, pollution of environment, loss in term of cost and human life in term of accident. Severity of corrosion problem varies from place to place because the process of corrosion depends on a number of factors. Ignorance sometimes is the cause of many premature unexpected and expensive failures due to corrosion problems [2].

Electrolytic Tinplate 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.

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 method [3] and their purities were checked by noting their melting points, solubility and crystallization method [4].

For weight loss studies, rectangular specimens of area 6 cm × 3 cm (thickness 0.21mm) with a small hole of about 2 mm diameters just near the one end (3 cm side end) of the specimen for suspension has been used.

Each specimen was first washed with distilled water and dried. The specimen was finally degreased by A.R. carbon tetrachloride. The test specimens were exposed to 0.5M solution of monochloroacetic acid containing controlled additions of various chromates and dichromates viz., Potassium chromate, Sodium chromate, Potassium dichromate, Sodium dichromate and Ammonium dichromate.

The specimen was weighted in single pan balance (Matelar Tolado AB 204 electronic balance) to an accuracy of $\pm 0.0001\text{gm}$. Then one specimen at a time was suspended by a glass-hook in each beaker (Borosil) which contained 230 ml of the test solution, the solution being open to air at $35 \pm 0.1^\circ\text{C}$ and left exposed to the air for various immersion periods (1 to 4 hours). Similar experiments were also carried out at other temperatures, viz., 40° , 45° , 50° and 55°C . For maintaining temperature the specimen were placed in a corrosive medium 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 solution [5-6]. But in present study only distilled water was used to remove corrosion products of tin coated steel in monochloroacetic acid.

Results and discussion :

The weight loss of the Tin coated steel coupons in 0.5M monochloroacetic acid in the absence and presence of different concentrations of chromates and dichromates at 35 ± 0.1 °C were determined. From the weight loss values determined, the % inhibition efficiencies (% I) were calculated using the following equation [7-8].

$$\% I = \frac{W_u - W_i}{W_u} * 100 \text{ ----- i}$$

Where W_u and W_i are weight loss of metal for tin coated steel in the absence and presence of inhibitor respectively in monochloroacetic acid at the same temperature.

Effect of inhibitor concentration :

The effect of inhibitor concentration on inhibitor efficiency in 0.5M monochloroacetic acid is given in table - 1 and fig. 1

Table : 1
Effect of Concentration of Inhibitor on Corrosion loss (mg/dm²) of Tin Coated Steel in 0.5M Monochloroacetic acid at Temperature 35 ± 0.1 °C
(Efficiency is shown in paranthesis)

Inhibitor	Period of Immersion : 1 Hour			
	Inhibitor Concentration			
	0.5%	1%	1.5%	3%
Nil	4.40	4.40	4.40	4.40
Potassium chromate	2.20 (50)	0.55 (88)	1.38 (69)	2.20 (50)
Sodium chromate	3.58 (19)	0.28 (94)	2.20 (50)	0.83 (81)
Potassium dichromate	3.30 (25)	0.55 (88)	2.20 (50)	3.30 (25)
Sodium dichromate	7.43 (-69)	0.83 (81)	1.65 (63)	2.48 (44)
Ammonium dichromate	2.20 (50)	0.28 (94)	1.10 (75)	1.65 (63)

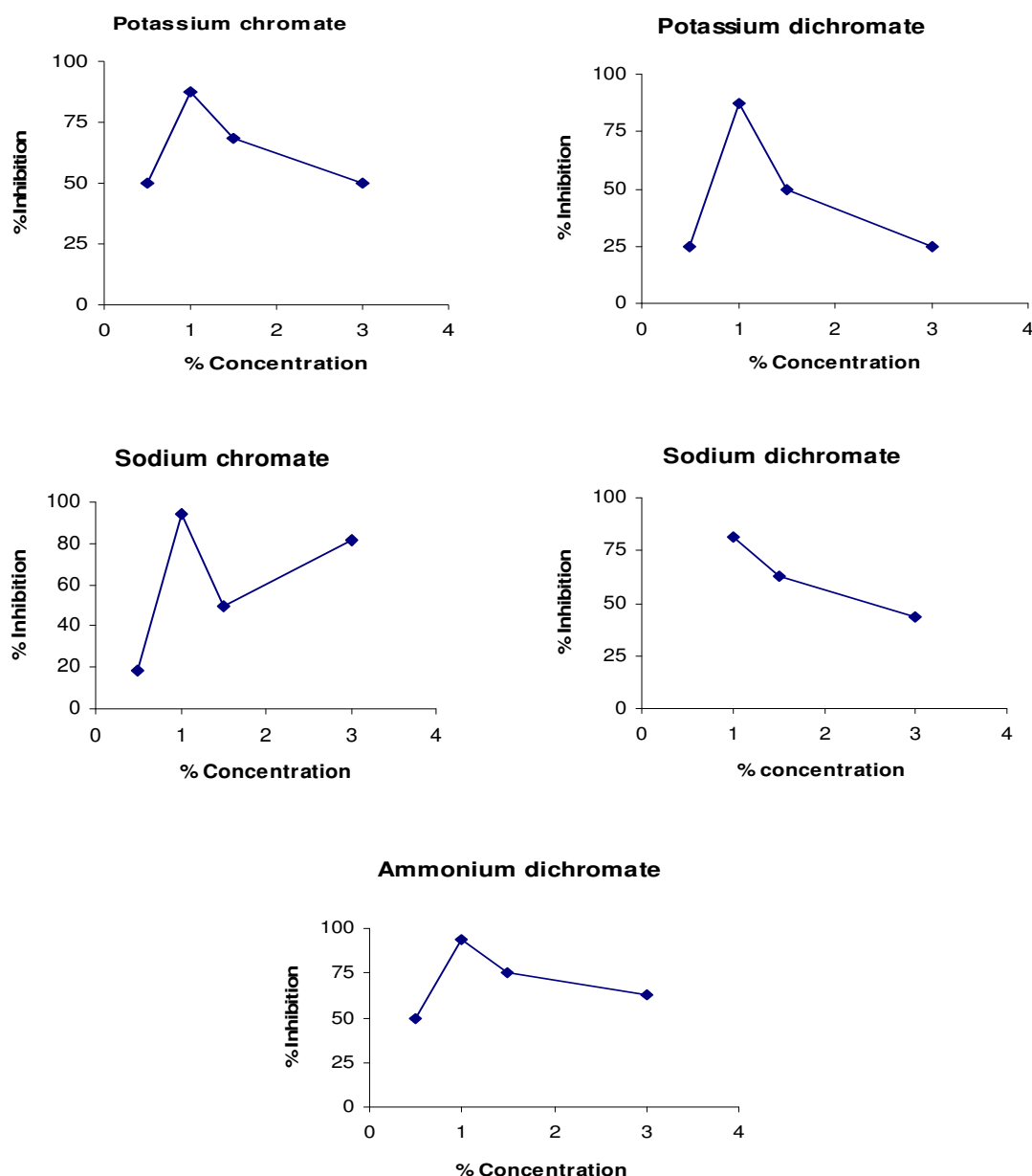


Fig. 1 : Effect of Concentration on inhibitor efficiency of tin coated steel in 0.5M monochloroacetic acid at temperature $35 \pm 0.1^\circ\text{C}$ and period of immersion 1 hour.

Of the inhibitors studied in this programme of work, Sodium chromate and Ammonium dichromate have proved to be the best inhibitor giving 94% protection at 1% concentration and also potassium chromate, potassium dichromate and sodium dichromate have proved to be the good inhibitor giving 88%, 88% and 81% protection at 1% concentration to Tin coated steel in 0.5M monochloroacetic acid solution at temperature $35 \pm 0.1^\circ\text{C}$ and for period of immersion of 1 Hour respectively.

At 1% concentration in 0.5M monochloroacetic acid the order of efficiency of inhibitor are as under :

Sodium dichromate (81%) < Potassium dichromate (88%) < Sodium dichromate (88%) < Ammonium dichromate (94%) < Sodium chromate (94%).

Effect of immersion period :

To determine the effect of immersion period on inhibitive efficiency, weight losses were determined in 0.5M monochloroacetic acid containing 1% inhibitor for immersion periods of 1, 2, 3 and 4 hours (fig. 2). From the inhibitive efficiencies given in table - 2 it may be generalized that the efficiency of Sodium chromate and Ammonium dichromate decrease with time up to an immersion period of 4 hours.

Table : 2

Effect of Period of immersion on corrosion of Tin coated steel in 0.5M monochloroacetic acid at 35 ± 0.1 °C

Period of immersion	Weight loss in mg /dm ²					
	Nil	1% K ₂ CrO ₄	1% K ₂ Cr ₂ O ₇	1% Na ₂ CrO ₄	1% Na ₂ Cr ₂ O ₇	1% (NH ₄) ₂ Cr ₂ O ₇
1	4.4	0.55 (88)	0.55 (88)	0.28 (94)	0.83 (81)	0.28 (94)
2	10.73	1.75 (84)	2.15 (80)	1.1 (90)	3.19 (70)	1.1 (90)
3	17.33	4 (77)	2.75 (84)	2.7 (84)	4.54 (74)	2.75 (84)
4	33	6.88 (79)	7.43 (78)	4.4 (87)	7.43 (78)	4.4 (87)

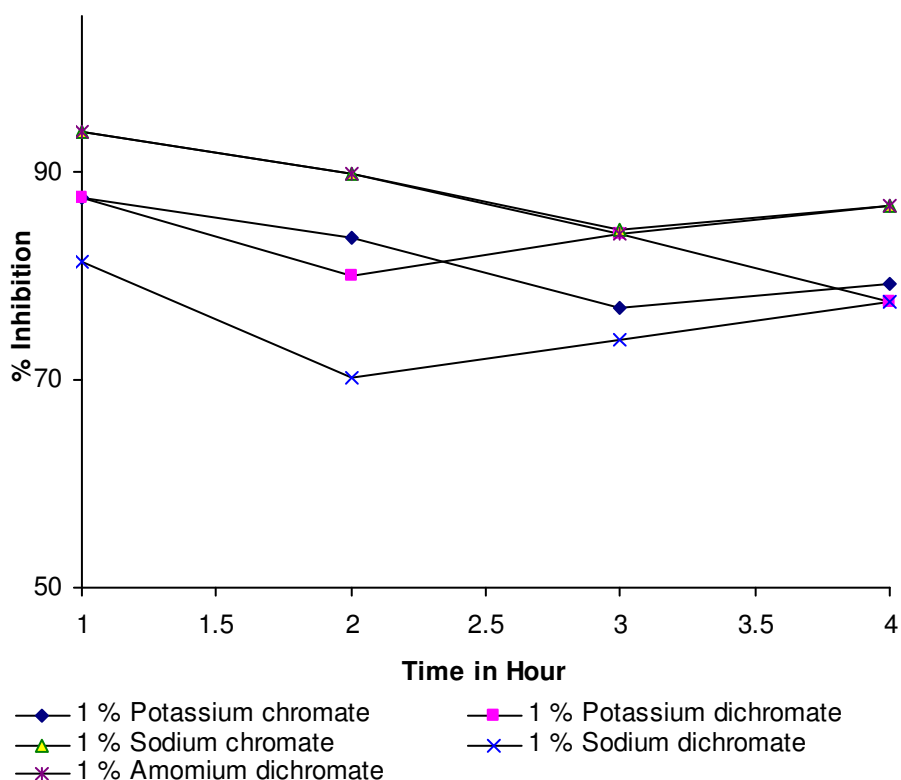


Fig. 2 : Effect of Time on Inhibitor Efficiency of Tin Coated Steel in 0.5M Monochloroacetic acid at Temperature 35 ± 0.1 °C

Out of Potassium chromate, Potassium dichromate and Sodium dichromate is almost similar to that of Sodium chromate.

It is observed that the inhibitor efficiency decreases in most of cases with increase in period of immersion. This may be due to the desorption of the adsorbed inhibitor molecules at more duration of time and thus exposing the metal surface to further attack [9].

For immersion periods ranging from 2 to 4 hour, the general order of inhibitor efficiency is as under :

Sodium dichromate < Potassium dichromate < Potassium chromate < Sodium chromate < Ammonium dichromate.

However, for 1 hour immersion period, the efficiency increases in the same order as 2 to 4 hours.

Effect of temperature on inhibitive efficiency :

To determine the effect of temperature on inhibitive efficiency, weight losses were determined in 0.5M monochloroacetic acid containing 1% inhibitor at solution temperatures of 35°, 40°, 45°, 50° and 55°C in table - 3 and fig. 3. It is seen that the extent of corrosion in inhibited as well as uninhibited acid increases with a rise in temperature, the loss in weight being much higher in plain acid. The result also show that all the five compounds studied decrease the corrosion rate to an appreciable extent, the extent of inhibition ranging from 34 % to 94 %. From the weight losses it may be generalized that here also Sodium chromate and Ammonium dichromate appears to be the best inhibitors.

Table : 3

Effect of Temperature (°C) on Corrosion loss (mg/dm²) of Tin Coated Steel in 0.5M Monochloroacetic acid for immersion period of 1 Hour

Inhibitor (inhibitors concentration)	35 ± 0.1	40 ± 0.1	45 ± 0.1	50 ± 0.1	55 ± 0.1
(Efficiency is shown in parenthesis)					
Nil (mg/dm ²)	4.4	5.8	6.9	8.7	10.5
Potassium chromate (1.0%) mg/dm ²	0.6	0.9	1.1	1.2	2.2
	(88)	(85)	(84)	(87)	(79)
Sodium chromate (1.0%) mg/dm ²	0.3	0.8	0.8	4.0	6.9
	(94)	(86)	(88)	(55)	(34)
Potassium dichromate (1.0%) mg/dm ²	0.6	1.1	2.0	2.2	2.8
	(88)	(81)	(72)	(75)	(74)
Sodium dichromate (1.0%) mg/dm ²	0.8	1.7	1.9	5.2	6.3
	(81)	(70)	(72)	(40)	(40)
Ammonium dichromate (1.0%) mg/dm ²	0.3	0.7	0.7	2.4	2.8
	(94)	(89)	(90)	(73)	(74)

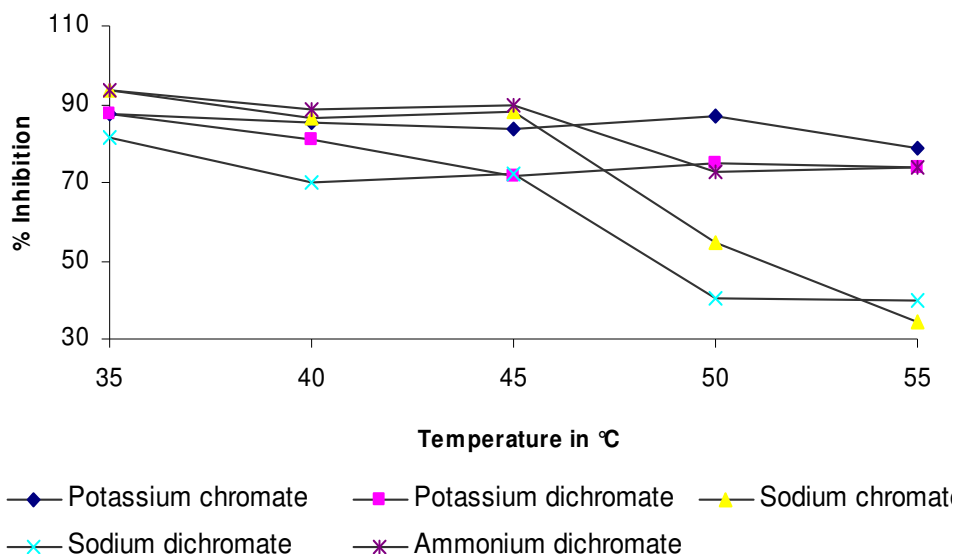


Fig. 3 : Effect of temperature on Inhibitor Efficiency of Tin Coated steel in 0.5 M Monochloroacetic acid

The value of Energy of activation, E_a were calculate with the help of the equation

$$\log\left(\frac{p_2}{p_1}\right) = \frac{E_a}{-2.303} * \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{ ----- ii}$$

and also from the plot of $\log p$ Vs $1/T$ where p is the corrosion rate at temperature T (K) and R is the gas constant. From the E_a value (table - 4), it is apparent that for the corrosion of Tin coated steel in uninhibited acid the E_a value is 8.66kcal/mol where as inhibited acid the values are higher and range from 14.12kcal/mol (Potassium chromate) to 32.35kcal/mol (Sodium chromate). In inhibited acid, the E_a values, thus vary and depend on the inhibitive power of the inhibitor. It appears that the exponential term in the Arrhenius equation appreciably changes the E_a value with a slight change in the corrosion rate. The higher value of activation energy in inhibited acid suggest that the adsorption of the inhibitor on the metal surface may be physical or weak in nature [10]. According to Putilova [11] et. al. the behavior of those inhibitors whose activity decreases with a rise in temperature and in whose presence the activation energies are higher in inhibited than in uninhibited acid may be compared with that of unstable catalyst poisons whose adsorption decreases with increasing temperature.

**Energy of Activation (E_a) for the corrosion of Tin Coated Steel in 0.5M
Monochloroacetic acid in presence and in absence of Inhibitors at different
Temperature**

Period of Immersion : 1 Hour

Name of Inhibitor	E_a kcal/mol				Mean E_a kcal/mol
	(35 - 40) °C	(40 - 45) °C	(45 - 50) °C	(50 - 55) °C	
Nil	10.53	6.77	9.84	7.49	8.66
1 % Potassium chromate	16.79	11.05	0.99	27.66	14.12
1 % Sodium chromate	40.87	1.27	64.01	23.26	32.35
1 % Potassium dichromate	26.47	22.77	4.89	9.40	15.88
1 % Sodium dichromate	28.24	4.36	40.63	7.82	20.26
1 % Ammonium dichromate	33.10	2.07	50.77	6.01	22.99

Adsorption characteristics :

The surface coverage (θ) of the Tin coated steel by adsorbed chromates and dichromates were calculated from the corrosion rate by using following equation [12].

$$\theta = \frac{W_u - W_i}{W_u} \quad \text{..... iii}$$

Where W_u and W_i are the corrosion rates in the absence and presence of chromates and dichromates in the 0.5M monochloroacetic acid solution. The θ was found to uncertain with increase inhibitor concentration at the $35 \pm 0.1^\circ\text{C}$ temperature studied.

The nature of inhibition on the corroding surface during corrosion inhibition of metals and alloys has been deduced in terms of adsorption characteristics of the inhibitors [13-14]. The way in which the value of θ for 1% Sodium chromate varied at constant temperature with the logarithm of

Inhibitor concentration show in fig. 4 conformed to the Temkin isotherm, which is formulated as [15]

$$\text{Exp} (-2a\theta) = k c \quad \text{----- iv}$$

Where 'a' is molecular interaction parameter, θ is the surface coverage area. And k is the equilibrium constant which is related to the standard free energy of adsorption below [16].

$$K = \frac{1}{55.5} \cdot \exp \left(\frac{-\Delta G}{RT} \right) \quad \text{----- v}$$

Diagram has been plotted to show dependency of coverage degree on logarithm of inhibitor concentration. The fig. 4 shows that this dependency is in confirmation with Freundlich adsorption isotherm equation written as follows.

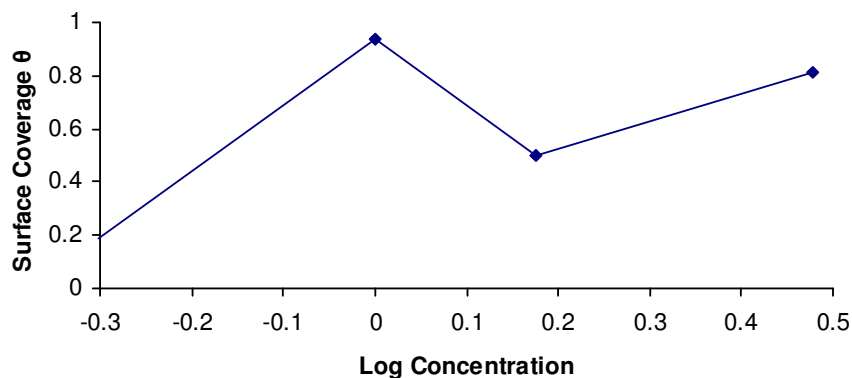
$$\log \theta = \frac{RT}{q_m} - \log a + \frac{RT}{q_m} \log c \quad \text{----- vi}$$

Where 'a' and 'q_m' are constants characterization for given adsorption system.

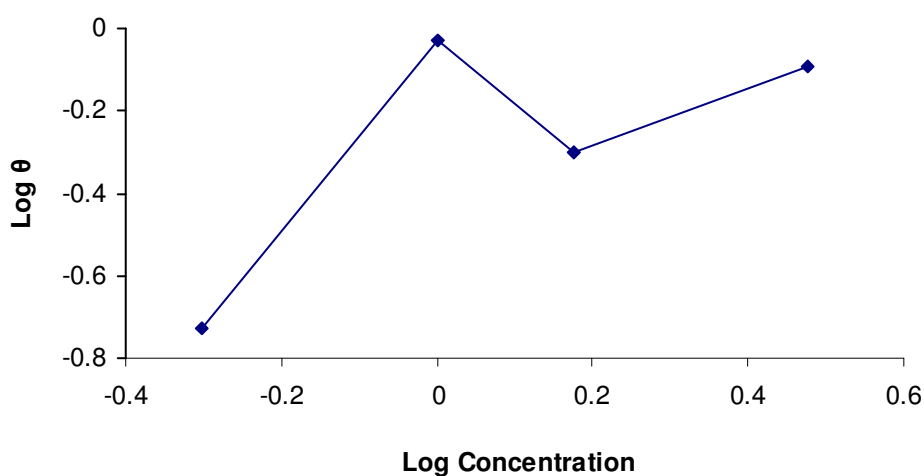
Diagram has been plotted to logarithm of ($\theta/1-\theta$) against logarithm of inhibitor concentration. The fig. 4 show that this dependency is in the confirmation with Langmuir adsorption isotherm equation as follows.

$$\log \left(\frac{\theta}{1-\theta} \right) = \log k + y \log c \quad \text{----- vii}$$

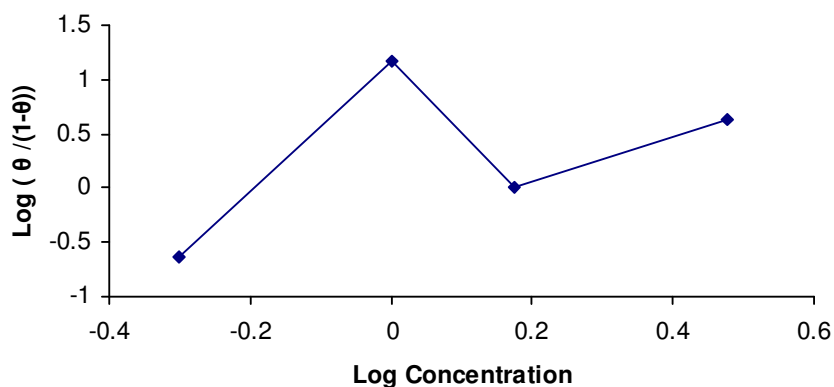
The facts indicate that chemisorptions occurs according to Temkin, Freundlich and Langmuir adsorption model and that the metal surface is heterogeneous.



Temkin adsorption isotherm



Freundlich adsorption isotherm



Langmuir adsorption isotherm

Fig. 4 : Adsorption isotherm in presence of Sodium Chromate as inhibitor in 0.5M Monochloroacetic acid

Study of Thermodynamic Parameters:

The thermodynamic functions like standard free energy of adsorption (ΔG), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) are estimated in the presence of inhibitors for 0.5M monochloroacetic acid and are given in table - 5

Table : 5

Thermodynamic Parameters of Free energy of adsorption (ΔG), Enthalpy of adsorption (ΔH) and Entropy of adsorption (ΔS) for various Inhibitors in 0.5M Monochloroacetic acid

Temperature : 35 ± 0.1 °C

Period of Immersion : 1 Hour

Sr.No.	Name of Inhibitor	ΔG	ΔH	ΔS
		$kcal\ mol^{-1}$	$cal\ mol^{-1}\ K^{-1}$	$cal\ mol^{-1}$
1	1 % Potassium chromate	-5.38	0.67	17.48
2	1 % Sodium chromate	-4.62	-5.63	14.97
3	1 % Potassium dichromate	-3.84	1.07	12.48
4	1 % Sodium dichromate	-7.80	6.92	25.34
5	1 % Ammonium dichromate	-6.54	-0.35	21.22

[I] Free energy of adsorption

Free energy of adsorption (ΔG) was calculated from the thermodynamic kinetic model (a modified langmuir adsorption isotherm fit) [17-20].

$$\frac{\theta}{1-\theta} = k_c * \exp\left(\frac{-\Delta G}{RT}\right) \quad \text{----- viii}$$

The equilibrium constant is related to the free energy of adsorption by the equation below [21].

$$k = -1.74 - \left(\frac{\Delta G}{2.303RT}\right) \quad \text{----- ix}$$

The relation $\log (\theta/1-\theta)$ against $\log c$, where c is the inhibitor concentration is linear showing an adsorption on the metal and alloy surface electrode according to the Langmuir isotherm [19].

Negative values [22] of ΔG indicates strong interaction of inhibitor molecule and spontaneous adsorption of inhibitor on the Tin Coated Steel surface. The standard free energy of adsorption values in 0.5M monochloroacetic acid for inhibitors under investigation are within limit of -7.80 to -3.84 kcal/mol. Such results have been observed in majority of inhibitors of various types in acid aqueous media [23-26].

However in 0.5M acid, where in inhibitor efficiency are more differentiated because ΔG values are more negative for good inhibitor like for Sodium dichromate and Ammonium dichromate than those of less efficient inhibitors like Potassium dichromate.

[II] Enthalpy and Entropy of adsorption

Enthalpy of adsorption and Entropy of adsorption were calculated this equation as under

$$\Delta H = - \text{slope} \times 2.303 R \quad \text{----- x}$$

Where R is gas constant.

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad \text{----- xi}$$

This agrees with general suggestion that more negative values of ΔG and positive value of ΔS leads to increase in inhibitor efficiency [27].

The positive values of entropy of adsorption ΔS suggest the adsorption to be a spontaneous process. But order of efficiency of different inhibitors and the order of decrease or increase w.r.t. ΔS do not agree and these suggest decrease in free energy is the controlling factor in adsorption process.

Conclusion.

In general for all selected inhibitors, rate of corrosion increases with rise of temperature and increase in immersion period; and efficiency of inhibitors decreases with rise of temperature. From weight loss data it may be generalized that corrosion protection is high for short period of time for all the

inhibitors. The negative value of free energy and small value of heat of adsorption for all inhibitors suggest for strong interaction of inhibitor molecules and spontaneous adsorption on metal surface and adsorption may be physical type. Dichromates and Chromates are passivator type of corrosion inhibitors and as per electrochemistry passivators reduce cathodic areas at a current density equivalent to that at anodic areas which is itself greater than critical current density of metal and passivation of metal occurs. Passive areas became noble to adjacent areas and passivity results over the entire metal surface.

References

- [1] R. Balasubramaniam, *Current science*, **84**(2), pp25, 2003.
- [2] G. Mars Fontana, '*Corro. Engineering*', 3rd edition, Mc Graw Hill Book Company, 4, 1987.
- [3] G.H. Jeffery and J. Basset et. al., '*Vogel's Text Book of Quantitative Chemical Analysis*', 5th edition, Longman, 1989.
- [4] The Merck Index, '*An Encyclopedia of Chemical, Drugs and Biologicals*', 12th edition, Merck and Co. Inc., 1996.
- [5] F.A. Champion, '*Corrosion testing procedures*', Chapman and Hall, London, pp194, 1964.
- [6] F.N. Speller, '*Corrosion causes and prevention*', Mc Graw Hill, New York, pp38, 1951.
- [7] J.D. Talati and R.M. Modi, *Trans. SAEST*, **11**, pp259, 1986.
- [8] L.A. Al-Shamma, J.M. Saleh and N.A. Hikmat, *Corros. Sci.*, **27**, pp221, 1987.
- [9] N.S. Rawat and A.K. Singh, *Bull. Electrochem.*, **3**, pp7, 1987.
- [10] P.K. Ghosh, D.K. Ghasarkar and V.S. Gupta, *British Corros. J.*, **18**, pp287, 1983.
- [11] I.N. Putilova, S.A. Balezin, and V.P. Barannik, '*Metallic Corrosion Inhibitors*', Pergamon Press, pp31, 1960.
- [12] B.G. Ateya, B.E. Anadouli and F.M.A. El-Nizamy, *Bull. Electrochem.*, **17**, pp437, 2001.
- [13] R.K. Dinnapa and S.M. Mayanna, *J. Appl. Electrochem.*, **11**, pp111, 1982.
- [14] R.K. Dinnapa and S.M. Mayanna, *Corrosion*, **38**, pp525, 1982.
- [15] U.J. Ekpe, U.J. Ibok, O.E. Offiong, B.I. Ita and E.E. Ebenso, *Mater Chem. Phys.*, **40**, pp87, 1995.
- [16] S. Bilgic and M. Sahin, *Mater. Chem. Phys.*, **70**, pp292, 2001.
- [17] S. Murlidharan, M.A. Quraishi and S.V.K. Lyer, *Corros. Sci.*, **37**, pp1739, 1995.
- [18] A. El-Away, A. Abd El-Nabey and S. Aziz, *J. Electrochem. Soc.*, **139**, pp2149, 1992.
- [19] I. Langmuir, *J. Amer. Chem. Soc.*, **39**, pp1848, 1947.

- [20] A.M.S. Abdel and E.L.A. Saiyed, *Trans. SAE*, **16**, pp197, 1981.
- [21] H.M. Bhajiwala and R.T. Vashi, *Bull. Electrochem.*, **17**, pp446, 2001.
- [22] H.B. Rudresh and S.M. Mayanna, *J. Electrochem. Soc. India*, **31**, pp109, 1982.
- [23] D. Prasad, G.S. Jha, B.P. Chaudhary and S. Sanyal, *J. Indian Chem. Soc.*, **79**, 264, 2002.
- [24] N.C. Subramanyam, R.S. Seshadri and S.M. Mayanna, 'Tenth International Congress on Metallic Corrosion', Oxford and I.B.H., New Delhi, **3**, pp3007, 1987.
- [25] D. Prasad and S. Sanyal, *J. Indian Chem. Soc.*, **74**, pp637, 1997.
- [26] S. Sanyal, *Indidan J. Technol.*, **30**, pp16, 1992.
- [27] S. Sanyal, *J. Electrochem. Soc. India*, **39**, pp192, 1990.