

ELECTROCHEMICAL BEHAVIOUR OF MILD STEEL AND BENZOTRIAZOLE IN DILUTE SULPHURIC ACID MEDIUM IN THE PRESENCE OF SODIUM FLUORIDE

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Abstract - Benzotriazole is a good inhibitor for the mild Steel in dilute Sulphuric acid medium. The corrosion of mild steel goes on increasing with increasing the concentration of fluoride ions. After the concentration of 5×10^{-2} M of fluoride ions, it decreases on increasing the concentration of fluoride ions with fixed concentration of Benzotriazole, the inhibitive power is not affected up to certain extent but latter it is diminished. Adsorption of inhibitor on the mild steel follow the Langmuir Adsorption Isotherm. Potentiometric and thermodynamic studies are made to verify the result. Potentiometric study shows the cathodic nature of inhibitor.

Key Words – Benzotriazole, Langmuir adsorption, cathodic inhibitor, sodium fluoride.

Introduction – Loss due to corrosion constitute a public hazard both economically and physically¹. So, this becomes necessary to develop materials like corrosion inhibitor². Generally, It has been found that the organic compound containing Nitrogen has been found to be great effective for the inhibitor of several metals and their alloys in the acidic medium. Now a days, these are used in the mining and petroleum industries. The inhibitors on adsorbing of the metallic surface forms a protective layer of the blockage present at the metallic surface. So the rate of corrosion of the metals decreases. Nitrogen, present in the

structure of the organic inhibitor has significant importance as they provide excellent inhibition properties due to their molecular structure^{3to15}.

The aim of this work is to envisage the performance of BTA as corrosion inhibitor in the presence of Fluoride ion for mild steel in the sulphuric acid medium. The inhibition property of BTA in acid medium for copper and brass

has been studied in the corrosion lab. present in the University Deptt. of Chemistry V. K.S.U. Ara by Singh and et al^{16 to 17}. But, a better result has been obtained for the mild steel in different environmental conditions of the solution. The effect of temperature, on corrosion rate has been found very effective. The synergistic effect of Fluoride ions with BTA has also been studied^{18 to 20}.

Experimental Essay – 99.9% pure NaF, made in Germany. 1,2,3-Benzotriazole of synthetic grade manufactured by LOBA CHEMIE Indo. Australian CO Bombay India as inhibitor. Mild steel used for the study was size 2 inch x 1 inch (Surface area 4 Sq inch)

Mild steel having percentage of Fe = 99.746, Mn = 0.1, C = 0.058, Al = 0.033, Cr

= 0.008, Cl = 0.010, Cu = 0.004, Mo = 0.002 and Ni = 0.0029 was used for panel of mild steel, concentration of Acid was of PH = 3.0, 3.5 and 4.0.

Experiment

Weight Loss method - The Specimens were immersed in the Sulphuric acid of different concentrations of PH = 3.0, 3.5 and 4.0 in presence and in the absence of inhibitor. one specimen was suspended in each breaker containing 230 ml of the test Solution at room temperature for 6 h and 18 h respectively. After the immersion surface of the specimen was cleaned with distilled water and also

ringed with acetone. The specimen was again weighed to calculate inhibition by the use of following formulae

$$Pi = 100 \frac{w_1 - w_2}{w_2}$$

Where, w_1 = corrosion rate in the absence of inhibitor
 w_2 = corrosion rate in the presence of inhibitor

The different sets of experiment were performed and weight loss data for each set was calculated.

To study the effect of temperature on corrosion rate, the specimens were immersed in 230 ml of concentrations PH = 3.0 with Benzoriazole as inhibitor of different concentrations. The rate of corrosion was also measured at different temperature 30^0 , 40^0 , 50^0 and 60^0 c. To study the temperature, thermostat was used. From the weight loss measurement; inhibition efficiency, energy of activation and heat of adsorption were calculated.

Polarization Study -To study the polarization, metal specimens were exposed to the solutions, mild steel was as working electrode ,saturated calomel electrode was used as reference electrode and was placed in 230 ml of corrosion media. After that, current was supplied externally from computerized polarization instrument ,potential different was measured by potentiostat . The study was made with and without inhibitors and the synergistic effect of fluoride ions.

Result and Discussion –From the table 1.0 and figure 1.0, on increasing the concentration of BTA, percentage inhibition rate increases up to concentration of BTA 1.0×10^{-3} M, but after addition of more BTA there is no remarkable change takes place in the efficiency of inhibitor. It is due to the fact that on increasing the concentration of BTA the more and more metal gets covered with inhibitor till the whole metal surface gets covered. After that there will be no change in the Inhibition efficiency.

At higher value of PH for the same concentration of BTA (1.0×10^{-3} M) shows relatively high efficiency due to the formation of Benzotriazolium ions with BTA, which are adsorbed on the metal surface (Table 02 and figure02).

In the present study, with rise of temperature from 30° to 50° c, the rate of corrosion increases for the PH = 3.0, and then is decreased . It is due to the fact that the depolarization of oxygen takes place with corrosion of mild steel on increasing the temperature but at higher temperature, dissolved Oxygen becomes less and so the depolarization of Oxygen reaction becomes slow and rate of corrosion decreases (Table03).

The plot of temperature $-1\left(\frac{1}{T}\right)$ and log corrosion rate is found linear in accordance with the equation (1)

$$\log k = -\frac{A}{T} + B \quad \text{--- (1)}$$

Where A and B are constant and K is corrosion rate.

On increasing the temperature, effect of inhibitor is adverse. This may be due to desorption of adsorbed Inhibitor at higher temperature, at PH = 3.0 for 3 Hrs from table (04).

In our study, the rate of corrosion of mild steel goes on increasing with increase in the concentration of fluoride ions but after the concentration of fluoride ion of concentration 5.0×10^{-2} M, It decreases. This is due to the fact that at higher concentration, It has been adsorbed strongly but desorption may not be taking place after hydrolysis. This has been observed from the table(05).

The heat of activation is calculated of from the slope on the plot of log corrosion rate and T . In the absence of the inhibitor, the reaction is fast and therefore, energy of activation is lower. The energy of activation for different concentration of fluoride ions, energy of activation increases on increasing the concentration of fluoride ions as from table (06 to 08)and(figure 03) for fixed PH = 3 of the solution.

When increasing the concentration of fluoride ions with the fixed Concentration of BTA, the inhibitions power is in effective up to certain extent but later on It is diminished (Table 09) . The reason behind, it may be hydrolysis of compound which is formed during the reaction, the hydrolyzed product goes into the solution rather than being adsorbed at the surface of the metal

The Potential-time Study in the Solution in the absence of inhibitor and in the presence of to inhibitor was carried cut on the constant (pH = 3.0). Initially, in the absence of inhibitor, the corrosion potential was - 182 mV. It has been found by the experiment that the change in potential with respect to time, potential increases up to 25 minutes then it rises in the direction of negative potential value and after 40 minutes it becomes more negative. In one hour, the potential of the mild Steel in absence of inhibitor it becomes -187 mV and after 2 hours it again came down to -177 mV, after three hours, Itbecomes

- 172 mV then it becomes constant. After the addition of BTA of concentration (1.0×10^{-4} M) the potential becomes -014mV but in one hour it becomes - 128 mV and again it comes down to – 122 mV after the 15 minutes. but after one hour, it became more active and potential becomes -13 4 mV, and in another 1 hour there is not appreciable change in the potential takes place and almost constant. It has been found the effect of fluoride on corrosion rate and after the addition of BTA at zero time the potential was found -018 mV, when only fluoride was added then after one hour the potential was observed - 097mV but after in another one hour, It did not attain the active range and it was only – 109 mV and final hour, increase in potential towards active region was found much less and it was observed -119 mV. It shows the increase in time, potential accelerates slowly. After the addition of fluoride with Benzotriazole, the potential at zero time was found to 012 mV and then it became nobler. After one hour it was found 031 mV and after two hours, It became 033 mV and in three hours 033 mV, thus It became more passive and the rate of corrosion will be stopped to the extent as shown in the figure(04).

Table -1

Result of Immersion test for mild steel in Sulphuric acid medium for
PH = 03 with different Concentration of BTA

Period of Immersion – 18 Hrs, Temperature –Room Temperature

Inhibitor	concentration of BTA	Percentage of Inhibition
BTA	Zero	Nil
	0.1×10^{-3} (M)	59.010
	0.2×10^{-3} (M)	82.100
	1.0×10^{-3} (M)	90.500
	2.0×10^{-3} (M)	83.200
	3.0×10^{-3} (M)	77.090
	4.0×10^{-3} (M)	73.000

Table -2

Result of Immersion test for mild steel in Sulphuric acid medium for
PH = 03 with different Concentration of BTA

Period of Immersion – 18 Hrs, Temperature –Room Temperature

Concentration of Solution in PH	Rate of Corrosion in mpy
3.0	7.780
3.5	5.330
4.0	5.120

Table -3

Result of Immersion test for mild steel in Sulphuric acid medium (PH = 3.0) at temperature 30^0 , 40^0 , 50^0 and 60^0 c

Period of Immersion = 3Hrs,

Temperature	Rate of corrosion (mpy)	Log corrosion rate	Energy of activation in Kcal per mole
30^0 c	9.726	0.980	5.740
40^0 c	18.583	1.270	
50^0 c	31.550	1.490	
60^0 c	13.840	1.140	

Table -4

Result of Immersion test for mild steel in Sulphuric acid medium inhibition by 1.0×10^{-3} M BTA and Sulphuric acid Solution of PH = 3.0

Period of Immersion = 3Hrs,

Temperature	Rate of corrosion (mpy)	Log corrosion rate (mpy)	Energy of activation Kcal per mole
30^0 c	4.10	0.612	10.225
40^0 c	6.20	0.792	
50^0 c	7.40	0.900	
60^0 c	0.31	-0.500	

Table -5

Result of Immersion test for mild steel in Sulphuric acid, solution of PH = 3.0 in the presence of Fluoride ions.

Period of Immersion = 18 Hrs, At Room Temperature

concentration of BTA	Percentage of Inhibition
1.0×10^{-2} (M)	1.890
3.0×10^{-2} (M)	2.490
5.0×10^{-2} (M)	5.000
7.0×10^{-2} (M)	2.290
9.0×10^{-2} (M)	1.869

Table -6

Result of Immersion test for mild steel in Sulphuric acid medium for PH = 3.0 and F^- ions of concentration 3.0×10^{-2} M

Period of Immersion = 3Hrs,

Temperature	Rate of corrosion (mpy)	Log corrosion rate (mpy)	Energy of activation in Kcal per mole
30^0C	16.311	1.213	9.213
40^0C	17.501	1.246	
50^0C	12.341	0.098	
60^0C	21.001	1.323	

Table -7

Result of Immersion test for mild steel in Sulphuric acid medium for
PH = 3.0 and F⁻ ions of concentration 5.0×10^{-2} M

Period of Immersion =3Hrs,

Temperature	Rate of corrosion (mpy)	Log corrosion rate (mpy)	Energy of activation in Kcal per mole
30 ⁰ c	10.860	1.036	16.590
40 ⁰ c	13.470	1.130	
50 ⁰ c	12.041	1.079	
60 ⁰ c	23.580	1.373	

Table -8

Result of Immersion test for mild steel in Sulphuric acid medium for PH = 3.0 and Fluoride ions of concentration 7×10^{-2} M

Period of Immersion = 3Hrs,

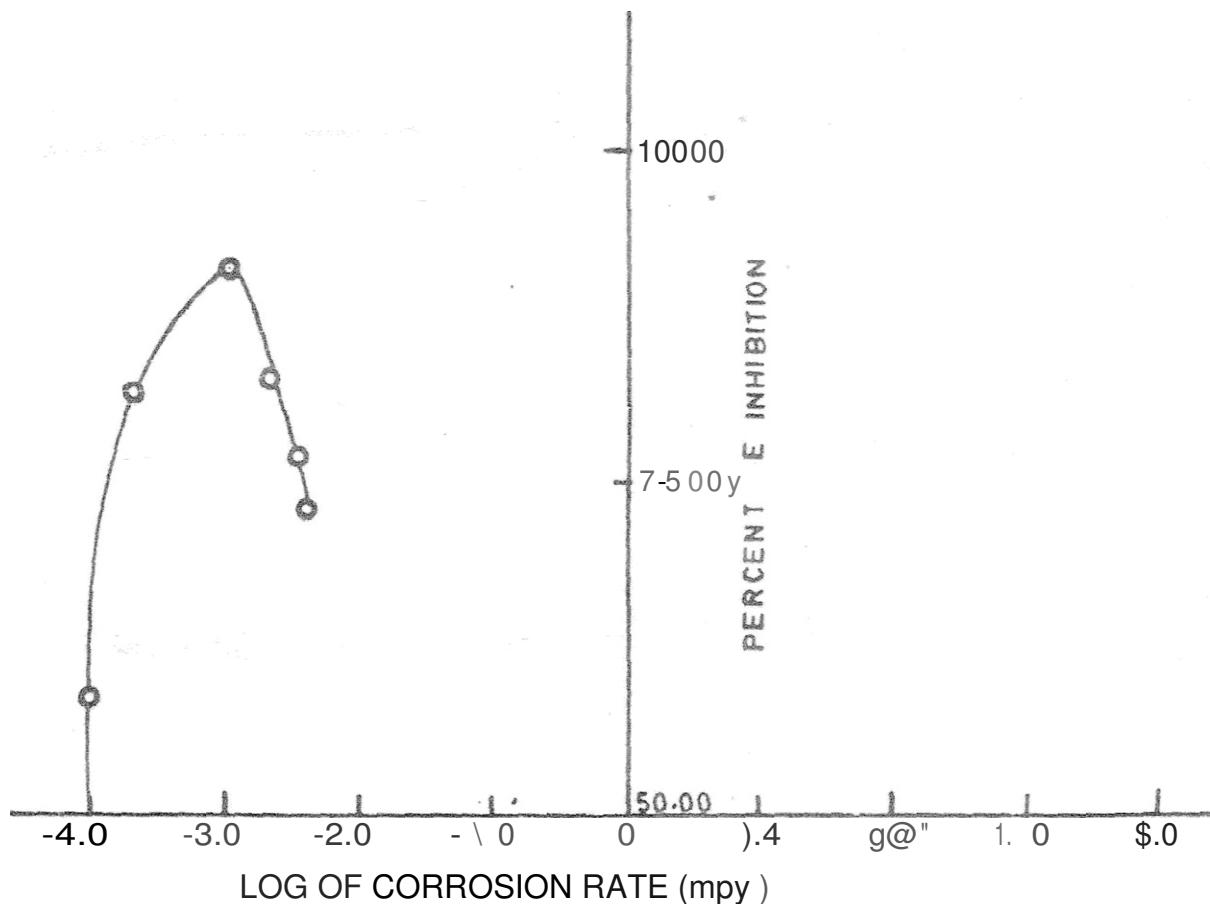
Temperature	Rate of corrosion (mpy)	Log corrosion rate (mpy)	Energy of activation in Kcal per mole
30 ⁰ c	13.100	1.116	25.340
40 ⁰ c	17.220	1.234	
50 ⁰ c	15.350	1.186	
60 ⁰ c	19.090	1.281	

Table -9

Test of Immersion for mild steel in Sulphuric acid medium for PH = 3.0
with a definite concentration of BTA and different concentration of
Fluoride

Period of Immersion = 18 Hrs, At Room Temperature

concentration of BTA	concentration of Fluoride ions (M)	Percentage of Inhibition
0.1×10^{-3} (M)		
	1.0×10^{-3}	93.00
	3.0×10^{-3}	72.090
	5.0×10^{-3}	70.100
	7.0×10^{-3}	40.030
	9.0×10^{-3}	37.040



r \/\\$ O E P E H6E NC E 0 F PE RCE N TAGE INNI BI TI0 N WI TH C0I4 C ENT RA TION OF B T A

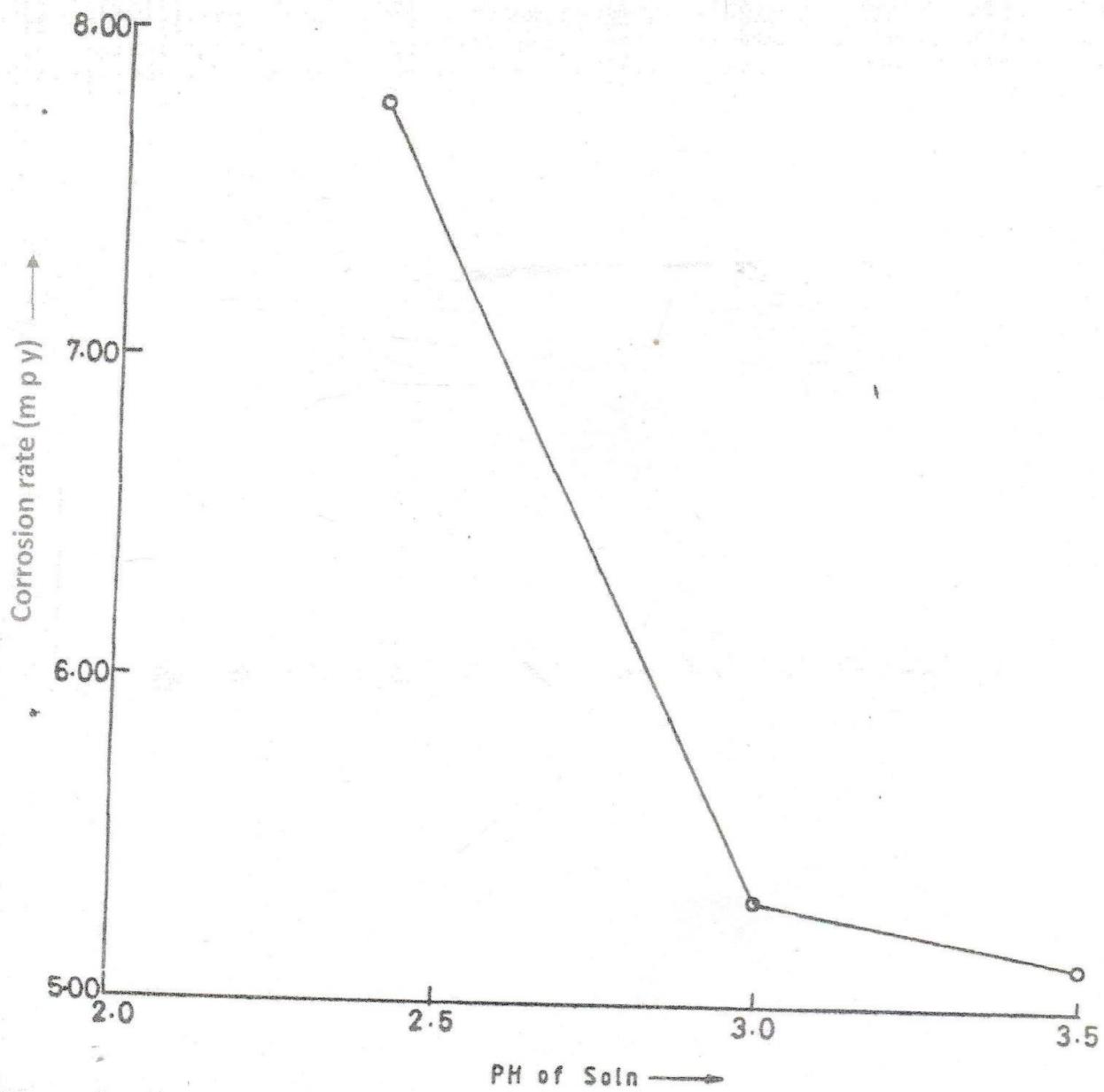


Fig. 2.0 Dependence of corrosion rate of mild steel on PH
of PAW

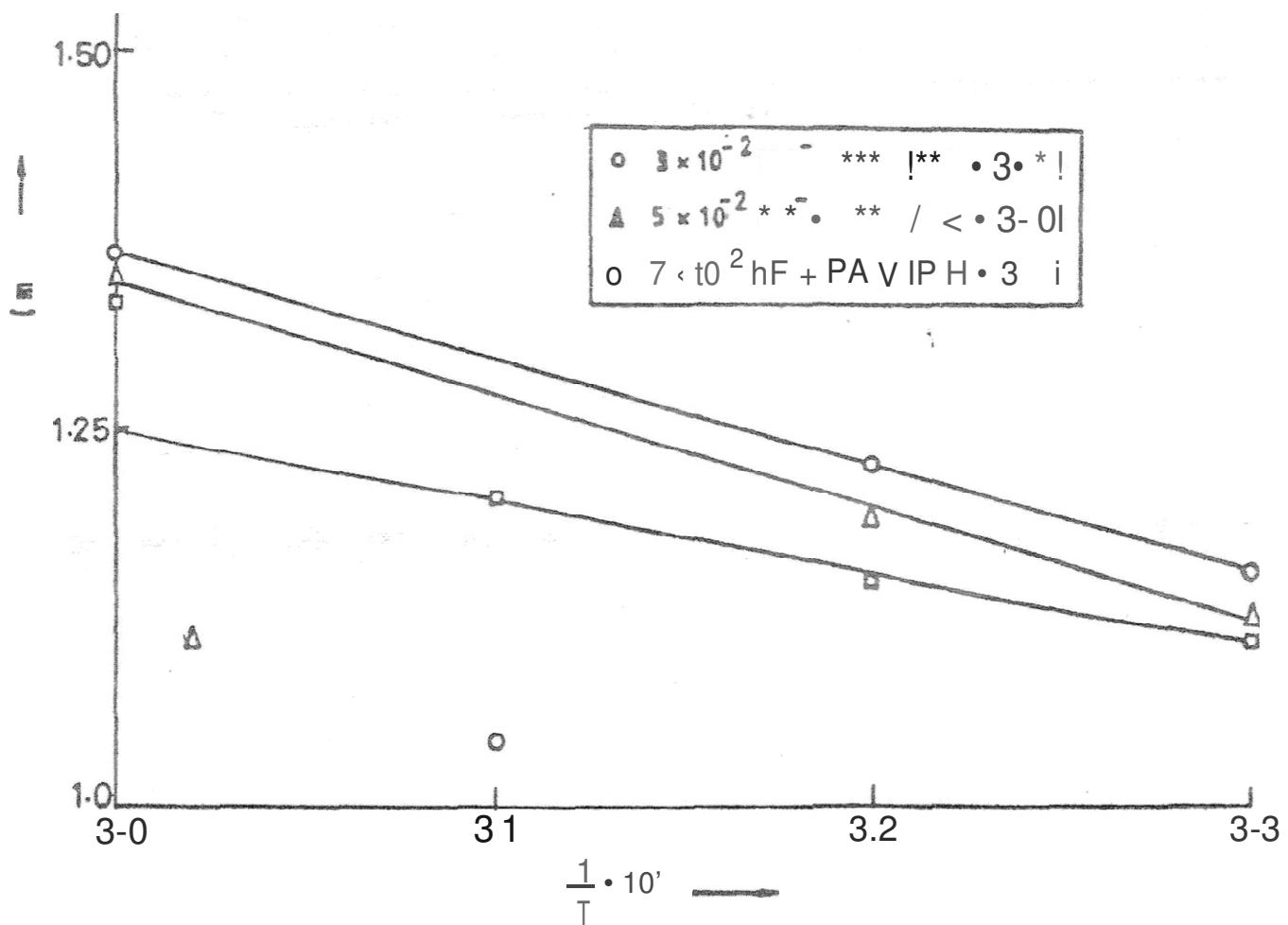
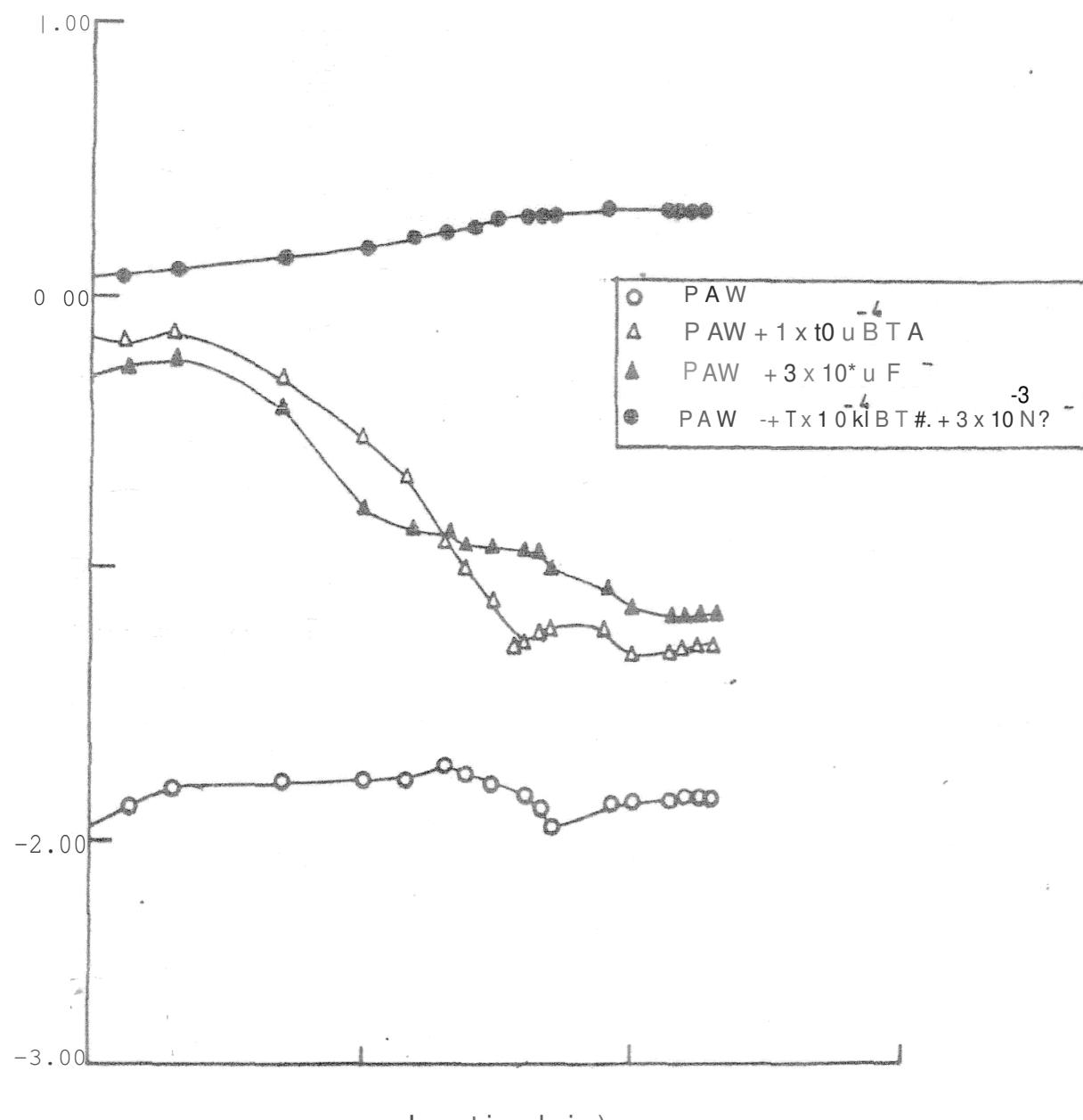


Fig- 3-0 Plot of tog corrosion rate vs. 1yt in presence of differentl concentration of Florida



FJ0. 4 0 POTENTIAL VS TIME CURVES IN PRESENCE OF FLORIDE AND FLORrBE + BTA

Reference :-

1. NACE Glossaory of corrosion terms., mat. Pro., 4, No. 1, 79-80 (1965) Jan.
2. Schmitt, G. ; Application of inhibitor for acid media, Br. corros. J., 19 (4), 174 (1984).
3. Jr. Riggs, O.L. ; and Hurd, R.M. ; corrosion, 18 (7), 25t-269t(1962)
4. Hammer, N.F. ; Scope and importance of inhibitor technology, corrosion Inhibitors, NACF, Houston, Texas, 2 (1973).
5. calcott and whetzel ; Trans Am. Inst. chem. Engg ; 1, 35 (1953).
6. Gardner, G; Inhibitors in Acid system corrosion Inhibitor, NACE, Houston Texas, 156 (1973).
7. Raj Narayan ; An introduction to metallic corrosion and its prevention, oxford & IBH publishing co, 17-19(1983)
8. F. Bentias. M. Lehnini and M.I. Lagenee corrosion science 47, 2913-2915 (2005)
9. Ubling , H.H; corrosion control, 97 (1971)
10. Kruger, j. ; use of ellipsometry in the study of corrosion, corrosion, 22,88 (1966)
11. Moser, B. and Farqubar, G.B; Use of differential capacitance measurements to predict the inhibitive behavior of organic nitrogen compounds corrosion, 23, 349 (1967)
12. Foley, R.T. ; Role of chloride ion in iron corrosion, corrosion 26, 58-70 (1970) February.
13. Anderson, D.L., Floyd, D.E; JS Electro chem.. soc. , 104, 56 (1957).
14. Ross, T.P. ; Pittsburg International conference on surface reaction, 127 (1948).

15. Anderson, D.L. , Floyd, D.E., Glasser, D.W. and Wittcoff, H.; corrosion, 17 (12) 9 (1961).
16. A.K Singh and B.K Singh, Adsorption Isotherm of copper benzotriazole system in HCl, Asian Journal of chemistry Vol-14, No.-1 (2002)497-499
17. A.K. Singh and D.K. Singh , Dihalo acetic acids as corrosion inhibitors of Brass in dilute Nitric acid, Nappier advance Research Journal of Sciences. Vol.-5, Dec 2010 (P. 81-84)
18. M.M.E.I. Naggar, corrosion inhibitor of mild steel in acidic medium by some Sulpha drugs compounds, corros sci 49(2007), 2226.
19. S. sharma and A. K. Singh Electro Chemical Behavior of mild steel and Benzotriazole in dilute HCl medium in presence of Kcl ijetae Journal.vol.-5 issue 10, october 2019
20. S.Sharma, 2020, Benzotriazole as a corrosion inhibitor for mild steel in acidic medium and synergistic effect of halide ions Ph. D. Thesis V.K.S.U. Ara.