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Inhibition of acid corrosion on mild steel with agar in hydrochloric acid medium at different temperatures

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ABSTRACT

The inhibitive effect of (agar) on the corrosion of mild steel in 1M HCl has been investigated using gravimetric and electrochemical techniques. The percentage inhibition efficiency was found to increase with increasing the concentration of inhibitor and with decreasing temperature. From both gravimetric and electrochemical experiments, the inhibition efficiency of the agar was found to be in the 92 -98 % range for 1M HCl medium. Galvanostatic study indicates that this compound act as a mixed type corrosion inhibitor. The rate of corrosion of mild steel rapidly increases with temperature over the temperature range of 30°C to 60°C, both in absence and presence of inhibitor. Thermodynamic parameters for adsorption process have been calculated using the Langmuir's adsorption isotherm.

Key words: Corrosion, Inhibition, agar, HCl, Mild steel.

INTRODUCTION

Due to the wide use of acidic media in many industrial fields, several researchers devoted their attention to develop more effective and non toxic inhibitors to reduce both acid attack and protection aspects. Organic inhibitor are applied extensively to protect metals from corrosion in many aggressive acidic media (e.g. in the acid pickling and cleaning processes of metals)[1-3]. The chemical components of agar had been analyzed from 1859 to 1938 by many scientists, and verified to consist of D-galactose, 3, 6-anhydro-L-galactose and sulfate. From the 1940's to 1950's the substituted galactose such as methylated, sulfated and pyruvated galactoses were proved to be the constituents of the agar molecule as well. Araki (1956) offered the evidence proving the heterogeneity of the agar by separating the agar into two different polysaccharides named agarose and aparopectin using the acetylation method. The agarose is a virtually neutral polymer, while the agaropectin is an acidic polymer. Later, Araki et al and other scientists — by acid hydrolysis and enzymic degradation of agar — isolated the agarobiose and neoagarobiose, respectively, and revealed that the agarose is composed of agarobiose repeating disaccharide units alternating with 1, 3-linked-β-D-galactopyranose and 1, 4-linked-3, 6-anhydro-α-L-galactopyranose (Fig. 2). The agaropectin seems to have the same backbone as the agarose, but contains considerable amount of acid groups such as sulfate, pyruvate and glucuronate groups.

It is partially soluble in water at lower temperature but soluble in water above 30°C, it is rich in hydroxyl group and carboxyl group. Thus it is likely to be one of the good inhibitors. There are several ways to prevent atmospheric corrosion. Among the available methods of preventing corrosion, the use of inhibitor is the most promising method particularly for closed systems. The inhibitors find wide applications in the industrial field. The inhibition by organic additives on metals in acids has been studied[1-10]. The organic substances belonging to this group contain mainly oxygen, sulphur, nitrogen and multiple bonds in the molecules that facilitate the adsorption on the metal surface[13-14] are strongly polar. According to ref[15-16], sulphur compounds such as thiourea are very effective corrosion inhibitor for steel in acidic condition because sulphur atom is easily protonated in acidic solution and a stronger electron donor than nitrogen .Therefore sulphur atom is more strongly absorbed to the metal surface. It has been observed that adsorption mainly depends on the presence of "- electrons and heteroatom , which induce greater adsorption of the inhibitor molecules on the surface of metal. The study of corrosion of iron is a matter of tremendous theoretical and practical concern and has received a considerable amount of interest. Iron is widely used as constructional material in many industries due to its excellent mechanical properties and low cost. The highly corrosive nature of aqueous mineral acids on most metal require degree of restraint to achieve economic maintenance and operation of equipment, minimum loss of chemical product and maximum safety condition.

The aim of this work is to study the effect of agar–agar as corrosion inhibitors for dissolution of mild steel in 1M concentration of HCl acid , by chemical and electrochemical technique . The effect of temperature on the dissolution of the mild steel in free and inhibited acid solution was also investigated.

EXPERIMENTAL

Electrolyte

The aggressive solutions used were made of AR grade of HCl acids Appropriate concentration of acid were prepared using double distilled water. The concentration range of inhibitor employed was 100 ppm to 1000 ppm .

Specimens

The mild steel coupons of composition(C=0.5%, Mn=0.5%, Si=0.05%, S=0.025%, P=0.25% and balance Fe) and have been used for weight loss measurements. These coupons were mechanically polished with emery papers of 1/0 , 2/0 ,3/0 and 4/0 grade and degreased with acetone before use.

Weight loss Studies

The mild steel strips of size (i.e. 1 × 1 ×3 cm) were used for weight loss measurement studies. All the weight loss experiments were carried out at 30°C to 60° C temperatures and immersion time 24-hour .The experiments were performed as per ASTM G31-72 method[15]. The percentage inhibition efficiency was calculated using the following equation:

$$I\,\% = \frac{Wo - Wi}{Wo} \times 100 \qquad \text{...(1)}$$

where Wo and Wi are weight losses in the absence and in the presence of inhibitor respectively

Electrochemical Studies

For potentiodynamic polarization studies, mild steel strips of above-mentioned composition were used and the experiments were carried out at different temperatures and time period, up to 6 hours in the absence and presence of inhibitor. For polarization studies a cylindrical mild steel rod of the same composition, as that of weight loss, coated with araldite (exposed area of 1cm^2) was used. The electrodes were polished with emery papers and degreased with acetone before used. For accurate measurements of potential and current densities, galvanostatic polarization studies were carried out at different temperatures. A platinum foil and saturated calomel electrode were used as counter and reference electrode respectively. Polarization studies were carried out in 1M HCl in the absence and presence of inhibitor of varying concentrations and temperatures. The percentage inhibition efficiency was calculated using the following equation:

$$I.E\% = \frac{Icorr - Icorr'}{Icorr} \times 100 \qquad \text{...(2)}$$

where Icorr and Icorr' are the corrosion current density of in the absence and in the presence of inhibitor respectively.

RESULTS AND DISCUSSION

Weight loss measurements

Table 1 give the values of inhibition efficiencies for different concentrations of (agar–agar) in 1M HCl medium obtained from weight loss measurements. The percentage inhibition was calculated using the above described equation. The results are listed in table 1. The results show that the inhibition efficiency increases with increasing the concentration of inhibitor at higher temperature. As the temperature increases the inhibition efficiency also increases because Agar –Agar formed a strong protective jell on alloys surrounding at studied temperature. The inhibition efficiency is appreciably higher i.e. HCl acid in presence of 1000 ppm of (agar–agar) concentration at 60° C temperature.

Table - 1:Inhibition efficiency of Agar-Agar on mild steel in 1M HCl medium from weight loss at various temperatures

Temperature	Solution in ppm	Weight loss/gram	%I
30 ° C	1M HCl	0.5457	-
	100	0.1334	75.7
	200	0.1118	79.5
	500	0.0835	84.7
	1000	0.0668	87.7
40 ° C	1M HCl	0.7935	-
	100	0.1695	78.6
	200	0.1445	81.7
	500	0.1175	85.1
	1000	0.0725	90.8
50 ° C	1M HCl	0.8350	-
	100	0.1445	82.7
	200	0.1235	85.2
	500	0.0885	89.4
	1000	0.0382	95.4
60 ° C	1M HCl	0.8975	-
	100	0.1205	86.5
	200	0.0957	89.3
	500	0.0484	94.6
	1000	0.0175	98.0

Galvanostatic polarization measurements

The electrochemical parameters such as corrosion potential (E_{corr}), Tafel's slopes (b_a and b_c), corrosion current (i_{corr}) and inhibition efficiency (I.E%) for corrosion of mild steel in 1M HCl in absence and presence of gelatin (agar–agar) as inhibitor of different concentrations and temperatures are calculated using aboye mention equation and listed in Table 2. Figures 1 to 4 show the effect of inhibitor concentration on the current potential curves for both the cathodic and anodic reactions at different temperatures in 1M HCl. As the inhibitor concentration increases there is an increase in the values of both the Tafel's slopes in this acid solution. The values of Tafel's slopes (cathodic and anodic) are more in case of 1000ppm concentration of inhibitor in 1M HCl . . The percentage inhibition curve of agar-agar on mild steel in 1M HCl solution shows that the corrosion inhibition efficiency reached about 88% with solution containing 1000 ppm of inhibitor where as at the lower concentration of 100 ppm, the percentage inhibition was about 75% at temperature 30 °C. The percentage inhibition of (agar–agar) in 1M HCl is about 98% having concentration 1000 ppm while at lower concentration 100 ppm the percentage inhibition was about 86% at 60 °C temperature. The value of I_{corr} is found to be little more in case of lowest concentrations inhibitor compound in this medium. As the concentration increases there is a decrease in the values of I_{corr}. The inhibition efficiency of (agar–agar) depends on many factors including number of adsorption active center in the molecule and their charge density, which are affected by (–OH) group. The values of inhibition efficiency obtained by weight loss method and galvanostatic polarization studies show fairly good agreement.

Adsorption Isotherm

The adsorption isotherms were constructed by evaluating the Icorr value in the absence and presence of the inhibitor Icorr'. All measurments are carried out in normally oxygenated solutions without stirring at temperature 60° C .The Surface coverage values (θ) have been obtained from polarization measurements (inhibition efficiency), for various concentration of inhibitor (agar–agar).Thus on the basis of this consideration, the value of (θ) is calculated as:

Table - 2: Electrochemical parameters of mild steel in 1M HCl in presence of Agar-agar as additive

Temp.	Solution /mol (L^{-1})	E_{corr} mV	Log i_{corr} µA/cm^2	b_c mV/dec	b_a mV/dec	%I
30 ° C	1M HCl	478	2.73	29	40	-
	100	451	2.15	21	29	75.1
	200	439	2.06	30	32	79.6
	500	390	1.99	20	20	83.0
	1000	485	1.82	75	45	88.45
40 ° C	1M HCl	462	2.98	21	22	-
	100	427	2.32	18	18	78.2
	200	437	2.25	16	17	81.3
	500	420	2.16	13	20	84.8
	1000	475	1.88	22	24	91.50
50 °C	1M HCl	454	3.21	28	28	-
	100	451	2.44	14	16	82.9
	200	431	2.38	16	16	85.2
	500	420	2.26	20	20	89.6
	1000	468	1.98	25	20	94.75
60 °C	1M HCl	456	3.54	20	11	-
	100	442	2.66	17	16	86.7
	200	441	2.57	12	12	89.2
	500	457	2.29	18	08	94.3
	1000	475	1.81	31	32	98.25

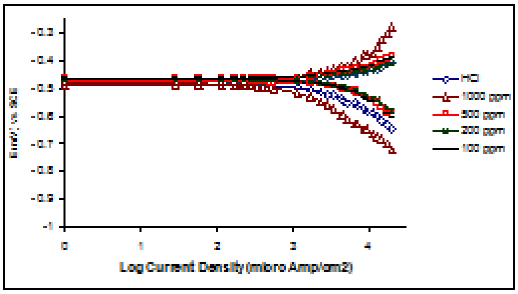

Fig. - 1: Galvanostatic polarization curves of mild steel in 1M HCl solution containing different concentrations of Agar-Agar at 30°C

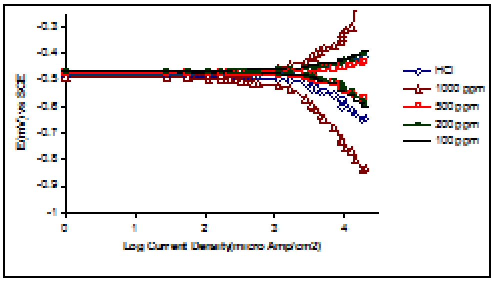

Fig. - 2: Galvanostatic polarization curves of mild steel in 1M HCl solution Containing different concentrations of Agar-Agar *at* 40°C.

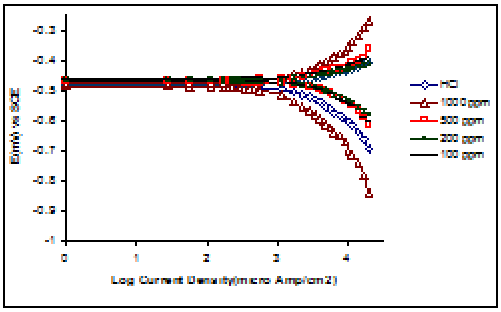

Fig. - 3: Galvanostatic polarization curves of mild steel in 1M HCl solution containing different concentrations of Agar-Agar at 50°C.

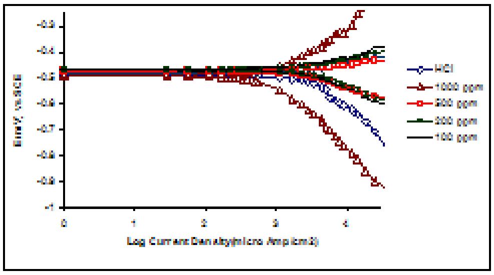

Fig.- 4: Galvanostatic polarization curves of mild steel in 1M HCl solution containing different concentrations of Agar-Agar at 60°C.

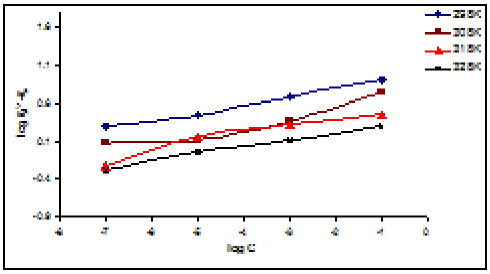

Fig. - 5: Variation of surface coverage vs concentration at different temperatures Of Agar Agar in 1M HCl.

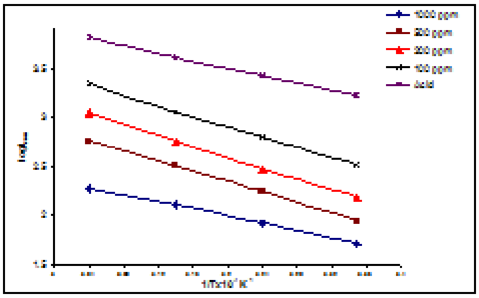

Fig. - 6: Arrhenius plots calculated from corrosion current density foe mild steel 1M HCl and 1M HCl + different concentrations of Agar –Agar in 1M HCl.

$$(\theta) = 1 - (I_{corr}' / I_{corr}) \qquad ...(3)$$

where, Icorr' = corrosion current in the presence of inhibitor. And Icorr = corrosion current in the absence of inhibitor. According to the literature[19-22] the adsorption process of aromatic containing compounds on ferrous metals can obey Langmuir, Temkin or Frumkin isotherm . The data shown in table (3) were tested graphically for fitting a suitable adsorption isotherm. A straight line is obtained by plotting a graph between log θ/1- θ vs. 1/T (Fig - 5). This clearly proves that the adsorption of Agar on mild steel surface obey Langumir's adsorption isotherm.

Effect of temperature

The change of the corrosion process rate with temperature increase was studied in 1M HCl, both in the absence and presence of inhibitor. We were interested in exploring the activation energy of the corrosion process and the thermodynamic of adsorption of Agar-Agar. This was accomplished by investigating the temperature dependence of the corrosion current, obtained using the Tafel Extrapolation method. Fig -4 shows Tafel plots, for the mild steel electrode in , 1M HCl with addition of 100 ppm to 1000ppm, in the temperature range 30°-60°C, It has been observed that the corrosion current density (Icorr) increased with increasing temperature. The Icorr increased with one order of magnitude with increase temperature, both in uninhibited and inhibited solutions. Corresponding data are given in table 4, the result of the blank (1M HCl) in the temperature range 30°–60°C reported previously[14] .It is seem that the Agar investigated have been inhibiting properties at all temperature studied and the values of inhibition efficiency of Agar increase with temperature increase. Thus, the Agar efficiencies were temperature – dependent.

Table - 3: Electrochemical parameters of Mild Steel in 1M H_2SO_4 in presence of N-(4,6-diphenylpyrimidin-2-yl)thiourea as additive

Temp.	Solution/mol (L^{-1})	E_{corr}mV	Log i_{corr}μA/cm^2	%I	θ	θ/1-θ
30 °C	1M HCl	478	2.73	-	-	-
	100	471	2.15	75.1	0.751	3.01
	200	453	2.06	79.6	0.796	3.90
	500	481	1.99	83.0	0.830	4.88
	1000	485	1.82	88.45	0.884	7.62
40 °C	1M HCl	462	2.98	-	-	-
	100	478	2.32	78.2	0.782	3.58
	200	481	2.25	81.3	0.813	4.34
	500	472	2.16	84.8	0.848	5.57
	1000	475	1.88	91.50	0.915	10.76
50 °C	1M HCl	454	3.21	-	-	-
	100	480	2.44	82.9	0.829	4.84
	200	464	2.38	85.2	0.852	5.75
	500	470	2.26	89.6	0.896	8.61
	1000	468	1.98	94.75	0.947	17.86
60 °C	1M HCl	456	3.54	-	-	-
	100	471	2.66	86.7	0.867	6.51
	200	470	2.57	89.2	0.892	8.25
	500	472	2.29	94.3	0.943	6.54
	1000	475	1.81	98.25	0.982	54.55

Table - 4: The influence of temperature on the electrochemical parameters for mild steel electrode immersed in 1M HCl , 1MHCl + 1000 ppm of Agar.

Inhibitors	Temperture (°C)	Icorr(micro A/cm2)	Erest. Pot(mV/SCE)	I.E. (%)
Blank	30	575	- 478	-
	40	960	- 462	-
	50	1635	- 454	-
	60	3512	- 456	-
Agar	30	66.45	- 485	88.4
	40	79	- 475	91.5
	50	97	- 468	94.7
	60	65	- 475.	98.2

The fact that (I.E.%) increases with temperature is explained by A.S.Founda et al, as the likely specific interaction between the mild steel surface and the inhibitor[15]. M.Lebrini[14] considers the increase the (I.E.%) with temperature increase as the change in the nature of the adsorption mode, the inhibitor is being physically adsorbed at lower temperatures , while chemisorptions is favored as temperature increases. The corrosion reaction can be regarded as an Arrhenius – type process, the rate is given by

$$I corr = k \exp\left(-\frac{Ea}{RT}\right) \quad ...(4)$$

Where Ea is the apparent activation corrosion energy, T is the absolute temperature, k is the Arrhenius pre-exponential constant and R is the universal gas constant. This equation can be used to calculate the Ea values of the corrosion reaction without and with the inhibitor. Plotting the natural logarithm of the corrosion current density vs 1/T , the activation energy can be calculated from the slope. The temperature dependence of mild steel dissolution in deaerated 1M HCl and in the presence inhibitor is presented in Arrhenius co-ordinates in Fig – 6. The calculated values of the apparent activation corrosion energy in the absence and presence of 1000ppm if Agar is 49.54 and 34.37 KJ / mol. respectively. The lower values of the activation energy of the process in an inhibitor's presence when compared to that in its absence is attributed to the chemisorptions of inhibitor on mild steel surface. This conclusion was in accordance with findings of other researchers[15-18].

CONCLUSION

Agar inhibits the corrosion of mild steel in 1M HCl and its percentage inhibition efficiency increased with the inhibitor concentration, polarization studies showed that this inhibitor is mixed type inhibitor. The performance of this compound as an inhibitor in this acid is very much encouraging. The inhibition efficiency increases with increase in concentration, inhibition efficiency also increases with increase in temperature, which indicate that it is a good organic inhibitor at high temperatures .The adsorption of Agar on mild steel surfaces obey Langmuir's adsorption isotherm.

REFERENCES

1. Y. Xiao-Ci, Z.Hong, L.Ming-Dao, R. Hong-Xuan, Y. Lu-An, *Corrosion Scinece.* **42** , 645 (2000).
2. M. Scendo, *Corrosion Science.* **47,** 2778 (2005).
3. M.M. Osman, M.N. Shalaby, *Mater. Chem. Phys.* **77** (2002).
4. M. El Azhar, M. Traisnel, B.Mernari, L.Gengembre, F. Bentiss, M. Largrenee, *Journal of Applied Surface Science.* **185,** 197 (2002) .
5. Y.K.Agrawal, J.D. Talati, M.D. Shah, M.N.Desai, N.K.Shah. Corrosion Science **46**, 633 (2004).
6. M.C. Garcia-Alonso, G.Macchi, C.Brugnoni, M.F. Stroosnijder, *Corrosion Science.***44,** 129 (2002) .
7. A.Popova, E. Sokolova, S Raicheva, M. Christov, *Corrosion Science.* **45**,33 (2003).
8. K. Takeuchi, A. Nishijima, K. Ui, N. Koura and C.K. Loong, *Journalof The Electrochemical Society,***152** (9)B 364-B368 (2005).
9. M.A.Quraishi ans S. Khanr*Indian Journal of Chemical. Technology.* **12**, September , pp. 576-581 2005.
10. P.Manivel and G. Venktachari. *Journal of Metallurgy and Materials Science* 46 ,No. 4 263-270 (2004).
11. H. J. Grabke, Mater. *Corrosion .* **54**, 736 (2003).
12. C.M. Chun and T.A. Ramanarayanan, *Oxide. Met.* **62**. 71 (2004).
13. S.D.Shetty, Prakash Shetty, H.V.S. Nayak, *Indian Journal of Chemical Technology.* **12**, 462 (2005).
14. M.Lebrini, M.Lagrenee, H.Vezin, L.Gengenbre, F.Bentiss. *Corrosion Science.* **47**, 485 (2005).
15. A.S.Founda, A.A.El-Bindary, A.A.Ai-Sarawy, E.E.El-Katori, *Bulletin of Electrochemistry. 21 (2005) 481.*
16. A.S.T.M, Standered Practice for Laboratory

Immersion Corrosion Testing of Metals, *Annual Book of Stan.,* G **31-72**, 3.02 (1990).

17. Y.K. Agrawal, J.D. Talati, M.D. Shah, M.N. Desai and N.K. Shah, *Corrosion Science*, **46** , 633 (2004) .
18. H.-B. Fan, C.-Y. Fu, H.-L. Wang, X.-P. Guo and J.-S. Zheng, *Brit. Corros. J.*, **37-2,** 122 (2002).
19. G. Blustein, J. Rodriguez, R. Romanogli and C. F. Zinola, *Corrosion Science,* **47,** 369-383 (2005).
20. Ilona Felhosi, Erika Kalman *Corrosion Science,* **47**, 695 – 708 (2005).
20. B. Muller *,* *Corrosion Science,* **46**, 159 – 167 (2004).
21. M.Abdallah, E.A.Hetal and A.S.Fouda. *Corrosion Science ,* **48**, 1639-1654 (2006).
22. I.A.Ammar, F.M. El Khorafi, *Werkst. Korr.* **24** 702 (1973).