Quaternary ammonium salt as effective corrosion inhibitor for carbon steel dissolution in sulphuric acid media

A. A. El Maghraby* and T. Y. Soror

Chemistry department, Faculty of Science, Cairo University, Giza, Egypt

ABSTRACT

The influence of cetyl trimethyl ammonium bromide (CTAB) on the corrosion of carbon steel in solutions of sulphuric acid has been investigated in relation to the concentration of the inhibitor and acid as well as temperature by various monitoring corrosion techniques. Results obtained revealed that CTAB is a good mixed-type inhibitor in sulphuric acid solutions and the inhibition efficiency increases with the inhibitor concentration, while decreases with increasing the sulphuric acid concentration. The adsorption of inhibitor on the carbon steel surface is in agreement with Langmuir adsorption isotherm.

Keywords: Corrosion inhibition, Cationic surfactant, Open circuit, Polarization.

INTRODUCTION

Corrosive environments have received a considerable amount of attention because of their attack on materials. Using inhibitors is one of the most important applications in corrosion protection of carbon steel in acidic media [1-4]. Among all inhibitors, the most important are the organic ones, also called adsorption inhibitors [5-12]. They control corrosion, acting over the anodic or the cathodic surface or both. Most commercial acid inhibitors are organic compounds containing heteroatoms such as nitrogen, oxygen, sulphur, phosphorous atoms, by which the inhibitor molecules are adsorbed on the metal surface in acidic media, thus resulting adsorption film acts as a barrier separating the metal from the corrosive medium and blocks the active sites [11, 13-17]. In this paper the effect of cetyl trimethyl ammonium bromide (CTAB) on corrosion inhibition of carbon steel in various concentrations of sulphuric acid solutions at different temperatures has been investigated using weight loss, open circuit potential, Tafel polarization and linear polarization techniques. In addition the adsorption isotherm of the inhibitor was investigated. The possible mechanism of CTAB surfactant onto C-steel surface has been proposed on the basis of results obtained.

MATERIALS AND METHODS

Carbon steel were used for the weigh loss measurement contains C = 0.7%, P = 0.03%, Mn = 0.3-0.6%, S = 0.035%, Si = 0.5-0.75% and iron is the remainder, of size (2.5 cm × 5 cm × 1 cm) were used. Strips were mechanically polished and degreased with acetone before use. A sheet cut of the same composition embedded in araldite with an exposed area of 2.1 cm^2 was used for both Tafel and linear polarization studies. The electrode was polished using different grades of emery papers and degreased. AR grade H_2SO_4 was used for preparing solutions. The inhibitor (CTAB) used was BDH made. All solutions were prepared using triply distilled water.

Inhibition efficiencies (IEs) for different concentrations of the inhibitor were calculated from weight loss values in the absence and presence of the inhibitor at temperature of 20, 40, and 60^{0}C. The effect of temperature on the performance of the inhibitor and the effectiveness of the inhibitor at higher acid strength were also studied.

Platinum sheet and saturated calomel electrode (SCE) was used as counter and reference electrodes respectively. The potentiokinetic current-voltage characteristics were recorded using potentiostat model 273/81 at 0.2 mVs^{-1} scan rate under stirring conditions. For linear polarization studies, the scan rate was 1.66×10^{-4} mVs^{-1} and the polarization resistance (R_p) values were measured in the absence and presence of different concentrations of the inhibitor at different temperatures (20- 45^{0}C). Open circuit potential studies were carried out to explore the direction of potential shifting in the presence and the absence of inhibitor.

RESULTS AND DISCUSSION

3.1. Effect of inhibitor dose and temperature on inhibition efficiency

The variation of the inhibition efficiencies obtained from the weight loss with different inhibitor doses in various H_2SO_4 concentrations (1-3M) at different temperatures (20, 40, and 60 ^{0}C) are shown in Figs 1-3. The results show that inhibition efficiency increases as the concentration of inhibitor increases from 25 to 300 ppm at 20, 40 and 60 ^{0}C. The maximum inhibition efficiency for CTAB inhibitor was found about 89% in 2M H_2SO_4 solution. The inhibition was estimated to be 72% at 20 ^{0}C even at very low concentrations (25 ppm), and at 300 ppm its protection was more than 85% (20 ^{0}- 40 ^{0}C). This trend may result from the fact that the adsorption amount and the coverage of surfactant on the C-steel increase with the inhibitor concentration, thus the C-steel surface is efficiently separated from the medium [18, 19]. Also, the inhibition efficiency decreases with an increase in corrosion temperature and H_2SO_4 at the same inhibitor dose Figs. 1-3, indicating that the high temperature might result in desorption of the inhibitor molecules from the C-steel surface [20].

3.2. Effect of exposure time

Effect of immersion time on corrosion inhibition at different concentrations of CTAB on the corrosion of C-steel in 1, 2 and 3M H_2SO_4 at 20, 40 and 60^{0}C was also studied. Figures 4-6 show the effect of changing immersion time at 20 ^{0}, 40^0 and 60^{0}C on the inhibition efficiency of CTAB at 300 ppm optimum dose in presence of 1, 2 and 3M H_2SO_4. It can be seen from Figs. 4-6 that the inhibition efficiency is higher than 65% when the immersion time is only 0.5 h, which indicates that the adsorption rate of CTAB on the C-steel surface is relatively high. The figures show that CTAB inhibits the corrosion of C-steel for all immersion time at all concentrations of CTAB. Generally increasing immersion time resulted in increasing IE. The most suitable results obtained in 2M H_2SO_4 at 20^{0}C give efficiency up to 80% at 2 h immersion time.

The high inhibition efficiency with longer immersion time can be attributed to the formation of a protective film which is time- dependent on the C-steel surface. It has been stated that stable two- dimensional layers of inhibitor molecules are formed on metal surfaces after longer immersion time [21].

3.3. Open circuit potential

Figs.7 and 8 show that a potential- time plots for carbon steel in 1M and 2M H_2SO_4 solutions at 25^0C in the presence of different doses of CTAB inhibitor. It was found that the potential for all inhibitor concentrations was shifted to less negative values while the blank potential went also to less negative direction but less than the inhibitor. Comparison between the behavior of CTAB in 1M and 2M H_2SO_4 solutions at 25^0C showed that increasing the inhibitor concentration to 300 ppm (Fig.8) in presence of 2M at 25^0C gives a more shift to the less negative values.

Table (I) variation of polarization parameters for carbon steel in 1M and 2M concentration of H_2SO_4 at 25^oC with different additives of CTAB inhibitor

Media	Inhibitor Dose	E_{corr}	β_a	β_c	I_{corr}	R_p	$(C.R.)_T$	I.E (%)	
	(PPM)	(mv)	(v/d)	(v/d)	(mA)	(Ohms)	(MPY)	Tafel	L.Polariz.
1M H_2SO_4	200	-530.2	150.7×10^{-3}	120.7×10^{-3}	881	9.63	406	21	72
	400	-510.8	182.8×10^{-3}	133.9×10^{-3}	575.1	13.97	264.7	48	79
	600	-491.7	210.8×10^{-3}	143.6×10^{-3}	374.7	14.1	172.5	66	81
	800	-489.9	181.5×10^{-3}	132.1×10^{-3}	327.1	17.87	150.5	71	85
	1000	-484.7	164.2×10^{-3}	127.8×10^{-3}	324.5	18.72	141.9	72	89
2M H_2SO_4	Blank	-531.3	193.8×10^{-3}	166.3×10^{-3}	2383	3.291	1018		
	200	-526.1	145.9×10^{-3}	138.7×10^{-3}	995.6	11.86	458.3	55	75.8
	400	-524.1	161.7×10^{-3}	142.5×10^{-3}	896.5	15.89	404	60	83.7
	600	-520.1	145.8×10^{-3}	136.6×10^{-3}	767.2	17.69	353.1	65	83.9
	800	-512.6	107.5×10^{-3}	123.5×10^{-3}	561.5	22.02	280.2	72.5	87.3
	1000	-513.8	132.5×10^{-3}	125.3×10^{-3}	469.2	30.52	216	79	87.6

3.4.Electrochemical polarization measurements

Figures 9 and 10 show the Tafel polarization curves measured on C-steel electrodes in 1M and 2M H_2SO_4 solutions at 25^0C in the absence and presence of CTAB inhibitor doses. The figures clearly indicate that the presence of inhibitor causes a markedly decrease in the corrosion rate, i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may be ascribed to adsorption of inhibitor over the corroded surface [22].The values of corrosion current densities *(I_{corr})*, corrosion potential *(E_{corr})*, the cathodic Tafel slope *(β_c)*, anodic Tafel slope *(β_a)*, and the inhibition efficiency *(IE)* as functions of CTAB concentration, were calculated from the curves of Figs.9 and 10 and given in Table 1. In the mean time the corrosion current decreases substantially, so the inhibition efficiency increases (Table 1), where the *IE%* was calculated from the relation [20]:

$$IE \quad \% = \frac{[I\ c.\ un - I\ c,\ inh]}{I\ c.\ un} \times 100$$

Where $I_{c.\ un}$ is the corrosion current in A cm^{-2} in the absence of inhibitor; $I_{c,\ inh}$ the corrosion current in A cm^{-2} in the presence of inhibitor. Table 1 reveals that the corrosion current decreases obviously and IE increases with the inhibitor concentration. The presence of CTAB does not remarkably shift the corrosion potential, while the anodic and cathodic Tafel slopes change upon addition of increasing inhibitor concentration. Therefore, CTAB can be arranged as mixed – type inhibitor in H$_2$SO$_4$. The same results have been reported with other organic surfactant compounds in acidic media [6, 23, 24]. Both anodic and cathodic reactions of electrode are drastically inhibited, probably being caused by a strong adsorption layer which covers both anodic and cathodic reactive sites on the C-steel surface.

Fig.11 shows the variation of the polarization resistance, R_p, with different CTAB concentrations in 1M and 2M H$_2$SO$_4$. The results showed that R_p increases with CTAB doses, and will attain its maximum value with 1000 ppm CTAB in 2M H$_2$SO$_4$. On the other hand, the change of R_p with inhibitor dose up to 1000 ppm at different temperatures (25, 35 and 45^{0}C) show that R_p decreases with increasing of temperature, Fig.12.This mean that the inhibition effect of the inhibitor decreases as the temperature increases. Previously it was found that the efficiency of the inhibitor decreased slightly with increasing of temperature [25]. The results of electrochemical polarization (Table 1) are in agreement with those of weight loss data and open circuit potential.

3.5. Adsorption Isotherm.
Corrosion inhibition of metal in acidic media by organic inhibitors is commonly attributed to the adsorption of organic molecules on metal surface, and the inhibition efficiency is directly proportional to surfactant coverage [26]. According to Langmuir adsorption model, the degree of surface coverage *(θ)* for surfactant molecules on the C-steel surface in acidic media could be evaluated from the following equation [27]:

$$\theta = \frac{(C.R.)o - (C.R.)}{(C.R.)o}$$

Where $(C.R.)_o$ and $(C.R.)$ are the corrosion rates in (mg Cm^{-2} min^{-1}) without and with different concentrations of inhibitor. Assuming the adsorption of CTAB on C-steel surface obeys Langmuir adsorption isothermal equation [6,18]:

$$\frac{C}{\theta} = \frac{1}{K} + C$$

where *C* is the concentration of inhibitor, *K* the adsorptive equilibrium constant and *θ* is the surface coverage. Fig.13 is the relationship between *C/θ* and *C* at 25^{0}C. The linear regression between *C/θ* and *C* were calculated. These results show that all the linear correlation coefficients (r) in case of 1M and 2M H$_2$SO$_4$ solutions are equal to 1.0 and all the slopes are very close to 1.0 which indicates the adsorption of CTAB inhibitor onto C-steel surface accords with the Langmuir adsorption isotherm. Also the adsorptive equilibrium constant K in case of 2M H$_2$SO$_4$ is more than K in case of 1M H$_2$SO$_4$ which indicates that the adsorption of CTAB molecules on C-steel surface in 2M H$_2$SO$_4$ media is easier than that 1M H$_2$SO$_4$ solution [20]. This result supports the conclusion that maximum inhibition corresponds to the formation of a monolayer of the additive on the active sites of the metal surface.

3.6. Apparent activation energy calculation
Arrhenius equation in the form

$$\frac{d \log Icorr}{d(1/T)} = \frac{-Ea}{2.303\ R}$$

gives a linear relation when plot *log I$_{corr}$* which is a measure of *log C.R* (corrosion rate) versus *1/T* [6,28-30]. Fig.14 gives plotted for 1M H$_2$SO$_4$ in presence and absence of 300 ppm CTAB inhibitor dose. From the slope of the straight lines, the activation energy for blank *(E$_a$)* $_{blank}$ = 28.721 k J mol^{-1} and it was in presence of inhibitor dose as *(E$_a$)$_{inh}$* = 46.662 k J mol^{-1}. It is clear that the value of *E$_a$* in the presence of CTAB is higher than that in the uninhibited acid solution. These results are according with the reported studies [20,31]. The increase of *E$_a$* in the presence of the inhibitor indicates that physical adsorption or weak chemical bonding between the CTAB molecules and the C-steel surface might occur [31]. Accordingly the higher *E$_a$* leads to the lower corrosion rate. Therefore, the decrease in C-steel corrosion rate is mostly decided by the apparent activation energy [20].

Fig.1.Inhibition efficiency as a function of inhibitor concentration in 1, 2 and 3M H$_2$SO$_4$ at 20^{0}C
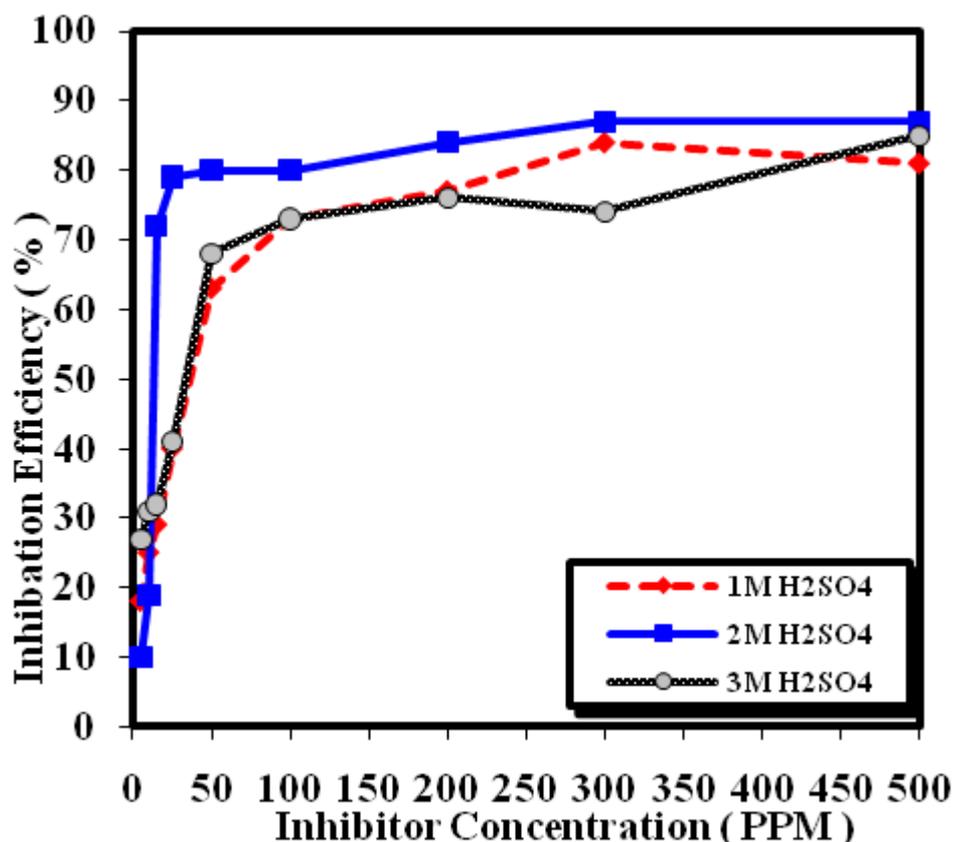
Fig.2.Inhibition efficiency as a function of inhibitor concentration in 1, 2 and 3M H$_2$SO$_4$ at 40^{0}C
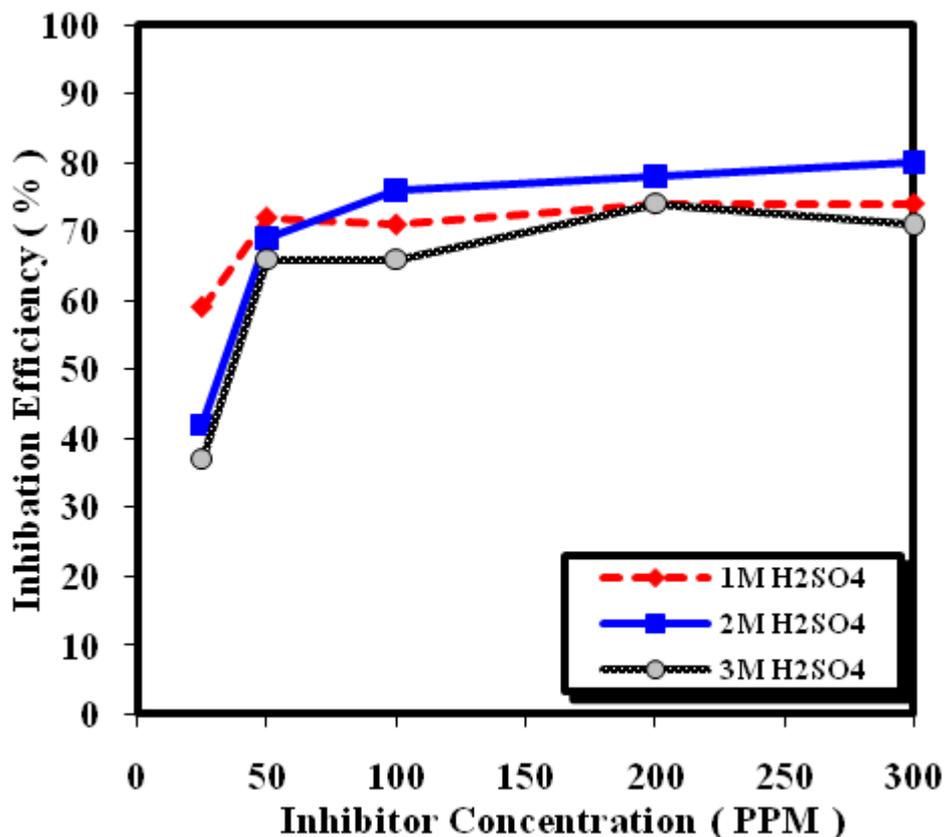
Fig.3.Inhibition efficiency as a function of inhibitor concentration in 1, 2 and 3M H$_2$SO$_4$at 60^{0}C
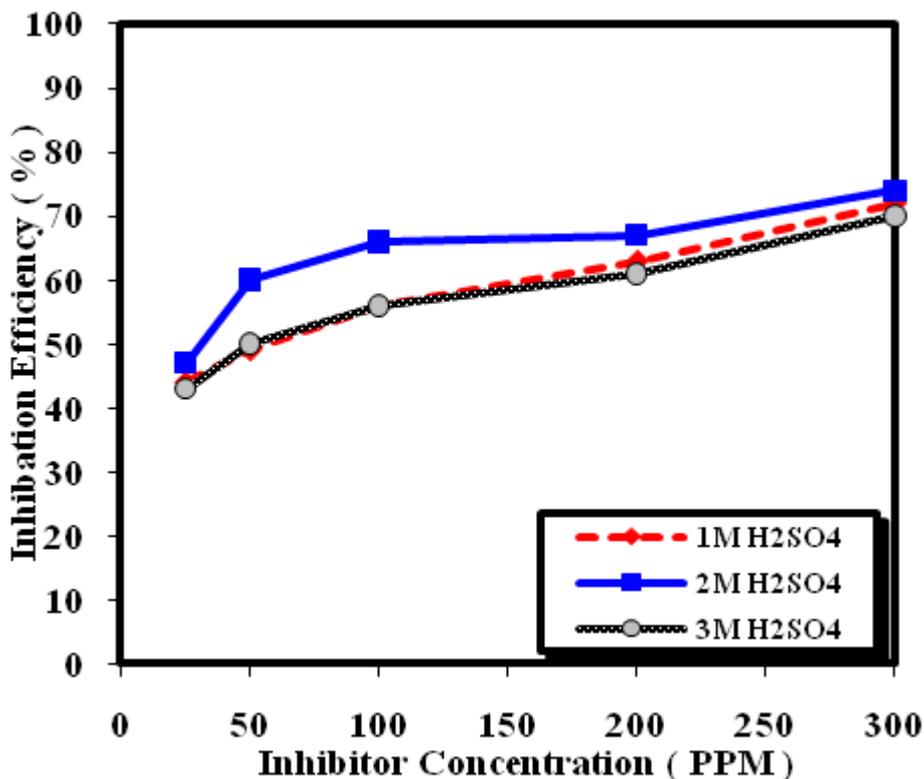
Fig.4. Effect of exposure time in 1, 2 and 3M H$_2$SO$_4$at 20^{0}C
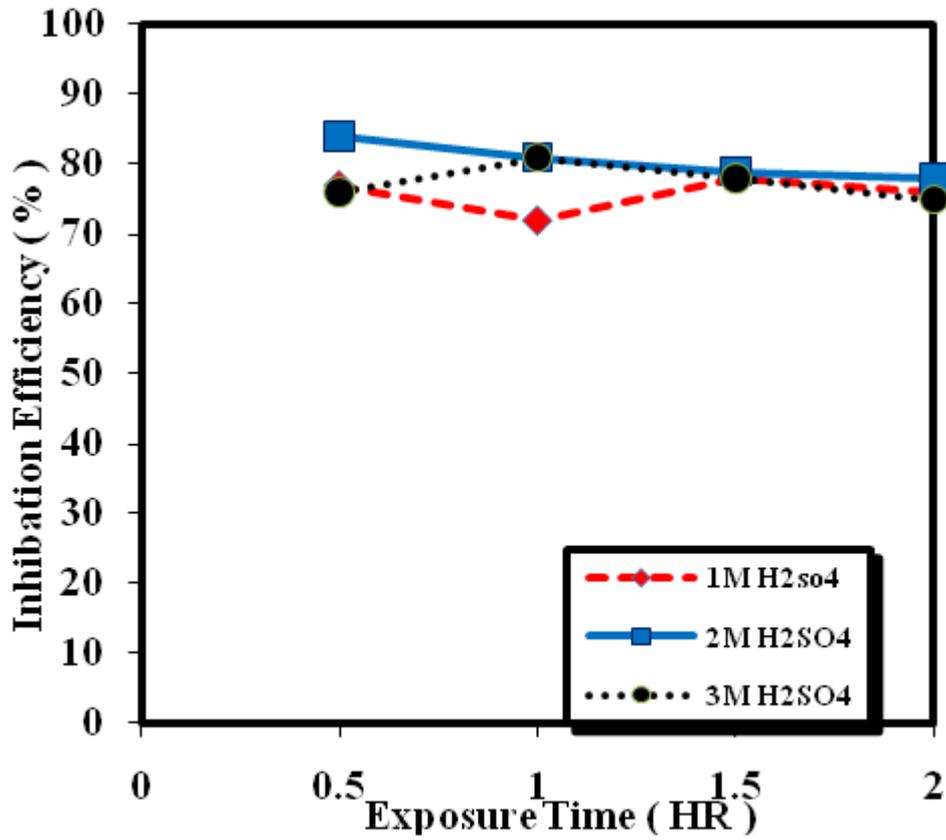
Fig.5. Effect of exposure time in 1, 2 and 3M H$_2$SO$_4$ at 40^{0}C

149
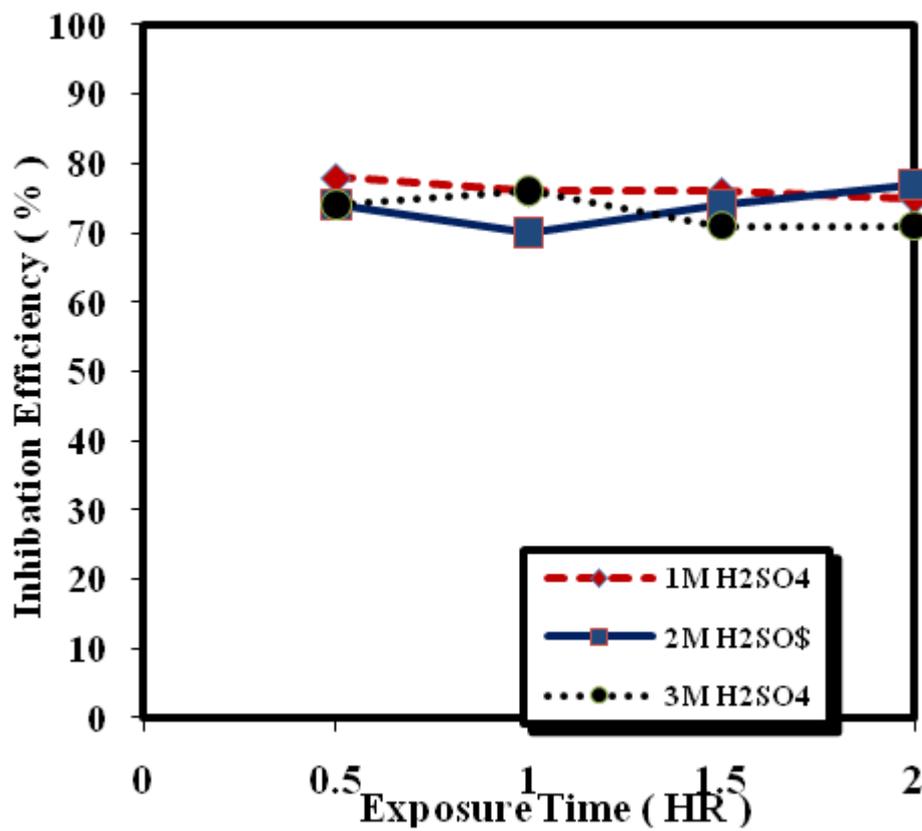
Fig.6. Effect of exposure time in 1, 2 and 3M H₂SO₄ at 60⁰C
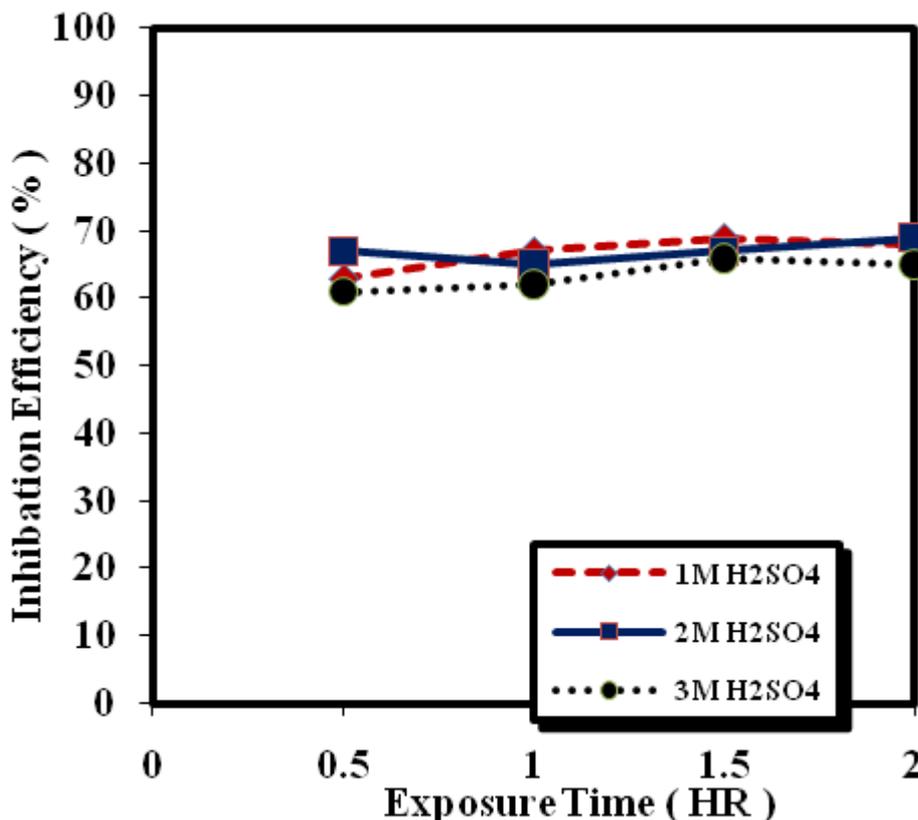
Fig.7. Potential vs. time plots for C-steel in 1M H₂SO₄ at 25⁰C with different CTAB doses
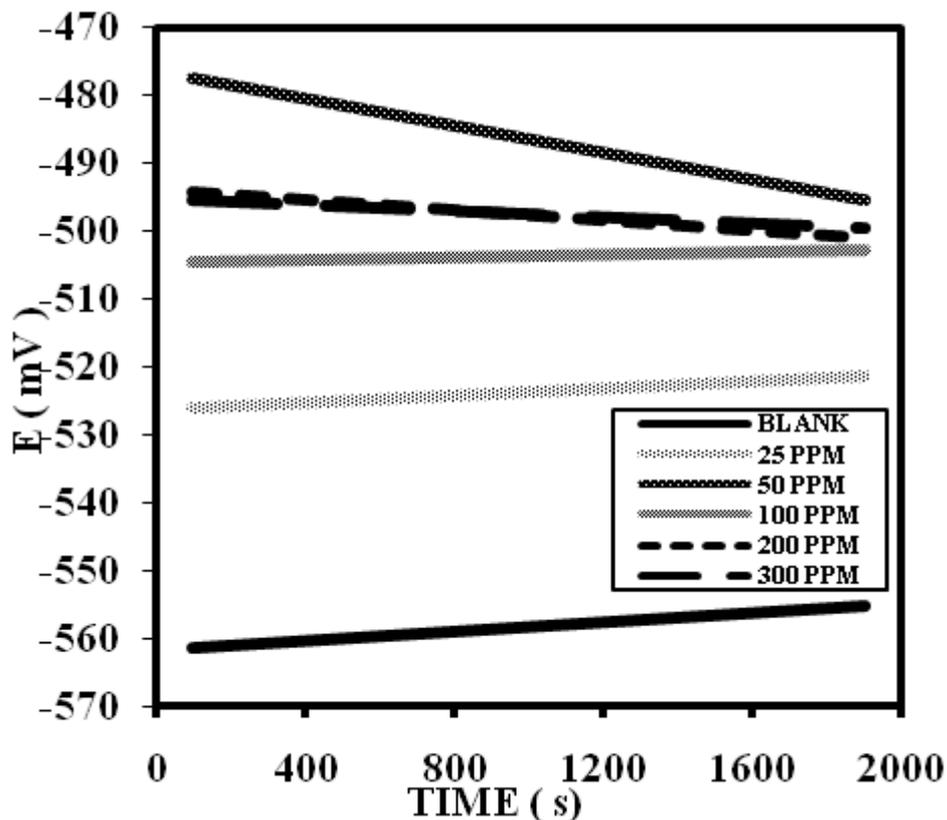
Fig.8. Potential vs. time plots for C-steel in 2M H$_2$SO$_4$at 25^{0}C with different CTAB doses
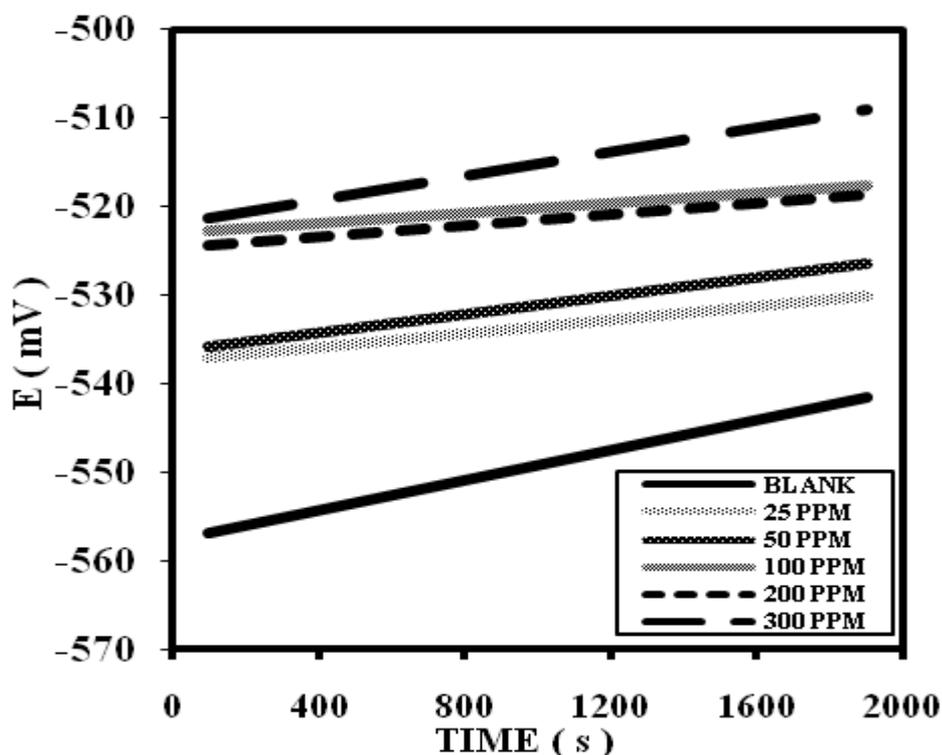
Fig.9.Tafel polarization curve for C-steel in 1M H$_2$SO$_4$ at 25^{0}C in absence and presence of CTAB
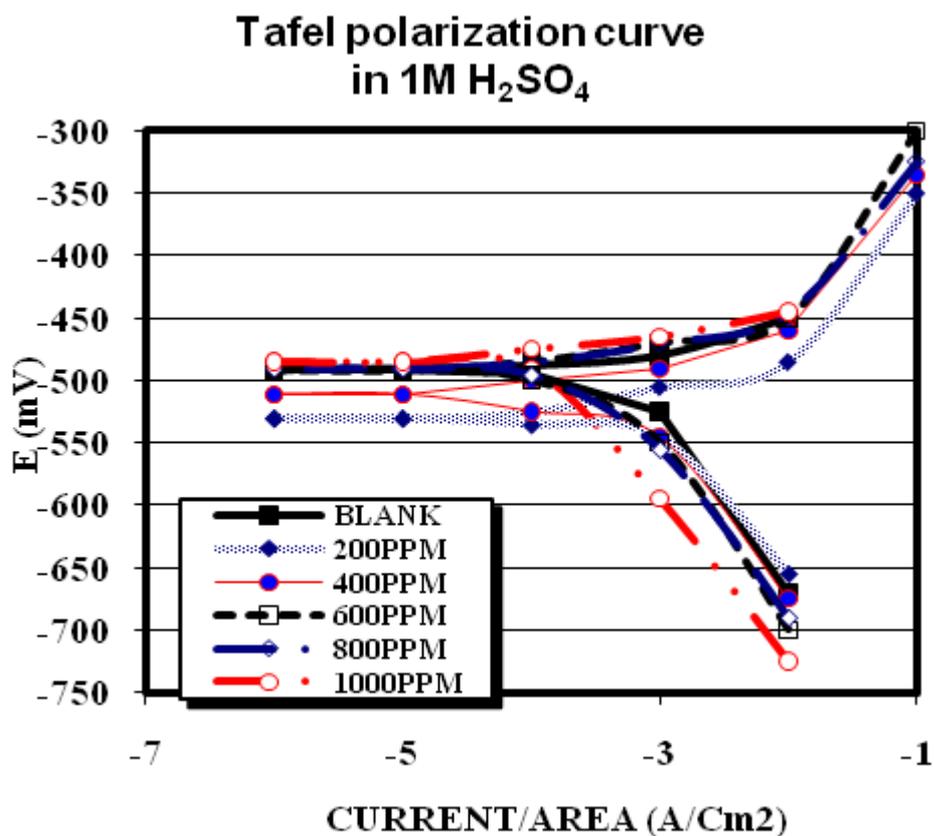
Fig.10.Tafel polarization curve for C-steel in 2M H$_2$SO$_4$ at 25^{0}C in absence and presence of CTAB

151
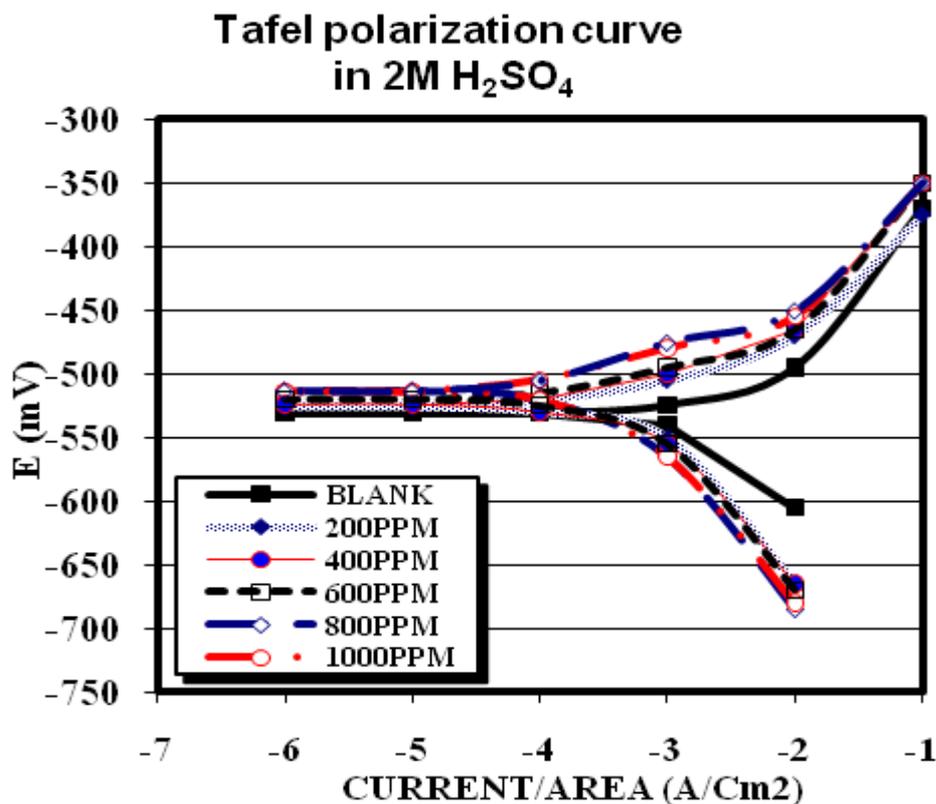
Fig.11. Polarization resistance measured for C-steel in 1M and 2M H₂SO₄ at 25⁰C
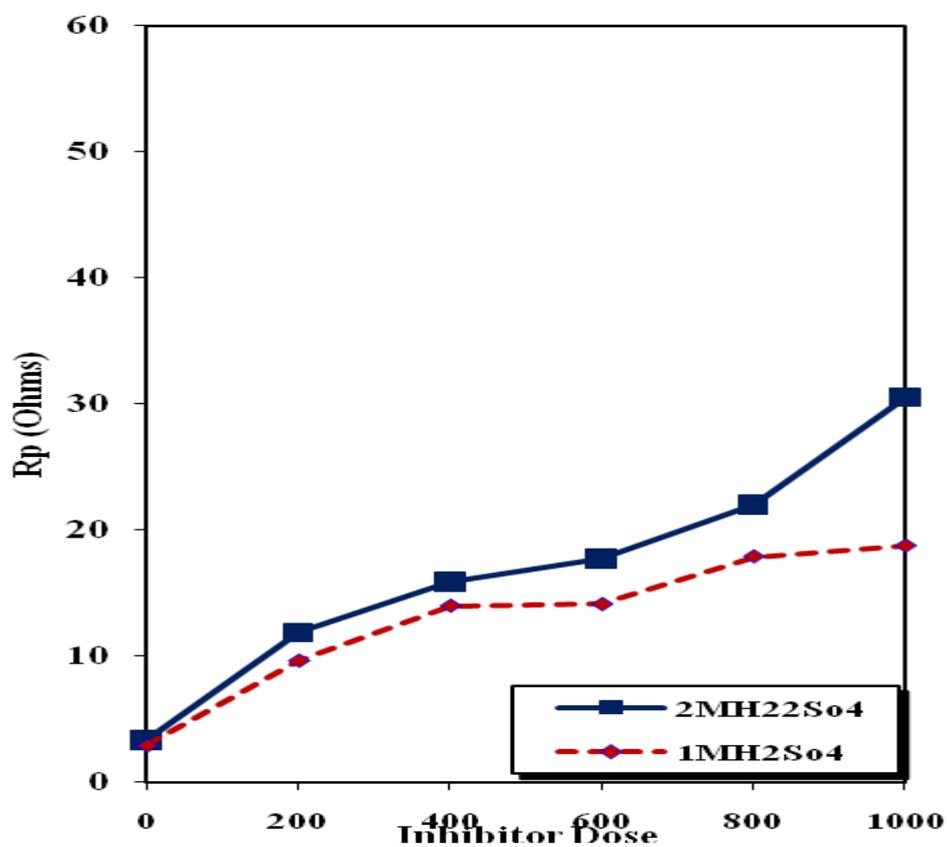
Fig.12. Polarization resistance measured for C-steel in 2M H₂SO₄ at 25, 35, and 45 ⁰C
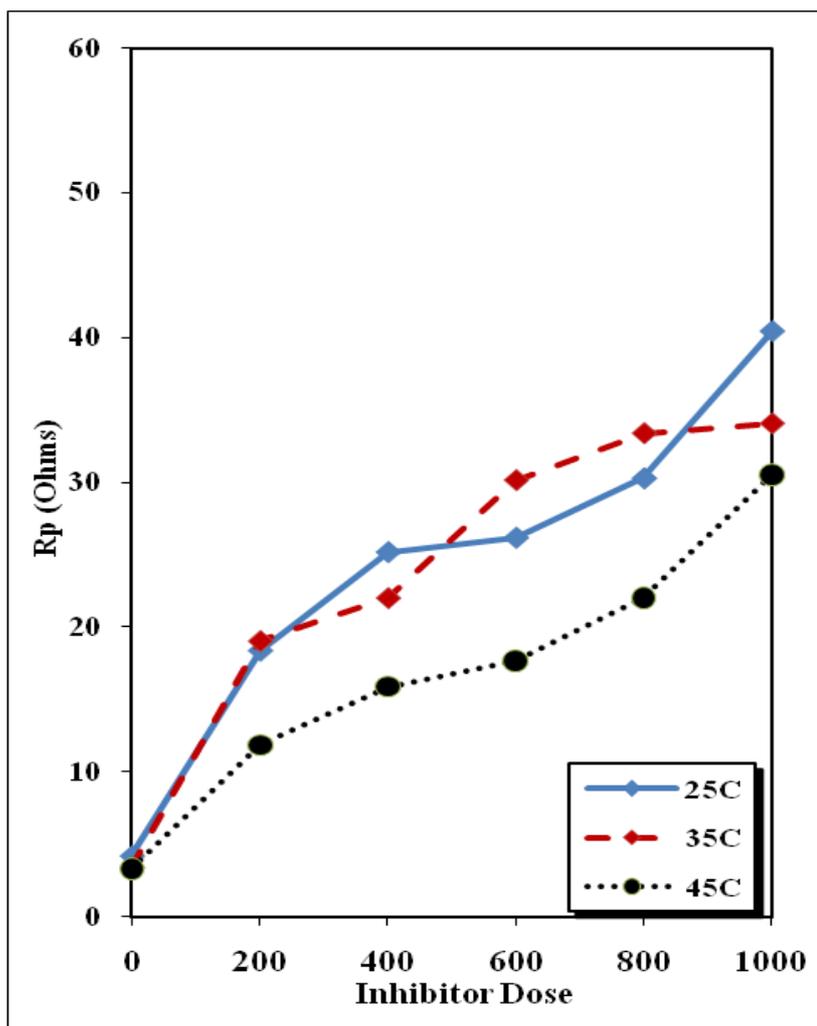
Fig.13. The relationship between C/θ and C at 25^{0}C in 1M and 2M H$_2$SO$_4$
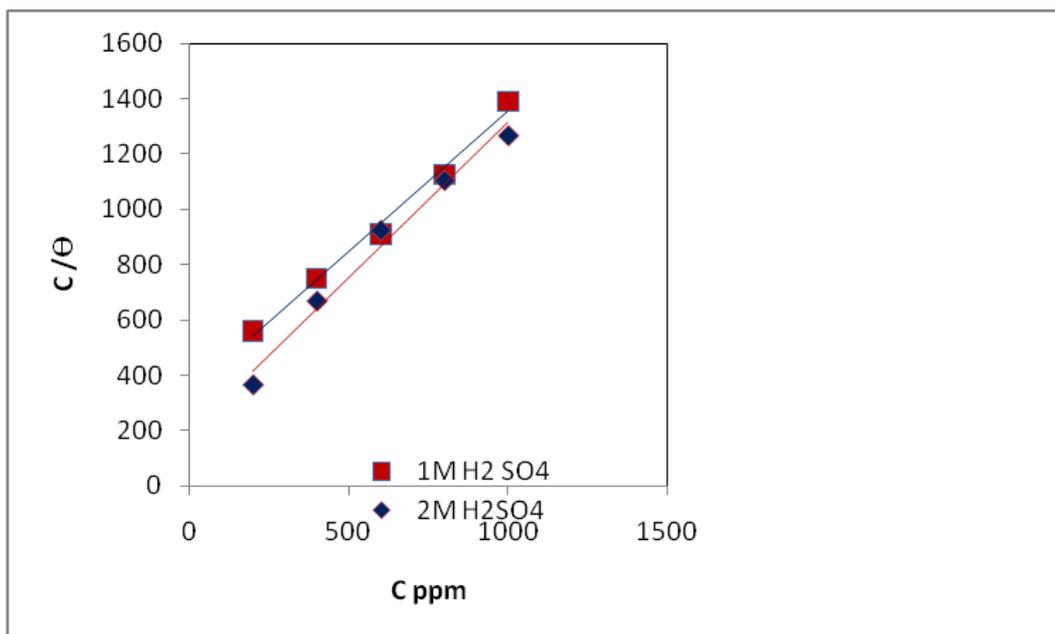
Fig.14. The relationship between log C.R and 1/ T in 1M H$_2$SO$_4$ in presence and absence of 300 ppm CTAB

153
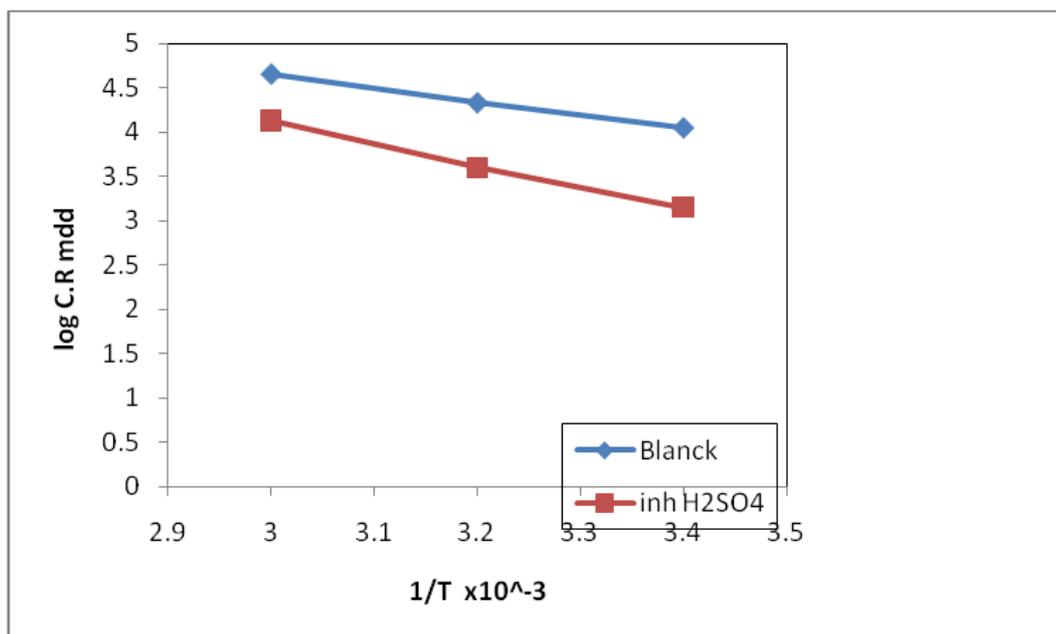
3.7. Mechanism of adsorption

The molecular weight of CTAB is large ($C_{16}H_{33} - N^+(CH_3)_3Br^-$), thus CTAB can relatively easily adsorb on the C-steel surface by Van der Waals force. In addition, the main hydrophilic part $^+N(CH_3)_3$ of CTAB may attack the C-steel surface while the main hydrophobic part ($-C_6H_{33}$) may extend to the solution face. Furthermore CTAB may chemisorb at steel / solution interface via chemical bond between positively charged nitrogen atoms and negatively charged C-steel surface as follows: In strong acidic solution, CTAB as a cationic surfactant, ionizes and carry a positive charge. As reported before [32], steel surface is positively charged in presence of sulfuric acid medium because of $E_{corr} - E_{q=0}$ (zero charge potential) >0, while bromide ion is negatively charged. As a result, the specific adsorption of bromide ion occurs onto C-steel surface, causing negatively charged surface of steel. By means of electrostatic attraction, ionized CTAB easily reaches C-steel surface, and the dipoles of the surface compound are oriented with their negative ends towards solution, preventing acid solution attach directly to C-steel surface. So, bromide ion acts as an adsorption mediator for bonding metal surface and CTAB. This gives rise to the formation of an adsorption composite film in which bromide ion are sandwiched between metal and positively charged part of the inhibitor. This film acts as a barrier facing corrosion process. Also it was found that the inhibition efficiency decreases with increases the experimental temperature, as previously reported by X. Li et al. [20], which indicates that the higher temperatures might cause desorption of CTAB from the C-steel surface.

CONCLUSION

Cetyl trimethyl ammonium bromide (CTAB) consider as effective corrosion inhibitor for C-steel dissolution in 1, 2 and 3M H_2SO_4 solutions. The maximum inhibition efficiency is about 89% in 2M H_2SO_4 solution. The inhibition efficiency values increase with the inhibitor dose, while decrease with increasing the sulphuric acid concentration and the temperature. The corrosion rate of C-steel in the presence and absence of CTAB acts as a function of immersion time. Increasing the immersion time resulted in increasing the inhibition efficiency. The weight loss and the electrochemical polarization studies are in good agreement. CTAB acts as a mixed-type inhibitor in 1M and 2M H_2SO_4. The adsorption of CTAB on C-steel surface obeys the Langmuir

154

adsorption isotherm. The value of both the adsorptive rate constant K and the apparent activation energy E_a are increases in the presence of CTAB in H_2SO_4 solutions. The inhibitive mechanism was proposed. When CTAB introduced into 1M and 2M H_2SO_4 solutions a film formed on the C-steel surface, which causes the decrease of the C-steel roughness and effectively protects C-steel from corrosion.

REFERENCES

[1] X. Li, L. Tang, H. Liu, G.Mu, G. Liu, *Materials Letters*,62(**2008**)2321.
[2] A. A. El Maghraby, *The Open Corros.J*. 2(**2009**)178.
[3] M. El Azhar, B. Mernari, M. Traisnel, F.Benties, M. Lagrenee, *Corros. Sci*. 43(**2001**)2229.
[4] M. Abdullah, *Corros. Sci*. 46(**2004**)1981.
[5] B. Sanyal, *Prog. Org. Coat*. 9(**1981**)165.
[6] L. B. Tang, G. N. Mu, G. H. Liu, *Corros. Sci*. 45(**2003**)2251.
[7] G. M. Abou- Elenien, A. A. El Maghraby, *J. Indian Chem. Soc*. 77(**2000**)473.
[8] L. B. Tang, X. M. Li, L. Li, G. N. Mu, G. H. Liu, *Surf. Coat. Technol*. 201(**2006**)384.
[9] L. B. Tang, X. M. Li, L. Li, Q. Qu, G. N. Mu, G. H. Liu, *Mater. Chem. Phys*. 94(**2005**)353.
[10] L. B. Tang, X. M. Li, L. Li, G. N. Mu, G. H. Liu, *Mater. Chem. Phys*. 97(**2006**)301.
[11] A. Popova, M. Christov, S. Raicheva, E. Sokolova, *Corros. Sci*.46(**2004**)1333.
[12] K. F. Khaled, *Appl. Surf. Sci*. 230(**2004**)307.
[13] A. Lagamri, H. A. El Makarimb, A. Guenbour, *Prog. Org. Coat*. 48(**2003**)63.
[14] F. Bentiss, M.Traisnel, N. Chaibi, et al., *Corros. Sci*. 44(**2002**)2271.
[15] M. A. Quraishi, H. K. Sharma, *Mater. Chem. Phys*. 78(**2002**)18.
[16] D. Chebabe, Z. A. Chikh, N. Hajjaji, et al. *Corros. Sci*. 45(**2003**)309.
[17] E.Elayyachy, A. El Idrissi, B. Hammouti*, Corros. Sci*. 48(**2006**)2470.
[18] T. P. Zhao, G. N. Mu, *Corros. Sci*. 41(**1999**)1937.
[19] M. Lebrini, F. Bentiss, H. Vezin, M. Lagrenee*, Corros. Sci*. 48(**2006**)1279.
[20] X. Li, S. Deng, G. Mu, H. Fu, F. Yang, *Corros. Sci*.50(**2008**)420.
[21] S. L. Granese, B. M. Rosales, C. Oviede, J. O.Zerbino, *Corros. Sci*. 33(**1992**)1439.
[22] G. N. Mu, X. H. Li, Q. Qu, J. Zhou, *Corros. Sci*. 48(**2006**) 445.
[23] F. Bentiss, M. Traisnel, M. Lagrenee, *Corros. Sci*. 42(**2000**)127.
[24] L. Elkadi, B. Marnari, M. Traisnel, F. Bentiss, M. Lagrenee, *Corros. Sci.*   42(**2000**)703.
[25] K. Gamal, Gomma, H. Mostafa Wahadan, *Bull. Chem. Soc. Jpn*. 67(**1994**)2621.
[26] M. Christov, A. Popova, *Corros. Sci*. 46(**2004**)1613.
[27] K. F. Khaled, *Electrochem. Acta* 53(**2008**)3484.
 [28] G. N. Mu, X. M. Li, F. Li, *Mater. Chem. Phys*. 86(**2004**)59.
[29] S. N. Banerjee, S. Misra, *Corrosion* 45(**1989**)780.
[30] E. S. Ferreira, C. Giacomelli, F. C. Giacomelli, A. Spineli, *Mater. Chem. Phys*. 83(**2004**)129.
[31] A. Popova, E. Soklova, S.Raicheva, M. Christov, *Corros. Sci*. 45(**2003**)33.
[32] H. Luo, Y. C. Guan, K. N. Han, *Corrosion* 54(**1998**)721.