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Electrochemical Studies On The Acidic Dissolution Of Carbon Steel In The Presence Of Inhibitors

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ABSTRACT

The effect of two corrosion inhibitors-namely, N,N′-dibenzyl ethane diammonium chloride and N,N′-dibenzyl butane diammonium chloride in 5% HCl under hot conditions has been studied by surface and electrochemical polarization measurements. Results obtained revealed that these better in 5% HCl at elevated temperatures. Tafel polarization studies showed that these inhibitors are anodic type inhibitors. Surface analysis using EDS measurement and SEM for the film formed and surface morphology showed high coverage of inhibitors on the carbon steel surface. The adsorption of these inhibitors on the C-steel surface in acidic media followed a Langmuir-adsorption isotherm.

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KEYWORDS

Carbon steel;
Acidic media;
Cationic surfactant;
Corrosion inhibitors;
Polarization;
Adsorption;
SEM;
EDS.

INTRODUCTION

The corrosion of iron and steel is a fundamental academic and industrial concern that has received a considerable amount of attention[1]. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media[2]. Progress in this field has been phenomenal in recent years and is borne out by the output of literature[3]. Acid solutions are used widely in industry, the most important field of application being acid pickling, industrial acid cleaning, acid descaling, and oil well acidizing. Because of the general aggressiveness of acid solutions, inhibitors commonly are used to reduce the corrosive attack on metallic materials.

Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms. The influence of organic nitrogen compounds on the corrosion of steel in acid solutions has been investigated by several researchers[4-11]. Quaternary ammonium compounds have been tried as inhibitors for corrosion of steel in acid media[12-14]. The parameters influencing their inhibitory effect have been described those including, influence of active groups, increase in alkyl chain length, combined action, formation of barrier film, the attractive Van der Waal's forces, a bimolecular layer and critical micelling concentration (CMC)[15].

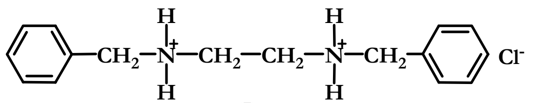
Existing data show that most organic inhibitors act by adsorption on the metal surface[16]. The most important prerequisites for compounds to be efficient inhibitors are that substances should form a compact barrier film and should adsorb strongly on the metal surface.

This work represents an extention to the previous one[17], where gravimetric, open circuit potential and linear polarization techniques have been tried to study the inhibitive behavior of our inhibitors in hot 5 % HCl solution.

In the present study, the effect of addition of two cationic surfactants namely N,N′-dibenzyl ethane diammonium chloride (I) and N,N′-dibenzyl butane diammonium chloride (II) on the corrosion inhibition of C-steel in 5 % HCl solutions was studied at temperature 30°C–90°C. The inhibition behavior was investigated by electrochemical polarization technique. Surface morphology of C-steel was studied by scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDS) in both corroded and inhibited conditions. Adsorption mode and corrosion inhibition mechanism on the C-steel surface in acidic solutions were discussed.

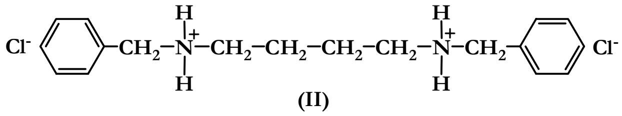
EXPERIMENTAL

Figure 1 shows the molecular structure of the investigated compounds. Inhibitors were prepared by condensing stoichiometric amounts of 1,2-ethylenediamine and 1,4-butylenediamine separately in aqueous alcohol with benzyl chloride[18]. Tests were performed on a carbon steel of the following composition: 98.43 % Fe, 0.7 % C, 0.3-0.6 % Mn, 0.03 % P, 0.5-.75 % Si and 0.035 % S. The aggressive solution, 5 % HCl was prepared from analytical grade with bi-distilled water. The concentration range of inhibitors used was 5-500 ppm.



(I)

N,N'-dibenzyl ethane diammonium chloride (I)



(II)

N,N'-dibenzyl butane diammonium chloride (II)

Figure 1: Molecular structure of the investigated compounds

Polarization experiments were carried out with a fine Luggin capillary to avoid ohmic polarization. All tests were performed at 30 °C-90 °C in magnetically stirred solutions, using EG & G potentiostat/ galvanostat model 352/252, interfaced to an IBM Ps/ 3 computer software V.-5.36 at 2 x 10^{-1} mV/s scan rate. The electrodes are of the form of sheet of 2.1 cm^2 exposed surface area, connected to a copper wire, enclosed in pyrex glass tube and mounted by araldite resin. A saturated calomel electrode (SCE) was used as reference electrode, with platinum net as a counter electrode. Before measurements, the electrodes were polished by emery papers of grades no. 600 and 1200. They were degreased with acetone, washed with bi-distilled water and dried at room temperature before use.

EDS (Energy dispersive X-ray spectroscopy) measurements were carried out using JSM-T 200 SEM/ EDS instrument (Jeol, Japan) in order to investigate the change in the composition of the surface film formed in absence and presence of optimum inhibitor dose on carbon steel samples (2.0 cm^2 exposed surface area) in 5 % HCl solution at temperature range 30 - 90 °C for 1h immersion time. Before the introduction into the EDS chamber the samples were thoroughly rinsed with distilled water and dried. When electrons emitted from such emitters and hit the specimen surface a survey analysis identifying all elements constituting the film surface of carbon steel was obtained.

RESULTS AND DISCUSSION

Electrochemical polarization measurement

Anodic and cathodic polarization curves for carbon steel in 5 % HCl at various concentrations [5-500 ppm] of inhibitor I and II at room temperature (30 °C) are shown in figure 2 and 3. Also, the electrochemical parameters, i.e. corrosion potential (E_c), corrosion current (I_c), the anodic and cathodic Tafel slopes (β_a, β_c), and the inhibition efficiency (I.E., %) obtained from Tafel line are listed in TABLE 1. I.E., % is calculated as follows

$$E.,\% = \frac{I_{c(uninh.)} - I_{c(inh.)}}{I_{c(uninh.)}} X100$$

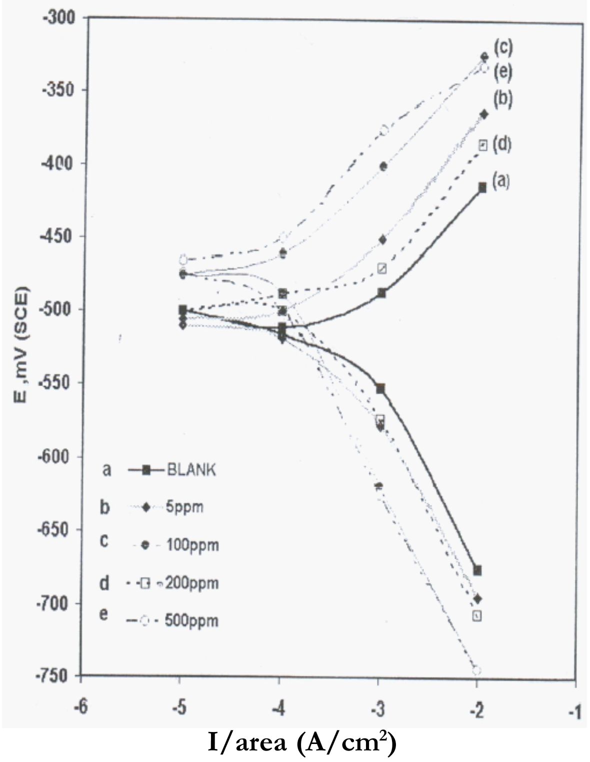


Figure 2: Polarization curves of carbon steel in 5 % HCl solution containing different additions of inhibitor I

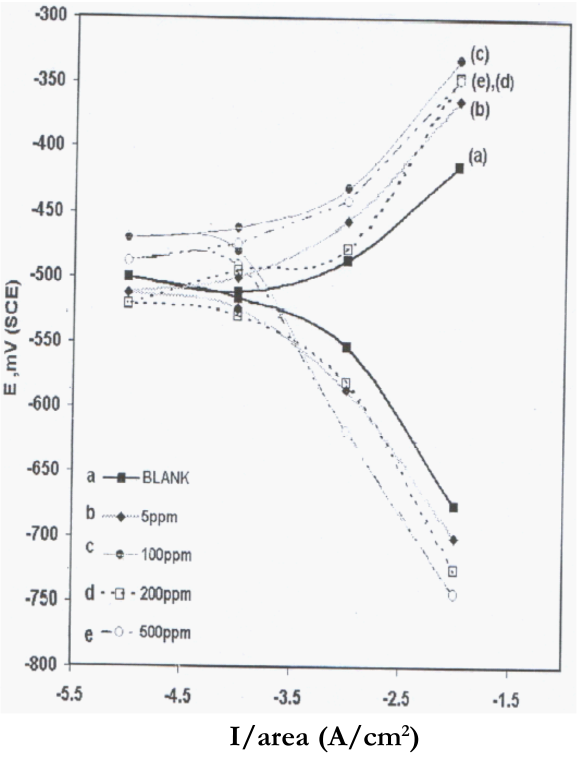


Figure 3: Polarization curves of carbon steel in 5% HCl solution containing different additions of inhibitor II

TABLE 1: Effect of different concentrations of inhibitors I & II on the electrochemical parameters obtained from Tafel Line (T.L.)

Inh.	Inh. Conc. ppm	$E_{corr.}$ (mV)	$I_{corr.}$ μA/cm²	β_a x 10^{-3} V/decade	β_c x 10^{-3} V/decade	C.R. mpy	I.E. %
	Blank	-516	719.6	103.5	144.6	331.2	
I	5	-511	356	82.6	135.4	164.1	50.4
	25	-511	380	81.6	132.9	175.7	46.9
	50	-506	340	84.8	151.7	170.2	48.6
	100	-504	250	50.9	157.3	151	54.4
	200	-492	190	41.2	128.5	110.8	66.5
	300	-485	150	40.4	140.9	51.2	84.5
	500	-476	102	40.8	146.5	42.0	87.3
II	5	-514	449	79.4	139.5	165.9	49.4
	25	-503	450	73.5	125.7	133.8	59.6
	50	-491	450	77.8	147	138.4	58.2
	100	-482	440	66.4	151.3	127.8	61.4
	200	-475	270	96.7	141.8	110	66.5
	300	-474	170	37.6	148.5	49.68	85
	500	-465	150	53.8	152.9	36.4	89

Generally, comparison between the behavior of inhibitor I and II showed that each concentration from inhibitor II would cause a higher shift in E_c (TABLE 1) towards a less negative direction than inhibitor I, this means that inhibitor II has a better performance than inhibitor I. This trend may be attributed to an increase of the number of carbon atoms in the alkyl groups of inhibitor II than inhibitor I[17]. The approximately constant values of the cathodic Tafel slopes (β_c) and the oscillating values of the anodic Tafel slopes (β_a) at TABLE 1 suggests that the inhibiting action of such compounds (inhibitors I & II) occurs by simple blocking of the electrode surface area, thus decreasing the surface area available for hydrogen evolution without affecting the reaction mechanism[19]. In this study, it has been observed that the magnitude of the displacement and the polarization curves appear to be dependent on the molecular structure of the inhibitor[20].

Figures 4 to 7 show the study of the effect of temperature (45 – 90 °C) on the polarization curves of C-steel dissolution in 5 % HCl, in absence and presence of the optimum dose (500 ppm) of the inhibitors (I&II). At every temperature, all the polarization curves shift towards lower values of current density, and the corrosion potential (E_c) shift to more noble values. As temperature increases (45 – 90 °C) the corrosion rate increases [TABLE 2] compared with that obtained at room temperature (30 °C), while the inhibition efficiency (I.E.) still at higher values. The rise of temperature causes an increase in the kinetic energy of molecules and therefore increase the aggregates of inhibitor molecules on the surface (increasing degree of surface coverage). At certain concentration, near its critical micellar value, higher efficiency appears which correspond to the formation of bimolecular layer at the electrode solution surface as described by Hajjaji et al.[13].

Adsorption isotherm

In formulating organic inhibitor system, it is required to know the inhibition mechanism and application field of the molecules concerned. It is generally accepted that organic molecules inhibit corrosion

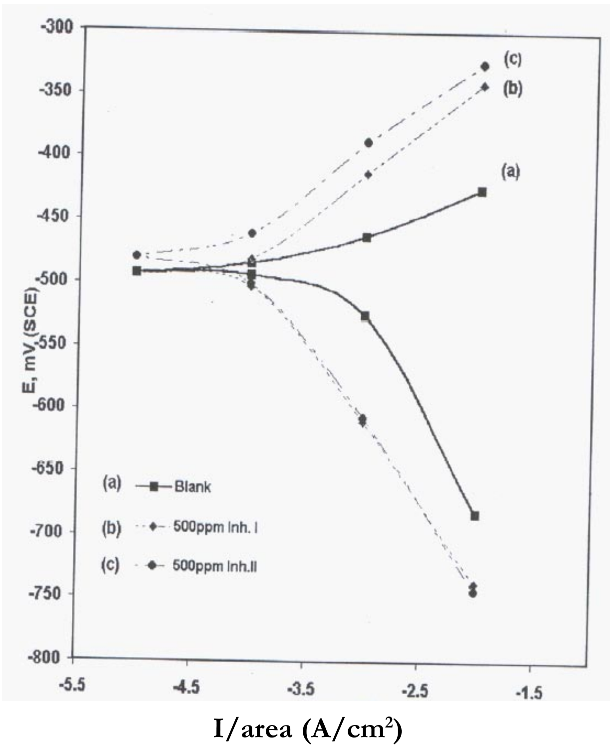


Figure 4: Polarization curves of carbon steel in 5% HCl solution in presence of 500 ppm dose of inhibitor I & II at 45 °C.

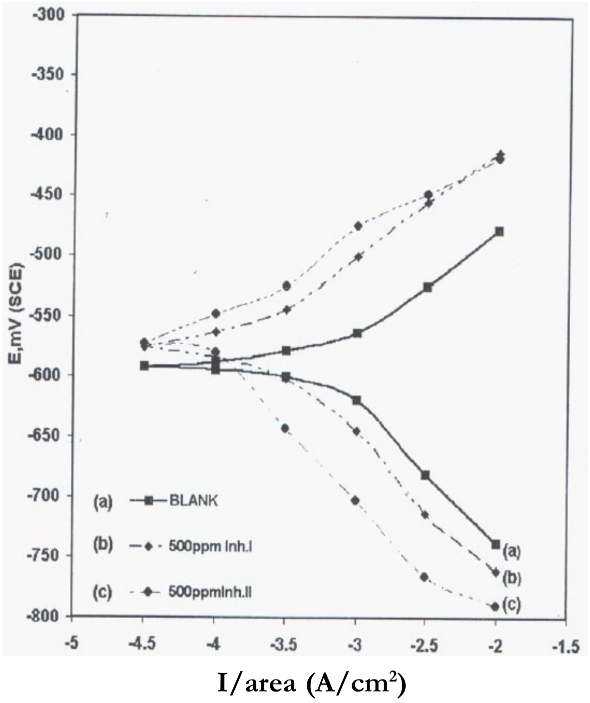


Figure 5: Polarization curves of carbon steel in 5 % HCl solution in presence of 500 ppm dose of inhibitor I & II at 60 °C.

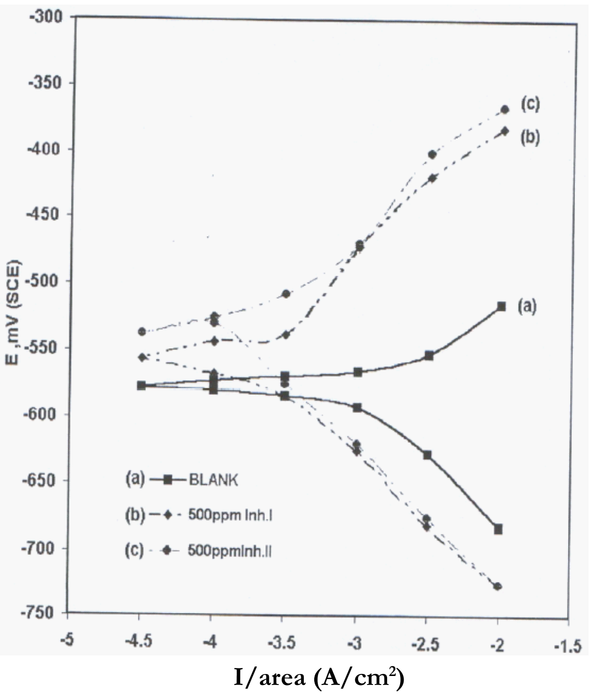


Figure 6: Polarization curves of carbon steel in 5 % HCl solution in presence of 500 ppm dose of inhibitor I & II at 75 °C.

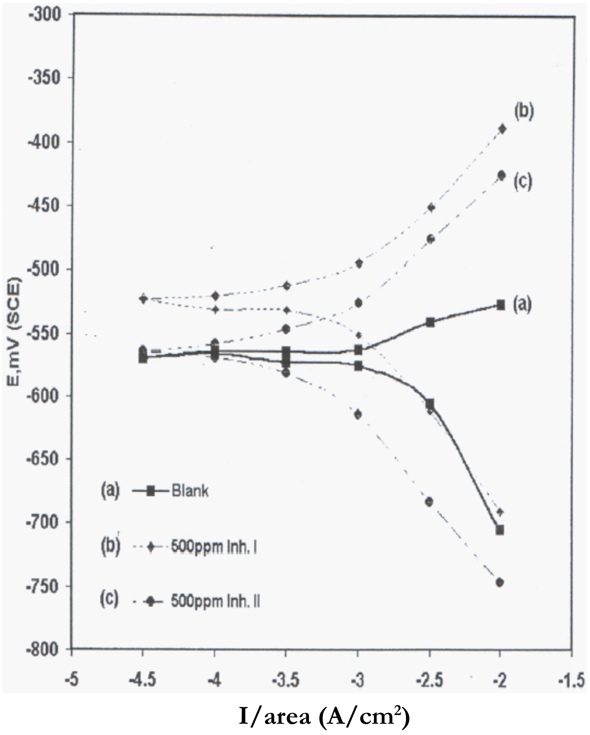


Figure 7: Polarization curves of carbon steel in 5% HCl solution in presence of 500 ppm dose of inhibitor I & II at 90 °C.

by adsorption at metal / solution interface and the degree of adsorption depends on the molecules chemical structure, the solution's chemical composition, the nature of metal surface, the temperature and the electrochemical potential at the metal / solution interface[21-26]. Adsorption provides information about the interaction among the adsorbed molecules as well as their interaction with the electrode surface[16]. A useful method that assists in the understanding of the mechanism of adsorption processes is the adsorption isotherm[27].

The corrosion data of the C-steel in 5 % HCl with different additives are fitted by the Langmuir ad-

TABLE 2: Effect of different temperatures on the electrochemical parameters (obtained from Tafel Line) of carbon steel in 5 % HCl solution in presence of 500 ppm of inhibitors I and II

Temp. °C	Inh. Conc. ppm	$E_{corr.}$ mV/SCE	$I_{corr.}$ μA/cm²	β_a x 10^{-3} V/decade	β_c x 10^{-3} V/decade	C.R. mpy	I.E. %
30	Blank	-516	719.6	103	144.6	331.2	
	Inh. I	-476	102	40.8	146.5	42	87.3
	Inh. II	-465	150	53.8	152.9	36.4	89
45	Blank	-592.4	742.3	73.7	180.5	341.7	
	Inh. I	-492.7	146.4	46.1	154.1	67.4	80.3
	Inh. II	480.7	159.9	44.5	151.1	73.6	78.4
60	Blank	-592.2	822.1	190.5	146.5	378.4	
	Inh. I	-576	321.1	104.2	144.8	147.8	60.9
	Inh. II	574.7	58.9	68.4	107.8	27.11	92.8
75	Blank	-578.2	232.5	195.4	174.9	1070	
	Inh. I	-556.6	208.1	90.16	105.7	95.79	91
	Inh. II	-538.9	269	94.27	122.6	123.8	88.4
90	Blank	-570.1	4713	37.14	197.3	269	
	Inh. I	-522.5	1424	113	194	655.5	69.7
	Inh. II	-563.5	501.8	105.6	148	231	89.3

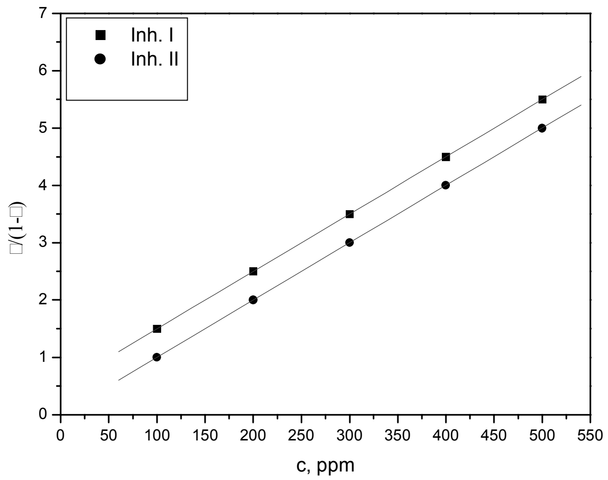


Figure 8: The langmuir adsorption isotherm for inhibitor I & II

sorption isotherm shown in figure 8, where the relation between θ/1- θ vs. C gives straight line, according to the following equation

$$\frac{\theta}{1-\theta} = K[C]$$

Where

θ : the degree of surface coverage.

C : the inhibitor concentration in the electrolyte.

K : the equilibrium constant of the adsorption process.

θ can be calculated from the results of electrochemical measurements, as follows:

$$\theta = \frac{I_{c,uninh.} - I_{C,inh}}{I_{C,uninh.}}$$

Where

$I_{C,uninh.}$: the corrosion current in μA / cm^2 in the absence of inhibitors.

$I_{C,inh.}$: the corrosion current in μA / cm^2 in the presence of inhibitors.

Langmuir equation is accepted generally as the most appropriate for steel / inhibited acid system[28].

The adsorption of inhibitors on the metal surface occurs either directly, on the basis of donor-acceptor interactions between the quaternary ammonium compound and the iron surface atoms, or interaction of inhibitors with already adsorbed chloride ions[29]. The better performance of inhibitors in 5 % HCl can be explained. In aqueous acidic solutions, the inhibitor exists in the form of cations. The compound may adsorb through electrostatic interactions between the positively charged nitrogen atom and negatively charged metal surface[30]. It has been observed that the adsorption of the inhibitor can be influenced by the nature of anions in acidic solution[31,32]. The specific adsorption of anions having a smaller degree of hydration, such as chloride ions, is expected to be more pronounced. Being specifically adsorbed, they created an excess negative charge toward the solution and favor more adsorption of the cations[33].

Surface analysis

SEM measurement

The results of these investigations are shown in figures 9 to 12. SEM of the mechanically polished C-steel electrode without any treatment, figure 9 shows no sites of corrosion area. The treated sample by 5 % HCl has true corrosion areas figure 10. The presence of such regions can be attributed to the surface attack of aggressive chloride ions leading to the dissolution of C-steel.

Immersion of C-steel samples in 5 % HCl solutions containing the optimum dose 500 ppm of both inhibitors I and II are shown in figure 11 and 12. As can be seen, an improvement in the surface morphology possibly by diminishing the corrosion areas due to covering of the active sites responsible for dissolution by protective film. This reflects the decrease in

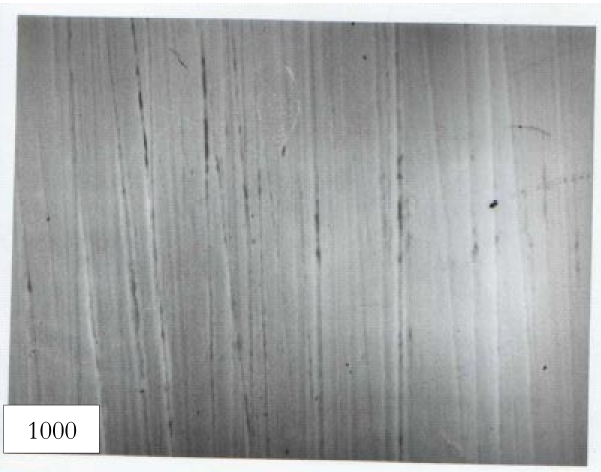


Figure 9: (X-1000) sample without immersion (Clean Sample) Sample A.

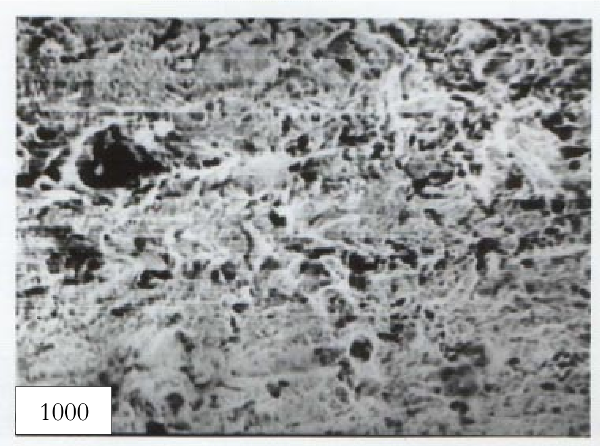


Figure 10: (X-1000) after 1hr immersion in 5 % HCl solution sample B

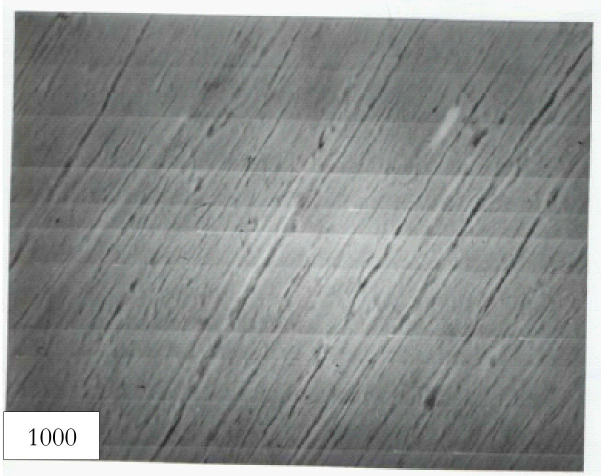


Figure 11: (X-1000) after 1hr immersion in 5% HCl containing 500 ppm dose of inhibitor I sample C.

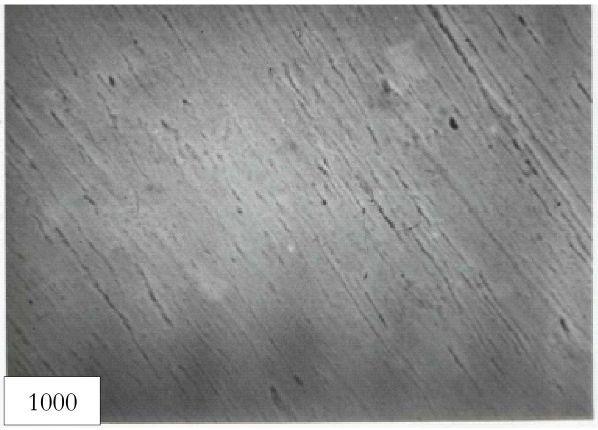
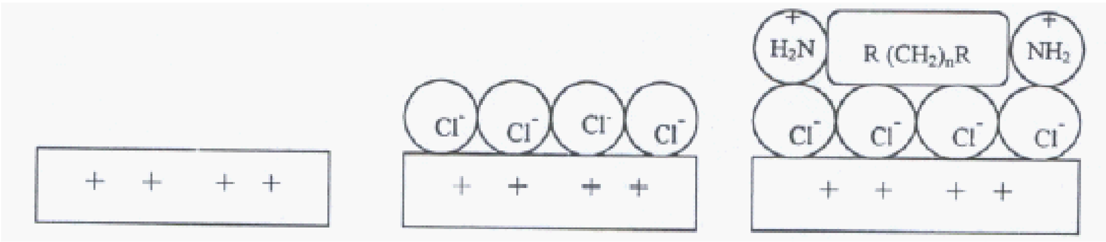


Figure 12: (X-1000) after 1hr immersion in 5 % HCl containing 500 ppm dose of inhibitor II sample D.

corrosion rate of C-steel in the presence of two inhibitors than inhibitor free solution.

Mechanism

In view of many investigations carried out[34] concerning the nature of organic inhibitor film, it is intended to try to explain the adsorption mechanism of the investigated inhibitors. McCafferty and Hackerman[35,36] showed the importance of molecular configuration and the steric effect by studying organic diamines, which were of great interest because of their possibility of adsorption at the metal/solution interface in several different configurations or orientations. These configurations include the vertical position in which only one of the two end groups is adsorbed with the hydrocarbon chain existing out-



Positively charged metal surface
(a)

Halide ion adsorbed
(b)

Organic cation adsorbed
(c)

Figure 13: Schematic adsorption mechanism positively charged metal surface in presence of 5 % HCl solution.
Adsorption of Cl^- ions on the positively charged metal surface.
Adsorption of organic cations on Cl^- ions.

ward, and the flat position in which both end groups are adsorbed with the hydrocarbon network parallel to the surface. In addition, if the molecule is long enough to be flexible, the hydrocarbon chain can be buckled between the two adsorbed end groups to present a hydrophobic "hump" to the solution.

From these point, and from the data previously stated, we can conclude that tetraalkyl diammonium cations like $^+[RNH_2(CH_2)_nNH_2R]^+$ are weakly adsorbed on carbon steel, since the metal surface is positively charged in acid media. However, the chloride ions produced as a result of dissociation of organic inhibitor salt are adsorbed on the surface of C-steel and decrease its positive charge and producing a negative adsorption potential, thus facilitating the adsorption of organic cation and stabilizing the formation of compact film. The schematic adsorption mechanism is shown in figure 13.

CONCLUSIONS

1. Electrochemical studies on the corrosion inhibition behavior of C-steel in 5% HCl show that both inhibitors (I, II) behaves as anodic type inhibitors.
2. The two inhibitors are able to inhibit the corrosion even at higher temperatures (45°C - 90°C).
3. Inhibitors I and II obey the Langmuir isotherm, and compounds acted through adsorption mechanism, where compounds are dissociated in acid medium producing chloride ions and organic cations. Chloride ions decrease the positive charge on C-steel thus facilitating the adsorption of organic cation.
4. SEM investigation show an improvement in the surface morphology possibly by dimensioning the corrosion ares due to covering of the active sites responsible for dissolution by protective film.
5. Finally, the two cationic surfactants behave as an efficient corrosion inhibitors for C-steel-acid pickling due to the formation of protective film.

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