



## Preparation of Amino nictino nitril and its application as corrosion inhibitor for carbon steel

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### Abstract

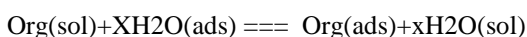
In this study , the inhibition effect of amino nictino nitril on carbon steel corrosion in 0.5 M Hcl solution was studied . for this aim , electrochemical techniques such as potentiodynamic polarization curves, weight loss(WL) were used . it was shown that , the amino nictino nitril has aremarkable inhibition efficiency on the corrosion of carbon steel in 0.5 M Hcl solution . polarization measurements indicated that,the studied inhibitor acts as mixed type corrosion inhibitor with predominatly control of cathodic reaction. The inhibition efficiency debends on Athe concentration of inhibitor and reaches 92 % at .001 M Amino nictino nitril was discussed in terms of blocking of electrode surface by adsorption of inhibitor molecules through active centers . the adsorption of amino nictino nitril molecules on the carbon steel surface obeys Langmuir adsorption isotherm.

**Key words:** C-steel, organic synthesis, Corrosion inhibition

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### 1. Introduction

The investigation of adsorption of surfactants at solid/liquid interfaces is extremely important in electrochemical studies [ 1]. Their adsorption on the metal surface can markedly change the corrosion resisting properties of metals [2]. The study of relationship between adsorption and corrosion inhibition is of great importance;science the corrosion inhibition is a surface process and the degree of protection of metal is a function of adsorption [2,3].corrosion in mineral acids represents a terrible waste of both resources and money [4]. Corrosion prevention systems favour the use of environmental chemicals with low or zero environmental impacts. The use of organic molecules as corrosion inhibitor is one of the most practical methods for protecting against the corrosion and it is becoming increasingly popular.the existing data showed that organic inhibitors act by the adsorption on the metal surface and protective film formation.the adsorption of organic inhibitors at the metal/solution interface takes place through the replacement of water molecules by organic inhibitor molecules according to the following process [5]



Where Org(sol) and Org (ads) are organic molecules in the solution and adsorped on the metal surface ,respectively. x is the number of water molecules replaced by the organic molecules. It was shown that organic compounds containing hetero atoms with high electron density such as phosphorous,nitrogen,sulpher,oxygen as well as those containing multiple bonds which are considered as adsorption centerers,are effective as corrosion inhibitor [ 6-9] . it has been also found that the molecules contain both nitrogen and sulpher in their molecular structure have exhibited greater

Corrosion inhibition efficiency in comparison with these atoms[10-14] Recently schiff base compounds have been of Ag/Agcl reference electrode. The working electrode was immersed in test solution for 15 m to establish steady state open circuit potential.

### 2. Experimental

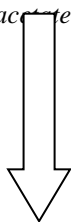
#### 2.1. preparation of Amino nictino nitril:

Inhibitor (I)(1.41 gm of cloro benzaldehyde)+(0.66 gm of malono nitril)+(1.21 gm of ketone)+(1.15 gm of amino acetate) was dissolved in ethanol and then reflux for four hours and wait for cooling and make filtration using filter

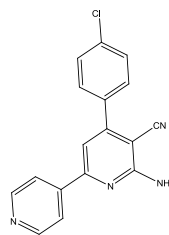
paper and wait for drying and recrystallized from hot ethanol to give the desired product.

Scheme 1. preparation of amino nictino nitril .

Chlorobenzaldehyde + malononitril + ketone =+ amonium acetate



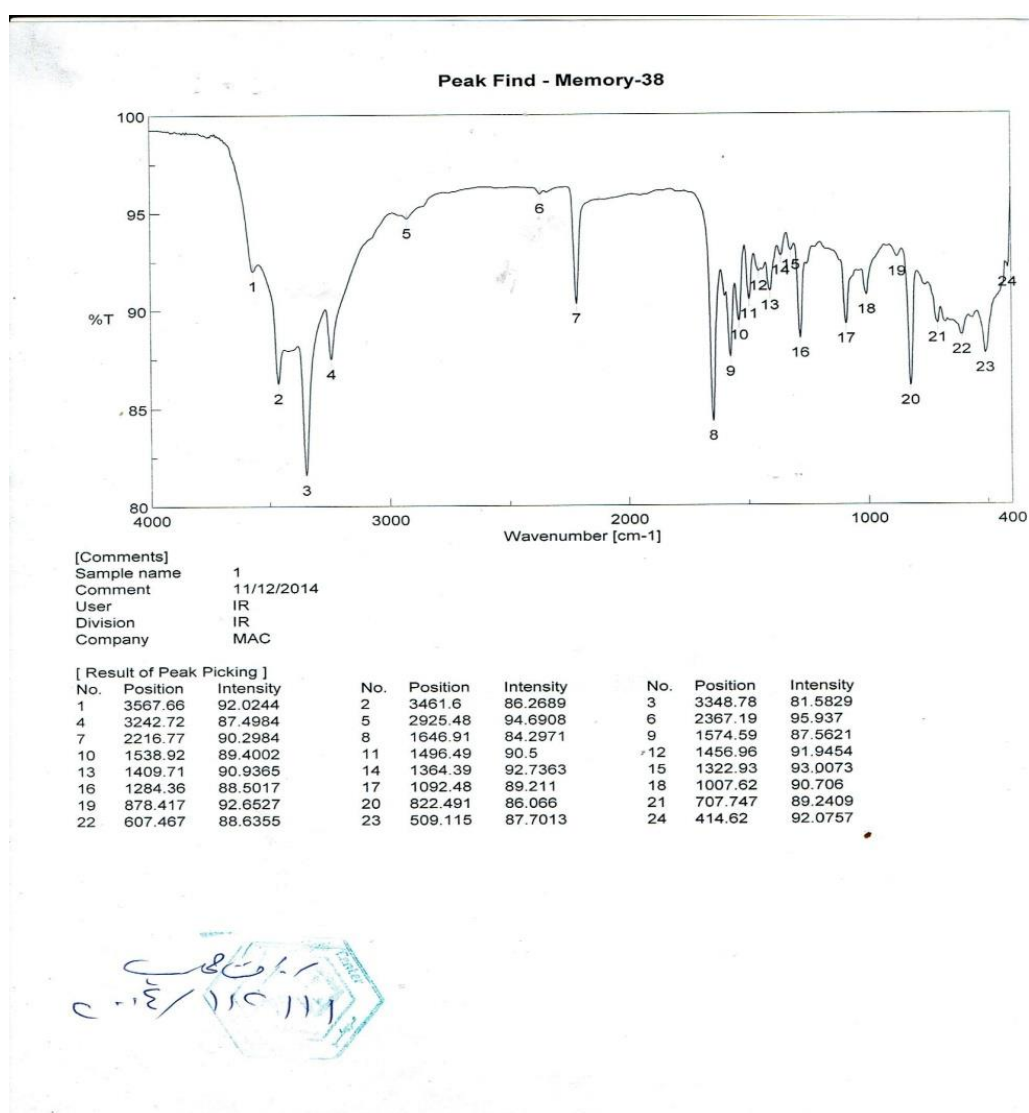
- 1\_ Dissolve in 20 ml ethanol
- 2\_ Reflux for 4 hrs
- 3\_ Cool
- 4\_ filtration



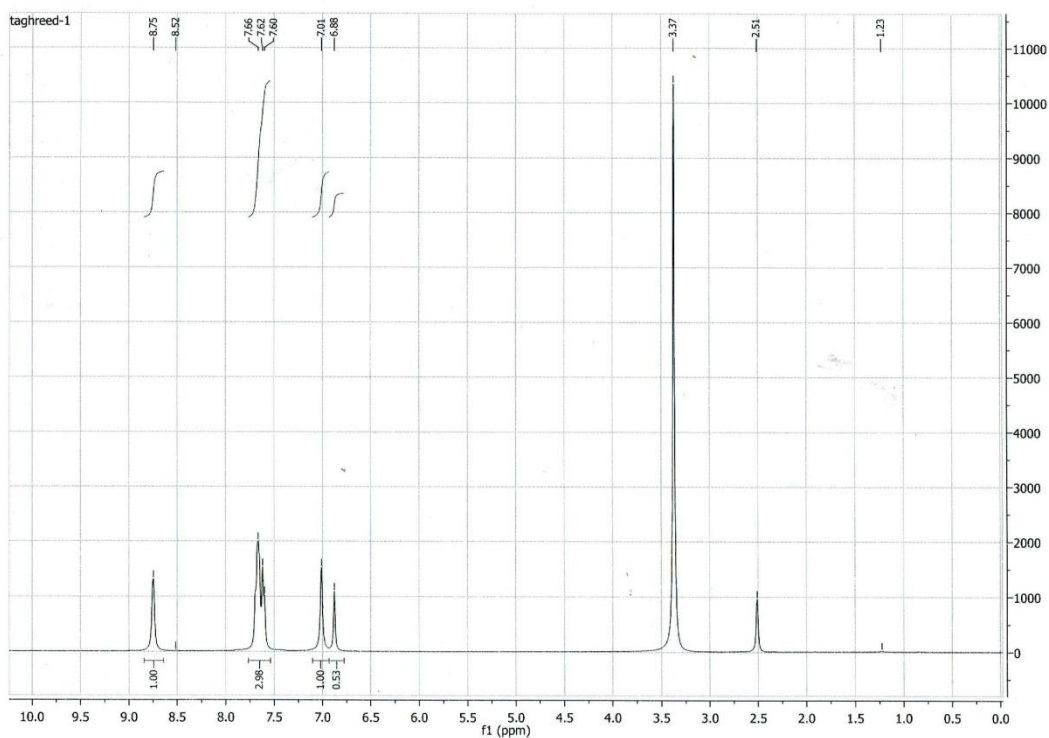
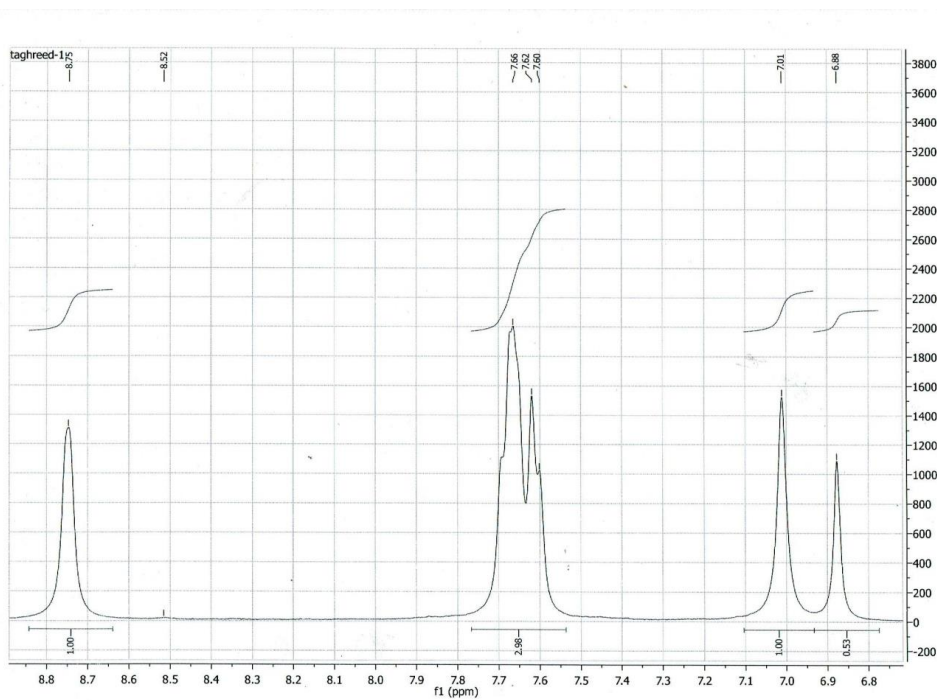
I.R and NMR spectra of amino nictino nitril

The synthesized compound was elucidated by IR and HNMR spectra. IR spectrum showed characteristic bands at( 3461 -3242 ) cm-1 ( NH2 ) , 2216.77 cm-1 (  $\nu$  C  $\equiv$  N ) , 1646.91 cm-1 (  $\nu$  C = N ).

HNMR dppm : 8.75 (S,2H,NH variable), 6.88-7.66 (m,4H Ar H),



2.51-3.37DMSO solvent



## 2.2. Test solutions

The corrosive medium was 1 M HCl acidic solution was prepared by diluting the appropriate volume of the concentration chemically pure acid (37 % merck), with bi-distilled water. The various concentrations of the synthesized cationic surfactant inhibitors used were ( $1 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $3 \times 10^{-4}$ , and  $5 \times 10^{-4}$  M). All test

solutions were prepared from bi-distilled water. For each experiment, a freshly prepared solution was used.

## 2.3. Weight loss measurements

Weight loss experiments were carried out using the specimens of carbon steel (CS) which have the following composition: 0.025 % Si, 0.09 % P, 0.1 % C, 0.05 % Ni, 0.02 % Cr, 0.01 % Mn, 0.03 % Cu, 0.001 % V, and the

remainder Fe. Carbon steel specimens were machined to be a rectangular with dimensions of (length 4.8, width 2, and thickness 1.1 cm) with an exposed total surface area of 34.16 cm<sup>2</sup> was used for gravimetric measurements. The specimens were mechanically polished with different grade emery papers, washed with distilled water, acetone and water again. The specimens were accurately weighted and then immersed in 1 M HCl acid solution without and with various concentrations of the synthesized surfactant inhibitors (ACS3.1 and ACS3.2) at various temperatures at 20–60 °C. The temperature for weight loss measurements was dominated by water bath provided with thermostat control ±2 °C. After 24 hours exposure, the specimens were taken out rinsed thoroughly with distilled water, dried and weighted accurately. All tests in this study were done under aerated conditions.

#### 2.4. Potentiodynamic polarization measurements

The polarization measurements were recorded by a Meinsberger Potentiostat/ Galvanostat (PS6) with

controlling software PS remote in a personal computer. Platinum electrode and a saturated calomel electrode was utilized as a counter electrode and reference electrode, respectively. The working electrode was a cylinder of carbon steel, embedded in epoxy resin with a surface area of 1.56 cm<sup>2</sup> exposed to the corrosive acidic solution. All measurements were carried out at a scan rate 1 mV Sec<sup>-1</sup>.

### 3-Results and discussion

#### 3.1 weight loss measurements

The weight loss of carbon steel specimens after exposure to .5 MHCl solution with and with out addition of various concentration of Amino Nictino Nitril was calculated in (1/cm<sup>2</sup>.hr) . and the data obtained were given in table 2. It is clear in table 2 that the addition of inhibitor to the aggressive solution reduce dissolution rate of carbon steel efficiency . The WL was reduced with increasing Schiff base concentration indicates that the inhibitor molecules act by adsorption on the metal surface.

Table (1): Data of Carbon steel corrosion in0.5MHCl solution devoid of and containing different inhibitor concentrations at different exposure times.

Exposure Time, h	1		2		3		4		24	
CONC. M	R mg/cm <sup>2</sup> .hr	I.E%	R mg/cm <sup>2</sup> .hr	IE%	R mg/cm <sup>2</sup> .hr	IE%	R mg/cm <sup>2</sup> .hr	IE%	R mg/cm <sup>2</sup> .hr	IE%
Free	130X10 <sup>-5</sup>	—	41X10 <sup>-5</sup>	—	22X10 <sup>-5</sup>	—	16X10 <sup>-5</sup>	—	13X10 <sup>-5</sup>	—
1x10 <sup>-5</sup>	49X10 <sup>-5</sup>	62	9.7 X10 <sup>-5</sup>	76	6.4X10 <sup>-5</sup>	71	4.8X10 <sup>-5</sup>	69.5	4.3X10 <sup>-5</sup>	67
5x10 <sup>-5</sup>	45X10 <sup>-5</sup>	65	7.8X10 <sup>-5</sup>	81	5.1X10 <sup>-5</sup>	77	4.1X10 <sup>-5</sup>	74	3.9X10 <sup>-5</sup>	70
1x10 <sup>-4</sup>	28X10 <sup>-5</sup>	78.5	6.2X10 <sup>-5</sup>	85	3.6X10 <sup>-5</sup>	83.5	2.7X10 <sup>-5</sup>	83	2.2X10 <sup>-6</sup>	83
5x10 <sup>-4</sup>	14.5X10 <sup>-5</sup>	88.5	4.1X10 <sup>-5</sup>	90	2.3X10 <sup>-5</sup>	89.5	1.9X10 <sup>-5</sup>	88	1.7X10 <sup>-5</sup>	87
1x10 <sup>-3</sup>	11.6X10 <sup>-5</sup>	91	3.3x10 <sup>-5</sup>	92	1.7X10 <sup>-5</sup>	91.5	1.4X10 <sup>-5</sup>	91	1.3X10 <sup>-5</sup>	90

The effect of increasing concentration of inhibitor (I) on the corrosion rate of Carbon steel in 0.5 M HCl solution was studied using weight loss technique. Figure (1) that represented the Relation between Inhibitor (I) exposure time and inhibition efficiency reveals that inhibition efficiency decrease as the exposure time is increased .

Inspection of Fig (1) reveals a fast absorption on metal leads to high inhibition efficiency in first hours and decrease with increasing time this result may be interpreted taking into account that the inhibitor is consumed in solution with increasing time of exposure. This consumption happen slowly in high concentrations and increases with low concentrations.

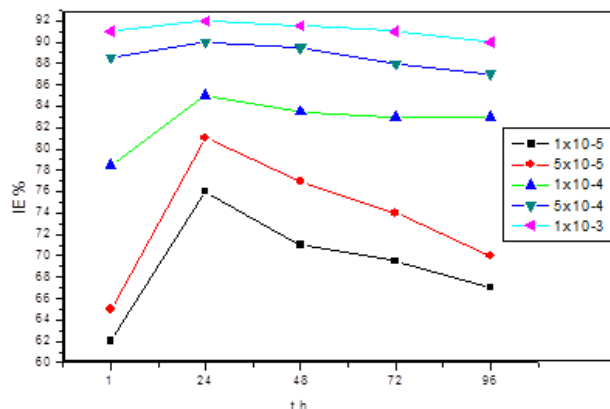


Fig (1): Relation between Inhibitor (I) exposure time and inhibition efficiency.

### 3.2. Potentiodynamic polarization

The representative potentiodynamic polarization curves of carbon steel in 1 M HCl solution in the absence and presence of various concentrations of cationic surfactant inhibitors (ACS3.1 and ACS3.2) are shown in Figure (2). The corresponding electrochemical parameters, i.e., corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), cathodic and anodic Tafel slopes ( $\beta_c$  and  $\beta_a$ ) and inhibition efficiency ( $\eta_p$ ) values were calculated from Figure (2) and are given in Table (2). It is apparent from Table (2) that, when the concentrations of the studied cationic surfactant inhibitors were increased, the inhibition

efficiencies ( $\eta_p$ ) increased while the corrosion current densities decreased. The inhibitive action of this inhibitor was discussed in terms of blocking the electrode surface by adsorption of the molecules through the active centers contained in its structure. The corrosion potential ( $E_{corr}$ ) of this inhibitors shifted slightly in the negative direction as shown in Table (2). This behavior indicated that the inhibitor predominantly controls both anodic and cathodic reactions. The values of the cathodic Tafel slope ( $\beta_c$ ) and the anodic Tafel slope ( $\beta_a$ ) for the inhibitor were shifted slightly. The slight variations in the Tafel slope suggested that the cationic inhibitor is blocking the cathodic and anodic sites without changing the corrosion mechanism.

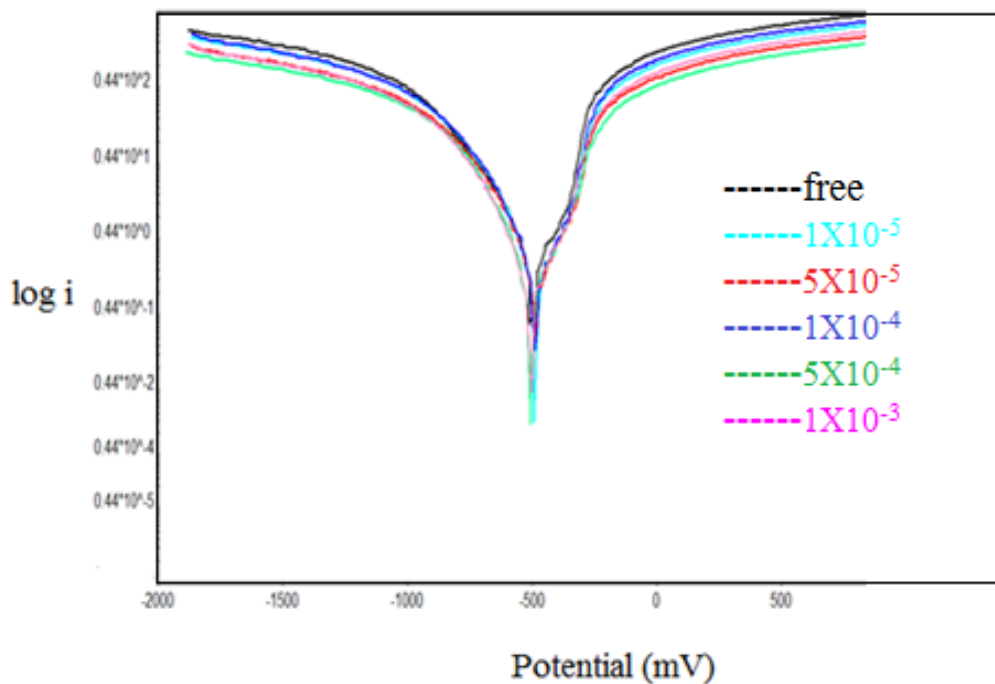


Fig (2): Polarization curves of Carbon steel in 0.5 M HCl in absence and presence of various concentrations of Inhibitor.

Table (2): Corrosion parameters of Carbon steel in 0.5 M HCl solutions devoid of and containing different concentrations of Inhibitor.

CONC.	-Ecorr (mv)	$\beta_a$ (mV/Decade)	$\beta_c$ (mV/Decade)	Icorr (mA)	IE %	$\theta$
Free	495	104	145	0.32	-----	-----
1X10 <sup>-5</sup>	515	98	159	0.28	12.5	0.12
5X10 <sup>-5</sup>	510	97	132	0.25	16	0.16
1X10 <sup>-4</sup>	526	97	134	0.2	33	0.33
5X10 <sup>-4</sup>	515	99	110	0.14	53	0.53
1X10 <sup>-3</sup>	513	100	101	0.11	63	0.63

### 3.3. Effect of Temperature

The effect of temperature (in the range of 303 – 343 K), on the corrosion of Carbon steel in 0.5M HCl solutions devoid of and containing 1x10<sup>-3</sup>M of the three tested inhibitors was studied using potentiostatic polarization.

The Potentio dynamic polarization curves for the tested inhibitor are represented in Fig (3) and the data are presented in table (3). The results show that, as the temperature increases the cathodic curves shift toward less negative values where as the anodic curves shift toward more negative values. Both branches are shifted toward high current values upon increasing the temperature .

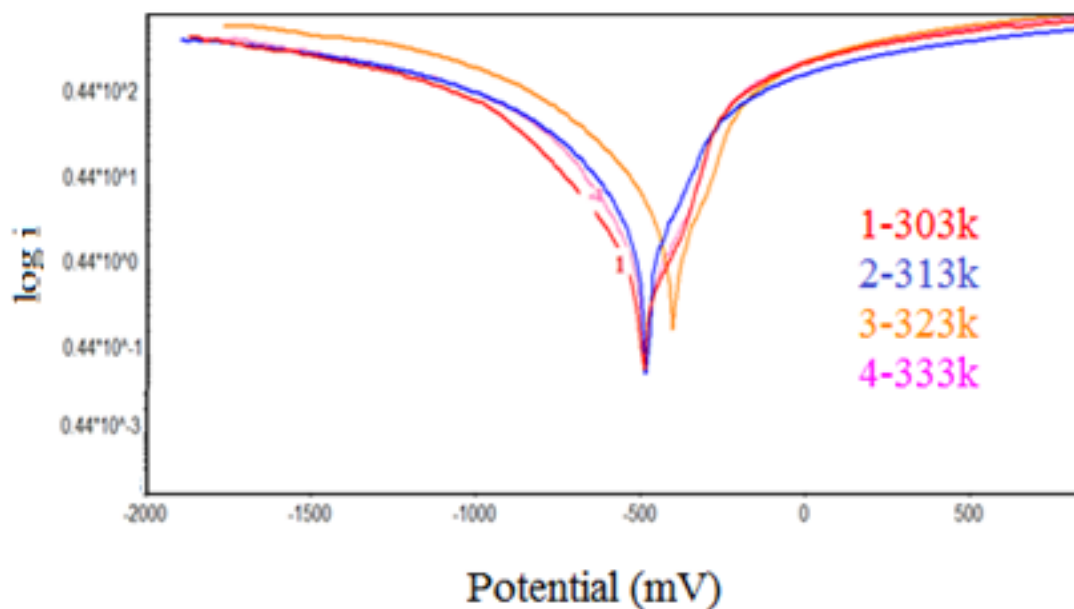


Fig (3): Polarization curves at different temperatures.

Table (3): Corrosion parameters of Carbon steel in 0.5M HCl solutions devoid of and containing  $1 \times 10^{-3}$  M of different inhibitors at different temperatures.

Medium	Temp. K	$-E_{\text{corr}}$ mV	$\beta_a$ mV/decade	$-\beta_c$ mV/decade	$I_{\text{corr}}$ mA/cm <sup>2</sup>	IE%	$\theta$
0.5 M HCl	303	495	104	145	0.32	--	
	313	490	96	153	0.7		
	323	405	87	178	1.0		
	333	496	94	139	1.6		
INHIBITOR	303	510	99	100	0.11	63	0.63
	313	541	119	113	0.31	55.7	0.557
	323	500	133	118	0.48	52	0.52
	333	528	146	102	0.89	44.3	0.443

Interest in order to obtain efficient corrosion inhibitors science they provide much greater inhibition compared to corresponding amines and aldehydes [15-19].the presence of -CN-

Group in schiff base molecules enhances their adsorption ability and corrosion inhibition efficiency [20,21]. We have recently reported amino nictino nitril as corrosion inhibitor for carbon steel[22]

In this study, we have further improved inhibition efficiency of amino nictino nitril br preparing its Schiff

base using benzaldehyde . the synthized Schiff base molecule has additional  $\pi$  bonds as well as aphenyl group which are assumed to be active centers of adsorption .

Therefore the molecules is expected to show better adsorption ability and corrosion inhibition efficiency . the aim of this study is to investigate inhibition effect of amino nictino nitril on the carbon steel corrosion in 0.5 M HCl solution . for this purpose ,potentiodynamic polarization , WL techniques were used.

#### 4. Conclusions

1. All measurements show that the tested compound has excellent inhibition properties for the corrosion of carbon steel in 1 M HCl solution.
2. The inhibition efficiency increases with increasing the concentration, but decreases with increasing the temperature.

#### 5- References

[1] M.A.Quraishi,J.Rawat,Inhibition of mild steel corrosion by some macrocyclic compounds in hot and concentrated hydrochloric acid, Mater.Chem.phys.73(2002)118-122.

[2] S.Kertit,B.Hammouti,Corrosion inhibition of iron in 1 M Hcl by 1 phenyl-5-mercapto-1,2,3,4-tetrazole,Appl.surf.sci.93(1996)59-66.

[3] O.K.Abiola,Adsorption of 3-(4-amino-2-methyl-5-pyrimidyl methyl)-4-methyl thiazolium chloride on mild steel ,Corros.Sci.48(2006)3078-3090

[4] A.Chetouani,A.Aouniti,B.Hammouti,N.Benchat,T.Benhadda,S.Kertit,Corrosion inhibitors for iron in

3. The tested compound is adsorptive inhibitor and its adsorption is spontaneous.
4. The cathodic and anodic Tafel slopes reveal that the tested compound is mixed type inhibitor.

hydrochloric acid solution by newly synthesized pyridazine derivatives,Corros.Sci.45(2003)1675-1684.

[5] J.O.M.Bockris,A.K.N.Reddy,Modern Electro Chemistry,vol.2,Plenum Publishing Corporation, New York,1976.

[6]M.ElAchouri,S.Kertit,H.M.Gouttaya,B.Nciri,Y.Bensouda,L.Perez,M.R.Infante,K.Elkacemi,Corrosion inhibition of iron in 1M Hcl by some gemini surfactants in the series of alkanediyl-bis-(di methyl tetradecyl ammonium bromide), Prog. Org.Coat.43(2001)276-273.

[7] S.A .Abdel Maksoud,Studies on the effect of Pyranocoumarin derivatives on the corrosion of iron in 0.5 M Hcl ,Corros.Sci.44(2002) 803-813.

- [8] M.Abdallah,Rhodanine azosulpha drugs as corrosion inhibitors for corrosion of 304 stainless steel in hydrochloric acid solution ,*Corros.Sci.*44(2002)717-728.
- [9] K.F.Khaled,The inhibition of benzimidazole derivatives on corrosion of iron in 1M Hcl solutions,*Electrochim.Acta* 48(2003) 2493-2503.
- [10] M.Behpour,S.M.Ghoreishi,N.Soltani,M.Salavati-Niasari,The inhibitive effect of some bis –N,S-bidentate Schiff bases on corrosion behaviour of 304 stainless steel in hydrochloric acid solution,*Corros.Sci.*51(2009) 1073-1082.
- [11] G.Karadas,R.Solmaz,Electrochemical investigation of barbiturates as green corrosion inhibitors for mild steel protection ,*Corros.Rev.*24(2006) 151-171.
- [12] R.Solmaz,G.Kardas,B.Yazici,M.Erbil,The rhodanine inhibition effect on the corrosion of amild steel in acid along the exposure time,*Prot.Met.+5*(2007) 476-482.
- [13] R.Solmaz,G.Kardas,B.Yazici,M.Erbil,Inhibition effect of rhodanine for corrosion of mild steel in hydrochloric acid solution ,*Prot.Met.*41 (2005) 581-585.
- [14] H.Keles,M.Keles,I.Dehtri , O.Serindag,Osman Serindag,Adsorption and inhibitive properities of aminobiphenyl and its schiff base on mild steel corrosion in 0.5 M Hcl medium , *colloid Surf.A* 320(2008) 138-145.
- [15] A.Barbosa da Silva,E.D'Elia, J.A.C.P. Gomes,Carbon steel corrosion inhibition in hydrochloric acid solution using areduced schiff base of ethylenediamine,*Corros.Sci.*52(2010) 788-793.
- [16] A.M.Abdel Gaber , M.S.Masoud ,E.A.Khalil,E.E.Shehata ,electro chemical study on the effect of schiff base and its cobalt complex on the acid corrosion of steel ,*Corros. Sci.* 51 (2009) 3021-3024.
- [17] N.A .Negm ,M.F.Zaki, Corrosion inhibition efficiency of non ionic schiff base amphiphiles of p-amino benzoic zcid for aluminum in 4N Hcl,*Colloid surf.A* 322(2008) 97-102.
- [18] I.Ahmad,R.Prasad ,M.A.Quraishi,Thermodynamic ,Electrochemical and Quantem chemical investigation of some schiff bases as corrosion inhibitors for mild steel in hydrochloric acid solutions ,*Corros.Sci.* 52 (2010) 933-942.
- [19] E.Baylo ,T.Gurten ,M.Erbil, Interactions of some schiff base compounds with mild steel surface in hydrochloric acid solutions ,*Mater .Chem .Phys.*112 (2008) 624-630.
- [20] K.C.Emregul, O.Atakol , Corrosion inhibition of mild steel with schiff base compounds in 1M Hcl ,*Mater.Chem.Phys.* 82 (2003) 188-193.
- [21] M.Behpour ,S.M.Ghoreishi ,M.Salavati-Niasari,B.Ebrahimi,Evaluating two new synthesized S—N Schiff bases on the corrosion of copper in 15% hydrochloric acid ,*Mater .Chem .Phys.*107 (2008) 153-157.
- [22] R.Solmaz,G.Kadas, B.Yazici ,M.Erbil , Adsorption and corrosion inhibitive properities of 2- amino -5-mercapto -1,3,4 thiadiazole on mild steel in hydrochloric acid media ,*Colloid Surf. A* 312 (2008)7-17.