



Inhibition Effect of Some Organic Compounds Toward the Corrosion of Steel Electrode in Citric Acid Solution in presence of Chloride Ions

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ABSTRACT

The chemistry behavior of steel electrode in acid solutions has been studied by galvanostatic polarization technique. The consequences of concentrations of acid and temperature of solution are examined. It was found that greater the citric acid concentration or reducing of temperature of the solution assist the passivation process. The values of i_{corr} decreased with greater concentrations of citric acid solutions and lowering of the temperature of solution. The free activation energy of passive film formed is determined and found to be 7.45 kJ/mole. Addition of increasing concentrations of some aggressive anions such as Cl^- and SO_4^{2-} was also investigated. With increasing concentrations of those anions result in the destruction of the passive film due to the increasing of corrosion current density, i_{corr} , and therefore the shift of corrosion potential, E_{corr} , to more negative potentials. Trials had been made to inhibit the corrosion process via including a few organic compounds as, urea, phenylhydrazin and 1,2-phenylenediamine.

Keywords: Steel, Citric acid, Passivation, Galvanostatic, Kinetic, Parameters.

INTRODUCTION

Corrosion process can be defined as gradual physio chemical destruction of metals and alloys by the action of environment. This is process usually begins at a surface of materials, nonetheless it may be prevented and controlled using the suitable blocking measures such as anodic protection, cathodic protection, metallic coating and using inhibitors, etc. Inhibitors are playing very good part

in the controlling of corrosion process. The organic inhibitors containing hetero atoms like oxygen, nitrogen, sulphur and phosphorus, etc shows better corrosion inhibition by forming protective layer over the metal surface. Also the corrosion inhibition efficiency follows the order $O < N < S < P$ ^{1,4}.

Organic compounds used as inhibitors, occasionally, they act as cathodic, anodic or together, as cathodic and anodic inhibitors, nonetheless,

as a preferred rule, act via a method of surface adsorption, designated as a film-forming. Obviously the prevalence of molecules showing a sturdy affinity for steel surfaces compounds showing top inhibition efficiency and occasional environmental hazard⁵. Those inhibitors building up a defensive hydrophobic film adsorbed particles on the electrode surface, which presents a barrier to the destruction of the metal in the tested solution. They have to be soluble or dispersible in the medium surrounding the metal⁶.

The performance of an organic inhibitor depends of the: i- chemical structure, just like the size of the organic molecule; ii- conjugation system and/or aromaticity, because the arrangement of carbon chain; corrosion inhibitors – ideas, mechanisms and applications iii- type and wide variety of bonding atoms or businesses in the molecule (both π or σ); iv- nature and the fees of the metal surface of adsorption mode like bonding energy to steel substrate; v- capacity for a layer to emerge as compact or pass-linked, vi- functionality to form a complicated with the atom as a solid in the steel lattice; vii- form of the electrolyte solution like good enough solubility within the environment⁷. the efficiency of those organic corrosion inhibitors is associated with the presence of polar purposeful businesses with S, O or N atoms inside the molecule, heterocyclic compounds and pi electrons, normally have hydrophilic or hydrophobic components ionizable. The polar function is commonly seemed as the reaction center for the establishment of the adsorption procedure^{5,6}. The organic acid inhibitor that incorporates oxygen, nitrogen and/or sulfur is adsorbed on the steel floor blocking the energetic corrosion web sites. Despite the fact that the best and efficient natural inhibitors are compounds that have π -bonds, it gift organic toxicity and environmental harmful traits⁸. Compounds containing nitrogen atom can be used as a good inhibitors in wide range. These compounds can attached to metal surfaces within a transfer of electrons and forming a coordinated bond and therefore inhibition process taken place⁹. Polarization experiments using organic compounds show that those compounds are cathodic inhibitors¹⁰. Comparison of the inhibition efficiencies of organic molecules are various and include, among others, weight loss determination, open circuit potential measurements, potentiodynamic polarization curves

depression of polarography highest, calculation of kinetic parameters and determination of elements dissolved by using of spectroscopy techniques¹¹. The inhibition process of carbon steel have been noticed potentiostatically by several workers¹², however, most of workers interested by studying the role of the type of functional groups of the organic inhibitors and the good inhibition of some inorganic molecules to complete protection.

In the present work has therefore been planned to analyze the galvanostatic technique is used to spotlight the behavior of steel in citric acid solutions free from and containing the aggressive ions SO_4^{2-} and Cl^- as pitting formers. The research additionally concerned the usage of urea, phenylhydrazine and 1,2-phenylene diamine as an inhibitor for the corrosion of steel infected via 0.1M NaCl.

EXPERIMENTAL

The working electrodes were prepared from steel samples produced by the Egyptian Mill steel Company (Helwan- Cairo) with the following chemical composition:

C	Si	Mn	P	S	Fe
0.32	0.24	0.89	0.024	0.019	98.507 mass %

The steel electrodes were mounted to salt glass tubes with epoxy glue so the overall exposed region was 1.33 cm². Electrical contacts were completed through thick copper wires linked to the ends of the steel rods not exposed to the electrolyte. Before being employed, the steel electrodes were scraped into uniform surfaces by a grinding machine (model Jean Wirtz TG 200, Germany) exploitation serial 0-, 00- and 000-grades emery papers, rinsed with acetone and at last washed with triply distilled water before immersing in the examined solution.

Measurements of polarization were carried out using galvanostatic technique. Before beginning the polarization, Immersion of steel electrode in the electrolyte taken place until the steady-state corrosion potential was reached. At first, low current density was used for polarization of the electrode cathodically or anodically, followed by higher ones. The potential

was determined on a digital multi meter. For each current density used, the steady-state potential of the metal was obtained when its value did not alteration by over than 1mV in 10 minutes. Each run was approved in a renewed naturally aerated citric acid solution and with a fresh polished electrode. The cell has a double wall jacket through which water, at the agreed temperature, was circulated. Measurements were accepted at a constant temperature $25 \pm 0.1^\circ\text{C}$, except those related to the influence of temperature. The cell temperature was measured using an ultra thermostat type poly science (USA). The main joint of the cell contains openings for, the working electrode, the reference electrode (SCE) and one opening for. This latter was fitted into a compartment separated from the main bulk of the electrolyte by means of G_4 sintered glass disc to complete separation between the anodic and the cathodic products.

Electrolytic solutions were ready from analytical grade reagents and triply-distilled water. Solutions of acid with totally different concentrations

were ready by dissolving the corresponding quantitative weights of solid acid within the applicable volumes of water. Temperature affect was accepted as mentioned above. The effect of adding increasing concentrations of NaCl and Na_2SO_4 ranged from 1×10^{-4} M to 1 M was tested within the presence of definite concentration of acid as 0.5 M. The addition of variable concentrations of some organic compounds such as urea, phenylhydrazine and 1,2-phenylenediamine were ready with a tested concentration of citric acid 0.5M and 0.1M NaCl.

RESULTS AND DISCUSSION

Effect of citric acid concentration

Fig.1 indicates the potentiodynamic polarization curves for the steel electrode in naturally aerated solutions of citric acid of variable concentrations at 25°C . The data show that, with increasing citric acid concentrations, the anodic polarization curves shift to more positive direction

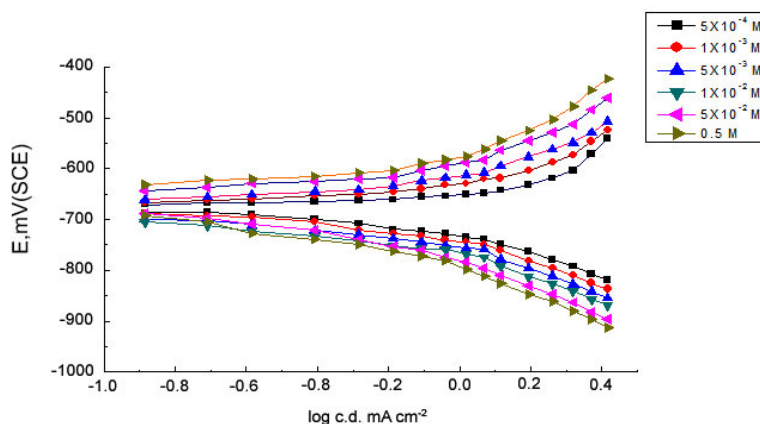


Fig. 1: potentiodynamic Polarization curves of the steel electrode in increasing concentrations of citric acid of increasing at 25°C .

Table 1: Variation of kinetic parameters, E_{corr} , I_{corr} , β_a , β_c , and Rp for steel electrode with the concentration of citric acid as calculated from Fig. 1.

Concentration, M	$-E_{\text{corr}}$, mV (SCE)	I_{corr} , mA.cm ²	β_a , mV decade ⁻¹	β_c , mV decade ⁻¹	Rp KΩ
5×10^{-4} M	569	0.339	56.878	-86.427	0.04394
1×10^{-3} M	546	0.309	127.78	-92.28026	0.0753
5×10^{-3} M	535	0.275	141.257	-80.557	0.081
1×10^{-2} M	502	0.257	143.232	-100.993	0.10007
5×10^{-2} M	476	0.24	197.862	-188.917	0.17485
0.5 M	421	0.229	245.579	-228.65	0.22451

and the cathodic polarization curves shift to more negative direction. The corresponding values of the anodic and cathodic Tafel slopes, β_a and β_c , also, the corrosion potential, E_{corr} , corrosion current, i_{corr} , and polarization resistance, R_p , are presented in Table 1. The corrosion current, i_{corr} , was achieved by extrapolation of the Tafel lines to the steady state potential. The polarization resistance, R_p , can be obtained from the Stern-Geary relationship¹³ as:

$$i_{corr} = (\beta_a \beta_c / 2.303(\beta_a + \beta_c) R_p) = B/R_p \quad \dots(1)$$

Inspection of Fig.1 and the results of Table 1, reveals that both the Tafel slopes, β_a and β_c are influenced by increasing the citric acid concentration. Simultaneously, the corrosion current density, i_{corr} , reduces markedly while the corrosion potential becomes more noble.

This performance could easily be elucidated on the basis of the passivating oxide film formation on the steel electrode surface¹⁴.

Citric acid is a multi dentate chelating agent, which forms stable complexes with metal ions such as Fe^{2+} , Ca^{2+} , Mg^{2+} and Fe^{3+} in aqueous solutions¹⁵. In spite of the perceived importance and various research of metal-citrate equilibrium, the citrate complexes of both Fe^{2+} and Fe^{3+} have remained poorly characterized. Such uncertainties arise from considerable experimental difficulties, such as: (i) number and strength of the complexes formed, (ii) tendency to form numerous ternary complexes, $Fe_xCit_y(OH)_z$, (iii) extensive hydrolysis of both Fe^{2+} and Fe^{3+} , (iv) facile oxidation of Fe^{2+} by atmospheric oxygen and (v) relatively weak interaction between Fe^{2+} and citrate¹⁶. Field et al.¹⁷ studied the stability constants for different Fe^{2+} and citrate complexes.

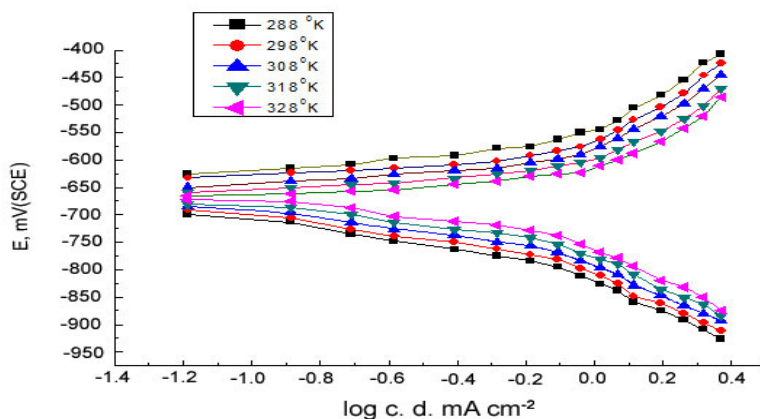


Fig. 2: Polarization curves of steel electrode in 0.5 M citric acid solution at different temperatures.

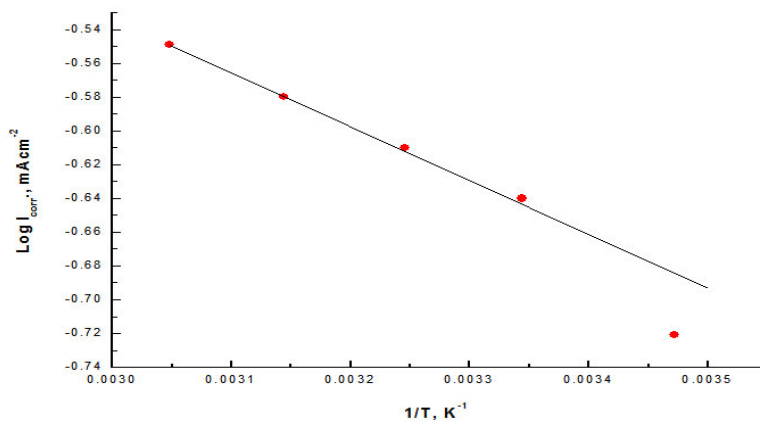


Fig. 3: Arrhenius plot of $\text{Log } I_{corr}$ versus $1/T$ for steel electrode in 0.5 M citric acid solution.

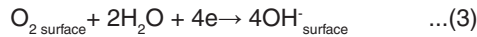
According to their study, the $[\text{FeHCit}]^-$ and $[\text{FeCit}]^{2-}$ complexes can be formed with dissociation constants of 2.4×10^{-9} and 1.58×10^{-5} respectively. These lower values enhanced the formation of citrate complexes with Fe^{2+} .

According to the above descriptions, we can now consider the processes in the studied system¹⁸:

Anodic reaction:



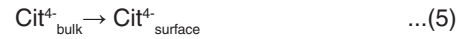
Cathodic reaction:



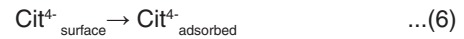
The resulted Fe^{2+} ions diffuse from surface of metal into the bulk of solution,



Furthermore the citrate ions migrate from bulk of solution into the electrode surface:



A part of the surface citrate ions are adsorbed on steel surface:



In addition, some of them form complexes with Fe^{2+} ions:

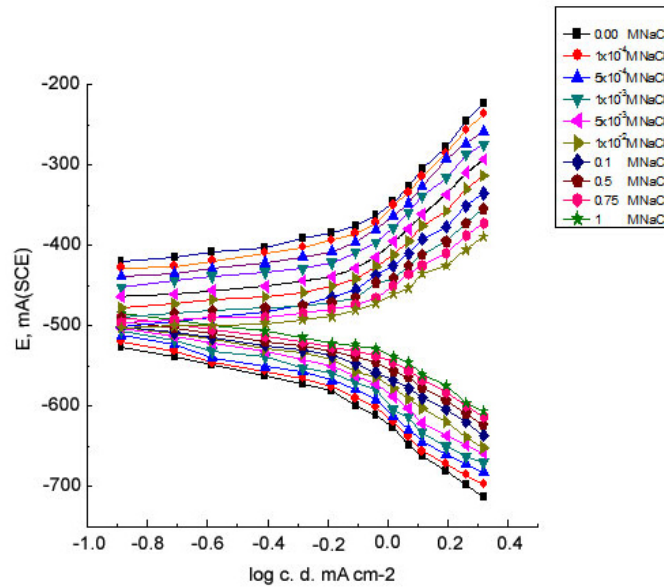
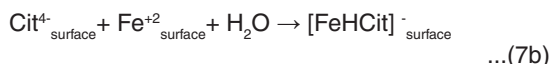


Fig. 4: Polarization curves of steel electrode in 0.5 M citric acid solution devoid of-and containing increasing concentrations of NaCl at 25°C

Table 2: Variation of kinetic parameters, E_{corr} , i_{corr} , β_a , β_c , and R_p for steel electrode in 0.5 M citric acid with Temperature as calculated from Fig. 2.

Temperature, °K	$-E_{\text{corr}}$, mV (SCE)	i_{corr} , mA.cm ²	β_a , mV decade	β_c , mV decade ⁻¹	R_p , KΩ
288	395	0.19	255.016	-239.18	0.28206
298	421	0.229	245.579	-228.65	0.22451
308	472	0.245	218.543	-199.057	0.18463
318	493	0.263	191.413	-191.639	0.15811
328	537	0.282	162.477	-185.402	0.13333



The produced complexes should be kept out of the surface; however, their mobility is less than smaller Fe^{2+} ions. This fact as well as the adsorption of citrate ions on metal surface may decrease the corrosion rate of the steel sample in the presence of citric acid. It is also obvious that the increase in concentration enhances the inhibiting action; that can be attributed to the enhancement of citrate surface concentration and subsequently increase of its adsorption on metal surface (eqs. 5 and 6)¹⁸.

Effect of Temperature

The effect of increasing the temperature from (25 °C-65 °C), on the potentiodynamic polarization curves of the steel electrode in naturally aerated 0.5M citric acid solution is shown in Fig.2.

Obviously, in figure 2 the raising of the temperature imposes the anodic polarization curves' shift into the cathodic direction in addition to the cathodic polarization curves into the anodic direction. In Table 2, the kinetic parameters values β_a , β_c , i_{corr} , E_{corr} and R_p are shown. From the values of i_{corr} and E_{corr} , increasing of temperature facilitates the

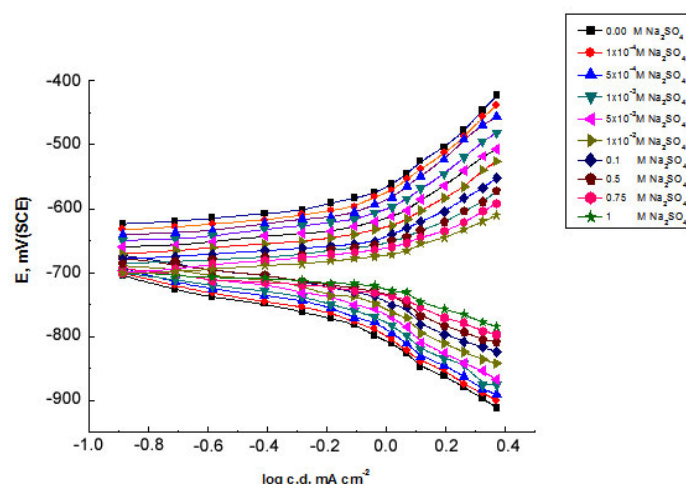


Fig. 5: Polarization curves of steel electrode in 0.5 M citric acid solution devoid of-and containing increasing concentrations of Na_2SO_4 at 25°C

Table 3: The kinetic parameters, E_{corr} , i_{corr} , β_c , β_a and R_p for steel electrode in 0.5 M citric acid solution at different concentrations of Na_2SO_4 and NaCl as calculated from Figs. 4. and 5.

Conc., M	$-E_{\text{corr}}$, mV(SCE)		i_{corr} , mAc m^{-2}		β_a , mV decade $^{-1}$		$-\beta_c$, mV decae $^{-1}$		R_p , K Ω		
	SO_4^{--}	Cl $^-$	SO_4^{--}	Cl $^-$	SO_4^{--}	Cl $^-$	SO_4^{--}	Cl $^-$	SO_4^{--}	Cl $^-$	
	0.00	M	421	421	0.229	0.229	245.5	245.5	228.6	228.6	0.224
1x10 $^{-4}$	M	449	441	0.245	0.234	234.2	226.4	208.1	208.9	0.195	0.201
5x10 $^{-4}$	M	497	481	0.269	0.257	207.1	205.9	197.6	184	0.163	0.164
1x10 $^{-3}$	M	538	509	0.288	0.263	193.8	191.5	184.6	151	0.142	0.139
5x10 $^{-3}$	M	568	532	0.309	0.282	155.3	174.6	169.8	131.7	0.114	0.115
1x10 $^{-2}$	M	579	553	0.331	0.302	132.9	161.5	143.4	119.4	0.09	0.098
0.1	M	656	571	0.355	0.324	119.1	146.7	125.1	96.4	0.074	0.078
0.5	M	611	612	0.363	0.331	102.8	124.9	117.2	87.2	0.065	0.067
0.75	M	671	639	0.38	0.347	91.9	109.1	98.3	82.7	0.054	0.058
1	M	711	658	0.407	0.355	84.2	92.3	86.2	74.5	0.045	0.05

dissolution of the passive film on the steel surface. This could be attributed to the lowering of solution viscosity and the consequent increase in the mobility of ions with elevation the solution temperature¹⁹. Arrhenius plot of $\log i_{\text{corr}}$ versus $1/T$ is shown in Fig 3. from which the free activation energy of passive film formation, E_a^* , is calculated:

$$\log i_{\text{corr}} = -E_a^* / 2.303 RT + \text{constant}$$

The value of E_a^* for the steel electrode in 0.5 M solution of citric acid is found to be

7.45 kJmol⁻¹. The lower value of activation energy (<40 kJ/mole) shows that the process of formation a passive film on the steel electrode is under diffusion control^{20,22}.

Effect of addition of the aggressive Cl⁻ and SO₄²⁻ anions

The influence of increasing concentrations of NaCl and Na₂SO₄ on the potentiodynamic polarization curves of the steel electrode in 0.5 M naturally aerated solution of citric acid at room temperature is examined.

Table 4: Variation of kinetic parameters, E_{corr} , I_{corr} , β_a , β_c , and R_p for steel electrode in 0.5 M citric acid + 0.1 M NaCl solution at different concentrations of inhibitors as calculated from figs. 7-9.

Inhibitor	Concen., M	$-E_{\text{corr}}$, mV (SCE)	I_{corr} , mA.cm ⁻²	I.E	β_a , mV decade ⁻¹	β_c , mV decade ⁻¹	R_p K Ω
Urea	0.00	571	0.324	-	146.7	- 96.4	0.078
	1x10 ⁻⁴	563	0.320	1.23	152.458	-103.524	0.08366
	5x10 ⁻⁴	554	0.311	4.01	165.232	-110.354	0.09238
	1x10 ⁻³	548	0.289	10.8	166.258	-125.325	0.10737
	5x10 ⁻³	543	0.278	14.19	178.455	-132.859	0.11895
	1x10 ⁻²	537	0.271	16.35	182.258	-139.421	0.12657
	0.1	533	0.263	18.82	199.322	-144.563	0.13834
	0.5	523	0.255	21.29	204.329	-157.201	0.15129
	0.75	517	0.250	22.84	209.985	-166.110	0.16108
1	510	0.241	25.61	211.346	-170.021	0.16976	
Phenyl hydrazine	0.00	571	0.324	-	146.7	- 96.4	0.078
	1x10 ⁻⁴	554	0.319	1.54	149.528	- 109.522	0.08605
	5x10 ⁻⁴	548	0.301	7.1	158.663	- 114.695	0.09603
	1x10 ⁻³	544	0.283	12.65	178.855	- 121.565	0.10726
	5x10 ⁻³	535	0.272	16.05	181.687	- 133.601	0.11648
	1x10 ⁻²	522	0.265	18.21	197.101	- 145.220	0.13107
	0.1	511	0.210	35.18	201.233	- 150.012	0.17771
	0.5	508	0.198	38.88	214.667	-167.302	0.2062
	0.75	498	0.187	42.28	220.122	-179.990	0.22993
1	495	0.181	44.13	229.710	- 181.123	0.24295	
1,2-Phenylen diamine	0.00	571	0.324	-	146.7	- 96.4	0.078
	1x10 ⁻⁴	517	0.308	4.94	157.248	- 110.232	0.09136
	5x10 ⁻⁴	541	0.297	8.33	163.012	- 131.985	0.10663
	1x10 ⁻³	535	0.279	13.88	174.365	- 149.211	0.12123
	5x10 ⁻³	528	0.262	19.13	189.584	- 152.326	0.13998
	1x10 ⁻²	517	0.251	22.53	209.101	-171.895	0.1632
	0.1	507	0.149	54.01	218.421	- 189.142	0.2954
	0.5	498	0.142	56.17	228.214	- 197.597	0.32383
	0.75	495	0.135	58.33	249.652	- 203.145	0.36025
1	491	0.129	60.18	261.550	- 212.753	0.3949	

The curves of Figs. 4, 5 reveal that, adding higher concentrations of NaCl and Na₂SO₄ shifts the cathodic polarization curves into the noble direction and the anodic polarization curves into the more active direction. The kinetic parameters, i_{corr} , E_{corr} , R_p , as well as, the corresponding anodic and cathodic Tafel slopes are given in Table 3.

Inspection of the data of Table 3 reveals that the presence of SO₄²⁻ and Cl⁻ ions has a marked effect on the anodic Tafel slope, β_a , while the cathodic Tafel slope, β_c , keeps on more/or less unchanged, showing the increasing effect of the SO₄²⁻ and Cl⁻ ions on the anodic reaction. Thus, the presence of, SO₄²⁻ and Cl⁻ ions increases the ease of anodic reaction²³.

The effect of Cl⁻ and SO₄²⁻ ions on the destruction of passive film on steel can be deduced on the basis of a balance between two processes competing on the metal surface; stability of the passive film by complex formation and dissolution of the film by adsorption of Cl⁻ and/or SO₄²⁻ ions on the electrode surface^{24,25}.

More inspection of the data of Table 3 reveals that the aggressiveness of NaCl and Na₂SO₄ depends on the concentration of citric acid. Thus, in one and the same citric acid concentration, the corrosion current density reported in the case of SO₄²⁻ is much higher than that reported in presence of the same concentration of Cl⁻ ions, while R_p values are lower

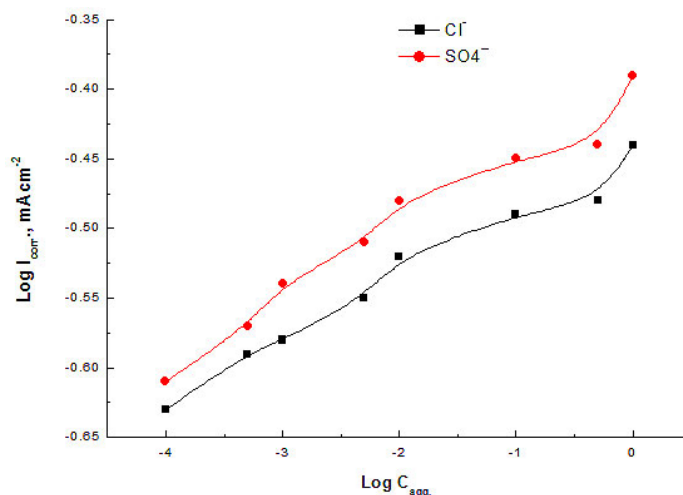


Fig. 6: Variation of the corrosion current density, I_{corr} , of the steel electrode with the molar concentration of the aggressive anions in 0.5M citric acid solution.

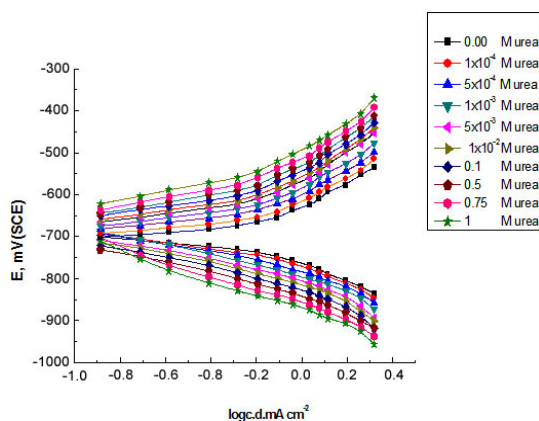


Fig. 7: Polarization curves of the steel electrode in 0.5 M citric acid+0.1 M NaCl at different concentrations of urea at 25°C.

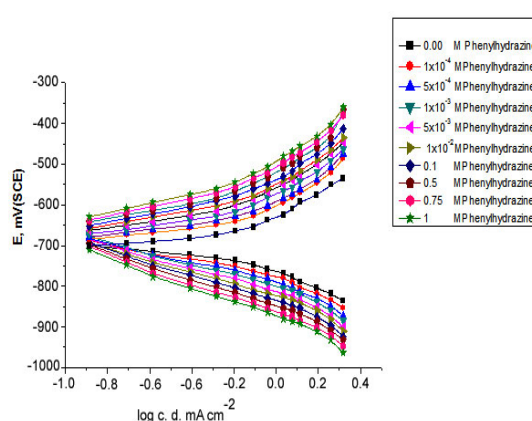


Fig. 8: Polarization curves of the steel electrode in 0.5 M citric acid+0.1 M NaCl at different concentrations of phenylhydrazin at 25°C.

for SO_4^{2-} than those reported for Cl^- ions. At the same time, the anodic slope, β_a , determined in presence of SO_4^{2-} ions is markedly lower than that determined in the case of Cl^- ions. These observations reveal that SO_4^{2-} ions are more aggressive than Cl^- ions in the process of breakdown of the passive film on the steel surface²⁶. The dependence of the corrosion current densities, i_{corr} , on the concentration of the aggressive SO_4^{2-} and Cl^- anions, is shown in Fig. 6. It is clear that with increasing the concentration of the aggressive anions, i_{corr} increases and varies with $\log C_{\text{agg}}$ according to:

$$\log i_{\text{corr}} = X + Y \log C_{\text{agg}} \quad \dots(9)$$

where X and Y are constants. From the curves of Fig. 6, one can conclude that with increasing the concentration of the aggressive anions, the corrosion current densities, i_{corr} , increase. Approximately, a like S shaped curves are obtained; this established that the mechanism of passive film dissolution caused by these anions is the same.

Table 5: The values of the adsorb ability constant, K, and the standard free energy of repassivation, ΔG° , for the used inhibiting organic molecules.

	Urea	Phenylhydrazine	1,2-Phenylene-diamine
$-\Delta G^\circ, \text{KJmol}^{-1}$	2.31	2.62	2.73
K	0.41	0.33	0.29

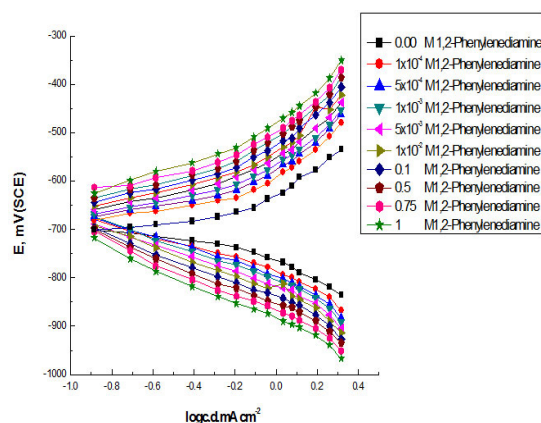


Fig. 9: Polarization curves of the steel electrode in 0.5 M citric acid + 0.1 M NaCl at different concentrations of 1,2-phenylenediamine at 25°C.

Effect of organic compounds as corrosion inhibitors

The effect of addition of increasing concentrations of some organic compounds, such as urea, phenylhydrazin and 1,2-phenylenediamine on the galvanostatic anodic and cathodic polarization curves of steel electrode immersed in naturally aerated 0.5 M citric acid + 0.1 M NaCl solution, at room temperature, is shown in Figs.7 – 9, successively. From these curves, it is clear that the behavior of all organic compounds used is similar. The kinetic parameters β_a , β_c , i_{corr} , R_p , E_{corr} and IE are shown in Table 4.

The percentage inhibition efficiency (I.E.) of the inhibitors was determined as following:

$$\% \text{I.E.} = \left(1 - \frac{i_2}{i_1} \right) \times 100 \quad \dots(10)$$

where i_1 and i_2 are the current density, in mA cm^{-2} , measured in absence and in presence of inhibitors, respectively. The dependence of the corrosion current densities, i_{corr} , of steel electrode in 0.5 M citric acid solution + 0.1M NaCl on the concentration of the organic inhibitors used, is shown in Fig. 10. It is clear that with increasing the concentration of the organic compounds, i_{corr} decreases and varies with $\log C_{\text{inh}}$ according to:

$$\log i_{\text{corr}} = A - B \log C_{\text{inh}} \quad \dots(11)$$

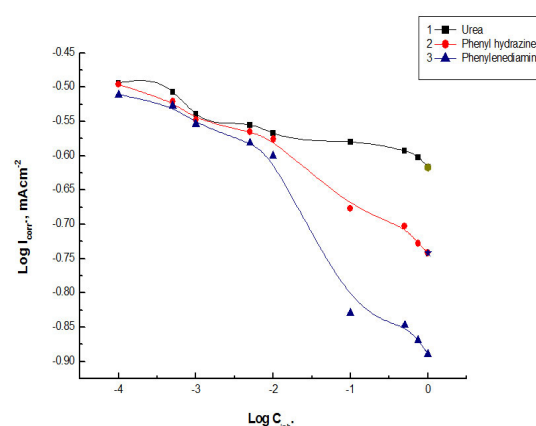


Fig. 10: The dependence of corrosion current density, i_{corr} , of the steel electrode in 0.5 M citric acid + 0.1M NaCl on the concentration of inhibitors used.

Where A and B are constants. Inspection of the curves of Figs. 7 – 11 and data in Table 4, reveals the following conclusions:

- i) On increasing the concentrations of all the inhibitors used, the anodic polarization curves are shifted into the positive direction with a marked increase in the value of β_a , and the cathodic polarization curves into the negative direction while β_c remains more/ or less unchanged. A behavior which indicates that the effect of these organic compounds is restricted to the anodic partial reaction.
- ii) In presence of one and the same organic compound concentration, β_a increases; E_{corr} is shifted into the noble direction; i_{corr} is markedly decreased while R_p and the percentage inhibition efficiency, IE, are markedly increased. This behavior reveals increased inhibition of corrosion on increasing each inhibitor concentration.
- iii) In presence of constant inhibiting concentration, the inhibition efficiency, IE, increased in the order: urea < phenylhydrazin < 1,2-phenylenediamine, which is the same order previously found using other techniques¹⁴.

One of the ways an anodic inhibitor can reduce the corrosion rate is by aiding the passivation reaction by acting as a catalyst, or by increasing the activation energy barrier for the reduction reaction. In other words, it can reduce the corrosion rate by either increasing the anodic Tafel slope or by increasing

the rest potential, or both²³ and/or the inhibitive compound may be incorporated into the passive layer on the metal surface, forming an improved stability against the aggressive ions²⁷.

Urea and its derivatives consider as a significant corrosion inhibition of metals and alloys because of the present of the nitrogen and oxygen atoms in their structures²⁸. M. Manivannan studied the effect of urea as inhibitor on carbon steel in seawater and reported that the efficiency of urea increases by the addition of Zn^{2+} ion²⁸. Urea fertilizer of certain concentration was reported to be a good corrosion inhibitor for concrete reinforced steel immersed in 3% NaCl (86.5% IF at 0.5 % concentration)²⁹. The reduction in the dissolution of metal in the presence of urea may be attributed to nitrogen and oxygen atoms present in the functional group. These groups are electro active and interact with the metals surface to a greater extent. Adsorption can be electrostatic or chemisorptive or the inhibitor can act simply by physically blocking the active sites³⁰ or the inhibition due to the formation of a compact protective film of Fe^{2+} - urea complex³¹.

Phenylhydrazin, is assumed to inhibit the corrosion by the formation of phenylhydrazine-complex which is precipitated on the metal surface. However, its lower inhibition efficiency could be attributed to its lower tendency to form its corresponding salt or to the presence of the benzene ring which lying parallel to the electrode surface affecting thus the p electrons interaction

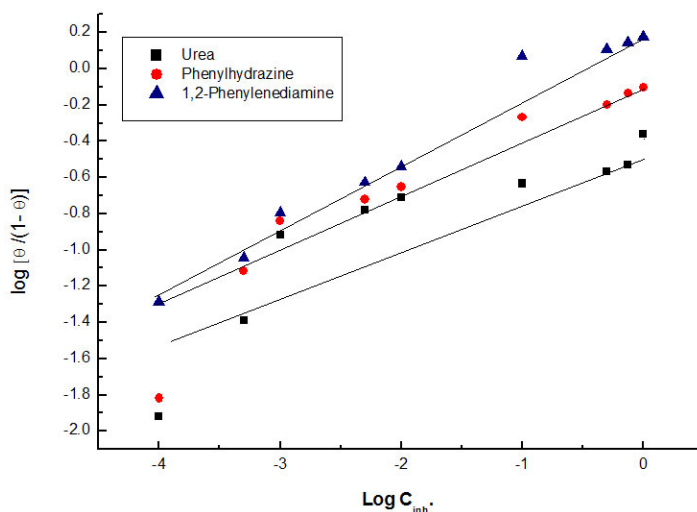


Fig. 11: Variation of $\log (\theta/1-\theta)$ with logarithm concentration of inhibitors, $\log C_{inh}$

with the metal surface³². The corrosion inhibition by phenylhydrazine can also be explained in terms of the anchoring atom in the function group. This compound is anchored on to the metal surface by the nitrogen atom of the –NH– group. The higher inhibition efficiency of this compound is attributed to reduce the electron density at anchoring nitrogen atom³³.

It is apparent that the adsorption of 1,2-phenylenediamine on the steel surface could occur directly on the basis of donor acceptor between the lone pairs of the hetero atoms, the extensively delocalized electrons over the C6 ring of benzene, the 1,2-phenylenediamine molecule and the vacant d-orbitals of iron surface atoms³⁴. The functional group responsible for 1,2-phenylenediamine adsorption on metal surface is the lone pair of the nitrogen atom: iron ions on metal surface which act as a Lewis acid because they accept electrons from a donor group³⁵. 1,2-phenylenediamine has ability to form a thin layer of adsorbed amino quinone on steel surface which is responsible for the greater reduction of corrosion rate³⁶.

In order to understand the mechanism of corrosion inhibition the adsorption behavior of the organic adsorbate on the metal surface must be known. At any instant a fraction θ of the metal surface is covered by the inhibitor molecules and the uncovered fraction $(1 - \theta)$ reacts with acid. The surface coverage θ values are very useful in explaining the adsorption characteristics. The surface coverage increases thereby increasing the percentage inhibition (Table 4). To examine the adsorption behavior of the inhibitor, the data were fitted to the Langmuir's adsorption isotherm. A plot of $\log (\theta / (1 - \theta))$ versus $\log C$ (conc. of inhibitor) was a straight line supporting the monolayer adsorption of the inhibitor on the metal surface (Fig. 11):

$$\log [\theta / (1 - \theta)] = -\Delta G^\circ / 2.303 RT + \log C_{inh} \quad \dots(12)$$

where ΔG° is the standard free energy for pit repassivation by the inhibiting organic molecule, and K is the adsorbability constant of the inhibiting organic molecule on the steel surface:

$$K = \exp (-\Delta G^\circ / 2.303 RT) \quad \dots(13)$$

Inspection of Table 5, shows that the values of both the adsorb ability constant and the standard free energy of repassivation, ΔG° , by the used inhibiting organic molecules decrease in the order: urea > phenylhydrazin > 1,2-phenylenediamine, which is the same order reported before for their inhibition efficiencies. The presence of G° with moderate negative values indicates that these compounds act as pitting corrosion inhibitor by adsorption in competition with Cl^- ions for the active sites on the passive film covering the steel electrode³⁷.

CONCLUSIONS

The different factors affecting the electrochemical behavior of steel electrode in citric acid solutions by using polarization measurements were studied. Such factors were citric acid concentrations, temperature, addition of NaCl, and Na_2SO_4 and addition of some organic compounds. The following conclusions could be drawn:

- (1) The higher citric acid concentrations and decreasing of temperatures assist the passivation of steel electrode by shifting E_{corr} towards more noble direction and reducing the corrosion current density, i_{corr} .
- (2) The free activation energy of passive film formation is calculated and found to be 7.45 $kJmol^{-1}$, indicating that the process of passive film formation is under diffusion control.
- (3) Addition of increasing concentrations of NaCl and Na_2SO_4 to the adjusted concentration of citric acid increase the passive film dissolution, which investigated from shifting of corrosion potentials, E_{corr} , to more active direction and increasing the values of corrosion current densities, i_{corr} .
- (4) The addition of increasing concentrations of some organic compounds such as 1,2-phenylenediamine, phenyl hydrazine and urea inhibit the destruction of the passive film on steel electrode and the inhibition effect of these compounds decreases in the order: (the highest) 1,2-phenylenediamine phenylhydrazine urea (the lowest), which is the same sequence of increasing the inhibitive actions of these anions towards pitting corrosion of the steel.
- (5) The inhibition efficiency of each inhibitor increases with increasing its concentration.

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