

Study on the performance of Ajowan seeds extract on the corrosion of steel in acidic solution by effect of temperature

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ABSTRACT

Electrochemical measurements (EIS and PDP) have been used to study the temperature effect in the range (30p C - 70p C) on the performance of Ajowan seeds extract (ASE) and its inhibitive effects on the corrosion of steel in 2.0M H₂SO₄. A good agreement between the data obtained by impedance and polarization measurements was found. Results obtained reveal that ASE reduces the corrosion rate at all temperatures studied. The inhibition efficiency increases with rise temperature and the activation corrosion energy decrease in presence of ASE suggest a chemical adsorption model for the corrosion processes. Thermodynamic parameters, E_a , ΔH^\ddagger , ΔS^\ddagger have been calculated and are discussed.

Key words: Steel, Acidic inhibition, Temperatur effect, Acidic corrosion.

INTRODUCTION

The inhibition of corrosion for steel is the subject of tremendous technological importance due to the increased industrial applications of these material. Several authers (1-4) have studied the corrosion of steel and its inhibition by organic and natural inhibitors in acid solutions.

Inhibition are widely used for protection of materials from corrosion in acid environments. Usually, inhibitors protect the metal by adsorbing onto the surface and retard metal corrosion in aggressive media, so selecting the appropriate inhibitor for metal is very important. Furthermore, in order to improve the performance of inhibitor and reduce the corrosion of metal in acidic media, the temperature effect are widely used in case of acidic corrosion, mainly in hydrochloric and sulphuric acids¹⁻¹¹.

The study of the mechamism of corrosion inhibitors action has a great importance both for the formulation of new inhibitors and for the correct

use of these inhibitors under different conditions. In many industrial operations, like pickling, acid cleaning, acid descaling and oil well acidizing, the choice of optimum working temperature and process duration is of particular importance. The inhibitors used are expected to be chemically stable and to provide high protective effect under the condition discussed.

The temperatures has a great effect of the rate of metal electrochemical corrosion. In case of corrosion in acid medium (hydrogen depolarization), the corrosion rate increases exponentially with temperature increase because the hydrogen evolution over-potential decreases¹². An experimental dependence of Arrhenius type is observed between the corrosion rate and temperature.

The purpose of this study is the effect of temperature on steel corrosion in presence of Ajowan seeds extract (ASE) to improve the performance of ASE as safe inhibitor.

EXPERIMENTAL

The steel used had the following chemical composition (wt%): 0.38% C, 0.15% Mo, 0.50% Mn, 0.40% Si, 0.03% S, 0.035% P and 97.61% Fe.

Two electrochemical measurements: impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) were used to determine the corrosion inhibition characteristics of ASE.

Electrochemical measurements are carried out in a conventional three electrodes electrolysis cylindrical pyrex glass. A steel cylinder pressed into a Teflon holder acted as a working electrode (WE). Its working area of 0.791cm² remained precisely fixed. A saturated silver/silver chloride electrode connected through a salt bridge was used as reference electrode (RE), while a large area platinum leaf was used as counter electrode (CE). The measurements were made by connecting the electrochemical cell to ACM Gill AC and to a Samsung computer (Bridge DVD

ASUS 8X max. Impedance data were obtained in the frequency range 0.5Hz- 30KHz and potentiodynamic polarization curves were recorded at scan rate between -200mV -700mV.

Prior to each electrochemical experiment the WE was wet polished with 60 to 1200 grade emery paper, rinsed with bi-distilled water and acetone, then immediately inserted into the glass cell, that contained 250 ml of electrolyte solution. Hence, all the electrochemical experiments were carried out after 20 mins. of exposure to the solution.

RESULTS AND DISCUSSION

Temperature has a great influence on the rate of steel corrosion in acidic medium. An increase in temperature results in an exponential increase in corrosion rate due to decrease in hydrogen evolution overpotential (11,13).

To gain insight into the nature of inhibitor

Table 1: Electrochemical parameters for steel corrosion in 2.0 M H₂SO₄ at different temperatures

t ^o c	Impedance(EIS)			Polarization(PDP)				
	R _{sol} [*] Ωcm ²	R _{ct} Ωcm ²	C _{dl} [*] μF	-E _{corr.} μV	b _a V/dec	b _c V/dec	I _{corr} [*] mAcm-2	R _{corr} [*] mm/day
30	0.9392	9.134	2.054×10 ⁻³	404.16	58.408	102.57	8.0176	92.925
40	0.9042	3.311	2.417×10 ⁻³	401.77	39.632	84.304	8.4204	97.892
50	0.9535	1.518	8.398×10 ⁻⁴	425.76	77.330	117.12	15.414	178.65
60	0.9864	0.9485	1.418×10 ⁻³	425.14	73.205	121.56	19.632	227.53
70	1.025	0.5336	1.445×10 ⁻³	403.01	88.193	82.251	30.757	356.48

Table 2: Electrochemical parameters for steel corrosion in 2.0 M H₂SO₄ in presence of 2.0%v/v of ASE at different temperatures

t ^o c	Impedance(EIS)			Polarization(PDP)				Inhibition		
	R _{sol} [*] Ωcm ²	R _{ct} Ωcm ²	C _{dl} [*] μF	-E _{corr.} μV	b _a V/dec	b _c V/dec	I _{corr} [*] mAcm-2	R _{corr} [*] mm/day	ESI	PDP
30	1.040	20.28	6.078×10 ⁻⁴	422.10	35.662	75.909	4.0998	47.493	48.89	54.98
40	0.9255	8.103	2.949×10 ⁻³	415.20	33.418	103.63	4.7097	66.176	55.94	56.67
50	1.528	3.599	1.116×10 ⁻³	418.67	81.110	93.451	5.9371	68.811	61.48	57.81
60	0.6666	3.207	3.070×10 ⁻³	429.31	33.307	91.714	6.2242	72.139	62.58	77.28
70	0.0565	2.459	4.379×10 ⁻³	401.06	46.666	83.765	6.4297	74.620	79.10	78.30

adsorption, the effect of temperature in the range from 30° C to 70° C on the corrosion behavior of steel in absence and presence of fixed concentration of ASE was investigated using electrochemical technique (impedance (Figs. (1 and 3)) and polarization (Figs. (2 and 4)). The results obtained indicate that the rates of steel corrosion in absence and presence of ASE increased with rise in temperature and the ASE molecule was adsorbed

on the steel surface at all temperatures studied.

Figs. (1 and 3) show the Nyquist plots of steel in 2.0M H₂SO₄ in absence and presence of ASE at 30, 40, 50, 60 and 70p C, respectively. The complex impedance plots have the appearance of adepressed semicircle with centers below the Z'-axis for all solution examined in Fig. 1, the plots refer to non-ideal capacitive semicircle.

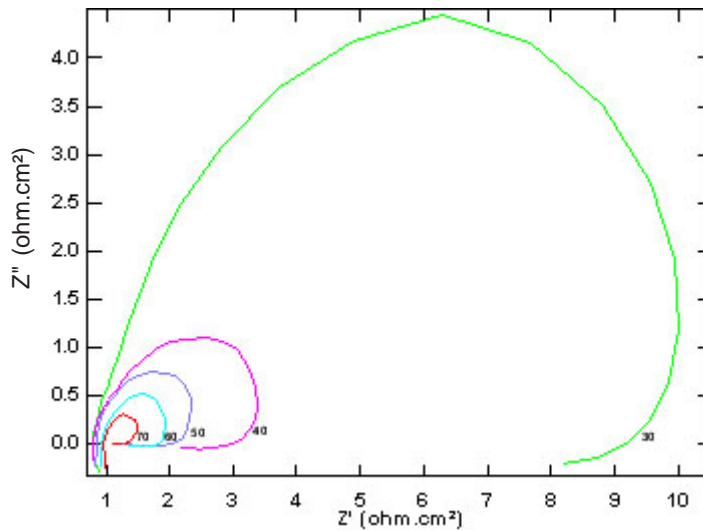


Fig. 1: Nyquist plots for steel sample in 2.0 M H₂SO₄ at different temperatures

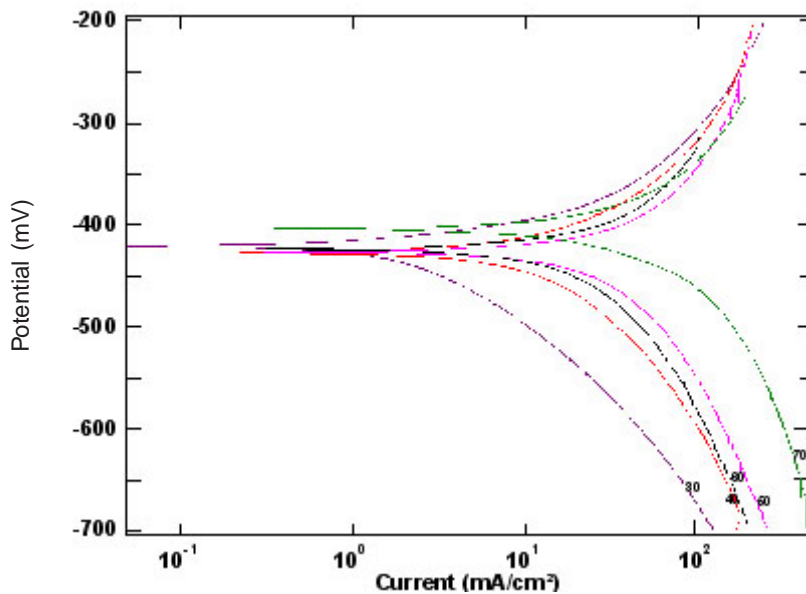


Fig. 2: Polarization plots for steel sample in 2.0 M H₂SO₄ at different temperatures

A characteristic feature of the results is the absence of a diffusive contribution to Z'' at low frequencies. This indicates that the charge transfer control the dissolution mechanism of steel across the phase boundary in the absence of the inhibitor. The results

also indicate that as the temperature increases, the rate of steel corrosion increases. Similar Figure (3) in presence of 5%v/v of ASE inhibitor at different temperatures. The results indicate that rising up the temperature leads to a decrease in

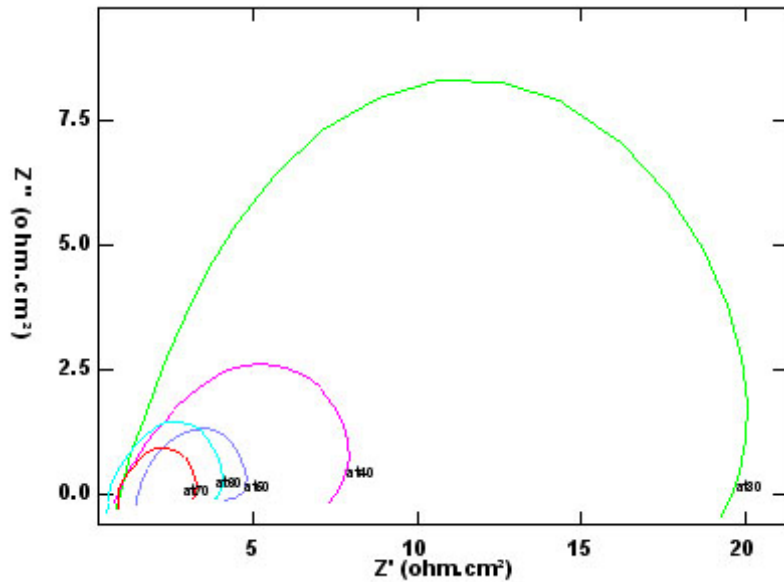


Fig. 3: Nyquist plots for steel sample in 2.0 M H_2SO_4 in presence of 1.0%v/v of Ajowan plant extract at different temperatures

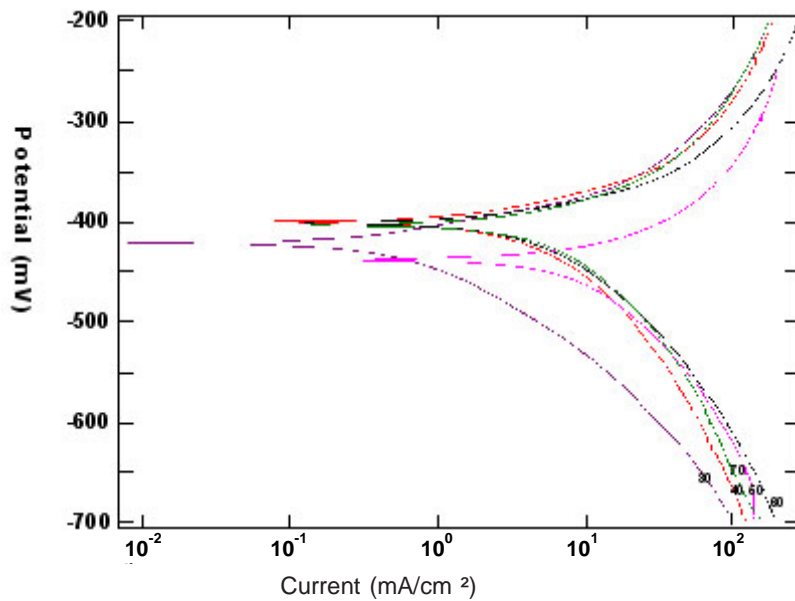


Fig. 4: Polarization plots for steel sample in 2.0 M H_2SO_4 in presence of 1.0%v/v of Ajowan plant extract at different temperatures

the charge transfer resistance, hence an increase of the corrosion rate of steel is observed. Similar behavior are obtained by E. Khamis *et al.*¹⁴.

It obvious from Figs. (2) and 4) that with increasing temperature, the anodic and cathodic current densities I_{corr} also increase, indicating that the rate of the corresponding electrode processes (metal dissolution and hydrogen evolution) increases, but the E_{corr} for steel increased more rapidly with temperature in the absence of inhibitor. These results confirmed that ASE acts as an efficient inhibitor in the range of temperature studied. The corresponding data are shown in Tables (1&2).

It could be seen, from Tables (1&2) that the rise in temperature lead to an increase in corrosive rate without and with inhibitor. It was also noted that the inhibition efficiency of Ajowan extract increased with rise in temperature. This may be attributed to chemical adsorption of Ajowan extract molecules on steel surface and it can be explained by the specific interactions between the steel surface and the inhibitor¹⁵⁻¹⁷.

Arrhenius plots for the charge transfer resistance (R_{ct}) and/or the corrosion current densities (I_{corr}) of steel in absence and presence of ASE are given in Figures (5-6). The activation energies from EIS and PDP methods can be calculated from the following relationships:

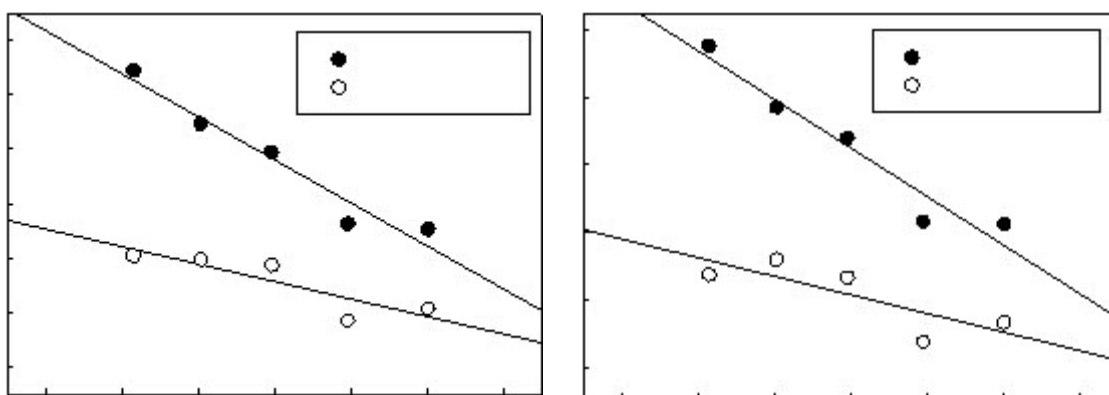


Fig. 5: Arrhenius relationship of the corrosion rates for steel in 2.0 M H_2SO_4 a) $\log I_{corr}$. b) $\log I_{corr}/T$.

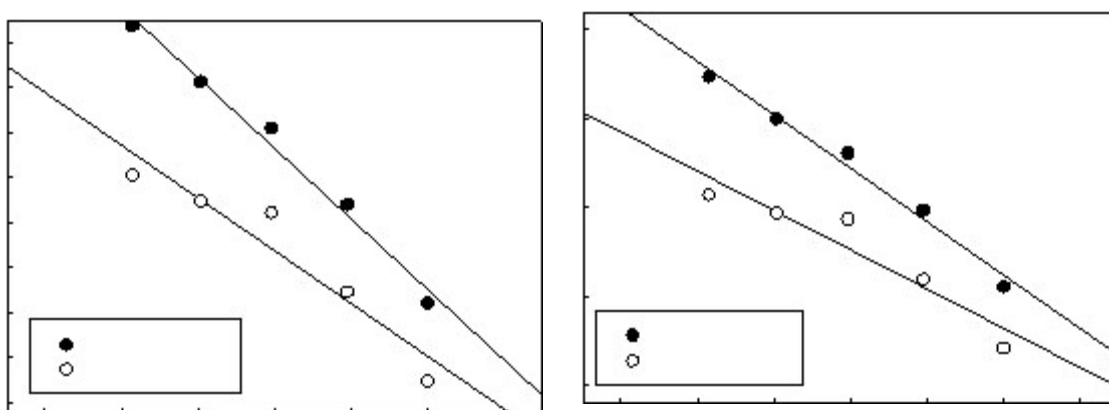


Fig. 6: Arrhenius relationship of the corrosion rates for steel in 2.0 M H_2SO_4 a) $\log 1/R_{ct}$ b) $\log 1/R_{ct}/T$

$$1/R_{ct} \text{ and/or } I_{corr} = K \exp(-E_a / RT) \quad \dots(1)$$

$$\log(1/R_{ct}) \text{ and/or } \log I_{corr} = \log K - E_a/RT \quad \dots(2)$$

where $1/R_{ct}$ and/or I_{corr} represents the corrosion rate, K is constant, R is the universal gas constant and T is temperature in Kelvin. The values of E_a from EIS and PDP measurements were recorded in Table 3.

It obvious that E_a values from EIS and PDP methods in presence of **ASE** were lower than that in their absence, respectively, this means that an inhibitor becomes more effective as the temperature increases¹⁸ which it can explained as due to each of the following:

- An increase in surface area of the metal covered by inhibitor molecules as the temperature rises¹⁹.
- The chemisorptions of Ajowan inhibitor on steel surface^{11,20-23}.
- Such inhibitor **ASE**, like the catalysts which do not change the temperature coefficient of the reaction are firmly held on the metal surface¹⁹.
- Machu²⁴ suggest that, the kinetic of such corrosion process acquires the character of a diffusion process, in which, at high temperatures the amount of inhibitor present at the metal surface is greater than that at lower temperatures. This increase the surface area of the metal covered by the inhibitor molecules. Then, the reaction between the metal and the inhibitor can then only take place by diffusion of acid anions through the pores of the protective layer formed.
- Hoar and Holliday²⁶ suggest that the enhancement of inhibitive efficiency at higher

temperatures may be due to the higher of activation energy available for adsorption, and the higher rate of diffusion of inhibitor molecules.

Singh *et al.*²⁷, consider that with increase in temperature some chemical changes occur in the inhibitor molecules leading to an increase in the electron densities at the adsorption centers of the molecule causing an improvement in inhibitor efficiency.

For calculating the enthalpy ΔH^\ddagger and entropy ΔS^\ddagger of activation, the alternative formulation of the Arrhenius equation is the transition state equation²⁸⁻³⁰:

$$(1/R_{ct} \text{ or } I_{corr}) = RT/Nh \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT) \quad \dots(3)$$

$$\log(1/R_{ct}/T) = \log(R/Nh) + \Delta S^\ddagger/2.303R - \Delta H^\ddagger/2.303RT \quad \dots(4a)$$

$$\log(I_{corr}/T) = \log(R/Nh) + \Delta S^\ddagger/2.303R - \Delta H^\ddagger/2.303RT \quad \dots(4b)$$

being h the blank's constant and N Avogadro's number. Figs. (5 & 6) show straight lines of plots of $\log R_{ct}/T$ and/or $\log I_{corr}/T$ vs. $1/T$ with a slope of $\Delta H^\ddagger/R$ and intercept of $\log(R/Nh) + \Delta S^\ddagger/R$. Values of E_a , ΔH^\ddagger and ΔS^\ddagger are collected in Table(3). The data show that the thermodynamic parameters (ΔH^\ddagger and ΔS^\ddagger) of the dissolution reaction of steel in 2.0M H_2SO_4 in the presence of **ASE** are higher than those of the non- inhibited solution from both EIS and PDP methods. The negative values of ΔH^\ddagger suggest that the dissolution process is an exothermic phenomenon and the dissolution of steel is difficult. Also, the entropy ΔS^\ddagger widely decreases with the content of the inhibitor. This means the

Table 3: Activation parameters for steel corrosion in 2.0 M H_2SO_4 in absence and presence of 2.0%v/v of **ASE at different temperatures from EIS and PDP measurements**

Method	2.0M H_2SO_4			2.0M H_2SO_4 + 2%v/v ASE		
	E_a kJmol. ⁻¹	ΔH^\ddagger kJmol. ⁻¹	ΔS^\ddagger Jmol. ⁻¹ k ⁻¹	E_a kJmol. ⁻¹	ΔH^\ddagger kJmol. ⁻¹	ΔS^\ddagger Jmol. ⁻¹ k ⁻¹
EIS	60.139	-6.911	-8.737	44.963	-5.085	-15.462
PDP	30.411	-3.335	-16.529	12.456	-1.272	-23.941

formation of an ordered stable layer of inhibitor on steel surface^{23,31}.

CONCLUSION

The principal finding of the present work could be summarized as follows:

The corrosion rate of steel in 2.0M H₂SO₄ from both impedance and polarization methods is directly proportional to an

increase in temperature from 20°C to 70°C. The inhibition efficiency of Ajowan seeds extract (ASE) increases with the temperature and the activation corrosion energy decreases in presence of inhibitor from both EIS and PDP, which indicate that the chemisorptions mode is more probable. ASE has a better performance for inhibit the corrosion of steel in 2.0M H₂SO₄ at high temperatures.

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