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Corrosion Inhibition of Steel in 1 M Hydrochloric Acid Medium by *Chamomile Essential Oils*

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Chamomile oil was tested as corrosion inhibitor of steel in 1 M HCl using electrochemical impedance spectroscopy (EIS), Tafel polarisation methods and weight loss measurements. The inhibition efficiency of chamomile oil was calculated and compared. We note good agreement between these methods. The results obtained revealed that the inhibitor tested reduce differently the kinetic of corrosion process of steel. Its efficiency increases with the concentration and attained 90% at 2 g/l. Effect of temperature on the corrosion behaviour of steel in 1M HCl was also studied in the range 298 K and 328 K. The thermodynamic data of activation are determined. The analysis of chamomile oil, obtained by hydro-distillation, using Gas Chromatography (GC) showed that the major components were were Linoleic acid (54.8 %), Oleic acid (23.5 %), Palmitic acid (10.7 %) and Linolenic acid (6.2).

Keywords: Corrosion; Steel; Inhibition; Chamomile essential oils; Acid medium

1. INTRODUCTION

Steel is widely used in most industries because of its low cost and availability for the manufacture of reaction vessels such as cooling tower reservoirs, pipelines, etc…[1]. Several researchers [2–14] studied the effect of some synthetic organic inhibitors on the corrosion of steel in hydrochloric and sulphuric acid solutions.

The toxic nature of these organic inhibitors has required research activities in recent times toward finding alternative environmentally friendly acid corrosion inhibitors. These advantages have incited us to draw a large part of program of our laboratory to examine natural substances as corrosion inhibitors such as: *Rosemary oil* [15-17], *Thymus oil* [18-19], *Artemisia* [20-22], *Lavender oil* [23], *Jojoba oil* [24], *Pennyroyal Mint oil* [25], *Argan oil* [26-27] and *prickly pear seed oil* [28].

However, to our best of knowledge, *chamomile oil* (CO) has not been used as a corrosion inhibitor for steel.

Chamomile (Chamomilla recutita) belongs to the compositae family and grows in Europe, North East Asia, North and South America. Some countries that produce chamomile for the international market are: Argentina, Egypt, Bulgaria, Hungary, Spain, Czech Republic, Germany, Brazil, Chile and Peru [29]. Due to its pleasant fruity odour, the oil has found widespread application in flavour and fragrance industry. The anti-inflammatory, anti-allergic, antidepressant and antiseptic properties of the oil contribute to its traditional use in aromatherapy [30-31].

The objective of the present work is to investigate the inhibition effect of chamomile oil on the corrosion of C38 steel in 1 M hydrochloric acid by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. It is expected to accumulate useful information on the adsorption and inhibition effect of Chamomile oil on steel in acid solution.

2. MATERIALS AND METHODS

2.1. Solutions preparation

The solution 1M HCl was prepared by dilution of analytical grade 37% HCl with double distilled water. The solution tests are freshly prepared before each experiment by adding the oil directly to the corrosive solution. The test solutions were freshly prepared before each experiment by adding the oil directly to the corrosive solution. The test solution is there after de-aerated by bubbling nitrogen. Gas pebbling is maintained prior and through the experiments. Experiments were carried out in triplicate to ensure the reproducibility.

2.2. Plant collection and essential oil extraction

Chamomile (Chamomilla recutita) was collected in the food supermarket of Agadir, Morocco. It was taxonomically identified at laboratory of Establishment of Autonomous Control and Coordination of Export in Morocco. A voucher specimen sample was deposited in the herbarium of the laboratory of Environmental Engineering and Biotechnology in the National School of Applied Sciences, Ibn Zohr University. Agadir, Morocco. The aerial parts of the plant were air-dried in the laboratory at room temperature. A sample of 100 g was subjected to water distillation for 2 hours using a Clevenger-type apparatus recommended by the French Pharmacopoeia [32].

2.3. Fatty acid composition

The fatty acid composition was determined following the ISO standard ISO 5509:2000 (ISO 2000) [33]. In brief, one drop of the oil was dissolved in 1 mL of n-heptane, 50 µg of sodium methylate was added, and the closed tube was agitated vigorously for 1 min at room temperature. After addition of 100 µL of water, the tube was centrifuged at 4500 × g for 10 min and the lower aqueous phase was removed. Then 50 µL of HCl (1 mol with methyl orange) was added, the solution was shortly mixed, and the lower aqueous phase was rejected. About 20 mg of sodium hydrogen sulphate (monohydrate, extra pure; Merck, Darmstadt, Germany) was added, and after centrifugation at 4500 × g for 10 min, the top n-heptane phase was transferred to a vial and injected in a Agilent Technologies 6890N gas chromatograph equipped with a capillary column (30 m x 0.32 mm; Supelco, Bellefonte, PA, USA) and flame ionization detection. The column was programmed to increase from 135 to 160°C at 2°C/min and from 160 to 205°C at 1.5°C/min; the detection temperature was maintained at 220°C, injector temperature 220 °C. The vector gas was helium at a pressure of 5520 Pa. Peaks were identified by comparing retention times with those of standard fatty acid methyl esters.

2.4. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster software. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was the same used for gravimetric measurements. The surface area exposed to the electrolyte is 0.056 cm^2.

Potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5 mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from −800 mV to −400 mV at 298 K. The solution test is there after de-aerated by bubbling nitrogen. Gas bubbling is maintained prior and through the experiments. In order to investigate the effects of temperature and immersion time on the inhibitor performance, some test were carried out in a temperature range 298–328 K.

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at E_{corr} after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

2.5. Weight loss measurements

Coupons were cut into 2 × 2 × 0.08 cm^3 dimensions having composition (0.179% C, 0.165% Si, 0.439% Mn, 0.203% Cu, 0.034% S and Fe balance) are used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water, degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 80 cm^3. The immersion time for the weight loss is 8 h at 298 K.

3. RESULTS AND DISCUSSION

3. 1. Fatty acid composition

The fatty acid composition of the *chamomile essential oil* is given in Table 1.

Table 1.Chemical composition of chamomile essential oil.

Fatty acid methyl esters	**%**
Myristic acid (C14 :0)	0.1
Palmitic acid (C16:0)	10.7
Palmitoleic acid (C16:1)	0.1
Heptadecanoic acid (C17:0)	0.1
Stearic acid (C18:0)	3.6
Oleic acid (C18:1)	23.5
Linoleic acid (C18:2)	54.8
Linolenic acid (C18:3)	6.2
Arachidic acid (C20:0)	0.3
Gadoleic acid (C20:1)	0.2

The main constituents were Linoleic acid (54.8 %), Oleic acid (23.5 %), Palmitic acid (10.7 %) and Linolenic acid (6.2).

3.2. Effect of concentration

3.2.1. Gravimetric measurements

Table 2. regroups the gravimetric parameters (W_{corr} and E_G / %) of steel in 1M HCl with and without the addition of various concentrations of the *chamomile oil*. The value of the inhibition efficiency (E_G / %) was determined using the equation (1).

$$E_G = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \qquad (1)$$

where W_{corr} and W'_{corr} are the corrosion rate in absence and presence of the inhibitor, respectively.

Table 2. Corrosion rate of steel in 1M HCl with and without *chamomile oil* at various concentrations, and the corresponding inhibition efficiency

Inhibitor	Conc (g / L)	W_{corr} (mg. cm^{-2})	E_G (%)
Blank	0.0	1.8614	-
Chamomile oil	0.1	0.9307	50
	0.5	0.6328	66
	1.0	0.4095	78
	2.0	0.2047	89

According to this data, it's clear that the corrosion rate of steel in the blank is higher in comparison with the blank containing CO. The addition of 0.1 g L^{-1} chamomile oil into the aggressive medium reduces this corrosion rate by 50% and reaches 89% at 2.0 g L^{-1}. The inhibition efficiency of chamomile oil increases as function of its concentration.

3.2.2. Polarization measurements

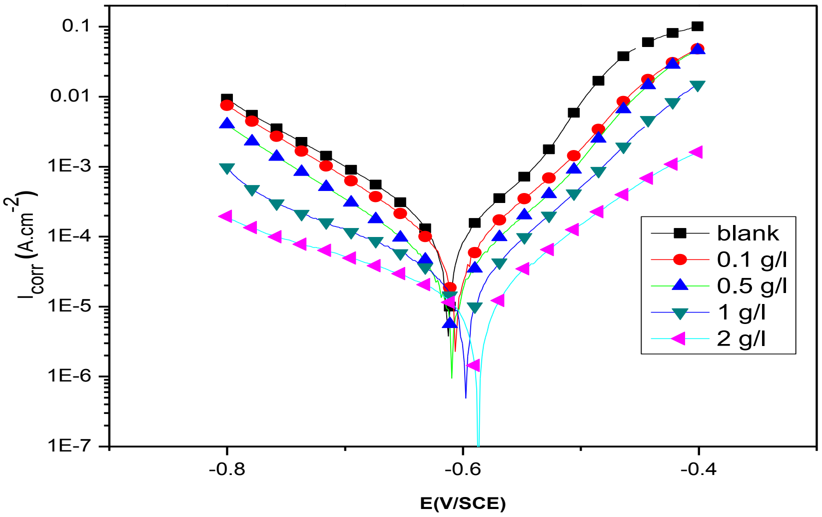

Figure 1. Potentiodynamic polarisation curves of steel in 1M HCl in the presence of different concentrations of *chamomile oil*.

Fig.1 show potentiodynamic polarisation curves obtained in presence of *chamomile oil* at different concentrations at 298 K. Table 3. shows the values of corrosion current density, corrosion potential, and E% as functions of CO concentration.

The values of corrosion current density were obtained by extrapolation of cathodic Tafel (b_c) lines to the respective free corrosion potential (E_{corr}). In this case, the inhibition efficiency is defined as follows:

$$E\% = (1 - \frac{I'_{corr}}{I_{corr}}) \times 100 \qquad (2)$$

Where I_{corr} and I'_{corr} are current density in absence and presence of chamomile oil respectively.

Table 3. Electrochemical parameters of C38 steel in 1M HCl solution without and with *chamomile oil* at different concentrations.

Inhibitor	**Concentrations (g/L)**	**E_{corr} (mV/SCE)**	**I_{corr} (µA/cm^2)**	**$-b_c$ (mV/dec)**	**E (%)**
Blank	0.0	-612	124	103	-
Chamomile oil	0.1	-605	66	98	50
	0.5	-609	37	100	70
	1.0	-600	24	121	80
	2.0	-586	12	165	90

It can be seen that the decrease of cathodic current densities more marqued at high inhibitor concentrations. *Chamomile oil* (CO) acts as an excellent and mixed-type inhibitor in 1 M HCl.

We also remark that the cathodic current–potential curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled and that the addition of the *chamomile oil* does not modify the mechanism of this process (Fig.1) [34].

From Table 3, it could be noted that E% increased with increasing inhibitor concentration, reaches 90% at 2.0 g/L. The results obtained from electrochemical are in good agreement with weight loss studies.

3.2.3. Electrochemical impedance spectroscopy measurements

The corrosion behaviour of steel, in acidic solution with and without *chamomile oil*, is also investigated by electrochemical impedance spectroscopy (EIS) measurements at 298 K (Fig.2).

The electrochemical impedance parameters derived from these investigations are mentioned in Table 4.

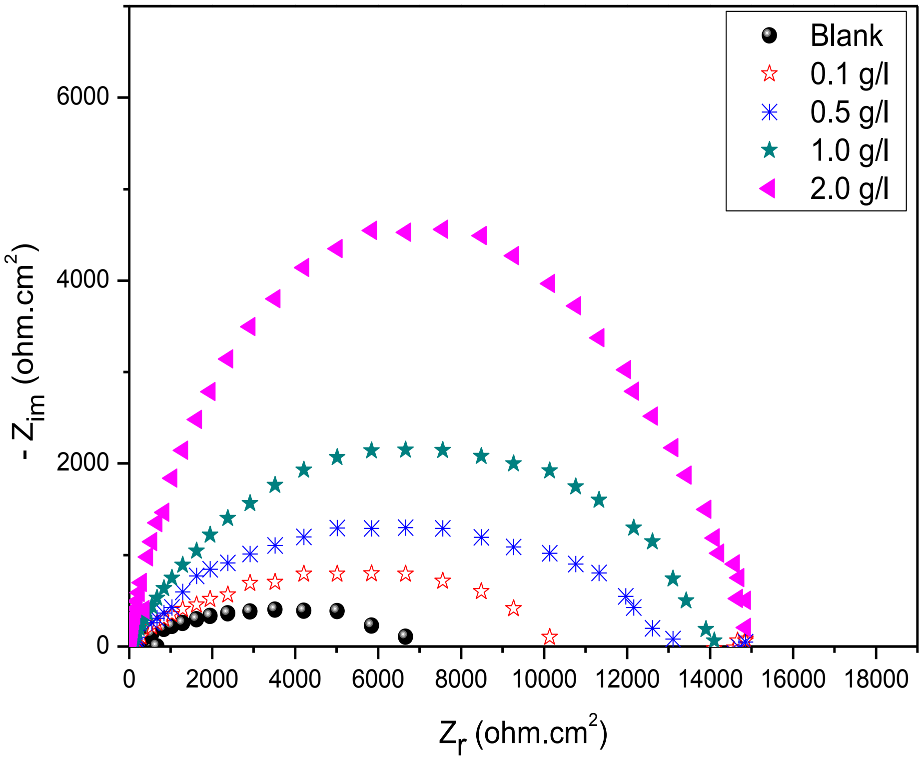

Figure 2. Nyquist plots of steel in 1 M HCl containing various concentrations of *chamomile oil* at E_{corr} after 30 min of immersion.

The inhibition efficiency got from the charge transfer resistance is calculated by:

$$E_{Rt}\% = \frac{(R_t - R^\circ{}_t)}{R_t} x100 \qquad (3)$$

Were R_t and $R^0{}_t$ are the charge transfer resistances in inhibited and uninhibited solutions respectively.

The charge transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [35]. The double layer capacitance (C_{dl}) values were obtained at maximum frequency (f_{max}), at which the imaginary component of the Nyquist plot is maximum and calculated using the following equation:

$$C_{dl} = \frac{1}{2.\pi.f_m.R_t} \qquad (4)$$

With C_{dl}: double layer capacitance (µF.cm^{-2}); f_{max}: maximum frequency (Hz) and R_t: Charge transfer resistance (Ω.Cm^2).

Table 4. Impedance parameters for corrosion of steel in 1 M HCl in the absence and presence of different concentrations of CO at 298 K.

Inhibitor	C (g/L)	Rt (kΩ.cm^2)	f_{max}(Hz)	C_{dl} (ŋF/cm^2)	E_{Rt} (%)
Blank	0.0	10	50	318	-
Chamomile oil	0.1	18	40	221	45
	0.5	29	31	177	65
	1.0	63	25	101	84
	2.0	141	20	56	92

As it can be seen from Fig. 2, impedance diagrams show a semi-circular appearance, indicating a charge transfer process mainly controls the corrosion of steel [36]. From the impedance data, we notice an increase of the charge transfer resistance and decrease of the double layer capacitance with increasing inhibitor concentration indicate that CO inhibits the corrosion rate of C38 steel by an adsorption mechanism [52]. A comparison may be made between inhibition efficiency E (%) values obtained by different methods (weight loss, polarization curves and EIS methods). Fig. 3 shows a histogram that compares the E (%) values obtained. One can see that whatever the method used, no significant changes are observed in E (%) values. We can then conclude that there is a good correlation with the three methods used in this investigation at all tested concentrations and that *chamomile oil* is an efficient corrosion inhibitor.

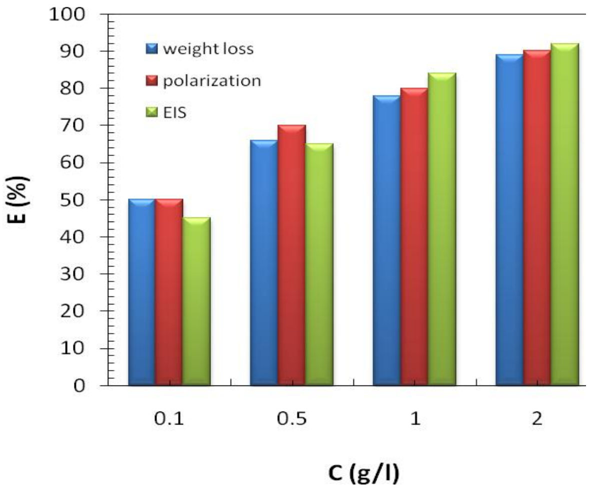

Figure 3. Comparison of inhibition efficiency (E%) values obtained by weight loss, polarization and EIS methods.

3.3. Effect of temperature

Temperature has a great effect on the corrosion phenomenon. Generally the corrosion rate increases with the rise of the temperature. Table 5. shown the effect of temperature on the corrosion rate of steel in absence and presence of *chamomile oil* at 2g/L.

Table 5. Electrochemical parameters of steel in 1 M HCl at different 2 g/L of *chamomile oil* and corresponding corrosion inhibition efficiency.

Inhibitor	Temperature (K)	E_{corr} (mV/SCE)	I_{corr} (µA/cm^2)	$-b_c$ (mV/dec)	E (%)
Blank	298	-612	124	103	-
	308	-544	177	132	-
	318	-545	280	133	-
	328	-537	435	140	-
Chamomile oil	298	-586	12	165	90
	308	-607	27	89	84
	318	-605	42	95	85
	328	-615	59	106	86

The results show that the inhibition efficiency (E%) is independent of temperature, showing that *chamomile oil* is an efficient inhibitor in the range of temperature studied.

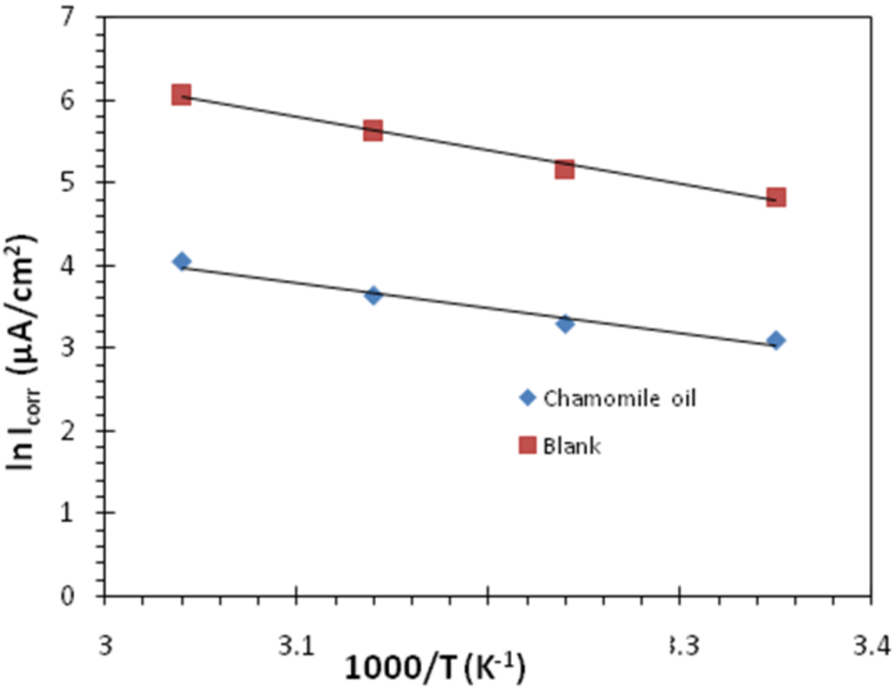

Figure 4. Arrhenius plots of steel in 1 M HCl with and without 2 g/L *chamomile oil*.

Fig. 4 also shows that the corrosion reaction can be regarded as an Arrhenius-type process (Equation (5)). The activation parameters for the studied system (E_a, ΔH_a^* and ΔS_a^*) were estimated from the Arrhenius equation and transition state equation (Equation (6)) :

$$I_{corr} = A\exp(-\frac{E_a}{RT}) \qquad (5)$$

$$I_{corr} = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^*}{R}\right)\exp\left(-\frac{\Delta H_a^*}{RT}\right) \quad (6)$$

where A is Arrhenius factor, E_a is the apparent activation corrosion energy, N is the Avogadro's number, h is the Plank's constant, and ΔH_a^* and ΔS_a^* are the enthalpy and the entropy changes of activation corrosion energies for the transition state complex. R is the perfect gas constant.

The apparent activation energy was determined from the slopes of Ln I_{corr} vs 1/T graph depicted in Fig.4.

Fig. 5 shows a plot of Ln (I_{corr} /T) against 1/T of chamomile oil. Straight lines are obtained with a slope of ($-\Delta H^*_a/R$) and an intercept of ($\ln R/Nh + \Delta S^*_a/R$) from which the values of ΔH_a^* and ΔS_a^* are calculated respectively (Table 6).

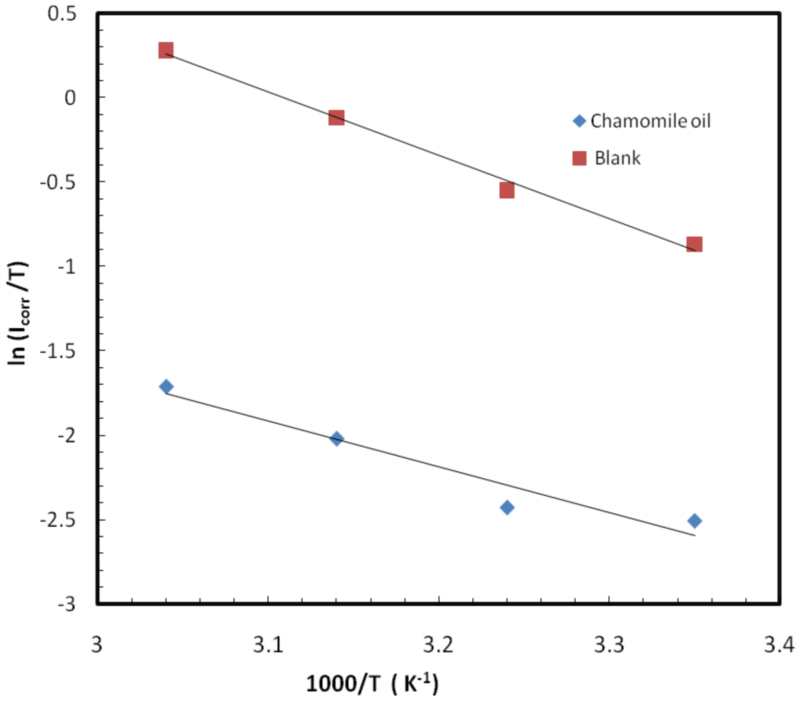

Figure 5. Relation between Ln (I_{corr}/T) and 1000/T at different temperatures.

Table 6. The values of activation parameters ΔH_a^* and ΔS_a^* for C38 steel in 1M HCl in the absence and the presence of 2 g/L of *chamomile oil*.

Inhibitor	E_a (kJ/mol)	ΔH^*_a (kJ/mol)	ΔS^*_a (J/mol)	$E_a - \Delta H^*_a$ (KJ/mol)
Blank	33.90	31.21	-100.32	2.69
Chamomile oil	25.01	22.53	- 143.52	2.48

From the following results, it can be concluded that:

- The decrease in activation energy in presence of the inhibitor studied.
- The E_a and ΔH_a^* values vary in the same way with the inhibitor concentration. This result permit to verify the known thermodynamic relation between E_a and ΔH_a^* [37]:

$$E_a - \Delta H_a^* = RT \qquad (7)$$

The calculated values are very close to RT which is equal 2.48 kJ mol^{-1} at 298 K.

- The positive values of ΔH_a^* show that the corrosion process is an endothermic phenomenon.
- The negative values of ΔS_a^* show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [38].

4. CONCLUSION

We have studied the inhibiting effect of *chamomile oil* in 1M HCl on the steel by using various methods. The results obtained are in good agreement and are given as follows.

- The major constituents of chamomile oil were Linoleic acid (54.8 %), Oleic acid (23.5 %), Palmitic acid (10.7 %) and Linolenic acid (6.2).
- The *chamomile oil* provides a good inhibition of corrosion of steel in normal hydrochloric acid medium.
- The inhibition efficiency increases with increased chamomile oil concentration to attain a maximum value of 90% at 2 g/L.
- The inhibition efficiency of *chamomile oil* is independent of temperature.

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