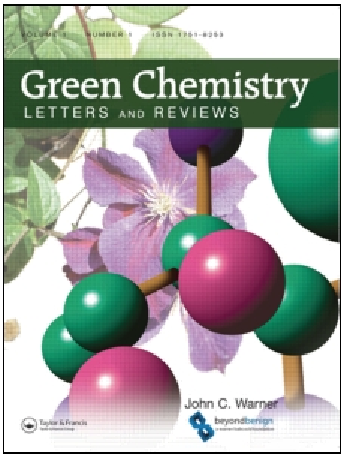

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Thermodynamic properties of *Thymus satureioides* essential oils as corrosion inhibitor of tinplate in 0.5 M HCl: chemical characterization and electrochemical study

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RESEARCH REVIEW

Thermodynamic properties of *Thymus satureioides* essential oils as corrosion inhibitor of tinplate in 0.5 M HCl: chemical characterization and electrochemical study

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Thymus satureioides (*TS*) oil was hydrodistillated and analyzed by chromatography. The natural oil was tested as a green inhibitor for tinplate in 0.5 M HCl solution. Electrochemical parameters of different concentrations of *TS* oil and the corresponding corrosion inhibition efficiencies were reported. Polarization data indicated that the studied oil acts as a mixed type inhibitor without changing the mechanism of hydrogen evolution reaction. The effect of temperature (25–60°C) on the inhibition efficiency at different concentrations of the oil studied was investigated. The data revealed that the *TS* oil might exhibit good inhibition even at moderate to high temperatures. The corrosion activation parameters (E_a, ΔH^*, ΔS^*, and ΔG^*) were estimated and discussed. It was found that the E_a values for tinplate corrosion in the inhibited solutions were higher than that for the uninhibited solution, indicating good inhibitor characteristics with a physical adsorption mechanism.

Keywords: corrosion; green inhibitor; *Thymus satureioides*; tinplate; activation

Introduction

Tinplate is widely used in industry. This is due to several factors including good resistance to corrosion and its low toxicity. The layer of tin deposited on the surface of the material consists essentially of a thin sheet of carbon rolled steel and tin plated by a layer of pure tin on both sides. Between the layer of pure tin and steel, it forms an intermediate layer composed of a solid solution Fe–Sn (*1*). Among the industrial sectors where there is high use of this material are the units of canned fish (*2*). Some special performances of tinplate are required because of the unique circumstances of the canned food. Firstly, protein and amino acid in the canned food usually contain chloride and sulfur, resulting in the wall of can being attacked seriously and food in the can being polluted as well. Secondly, the conditions in the food can are usually aggressive, and it is required that tinplate cannot seriously corrode during the can's storage life (about one year) (*2*).

Over the past couple of decades, studies have focused on the application of non-toxic inhibitors called green or eco-friendly environmental inhibitors. Natural plants in the form of extracts, oils or pure compounds may play major roles in keeping the environment more healthy, safe, and under pollution control. Among the various natural products, such as the Lawsonia extract (*3*), *Hibiscus sabdariffa* extract (*4*), *Garcinia kola* extract (*5*), fenugreek extract (*6*), *Phyllanthus amarus* extract (*7*), eucalyptus oil (*8,9*), *Azadirachta indica* (*10*), and black peper (*11*), all of which have been reported to be good inhibitors for steel in acidic solutions. In our laboratory, several oils of natural plants, such as jojoba oil (*12*), Artemisia oil (*13*), Pennyroyal oil from *Mentha oulegium* (*14*), and cedar oil (*15*) were tested and may be used as efficient inhibitors.

This work is a continuation of the earlier works and an attempt to evaluate the inhibitive action of the natural oil of *Thymus satureioides* (*TS*) on the corrosion of tinplate alloy in 0.5 M HCl using potentiodynamic polarization and polarization resistance measurements. Identification of the composition of *TS* oil was made by the GC-mass method.

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Materials and methods

Plant collection and essential oil extraction

TS belonging to Labiateae was collected in the region of Agadir, Morocco. It was taxonomically identified at the National Scientific Institute of Rabat (Laboratory of Botany, Department of Plant Biology). A voucher specimen sample was deposited in the Herbarium of the Laboratory, 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 200 g was subjected to water distillation for two hours using a Clevenger-type apparatus recommended by the French Pharmacopoeia (*16*). The yield was determined as grams over the 200 g of powder analyzed in percentage, and is shown in Table 1.

The oil was analyzed using a Hewlett-Packard 5972 MS, fitted with a HP 5890 Series II GC, and controlled by a G1034C Chemstation. A sample of 1μl was injected under the following conditions: DB-1 fused silica capillary column (20 m × 0.20 mm, film thickness 0.2 μm); carrier gas helium (0.6 ml/min); injector temperature 250°C; column temperature 50–250°C at 3°C/min; and MS electronic impact 70 eV. The identification of the compounds was achieved by comparing retention times and mass spectra with those of the published standards (*17,18*).

Preparation of the electrode

The employed material in this study is tinplate. It has been selected based on its diverse uses in packing food and beverage cans. For electrochemical tests, the commercial tinplate samples are in the form of a surface disc of 0.78 cm^2 used as a work electrode that is rinsed with acetone then with distilled water before plunging the electrode in the solution.

Electrochemical tests

The electrochemical study was carried out using a potentiostat PGP 201 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 electrode, respectively. The working electrode is the tinplate.

Potentiodynamic polarization curves were plotted from −1.0 to 0 V vs. SCE at a polarization scan rate of 0.5 mV/s and linear polarization resistance (R_p) was applied using an interval of ±10 mV from the corrosion potential (E_{corr}). After all experiments, the potential is stabilized at free potential for 30 min.

An aggressive solution of 0.5 M HCl was prepared by dilution of concentrated HCl with double distilled water. The solution tests are freshly prepared before each experiment by adding the *TS* oil directly to the corrosive solution. The solution test is thereafter deaerated by bubbling nitrogen. Gas pebbling is maintained prior and through the experiments. Experiments are repeated three times to ensure reproducibility.

Results and discussion

Thymus satureioides (TS) oil analysis

GC-mass spectrum analyzes permit the identification of the composition of *TS* oil. The main components are listed in Table 1. *TS* essential oil mainly contains borneol, α-terpineol, and low percentages of terpinen-4-ol, β-caryophyllene, bornyl acetate, camphene, γ-terpinene, thymol, carvacrol, and α-pinene (Scheme 1).

Corrosion tests

Anodic and cathodic polarization curves of tinplate in 0.5 M HCl in absence and presence of various concentrations of natural oil at 25°C are shown in Figure 1. The electrochemical parameters, such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), polarization resistance (R_p), anodic (b_a), and cathodic (b_c) Tafel slopes, are estimated by using Tafel ruler and reported in Table 2. The inhibition efficiency (E_i%) can be given by the following equation:

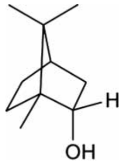
$$E_i\% = \frac{i_{corr} - i_{corr}^{inh}}{i_{corr}} \times 100, \qquad (1)$$

Table 1. Chemical composition of *Thymus satureioides* essential oils.

Family	Plant species	Yield (%)[a]	Major constituents (%)[b]
Labiateae	*Thymus satureioides*	1.5	Borneol (36.2), α-terpineol (17.1), terpinen-4-ol (6.7), β-caryophyllene (4.9), bornyl acetate (3.0), camphene (4.4), γ-terpinene (4.4), thymol (2.5), carvacrol (2.2), α-pinene (1.7)

[a] Grams of extracted oil as percentage over the 200 g of powder analysed.

[b] Grams over total extracted oil in percentage.



Scheme 1. Molecular structure of borneol (36.2%, $C_{10}OH_{17}$ M 155 g/mol).

where i_{corr} and i_{corr}^{inh} are the corrosion current density values without and with the inhibitor, respectively, determined by extrapolation of the cathodic Tafel lines to the corrosion potential:

$$E_{R_p}\% = \frac{R_p^{inh} - R_p}{R_p^{inh}} \times 100, \qquad (2)$$

where R_p and $R_p^{inh}$are the polarization resistance value without and with the inhibitor, respectively. Rp is the reciprocal slope of plots of polarization curves around E_{corr} (at ±10 mV).

We note that the anodic and cathodic branches of polarization curves show the same characteristics in the absence and presence of inhibitor. Extrapolation of this linear corrosion potential leads to the current density of corrosion. In anodic domain, an anodic active passive transition is observed in uninhibited and inhibited acid. The peak of activity state followed by a decrease in anodic current density. This phenomenon could be attributed to the formation of an oxide film based on Sn (II) and confirmed by the presence of a minimum current density. At higher potentials, the increase observed in anodic current density is attributed to the oxidation of Sn (II)–Sn (IV) (*19,20*).

Analysis of the polarization curves indicates that the presence of the natural oil studied leads to decreases in both the cathodic and anodic current densities. The inhibited systems were slightly shifted toward cathodic potentials, emphasizing that the studied compounds act as a mixed type inhibitor. We remark that b_c values are much higher in deaerated acid solution while b_a values are around 40 mV/dec. In a reducing acid where hydrogen is evolved from a tin surface, the exchange current is relatively small. It may be increased and the cathodic Tafel slope decreased by providing local noble-metal cathodes. In other words, the dissolution of tin is possible but the rate of corrosion may be very slow. The hydrogen overpotential of tin is high (*21*).

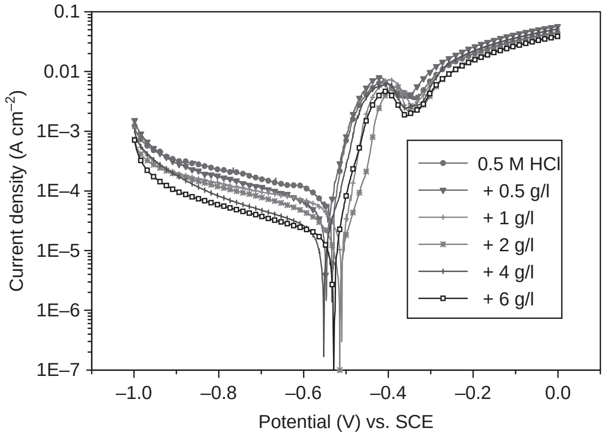


Figure 1. Anodic and cathodic polarization curves of tinplate in 0.5 M HCl at various concentrations of natural oil at 25°C.

Effect of temperature

The influence of temperature on the inhibitory effect of natural oil was conducted at various concentrations in the range of 25–65°C. The representative curves in the absence and presence of 6 g/l of *TS* oil are shown in Figures 2 and 3, respectively. The electrochemical parameters deduced are gathered in Table 2.

The variation of the logarithm of I_{corr} of tinplate in 0.5 M HCl at various concentrations of oil as function of the reciprocate of temperature was illustrated in Figure 4. Examination of Figure 4 and data of Table 2 revealed that the corrosion rate increases with temperature for all the studied systems and its extent was more pronounced in the uninhibited system, indicating the good inhibitive properties of the studied compound under the severe conditions of acid content and in temperature range. The variation of inhibitor efficiency (E%) with temperature, Table 2, shows that natural oil may be a good pickling inhibitor.

Figure 4 also shows that the corrosion reaction can be regarded as an Arrhenius-type process (Equation (3)). The activation parameters for the studied system (E_a, ΔH^* and ΔS^*) were estimated from the Arrhenius equation and transition state equation (Equation (4)):

$$I_{corr} = A \exp\left(-\frac{E_a}{RT}\right) \qquad (3)$$

$$I_{corr} = \frac{RT}{N.h}\exp\left(\frac{\Delta S_a^0}{R}\right)\exp\left(-\frac{\Delta H_a^0}{RT}\right), \qquad (4)$$

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^* and ΔS^* are the enthalpy and the entropy changes of activation corrosion energies for the transition state complex.

Transition state plots for the corrosion rates (I_{corr}) of the tinplate in the absence, and in presence of different concentrations of the inhibitor are given in Figure 5 and the corresponding activation parameters

Table 2. Electrochemical parameters of tinplate in 0.5 M HCl at different *TS* oil concentration and corresponding corrosion inhibition efficiency.

C (g/l)	T (C)	E_{corr} (V/SCE)	I_{corr} ($\mu A/cm^2$)	b_c (V/dec)	b_a (V/dec)	R_p(Ωcm^2)	Ei (%)	E_{Rp} (%)
Blank	25	−0.534	92	−0.638	0.042	212	–	–
	35	−0.569	118	−0.443	0.049	203	–	–
	45	−0.554	141	−0.477	0.044	150	–	–
	55	−0.553	148	−0.486	0.045	146	–	–
	65	−0.556	151	−0.479	0.044	140	–	–
0.5	25	−0.543	68	−0.546	0.039	269	26	21
	35	−0.549	105	−0.468	0.050	232	11	13
	45	−0.551	118	−0.469	0.043	174	16	14
	55	−0.556	120	−0.465	0.043	170	19	15
	65	−0.561	128	−0.451	0.044	166	15	16
1	25	−0.495	49	−0.680	0.039	367	47	42
	35	−0.509	77	−0.635	0.048	293	35	31
	45	−0.550	85	−0.461	0.044	249	40	40
	55	−0.523	90	−0.467	0.041	220	38	34
	65	−0.508	94	−0.455	0.043	204	37	31
2	25	−0.490	29	−0.508	0.041	669	69	68
	35	−0.513	52	−0.551	0.047	430	56	53
	45	−0.536	65	−0.464	0.046	370	54	59
	55	−0.492	73	−0.437	0.041	290	51	50
	65	−0.526	78	−0.421	0.047	258	48	46
4	25	−0.539	18	−0.431	0.033	1179	80	82
	35	−0.489	34	−0.562	0.048	671	71	70
	45	−0.497	55	−0.522	0.041	334	61	55
	55	−0.502	67	−0.500	0.038	387	55	62
	65	−0.489	77	−0.460	0.035	296	49	53
6	25	−0.525	11	−0.500	0.037	1572	88	87
	35	−0.502	19	−0.436	0.041	1036	84	80
	45	−0.490	25	−0.392	0.047	929	82	84
	55	−0.516	31	−0.403	0.039	606	79	76
	65	−0.516	36	−0.416	0.042	564	76	75

(E_a, ΔH^*, and ΔS^*) for the corrosion process were estimated and listed in Table 3. The change in the activation free energy (ΔG^*) of the corrosion process can be calculated at each experimental temperature by applying the well known equation:

$$\Delta G^* = \Delta H^* - T\Delta S^*. \quad (5)$$

The obtained ΔG^* values were also listed in Table 3. From the data recorded in Table 3, we conclude:

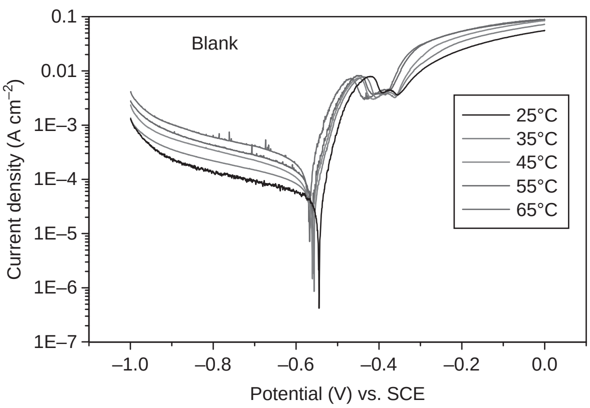


Figure 2. Polarization curves of tinplate in free 0.5 M HCl at various temperatures.

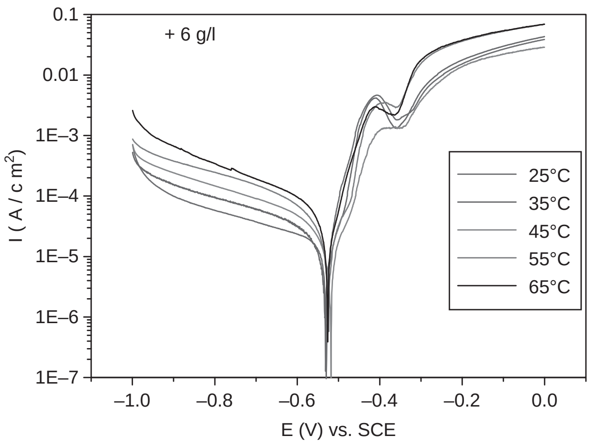


Figure 3. Polarization curves of tinplate in 0.5 M HCl+ 6 g/l oil at different temperatures.

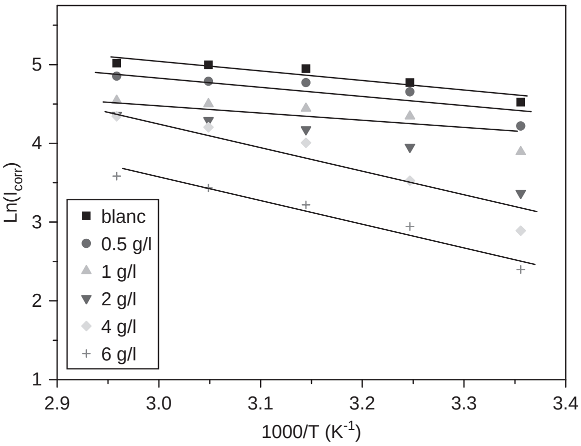


Figure 4. Arrhenius plots at various oil concentrations.

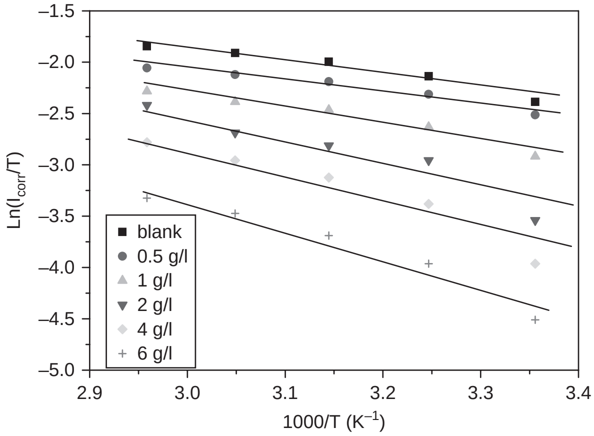


Figure 5. Variation of Ln (I_{corr}/T) versus 1000/T at various oil concentrations.

- The results showed positive signs for both E_a and ΔH^*, reflecting the endothermic nature of the corrosion process. It is obviously that the activation energy strongly increases in the presence of the inhibitor. Some authors (*20,22,23*) have attributed this result to the inhibitor species being physically adsorbed on the metal surface. In this respect, the comparison of the inhibiting action of the investigated compounds in HCl will be of definite interest.
- As observed, the trend of E_a for the studied inhibitor is not the same with that obtained from inhibition efficiency. The higher activation energy for oil as compared to that of free acid may be explained according to Riggs and Hurd (*24*), as they stated that at higher levels of surface coverage the corrosion process may proceed on the adsorbed layer of inhibitor and not on the metal surface leading to a decrease in the apparent activation energy and in some cases become less than that obtained in the absence of inhibitor.
- The negative values of ΔS^* pointed to a greater order produced during the process of activation. This can be achieved by the formation of an activated complex representing an association or fixation with consequent loss in the degrees of freedom of the system during the process (*25*).
- The values of ΔG^* were positive and showed a limited increase with rise in temperature, indicating that the activated complex was not stable and the probability of its formation decreased somewhat with rise in temperature. Therefore, the increase in the rate of corrosion with rise in temperature (Table 2) can be attributed to the large number of corrosion species passing into an activated state with a less stable configuration (*20*). However, ΔG^* values for the inhibited systems were more positive than that for the uninhibited systems revealing that in presence of inhibitor addition the activated corrosion complex becomes less stable as compared to its absence.

Conclusion

From the present work, it is found that *TS* oil can be used as an inhibitor for tinplate corrosion in HCl medium. The green natural oil tested acts as a mixed type green inhibitor. The inhibitive action of the oil increases with the concentration to attain 87% at 6 g/l. But, E% decreases at elevated temperature to reach 75% at 65°C. The activation energy increases with the inhibitor concentration.

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Table 3. Activation parameters (E_a, ΔH^*, ΔG^*, and ΔS^*) of tinplate in 0.5 M HCl at different *TS* oil.

C (g/l)	E_a (kJ/mol^{-1})	ΔH^* (kJ/mol^{-1})	ΔS^* (J.mol^{-1}.K^{-1})	ΔG^* (kJ/mol^{-1})
Blank	11.06	11.06	−122.35	47.52
0.5	9.35	11.56	−129.24	50.07
1	12.82	12.82	−120.82	48.82
2	21.19	21.19	−97.33	50.19
4	23.59	23.59	−92.73	51.22
6	24.17	24.16	−95.50	52.62

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