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Acid extract of *Mentha pulegium* as a potential inhibitor for corrosion of 2024 aluminum alloy in 1 M HCl solution

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Abstract

Inhibitive effect of *Mentha pulegium* extract on the acid corrosion of aluminum in 1 M HCl solution was studied using gravimetric, gasometric and EIS techniques. It was shown that the presence of acid extract of *Mentha pulegium* extract inhibited the corrosion of aluminum in the test solutions and the inhibition efficiency depended on the concentration of the plant extract as well as on the time of exposure of the aluminum samples in HCl solutions containing the extract. Effect of temperature on the corrosion behavior of aluminum in 1M HCl was also studied in the range 298 K and 318 K. The thermodynamic data of activation are determined. *Mentha pulegium* extract is adsorbed on the aluminum surface according to a Temkin adsorption model.

Keywords: Green corrosion inhibitor. Aluminum alloys. *Mentha pulegium* extract.

1. Introduction

Aluminum and its alloys have proved to be strategically important materials and have extensive use in many industries. They are used in the automotive, aviation and aerospace industries, in the making of household appliances, in ship building and military hardware [1-3]. Their usefulness is derived from their very good physical and mechanical properties such as their high strength-to-weight ratio, recyclability, good machining properties, as well as their outstanding resistance to corrosion.

Corrosion control of aluminum and its alloys can be enhanced by the addition of some inorganic substances to the corrodent. The substances include phosphates, chromates, dichromates, silicates, bromates, arsenates, tungstates, molybdates, chlorides and their likes [4-7]. These inorganic inhibitors exhibit toxic effects, expensive and are therefore not environmentally friendly [8]. Consequently, there has been a search for corrosion inhibitors which are not harmful to the environment.

Plant extracts and their derivatives in much greater numbers. It is needless to point out the importance of cheap, safe inhibitors of corrosion. Plant extracts have become important as an environmentally acceptable, readily available, having a heteroatoms (O, S, N) in functional groups and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. The extracts from the leaves, seeds, heartwood, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media [9-18]. Medicinal plants were previously used as corrosion inhibitors of aluminum alloys in various environments [19–35].

In Algeria, collection of medicinal and aromatic plants to extract, after distillation, essential oils for the manufacture of cosmetics, pharmaceuticals as well as flavors for food products, is a virgin field.

Many Researches are studies the influence of compounds structure, concentration on inhibition efficiency. Hammouti et al. [36] reported that the essential oil of *Mentha pulegium* appears to be a good inhibitor of steel in 1M HCl and it has very interesting and encouraging inhibition efficiency (85 %).

The present work is another trial to find a cheap and environmentally safe inhibitor for aluminum corrosion in the acidic solution. The *Mentha pulegium* belongs to the family Lamiacées; in Algeria and northern Africa, this aromatic plant is well known such as " *Fliyou".* Weight loss measurements, gasometry and electrochemical impedance spectroscopy techniques are used to evaluate the inhibition efficiency of the *Mentha pulegium* extract. The effect of temperature on the corrosion reaction rates in free and inhibited acid solutions was also investigated.

2. Materials and methods

2.1. Materials

An aluminum alloy (2024) specimen of dimension 20 x 10 x 2 mm with chemical composition: 4.5% Cu, 1..51% Mg, 0.63% Mn, 0,17% Fe, 0.08% Zn, 0.06% Si, 0.03% Ti, 0.01% Cr and Al balance was used as coupons for the corrosion study in 1M HCl solution.

The aerial parts (leaves and seeds) of the plant were air-dried in the laboratory at room temperature. Stock solutions of the plant extract were prepared by extracting weighed amounts of the dried and ground leaves and seeds of *Mentha pulegium* for 72 h in the 1M HCl at 298°K with a continues agitation. The solution was filtered and stored. The filtrate from both acid extractions had a reddish brown appearance. The filtrate was diluted by 1 M HCl to obtain inhibitor test solutions of 0.5–2.5 g/L concentrations.

2.2. Experimental methods

2.2.1. Gravimetric measurements

Gravimetric measurements were carried out in 60 ml of the corrosive solution. Rectangular aluminum specimens having a total surface area of 5.2 cm^2 were used. The sheets were abraded successively with fine emery papers (800 – 1200 grit), rinsed with distilled water, degreased with acetone, dried before being weighed, and then hanged in the corrosive medium. The duration time of immersion was extended up to 120 min at 298K in naturally aerated solutions. At the end of each experiment, the specimens were carefully washed by distilled water, dried between two filter papers and weighed.

2.2.2. *Gasometry*

The progress of the corrosion reaction was determined by volumetric measurement of the evolved hydrogen gas. The corrosion rate was taken as the slope of the straight line representing the variation of hydrogen volume and time of exposure at 298 K. The procedure was described elsewhere [37]. The material used for constructing the working electrode was the same as used for gravimetric measurements

2.2.3. *Electrochemical impedance spectroscopy measurements*

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the Analyzer of function of transfer model 5210, piloted by Powersuite software. The surface area exposed to the electrolyte is 1 cm^2. 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 30 min of exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

3. Results and discussion

3.1. Gravimetric technique and Corrosion Rates

The corrosion rates of the aluminum in 1 M HCl in the absence and presence of *Mentha pulegium* extract were determined at room temperature (298K) after 2 h of immersion period. Inhibition efficiency E (%) is calculated as follows:

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

Where W_{corr} and W'_{corr} are the corrosion rate of aluminum in 1M HCl in absence and presence of inhibitor, respectively. The degree of surface coverage θ is given by equation 2:

$$\theta = 1 - \frac{W'_{corr}}{W_{corr}} \qquad (2)$$

The weight loss data obtained are presented in figure 1 and table 2, indicating the variation of corrosion inhibition efficiency against concentration of the test inhibitor. Inhibition efficiency increased and corrosion rate decrease with the increase in the concentration of inhibitor, indicating that the *Mentha pulegium* extract acted as good inhibitor. The highest inhibition efficiency of 60.75 % was obtained for 1.5 g/L *Mentha pulegium* extract.

Table 1: Inhibition efficiencies of various concentrations of acid extract of *Mentha pulegium* for corrosion of aluminum in 1M HCl.

C (g/l)	W (mg/cm^{2}h)	E %
0	1.3696	0
0.5	0.9574	30.09
1	0.75471	44.89
1.5	0.5375	60.75
1.75	0.5921	56.77
2	0.8608	37.14
2.5	0.5585	59.22

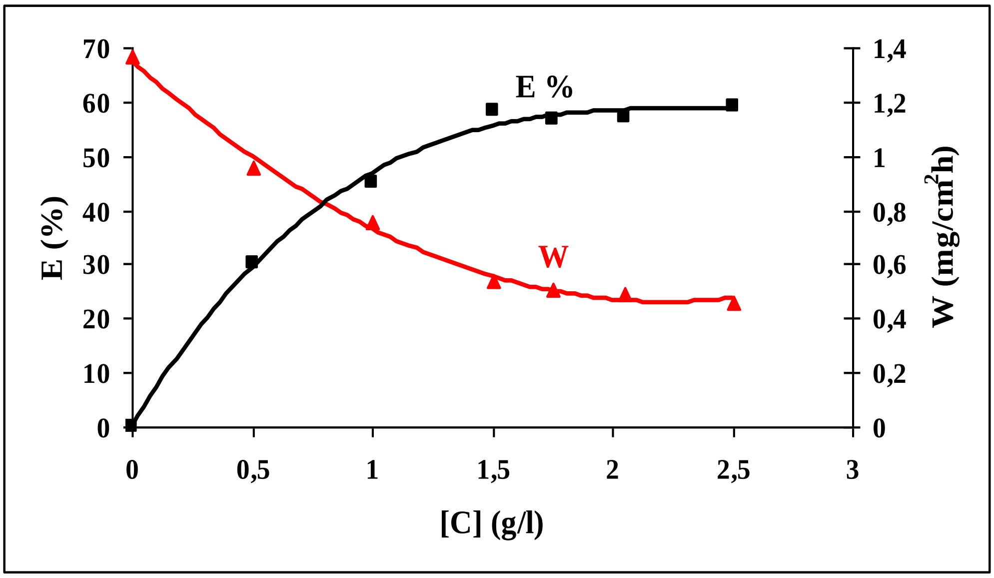

Figure 1: Dependence of the inhibition efficiency E (%) and corrosion rate, on the concentration of the inhibitor in 1M HCl at 298 K.

3.2. Gasometry

The volume of hydrogen evolved during the corrosion reaction of aluminum in 1 M HCl solution devoid of and containing different concentrations of extract is measured as a function of the reaction time, and the data are represented graphically in Figure. 2. The inhibition efficiency was calculated using equation 3:

$$E = \left(1 - \frac{V}{V^0}\right) \times 100 \qquad (3)$$

Where V, is the volume of H_2 gas evolved at time t for inhibited solution and V^0 for uninhibited solution.
Inspection of this figure reveals that, the hydrogen evolution starts after a certain time from the immersion aluminum coupon in the test solution. It may be expected that this time corresponds to the period needed by the acid to destruct the oxide film before the start of the metal attack, and it is known as the incubation period.
Further inspection of figure 2, reveal a relationship between the time of reaction and the volume of hydrogen gas evolved, in all of the tested solutions. However, the presence of the extract decreases, markedly, the slope of

the straight line. Since the slope of the line represents the corrosion reaction rate, it could be concluded that the *Mentha pulegium* extract has an ability to inhibit the corrosion of aluminum in the acid solution. The highest inhibition efficiency of 59.84% was obtained at 1.5g/L of acid extract of *Mentha pulegium*.

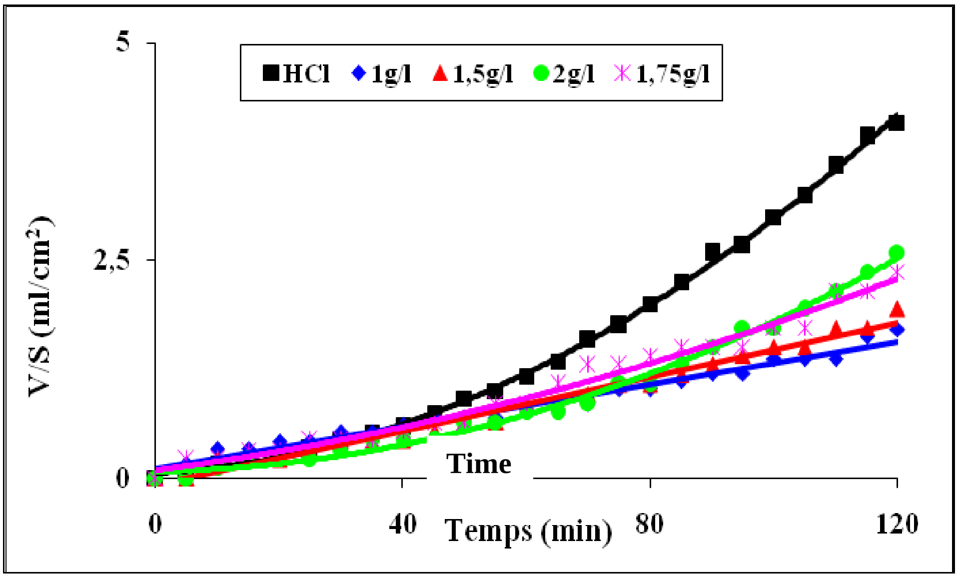

Figure 2: variation of the volume of hydrogen gas evolved with time for the corrosion of aluminum in 1 M HCl containing various concentrations of acid extract of *Mentha pulegium* at 298 K.

3.3. *Electrochemical impedance spectroscopy measurements*

The corrosion behaviour of aluminum, in acidic solution with and without *Mentha pulegium* extract, is also investigated by electrochemical impedance spectroscopy (EIS) measurements at 298 K (Figure.3).

The electrochemical impedance parameters derived from these investigations are mentioned in Table 2. The inhibition efficiency got from the charge transfer resistance is calculated by:

$$E_{Rt}\% = \frac{(R_t - R°_t)}{R_t} x100 \qquad (4)$$

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. [38].

The Nyquist plots of figure 3 show two parts: the capacitive loop in the high-frequency region, the inductive loop in the low-frequency region. The high-frequency capacitive loop can be attributed to the charge transfer resistance (Rt). The inductive loop might have been caused by the adsorbed intermediate complex. Adsorption or desorption equilibrium of surface-active species, or corrosion inhibitors, on a metal surface has also been reported as a possible source of induction in EIS spectra [39].

However, in literatures the inductive loop of aluminum has also been attributed to some other phenomena [40]. For example, it has been referred to surface or bulk relaxation of species in the oxide layer [41]. Cinderey and Burstein's measurements [42–45] confirmed that the inductive loop was closely related to the existence of a passive film on aluminum.

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:

$$C_{dl} = \frac{1}{2.\pi.f_m.R_t} \qquad (5)$$

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

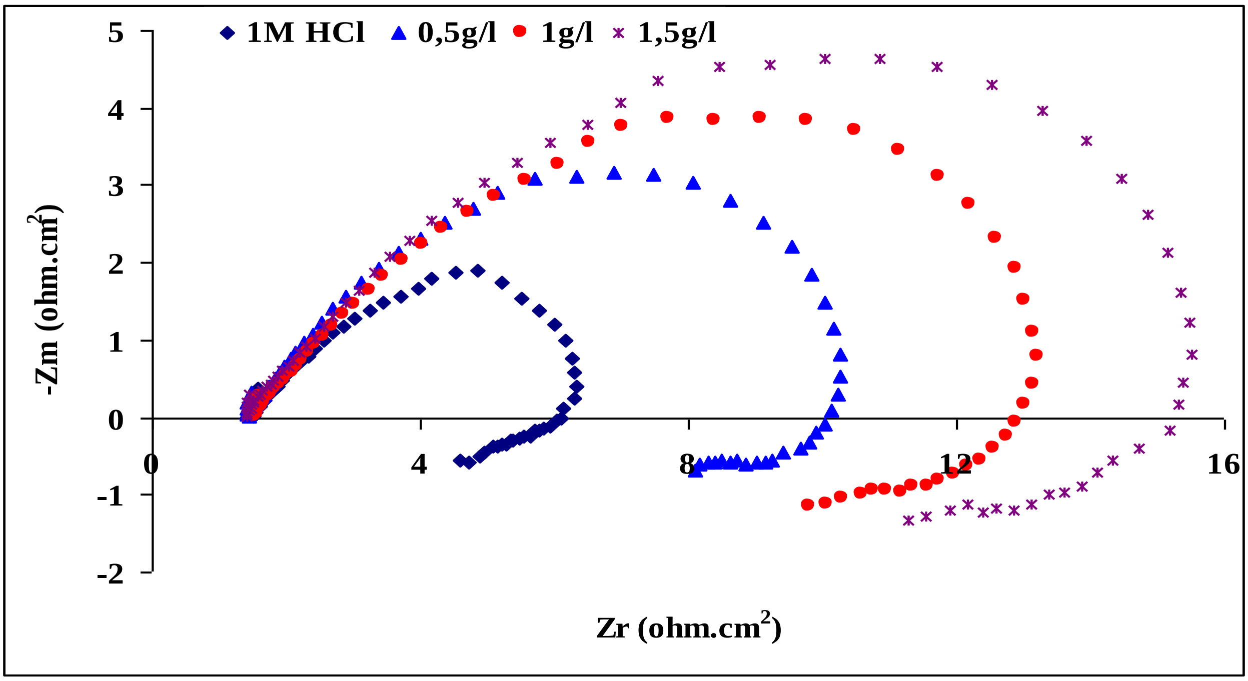

Figure 3. Nyquist plots of Al in 1 M HCl with and without different concentrations of *Mentha pulegium* extract at 298 K.

Table 2. Impedance parameters for corrosion of aluminum in 1 M HCl in the absence and presence of different concentrations *Mentha Pulegium* extract at 298 K.

Inhibitor	C (g/L)	Rt (kΩ.cm^2)	f_{max}(Hz)	C_{dl} (ŋF/cm^2)	E_{Rt} (%)
Blank	0.0	5.93	1.89	0.014	-
Mentha pulegium extract	0.5	9.90	3.18	0.005	40.01
	1	12.88	3.87	0.003	53.95
	1.5	15.17	4.64	0.002	60.90

As it can be seen from Figure 3, impedance diagrams show a semi-circular appearance, indicating a charge transfer process mainly controls the corrosion of aluminum. From the impedance data, we notice an increase in the charge transfer resistance and decrease of the double layer capacitance with increasing inhibitor concentration indicate that *Mentha pulegium* extract inhibits the corrosion rate of aluminum by an adsorption mechanism [9]. Therefore, the decrease in the C_{dl} value can be attributed to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules function by adsorption at the metal/solution interface as a consequence of the replacement of water molecules by the inhibitor molecules [46].

A comparison may be made between inhibition efficiency E (%) values obtained by different methods (weight loss, gasometry and EIS methods).We 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 the acid extract of *Mentha pulegium* acts as corrosion inhibitor for acid corrosion of aluminum.

3.4. Adsorption isotherms

Adsorption isotherms are important in understanding the mechanism of inhibition of corrosion reactions. Various isotherm models, with two or three parameters, are available for modeling equilibrium data. Two-parameter isotherms are the most commonly used isotherms because of their simplicity and possibility of linearization. However, transformation of non-linear isotherm models to linear forms usually results in parameter estimation error. Three-parameter isotherms (Sips adsorption isotherm) have three adjustable parameters and cannot be estimated by linear regression. The adjustable parameters of all isotherms analyzed here were calculated using linear regression analysis. In order to describe the goodness-of-fit of the experimental data to the proposed models, the correlation coefficient (R^2) was calculated. The most frequently used adsorption isotherms are Frumkin, Temkin, Freundlich, Flory-Huggins, and Langmuir isotherms.

The experimental data obtained in this study fits well into Temkin adsorption isotherm formulated as:

$$Exp(-2a.\theta) = K_{ads}.C \qquad (6)$$

where C is the *Mentha pulegium* extract concentration, *Kads* the equilibrium constant of the adsorption process

Figure.4 shows the variation of θ against the logarithm of the *Mentha pulegium* extract concentration. The data fit straight line, with slope nearly equal unity, indicating that these compounds adsorb according to Temkin adsorption isotherm. The linear correlation coefficient is 0.978 close to unity.

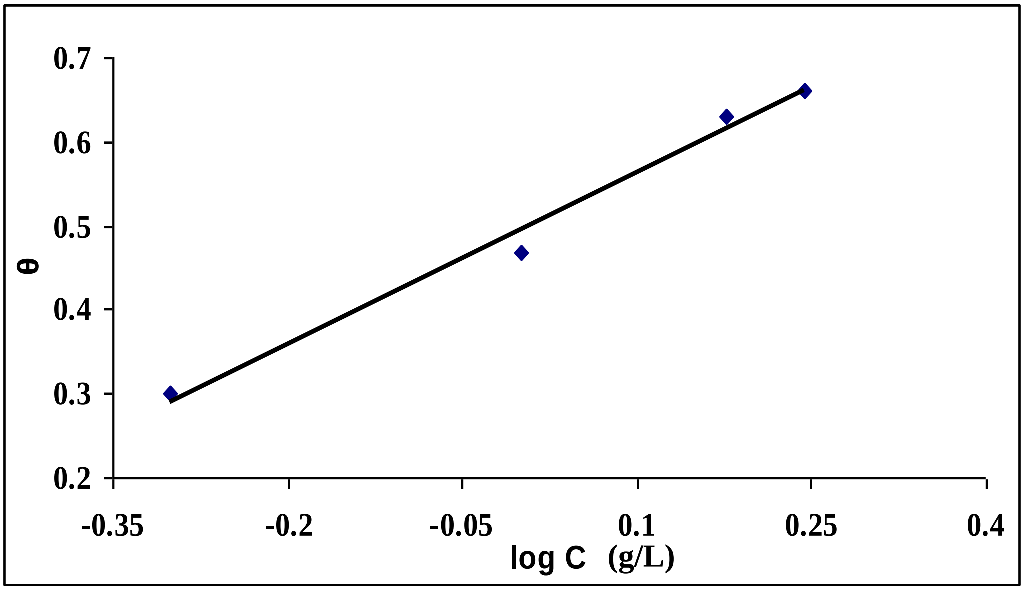

Figure 4. Plots of Temkin adsorption isotherm of *Mentha pulegium* extract on the aluminum surface at 298K.

3.5. Effect of temperature

The effect of temperature on the corrosion parameters of aluminum in free and inhibited solutions of 1 M HCl was studied using weight loss measurement in temperature range 298–318 K during 1 h. The acid solutions were inhibited by addition of *Mentha pulegium* extract. The obtained corrosion parameters are given in Table 3.

Inspection of Table 3 reveals that the corrosion rate of aluminum increases with increased temperature. On the other hand, the inhibition efficiency of *Mentha pulegium* extract increases as the temperature was increased. The activation energy for the studied system (Ea) was estimated from the Arrhenius equation:

$$W = A.\exp(-\frac{E_a}{R.T}) \qquad (7)$$

where A is Arrhenius factor, E_a is the apparent activation corrosion energy, N is the Avogadro's number, R is the perfect gas constant.

Table 3. Effect of temperature on the aluminum corrosion with and without 1.5 g/L acid extract of *Mentha pulegium* at 1h

T (K)	W ($mg/cm^2.h$)	W' ($mg/cm^2.h$)	E (%)
298	1,37	0,5	63
308	4,95	1,56	66
318	57,5	6,64	88

The apparent activation energy was determined from the slopes of Ln W vs 1000/T graph depicted in Figure.5 The values of activation energy calculated using the curves of Figure 5 are 147.13 and 99.08 kJ mol^{-1} for free and inhibited acid solutions, respectively.

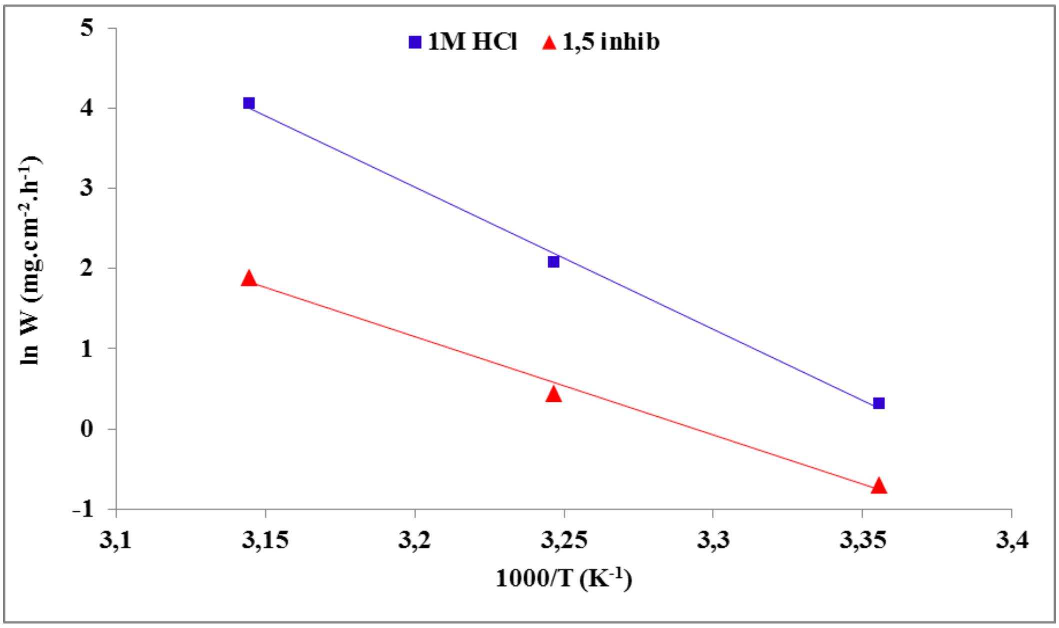

Figure 5. Arrhenius plots for the dissolution of aluminum in 1M HCl + 1.5 g/L *Mentha pulegium* extract.

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies with and without inhibitor gives some insight into the possible mechanism of inhibitor adsorption. Hammouti et al. [47] reported that an increase of the inhibition efficiency with a rise in temperature with a corresponding decrease in corrosion activation energy in the presence of an inhibitor compared to its absence is frequently interpreted as being suggestive of chemical adsorption.

Conclusion

The main conclusions are as follows:

1. The acid extract of *Mentha pulegium* shows good inhibitive action against the corrosion of Al in 1 M HCl.
2. The value of inhibition efficiency (E %) of the plant increases with increasing inhibitor concentration and with rise in temperature.
3. The adsorption of acid extract of *Mentha pulegium* on Al surface obeys Temkin adsorption isotherm.
4. The phenomenon of chemical adsorption is proposed from the activation and thermodynamic parameters obtained
5. There was good agreement between the data obtained from hydrogen gas evolution, *Gravimetric measurements* and electrochemical impedance spectroscopy measurements.

References

1. Caporali S, Fossati A, Lavacchi A, Perissi I, Tolstogouzov A, Bardi U. *Corros. Sci*., 50 (2008) 534.
2. Fang H, Chen K, Zhang Z, Zhu C, *Trans. Nonferrous Met. Soc. China*. 18 (2008) 28
3. Rosaliza R, Wan Nik WB, Senin HB, *Mater. Chem. Phys*., 107 (2008) 281.
4. Salghi R., Bazzi, L., Hammouti, B., Bouchtart, A.,Kertit, S., Ait Addi, Z.A., El Alami, Z. *Ann. Chim. Sci. Mater*. 25 (2000) 187.
5. Oguzie EE, *Port. Electrochim. Acta*, 26 (2008) 303.
6. Ebenso EE, *Bull. Electrochem*. 20 (2004), 551-559.
7. Mejeha I. M., Uroh A. A., Okeoma K. B., Alozie G. A., *Afr. J. Pure Appl. Chem*., 4(8) (2010) 158.

8. Khadraoui. A, Khelifa. A, Hamitouche. H, Mehdaoui. R, *Res. Chem. Intermed*, (2013) DOI: 10.1007/s11164-012-1014-y.
9. Khadraoui A, Khelifa A, *Res. Chem. Intermed*, (2012) DOI: 10.1007/s11164-012-0910-5.
10. Ebenso E.E., Ibok. U. J., Ekpe. U. J., Umoren. S., Jackson. E., Abiola. O. K., Oforka. N. C., Martinez. S., *Trans. of the SAEST* 39 (2004) 117.
11. Gunasekaran. G., Chauhan. L.R., *Electrochim. Acta* 49 (2004) 4387.
12. Okafor. P.C, Ekpe. U. J., Ebenso. E. E, Umoren. E. M., Leizou. K. E., *Bull. Electrochem*. 21 (2005) 347.
13. El-Etre. A.Y., Abdallah. M., El-Tantawy. Z.E., *Corros. Sci*. 47(2005) 385.
14. Oguzie. E.E., *Mater. Chem. Phys*. 99 (2006) 441.
15. Oguzie. E.E, Onuchukwu. A. I, Okafor. P. C, Ebenso. E. E., *Pigment Resin*. Tech. 35 (2006) 63.
16. Abdel-Gaber A.M., Abd-El-Nabey B.A., Sidahmed I.M., El-Zayady A.M., Saadawy M., *Corros. Sci*. 48 (2006) 2765.
17. Umoren S.A, Obot I. B, Ebenso E. E, Okafor P. C, Ogbobe O. Oguzie E. E. *Anti-Corros. Meth. Mater*. 53 (2006) 277.
18. Okafor, P.C, Ekpe, U. J, Ebenso, E. E, Oguzie, E. E, Umo, N. S, *Etor, Trans. SAEST* 41 (2006) 82.
19. Abdel-Gaber A.M., Abd El-Nabey B.A., Sidahmed I.M., El-Zayady A.M., Saadawy M. *Corros. Sci*. 48 (2006) 2765.
20. Znini M., Bouklah M., Majidi L., Kharchouf S., Aouniti A., Bouyanzer A., Hammouti B. , Costa J., Al-Dyab S.S., *Int. J. Electrochem. Sci.*, 6 (2011) 691.
21. Ahmed M.M. *Electrochimica Acta*, 24 (2006) 1.
22. Kharchouf S. , Majidi L., Bouklah M., Hammouti B., Bouyanzer A., Aouniti A., *Arab. J. Chem*, DOI : http://dx.doi.org/10.1016/j.arabjc.2010.12.002
23. Janaina Cardozo da Rocha, José Antônio da Cunha Ponciano Gomes, Eliane D'Elia *Corros. Sci*, 52 (2010) 2341
24. Mohammed R.A., Abdulwahab M., Madugu I. A., Gaminana J. O., Asuke F., *J. Mater. Environ. Sci.* 4 (2013) 93
25. Baccaria A.M. *Corros. Sci.* 41 (5) (1999), p. 885.
26. Chetouani A. , Hammoui B. and Benkaddour M. *Pigment and Resin Technology*, 33 (2004) 26.
27. Daufin G. , Labre J.P. and Pagetti J. (1977). *Corros. Sci.* 17 (1977) 901
28. M. Ramananda Singh. *J. Mater. Environ. Sci.* 4 (2013) 117.
29. El-Etre A.Y.. *Corros. Sci*. 43 (2001) 1031.
30. Benali O., Benmehdi H., Hasnaoui O., Selles C., Salghi R.. *J. Mater. Environ. Sci.* 4 (2013) 127
31. Gualdrón A.F., Becerra E.N., Peña D.Y., Gutiérrez J.C., Becerra H.Q.. *J. Mater. Environ. Sci.* 4 (2013) 143
32. Ekpe U.J. , Okafor P.C. , Ebenso E.E. ,Offiong O.E. and Ita B.I.. *Bull. Electrochem*. 17 (2001) 131.
33. Maayta A.K. and Al-Rawashdeh N.A.F. *Corros. Sci*. 46 (2004). 1129
34. Al-Turkustani A. M., Arab S. T., Al-Dahiri R. H.. *J. Mater. Environ. Sci.* 3 (2012) 1163
35. Saleh R.M. and El-Hosary A.A. *J. Electrochem. Soc*. 226 (1972).
36. Bouyanzer A., Hammouti B., Madjidi L *materials letters* 60 (2006) 2840.
37. El-Etre, A.Y. *Corros. Sci*. 43 (2001) 1031.
38. Tsuru. T, Haruyama. S, Gijutsu.B, *J. Jpn. Soc. Corros. Eng*. 27 (1978) 573.
39. Ashassi-Sorkhabi. H., Asghari. E ; *J. Appl. Electrochem.* 40 (2010) 631
40. Metikosˇ-Hukovic´ M, Baic´ R, Grubacˇ Z; *J Appl Electrochem* 32 (2002) 35
41. Freres SE, Stefenel MM, Mayer C, Chierchie T ; *J. Appl. Electrochem.* 20 (1990) 996
42. Brustein GT, Cinderey R.J. *Corros. Sci.* 32 (1991) 1195
43. Cinderey RJ, Brustein G.T. *Corros. Sci.* 33 (1992) 475
44. Cinderey RJ, Brustein G.T. *Corros. Sci.* 33 (1992) 493
45. Cinderey RJ, Brustein G.T. *Corros. Sci.* 33 (1992) 499
46. Ogundele GI, White WE, Corrosion 42 (1986) 71
47. Chaieb E, Bouyanzer A, Hammouti B, Benkaddour M., *Appl. Surf. Sci*. 246 (2005) 199.