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Temperature Effect, Activation Energies and Thermodynamic Adsorption Studies of L-Cysteine Methyl Ester Hydrochloride As Copper Corrosion Inhibitor In Nitric Acid 2M

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The inhibition of L-Cysteine Methyl Ester Hydrochloride (L-CMEH) on the corrosion of copper in 2M HNO_3, was studied by gravimetric method, in the range of temperatures from 303 to 343 K. Results obtained show that L-CMEH acts as inhibitor for copper in HNO_3 solution. The inhibition efficiency was found to increase with increase in L-CMEH concentration but decreased with temperature. The inhibition was assumed to occur via adsorption of the L-Cysteine Methyl Ester Hydrochloride on the metal surface. The adsorption of L-CMEH onto the copper surface was found to follow the Langmuir adsorption isotherm. Both kinetic parameters (activation energy, pre-exponential factor, enthalpy of activation and entropy of activation) and thermodynamics of adsorption (enthalpy of adsorption, entropy of adsorption and Gibbs free energy) were calculated and discussed.

Keywords: Corrosion, Inhibition, Copper, Nitric Acid, Cysteine, Adsorption, Thermodynamics.

1. INTRODUCTION

Pickling in nitric acid is commonly practised in industry for finishing metal surfaces. The use of inhibitors during the pickling operation is of very recent origin. The mechanism of the action of inhibitors for nitric acid has not been studied exhaustively [1]. Dilute nitric acid is one of the best sovlents for copper. According to Veley [2], copper readily dissolves in nitrous acid, less readily in a mixture of nitrous and nitric acid and still less rapidly in nitric acid alone. The reaction of nitric acid on copper is conditioned by (1) concentration of the acid, 2) temperature 3) presence of nitrous acid, and 4) solubility of the reaction products in the acid. Quinine and Strychnine [3], Caffeine [4],4 *n*-decylamine [5],5 2,4- dinitrophenyl hydrazine [6],6 substituted phenols [7],7 benzoyl benzaldehyde hydrazone derivatives [8], ethylamine [9], thiophene and its derivatives [10], some benzotriazole derivatives [11], quinoxalines and pyridazines derivatives[12, 13], cysteine [14], have been used as effective corrosion inhibitors for copper. Copper is widely used in various industrial operations, therefore the study of the corrosion inhibition of copper is a subject of pronounced practical significance. The purpose of the present contribution is to determine the influence of L-Cysteine Methyl Ester Hydrochloride (L-CMEH) towards the corrosion of copper in nitric acid, to throw some light on the mechanism of inhibition and to study the influence of temperature on the corrosion of copper in HNO_3 solution at different concentration of L-Cysteine Methyl Ester Hydrochloride (L-CMEH). The molecular structure of L-CMEH is shown in Fig. 1. The thermodynamic parameters describing the kinetic of corrosion as well as adsorption process when varying temperature and inhibitor concentration are evaluated and discussed.

2. EXPERIMENTAL DETAILS

Copper strips containing 99.5 wt.% Cu, 0.001wt.% Ni, 0.019 wt.% Al, 0.004 wt.% Mn, 0.116 wt.% Si and balance impurities was used. Prior to all measurements, are abraded with a series of emery paper from 180 to 2000 grade. The specimens are washed thoroughly with bidistilled water degreased and dried with acetone. The aggressive solution (2M HNO_3) was prepared by dilution of Analytical Grade 67 % HNO_3 with double-distilled water.

Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 50 cm^3. The copper specimens used have a rectangular form (2cm × 2cm × 0.20cm). The immersion time for the weight loss is 1h.

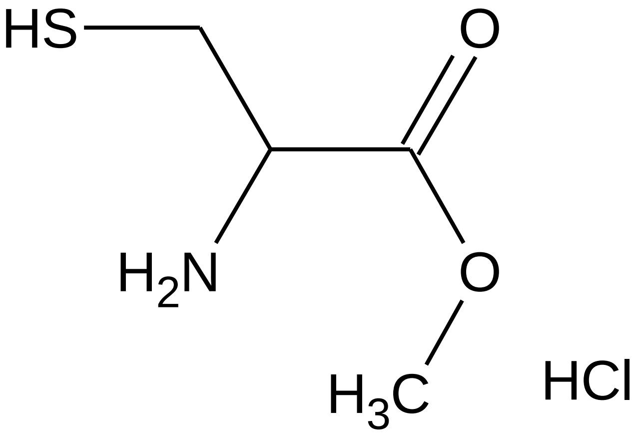

Figure 1. The molecular structure of L-CMEH.

3. RESULTS AND DISCUSSION

3.1. Effect of immersion time

The effect of addition of L-Cysteine Methyl Ester Hydrochloride derivative tested (L-CMEH) at 10^{-3}M on the corrosion of copper in 2M HNO_3 solution was studied by weight loss at 303 K at various immersion periods. Inhibition efficiency (E_w%) is calculated as follows:

$$E_W\% = \left(1 - \frac{W_{corr}}{\overset{\circ}{W}_{corr}}\right) \times 100 \qquad (1)$$

Where W^{o}_{corr} and W_{corr} are the corrosion rates of copper samples in the absence and presence of the organic compound, respectively.

The weight loss of copper in 2M HNO_3 is nearly varied linearly with immersion period in the absence and presence of different concentrations of compound (L-CMEH) at 303 K as shown in Fig. 2. The linearity of the weight loss with time from the beginning was interpreted by El-Hosary et al. [15], as the breakdown of the oxide film at the start of the attack. The variation of the inhibition efficiency of this compound inhibitor with time is shown in Fig. 3. So, we can deduce that this quantity is almost constant from the first 30 minutes of immersion, which allowed us to say that the immersion time has no significant effect on the corrosion inhibition of copper in 2M HNO_3 by L-Cysteine Methyl Ester Hydrochloride.

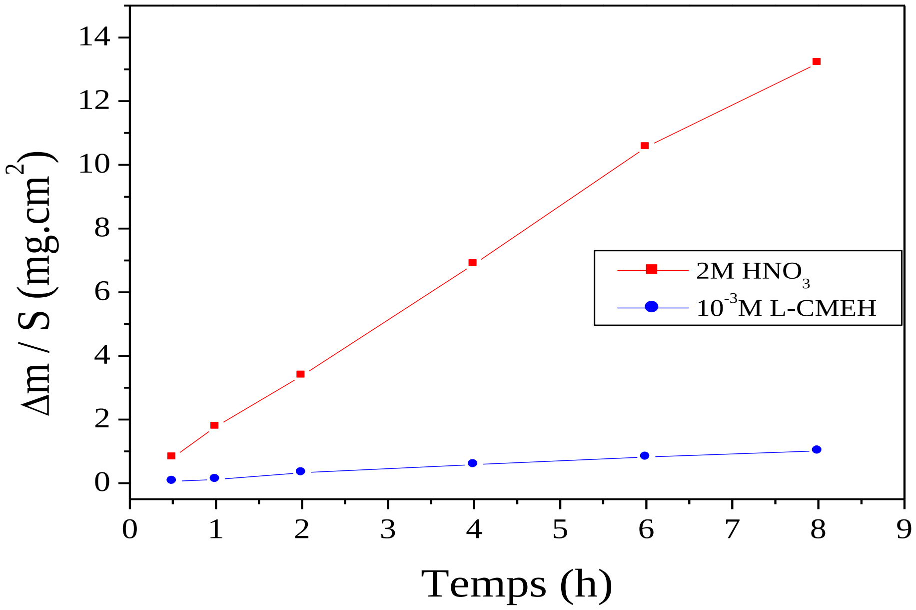

Figure 2. Weight loss as a function of immersion time of copper in 2M HNO_3 without and with 10^{-3}M of L-CMEH at 303 K.

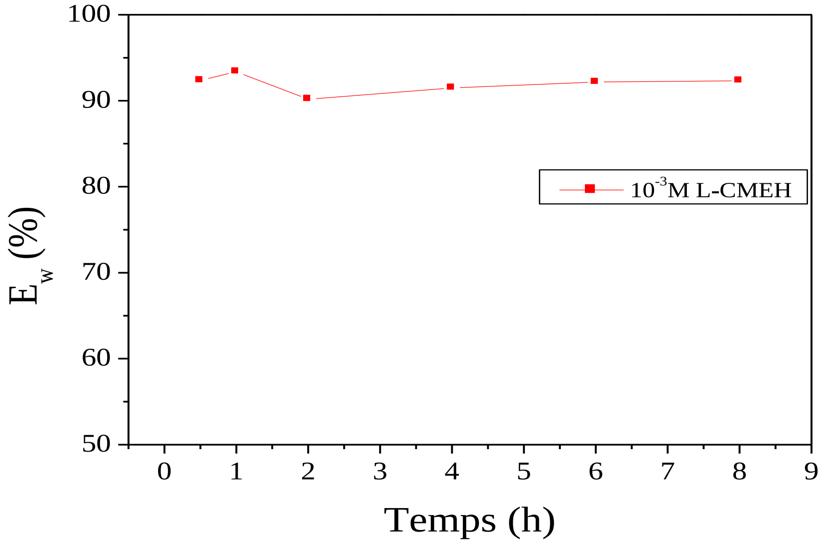

Figure 3. Variation of E_W(%) with immersion time for copper in 2M HNO_3 containing 10^{-3}M of L-CMEH at 303 K.

3.2. Effect of temperature

Table 1. The values of inhibition efficiency obtained from the weight loss for L-CMEH at different concentration in 2M HNO_3 and at different temperatures.

T (K)	Conc (M)	W(mg/cm^2.h)	E_w (%)	Θ
	BlanK	1,78	-	-
	10^{-3}	0.0618	96.53	0.9653
303	5×10^{-4}	0.1004	94.36	0.9436
	10^{-4}	0.1762	90.10	0.9010
	5×10^{-5}	0.2629	85.23	0.8523
	Blank	7.3300	-	-
	10^{-3}	0.5793	92.10	0.9210
313	5×10^{-4}	0.9717	86.75	0.8675
	10^{-4}	1.5429	78.96	0.7896
	5×10^{-5}	2.3313	68.21	0.6821
	Blank	24.9700	-	-
	10^{-3}	3.5833	85.65	0.8565
323	5×10^{-4}	4.4323	82.25	0.8225
	10^{-4}	6.0878	75.62	0.7562
	5×10^{-5}	9.3190	62.68	0.6268
	Blank	70.8200	-	-
	10^{-3}	15.0876	78.70	0.7870
333	5×10^{-4}	18.6399	73.68	0.7368
	10^{-4}	23.6682	66.58	0.6658
	5×10^{-5}	31.9967	54.82	0.5482
	Blank	186.6100	-	-
	10^{-3}	63.2473	66.11	0.6611
343	5×10^{-4}	71.6971	61.58	0.6158
	10^{-4}	84.2170	54.87	0.5487
	5×10^{-5}	102.1153	45.28	0.4528

The effect of temperature on the anti-corrosion effectiveness of L-CMEH studied at various concentration of L-CMEH in the temperature domain (303–343 K) at 1 h of immersion is summarized in Table 1. The collected curves in Fig. 4 show the evolution of corrosion rate (W) with L-CMEH concentration (C) at different temperatures.

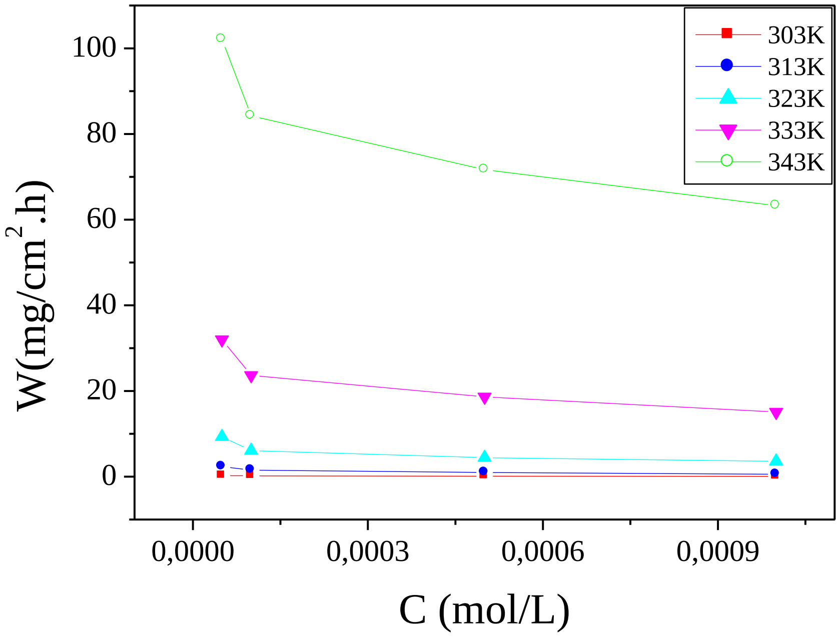

Figure 4. The relationship between corrosion rate and inhibitor concentration of L-CMEH.

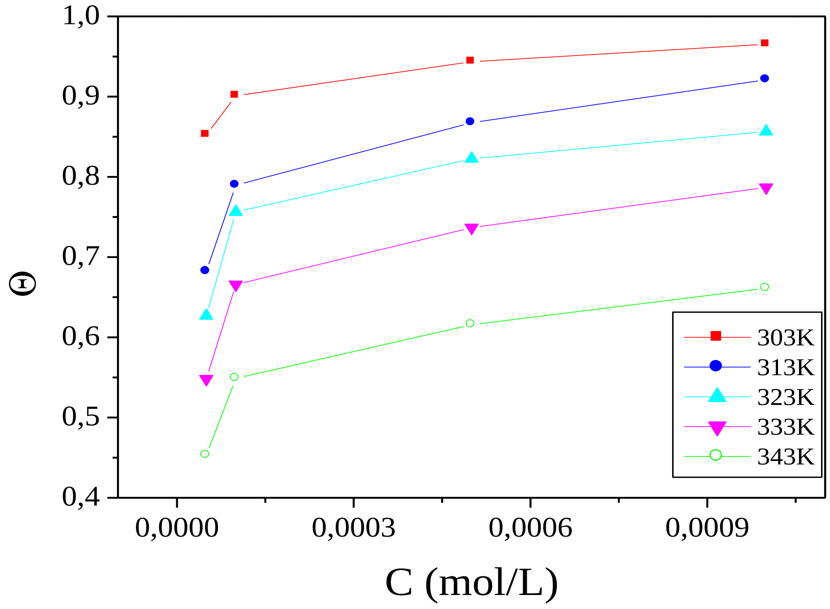

Figure 5. Relationship between inhibition efficiency and concentration of L-CMEH in 2 M HNO_3.

Fig. 4 indicates that at a given L-CMEH concentration the corrosion rate of copper increased with temperature. The increase is more pronounced at weak concentration. The results also indicate that for a given temperature, the corrosion rate of copper decreased with increasing inhibitor concentration. The values of inhibition efficiency obtained from the weight loss for different inhibitor concentrations and at various temperatures in 2M HNO_3 are given in Table 1 and Fig. 5. The results show that the inhibition efficiency decreases with increasing temperature indicating that higher temperature dissolution of copper predominates on adsorption of L-CMEH at the surface.

3.3. Kinetic parameters of activation.

The adsorption process was well elucidated by using a thermodynamic model; a kinetic model was another useful tool to explain the mechanism of corrosion inhibition for the inhibitor. The logarithm of the corrosion rate (W) could be represented as a straight line function of 1/T of copper in acid medium:

$$Ln W = \frac{-E_a}{RT} + \ln A \qquad (2)$$

Where E_a represents the apparent activation energy, R is the universal gas constant, T is the absolute temperature, and A is the pre-exponential factor.

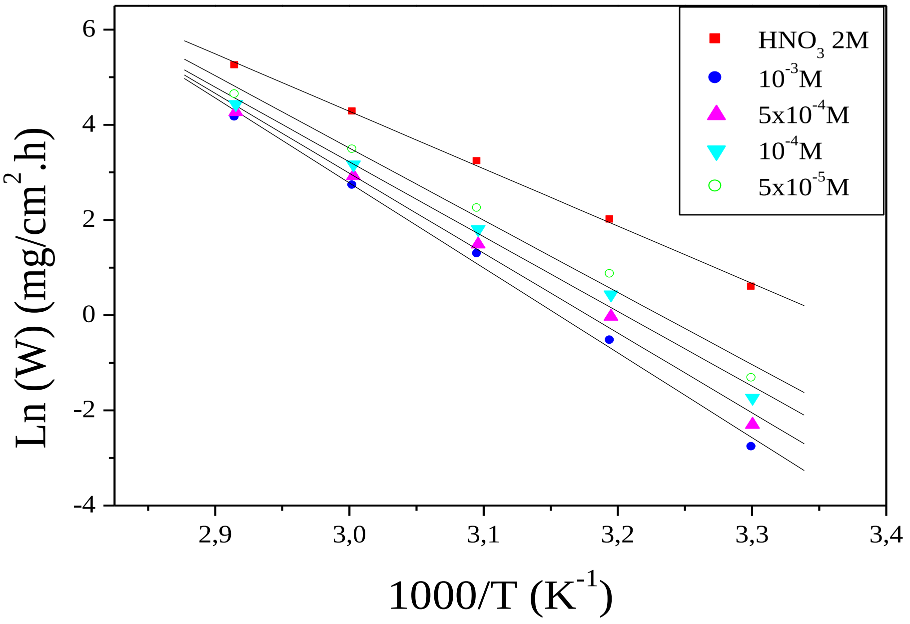

Figure 6. Arrhenius plots of copper in acid with and without different concentrations of L-CMEH.

The linear regression plots between Ln (W) and 1/T are presented in Fig.6. The calculated activation energies, E_a, and pre-exponential factors, A, at different concentrations of the inhibitor are collected in Table 2. The change of the values of the apparent activation energies may be explained by the modification of the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules [16].

Literature [16-18] discussed the variation of the apparent activation energy E_a in the presence and absence of inhibitor. Higher values for E_a were found in the presence of inhibitors. Other studies [1,19,20] showed that in the presence of inhibitor the apparent activation energy was lower than that in the absence of inhibitor. However, in our study, E_a increases with increasing the L-CMEH concentration, and all values of E_a were higher than that in the absence of L-Cysteine Methyl Ester Hydrochloride compound. This type of inhibitor retards corrosion at ordinary temperatures but inhibition is diminished at elevated temperature. Arrhenius law predicts that corrosion rate increases with the temperature and E_a and A may vary with temperature (Eq. 2). The obtained values seem that A and E_a increase continuously with the inhibitor's concentration.

Kinetic parameters such as enthalpy and entropy of corrosion process may be evaluated from the temperature effect. An alternative formulation of Arrhenius equation is [21]:

$$W = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^O}{R}\right)\exp\left(-\frac{\Delta H_a^O}{RT}\right) \tag{3}$$

h is plank's constant, N is Avogrado's number, $\Delta S°_a$ and $\Delta H°_a$ are the entropy and enthalpy of activation, respectively. Straight lines are obtained with a slope ($-\Delta H°_a /R$) and intercept ($\ln R/Nh + \Delta S°_a /R$) from which the $\Delta H°_a$ and $\Delta S°_a$ values are calculated (Table 2). The positive sign of the enthalpy ($\Delta H°_a$) reflects the endothermic nature of the copper dissolution process. The entropy of activation ΔS_a° in the absence of inhibitor is positive and this value increases positively with the L-CMEH concentration. The increase of ΔS_a° implies that an increase in disordering takes place on going from reactants to the activated complex [1].

Table 2. The values of activation parameters for copper in 2M HNO_3 in the absence and the presence of different concentrations of L-CMEH.

Conc of L-CMEH (M)	Pre-exponential factor (mg/cm^2.h)	Linear regression coefficient (r)	E_a (kJ/mol)	ΔH_a° (kJ/mol)	ΔS_a° (J/mol.K)	$E_a - \Delta H_a^{\circ}$ (kJ/mol)
Blank	3.6627×10^{17}	0.99908	100.21	097.53	082.36	2.68
10^{-3}	2.8797×10^{24}	0.99782	148.37	145.70	214.37	2.67
5×10^{-4}	1.43×10^{23}	0.99703	139.49	136.82	189.40	2.67
10^{-4}	7.3433×10^{21}	0.99664	130.60	127.93	164.72	2.67
5×10^{-5}	1.9807×10^{21}	0.99467	126.16	123.48	153.82	2.68

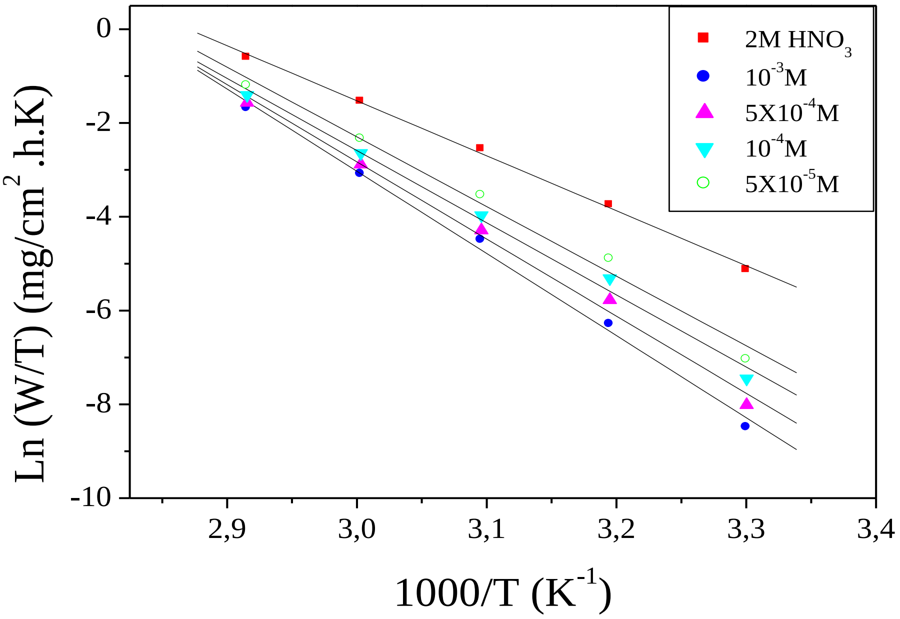

Figure 7. The relationship between Ln (W/T) and T^{-1} for different concentrations of L-CMEH.

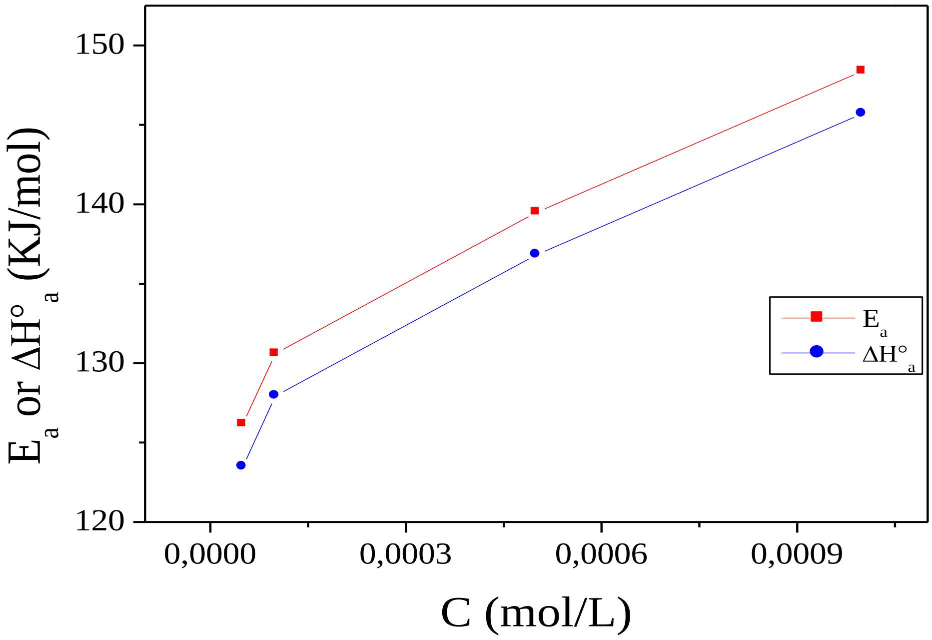

Figure 8. The relationship between E_a and ΔH_a° with concentration of L-CMEH.

The increase of E_a and $\Delta H°_a$ accompanying the increase in the inhibitor concentration is explained by an increase of the energy barrier of corrosion reaction. In case of endothermic H adsorption, with a high activation energy barrier for the transition between strongly bonded H_{ads} and H_{diss} [16]. The higher activation energy in the inhibitor's presence further supports the proposed physisorption mechanism. Unchanged or lower values of E_a in inhibited systems compared to the blank to be indicative of chemisorption mechanism, while higher values of E_a suggest a physical adsorption mechanism.

We remark that E_a and $\Delta H°_a$ values vary in the same way with the inhibitor concentration (Fig. 8). This result permits to verify the known thermodynamic relation between E_a and $\Delta H°_a$ as shown [22]:

$$E_a - \Delta H_a^{\circ} = RT \tag{4}$$

The calculate values are too close to RT is 2.67 kJ/mol. This result shows the inhibitor acted equally on E_a and ΔH_a°.

3.4. Thermodynamic parameters and adsorption isotherm.

The primary step in the action of inhibitors in acid solution is generally agreed to be the adsorption on the metal surface.

This involves the assumption that the corrosion reactions are prevented from occurring over the area (or active sites) of the metal surface covered by adsorbed inhibitor species, whereas these corrosion reactions occur normally on the inhibitor-free area [23]. Accordingly, the fraction of surface covered with inhibitor species ($\Theta = IE\%/100$) can follow as a function of inhibitor concentration and solution temperature.

The surface coverage Θ data are very useful on discussing the adsorption characteristics. When the fraction of surface covered is determined as a function of the concentration at constant temperature, adsorption isotherm could be evaluated at equilibrium condition.

The dependence of the fraction of the surface covered Θ on the concentration C of the inhibitor was tested graphically by fitting it to Langmuir's isotherm, which assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species.

Fig. 9 shows the linear plots for C/Θ versus C, suggesting that the adsorption obeys the Langmuir's isotherm:

$$\frac{C}{\Theta} = \frac{1}{K_{ads}} + C \tag{5}$$

Where C is the inhibitor concentration, and K_{ads} the adsorptive equilibrium constant, representing the degree of adsorption (i.e., the higher value of K_{ads} indicates that the inhibitor is strongly adsorbed on the metal surface); the value of K_{ads} obtained from the reciprocal of intercept of Langmuir plot lines and the slope of these lines is near unity, meaning that each inhibitor molecule occupies one active site on the metal surface.

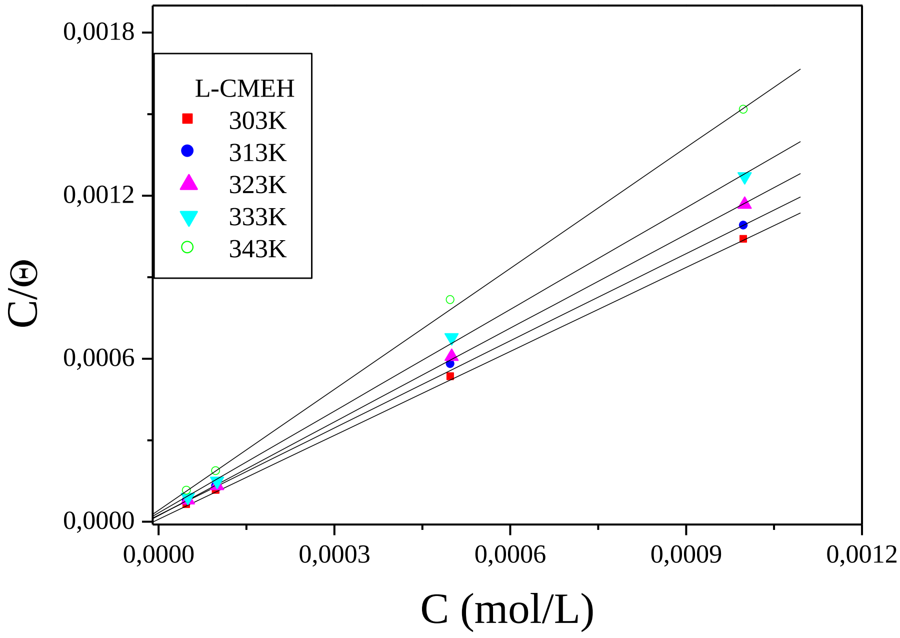

Figure 9. The relationship between C/Θ and C of L-CMEH at various temperatures.

Thermodynamic model is very useful to explain the adsorption phenomenon of inhibitor molecule. The adsorption heat could be calculated according to theVan't Hoff equation [17, 24]:

$$\mathrm{Ln}(K_{ads}) = -\frac{\Delta H^{\circ}_{ads}}{RT} + Constant \qquad (6)$$

Where ΔH°_{ads} and K_{ads} are the adsorption heat and adsorptive equilibrium constant, respectively.

To obtain the adsorption heat, the regression between Ln (K_{ads}) and 1/T was dealt with. Fig. 10 is the straight line Ln (K_{ads}) versus 1/T. The adsorption heat (ΔH) can be approximately regarded as the standard adsorption heat (ΔH°_{ads}) under the experimental conditions [17, 25].

K_{ads} values are also related to the standard free energy of adsorption, ΔG°_{ads}, with the following equation [26]:

$$K_{ads} = \frac{1}{55.55}\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \qquad (7)$$

Where R is the universal gas constant and T is the absolute temperature. The value 55.55 in the above equation is the concentration of water in solution in mol L^{-1}.

The negative value of ΔG°_{ads} (Table 3) means that the adsorption of L-CMEH on copper surface is a spontaneous process, and furthermore the negative values of ΔG°_{ads} also show the strong interaction of the inhibitor molecule onto the copper surface [27-28].

Generally, values of ΔG°_{ads} around - 20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). Those more negative than - 40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [29-30]. The calculated values of ΔG°_{ads} are greater than -20 kJ mol^{-1} but less than - 40 kJ mol^{-1}, indicating that the adsorption of mechanism of L-CMEH on copper in 2M HNO_3 solution at the studied temperatures may be a combination of both physisorption and chemisorption (comprehensive adsorption) [31]. However, physisorption was the major contributor while chemisorption only slightly contributed to the adsorption mechanism judging from the decrease of E_w% with increase in temperature and the higher values of E_a obtained in the presence of inhibitor when compared to its absence. The negative values of ΔH°_{ads} also show that the adsorption of inhibitor is an exothermic process [32]. Generally, an exothermic process signifies either physior chemisorption while endothermic process is attributable unequivocally to chemisorption [33]. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of a physisorption process is lower than 40 kJ mol^{-1} while the adsorption heat of a chemisorption process approaches 100 kJ mol^{-1} [34]. In the present case; the standard adsorption heat -29.376 kJ mol^{-1} shows that a comprehensive adsorption (physical adsorption) might occur [24]. The adsorption of inhibitor molecules is accompanied by positive values of ΔS°_{ads} .

ΔH°_{ads} = -29.376 kJ mol^{-1} found by the Van't Hoff equation, may be also evaluated by the Gibbs–Helmholtz equation, which is defined as follows :

$$\left[\frac{\partial(\Delta G^{\circ}_{ads}/T)}{\partial T}\right]_P = -\frac{\Delta H^{\circ}_{ads}}{T^2} \quad (8)$$

Which can be arranged to give the following equation:

$$\frac{\Delta G^{\circ}_{ads}}{T} = \frac{\Delta H^{\circ}_{ads}}{T} + A \quad (9)$$

The standard adsorption entropy ΔS°_{ads} may be deduced using the thermodynamic basic equation:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad (10)$$

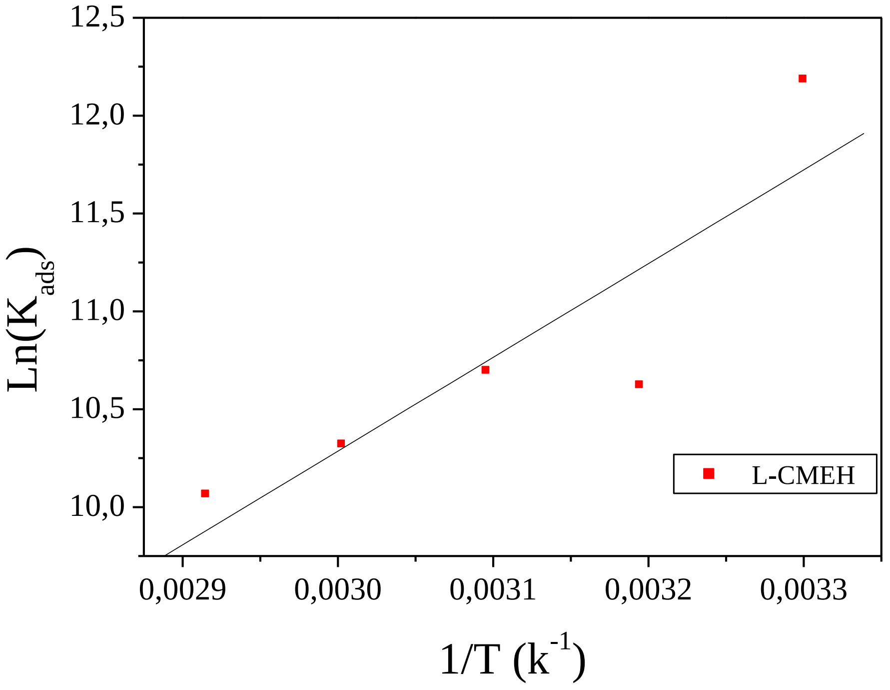

Figure 10. The relationship between Ln(K_{ads}) and 1/T for L-CMEH

The variation of ΔG°_{ads}/T with 1/T gives a straight line with a slope that equals ΔH°_{ads} = -29.381 kJ.mol^{-1} (Fig. 11). It can be seen from the figure that ΔG°_{ads}/T decreases with 1/T.

The value of the enthalpy of adsorption found by the two methods such as Van't Hoff and Gibbs–Helmholtz relations are in good agreement [35-37].

Table 3. Thermodynamic parameters of adsorption of L-CMEH on the copper surface at different temperatures.

T (K)	Linear regression coefficient (r)	K (L/mol)	ΔG°_{ads} (kJ/mol)	ΔH°_{ads} (kJ/mol)	ΔS°_{ads} (J/mol.K)
303	0.99994	108615.14	-39.329	-29.376	32.85
313	0.99970	40894.28	-38.087		27.83
323	0.99990	44083.74	-39.505		31.36
333	0.99964	30235.05	-39.684		30.95
343	0.99959	23418.93	-40.145		31.40

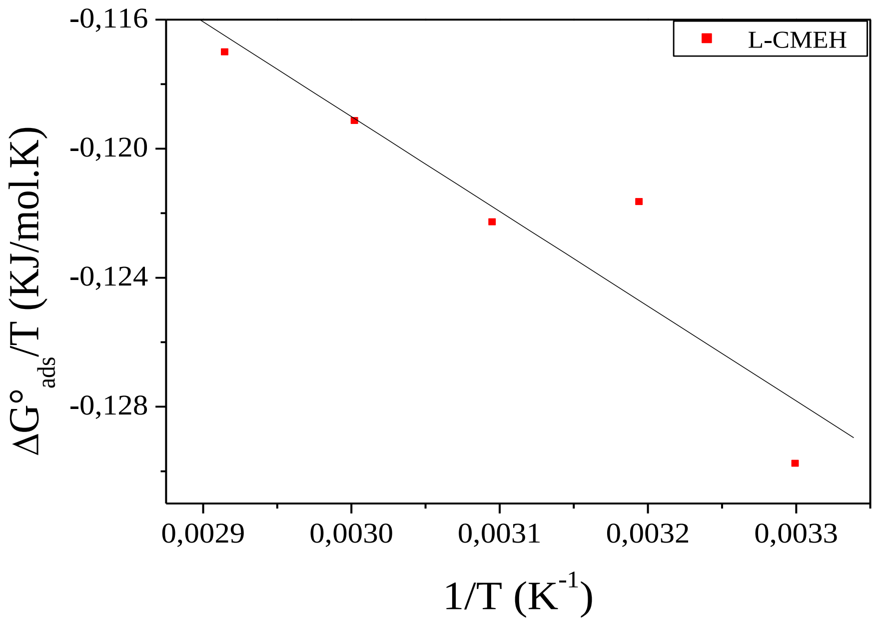

Figure 11. Relationship between ΔG°_{ads}/T and the reverse of absolute temperature

4. CONCLUSION

The following conclusions may be drawn from the study:

- Results obtained qualified that cysteine tested is an efficient inhibitor.
- Increase of temperature leads in a decrease of efficiency and an increase of the activation corrosion energy.
- The adsorption of L-CMEH on the copper surface from 2M HNO_3 obeys a Langmuir adsorption isotherm. The adsorption process is a spontaneous and exothermic process.
- Kinetic and adsorption parameters were evaluated and discussed.

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References

1. I.N. Putilova, S. A. Balezin, V. P. Barannik, Metallic Corrosion Inhibitors; Pergamon Press Ltd.: Oxford, 1960.
2. V. H. Veley, In Comprehensive Treatise on Inorganic and Theoretical Chemistry; Mellor, J. W., Ed.; Longmans, Green and Co. Ltd.: London, 1952.
3. N. C. Subramanyan, B. S. Sheshadria, S. M. Mayanna, *Br. Corros. J.* 19 (1984) 177.
4. M. F. Ahmed, S. M. Mayanna, F. Pushpanaden, *J. Electrochem. Soc.* 124 (1977) 1667.

5. H. B. Rudresh, S. M. Mayanna, *Br. Corros. J*. 12 (1977) 54.
6. S. Siddagangappa, S. M. Mayanna, F. Pushpanaden, *Anti Corros. Methods Mater*. 23 (1976) 11.
7. A.S. Fouda, A. K. Mohamed, *Werkst. Korros*. 39 (1988) 23.
8. S. M. Abdel Maksoud, A. A. El-Shafie, H. A. Mostafa, A. S. Fouda, *Material and Corrosion*. 46 (1995) 468.
9. A.S. Fouda, A. K. Mohamed, *J. Electrochem. Soc. Ind*. 39 (1990) 246.
10. A.S. Fouda, H. A. Wahed, *Arab. J. Chem*. (2011) Article In Press.
11. K. F. Khaled , Mohammed A. Amin, *Corros. Sci*. 51 (2009) 2098.
12. A.Zarrouk, A. Dafali, B. Hammouti, H. Zarrok, S. Boukhris, M. Zertoubi, *Int. J. Electrochem. Sci*. 5 (2010) 46 .
13. A.Zarrouk, T. Chelfi, A. Dafali, B. Hammouti, S.S. Al-Deyab, I. Warad, N. Benchat, M. Zertoubi, *Int. J. Electrochem. Sci*. 5 (2010) 696.
14. A.Zarrouk, B. Hammouti, A. Dafali, H. Zarrok, *Der Pharma Chemica*. 3 (2011) 266.
15. A.A. El-Hosary, R. M. Saleh, A. M. Shams El Din, Corros. Sci. 12 (1972) 897.
16. S. Al-Luaibi Salah, S. Azad, H. Taobi Abdel-Amir, *J. Mater. Environ. Sci.* 2 (2011) 148.
17. T. P. Zhao, G. N. Mu, *Corros. Sci*. 41 (1999)1937.
18. B. A. Abd-El-Nabey, E. Khamis, M. Sh. Ramadan, A. El-Gindy, *Corrosion*. 52 (1996) 671.
19. O. Benali, L. Larabi, S. Merah, Y., Harek, *J. Mater. Environ. Sci.* 2 (2011) 39.
20. Q. H. Cai, Y. K. Shan, B. Lu, X. H. Yuan, *Corrosion*. 49 (1993) 486.
21. J. O. M. Bockris, A. K. N. Reddy, Modern Electrochem. Plenum Press, New York, 2 (1977) 1267.
22. M. Stern, A. L. Geary, *J. Electrochem. Soc*. 104 (1957) 56.
23. L. L. Shereir, Corrosion, vol. 2, 2nd edition, Newnes-Butterworths, London, 1977.
24. L. B. Tang, G. N. Mu, G. H. Liu, *Corros. Sci*. 45 (2003) 2251.
25. G. N. Mu, X. M. Li, F. Li, *Mater. Chem. Phys*. 86 (2004) 59.
26. E. Khamis, *Corrosion*. 46 (1990) 476.
27. M. Elachouri, M. S. Hajji, M. Salem, S. Kertit, J. Aride, R. Coudert, E. Essassi, *Corrosion*. 52 (1996) 103.
28. B.V. Savitri, S. Mayanna, *Ind. J. Chem. Technol*. 3 (1996) 256.
29. F. M. Donahue, K. Nobe, *J. Electrochem. Soc*. 112 (1965) 886.
30. E. Khamis, F. Bellucci, R. M. Latanision, E. S. H. El-Ashry, *Corrosion*. 47 (1991) 677.
31. G. Moretti, F. Guidi, G. Grion, *Corros. Sci*. 46 (2004) 387.
32. G. K. Gomma, M. H. Wahdan, *Mater. Chem. Phys*. 39 (1995) 211.
33. W. Durnie, R. De Marco, B. Kinsella, A. Jefferson, *J. Electrochem. Soc*. 146 (1999) 1751.
34. S. Martinez, I. Stern, *Appl. Surf. Sci*. 199 (2002) 83.
35. M. Dahmani, A. Et-Touhami, S.S. Al-Deyab , B. Hammouti, A. Bouyanzer, *Int. J. Electrochem. Sci.*, 5 (2010) 1060.
36. A. Zarrouk, B. Hammouti, R. Touzani, S.S. Al-Deyab, M. Zertoubi, A. Dafali, S. Elkadiri, Int. *J. Electrochem. Sci.*, 6 (2011) 939.
37. M. Bouklah, N. Benchat, A. Aouniti, B. Hammouti, M. Benkaddour, M. Lagrenée, H. Vezin, F. Bentiss, *Prop. Org. Coat.* 51 (2004) 118