Carboxymethyl Cellulose as Corrosion Inhibitor of Iron in Presence of Magnetic Field; Kinetic Investigation

Mohammad M. Fares [1],*, A. K. Maayta [1], Ali F. Al-shawabkeh [2]

[1]*Department of Applied Chemistry, Jordan University of Science & Technology, P.O. Box 3030, 22110, Irbid, Jordan*

[2] *Department of Chemistry, Faculty of Engineering Technology, Al-Balqa Applied University, Amman, Jordan*

*Correspondence: fares@just.edu.jo

_____

Abstract

The effect of Carboxymethyl cellulose natural polymer, CMC, as corrosion inhibitor on the surface of iron metal in acidic media and in the presence of magnetic field had been studied. Kinetic and thermodynamic parameters determined using *Arrhenius* and *Eyring* equations revealed several insight views. Dominant inhibitory role of CMC in corrosion resistance in 0–20 °C range were observed, whereas detachable CMC-Fe layers and adsorption weakening on the surface of the metal in 30–50 °C range were investigated.

The role of magnetic field was abstracted in topology enhancement, alignment of CMC polymeric chains on the surface of Iron metal and hence better oriented adsorption layers. In addition, larger spontaneouty and adsorption equilibrium constant at 0 °C and in the presence of magnetic field were determined. Adsorption of CMC polymeric chains on Iron surface exhibit Langmuir adsorption isotherms fit.

_____

Keywords: Carboxymethyl cellulose polymer, corrosion, kinetic and thermodynamic parameters, magnetic field

INTRODUCTION

The use of polymers in corrosion resistance processes have been well documented in the literature. The formation of self-assembled monolayers (SAM) [1-3], conducting polymer or self doped conducting polymer layers [4-8], the use of carbon nanotube [9,10], composite coatings [11], plasma polymer coatings [12], and use of polymers as surface-active agents that have high chelating ability with metals [13,14] were all intended to isolate iron metal surface from corrosive agents and prevent electrochemical corrosion. Polymers, as carbon fiber, have been extended to be used for corrosion prevention in concrete through composite wrap formations [15].

The presence of organic molecules containing functional electronegative groups, such as sulfur, phosphorus, nitrogen and oxygen together with π-electron in conjugated double bonds has drastic effect on corrosion efficiency. These polar and nonpolar plays as reaction centre for adsorption processes and hence exhibit strong affinity for metal surfaces [16–21]. The efficiency of these inhibitors mainly depends on their ability to be adsorbed on the metal surface that results with replacement of water molecules as follows;

$$Inhib._{(sol.)} + H_2O_{(ads.)} \longrightarrow Inhib._{(ads.)} + H_2O_{(sol.)}$$
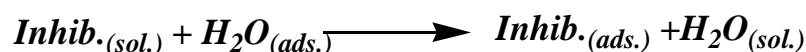
The use of magnetic field for promoting the inhibition processes could further provide better properties and characteristics including micro-roughness, hydrophilicity and micro-topography enhancement through minimizing the actual surface area in micro- and nano-scales exposed to corrosive agents [22].

In this study, the use of cellulose modified natural polymers (*i.e.* CMC), scheme 1, as corrosion inhibitors have been investigated in the absence and presence of magnetic field in acidic media. Kinetic and thermodynamic parameters were verified to interpret and elucidate the output data. Weight loss measurement and hydrogen evolution method techniques were used in 1.0 to 3.0 M HCl concentration range.
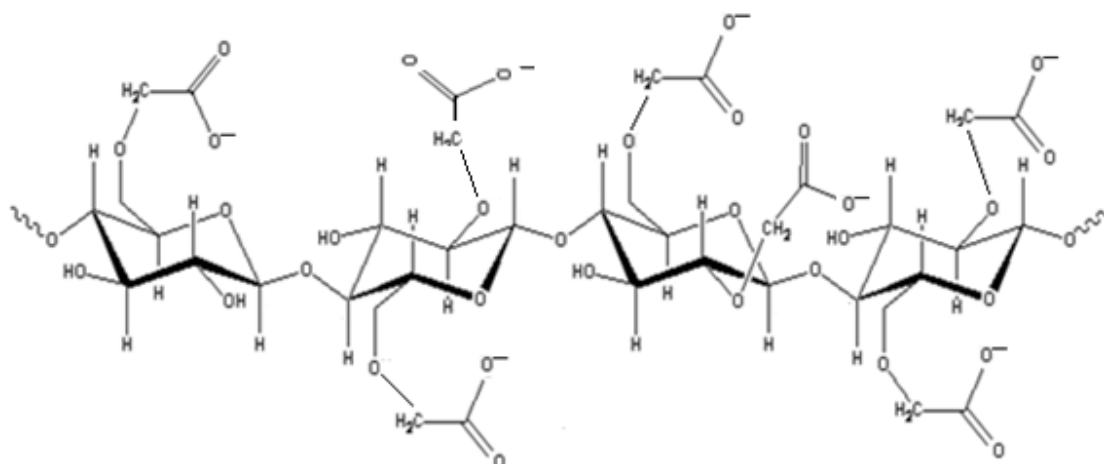
Scheme 1. Chemical structure of Carboxymethyl cellulose (CMC) natural polymer based on β-(1⟶4)-D-glucopyranose repeating units.

EXPERIMENTAL

Materials

Mild iron sheets with 30x10x0. 5 mm dimensions were degreased with acetone, polished, dried, and weighed until used. CMC inhibitor (molar mass = 400,000 g/mol), supplied by BDH-lab supplies, GPR[TM], was diluted to the appropriate concentrations using triple distilled water. Magnetic field was supplied by two magnet plates with 7.0x7.0x1.9 cm dimensions. The strength of magnetic field was measured to be 100 mT using Holl-Probe, Leybold-Hereaus instrument.

Weight loss measurements

Mild Iron sheets were immersed in 10 ml of 1.0 M HCl that contains different concentrations of CMC inhibitor (*i.e.* 0, 200, 600, and 1000 ppm) solutions, once at a time, for 1.0 hour at 25 °C. The process was repeated using 2.0 M, and 3.0 M, HCl solutions at the same temperature. In addition, the same process were repeated at different temperatures (*i.e.* 0, 10, 20, 30, 40, and 50 °C) using fixed HCl and CMC concentrations in absence of magnetic field. For magnetic field measurements, the samples were placed between two magnets that supply 100 mT magnetic strength. The inhibition efficiency (*%IE*) was calculated as follows;

$$\%IE = \frac{W_0 - W_i}{W_0} x100 \qquad (1)$$

where w_0 and w_i are corrosion weight losses of iron in un-inhibited and inhibited solutions, respectively. The rate of corrosion (R_c) of iron was calculated (in mg/cm^2.sec) using the relation:

$$R_c = \frac{W}{St} \qquad (2)$$

where W is weight loss, S is area of Iron sheet and t is the exposure time of specimens. All weight measurements were performed using semi-micron balance (Saratorius 2024 MPb) with precision of $\pm 0.01\ mg$ and doublicated replications.

Hydrogen evolution method

The Iron sheets were placed in specific concentration of CMC and HCl solution in 10 ml test tube, sealed and connected to a thin PVC tube to enable hydrogen gas collection over water by graduated cylinder according to:

$$Fe_{(s)} + 3HCl_{(aq)} \rightarrow FeCl_{3(aq)} + 3/2H_{2(g)}$$
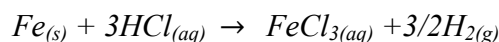
Adsorption isotherms

The degree of surface coverage of inhibitor on iron sheet surface, θ-value, was calculated using the relation:

$$\theta = \frac{W_0 - W_i}{W_0} \qquad (3)$$

Different adsorption isotherms were tested to show the best regression coefficients, R^2, (*i.e.* very close to 1.0) such as Tempkin [23], Langmuir [24], and Frumkin [25] using the following formulae (equations 4-6 respectively);

$$\theta = \left(\frac{1}{f}\right) \ln\left(K[CMC]\right) \qquad (4)$$

$$log\left(\frac{\theta}{1-\theta}\right) = logK + log[CMC] \qquad (5)$$

$$log\left(\frac{\theta}{(1-\theta)[CMC]}\right) = logK + g\theta \qquad (6)$$

Where θ is the degree of surface coverage of inhibitor on iron sheet surface, and K is equilibrium constant of the adsorption process, g is adsorbate interaction parameter, and f is heterogeneous factor of metal surface.

RESULTS & DISCUSSIONS

Weight loss measurements

In Absence of magnetic field

Weight loss, evolved volume of H_2 gas, and inhibition efficiency(*%IE*) were plotted versus caboxylmethyl cellulose (CMC) concnetration in Figures 1a, 1b and 1c respectively. The linear decrease of weight loss and evolved volume of H_2 gas as CMC concentration increases confirms the role of CMC polymeric chains reforming shielding layers, via chemisorption, that separates metal from corrosive environment . The linear increase of Inhibition efficiency (Figure 1c) at elevated CMC concentration confirms the inhibitory effect of CMC polymeric chains to re-orient itself and be adsorbed on the surface of the metal through the formation of electrostaic interactions of negatively charged carboxylate groups (COO⁻) with Fe^{+2} and Fe^{+3} and/or formation of coordinative bond via iron which may act as Lewis acid, with oxygen atoms in carboxylate group that contain two lone-pairs and might act as Lewis base.
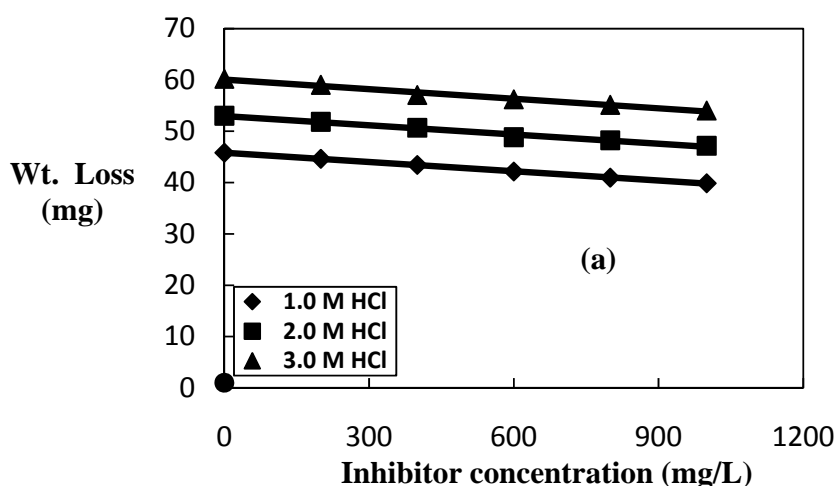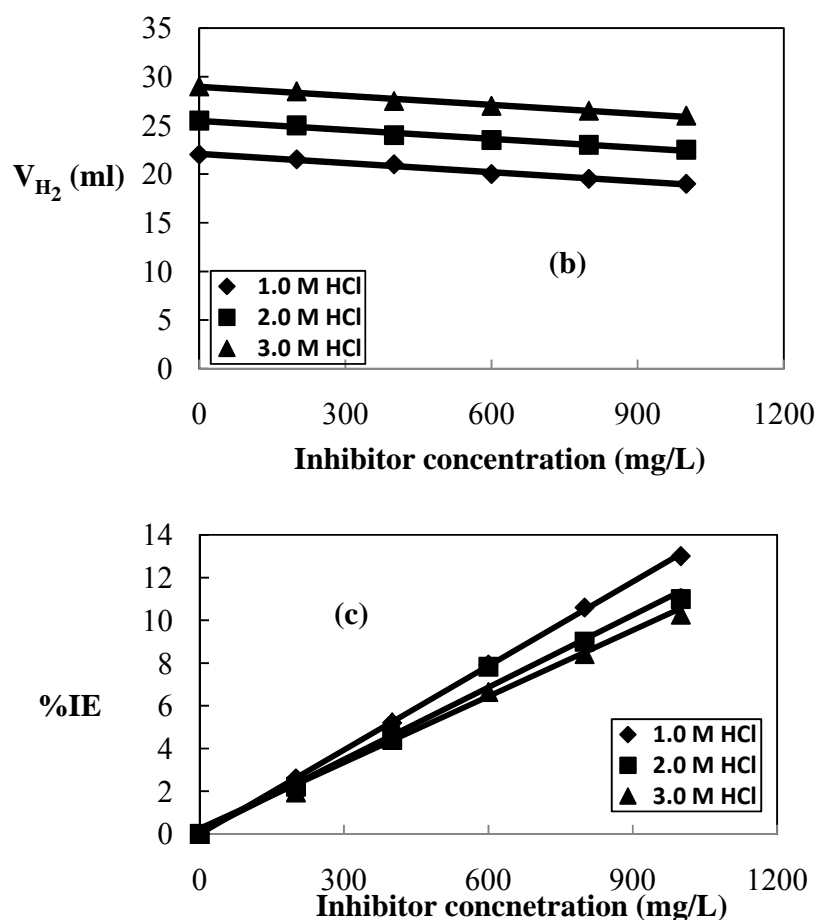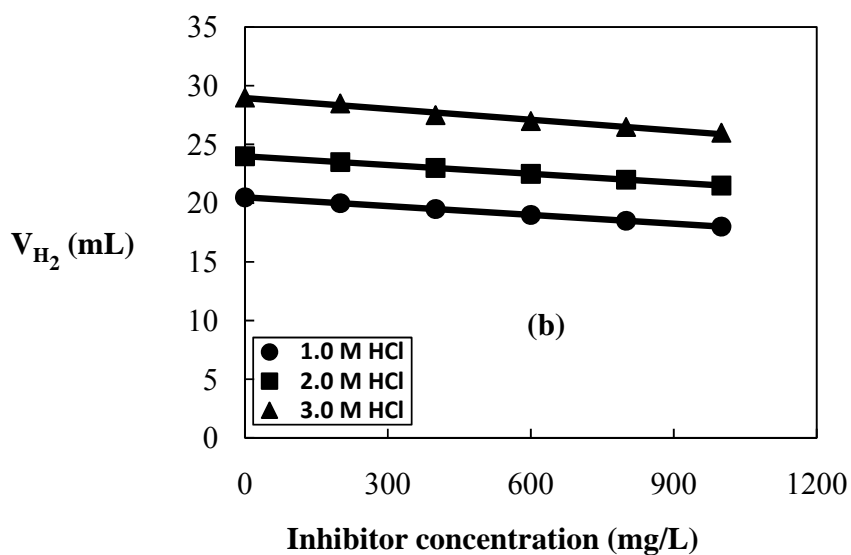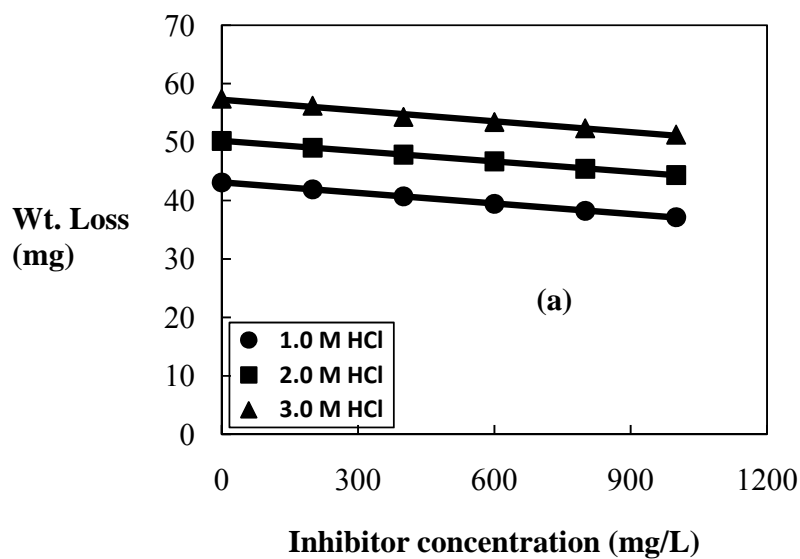
Figure 1.   Weight loss (a), Volume of H_2 gas (b) and Inhibition efficiency (%IE) (c) versus CMC inhibitor concentration in absence of magnetic field for 1.0 hour exposure at room temperature.

In Presence of magnetic field

The use of magnetic field was found to change the inhibition efficiency with almost 50% increase. It also helps in topology enhancement through minimizing the actual surface area in micro- and nano-scales exposed to corrosive agents [22], which would lead to formation of well-oriented and well-accumulated polymeric chains across the surface, and eventually would lead to better shielding, least entropy and better inhibition process.
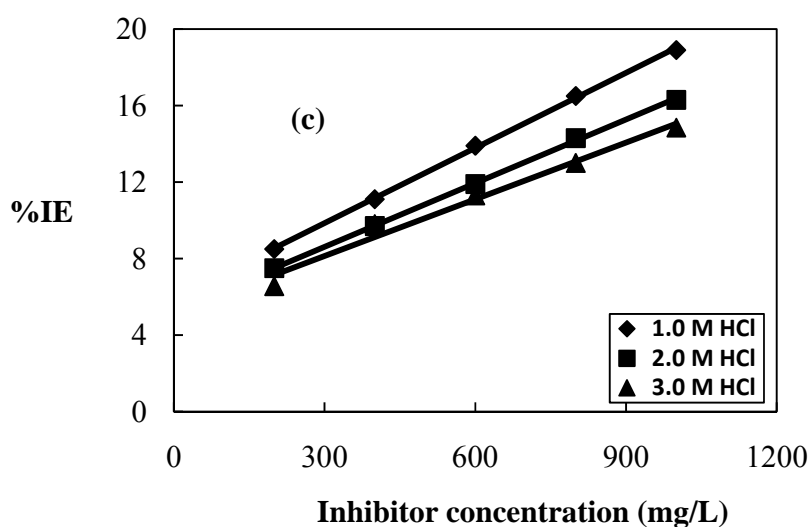
Figure 2.   Weight loss (a), Volume of H_2 gas (b) and Inhibition efficiency (%IE) (c) versus CMC inhibitor concentration in presence of magnetic field for 1.0 hour exposure at room temperature.

Corrosion Kinetic Investigation

The determination of activation energies in the absence and presence of inhibitor and magnetic field, through *Arrhenius* plot, could give deeper insight and elucidation for corrosion inhibition processes [26, 27]. If rate of corrosion (R_C), determined using equation (2), increases with temperature increase, then the determined activation energy is said to be *Arrhenius* activation energy *(i.e. E_a (A))*, whereas if rate of corrosion (R_C) decreases with temperature increase, then the determined activation energy is said to be *non-Arrhenius* activation energy *(i.e. E_a (non-A))*.

In addition, the successful implementation of *Eyring* equation could give rise valuable information about thermodynamic parameters such as is the enthalpy of activation ($\Delta H^{\neq}$) and the entropy of activation ($\Delta S^{\neq}$) through the following equation;

$$\frac{R_C}{T} = \frac{k_B}{h} \; exp\left(\frac{\Delta S^{\neq}}{R}\right) \; exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{7}$$

where k_B is Boltzmann constant, h is the Planck constant, $\Delta H^{\neq}$ is the enthalpy of activation and $\Delta S^{\neq}$ is the entropy of activation. As a result, a plot of $ln\left(\frac{R_C}{T}\right)$ versus $1/T$ would determine $\Delta H^{\neq}$ and $\Delta S^{\neq}$ from the slope and intercept respectively [28, 29].

In Absence of Magnetic Field

Kinetic and thermodynamic parameters determined using *Arrhenius* and *Eyring* equations in the absence of magnetic field are summarized in Table 1. Two distinct zones could be seen namely, *Non-Arrhenius* behavior in the 0–20 °C temperature range and *Arrhenius* behavior in the 30–50 °C temperature range. In the *Non-Arrhenius* zone, it could be seen that as the concentration of inhibitor increases the activation energy were increased larger than activation energy at [CMC] = 0.0 mg/L, which confirm the dominant inhibitory role of CMC in corrosion resistance. Furthermore, at larger inhibitor concentration, smaller entropy of activation ($\Delta S^{\neq}$) values were obtained. The decrease in entropy of activation values accompanied with desorption of water molecules and adsorption of CMC polymeric chains on the surface of the metal confirms the adsorption process of the large macromolecules of CMC on the surface of the metal as follows,
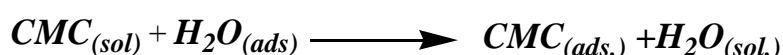
$$CMC_{(sol)} + H_2O_{(ads)} \longrightarrow CMC_{(ads.)} + H_2O_{(sol.)}$$

Table 1. Kinetic and thermodynamic parameters of corrosion process in 1.0 M HCl solution and in the absence of magnetic field.

[CMC] (mg/L)	T (°C)	R_C (mg/cm^2.sec.)	E_a(non-A) (kJ/mol)	E_a(A) (kJ/mol)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/mol.K)
0.0	0	2.5×10^{-3}	6.8		9.8	−329.6
	10	2.3×10^{-3}				
	20	2.0×10^{-3}				
	30	2.8×10^{-4}		80.1	77.4	−174.0
	40	8.1×10^{-4}				
	50	2.0×10^{-3}				
200	0	2.6×10^{-3}	9.7		12.9	−340.4
	10	2.5×10^{-3}				
	20	1.9×10^{-3}				
	30	1.6×10^{-4}		78.7	75.8	−174.7
	40	4.5×10^{-4}				
	50	1.1×10^{-3}				
600	0	2.7×10^{-3}	13.2		15.8	−350.7
	10	2.6×10^{-3}				
	20	1.8×10^{-3}				
	30	1.6×10^{-4}		75.0	72.1	−175.5
	40	4.3×10^{-4}				
	50	1.0×10^{-3}				
1000	0	2.9×10^{-3}	16.9		19.9	−365.1
	10	2.7×10^{-3}				
	20	1.7×10^{-3}				
	30	1.5×10^{-4}		76.7	74.6	−174.9
	40	5.0×10^{-4}				

50	9.8×10^{-4}

On the other hand, in the *Arrhenius* zone (*i.e.* 30–50 °C temperature range) the increase in CMC concentration result with activation energy lowering below activation energy value at [CMC] = 0.0 mg/L. This lowering, which confirms the catalytic action of CMC macromolecules on iron surface, could be attributed to higher kinetic energy of CMC molecules and or partial hydrolysis CMC polymer chains [30], that were capable to detach CMC-Fe molecules away from Iron surface and hence expose lower layers of Fe to HCl solution, which might exhibit more weight loss and corrosion. This could be further confirmed through the large increase of entropy of activation in 30–50 °C range than that in 0–20 °C range. Furthermore, the unchanged value of entropy of activation in 30–50 °C range, regardless to CMC concentration, confirms the detachment of CMC-Fe layers and weakens the adsorption of CMC on the surface of the metal (Scheme 2).

Low temperature   *High temperature*
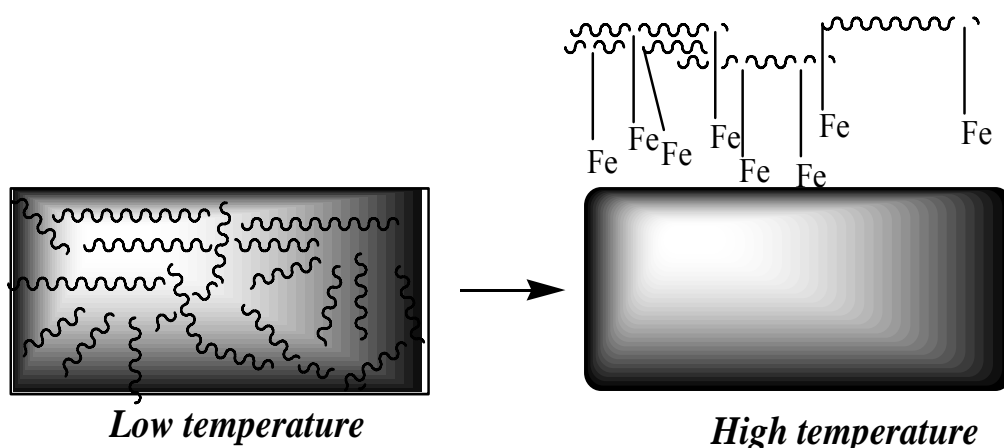
Scheme 2: CMC polymeric Chains, as inhibitor, show adsorbed layer at lower temperature and detached CMC-Fe^{+2} layers at higher temperatures.

Enthalpy of activation values were in accordance with activation energy values. Thus, not too much conclusive remarks could be deduced from its change throughout Tables 1 and 2.

In Presence of Magnetic Field

Kinetic and thermodynamic parameters determined in the presence of magnetic field were illustrated in Table 2. It could be seen that larger activation energies and lower corrosion rates were determined in presence of magnetic field, which was mainly due to the role of magnetic field in topology enhancement of the surface of Iron metal [22] and consequent alignment and accumulation of CMC polymeric chains near and above each other on the metal surface, which would lead to better shielding, least entropy and better inhibition process.

Table 2. Kinetic and thermodynamic parameters of corrosion in HCl solution in the presence of magnetic field.

[CMC] (mg/L)	T (°C)	R_C (mg/cm^2.sec.)	E_a (kJ/mol)	$\Delta H^{\neq *}$ (kJ/mol)	$\Delta S^{\neq}$ (J/mol.K)
0.0	20	1.9×10^{-3}	7.0	4.6	−281.2
200	20	1.8×10^{-3}	9.8	7.4	−272.1
600	20	1.7×10^{-3}	13.3	10.9	−260.6
1000	20	1.6×10^{-3}	17.2	14.8	−247.8

*Calculated based on the assumption of unimolecular reaction where $E_a = \Delta H^{\neq} + RT$ [24].

Furthermore, solvent entropy of activation (*i.e.* $\Delta S^{\neq}$) in presence of magnetic field was larger than in the absence of magnetic field (*i.e.* $\Delta S^{\neq}_{present\ MF} > \Delta S^{\neq}_{absent\ MF}$). This necessarily imposes larger entropy decrease in the system (Iron sheet with inhibitor), according to second law of thermodynamics, which confirms that there had been more alignment, more orientation of CMC polymeric chains on the surface of the metal and hence better aligned adsorption layers.

Adsorption Isotherms

The most fitting isotherm with 0.99 regression coefficients, R^2, was Langmuir adsorption isotherms as Figure 3 suggested. Adsorption equilibrium constant (K) determined using equation (7), could be further used to determine free energy of adsorption as follows;

$$-\frac{\Delta G_{ads.}}{RT} = \ln(55.5\ K) \tag{8}$$

where 55.5 is the molar concentration of water, R is the universal gas constant and T is the thermodynamic temperature.
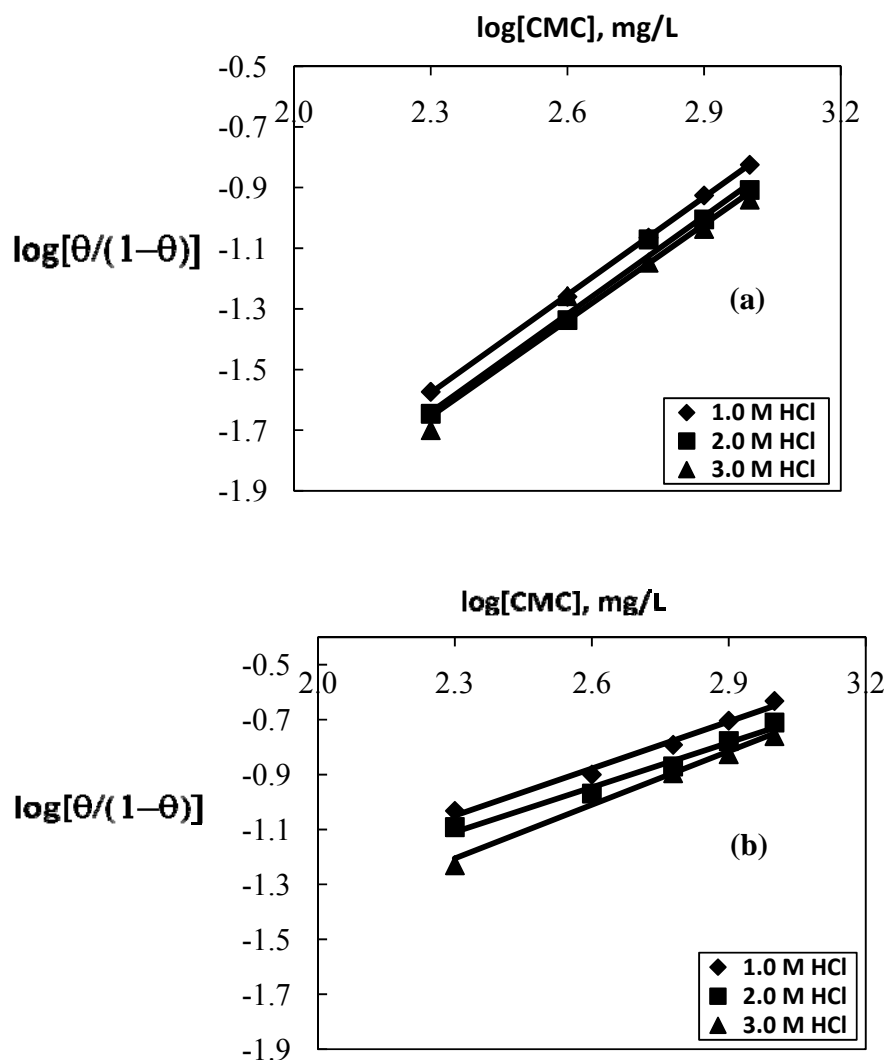

Figure 3. Langmuir adsorption isotherms, (a) in the absence of magnetic field, (b) in the presence of magnetic field.

The equilibrium constant and free energy of adsorption values in presence and absence of magnetic field are summarized in Table 3.

Table 3. Equilibrium constant and free energy of adsorption values in HCl solutions, in presence and absence of magnetic field

T ($°C$)	K (L/g)	$\Delta G_{ads.}$ (kJ/mol)	Magnetic field
20	4.36	−13.4	Present
0	1.25	−9.63	Absent
10	1.07	−9.61	Absent
20	0.94	−9.64	Absent
30	0.82	−9.62	Absent
40	0.62	−9.21	Absent
50	0.52	−9.03	Absent

In the absence of magnetic field it could be seen that adsorption equilibrium constant (*i.e.* K) and spontaneouty (*i.e.* $\Delta G_{ads.}$) decrease with temperature increase. The elevated temperature had an adverse effect on adsorption process, where electrostatic interactions, and coordinative interactions, were weaken, loosen and encourage the possibility of detachment of CMC macromolecules with Fe and Fe^{+2} atoms. On the other hand, presence of magnetic field led to larger equilibrium constant value and larger adsorption spontaneouty, which could be explained by the role of magnetic field to align adsorbed and accumulated molecules on the surface of metal, decreases free volume of metal exposed to HCl solution, and finally form consistent shielding layers that resist corrosion.

CONCLUSIONS

The inhibitory effect of Carboxymethyl cellulose natural polymer, CMC, on the surface of iron metal in acidic media and in the presence of magnetic field was investigated. The inhibitory effect was dominant in 0–20 °C range, whereas detachable CMC-Fe layers and adsorption weakening on the surface of the metal in 30–50 °C range have been investigated. Magnetic field were found to induce CMC polymeric chains alignment and topology enhancement, and hence better oriented adsorption layers were formed. Adsorption of CMC polymeric chains on Iron surface exhibited Langmuir adsorption isotherms match. Optimum adsorption properties to exhibit largest spontaneouty and equilibrium constant values were at 0 °C and in the presence of magnetic field.

ACKNOWLEDGMENT

REFERENCES

1. K. Aramaki, T. Shimura, *Corrosion Science* **51** (2009) 1887–1893
2. K. Aramaki, T. Shimura, *Corrosion Science* **52** (2010) 1–6
3. K. Aramaki, T. Shimura, *Corrosion Science* **50** (2008) 596–604
4. P. Oco´n, A.B. Cristobal, P. Herrasti, E. Fatas, *Corrosion Science* **47** (2005) 649–662
5. D.P. Le, Y.H. Yoo, J.G. Kim, S.M. Cho, Y.K. Son, *Corrosion Science* **51** (2009) 330–338
6. S. Kumar Shukla, M.A. Quraishi, R. Prakash, *Corrosion Science* **50** (2008) 2867–2872
7. R. Hasanov, S. Bilgic, *Progress in Organic Coatings* **64** (2009) 435–445
8. S. Y. Huang, P. Ganesan, B. N. Popov, *Applied Catalysis B: Environmental* **93** (2009) 75–81
9. Y. B. Lee, C. H. Lee, D. S. Lim, *International Journal of Hydrogen Energy* **34** (2009) 9781 – 9787
10. Y. J. Ko, H. S. Oh, H. Kim, *Journal of Power Sources* **195** (2010) 2623–2627
11. M. Rohwerder, Le Minh Duc, A. Michalik, *Electrochimica Acta* **54** (2009) 6075–6081
12. T. Titz, F. Hrzenberger, K. Van den Bergh, G. Grundmeier, *Corrosion Science* **52** (2010) 378–386
13. G. Achary, Y. Arthoba Naik, S. Vijay Kumar, T.V. Venkatesha, B.S. Sherigara, *Applied Surface Science* **254** (2008) 5569–5573
14. R. Uffana, S.M. Ashraf, S. Ahmad, *Progress in Organic Coatings* **59** (2007) 138–145.
15. L. K. Spainhour, I. A. Wootton, *Cement & Concrete Composites* **30** (2008) 535–543
16. H. Ju, Z.P. Kai, Y. Li, *Corrosion Science* **50** (2008) 865–871
17. G. Schmitt, *Br. Corrosion Science* **19** (1984) 165.
18. J.M. Sykes, *Br. Corrosion Science* **25** (1990) 175.
19. S. Kertit, J. Aride, A. Ben-Bachir, A. Sghri, A. Elkoly and M. Etman, *J. Appl. Electrochem.* **19** (1989) 83.
20. S.S. Abd El-Rehim, M. A. M. Ibrahim and K.F. Khaled, *J. Appl. Electrochem.* **29** (1999) 593
21. P.R. Roberge, Corrosion inhibitors, in: *Handbook of Corrosion Engineering*, McGraw-Hill, New York, 1999, pp. 833–862.
22. T. Hryniewicz, K. Rokosz, R. Rokicki, *Corrosion Science* **50** (2008) 2676–2681
23. M. I. Tempkin, *Zh. Fiz. Khim.* **15** (1941) 296
24. L. Langmuir, *J. Am. Chem. Soc.* **38** (1916) 2221
25. A. N. Frumkin, *Z Phys. Chem.*, **116** (1925) 466.
26. M.A.B. Christopher, A.R.G. Isabel, P.S.M. Jenny, *Corrosion Science* **36** (1994) 915.
27. M. Bouklah, B. Hammouti, M. Lagrenee, F. Bentiss, *Corrosion Science* **48** (2006) 2831.

28. I. Ahmad, M.A. Quraishi, *Corrosion Science* **51** (2009) 2006–2013

29. K. J. Laidler, J. H. Meiser, Physical Chemistry, 3ʳᵈ ed., Houghton-Mifflin, 1999, p.397-398.

30. V. D. Athawale and V. Lele, *Carbohydrate Polymers*, **35**, 21 (1998).