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# Adsorption Behavior and Inhibition Corrosion Effect of Sodium Carboxymethyl Cellulose on Mild Steel in Acidic Medium

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**Abstract:** The effect of sodium carboxymethyl cellulose (Na-CMC) on the corrosion behavior of mild steel in 1.0 mol  $\cdot$  L<sup>-1</sup> HCl solution has been investigated by using weight loss (WL) measurement, potentiodynamic polarization, linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS) methods. These results showed that the inhibition efficiency of Na-CMC increased with increasing the inhibitor concentration. Potentiodynamic polarization studies revealed that the Na-CMC was a mixed type inhibitor in 1.0 mol  $\cdot$  L<sup>-1</sup> HCl. The adsorption of the inhibitor on mild steel surface has been found to obey the Langmuir isotherm. The effect of temperature on the corrosion behavior of mild steel in 1.0 mol  $\cdot$  L<sup>-1</sup> HCl with addition of 0.04% of Na-CMC has been studied in the temperature range of 298–328 K. The associated apparent activation energy ( $E_a^*$ ) of corrosion reaction has been determined. Scanning electron microscopy (SEM) has been applied to investigate the surface morphology of mild steel in the absence and presence of the inhibitor molecules.

Key Words: Corrosion; Mild steel; Adsorption; Sodium carboxymethyl cellulose; Electrochemical impedance spectroscopy

Iron and its alloys find utility in a wide spread spectrum of many industrial units because of its low-cost and excellent mechanical properties. For this reason, the corrosion behavior of these materials has attracted the attention of several investigations. Steel is the most corrosion vulnerable metal. Thus, much attention is given for its protection from the hostile environments. Acid solutions are widely used in industry. The most important areas of application are acid pickling, industrial acid cleaning, acid descaling, and oil-well acidizing<sup>[1-6]</sup>. Polymers are used as corrosion inhibitors, when they are used in some particular functional groups. They can often form complexes with metal ions. These complexes occupy a large surface area on the metal surface, thereby blocking the surface and protecting the metal from corrosive agents present in the solution<sup>[7-11]</sup>. Furthermore, some low-cost polymeric compounds are good corrosion inhibitors for metallic materials in an acidic medium<sup>[12]</sup>.

Sodium carboxymethyl cellulose (Na-CMC) is an anionic water-soluble polymer derived from cellulose. Due to its innocuousness, it is used as a stabilizer, binder, thickener, for suspension and as water retaining agent in food industry, pharmaceuti cal, cosmetic, paper, and other industrial areas<sup>[13–15]</sup>. However, most of the corrosion inhibitors used in aqueous heating and cooling systems are hazardous for health. Their toxic properties limit their application areas<sup>[16]</sup>. The study of Na-CMC as acid inhibitor is particularly important because of its cheapness, water solubility, nontoxicity, and as an environmentally acceptable polymer.

In this study, mild steel corrosion with various concentrations of Na-CMC in 1.0 mol·L<sup>-1</sup> HCl using weight loss test and electrochemical techniques such as potentiodynamic, linear polarization resistance (LPR), and impedance measurements have been investigated. Temperature effect on the dissolution of mild steel in 1.0 mol·L<sup>-1</sup> HCl containing 0.04% Na-CMC was also studied and activation energy of the corrosion reaction was computed from  $i_{corr}$  values obtained from the Tafel extrapolation method.

### **1** Experimental

#### 1.1 Weight loss measurement

The mild steel coupons of 4.0 cm×2.0 cm×0.07 cm with an exposed total area of 16.84 cm<sup>2</sup> were cleaned using 20% NaOH solution containing 200 g·L<sup>-1</sup> of zinc dust for 12 h. They were washed with distilled water, dried in acetone, weighed, and stored in a moisture free desiccator prior to use<sup>[17]</sup>. The precleaned and weighed coupons were dipped in beakers containing 1.0 mol·L<sup>-1</sup> HCl solution and different mass fractions of Na-CMC containing 0, 0.001%, 0.005%, 0.01%, 0.02%, 0.03%, and 0.04%, respectively (for 250 mL solution consist of 1.0 mol·L<sup>-1</sup> HCl and Na-CMC), for the gravimetric experiments in which

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immersion time for weight loss was 24 h at 298 K. All tests were performed in aerated solutions and were run in triplicate. At the end of the test, the specimens were carefully washed with distilled water, dried, and weighed. The weight loss was calculated from the difference between before and end of the experiment. This allowed calculation of the mean corrosion rate expressed in  $mg \cdot cm^{-2} \cdot h^{-1}$ .

#### 1.2 Electrochemical measurement

Mild steel with mass fraction of 0.097% C, 0.00321% Pb, 0.488% Cu, 0.117% Cr, 0.032% P, 0.099% Si, 0.012% V, 0.004% Nb, 0.054% Mo, 0.07% S, 0.018% Sn, 0.01% W, 0.0042% Co, 0.137% Ni, and 0.459% Mn and the remaining iron was used for the electrochemical measurements. The specimens were embedded in polyester; 0.5 cm<sup>2</sup> surface area was in contact with the corrosive media and the electrical conductivity was provided by a copper wire. Prior to each experiment, the mild steel surfaces were mechanically polished with different grades of emery paper (150, 600, and 1200), degreased with acetone, rinsed with distilled water, and placed in the cell. All the reagents used were of analytical grade purchased from Sigma-Aldrich (Na-CMC, Cat No: 41931-1) and Merck (HCl). The molecular structure of Na-CMC is shown in Fig.1.

Electrochemical experiments were carried out in a conventional three-electrode cell. The working electrode with a shape of a disc was cut from the mild steel sheet. A platinum electrode and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. The temperature conditions were thermostatically controlled by using wear-jacketed cell. Electrochemical measurements were carried out using a CHI 660B electrochemical analyzer under computer control. The mild steel electrode was immersed in the solution for 30 min and then the free corrosion potential ( $E_{corr}$ ) was recorded. For each test, freshly prepared solutions were used.

Electrochemical impedance measurements were obtained at the corrosion potential when sinusoidal potential wave of 5 mV of amplitude was applied at frequencies ranging from  $10^5$  to  $10^{-2}$  Hz. The impedance diagrams are given in the Nyquist representation.

In the linear polarization resistance measurements, the mild steel was polarized to  $\pm 10$  mV of the corrosion potential at a scan rate of 0.1 mV  $\cdot$  s<sup>-1</sup>. The mild steel was polarized from the negative to the positive side of the corrosion potentials to a sin-



Fig.1 Molecular structure of Na-CMC

gle cycle at each measurement. The resulting current *versus* potential was plotted. Polarization resistance  $(R_p)$  values were obtained from the current potential plot.

Potentiodynamic polarization was carried out at -170 mV cathodic potential and at +170 mV anodic potential of the corrosion potential at 1 mV · s<sup>-1</sup> sweep rate in order to observe the corrosion inhibition effect of Na-CMC. The corrosion current densities ( $i_{corr}$ ) before and after adding the Na-CMC were determined using the Tafel extrapolation method.

## 1.3 Scanning electron microscopy

The micrographs of polished, corroded, and inhibited mild steel surfaces were taken using scanning electron microscope (SEM) (Leon 440). The energy of the acceleration beam employed was 20 kV. Thousand fold of magnification was applied for all micrographs.

## 2 Results and discussion

## 2.1 Gravimetric measurement

The effect of different concentrations of Na-CMC on the mild steel corrosion in 1.0 mol·L<sup>-1</sup> HCl was studied by weight loss at 298 K after 24 h of immersion period. The corrosion rate (w) of mild steel was determined by using the following relation:

$$W = \frac{\Delta m}{St}$$

where  $\Delta m$ , *S*, and *t* are mass loss, surface area of the electrode (here 16.84 cm<sup>2</sup>), and immersion period (here 24 h), respectively.

The inhibition efficiency (IE) of corrosion inhibitor is defined by the following expression:

$$IE = \left(\frac{W_0 - W}{W_0}\right) \times 100\%$$

where  $W_0$  and W are the corrosion rates in the absence and presence of inhibitor, respectively.

Table 1 includes the corrosion rate values of mild steel and inhibition efficiency of Na-CMC. According to Table 1, the distribution of corrosion rate varied from 0.319 to 0.088 mg  $\cdot$  cm<sup>-2</sup>  $\cdot$  h<sup>-1</sup> and the inhibition efficiency increased with increasing the inhibitor concentration. Inhibition efficiency reached a value of 72% at 0.04% Na-CMC. The electrochemical results partially showed similarity to the inhibition efficiency in the sense that they increased as inhibitor concentration increased.

#### 2.2 EIS and LPR

The corrosion behavior of mild steel in 1.0 mol·L<sup>-1</sup> HCl solu-

Table 1Inhibition efficiencies for various concentrationsof Na-CMC for the corrosion of the mild steel in 1.0 mol·L<sup>-1</sup>HCl obtained from weight loss measurement

w(Na-CMC)	$W/(\mathrm{mg}\cdot\mathrm{cm}^{-2}\cdot\mathrm{h}^{-1})$	IE(%)
0	0.319	-
0.001%	0.163	49
0.005%	0.153	52
0.01%	0.147	54
0.02%	0.137	57
0.03%	0.105	67
0.04%	0.088	72



Fig.2 Nyquist diagrams for mild steel electrode in 1 mol·L<sup>-1</sup> HCl with and without Na-CMC

tions with 0.001%–0.04% Na-CMC and without Na-CMC was investigated by electrochemical impedance spectroscopy (EIS) at 298 K. Nyquist plots of mild steel in acidic solutions with and without inhibitor displayed only one depressed semi-circle, as seen in Fig.2.

The polarization resistance ( $R_p$ ) values were calculated from the difference in the impedance at lower and higher frequencies<sup>[18]</sup>. The electrochemical equivalent circuit model employed for this system is presented in Fig.3. According to the equivalent circuit, the real impedance at lower and higher frequencies is permitted to obtain the polarization resistance ( $R_p$ ). The polarization resistance includes charge transfer resistance ( $R_a$ ), which corresponds to resistance between the metal/outer Helmholtz plane, diffuse layer resistance ( $R_d$ ) attributed to the adsorbed inhibitor molecules, corrosion products, ions, and accumulated species on the metal surface of the semi-ellipse model. This has been reported by Erbil<sup>[19,20]</sup> and Solmaz<sup>[21]</sup>*et al.*. The  $R_{ct}$  and  $R_d$  resistance values calculated using the semi-ellipse model are given in Table 2. The impedance parameters determined from Nyquist diagram such as  $R_s$ ,  $R_p$ ,  $Q_{db}$ ,  $\alpha$ , and IE are given in Table 2.

In an acidic medium, the impedance response of mild steel significantly changes with Na-CMC concentration and the size of semicircle, which corresponds to the polarization resistances of mild steel. The  $R_p$  values increased from 44 to 222  $\Omega$  and the capacitance values decreased from 114 to 49  $\mu$ F by the addition of Na-CMC (Table 2). As the inhibitor concentrations increased, the  $R_p$  values increased, the capacitance values tended to decrease: this is probably due to the adsorption of the inhibitor on



Fig.3 Equivalent electrical circuit model

 $R_{p} = R_{a} + R_{a}, R_{a} = R_{t} + R_{a}; R_{s}$ : solution resistance,  $R_{a}$ : charge transfer resistance,  $R_{d}$ : diffuse layer resistance,  $R_{t}$ : film resistance,  $R_{a}$ : accumulated resistance,  $Q_{a}$ : differential capacitance

Table 2Impedance and LPR parameters for corrosion ofmild steel in 1 mol·L<sup>-1</sup> HCl at various contents of Na-CMC

		Impedance method					LPR n	LPR method	
u(INd-CIVIC)	$R_{\rm s}/\Omega$	$R_{\rm ct}/\Omega$	$R_{\rm d}/\Omega$	$R_{\rm p}/\Omega$	$Q_{\rm dl}/\mu F$	α	IE(%)	$R_{ m lp}/\Omega$	IE(%)
0	1.5	24	20	44	114	0.90	-	45	-
0.001%	1.8	50	45	95	94	0.90	54	96	53
0.005%	1.7	55	52	107	84	0.89	59	100	55
0.01%	1.8	65	58	125	72	0.89	65	131	66
0.02%	1.7	80	77	157	69	0.88	72	161	72
0.03%	3.6	87	105	192	56	0.84	77	190	76
0.04%	4.6	108	114	222	49	0.86	80	205	78

the metal surface<sup>[10,21]</sup>. The presence of a low-frequency inductive loop is typical for iron and mild steel and could be attributed to the molecules that are scattered at the high frequency region. These molecules are reoriented and accumulated on the electrode surface in the low frequency region.

The corroded metal represents a general behavior where the double layer on the interface of metal-solution does not behave as a real condenser. The potential trend is exponential going from metal to solution. If the potential drop at the distance dx is dE, the capacitance lowering will be equal to dC. The capacitance of the whole system is the integral of dC values, called differential capacitance ( $Q_{dl}$ )<sup>[2223]</sup>. In modelling corrosion process, the term  $Q_{dl}$ , a constant phase element (CPE) that could be substituted by  $C_{dl}$  in the time constants associated with the corrosion process, is represented as an experimental deviation from a semi-circle<sup>[23]</sup>. In order to obtain the differential capacitance, the frequency at which the imaginary component of the impedance is maximum, ( $-Z'_{max}$ ) was determined and  $Q_{dl}$  values were also calculated from the following equation:

$$Q_{\rm dl} = \left( B \cdot \frac{1}{(j\omega)^{\alpha}} \right)$$

where *B* is a constant depending on the specific analyzed system, j is the imaginary unit  $(\sqrt{-1})$ ,  $\omega$  is the angular frequency, and  $\alpha$  is a surface inhomogeneity coefficient ranging between 0 and 1. The CPE ( $Q_{dl}$ ) is related to the capacity of the double layer and the exponent ( $\alpha$ ) of  $Q_{dl}$ , relevant to the capacitive semi- circle of electrode/electrolyte system<sup>[22,24]</sup>.

The differential capacitance is considered as the electrical capacitor between charged metal surface and solution. It is generally assumed that acid corrosion inhibitors adsorb on the metal surface and the structure of double layer changes with reducing electrochemical partial reaction rate. Inhibition process takes place by a decrease in the electrical capacity of the mild steel surface in the presence of the inhibitor and this could be related with the decrease in the corrosive area on the mild steel surface owing to the increase of the inhibitor covered area. The decrease of capacitance values may be due to the adsorption of Na-CMC on metal surface thus leading to a film formation on the mild steel surface that has led to an increase in percentage inhibition efficiency (IE)<sup>[25,26]</sup>. The capacitance values decrease due to an increase in the thickness of the electrical double layer and/or a decrease in local dielectric constant that are caused by the adsorption of Na-CMC molecules on the mild steel surface<sup>[27-29]</sup>.

The LPR ( $R_{ip}$ ) values in the absence and presence of inhibitor are given in Table 2. The  $R_{ip}$  values showed an increase from 45 to 205  $\Omega$  by the addition of Na-CMC. These high values of  $R_{ip}$ seem to validate the hypothesis of high protection of the interface against H<sup>+</sup> reduction and Fe dissolution. An inhibitor efficiency of 78% has been observed for 0.04% Na-CMC concentration.

#### 2.3 Potentiodynamic polarization measurements

Anodic and cathodic potentiodynamic polarization curves for mild steel in 1.0 mol  $\cdot$ L<sup>-1</sup> HCl in the absence and presence of Na-CMC were studied at 298 K. Potentiodynamic polarization curves of mild steel in 1.0 mol  $\cdot$ L<sup>-1</sup> HCl in the absence and presence of different amounts (0.001%–0.04%) of Na-CMC are given in Fig.4.

These values were determined by extrapolation of the anodic and cathodic Tafel lines to the respective free corrosion potential. The values of the corrosion current density ( $i_{corr}$ ), corrosion potential ( $E_{corr}$ ), anodic Tafel slopes ( $\beta_a$ ), cathodic Tafel slopes ( $\beta_c$ ), and IE were obtained as a function of Na-CMC concentrations and are given in Table 3.

From the electrochemical polarization measurements, it is clear that the addition of an inhibitor causes a decrease in both anodic and cathodic currents. The anodic current decrease is more significant than that of cathodic current as shown in Fig.4. The increase in concentration of Na-CMC causes a slight shift of corrosion potentials to the noble direction. The addition of Na-CMC in corrosive media produces a light modification in cathodic Tafel slope ( $\beta_c$ ). This result suggests that the mechanism of hydrogen reduction on the surface of mild steel is not significantly modified by the addition of Na-CMC. The cathodic current-potential curves give parallel rises to Tafel lines indicating that the hydrogen evolution is controlled by the activation. In the anodic range, current densities of mild steel in 1.0 mol·L<sup>-1</sup> HCl decreased with the addition of Na-CMC at the related potential. This result indicated that Na-CMC exhibited both cathodic and anodic inhibition effects. Hence, this molecule can be classified as mixed type inhibitor in acidic solution<sup>[30,31]</sup>.

It can be seen from Table 3 that the corrosion current density



Fig.4 Potentiodynamic polarization curves for the mild steel in 1.0 mol·L<sup>-1</sup> HCl containing different concentrations of Na-CMC

Fable 3	Corrosion data obtained with the potentiodynamic					
tests	of mild steel in 1.0 mol $\cdot$ L <sup>-1</sup> HCl with and without					
Na-CMC at 298 K						

w(Na-CMC)	<i>E</i> <sub>corr</sub> /mV ( <i>vs</i> Ag/AgCl)	$\frac{\beta_{a}}{(\mathrm{mV}\boldsymbol{\cdot}\mathrm{dec}^{-1})}$	$\frac{-\beta_{\rm c}}{({\rm mV}\cdot{\rm dec}^{-1})}$	$\frac{i_{\rm corr}}{(\mu {\rm A} \cdot {\rm cm}^{-2})}$	IE(%)
0	-478	130	116	478	-
0.001%	-476	149	102	229	52
0.005%	-466	132	101	221	54
0.01%	-465	95	99	169	65
0.02%	-467	111	97	159	67
0.03%	-464	119	97	135	72
0.04%	-465	97	97	105	78

 $(i_{corr})$  decreased from 478  $\mu$ A·cm<sup>-2</sup> for the inhibitor free solution to 105  $\mu$ A·cm<sup>-2</sup> at the highest concentration of Na-CMC studied. IE values increased with the increase in the concentration of the polymer and attained a value of 78% at 0.04% Na-CMC concentration.

The comparison of inhibiting-efficiency data obtained from the electrochemical methods used in the determination of the corrosion of mild steel in HCl is presented in Fig.5. Inhibition efficiencies or the degree of surface coverage ( $\theta$ ) values derived from  $R_{lp}$ ,  $R_p$ , and Tafel measurements agreed satisfactorily with each other. The arithmetic average of the surface coverage values obtained by the electrochemical test methods are used for plotting the adsorption isotherms.

#### 2.4 Adsorption isotherm

Basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. The metal surface in aqueous solution is always covered with adsorbed water dipoles. The adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasisubstitution process between the organic compounds in the aqueous solution and water molecules adsorbed on the electrode surface<sup>[32]</sup>.

In order to investigate the adsorption isotherm, the degree of surface coverage was evaluated graphically by fitting a suitable adsorption isotherm. Attempts were made to fit  $\theta$  values to various isotherms including Frumkin, Langmuir, Temkin, and Freundlich isotherms. By far the best fit was obtained from Lang-



Fig.5 Inhibition efficiencies derived from electrochemical measurements in 1.0 mol·L<sup>-1</sup> HCl containing different concentrations of Na-CMC



Fig.6 Langmuir adsorption plot for the mild steel in 1.0 mol·L<sup>-1</sup> HCl containing different concentrations of Na-CMC

muir isotherm with correlation coefficient of 0.9967. According to this isotherm,  $\theta$  is related to the inhibitor concentration  $C_{\text{(inh)}}^{[33]}$ :

$$\frac{C_{\text{(inh)}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{(inh)}}$$

where  $K_{ads}$  is the adsorption equilibrium constant of the adsorption process (Fig.6).

The adsorption equilibrium constant is related to the free energy of adsorption  $\Delta G_{ads}$  as shown in the equation below

$$K_{\text{ads}} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{\text{ads}}}{RT}\right)$$

where R is the gas constant (8.314 J·K<sup>-1</sup>·mol<sup>-1</sup>), T is the absolute temperature (K), and the value 55.5 is the concentration of water in solution expressed in mol  $\cdot L^{-1}$ . In order to calculate the free adsorption energy ( $\Delta G_{\rm ads}$ ), it is necessary to know the average molecular weight of Na-CMC. Since Na-CMC is a polymer with an average molecular weight ( $M_w$ =250000), it was used in the determination of the molar concentrations of the studied polymeric solution. Obviously, the adsorptive equilibrium constant  $K_{ads}$  has a unit of L·mol<sup>-1</sup>. Therefore, adsorptive equilibrium constant  $K_{ads}$ unit L·mg<sup>-1</sup> should be converted into L·mol<sup>-1</sup> as 45  $M_{\rm w}$  L·mol<sup>-1</sup> [34]. The free energy of adsorption ( $\Delta G_{ads}$ ) can be obtained from the equation of  $\Delta G_{ads}$ =-20.23-2.48ln $M_w$ . The values of equilibrium constant and free energy of adsorption of the mild steel are 1.1× 107 L·mol<sup>-1</sup> and -51.0 kJ·mol<sup>-1</sup>, respectively. The negative value of  $\Delta G_{ads}$  suggests that the adsorption of Na-CMC molecule on the mild steel surface is a spontaneous process. A value of -40



Fig.7 Effect of temperature on the cathodic and anodic responses for mild steel in 1.0 mol·L<sup>-1</sup> HCl



Fig.8 Effect of temperature on the cathodic and anodic responses for mild steel in 1.0 mol·L<sup>-1</sup> HCl+0.04% Na-CMC

kJ ·mol <sup>-1</sup> is usually adopted as a threshold value between chemisorption and physisorption<sup>[35,36]</sup>. Generally, the value of  $\Delta G_{ads}$  for chemisorption is more negative than -40 kJ ·mol <sup>-1</sup>. Such a value implies either transfer of electrons or sharing with inhibitor molecules on the metal surface, which forms a coordinate type of bond that explains the strong adsorption of Na-CMC on the mild steel surface. Similar interpretations about the adsorption of water-soluble polymer on the metal surface have been reported by other researchers<sup>[34,37]</sup>.

# 2.5 Effect of temperature

Temperature could affect the interaction between the mild steel electrode and the acidic medium in the absence and presence of the inhibitor. Polarization curves for the mild steel in 1.0 mol·L<sup>-1</sup> HCl and 1.0 mol·L<sup>-1</sup> HCl containing 0.04% Na-CMC at the temperature range 298–328 K are given in Figs.7 and 8 and the corresponding data are given in Table 4.

Table 4 shows that the corrosion current density increases with increasing temperature, whereas inhibitor efficiency decreases as temperature increases. The decrease in inhibition efficiency shows that the film formed on the metal surface is less protective at higher temperatures, since desorption rate of the inhibitor is greater at higher temperatures.

The corrosion reaction can be regarded as an Arrhenius-type process and corrosion rate is given by the following equation:

$$i_{corr} = kexp \frac{E_a^*}{RT}$$

where  $E_a^*$  is the apparent activation corrosion energy, T is the ab-

Table 4Influence of temperature on the electrochemicalparameters for mild steel electrode immersed in 1.0 mol $\cdot$ L<sup>-1</sup>HCl and 1.0 mol $\cdot$ L<sup>-1</sup>HCl + 0.04% Na-CMC

T/K	w(Na CMC)	$E_{\rm corr}/{\rm mV}$	$\beta_{a}$	$-\beta_{c}$	i <sub>corr</sub>	IE(%)
TK W(INA-CIVIC)	(vs Ag/AgCl)	$(mV \cdot dec^{-1})$	$(mV \cdot dec^{-1})$	$(\overline{\mu A \cdot cm^{-2}})$	IL(%)	
298	0	-478	222	116	478	-
	0.04%	-465	97	97	105	78
308	0	-472	209	132	872	-
	0.04%	-461	118	105	218	75
318	0	-466	224	144	1426	-
	0.04%	-458	151	117	417	71
328	0	-461	231	162	4065	-
	0.04%	-452	157	138	1712	58



Fig.9 Arrhenius plots of mild steel in 1.0 mol·L<sup>-1</sup> HCl in the absence (■) and presence (▲) of Na-CMC

solute temperature, k is the Arrhenius pre-exponential constant and R is the universal gas constant.  $E_a^*$  values of the corrosion reaction in the absence and presence of 0.04% of Na-CMC can be derived from the above-mentioned equation. By plotting the natural logarithm of the corrosion current density versus 1/T, the activation energy can be calculated from the slope. The temperature dependence of mild steel dissolution in 1.0 mol ·L<sup>-1</sup> HCl and in the presence of Na-CMC is presented in Arrhenius co-ordinates in Fig.9. The calculated values of the apparent activation corrosion energies in the absence and presence of Na-CMC are 55.92 and 72.93 kJ·mol<sup>-1</sup>, respectively. These results are in accordance with the findings of the other researchers<sup>[38-40]</sup>. It was clear that the  $E_a^*$  values in the presence of Na-CMC are higher than those in the noninhibited acid solution. The increase of  $E_a^*$ in the presence of the inhibitor indicates either physical adsorption or weak chemical bonding between the Na-CMC molecules and the mild steel surface<sup>[23,27,41]</sup>.

# 2.6 Scanning electron microscopy

The surface morphology of mild steel specimen before immersion is shown in Fig.10(a), where one can see the irregularities due to the mechanical treatment. Fig.10(b) shows the SEM image of the surface of mild steel specimen after immersion in 1.0 mol  $\cdot L^{-1}$  HCl solution for 24 h. Comparisons of the micrographs reveal that the surface was badly corroded and corrosion products can be seen all over the surface of the specimen clearly. Fig.10(c) shows the SEM image of another mild steel surface in the presence of 0.04% Na-CMC.

The micrograph of the mild steel without inhibitor (Fig.10b) shows some cracks and pits due to the attack of the aggressive medium. However, a uniform modification of the mild steel surface is observed in the presence of Na-CMC that has provided a protective film on the mild steel surface after immersion for 24 h interval (Fig.10c)).

Generally, adsorption of inhibitors is attributed to the presence of heteroatoms, such as oxygen, sulfur, and nitrogen, which allow adsorption on the electrode surface. The experimental results showed that the effectiveness of the Na-CMC as a corrosion inhibitor depends primarily on sufficient surface coverage with the strongly adsorbed Na-CMC: this polymer contains active hydroxyl groups that could be bridged with the metal sur-



Fig.10 SEM images of mild steel samples
 (a) after polishing, (b) after immersion in 1.0 mol·L<sup>-1</sup> HCl without,
 (c) after immersion in 1.0 mol·L<sup>-1</sup> HCl+0.04% Na−CMC

face. The observed results on the adsorption of the Na-CMC with other organic compounds on the corrosion inhibition in acidic solution have been well correlated with those reported in Refs. [11,42].

# **3** Conclusions

The corrosion inhibition of mild steel by Na-CMC was studied by weight loss, electrochemical measurements, and SEM. The main conclusions of this study are given below.

(1) The Na-CMC is found to be a good inhibitor for mild steel corrosion in 1.0 mol· $L^{-1}$  hydrochloric acid solution.

(2) Inhibition efficiency values obtained from the electrochemical and analytical methods increase with the increase of Na-CMC concentration.

(3) The corrosion potential values are slightly affected by the addition of inhibitor and Na-CMC is a mixed type inhibitor.

(4) The Na-CMC adsorbed on the mild steel surface followed Langmuir adsorption isotherm, indicating that there is no interaction between the adsorbed molecules on the metal surface.

(5) The calculated values of activation energy  $(E_a^*)$  in the presence of Na-CMC are found to be higher than the values obtained in the absence of Na-CMC.

(6) SEM reveals the formation of a smooth, dense protective layer on mild steel surface in the presence of Na-CMC.

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