Original Article

Inhibitory effect of sodium carboxymethylcellulose and synergistic biodegradable gemini surfactants as effective inhibitors for MS corrosion in 1 M HCl

Ruby Aslam\textsuperscript{a}, Mohammad Mobin\textsuperscript{a,}\textsuperscript{*}, Jeenat Aslam\textsuperscript{b}, Hassane Lgaz\textsuperscript{c}, Ill-Min Chung\textsuperscript{c}

\textsuperscript{a} Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, India
\textsuperscript{b} Department of Chemistry, College of Science, Taibah University, Yanbu 30799, Al-Madina, Saudi Arabia
\textsuperscript{c} Department of Applied Bioscience, College of Life & Environment Science, Konkuk University, 120 Neungdong-ro, Guanjin-gu, Seoul 05029, South Korea

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A B S T R A C T

The aim of this paper is to study the anticorrosive performance of the polymer–surfactants system comprising of mixed solutions of varying concentrations (10–700 ppm) of sodium salt of carboxymethylcellulose (NaCMC) and fixed concentration (1 ppm) of oppositely charged synthesized green cationic di-ester bonded gemini surfactants i.e., ethane-1,2-diylbis(N,N-dimethyl-N-alkylammoniumacetoxy)dichloride,referred as m-E2-m, where m = 12, 14, 16, respectively for mild steel in 1 M HCl solution. The inhibition effect of mixed NaCMC - gemini surfactant system was examined using weight reduction technique, potentiodynamic polarization (PP) measurements, electrochemical impedance (EIS) measurements, surface morphological observation (SEM), and molecular dynamics simulation study. NaCMC alone was observed to offer moderate inhibition efficiency (IE) of 57.3% at 500 ppm, which was synergistically increased in the presence of very small amount of synthesized gemini surfactants. The improvement in IE was highly dependent on the surfactant tail length; the maximum improvement in IE of 90.1% was observed in presence of 16-E2-16. The adsorption of the studied systems followed Langmuir adsorption isotherm. PP result showed that all the examined systems behave as mixed type inhibitors. EIS results supported the existence of protective layer by the adsorption of inhibitor molecules on the metal surface. The formation of protective layer of studied systems on the mild steel surface was confirmed by FT-IR and SEM results. Molecular dynamics simulation was further performed to provide molecular level insights into the adsorption mechanism with the structure of studied systems.

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1. Introduction

Mild steel (MS) finds wide application in a broad field of industry and machinery. Extensive studies are being carried...
out to protect the MS due to its low corrosion resistance in different aggressive environments i.e. Cl−, CO32− and \(\text{SO}_4^{2−}\), etc. [1,2]. The corrosion of steel is a continuous process which cannot be stopped but it can be minimized or slow down/reduced by using different protective schemes. Hence to minimize the metal loss, several types of protective programmes are being adopted to control the corrosion of freshly erected or rusted surface after their proper cleaning. One of the popular schemes of corrosion control, which has gained wide acceptance in industries, is the use of corrosion inhibitors. However, most of the inhibitors employed are not cost effective and are toxic to humans and the environment [3]. Consequently, the new green and less toxic corrosion inhibitors should be found following environmental-friendly approaches and safety solutions, to replace the hazardous materials.

Sodium carboxymethyl cellulose (NaCMC) is an anionic water-soluble linear polymer derived from the partial substitution of 2, 3 and 6 hydroxyl groups of cellulose by hydrophilic carboxymethyl groups. NaCMC contains -OH and -COOH groups in its chemical structure, fulfilling an important criterion to work as a corrosion inhibitor. The use of NaCMC as an inhibitor is particularly important because of its cheapness, water solubility, non-toxicity, and as an environmentally acceptable polymer.

A review of literature reveals that the application of carboxymethyl cellulose (CMC) and NaCMC formulations have been scarcely reported to inhibit MS corrosion in acidic solution [4]. Solomon et al. [5], studied the inhibitive effect of CMC in 2 M \(\text{H}_2\text{SO}_4\) solution for MS corrosion at 30–60 °C employing hydrogen evolution, mass loss, and thermometric methods. The inhibitor offered a moderate inhibition efficiency of 64.8% at 500 ppm at 30 °C. Later, the authors studied the effect of halide ions (KCl, KBr and KI) on the corrosion inhibition performance of CMC under the same experimental conditions. The result showed that the addition of 5 mM KCl, downgraded the inhibition efficiency (51%) and the addition of the same concentration of KBr and KI, upgraded the inhibition efficiency (67 and 89% respectively). In another study, adsorption behavior and corrosion inhibition effect of NaCMC was investigated in 1.0 mol L−1 HCl [6]. The inhibition efficiency of NaCMC at 298 K was observed to be 78% at 400 ppm which decreased to 58% at 328 K.

In recent research, synergism has become one of the most important factors in the inhibition process. The synergistic formulation has been recommended as an effective means of improving the inhibitive performance of the inhibitor and decreasing the inhibitor dosage [5].

In our continuous quest of exploring environment friendly and cost effective corrosion inhibitors, the present work reports on the synergistic corrosion inhibition performance of NaCMC and biodegradable ester bonded gemini surfactants (GS) referred as m-E2-m (where E2 is diester group in gemini’s spacer part and m = 12, 14, 16, is the number of carbon atoms in the alkyl tail) for MS corrosion in 1 M HCl solution at 30 °C using weight loss measurements, electrochemical measurements, surface analytical and molecular dynamics simulation techniques. Influence of environmentally friendly GS on corrosion inhibition of metals using polymers have not yet been investigated though effect of some non-biodegradable monomeric surfactants has been reported in the recent past in the author’s laboratory [7–11].

2. Experimental section

2.1. Metal coupons and aggressive solutions for corrosion tests

MS specimens composition (wt. %: C-0.061%, Mn-0.181%, P-0.017%, Cr-0.035%, Mo-0.054%, Al-0.017%, V-0.033% and Fe-balance) with dimension 2.5 × 2 × 0.1 cm (exposed surface area 10.9 cm²) were used for weight loss measurements. Circular coupons with exposed surface area of 1 cm² were used for electrochemical studies. Before corrosion experiment, the coupons surface were polished via an abrading procedure with SiC papers (320, 400, 600 and 1200 grades). The coupons were degreased with acetone and washed with double-distilled water and then air dried. Sodium salt of carboxymethyl cellulose (NaCMC) (molecular formula - \(\text{C}_6\text{H}_{13}\text{NaO}_8\)) was commercially purchased from Merck and hydrochloric acid (HCl 37%) from Fischer Scientific.

2.2. Inhibitors

The ester bonded green cationic GS used in this work were synthesized and characterized as reported [12,13]. The chemical structures of NaCMC and m-E2-m were given in Fig 1.

2.3. Weight loss measurements

For gravimetric experiments, the test specimens were prepared and cleaned as described above. The pre-cleaned and weighed specimens were hanged in beakers containing 250 mL of the aerated and unstirred test solutions. The MS coupons were retrieved from test solutions after 6 h, appropriately cleaned, air-dried, and reweighed and then the weight loss was determined. All tests were run in triplicate and the data showed good reproducibility. Average values of weight loss for each experiment were obtained and used in subsequent calculations.

The corrosion rates (mg cm⁻² h⁻¹) and inhibition efficiencies (\(\eta_w\)%) were evaluated by Eqs. (1) and (2), respectively, where \(w_1\) and \(w_2\) is the weight loss before and after immersion, \(A\) is the surface area of the MS specimen (cm²); and \(T\) is the exposure time (h), \(\nu\) and \(\nu^0\) are the corrosion rates without and with the inhibitor, respectively.

\[
\nu = \frac{w_1 - w_2}{AT}
\]

\[
\eta_w = \frac{\nu^0 - \nu}{\nu^0} \times 100
\]

2.4. Electrochemical measurements

Metrohm Autolab Potentiostat/Galvanostat electrochemical system workstation (PGSTAT302N) was used to perform electrochemical experiments at 30±1 °C. The NOVA 1.11 software was used to analyze the data. A platinum wire was used as counter electrode (CE) and an Ag/AgCl/1 M KCl (sat.) as
reference electrodes (RE) and a MS specimen of 1 cm² dimension was used as working electrode (WE). To gain the stable status of the working electrode, the working electrode was immersed in aerated test solution for 1800s before each measurement, which allowed the open circuit potential (OCP) values to attain steady state (Fig. S1) (supporting information). The potentiodynamic anodic and cathodic polarization curves were scanned from +250 mV to −250 mV versus OCP at a scan rate of dE/dt = 0.1 mV/s. Impedance diagrams were obtained over a frequency range of 10⁻¹ Hz to 10⁶ Hz, and the ac voltage amplitude was 10 mV.

The protection efficiencies of inhibitors from potentiodynamic polarization measurement (%ηPP) and EIS measurements (%ηEIS) were estimated with the following formulas, respectively:

\[
\eta_{PP}(\%) = \frac{i_{corr} - i_{corr}^{(0)}}{i_{corr}} \times 100
\]

\[
\eta_{EIS}(\%) = \frac{R_p^{(0)} - R_p}{R_p^{(0)}}
\]

where, \(i_{corr}\) and \(i_{corr}^{(0)}\) is the corrosion current density and \(R_p^{(0)}\) is the charge transfer resistance of WE without and with the inhibitors, respectively.

### 2.5. Fourier transform infrared (FT-IR) analysis

FT-IR spectra were recorded using a Perkin Elmer spectrometer. The frequency ranges from 4000 to 400 cm⁻¹. The spectra for pure NaCMC, pure 16-E2-16 and the adsorbed NaCMC, 16-E2-16 NaCMC/16-E2-16 on the MS surface in 1 M HCl after 6 h immersion were obtained. For the spectra of adsorbed (Fe-NaCMC, Fe-16-E2-16 and Fe-NaCMC/16-E2-16) inhibitor, the film was scrapped, mixed with KBr, and transformed into pellets.

#### 2.6. Surface morphological study

Scanning electron microscopy (SEM) analysis was accomplished using JEOL JSM-6510LV scanning electron microscope to determine the extent of corrosion damage without and with the inhibitors in terms of surface roughness/heterogeneity, which in turn give an idea about the extent of protection offered by the adsorbed inhibitors layer. For SEM analysis, the MS coupons were prepared as described above. After completion of 6 h immersion, the specimens were retrieved, appropriately cleaned, thoroughly rinsed with distilled water, dried and subjected to SEM analysis.

#### 2.7. MD simulation and Radial distribution function

In this study, the Fe (110) surface with a slab of 5 Å was chosen for MD simulation, as this iron surface is associated with high stabilization energy with highly packed structure. To provide larger surface area for metal-inhibitor interactions, the simulations were carried out in simulation box (24.82 × 24.82 × 35.69 Å³) that included 9Cl⁻, 49H₂O, 9H₂O⁺ and inhibitor molecules. The simulations were constructed with the help of the Visualizer, Amorphous Cell and Discover modules implemented in BIOVIA Materials Studio® commercial software. MD simulations are performed at temperatures T = 303 K maintained constant by the Andersen thermostat, a time step of 0.1 fs, NVT (fixed atom number, system volume and temperature) ensemble and a simulation time of 2000 ps to reach simulation system under an equilibrium state. The energy minimization and MD calculation processes were carried using COMPASS (the Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies) force field [14]. The extent of the interactions of the inhibitor molecules adsorbed on Fe(110) surface can be demonstrated by their interaction \(E_{interaction}\) and binding \(E_{binding}\) energies derived using Eqs. (5) and (6) [15].

\[
E_{interaction} = E_{total} - (E_{surface+solution} + E_{inhibitor})
\]
The corrosion inhibition performance of MS in 1 M HCl solution as a function of different inhibitor concentrations was evaluated by using the weight loss method. The results obtained from the weight loss measurements, such as corrosion rates \( \nu \) (mg cm\(^{-2}\) h\(^{-1}\)) and corrosion inhibition efficiencies \( \eta \) (%) without and with various concentrations of inhibitors, at 30 °C are listed in Table 1. These data show that corrosion rates of MS decrease on increasing the inhibitors concentration. As indicated in Table 1, the inhibition efficiency and surface coverage values were found to be: NaCMC < NaCMC/12-E2-12 < NaCMC/14-E2-14 < NaCMC/16-E2-16. The maximum inhibition efficiency (90.1%) was obtained for NaCMC/16-E2-16 at 30 °C, while, the minimum (57.3%) for NaCMC at 30 °C.

The higher inhibition efficiency of NaCMC/m-E2-m compared to NaCMC is ascribed to the strong Coulombic interactions between the NaCMC and the oppositely charged gemini surfactants head groups, which resulted in larger surface coverage and hence higher inhibition efficiency. The higher inhibition efficiency of NaCMC/16-E2-16 compared to NaCMC/12-E2-12 and NaCMC/14-E2-14 is attributed to its longer hydrophobic chain length which leads to increase in hydrophobic interaction [16], thus favoring its greater adsorption on steel surface.

As evidenced by the calculated synergism parameter \( S_0 \) (Table 1) the effect of m-E2-m GS on the inhibition efficiency of NaCMC was observed to be synergistic in nature. The value of \( S_0 \) is calculated using the following expressions [17]:

\[
E_{\text{binding}} = -E_{\text{interaction}} \tag{6}
\]

where, \( E_{\text{total}} \) represents the energy of the entire system, the \( E_{\text{surface-solution}} \) denotes the entire energy of Fe (110) and electrolytic solution in the absence of inhibitor molecules and \( E_{\text{inhibitor}} \) denotes the whole energy of inhibitor molecules and \( E_{\text{binding}} \) represents the binding energy between Fe(110) and inhibitor molecules.

### 3. Results and discussion

#### 3.1. Weight loss measurements

**3.1.1. Effect of inhibitor concentration, hydrophobic chain length and immersion time**

The corrosion inhibition performance of MS in 1 M HCl solution as a function of different inhibitor concentrations was evaluated by using the weight loss method. The results obtained from the weight loss measurements, such as corrosion rates \( \nu \) (mg cm\(^{-2}\) h\(^{-1}\)) and corrosion inhibition efficiencies \( \eta \) (%) without and with various concentrations of inhibitors, at 30 °C are listed in Table 1. These data show that corrosion rates of MS decrease on increasing the inhibitors concentration. As indicated in Table 1, the inhibition efficiency and surface coverage values were found to be: NaCMC < NaCMC/12-E2-12 < NaCMC/14-E2-14 < NaCMC/16-E2-16. The maximum inhibition efficiency (90.1%) was obtained for NaCMC/16-E2-16 at 30 °C, while, the minimum (57.3%) for NaCMC at 30 °C.

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As evidenced by the calculated synergism parameter \( S_0 \) (Table 1) the effect of m-E2-m GS on the inhibition efficiency of NaCMC was observed to be synergistic in nature. The value of \( S_0 \) is calculated using the following expressions [17]:

\[
S_0 = \frac{1 - \theta_{1+2}}{1 - \theta_1 \theta_2} \tag{7}
\]

\[
\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2) \tag{8}
\]

where \( \theta_1 \) = surface coverage by m-2-m, \( \theta_2 \) = surface coverage by NaCMC and \( \theta_{1+2} \) = combined surface coverage by both m-2-m and NaCMC. Generally, when \( S_0 \) approaches 1, no interaction between surfactant and the additives exists; values of \( S_0 > 1 \) represent a synergistic effect, while values of \( S_0 < 1 \) indicate antagonistic behaviour.

#### 3.1.2. Effect of immersion time

The influence of immersion period (3–168 h) on the inhibition efficiency of optimum concentration of NaCMC/m-E2-m system at 30 °C was done to test their stability over prolonged exposure period and the result is given in Fig. S2 (supporting information). As the immersion period increases the inhibition efficiency of the inhibiting system increases up to 48 h (from 69.81 to 88.79% for 12-E2-12, from 80.48 to 98.89% for 14-E2-14 and from 86.71 to 98.98% for 16-E2-16) supporting the strengthening of protective film by the increased adsorption of inhibitor molecules. On further extending the
immersion period, there is a slight lowering in inhibition efficiency, this is followed by a near constant inhibition efficiency. The slight lowering in inhibition efficiency is because protective film is ruptured by the continuous attack of ions present in acid solution. There is a competition between the formation of iron-NaCMC complex and iron chloride/hydroxide complex. It is suggested that the formation of iron chloride complex is more favored than formation of complex (iron-NaCMC). However, after certain period of immersion an equilibrium is established between iron-NaCMC complex and iron chloride/hydroxide complex giving rise to a near constant inhibition efficiency.

3.1.3. Adsorption isotherm and thermodynamics parameters

To understand adsorption mechanism of NaCMC, NaCMC+12-E2-12, NaCMC+14-E2-14, NaCMC+16-E2-16 molecules on MS/solution interface, adsorption isotherms are deduced by fitting the surface coverage ($\theta$) as a function of the inhibitors concentration. The adsorption of tested inhibitors on steel surface is in well agreement with the Langmuir isotherm. This isotherm is defined by the equation below, where $\theta$: the surface coverage; $C$: the inhibitor concentration and $K_{ads}$: the adsorptive equilibrium constant.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

(9)

The plots of $C/\theta$ vs. $C$ gave straight lines as shown in Fig. S3 (supporting information). The obtained linear association coefficient ($R^2$) is $> 0.998$ (strong correlation) verifying that the adsorption of studied inhibitor molecules obeys Langmuir adsorption isotherm. The values of $K_{ads}$ (Table 2) were obtained from the intercept of $C/\theta$ vs. $C$ plot. The high value of $K_{ads}$ is indicative of high adsorption percentage of studied inhibitor molecules on the MS surface [18].

The free energy of adsorption, $\Delta G_{ads}$, of the inhibitors on the steel surface is obtained by using the following equation,

$$\Delta G_{ads} = -RT \ln(1 \times 10^6 K_{ads})$$

(10)

where $R$: the universal gas constant, $T$: the absolute temperature and the value of $1 \times 10^6$ is the concentration of water in solution in ppm. The calculated $\Delta G_{ads}$ values are given in Table 2. $\Delta G_{ads}$ values range between $-42.13$ to $-44.58$ (higher than $-40$ KJ mol$^{-1}$), this specifies dominant chemical mode of adsorption, which indicates a charge transferring from inhibitor molecules to the MS surface, to form a coordinate type of metal bond.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Slope</th>
<th>$R^2$</th>
<th>$K_{ads}$ (ppm/mol)</th>
<th>$\Delta G_{ads}$ (KJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCMC</td>
<td>1.73</td>
<td>0.993</td>
<td>0.018</td>
<td>$-42.13$</td>
</tr>
<tr>
<td>NaCMC+12-E2-12</td>
<td>1.37</td>
<td>0.996</td>
<td>0.036</td>
<td>$-43.82$</td>
</tr>
<tr>
<td>NaCMC+14-E2-14</td>
<td>1.18</td>
<td>0.996</td>
<td>0.038</td>
<td>$-43.97$</td>
</tr>
<tr>
<td>NaCMC+16-E2-16</td>
<td>1.12</td>
<td>0.999</td>
<td>0.048</td>
<td>$-44.58$</td>
</tr>
</tbody>
</table>

Fig. 2 – PP curves for MS in 1 M HCl solution without and with different concentrations of NaCMC+1 ppm 16-E2-16.

3.2. Electrochemical measurements

3.2.1. Potentiodynamic polarization (PP) method

Polarization curves of MS in uninhibited 1 M HCl and HCl inhibited with different concentrations of NaCMC alone and in combination with 1 ppm of m-E2-m were obtained at 30 °C (Fig. 2 and Fig. S4, supporting information) and parameters such as corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), Tafel slopes ($\beta_c$ and $\beta_a$) and percentage of inhibition efficiency ($\eta_{IPE}$, %) are listed in Table 3.

The displayed curves (Fig. 2) show that the addition of inhibitor shifts the $E_{corr}$ values to more negative direction compared to the blank solution. Since the shift in $E_{corr}$ is within 85 mV, it is confirmed that tested molecules inhibit both cathodic and anodic corrosion reactions on the electrode surface. From Table 3, it is also observed that $\beta_a$ and $\beta_c$ values of the inhibited acid solution do not follow a specific pattern with increase in inhibitor concentration. This suggests that the mechanism of corrosion reaction is not modified due to the presence of studied inhibitor [18]. The lower values of $i_{corr}$ (Table 3) at higher concentrations of the inhibitors might be due to increased number of inhibitors molecules leading to larger surface coverage of the molecules on MS surface.

All studied inhibitors reduce the MS corrosion and display similar polarization behavior. At the concentration of 500 ppm, the efficiencies of NaCMC, NaCMC+1 ppm 12-E2-12, NaCMC+1 ppm 14-E2-14, and NaCMC+1 ppm 16-E2-16 inhibitors are 58.5%, 73.6% 77.1% and 82.2%, respectively. Thus, NaCMC+1 ppm 16-E2-16 inhibitor is more effective to resist corrosion of MS in 1 M HCl solution. This is due to the better adsorption of NaCMC+1 ppm 16-E2-16 compared to
other combinations on the surface of the MS. This is attributed to the longer hydrophobic chain of 16-E2-16 than other two gemini surfactants thus having higher coverage fraction on the MS surface.

### 3.2.2. Electrochemical impedance spectroscopy (EIS) measurements

To further evaluate the corrosion protection performance of MS without and with investigated inhibitors, EIS measurements were performed. The inhibited and uninhibited MS specimens show single capacitive loop which indicates that MS dissolution in present case involves charge transfer mechanism [19,20]. Inspection of Figs. 3a and S5 (supporting information) showed that diameters of Nyquist plots increase on increasing concentrations of all three inhibitors which is attributed to their increased adsorption on metal/electrolyte interfaces [21].

The experimental parameters were derived with the help of a proper equivalent circuit shown in Fig. S6 (supporting information) and are listed in Table 4. This equivalent circuit consists of $R_S$ (solution resistance), $R_p$ (polarization resistance), and CPE (constant phase element) which is used at the place of pure capacitor to compensate the surface inhomogeneity [22-24] arising due to the surface roughness, dislocations, impurities, fractality of grain boundaries, and the distribution of active sites [25]. The impedance of CPE ($Z_{CPE}$) is given by the following equation [26,27]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n}$$  \hspace{1cm} (11)

where $Y_0$ is the CPE constant, $j$ is imaginary number and is equal to the square root of $-1$, $\omega$ is the angular frequency in Rads$^{-1}$ ($\omega = 2\pi f_{max}$, $f_{max}$ is the frequency) and factor $n$ is the phase shift. The values of $n$ equal to 1, 0, $-1$ and $\frac{1}{2}$ represent pure capacitive, resistive, inductive and Warburg impedance, respectively. The values of chi-square ($\chi^2$) (Table 4) was used to judge the quality of fitting results.

The values of double layer capacitance ($C_{dl}$) were calculated using the Eq. (12).

$$C_{dl} = Y_0(\omega_{max})^{n-1}$$  \hspace{1cm} (12)

where $\omega_{max}$: represents the frequency at which imaginary part of the impedance is maximum (rads$^{-1}$).

The $R_p$ values given in Table 4 are higher for the inhibited systems compared to 1 M HCl solution. This is attributed to decrease in solution conductivity by the addition of the studied inhibitors. The data of Table 4 revealed that the values of $R_p$ enhanced on enhancing the concentration of inhibitors which refers to greater blocking of the active area at the metal surface due to the adsorption of the studied inhibitor molecules onto the MS surface and the displacement of the adsorbed water molecules from the surface.

In general, when a corrosion inhibitor is added to a solution, the values of $C_{dl}$ will become small and this implies that the local dielectric constant decreases and/or thickness of double layer increases, advocating the inhibition of MS corrosion by the adsorption of inhibitors molecules at metal/solution interface [28,29].

Capacitance is the reciprocal of the thickness of the double layer and can be used to follow the adsorption process of inhibitor molecules on the MS surface. For example, for NaCMC (500 ppm) alone and in combination with 1 ppm m-E2-m gemini surfactants, the capacitance value $(2.41 \times 10^{-4}$ Fcm$^{-2}$) obtained for the uninhibited metal, which is declined to $0.97 \times 10^{-4}$ Fcm$^{-2}$ for NaCMC, $0.84 \times 10^{-4}$ Fcm$^{-2}$ for NaCMC+12-E2-12, $0.80 \times 10^{-4}$ Fcm$^{-2}$ for NaCMC+14-E2-12, and $0.62 \times 10^{-4}$ Fcm$^{-2}$ for NaCMC+16-E2-16, demonstrating that the later compound acts as a good capacitance reducer therefore better corrosion inhibitor. Further, a decrease in capacitance with increasing inhibitors concentrations was observed which may be attributed to the formation of a pro-

<table>
<thead>
<tr>
<th>$C$ (ppm)</th>
<th>GS (1 ppm)</th>
<th>$E_{corr}$ (V vs. Ag/AgCl)</th>
<th>$\beta_s$ (V/dec)</th>
<th>$-\beta_i$ (V/dec)</th>
<th>$i_{corr}$ (A) $\times 10^{-3}$</th>
<th>$n_{PP}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl NaCMC</td>
<td>-</td>
<td>-0.4151</td>
<td>0.1416</td>
<td>0.0885</td>
<td>0.199 ± 0.006</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-0.4126</td>
<td>0.1425</td>
<td>0.0817</td>
<td>0.146 ± 0.001</td>
<td>26.7</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>-0.4361</td>
<td>0.1059</td>
<td>0.0685</td>
<td>0.123 ± 0.001</td>
<td>38.0</td>
</tr>
<tr>
<td>300</td>
<td>-</td>
<td>-0.4200</td>
<td>0.1238</td>
<td>0.0644</td>
<td>0.093 ± 0.001</td>
<td>53.5</td>
</tr>
<tr>
<td>500</td>
<td>-</td>
<td>-0.4316</td>
<td>0.1188</td>
<td>0.0904</td>
<td>0.083 ± 0.001</td>
<td>58.5</td>
</tr>
<tr>
<td>-</td>
<td>12-E2-12</td>
<td>-0.4230</td>
<td>0.1020</td>
<td>0.0719</td>
<td>0.068 ± 0.001</td>
<td>65.7</td>
</tr>
<tr>
<td>-</td>
<td>14-E2-14</td>
<td>-0.4160</td>
<td>0.0916</td>
<td>0.0693</td>
<td>0.053 ± 0.0005</td>
<td>73.6</td>
</tr>
<tr>
<td>-</td>
<td>14-E2-14</td>
<td>-0.4052</td>
<td>0.1074</td>
<td>0.0699</td>
<td>0.100 ± 0.0002</td>
<td>49.4</td>
</tr>
<tr>
<td>-</td>
<td>14-E2-14</td>
<td>-0.4239</td>
<td>0.1246</td>
<td>0.0801</td>
<td>0.088 ± 0.0001</td>
<td>55.8</td>
</tr>
<tr>
<td>300</td>
<td>14-E2-14</td>
<td>-0.4149</td>
<td>0.1097</td>
<td>0.0751</td>
<td>0.069 ± 0.0004</td>
<td>64.9</td>
</tr>
<tr>
<td>500</td>
<td>14-E2-14</td>
<td>-0.4139</td>
<td>0.1038</td>
<td>0.0687</td>
<td>0.045 ± 0.0004</td>
<td>77.1</td>
</tr>
<tr>
<td>-</td>
<td>16-E2-16</td>
<td>-0.4139</td>
<td>0.1194</td>
<td>0.0679</td>
<td>0.094 ± 0.001</td>
<td>52.9</td>
</tr>
<tr>
<td>-</td>
<td>16-E2-16</td>
<td>-0.4233</td>
<td>0.1089</td>
<td>0.0719</td>
<td>0.068 ± 0.0009</td>
<td>65.7</td>
</tr>
<tr>
<td>300</td>
<td>16-E2-16</td>
<td>-0.4153</td>
<td>0.1022</td>
<td>0.0782</td>
<td>0.039 ± 0.0004</td>
<td>80.0</td>
</tr>
<tr>
<td>500</td>
<td>16-E2-16</td>
<td>-0.4197</td>
<td>0.1074</td>
<td>0.0743</td>
<td>0.035 ± 0.0003</td>
<td>82.2</td>
</tr>
</tbody>
</table>
Fig. 3 – (a) Nyquist and (b) Bode curves for MS in 1 M HCl solution without and with different concentrations of NaCMC+1 ppm 16-E2-16.

Protective layer by the adsorption of inhibitor molecules on the electrode surface [30].

Figs. 3b and S5 (supporting information) displays the Bode impedance and phase angle plots at various concentrations of tested inhibitors. As seen from Figs. 3b and S5 (supporting information), Bode plots refer to the existence of a single constant phase element at the metal/solution interface. The impedance at low frequencies increased due to the formation of inhibition film by the adsorption of inhibitors molecules, which protects MS from corrosive ions. The maximum phase angle at the intermediate frequency for ideal capacitor is −90°. In the absence of inhibitor, the phase angle value is lower than the values observed in presence of inhibitors. The increase in maximum phase angle with increase in the inhibitors concentrations supports the adsorption of more inhibitor molecules on MS surface [31,32] resulting decreased metal dissolution rate. In addition, the more negative values of phase angle are observed in the case of NaCMC+16-E2-16 which explains its better protection properties.

3.3. FT-IR spectroscopy

The FT-IR spectra were recorded for free inhibitor (NaCMC and 16-E2-16) and scrapped sample (Fe-NaCMC, Fe-16-E2-16 Fe-NaCMC/16-E2-16) and results are produced in Fig. S7 (supporting information). Spectrum of NaCMC shows the sharp and strong peaks at 3448 cm⁻¹ which could be assigned to −OH stretching of the carboxyl group of the NaCMC molecule, while that at 2920 cm⁻¹ is due to asymmetric −CH₂— stretching vibrations. Those at 1633 and 1426 cm⁻¹ are due to the COO⁻ asymmetric and symmetric vibrations, respectively and peaks at 1126 and 1032 cm⁻¹ are assigned to C—O—C and C—O stretch, respectively. In case of adsorbed NaCMC (Fe-NaCMC) spectra, most of peaks observed in the spectra of pure NaCMC, were also present. However some of the peaks got reduced in intensity and shifted to lower wavenumbers. The −OH peak shifts from 3448 cm⁻¹ to 3428 cm⁻¹ whereas the other characteristic peaks observed at 1633 cm⁻¹, 1426 cm⁻¹, 1126 cm⁻¹ and 1032 cm⁻¹ have
shifted to 1629 cm\(^{-1}\), 1411 cm\(^{-1}\), 1106 cm\(^{-1}\), and 1017 cm\(^{-1}\), respectively. Spectrum of free 16-E2-16 shows characteristic peaks at 1407 cm\(^{-1}\) (C\(\equiv\)O–C stretching), 1746 cm\(^{-1}\) (C\(\equiv\)O) and 1199 cm\(^{-1}\) (C\(\equiv\)N). The peaks value at 2920 and 2851 cm\(^{-1}\) corresponds to C–H stretching frequencies. In case of adsorbed 16-E2-16 (Fe-16-E2-16), the peak of C\(\equiv\)O has shifted to lower wavenumber (1743 cm\(^{-1}\)) which suggest that C\(\equiv\)O is involved in the adsorption process. FT-IR spectrum of the film formed on the MS surface (Fe-NaCMC/16-E2-16) shows similar FT-IR spectrum, and the peak regions of the adsorptive film are basically consistent with that of NaCMC and 16-E2-16. How- ever, it is demonstrated that intensities of some of the peaks are reduced and shift toward the lower wave numbers in the mixed system. In the case of adsorbed NaCMC/16-E2-16 molecules, the intensity of –OH and C\(\equiv\)O bond has shifted from 3448 to 3417 cm\(^{-1}\) and 1746 to 1626 cm\(^{-1}\), respectively. These results indicate an interaction between steel surface and NaCMC/16-E2-16 and formation of a layer of protective film on the MS surface [33].

### 3.4. SEM

To establish the corrosion inhibition of studied inhibitors in 1 M HCl, SEM was used to take the images of steel surface. Fig. S8(a–f) (supporting information) presents the steel surface after polishing (abraded state); (b) steel immersed in 1 M HCl solution for about 6 h; and (c) steel immersed in 1 M HCl solution containing 500 ppm NaCMC, (d) NaCMC+1 ppm 12-E2-12, (e) NaCMC+1 ppm 14-E2-14 and (f) NaCMC+1 ppm 16-E2-16 for about 6 h. The freshly polished MS surface (Fig. S8a) exhibits smooth surface. In the absence of studied inhibitors, the MS surface degraded significantly due to free acid corrosion resulting in rough surface of MS (Fig. S8b). In contrast, in the presence of studied inhibitors, the surface morphology of MS coupons improved resulting in the less corroded and smoother surfaces (Fig. S8c–f). Here the adsorbed studied inhibitors perform as a barrier film and protect steel from corrosion. Moreover, the MS surface with NaCMC/16-E2-16 (Fig. S8f) is smoother than counterpart with NaCMC/14-E2-14 and NaCMC/12-E2-12, which also support the results obtained from weight loss, PDP, and EIS measurements.

### 3.5. Molecular Dynamics (MD) simulations

Though experimental studies provided highly noteworthy progress in the understanding of phenomena underlying inhibition activity, an overview of corrosion issues has shown that a better theoretical understanding of the corrosion mechanism plays a relevant role in more accurate corrosion inhibition process. It means, on the one hand, reducing experiment costs and, on the other hand, providing significant help in designing effective corrosion inhibitors directed against metal dissolution. Recent advances in computation technologies have facilitated computer simulation of complex phenomena and provide a more complete understanding of corrosion inhibitor function [34]. MD simulation are used widely to study inhibitor molecule motions at an atomic level in detail. In most recent studies, they are used as a promising tool to generate a molecular understanding of processes related to the corrosion inhibition mechanism [35]. The aim of this section is to obtain detailed insight of the underlying inhibition processes that determine the success of synergistic effect and the failure of individual inhibitor molecules investigated in the current study. MD simulation was performed for all used inhibitors using Discover module implemented in Materials studio software. All simulation systems reach equilibrium only if both energy and temperature reach balance [36,37]. The temperature and energy fluctuation curves are represented in Fig. 4. From the data in Fig. S9 (supporting information), it is apparent that the system tends to attain equilibrium by the end of the simulation process. Fig. 5 shows

<p>| Table 4 – EIS results for MS in 1 M HCl solution without and with different concentrations of studied systems at 30 °C. |</p>
<table>
<thead>
<tr>
<th>NaCMC (ppm)</th>
<th>GS (1 ppm)</th>
<th>Rs (Ω cm(^2))</th>
<th>Rp (Ω cm(^2))</th>
<th>(\Delta)</th>
<th>C(_{eq} \times \times 10^{-4}) (F/cm(^2))</th>
<th>%EIS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl NaCMC</td>
<td>–</td>
<td>4.77</td>
<td>101.98 ± 1.01</td>
<td>0.0159</td>
<td>2.41</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>3.37</td>
<td>141.43 ± 1.3</td>
<td>0.002</td>
<td>1.82</td>
<td>28.61</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.45</td>
<td>166.59 ± 0.53</td>
<td>0.008</td>
<td>1.42</td>
<td>38.83</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>2.92</td>
<td>218.37 ± 2.4</td>
<td>0.006</td>
<td>1.01</td>
<td>53.71</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>7.79</td>
<td>260.98 ± 2.8</td>
<td>0.021</td>
<td>0.97</td>
<td>61.30</td>
<td></td>
</tr>
<tr>
<td>– 12-E2-12</td>
<td>10</td>
<td>4.82</td>
<td>194.43 ± 1.5</td>
<td>0.008</td>
<td>1.70</td>
<td>47.5</td>
</tr>
<tr>
<td>100</td>
<td>2.46</td>
<td>216.52 ± 2.0</td>
<td>0.005</td>
<td>1.27</td>
<td>53.42</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1.32</td>
<td>299.16 ± 3.0</td>
<td>0.032</td>
<td>0.94</td>
<td>65.91</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>2.44</td>
<td>426.97 ± 0.65</td>
<td>0.002</td>
<td>0.84</td>
<td>76.12</td>
<td></td>
</tr>
<tr>
<td>– 14-E2-14</td>
<td>10</td>
<td>1.17</td>
<td>231.14 ± 3.9</td>
<td>0.0609</td>
<td>0.96</td>
<td>56.30</td>
</tr>
<tr>
<td>100</td>
<td>3.85</td>
<td>312.67 ± 4.0</td>
<td>0.0090</td>
<td>0.94</td>
<td>67.38</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.55</td>
<td>490.55 ± 4.9</td>
<td>0.0627</td>
<td>0.84</td>
<td>79.21</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>3.57</td>
<td>729.72 ± 8.2</td>
<td>0.0195</td>
<td>0.78</td>
<td>86.15</td>
<td></td>
</tr>
<tr>
<td>– 16-E2-16</td>
<td>10</td>
<td>3.86</td>
<td>262.09 ± 1.8</td>
<td>0.0225</td>
<td>0.91</td>
<td>61.22</td>
</tr>
<tr>
<td>100</td>
<td>22.08</td>
<td>387.93 ± 2.0</td>
<td>0.3304</td>
<td>0.73</td>
<td>73.71</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>22.19</td>
<td>769.38 ± 6.5</td>
<td>0.1097</td>
<td>0.69</td>
<td>86.94</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>22.25</td>
<td>1209.01 ± 13.0</td>
<td>0.2997</td>
<td>0.62</td>
<td>91.61</td>
<td></td>
</tr>
</tbody>
</table>
bition effect may have resulted from a combination of effects induced by carbon chain length and heteroatoms that play a crucial role in several corrosion inhibition systems. The presence of several reactive sites such as nonbonding electrons present on nitrogen and oxygen atoms of the inhibitor molecules as well as functional groups enhances the tendency of said compounds to donate their electrons to the vacant d-orbitals of iron atoms [38].

Table 5 shows the binding ($E_{\text{binding}}$) and interaction ($E_{\text{interaction}}$) energies of all inhibitors obtained under equilibrium conditions for both systems. As can be seen from Table 5, all individual inhibitor systems have low values of binding energies. These findings are somewhat not surprising given the fact the previous observations. On the other hand, further inspection of the table shows that combination of NaCMC with 12-E2-12, 14-E2-14, and 16-E2-16 have high negative values of interaction energy, therefore, they are associated with strong, stable and spontaneous adsorption on Fe(110) surface [39]. The high magnitude of the binding energies for all inhibitor molecules indicates that they adsorbed through their more than one adsorption centers [40,41]. The heteroatoms and π-electrons are the potential reactive sites that can coordinate with iron surface through donation and back-donation of electrons.

Larger the value of binding energy, stronger the adsorption of inhibitor molecules would be obtained. The simulations result also indicate that 12-E2-12 and 14-E2-14 have significantly less interaction energy than 16-E2-16, although in contrast, a slight difference was observed in the adsorption profile of the three systems. The insights gained from this study provide further evidence of a strong association between heteroatoms and inhibitive performances. They also confirm that the synergistic effect has a marked influence on the corrosion inhibition process. These findings contribute in several ways to our understanding of synergistic effect and provide a basis for developing future strategies for corrosion inhibitor design.

To interpret deeply the role of heteroatoms on inhibitor-iron interactions; the radial distribution function (RDF) [42], which is used to calculate the distance between oxygen, carbon and nitrogen atoms of inhibitors and iron atoms in the uppermost layer after adsorption of inhibitor molecules, was examined. The RDF results for each mixed inhibitors are provided in Fig. 6. Referring to literature that if the distances between two atoms are 1–3.5 Å, and greater than 3.5 Å, the types of interaction will be chemisorption, and physisorption, respectively. In Fig. 6, we can observe that the RDF of heteroatoms and carbon atoms for all inhibitor molecules yielded

The most obvious finding to emerge from this figure is that 12-E2-12, 14-E2-14, and 16-E2-16 are generally placed into the water phase while little interactions were observed in the case of NaCMC. These results accord with our experimental observations, which showed that all tested inhibitor molecules are not suitable enough for effective protection. Then we shall move on to describe how synergistic effect can influence on the conformation and therefore the adsorption ability of the inhibitor molecules on Fe(110) surface. To this end, MD simulations have been done for NaCMC with 12-E2-12, 14-E2-14, and 16-E2-16 (Fig. 5).

It can be seen from the Fig. 5 that the inhibitor molecules are adsorbed on the iron surface in a parallel manner which can help ensure coverage of a maximum surface area of the corroded metal. Inhibitor molecules were allowed to interact with each other freely, and it can be observed that all molecules are adsorbed on Fe-atoms of the first layer surface in nearly parallel mode, which ensures strong interactions and by extension high inhibition effect. Therefore, it is thought that NaCMC with 12-E2-12, 14-E2-14, and 16-E2-16 have a synergistic inhibitory effect on steel corrosion, and the inhibition effect may have resulted from a combination of effects induced by carbon chain length and heteroatoms that play a crucial role in several corrosion inhibition systems. The presence of several reactive sites such as nonbonding electrons present on nitrogen and oxygen atoms of the inhibitor molecules as well as functional groups enhances the tendency of said compounds to donate their electrons to the vacant d-orbitals of iron atoms [38].

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Fig. 5 – Side and top view of the final adsorption of 12-E2-12, 14-E2-14, and 16-E2-E2 in combination with NaCMC on Fe(110) surface in solution.

4. Conclusions

All investigated inhibiting systems act as effective MS corrosion inhibitor in 1 M HCl solution and the inhibition efficiency follows the order NaCMC/16-E2-16 > NaCMC/14-E2-14 > NaCMC/12-E2-12 at 30°C. There is slight difference in their efficiency values obtained from different methods employed. Besides, the inhibition efficiencies increase with incremental concentration and alkyl chain attached to the ammonium group, which was further confirmed by PP, EIS, SEM and MD simulation observations. PP measurements showed that the inhibitors influence both the anodic and cathodic processes (mixed-type inhibitor). The adsorption of studied inhibitors on MS follows Langmuir adsorption isotherm. SEM images confirm the formation of protective film on the metal surface. MD simulation studies showed that the inhibitor molecules are adsorbed on the iron surface in a parallel manner which ensures coverage of a maximum surface area of the corroded metal. The high magnitude of the binding energies for all inhibitor molecules indicate that they are adsorbed through their more than one adsorption centers. Due to synergistic effect of NaCMC with 12-E2-12, 14-E2-14, and 16-E2-16, it is proposed that the inhibition effect may have resulted from a combination of effects induced by carbon chain length and heteroatoms.

a sharp first peak, indicating the strong affinity of inhibitors towards the iron atoms. The results show that the bonding length of Fe-C, and Fe-O are all less than 3.5 Å while Fe-N distances are higher than 3.5 Å. These results signify the close contact between inhibitor molecules and the iron surface and that the chemical interaction between inhibitors and iron atoms seems to be the most likely dominant inhibition mechanism [43]. Whereas the contribution of physical interactions is mainly from the interaction between protonated nitrogen atoms and iron surface.
Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.07.065.

REFERENCES


Mohd Mobin is a Professor in the Department of Applied Chemistry, Aligarh Muslim University Aligarh, India. He received his M.Sc., M. Phil. and Ph.D. degrees from the same university. He has also served as Corrosion Researcher at Saline Water Conversion Corporation, Saudi Arabia. His present research interests are in the area of corrosion.
inhibitors (surfactants, amino acids, natural and synthetic polymers) and conducting polymers as corrosion protective coatings.

Ruby Aslam is currently a Ph.D. student in the Department of Applied Chemistry, Aligarh Muslim University, Aligarh, India. She received her M.Sc. and M.Phil degrees from the same university.

Jeenat Aslam is currently an Assistant Professor department of Chemistry, College of Science, Taibah University, Yanbu, Al-Madina, Saudi Arabia. She received her M.Sc. and Ph.D. degrees from Aligarh Muslim University, Aligarh, India. Her present research interests are in the area of corrosion inhibitors, conducting polymers as corrosion protective coatings, nanoparticles and colloids & surface sciences.

Dr. Hassane Lgaz is a Research Assistant Professor at Konkuk University, Seoul, South Korea. His area of research is Physical Chemistry and quantum chemical modeling.