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Anti-Corrosion and Computational Study of Mild Steel in Hydrochloric Acid Using Calcium Gluconate as Inhibitor

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The inhibiting effect of calcium gluconate on the electrochemical behaviour of mild steel in dilute hydrochloric acid was evaluated through weight loss technique, open circuit measurement and potentiodynamic polarization tests at specific concentration of the organic compound. Corrosion rate were calculated from the potentiodynamic polarization measurements. The surface morphology of the mild steel was examined using scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS). A molecular dynamics simulations with Forcite quench molecular dynamics was used for the computational study of the system. The results revealed that corrosion rate of the mild steel decreased with addition of the inhibitor. Equally, increasing inhibitor concentration led to significant reduction in the corrosion rate of the mild steel with inhibitor efficiency values above 80 %. The potentiodynamic polarization data showed that calcium gluconate acts as mixed type corrosion inhibitor. The inhibition occurs by adsorption of films on the metal surface. The adsorption of calcium gluconate has been found to obey Langmuir adsorption isotherm at all the concentrations of calcium gluconate.

Keywords: Calcium gluconate, Metal interface, Langmuir adsorption, Corrosion inhibition.

INTRODUCTION

The application of steel and its alloys have been widely reported in the industry due to its excellent properties. However, in various service conditions the alloy is faced with corrosion problem usually in some aggressive environment [1]. More than millions of dollars are lost every year due to corrosion. Corrosion damage causes leakage of fluids or gases in devices and containers made of alloy materials. Even more dangerous is the loss of strength of engineering structures induced by corrosion leading to subsequent failure. Mild steel is widely used in many applications such as desalination plants, construction materials, pharmaceutical industry, thermal power plant, chemical cleaning and pickling process, oil and gas industry *etc*., due to their stability, good corrosion resistance, high strength, weldability [1]. The use of organic inhibitors is one of the most practical methods for protecting metals against corrosion. It has been reported that many heterocyclic compounds containing hetero atoms like N, O, S, have been proved to be effective inhibitors for the corrosion of steel in acid media [2-8]. The influence of such organic compounds, on the corrosion of mild steel in acidic solution has been investigated by several authors [8-10]. The corrosion inhibition property of these compounds is attributed to their molecular structure. The planarity and the lone pair electrons in the hetero atoms are important features that determine the adsorption of these molecules on the metallic surface. The effect of inhibitors adsorbed on metallic surfaces in acid solutions, is to slow down the cathodic reaction as well as the anodic process of dissolution of the metal. Such effect is obtained by forming a barrier of diffusion or by means of the blockage of the reaction sites and thereby reducing the corrosion rate [11]. Gluconate and gluconic acids are known to be cheap, effective, non-toxic and environmentally friendly inhibitors for iron and mild steel in cooling water [12]. There are several reports showing the ability of gluconate to hinder the corrosion of carbon steel and their environmental compatibility [13,14]. Rajendran *et al.* [15] reported the inhibition efficiency of calcium-gluconate for mild steel in neutral aqueous solution containing 60 ppm chloride ions. However most of the investigations on the inhibition effects of gluconates have been carried out in chloride free or in low chloride neutral aqueous environment in ideal condition [11,16-18]. These do not reflect the inhibition action in real situation. The objective of this work is to investigate

the corrosion inhibition efficiency and adsorption mechanism of calcium gluconate on mild steel in 0.5 M hydrochloric acid through weight loss, open circuit potential measurement and potentiodynamic polarization method.

EXPERIMENTAL

Mild steel used for this investigation has the following nominal chemical composition: 0.150C, 0.180Si, 0.450Mn, 0.031S, 0.010P, 0.008Ni, 0.005Al and the rest being Fe. Calcium gluconate was used as corrosion inhibitor in the present study. The structural formulae is shown in Fig. 1.

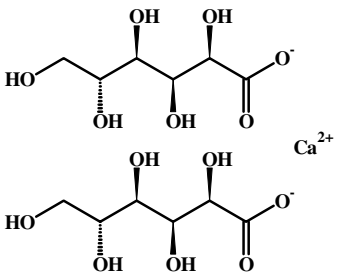

Fig. 1. Structure of calcium gluconate

The test media used for the investigation consists of 200 mL of 0.5 M dilute HCl of Analar grade prepared with distilled water in addition to the specified concentration of potassium gluconate. A mild steel of 20 mm × 20 mm × 2 mm was used for potentiodynamic measurement. A 3 mm hole was drilled at the centre for suspension for the weight loss coupons. These mild steel specimens were then thoroughly rinsed with distilled water and cleansed with acetone before analysis.

Weight-loss analysis: Weighted samples were fully and separately immersed in 200 mL of 0.5 M dilute HCl at specific concentrations of calcium gluconate for 360 h at ambient temperature of 27 °C. Each of the test specimens was taken out every 72 h, washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss (mg) and corrosion rate (mm/y) with exposure time (h) and those of percentage inhibition efficiency (IE, %) (calculated) with exposure time (h) were done.

The corrosion rate (R) calculated is from eqn. 1:

$$R = \left(\frac{87.6W}{DAT} \right) \quad (1)$$

where W is the weight loss in milligrams, D is the density in g/cm^2, A is the area in cm^2 and T is the time of exposure in hours. The inhibition efficiency (%) was calculated from the relationship in eqn. 2:

$$IE\ (\%) = \left(\frac{W_1 - W_2}{W_1} \right) \times 100 \quad (2)$$

W_1 and W_2 are the weight loss (in the absence and presence of calcium gluconate). The IE (%) was calculated for all the inhibitors every 72 h during the course of experiment, while the surface coverage (θ) is calculated from the relationship:

$$\theta = \left(1 - \frac{W_2}{W_1} \right) \quad (3)$$

where θ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent. W_1 and W_2 are the weight loss of mild steel coupon in free and inhibited acid solution.

Open circuit potential and linear polarization resistance measurement: A two-electrode electrochemical cell with silver/silver chloride was used as reference electrode. The measurement of open circuit potential was obtained with Autolab PGSTAT 30 ECO CHIMIE potentiostat. Resin mounted test electrode/specimens with an exposed surface of 250 mm^2 were fully and separately immersed in 200 mL of the test media (acid) at specific concentrations of calcium gluconate for total of 7200 s. Equally, the potential of each of the test electrodes was measured every 1200 s. The plots of potential E (mV) *versus* immersion time T (h) as shown in the figure for the test medium were made from the tabulated values in table. In the electrochemical test, a glass corrosion cell kit with a platinum counter electrode, a saturated Ag/Ag reference electrode and mild steel sample as working electrode were used. The working electrodes samples were positioned at the glass corrosion cell kit, leaving 250 mm^2 surfaces in contact with the solution. The polarization test was carried out in 0.5 M HCl static solution at room temperature using a potentiostat. The polarization curves were determined by stepping the potential at a scan rate of 2 mV s^{-1} at a potential initiated at -0.5V to +2 V. The polarization curves were plotted using Autolab data acquisition system Autolab PGSTAT 30 ECO CHIMIE potentiostat and both the corrosion rate and potential were estimated by the Tafel extrapolation method using both the anodic and cathodic branches of the polarization curves.

RESULTS AND DISCUSSION

Gravimetric measurement of the specimen: From the result, the rate of corrosion decreased with an increase in calcium gluconate addition at all concentrations. It can be seen that specimen in 2.0 %v/v of inhibitor has the lowest weight loss. Equally, it was demonstrated that at 0.5 % v/v addition of calcium gluconate, the corrosion rate decreased to the minimum. The concentration was able to interact enough with the anodic and cathodic region and cause a more passive activities rather than an active one (Tables 1 & 2 and Fig. 2). It is also important to note that the inhibitive tendency of the calcium gluconate is quite good for the studied conditions. Equally, the un-inhibited mild steel specimen demonstrated to be the least protected expectedly. On the other hand, the corrosion rate decreased with an increase in inhibitor concentration (Fig. 3).

TABLE-1
DATA OBTAINED FOR THE VALUE OF CORROSION RATE, INHIBITOR EFFICIENCY AND SURFACE COVERAGE OF ADSORPTION AT VARYING CONCENTRATION OF CALCIUM GLUCONATE FROM WEIGHT LOSS METHOD

Sample	Inhibitor conc. (%)	Corrosion rate (mpy)	Inhibition efficiency (%)	Surface coverage (θ)
A	0	11.1110	0	0
B	0.5	0.27255	97.55	0.9755
C	1.0	0.58570	94.73	0.9473
D	1.5	1.12430	89.88	0.8988
E	2.0	1.10420	90.06	0.9006

TABLE-2
DATA OBTAINED FROM POLARIZATION RESISTANCE MEASUREMENTS OF MILD STEEL IN 0.5 M HCl-CALCIUM GLUCONATE SOLUTION

Sample	Corrosion rate (mpy)	Inhibitor conc. (%)	ba (V/dec)	bc (V/dec)	E_{corr} (A/cm^2)		i_{corr} (A)	Polarization resistances (Ω)	Inhibition efficiency (%)
					Observed	Calculated			
A	11.111	0	0.160	0.324	-0.565	-0.571	9.560×10^{-4}	36.83	0
B	0.2726	0.5	0.092	0.220	-0.502	-0.510	2.324×10^{-5}	992.44	97.55
C	0.5857	1.0	0.078	0.153	-0.598	-0.598	5.039×10^{-5}	329.91	94.73
D	1.1243	1.5	0.132	0.220	-0.616	-0.617	9.673×10^{-5}	237.33	89.88
E	1.1042	2.0	0.219	0.314	-0.616	-0.665	9.502×10^{-5}	303.18	90.06

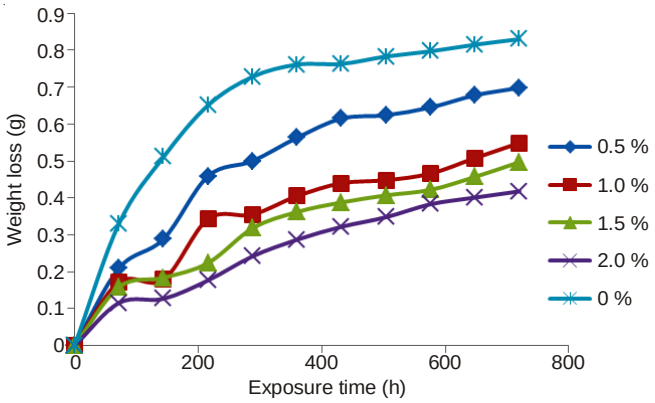

Fig. 2. Variation of weight loss with time for mild steel in HCl solution by calcium gluconate

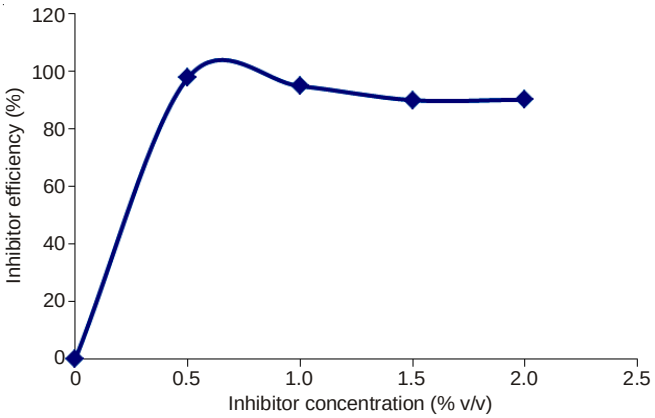

Fig. 4. Variation of the percentage inhibition efficiency with inhibitor concentration

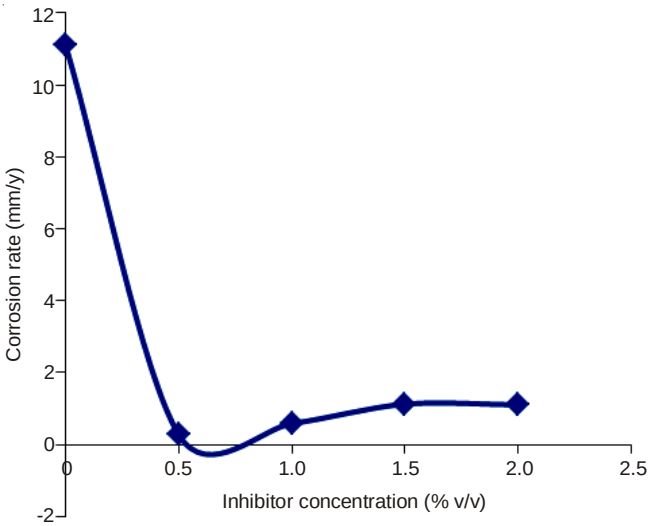

Fig. 3. Variation of corrosion rate with inhibitor concentration

Effect of inhibitor concentration and immersion time: The effect of inhibitor concentration on inhibition efficiency in 0.5 M HCl was presented in Fig. 4. The inhibition efficiency increases with increase in calcium gluconate and the maximum inhibition efficiency of 97.55 % was obtained at an optimum concentration of 0.5 % v/v using polarization technique (Tables 1 and 2). Further increase in the inhibitor concentration equally showed some significant change in inhibitor performance (Fig. 4). The values of corrosion rate (CR), percentage inhibition efficiency (IE %) and surface coverage (θ) at room temperature were summarized in Table-1.

The effect of immersion time on corrosion rate and inhibition efficiency of the calcium gluconate on a time scale, weight loss measurements were performed in 0.5 M HCl in absence and presence of calcium gluconate with optimum 2.0 % v/v concentration for up to 360 h immersion time at 27 °C. Inhibition efficiencies were plotted against inhibitor concentration as seen from Fig. 4. The result shows that inhibition efficiency of the calcium gluconate was increased with increasing concentrations. The increase in inhibition efficiency beyond 700 s indicates the strong adsorption of constituents present in the calcium gluconate on the mild steel surface, leading to a more protective layer formed at mild steel-hydrochloric acid solution interface.

Open circuit potential and potentiodynamic polarization studies: The corrosion potential, E (V), decreases with the electrochemical exposure time for all calcium gluconate additions (Fig. 5). This becomes stable (passive) with open circuit exposure time throughout the study. This shows that the resistances of the mild steel to corrosion attach increases with increasing exposure time and that the coupons later developed passivity against corrosion. At this 'stable-level', it is believed that the mild steel have some level of immunity as a result of the corroding products which covers the mild steel surface and retard/stabilizes corrosion attack. These observations are not uncommon. It can also be observed for example that 0.5 %v/v of calcium gluconate that gave best corrosion resistance still have moderate but higher corrosion potential.

Fig. 6 shows the potentiodynamic polarization curves for mild steel in 0.5 M HCl in acid solution and in presence of different concentration of calcium gluconate from 0.5-2.0 % v/v. The various electrochemical parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}) and Tafel constants (ba and bc) were given in Table-2. It was observed that addition of calcium gluconate lowers the current density (i_{corr}). The values of corrosion potential E_{corr} do not change but

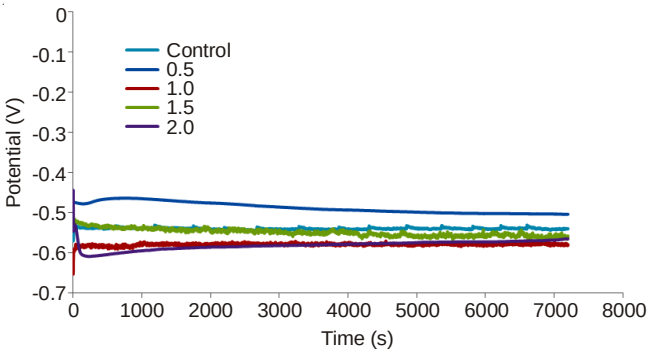

Fig. 5. Open circuit polarization curves for mild steel in 0.5 M HCl solution with and without calcium gluconate addition

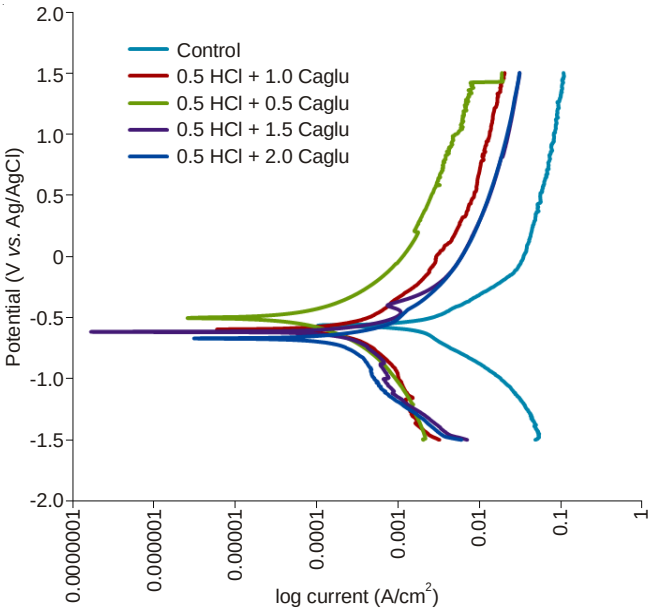

Fig. 6. Potentiodynamic polarization curves for mild steel in 0.5 M HCl solution with and without calcium gluconate (Caglu) addition

however; both Tafel constants were strongly changed in the presences of the inhibitor suggesting that calcium gluconate behave as mixed typed inhibitor. This is also in agreement with other reports [19,20].

Adsorption isotherm and free energy of adsorption: The degree of surface coverage (θ) from 0.5-2.0 % v/v of calcium gluconate in 0.5 M HCl at 27 °C for 360 h immersion time were evaluated from gravimetric method values. Attempts were made to fit these θ values to Langmuir isotherms. According to these isotherms, θ is related to the inhibitor concentration, C in h: A straight line was obtained on plotting C/θ *versus* C and a correction factor of 0.999 was obtained as shown in Fig. 7. This shows that the calcium gluconate inhibitor is assumed to obey Langmuir adsorption isotherm [19,21,22].

The value of free energy of adsorption (ΔG_{ads}) for all the concentration considered in this work are negative suggesting a spontaneous adsorption of inhibitor molecules on the surface of the mild steel. Generally, values of ΔG_{ads} up to -20 kJ/mol are consistent with physisorption while those around -40 kJ mol/or higher are associated with chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond.

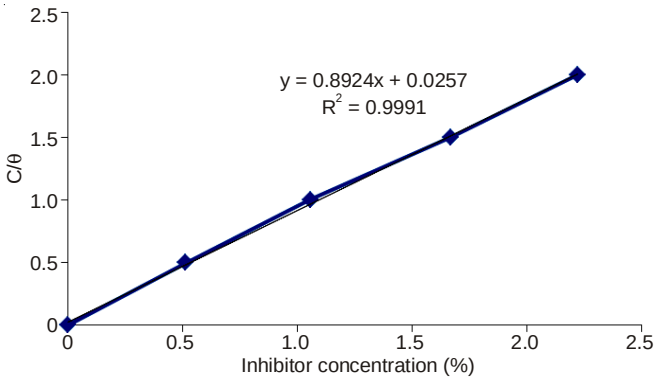

Fig. 7. Langmuir isotherm for the adsorption of the calcium gluconate on the mild steel surface in 0.5 M HCl solution at 27 °C

Based on our results, the values obtained for (ΔG_{ads}) using 0.5 % v/v calcium gluconate addition is -21.13846 kJ/mol. This suggest a physisorption, therefore, it can be said that the adsorption mechanism of molecules of calcium gluconate on the mild steel surface in HCl solution was proposed to be physisorption. Similarly to the previous report elsewhere [23,24]. This occurrence was also supported in Fig. 8, that at 0.5 %v/v calcium gluconate addition the mild steel have higher value of K_{ads} (79.63) corresponding to higher value of (ΔG_{ads}) (Table-3 and Fig. 8).

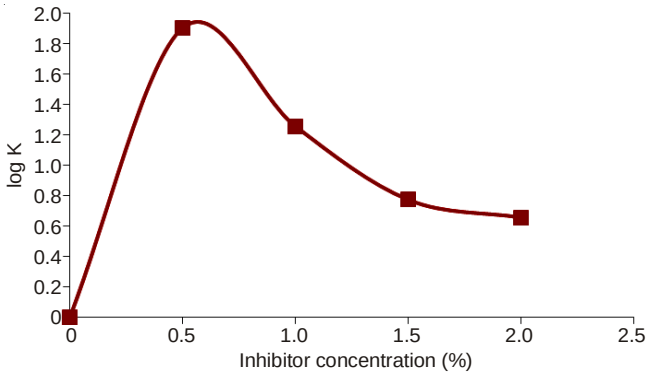

Fig. 8. Relationship between the log of the equilibrium constant of adsorption K and the inhibitor concentration C

TABLE-3
DATA OBTAINED FOR THE VALUE OF GIBBS FREE ENERGY, SURFACE COVERAGE AND EQUILIBRIUM CONSTANT OF ADSORPTION AT VARYING CONCENTRATION OF CALCIUM GLUCONATE

Sample	Inhibitor conc. (%)	Surface coverage (θ)	Equilibrium constant of absorption (K_{ads})	Gibb's free energy (G_{ads}) (J/mol)
A	0	0	0	0
B	0.5	0.9755	79.63	-21138.46
C	1.0	0.9473	17.975	-17398.72
D	1.5	0.8988	5.9209	-14600.73
E	2.0	0.9006	4.5302	-13926.18

Molecular dynamics (MD) simulations: Adsorption of calcium gluconate molecules on the metal surface was analyzed at a molecular level by molecular dynamics (MD) simulations, using Forcite quench molecular dynamics to sample many different low-energy configurations and identify the low-energy minima. Calculations were carried out, using the COMPASS

force field and the Smart algorithm, in a simulation box 30 Å × 25 Å × 29 Å with periodic boundary conditions to model a representative part of the interface, devoid of arbitrary boundary effects. The box composed of the Fe slab, cleaved along the (110) plane and a vacuum layer of 20 A° height (Fig. 9). The geometry of the bottom layer of the slab was constrained to the bulk positions, whereas other degrees of freedom were relaxed before optimizing the Fe (110) surface, which was subsequently enlarged into a 10 × 9 supercell.

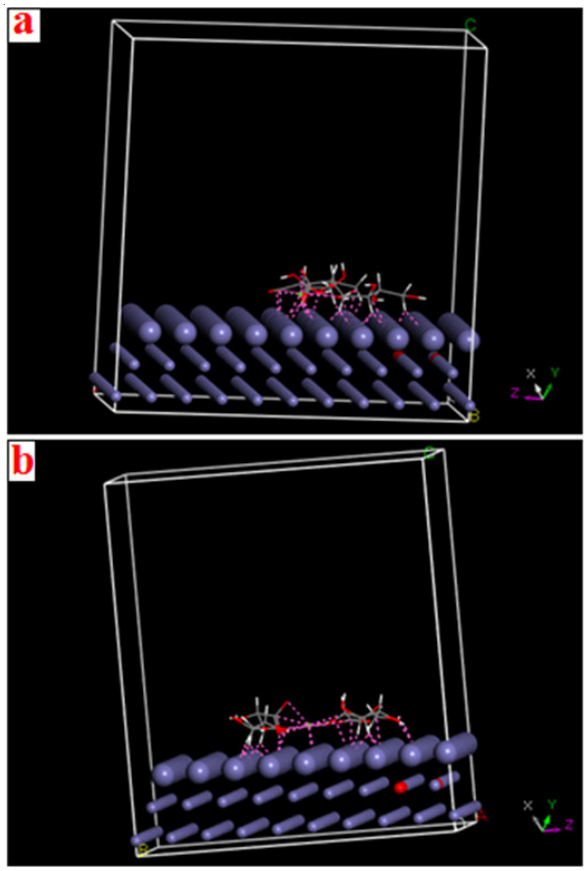

Fig. 9. Images are how the molecule adsorbs itself on the surface of the metal (a) top and (b) side view

The molecules were adsorbed on one side of the slab. Temperature was fixed at 350 K, with NVE (microcanonical) ensemble, with a time step of 1 fs and simulation time 5 ps. The system was quenched every 250 steps. Optimized structures of calcium gluconate and the Fe surface were used for the simulation. The molecule can be seen to maintain a flat-lying adsorption orientation on the Fe surface, as expected from the delocalization of the electron density all around the molecules. This orientation maximizes contact with the metal surface and hence augments the degree of surface coverage. The adsorption energy (E_{ads}) for the most stable configuration of the constituents on the Fe (110) surface was computed using the relationship below:

$$E_{ads} = E_{total} - (E_{mol} + E_{Fe}) \quad (4)$$

E_{mol}, E_{Fe} and E_{total} correspond to the total energies of the molecule, Fe (110) slab and the adsorbed mol/Fe (110) couple in the gas phase. A negative value of E_{ads} corresponds to a stable adsorption structure. The total energies were calculated by averaging the energies of the five most stable representative adsorption configurations. This strong affinity of the molecule for the Fe surface accounts for the remarkable corrosion inhibition efficacy of the compound as observed experimentally.

SEM/EDS for the surface morphology of the mild steel: The morphology of the polished, with and without inhibitor of calcium gluconate were examined and presented in Figs. 10-13. These show the surface morphology of the coupons without and with inhibitor addition. Fig. 10 shows the surface of as-received mild steel. The morphology of the inhibited surface with 0.5 %v/v indicates a fair surface degradation as compare to Figs. 12 and 13. There exist surface damage during corrosion and as expected rough, uneven surface covered with cracks were seen (Figs. 12 and 13). More severe cracks and pits were seen, especially with Fig. 12. However, no pits and cracks were observed in the morphology of the coupon with inhibitor (Fig. 11). The protective film formed on the surface of the mild steel confirmed by SEM/EDS also supports the high inhibition efficiency exhibited by the calcium gluconate in the study condition. This is in conformity with earlier reports [25,26].

Conclusions

• The corrosion rate decreased with an increase in addition of calcium gluconate and with its concentrations. • There was

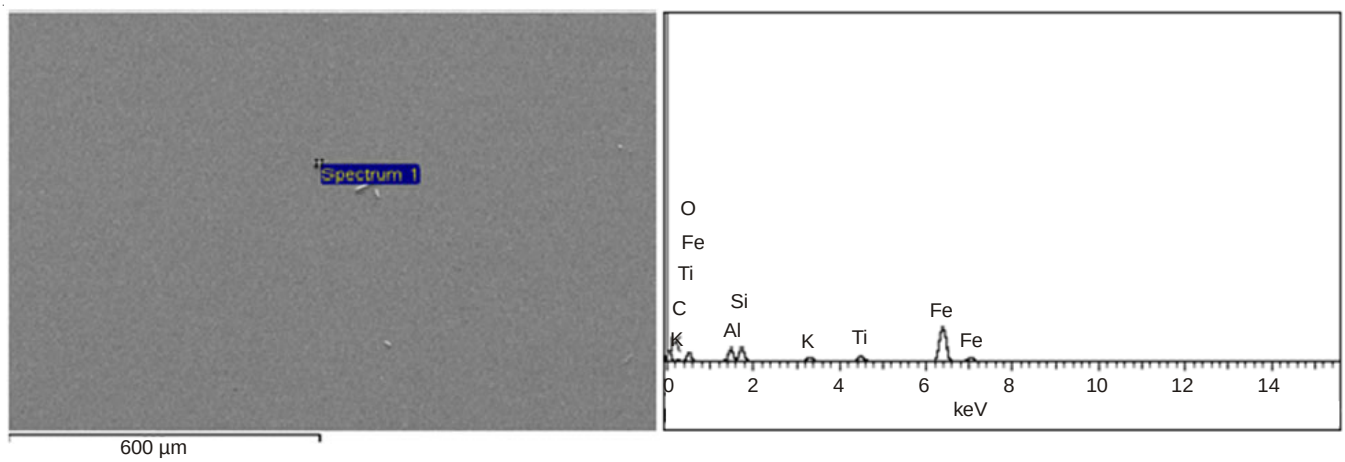

Fig. 10. SEM micrographs and EDS of as-received mild steel

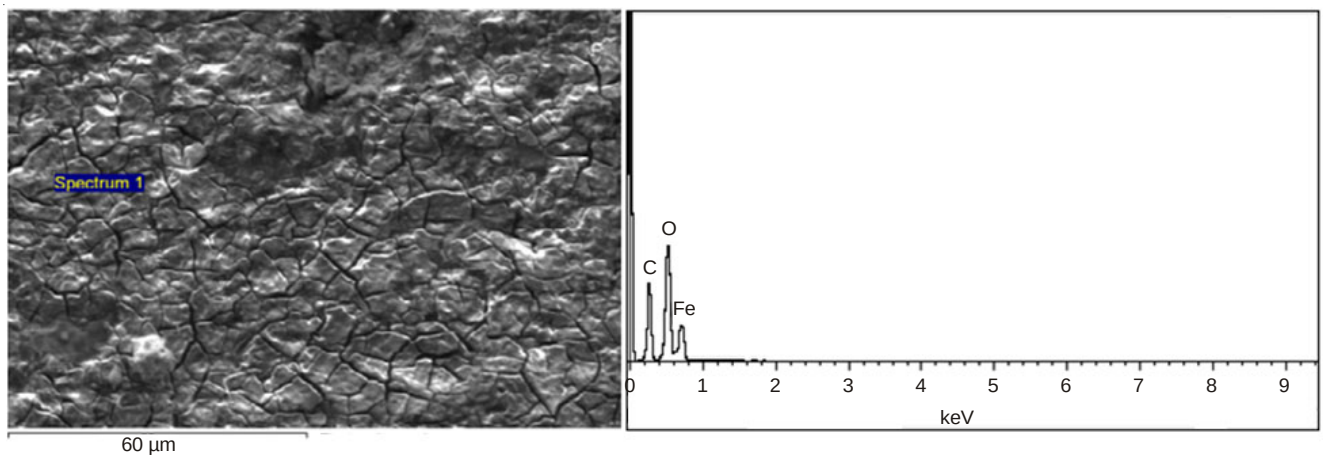

Fig. 11. SEM micrographs and EDS of 0.5 % calcium gluconate in mild steel-HCl solution

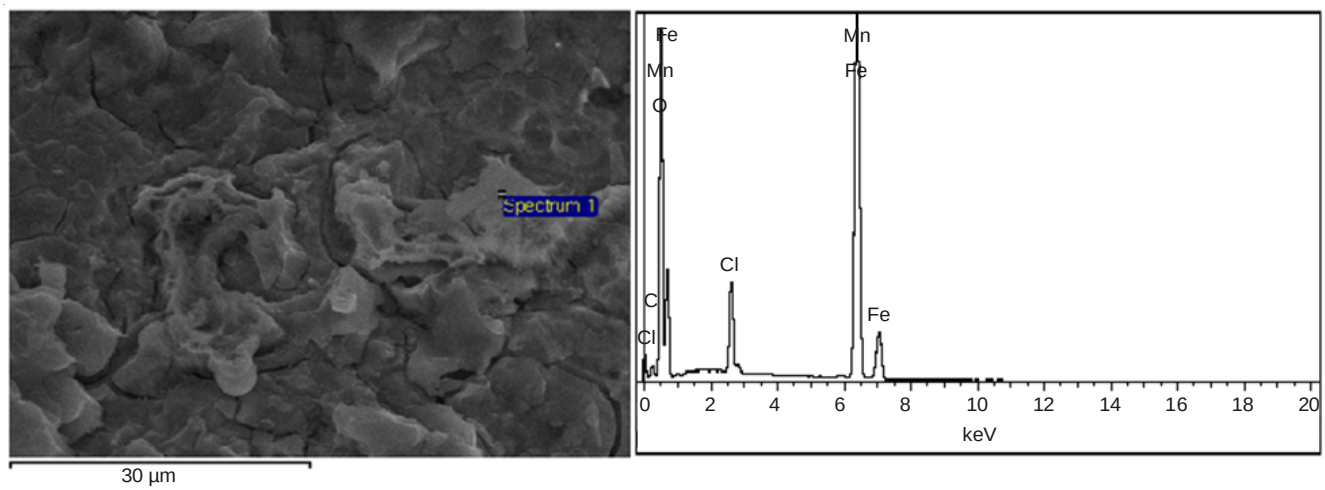

Fig. 12. SEM micrographs and EDS of 1.0 % calcium gluconate in mild steel-HCl solution

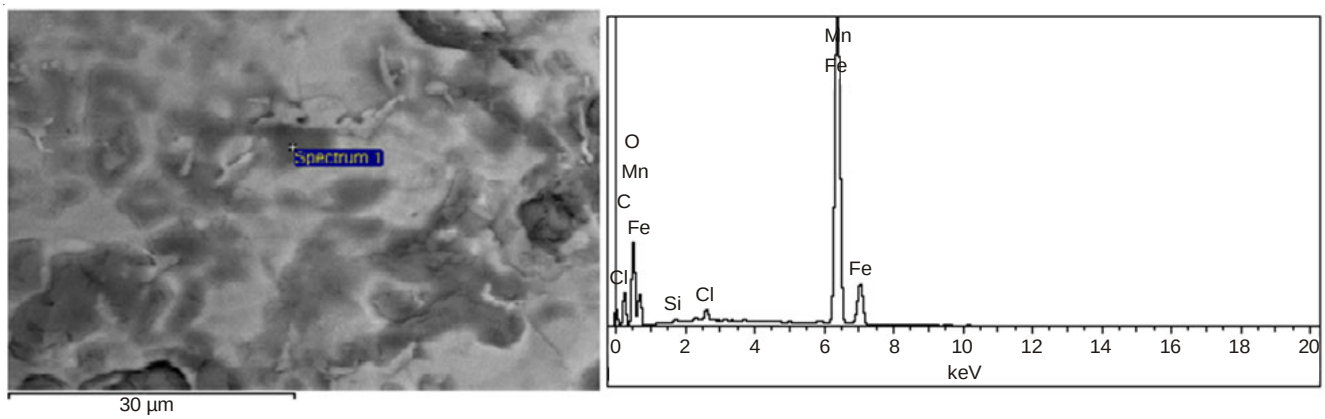

Fig. 13. SEM micrographs and EDS of 1.5 % calcium gluconate in mild steel-HCl solution

a reasonable inhibition efficiency that was exhibited by calcium gluconate for the corrosion of mild steel in HCl solution. • The Langmuir adsorption isotherm fits the experimental data obtained in this study. Hence a monolayer film was assumed to have formed on the mild steel surface. • That the adsorption mechanism of molecules of calcium gluconate on the mild steel surface in HCl solution has been proposed to be by physisorption process. • The molecular dynamics simulation showed how the molecule adsorbs itself on the surface of the metal and the strong affinity of the molecule for the Fe surface accounts for the remarkable corrosion inhibition efficacy of the compound as observed experimentally.

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