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Inhibition Effect of Hydrazine-Derived Coumarin on a Mild Steel Surface in Hydrochloric acid

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ABSTRACT

In this work, economy novel hydrazine-derived coumarin 4-(6-methylcoumarin)acetohydrazide (MCA) were synthesized, characterized, and tested as an inhibitor for the corrosion of a surface of mild steel in an acidic environment through weight loss and Scanning electron microscopy (SEM) techniques. Results showed that the synthesized inhibitor can inhibit the corrosion of mild steel surface in a 1 M hydrochloric acid environment. The corrosion inhibition efficiency of MCA increases with increasing MCA concentration and decreases with increasing temperature. SEM analysis showed the formation of a film as a protective layer from MCA molecules on the surface of mild steel. Adsorption of the MCA molecules on the mild steel surface in the presence of hydrochloric acid environment was obeyed Langmuir isotherm. The density functional theory (DFT) calculations were used to study the relationship between molecular structure and inhibition efficiency and they found in good agreement.

Keywords: 6-methylcoumarin, acetohydrazide, Corrosion inhibitor, DFT, NMR, MCA.

1. Introduction

Generally, one of the significant alloys used in many industrial processes is mild steel due to its superior mechanical characteristics and cost-effectiveness. Mild steel is quite sensitive to corrode in various acidic and basic solutions [1-3]. Unfortunately, widely acidic solutions were used in various industries such as pickling, cleaning, oil well acidizing, steel acid descaling, petroleum processes, rust removal, and ion exchangers as hydrochloric acid [4-6]. To control the corrosion of mild steel, various approaches have accordingly been used. The most efficient technique was used the corrosion natural inhibitors due to significant characteristics, such as eco-friendly, low cost, superior performance, and applicability in different approaches [7,8]. Organic molecules can be adsorbed on mild steel surface through nitrogen, sulfur, oxygen, and phosphorus heteroatoms, in addition to pi-bonds and ion-pairs [9]. Coumarins act as corrosion inhibitors due to the presence of aromatic systems and heteroatoms, which adsorb onto the mild steel surface via ion-pairs of electrons on heteroatom. This induces superior adsorption of the inhibitor molecules and excellent inhibition efficiency in addition to decreases the corrosion rate [10-13]. Physisorption and/or chemisorption are the techniques that inhibitors adsorb onto a surface of mild steel and form a film as a protective barrier from acidic solutions [14]. The formation of protective film was due to electrostatic forces between the positive charges of the mild steel surface and negative charges of inhibitor molecules, in addition to charge transfer of nonbonding and/or pi-electrons of inhibitor molecules to unoccupied d-orbitals of iron atoms of the mild steel surface. Moreover, iron donates the electrons to the inhibitor molecules (π*-orbitals of an aromatic system) and form feedback bonds, through chemisorption action [15]. Nature and chemical structure of inhibitor in addition to mild steel surface charge were the main parameters that influence the inhibition efficiency of inhibitors due to the formation of adsorbed layers on the surface of mild steel. Therefore, the impact of coumarins having pi-system, heteroatoms, and polar group on the corrosion impedance remains to be studied. We noted that the presence of donating groups such as methyl group will increase the inhibition efficiency of the inhibitors [16,17] and hence the effect substituted coumarin with amino atoms (heteroatom) and methyl group (donating group) was investigated in this study. In this study, a new coumarin compound as shown in Figure 1, namely "4-(6-methylcoumarin)acetohydrazide (MCA)" acts as a superior eco-friendly corrosion inhibitor of mild steel in 1 M HCl solution, was designed, synthesized, and spectroscopically characterized. The inhibition efficiency was tested by weight loss measurements and surface assessment technique (scanning electron microscopy). Results

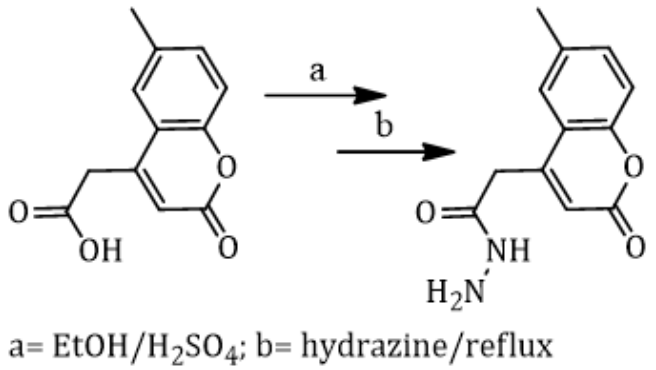


Figure 1. Chemical Structure of the Synthesized ecofriendly

demonstrate that MCA molecules have excellent inhibition efficiency, at high and low concentrations, compared to previous work of synthesis of new corrosion inhibitors [18-40].

2. Experimental section

2.1 Chemistry

Chemicals were used as supplied without further purification (Sigma-Aldrich, KL, Malaysia). The Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded using a Thermo Scientific Model Nicolate 6700 Spectrophotometer. CHN analysis was done using Carlo Erba 5500 CHN elemental analyzer. Nuclear magnetic resonance (NMR) spectra were recorded on an AVANCE III 600 MHz spectrometer.

2.2 Synthesis of 4-(6-methylcoumarin)acetohydrazide (MCA)

An ethanolic solution of 4-(6-methylcoumarin)-acetic acid (50 gm) was allowed to reflux for 6 h., in presence of concentrated sulfuric acid (few drops). The reaction mixture was poured into ice-water to obtain the ethyl (6-methylcoumarin)acetate. After that an equimolar quantities of ethyl (6-methylcoumarin)acetate (50 gm) and hydrazine hydrate was reflux for 12 h., then poured into ice, filtered, and recrystallized from ethanol. Solid yield (52%);mp over 300 °C. Anal. Calcd for $C_{12}H_{12}N_2O_3$: C, 62.06; H, 5.21; N, 12.06%. Found: C, 61.98; H, 5.17; N, 11.94%. ^{1}H NMR (DMSO-d6): δ (ppm), 2.31 (s, 3H, –CH_3), 3.27 (s, 2H, -CH_2), 6.03 (d, ^{1}H, -CH=C-), 8.05 (s, 1H, NH), s, 7.23-7.51 (^{1}H, Aromatic ring). ^{13}C{1H} NMR (DMSO-d6): δ (ppm), 19.8 -CH3, 117.4, 121.3, 126.8, 131.8, 134.9, 148.7, (benzene ring); 113.6, 154.8, 163.2 (pyron ring); 47.2 (CH_2); 167.9 (C=O).

2.3 Electrode and Electrolytes

Mild steel samples having a chemical composition of (wt %) 0. 0.21% C, 0.35% Mn, 0.05% Si, 0.38% S, 0.01% Al, 0.09% P, and balance Fe were used for gravimetric studies and surface analysis. The effective surface area of 4.5 cm^2. Initially, the coupons were polished using emery papers and washed with acetone, double distilled water, dried at

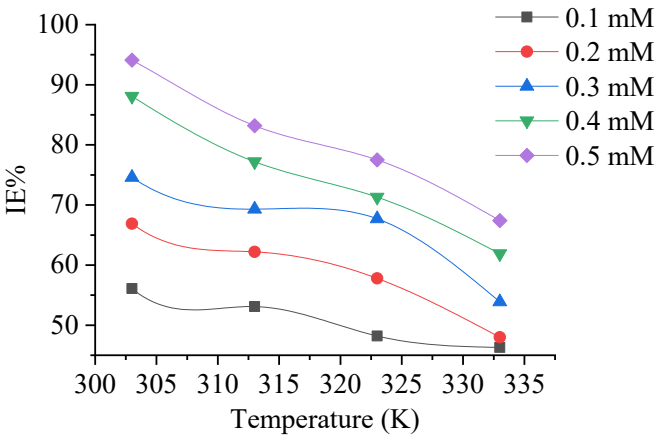


Figure 2. Inhibition Efficiencies measured by Weight Loss of Mild Steel in 1.0MHCl in presence of different Concentrations of MCA at Various Temperatures

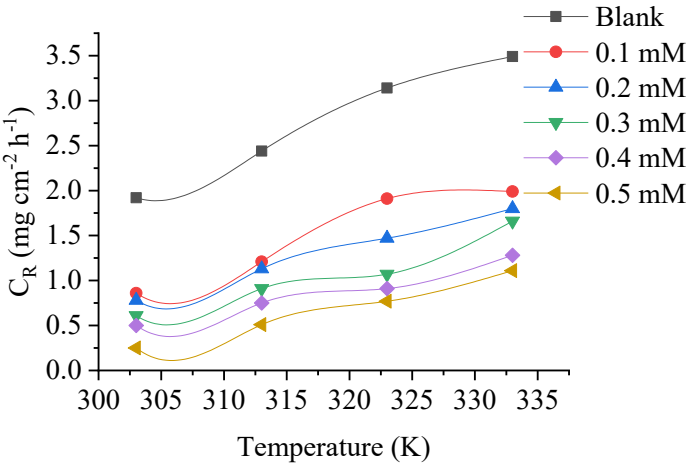


Figure 3. Corrosion rates measured by Weight Loss of Mild Steel in 1.0MHCl in presence of different Concentrations of MCA at Various Temperatures

room temperature, and immediately used for gravimetric studies and surface analysis [41]. Hydrochloric acid solutions of 1 M were prepared by using double distilled water. The concentrations of MCA were 0.1, 0.2, 0.3, 0.4 and 0.5 mM.

2.4 Weight Loss Measurements

Gravimetric techniques were performed by weighing the coupons before and after immersion in 500 mL of 1.0 M hydrochloric acid solution having various concentrations of MCA as an investigated inhibitor for 5 h at different temperatures. The experimental methods were carried out in atmospheric ambient. The thermostat was used to control the solution temperature. The mean results were calculated for each duplicate experiment and the inhibitive efficiencies (%IEs), surface coverage (θ), and corrosion rate (C_R) were calculated using equations 1, 2, and 3 [42,43] respectively.

$$IE\% = \frac{W_o - W_{in}}{W_o} \times 100 \quad (1)$$

$$\theta = \frac{W_o - W_{in}}{W_o} \quad (2)$$

$$CR = \frac{W_o - W_{in}}{at} \quad (3)$$

where Wo & Win =weight loss without & with MCA respectively, A = area and T=time (h).

Gravimetric techniques were repeated at various temperature (303, 313, 323, and 333 K) without and with the addition of various MCA concentrations, to calculate the impact of temperature on the inhibitive efficiencies of MCA.

2.5 Quantum Chemical Calculations

The molecular structure of the MCA molecules as corrosion inhibitor the main reason that responsible for the inhibition ability and impedance of the corrosion process upon the mild steel surface. The excellent comprehensive studies were achieved when compared and combined the results of experimental work and theoretical calculations through means of certain attributes on the inhibitive process [44]. Those attributes are determined by DFT calculations such as HOMO, LUMO, energy gap (ΔE), atomic charges, dipole moment (μ), electron affinity (A), chemical hardness (η), electronegativity (χ), ionization potential (I), and fraction of electrons transferred (ΔN) [45,46].

3. Results and discussion

Synthesis and Characterization of Inhibitor. hydrazine-derived coumarin, 4-(6-methylcoumarin)acetohydrazide (MCA) was synthesized from the reaction of methylcoumarin)acetic acid with hydrazine in ethanol under refluxing for 12 h. The yield of the reactions and melting points of the MCA were determined, and the structure of MCA was characterized by elemental analysis, and NMR, spectroscopy. The CHN analysis with ^{1}H and ^{13}C NMR spectra confirmed the structure. The ^{1}H NMR data for the MCA in DMSO-d6 demonstrate the doublet signal at δ 6.03 ppm is attributed to the proton of the vinyl group of the pyridine ring. The signal of the CH3 protons of the methyl group is observed at δ 2.31 ppm, and the absence of ethyl protons indicates the formation of an MCA. The expected resonance was observed in the ^{13}C NMR spectrum of MCA. The signal for the carbonyl carbon appears at δ 167.9 ppm.

3.1. Corrosion Inhibition Tests: Effect of MCA Concentration.

The data from gravimetric analysis of the mild steel coupons in an acidic environment in the presence and absence of different MCA concentrations at various temperatures are displayed in Figures 2 and 3. The data from gravimetric analysis of the mild steel coupons in an acidic environment in the presence and absence of different MCA concentrations at various temperatures are displayed in Figures 2 and 3.

From Figure 2, the inhibition efficiency for MCA as-synthesized inhibitor increase with increasing the concentration of inhibitor. The conducted experiments at higher concentrations of inhibitor (> 0.5 mM) imply that there was no significant increase in the inhibition efficiency and hence we found that the inhibitor at the concentration of 0.5 mm was found to be the optimal inhibition concentration.

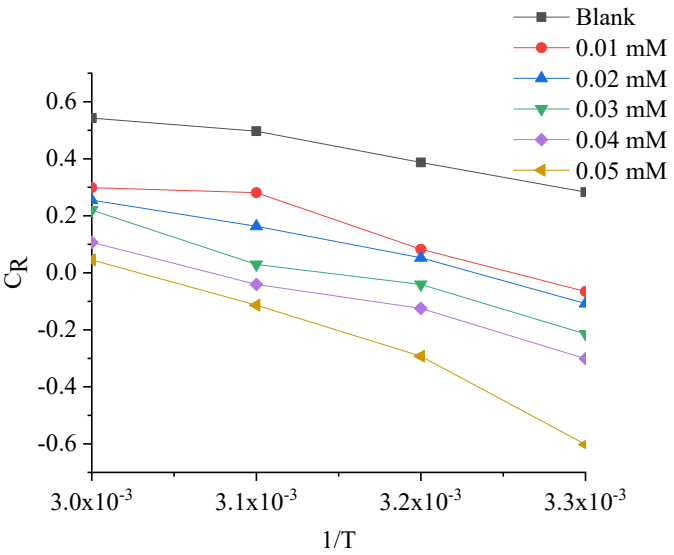


Figure 4. Arrhenius plot for corrosion of mild steel in presence of different concentrations of inhibitor.

3.2. Corrosion Inhibition Tests: Effect of Temperature and Activation Process.

To study the impact of temperature on the corrosion process of the coupon (mild steel) in acidic solution, the weight loss measurements were done at 303, 313, 323, and 333 K with and without the addition of various concentrations of MCA as corrosion inhibitor during 5 h immersion time. The impact of temperature on inhibition efficiency is shown in Figure 3. The inhibition efficiency decreases with elevated temperature due to desorption of MCA molecules from the surface of mild steel with increased temperature 303 to 333 K. Arrhenius equation represent the relation of the factors corrosion rate (C_R), temperature (T), activation energy (Ea) and gas constant (R) [47,48] as a display by the equation 4.

$$C_R = A\, exp(\frac{-Ea}{RT}) \quad (4)$$

A plot of the log of C_R vs 1/T which calculated by gravimetric analysis gave a straight line as demonstrated in Figure 4 for tested coupons in a hydrochloric acid environment in presence of various concentrations of MCA.

The slope (−Ea/2.303R) was determined activation energy Ea value and it was listed in Table 1.

Table 1. Activation Parameters of tested coupons in corrosive solution in the absence and presence of different concentrations of MCA at various Temperatures.

Conc. (mM)	Ea (kJ/mol)	ΔH^*_{corr} (kJ/mol)	$-\Delta S^*_{corr}$ (J/Mol.K)
0.0	16.74	13.95	188.84
0.1	23.96	18.74	172.40
0.2	24.91	20.99	169.23
0.3	25.44	24.27	163.39
0.4	28.30	28.61	159.35
0.5	32.83	31.23	146.34

The activation energy values of the tested coupons in corrosive solutions in presence of MCA are more than the activation energy value in absence of the MCA. Table 1 demonstrates the elevate of activation energy with an increase of MCA concentration, so the corrosion rate decrease [49]. The enthalpy (ΔHcorr *) and entropy (ΔScorr *) can be calculated from equation 5.

$$CR = \frac{RT}{N_A h}\, exp\left(\frac{\Delta S^*_{corr}}{R}\right) exp\left(\frac{\Delta H^*_{corr}}{RT}\right)$$

where h and NA are is Planck's constant the Avogadro number.

Figure 5 demonstrates plot of log(CR/T) versus 1/T obtained for tested coupons in a corrosive environment in the absence and presence of various concentrations of MCA gave straight line, The slope and intercept were –ΔHcorr * /2.303R and [log(R/NAh) +ΔScorr * /2.303R] respectively [50]. ΔHcorr * and ΔScorr * were determined from Figure 5 and were demonstrated in Table 1.

The $\Delta S_{corr}{}^*$ value was increase with an elevated concentration of MCA which proposes random reaction. The ΔHcorr* with positive value with and without MCA indicates the endothermic nature of the coupon of mild steel dissolution process proposing a slow dissolution rate of mild steel coupon with the addition of MCA. Moreover, the activation energy and enthalpy values were increased with the addition of MCA suggest that the energy barrier increases [51].

3.3. Scanning Electron Microscopy.

SEM images of the coupon surface without corrosion inhibitor and with the addition of corrosion inhibitor at the concentration of 0.5 mM for 5 h, immersion time in the acidic environment are demonstrated in Figure 6. The untreated coupon surface shows corroded and highly damaged as in Figure 6 a, on the other hand, the treated coupon surface has clear and smooth as in Figure 6 b.

3.4. Quantum Chemical Calculations.

In general, the energy of the highest occupied molecular orbital (HOMO) is associated with the electron-releasing ability of the molecule. The higher value of the lowest unoccupied molecular orbital (HOMO) denotes the nature of more electron-donating ability. ELUMO with low value indicates the accepting ability of the molecule [52]. A

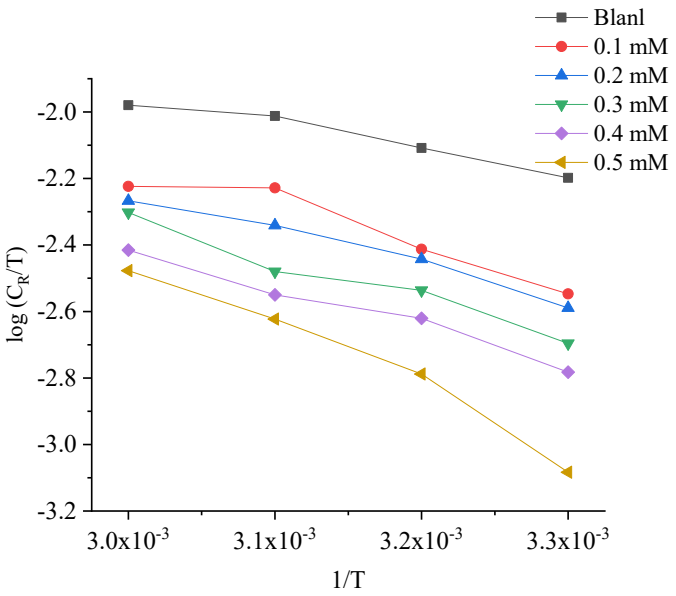


Figure 5. Arrhenius plot for corrosion of mild steel in corrosive solution in presence of different concentrations of inhibitor.

superior corrosion inhibitor has a higher value of EHOMO to contribute the electrons toward the vacant d-orbital of and also the value of ELUMO should below to accept the electrons transferred from the mild steel coupon. The MCA molecules have superior inhibition performance based on the low value of ΔE of 6.191 eV as in Table 2. The optimized geometrical structure and highest occupied molecular orbital with lowest unoccupied molecular orbital are demonstrated in Figure 7. highest occupied molecular orbital is located over carbonyl and amino residue while the lowest unoccupied molecular orbital is located over the pyrone and benzene rings, promote electron contribution toward mild steel surface and receive the pairs of electrons from donor atoms and may delocalize the electrons of the mild steel surface. The electrons pairs of nitrogen and oxygen in the MCA molecules can form coordination bonds with an occupied d-orbital of mild steel [53]. A Mulliken charges are demonstrated in Table 3 and analysis fortifies the best inhibition characteristic of MCA. The dipole moment is a significant characteristic, that determined the inhibition nature of the inhibitor molecules upon the mild steel surface [54]. The present investigations indicate that the MCA molecules have a dipole moment value of 2.6122 D, which confirms the excellent performance of MCA as a corrosion inhibitor. Chemical hardness and softness are significant factors to measure the stability and reactivity of a molecule. The hardness generally indicates the resistance towards the deformation or polarization of the electron cloud of molecules under small perturbation of chemical reaction. Hard molecules have energy gaps with high values and a soft molecule has energy gaps with low values [55]. Inhibitor with low hardness value is expected to have superior inhibition efficiency that is comfortable with our study. High electronegativity and low variation of electro

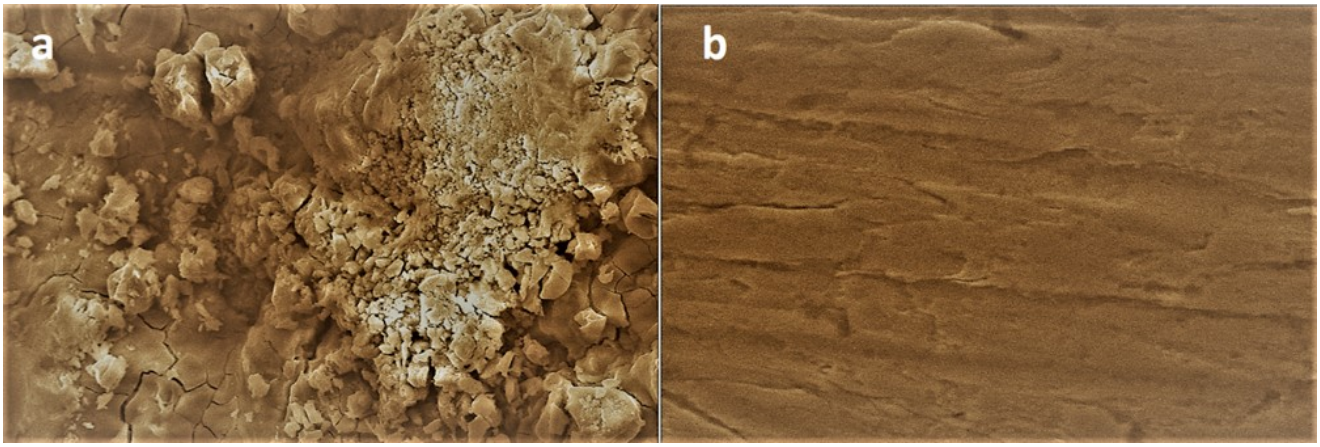


Figure 6. SEM pictures tested coupon surface 5 h of immersion time in corrosive solution: (a) in absence of inhibitor; (b) with 0.5 mM MCA.

Table 2. Quantum characteristics for the most stable conformation of *MCA*.

Function	Values
E_{HOMO}	-10.724
E_{LUMO}	-4.533
$E_{HOMO} - E_{LUMO}$	6.191
Dipole Moment (μ)	2.6122
I= -EHOMO (eV)	-10.724
A= - ELUMO (eV)	-4.533
$\eta = -0.5(E_{HOMO} - E_{LUMO})$	3.0955
$\sigma = 1/\eta$	0.3230
$\chi = -0.5(E_{HOMO} + E_{LUMO})$	7.6285
$\Delta N = -\frac{\emptyset - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}$	2.424

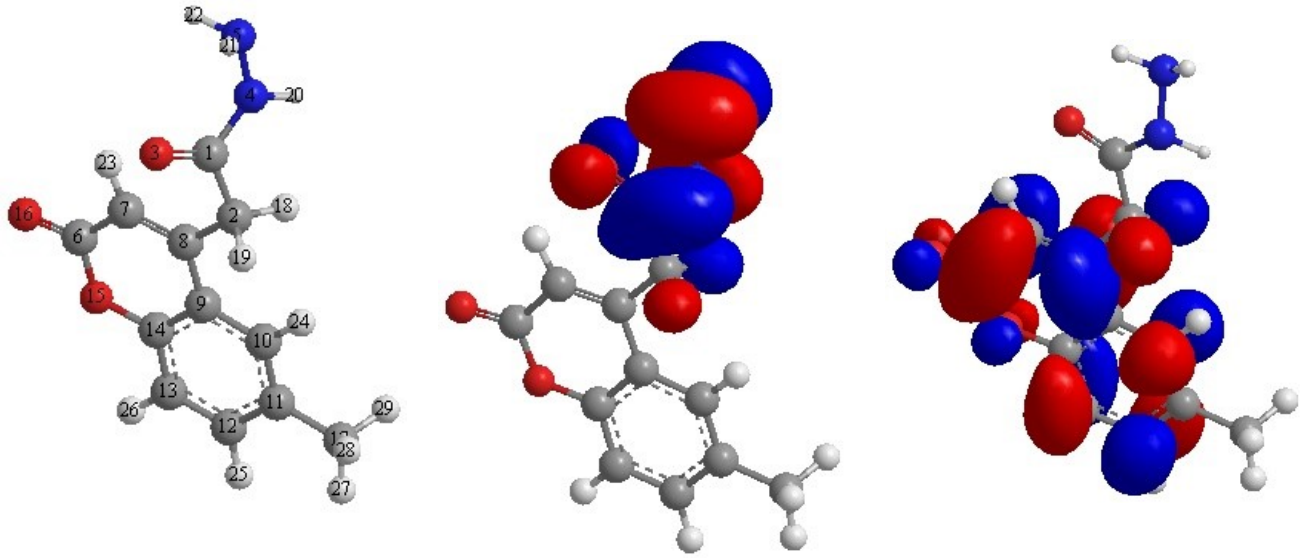
negativity expected low reaction are which in turn indicates low inhibitory efficiency. The ΔN has an intimate relationship with the adsorption phenomenon. Here, χFe and χinh denote absolute electronegativity of iron and the inhibitor, respectively. The ηFe and ηinh represent the absolute hardness of iron and the inhibitor molecule, respectively. The calculated fraction of electrons transferred, N for MCA, demonstrate inhibition impact resulting from electrons donation that approbates with Lukovits et al. 'S study. If N <3.6, the obligation efficiency increased with the increasing electron-donating ability at the metal surface. The η value of MCA is 3.0955. A similar trend is recognized as well, chemical characteristics (electronic chemical potential and electron affinity (A)) closely inter-related [11]. The calculated quantum chemical parameters imply the way to select MCA as a superior corrosion inhibitor against a corrosive environment.

3.5. Mechanism of Inhibition.

The adsorption phenomenon is the main factor that explains the mechanism of inhibition action. Generally, the adsorption is influenced by the surface charge of the mild steel, interaction type between MCA as an inhibitor, and mild steel surface in addition to the molecular structure of MCA. The MCA molecule has donor atoms (electronegative) nitrogen and oxygen in addition to pi-electrons of the benzene and pyrone rings. This donor sits cause efficient adsorption of inhibitor molecules onto the surface of tested coupons. In the mineral and halogenic acid environment, N atom becomes protonated because of hydration, chloride ions with a smaller degree adsorb at the electrode/environment interface, produce a more negative charge in the vicinity of the electrode/ environment interface, and prefer excess adsorption of the positive charge protonated MCA molecules (tested corrosion inhibitor) [56]. Protonated MCA molecules can adsorb onto the surface tested coupons via interaction of positive charge of MCA molecules and the negative charge of the mild steel surface, and imply physical adsorption. Chemical adsorption may occur via donating of electrons from the MCA molecules containing nitrogen and oxygen atoms that have unshared pairs of electrons with pi-electrons of pyrone and benzene rings and the unoccupied d-orbital of mild steel coupon surface [57]. In general, the transition elements with unoccupied d-orbitals such as Fe,

Table 3. Mulliken Atomic Charges of All Atoms in MCA.

At.	Cha.	At.	Cha.	At.	Cha.	At.	Cha.
1	0.28	8	0.02	15	-0.18	22	0.14
2	-0.14	9	-0.12	16	-0.28	23	0.18
3	-0.36	10	-0.08	17	-0.17	24	0.13
4	-0.34	11	-0.09	18	0.11	25	0.14
5	-0.17	12	-0.08	19	0.13	26	0.16
6	0.33	13	-0.14	20	0.25	27	0.08
7	-0.21	14	0.10	21	0.14	28	0.08



a b c

Figure 7. (a) Optimized geometry, (b) HOMO and (c) LUMO of MCA inhibitor.

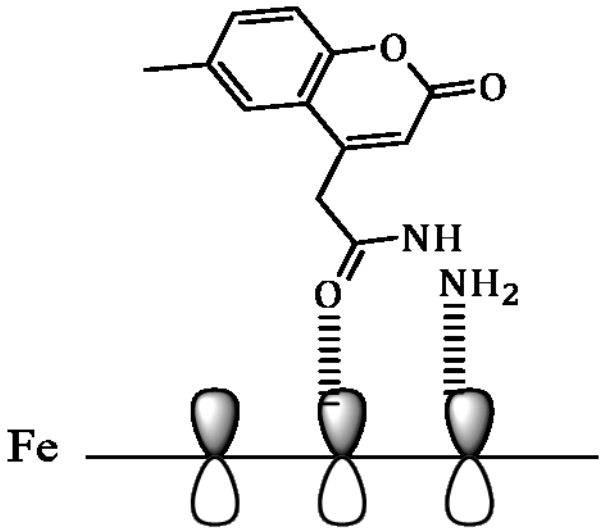


Figure 8. Adsorption of MCA molecules on the coupon surface of mild steel in corrosive solution

have complexation tendencies toward molecules containing atoms with unshared pairs of electrons and forming coordination bonds and hence the formation of protective barrier. The formation of a protective barrier on the surface of mild steel tested coupons through physical and/or chemical adsorption causes a decrease in the corrosion rate. Increase the concentration of MCA as a corrosion inhibitor, will increase the inhibition efficiency due to the coverage area of the tested coupon surface. Figure 8, demonstrate various adsorption types of surface of tested coupon/corrosive environment.

4. Conclusion

In this investigation, costly-effect novel hydrazine-derived coumarin 4-(6-methylcoumarin)acetohydrazide (MCA) as a corrosion inhibitor was synthesized and characterized vis spectroscopical techniques. MCA effectively acts as a corrosion inhibitor for mild steel coupons in a corrosive environment at low and high concentrations. The inhibition efficiency increase with increasing concentration of MCA. The interactions between MCA molecules as a corrosion inhibitor and tested coupon surface have been studied gravimetrical techniques. Adsorption of MCA molecules on the surface of tested mild steel coupons obeyed the Langmuir isotherm. SEM micrographs revealed a clear and smooth coupon surface in a corrosive environment compared to a solution without the addition of MCA, which suggests that a barrier layer was formed on the coupon surface. The quantum chemical calculations confirm the formation of a barrier layer via the reaction of unpaired electron pairs of nitrogen, oxygen, and pi-system with a surface of mild steel coupon and create a coordination complex. The superior inhibition performance of MCA can be explained according to the HOMO, LUMO, energy gap (ΔE), atomic charges, dipole moment (μ), electron affinity (A), chemical hardness (η), electronegativity, ionization potential (I), and a fraction of electrons transferred (ΔN). The quantum chemical calculations are in good agreement with the methodological results.

Acknowledgement

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Conflicts of Interest

The authors declare no conflict of interest.

References

[1] Wang, X.; Yang, H.; Wang, F. Inhibition performance of a gemini surfactant and its co-adsorption effect with halides on mild steel in 0.25 M H2SO4 solution. Corrosion Science. 2012, 55, 145– 152, DOI: 10.1016/j.corsci.2011.10.008

[2] El-Lateef, H. M. A.; Abo-Riyab, M. A.; Tantawy, A. H. Empirical and quantum chemical studies on the corrosion inhibitionperformance of some novel synthesized cationic gemini surfactantson carbon steel pipelines in acid pickling processes. Corrosion Science. 2016, 108, 94– 110, DOI: 10.1016/ j.corsci.2016.03.004

[3] Salarvand, Z.; Amirnasr, M.; Talebian, M.; Raeissi, K.; Meghdadi, S. Enhanced corrosion resistance of mild steel in 1 M HCl solution bytrace amount of 2-phenyl-benzothiazole derivatives: Experimental,quantum chemical calculations and molecular dynamics (MD) simulation studies. Corrosion Science. 2017, 114, 133– 145, DOI: 10.1016/j.corsci.2016.11.002

[4] Heakal, F. E. T.; Elkholy, A. E. Gemini surfactants as corrosion inhibitors for carbon steel. Journal of Molecular Liquids, 2017, 230, 395– 407, DOI: 10.1016/ j.molliq.2017.01.047

[5] Zana, R. Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review. Journal of Colloid and Interface Science. 2002, 97, 205– 253, DOI: 10.1016/S0001-8686(01)00069-0

[6] Okafor, P. C.; Zheng, Y. G. Synergistic inhibition behaviour of methylbenzyl quaternary imidazoline derivative and iodide ions on mild steel in H2SO4 solutions. Corrosion Science. 2009, 51, 850-859, DOI: 10.1016/j.corsci.2009.01.027

[7] Hegazy, M. A. A novel Schiff base-based cationic gemini surfactants: Synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid solution. Corrosion Science. 2009, 51, 2610– 2618, DOI: 10.1016/j.corsci.2009.06.046

[8] Kaczerewska, O.; Leiva-Garcia, R.; Akid, R.; Brycki, B. Efficiency of cationic gemini surfactants with 3-azamethylpentamethylene spacer as corrosion inhibitors for stainless steel in hydrochloric acid. Journal of Molecular Liquids, 2017, 247, 6– 13, DOI: 10.1016/j.molliq.2017.09.103

[9] Solmaz, R.; Kardaş, G.; Yazıcı, B.; Erbil, M. Adsorption and corrosion inhibitive properties of 2-amino-5-mercapto-1,3,4-thiadiazole on mild steel in hydrochloric acid media. Colloids and Surfaces A. 2008, 312, 7– 17, DOI: 10.1016/j.colsurfa.2007.06.035 17

[10] Li, X. H.; Deng, S. D.; Fu, H. Triazolyl blue tetrazolium bromide as a novel corrosion inhibitor for steel in HCl and H2SO4 solutions. Corrosion Science. 2011, 53, 302– 309, DOI: 10.1016/j.corsci.2010.09.036

[11] Qiu, L. G.; Xie, A. J.; Shen, Y. H. A novel triazole-based cationic gemini surfactant: synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid. Materials Chemistry and Physics. 2005, 91, 269– 273, DOI: 10.1016/j.matchemphys.2004.11.022

[12] Feng, L. W.; Yin, C. X.; Zhang, H. L.; Li, Y. F.; Song, X. H.; Chen, Q. B.; Liu, H. L. Cationic Gemini surfactants with a Bipyridyl Spacer as corrosion inhibitors for mild steel. ACS Omega 2018, 3, 18990– 18999, DOI: 10.1021/ acsomega.8b03043

[13] Salman, T.A.; Zinad, D.S.; Jaber, S.H.; Al-Ghezi, M.; Mahal, A.; Takriff, M.S.; Al-Amiery, A. Effect of 1,3,4 Thiadiazole Scafold on the Corrosion Inhibition of Mild Steel in Acidic Medium: An Experimental and Computational Study, Journal of Bio- and Tribo-Corrosion, 2019, 5, 1

[14] Habeeb, H.J.; Luaibi, H.M.; Dakhil, R.M.; Kadhum, A.A.H.; Al-Amiery, A.; Gaaz, T.S.; Development of new corrosion inhibitor tested on mild steel supported by electrochemical study, Results in Physics. 2018, 8, 1260

[15] Al-Amiery, A.; Kadhim, A.; Mohamad, A.; Musa, A.; Li, C. Electrochemical study on newly synthesized chlorocurcumin as an inhibitor for mild steel corrosion in hydrochloric acid, Materials, 2013, 6, 5466

[16] Ansari, K. R.; Quraishi, M. A.; Singh, A. Pyridine derivatives as corrosion inhibitors for N80 steel in 15% HCl: Electrochemical, surface and quantum chemical studies. Measurement, 2015, 76, 136-147

[17] Junaedi, S.; Kadhim, A.; Al-Amiery, A.; Mohamad A.; Takriff, M. Synthesis and characterization of novel corrosion inhibitor derived from oleic acid: 2-Amino5-Oleyl1,3,4-Thiadiazol (AOT), International Journal of Electrochemical Science. 2012, 7, 3543

[18] Kadhim, A.; Al-Okbi, A.; Jamil, D. M.; Qussay, A.; Al-Amiery, A.; Gaaz, T.; Kadhum, A.; Mohamad, A.; Nassir, M.H. Experimental and theoretical studies of benzoxazines corrosion inhibitors, Results in Physics. 2017, 7, 4013

[19] Al-Azawi, K.F.; Mohammed, I.M.; Al-Baghdadi, S.B.; Salman, T.A.; Issa, H.A.; Al-Amiery, A.; Gaaz, T.; Kadhum, A. Experimental and quantum chemical simulations on the corrosion inhibition of mild steel by 3-((5-(3,5-dinitrophenyl)-1,3,4- thiadiazol-2-yl)imino) indolin-2-one, Results in Physics. 2018, 9, 278

[20] Al-Baghdadi, S.B.; Hashim, F.G.; Salam, A.Q.; Abed, T.K.; Gaaz, T.S.; Al-Amiery, A.; Kadhum, A.A.H.; Reda, K.S.; Ahmed, W.K. Synthesis and corrosion inhibition application of NATN on mild steel surface in acidic media complemented with DFT studies, Results in Physics. 2018, 8, 1178

[21] Al-Obaidy, A.H.M.J.; Kadhum, A.; Al-Baghdadi, S.B.; Al-Amiery, A.; Kadhum, A.A.H.; Mohamad, A.B.; Yousif, E. Eco-friendly corrosion inhibitor: experimental studies on the corrosion inhibition performance of creatinine for mild steel in HCl complemented with quantum chemical calculations, International Journal of Electrochemical Science. 2015, 10, 3961

[22] Al-Amiery, A.; Kadhum, A.A.H.; Mohamad, A.B.;

Junaedi, S. A Novel Hydrazinecarbothioamide as a Potential Corrosion Inhibitor for Mild Steel in HCl, Materials, 2013, 6, 1420

[23] Ahmed, M.H.O.; Al-Amiery, A. ; Al-Majedy, Y.K.; Kadhum, A.A.H.; Mohamad, A.B.; Gaaz, T.S. Synthesis and characterization of a novel organic corrosion inhibitor for mild steel in 1 M hydrochloric acid, Results in Physics. 2018, 8, 728

[24] Salman, T.A.; Al-Amiery, A.A.; Shaker, L.M.; Kadhum, A.; Takriff, M.S.A. Study on the inhibition of mild steel corrosion in hydrochloric acid environment by 4-methyl-2-(pyridin-3-yl)thiazole-5-carbohydrazide. International Journal of Corrosion and Scale Inhibition. 2019, 8, 1035

[25] Salman, T.A.; Jawad, Q.A.; Hussain, M.A.; Al-Amiery, A.A.; Shaker, L.M.; Kadhum, A.; Takriff, M.S. Novel ecofriendly corrosion inhibition of mild steel in strong acid environment: Adsorption studies and thermal effects. International Journal of Corrosion and Scale Inhibition. 2019, 8, 1123

[26] Al-Taweel, S.S.; Al-Janabi, K.W.S.; Luaibi, H.M.; Al-Amiery, A.A.; Gaaz, T.S. Evaluation and characterization of the symbiotic effect of benzylidene derivative with titanium dioxide nanoparticles on the inhibition of the chemical corrosion of mild steel. International Journal of Corrosion and Scale Inhibition. 2019, 8, 1149

[27] Zinad, D.S.; Jawad, Q.A.; Hussain, M.A.M.; Mahal, A.; Shaker, L.M.; Al-Amiery, A.A. Adsorption, temperature and corrosion inhibition studies of a coumarin derivatives corrosion inhibitor for mild steel in acidic medium: gravimetric and theoretical investigations, International Journal of Corrosion and Scale Inhibition. 2020, 9, 134

[28] Al-Amiery, A.; Al-Majedy, Y.K.; Kadhum, A.A.H.; Mohamad, A.B. New Coumarin Derivative as an Eco-Friendly Inhibitor of Corrosion of Mild Steel in Acid Medium, Molecules 2015, 20, 366

[29] Rubaye, A.Y.I.; Abdulwahid, A.A.; Al-Baghdadi, S.B.; Al-Amiery, A.; Kadhum, A.A.H.; Mohamad, A.B. Cheery sticks plant extract as a green corrosion inhibitor complemented with LC-EIS/MS spectroscopy, International Journal of Electrochemical Science. 2015,10, 8200

[30] Kadhum, A.; Mohamad, A.; Kadhum, A.A.H.; Mohamad, A.B.; Hammed, L.A.; Al-Amiery, A.; San, N.H.; Musa, A.Y. Inhibition of Mild Steel Corrosion in Hydrochloric Acid Solution by New Coumarin, Materials 2014, 7, 4335

[31] Mohamad, A.; Kadhum, A.; Al-Amiery, A.; Ying, L.; Musa, A. Synergistic of a coumarin derivative with potassium iodide on the corrosion inhibition of aluminum alloy in 1.0 M H2SO4, Metals and Materials International. 2014, 20, 459

[32] Zinad, D.S.; Hanoon, M.; Salim, R.D.; Ibrahim, S.I.; Al-Amiery, A.; Takriff M.S.; Kadhum, A.A.H. A new synthesized coumarin-derived Schiff base as a corrosion inhibitor of mild steel surface in HCl medium: gravimetric and DFT studies. International Journal of Corrosion and Scale Inhibition. 2020, 9, 228

[33] Jawad, Q. A.; Zinad, D. S.; Salim, R. D.; Al-Amiery, A.; Gaaz, T. S.; Takriff, M. S.; Kadhum, A. Synthesis, Characterization, and Corrosion Inhibition Potential of Novel Thiosemicarbazone on Mild Steel in Sulfuric Acid Environment, Coatings 2019, 9, 729

[34] Sheet, E.; Yamin, J.; AL-Salihi, H.; Salam, A.; Reda, K. S.; Ahmed, W. K.; Mahdi, M. T.; Al-Amiery, A.A. N-(3-Nitrobenzylidene)-2-Aminobenzothiazole As New Locally Available Corrosion Inhibitor For Iraqi Oil. Industry Journal of the Balkan Tribological Association, 2020, 26, 194

[35] Yamin, J.A.A.; Sheet, E.; Al-Amiery, A. Statistical analysis and optimization of the corrosion inhibition efficiency of a locally made corrosion inhibitor under different operating variables using RSM, International Journal of Corrosion and Scale Inhibition. 2020, 9, 502

[36] Jamil, D.M.; Al-Okbi, A.K.; Al-Baghdadi, S.B.; Al-Amiery, A.; Kadhim, A.; Gaaz, T. Experimental and theoretical studies of Schiff bases as corrosion inhibitors, Chemistry Central Journal. 2018, 12, 1

[37] Salim, R.D.; Jawad, Q.A.; Ridah, K.S.; Shaker, L.M. Al-Amiery, A.; Kadhum, A.A.H.; Takriff, M.S. Corrosion inhibition of thiadiazole derivative for mild steel in hydrochloric acid solution, International Journal of Corrosion and Scale Inhibition. 2020, 9, 550

[38] Al-Amiery, A.; Shaker, L.M.; Kadhum, A.A.H.; Takriff, M.S. Corrosion Inhibition of Mild Steel in Strong Acid Environment by 4-((5,5-dimethyl-3-oxocyclohex-1-en-1-yl)amino)benzenesulfonamide, Tribology in industry 2020, 42, 89

[39] Al-Amiery, A.A.; Salman, T.A.; Alazawi, K.F.; Shaker, L.M.; Kadhum A. Takriff, M.S. Quantum chemical elucidation on corrosion inhibition efficiency of Schiff base: DFT investigations supported by weight loss and SEM techniques. International Journal of Low-Carbon Technologies 2020, 15, 202–209

[40] Al-Amiery, A.; Shaker, L. M.; Kadhum, A. A. H.; Takriff, M. S. Synthesis, characterization and gravimetric studies of novel triazole-based compound. International Journal of Low-Carbon Technologies 2020, 15, 164–170

[41] ASTM G77-98, Standard Test Method for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Wear Test, 1998.

[42] Khadom, A. Effect of temperature on corrosion inhibition of copper - nickel alloy by tetraethylenepentamine under flow conditions, Journal of the Chilean Chemical Society,.59 2014, 2545- 2549; DOI:10.4067/S0717-97072014000300004

[43] Yin, C. Kong, M. Zhang, J. Wang, Y. Ma, Q. Chen, Q. and Liu, H. Influence of Hydroxyl Groups on the Inhibitive Corrosion of Gemini Surfactant for Carbon Steel, ACS Omega 2020, 5, 6, 2620-2629; DOI: 10.1021/

acsomega.9b02989

[44] Lebrini, M.; Lagrenée, M.; Vezin, H.; Traisnel, M.; Bentiss, F. Experimental and Theoretical Study for Corrosion Inhibition of Mild Steel in Normal Hydrochloric Acid Solution by Some New Macrocyclic Polyether Compounds. Corrosion Science. 2007, 49, 2254–2269.

[45] John, S.; Joseph, A. Effective Inhibition of Mild Steel Corrosion in 1 M Hydrochloric Acid Using Substituted Triazines: an Experimental and Theoretical Study. RSC Advances 2012, 2, 9944–9951.

[46] Kovačević, N.; Kokalj, A. DFT Study of Interaction of Azoles with Cu(111) and Al(111) Surfaces: Role of Azole Nitrogen Atoms and Dipole-Dipole Interactions. The Journal of Physical Chemistry, 2011, 115, 24189–24197.

[47] Obot, I. B.; Obi-Egbedi, N. O.; Umoren, S. A. Antifungal drugs as corrosion inhibitors for aluminium in 0.1M HCl. Corrosion Science. 2009, 51, 1868– 1875, DOI: 10.1016/j.corsci.2009.05.017

[48] Morad, M. S.; Sarhan, A. A. O. Application of some ferrocene derivatives in the field of corrosion inhibition. Corrosion Science. 2008, 50, 744– 753, DOI: 10.1016/j.corsci.2007.09.002

[49] Deng, S.; Li, X.; Fu, H. Acid violet 6B as a novel corrosion inhibitor for cold rolled steel in hydrochloric acid solution. Corrosion Science. 2011, 53, 760– 768, DOI: 10.1016/j.corsci.2010.11.002

[50] Hegazy, M. A.; Zaky, M. F. Inhibition effect of novel nonionic surfactants on the corrosion of carbon steel in acidic medium. Corrosion Science. 2010, 52, 1333– 1341, DOI: 10.1016/j.corsci.2009.11.043

[51] Liu, Y.; Zou, C. J.; Yan, X. L.; Xiao, R. J.; Wang, T. Y.; Li, M. β-Cyclodextrin Modified Natural Chitosan as a Green Inhibitor for Carbon Steel in Acid Solutions. Industrial & Engineering Chemistry Research, 2015, 54, 5664– 5672, DOI: 10.1021/ acs.iecr.5b00930

[52] Ahamad, I.; Prasad, R.; Quraishi, M. A. Inhibition of mild steel corrosion in acid solution by Pheniramine drug: Experimental and theoretical study. Corrosion Science. 2010, 52, 3033– 3041, DOI: 10.1016/ j.corsci.2010.05.022

[53] min, M. A.; Ahmed, M. A.; Arida, H. A.; Kandemirli, F.; Saracoglu, M.; Arslan, T.; Basaran, M. A. Monitoring corrosion and corrosion control of iron in HCl by nonionic surfactants of the TRITON-X series-Part III. Immersion time effects and theoretical studies. Corrosion Science. 2011, 53, 1895– 1909, DOI: 10.1016/j.corsci.2011.02.007.

[54] El-Lateef, H. M. A.; Ahmed, H. T. Synthesis and evaluation of novel series of Schiff base cationic surfactants as corrosion inhibitors for carbon steel in acidic/chloride media: experimental and theoretical investigations. RSC Advances. 2016, 6, 8681– 8700, DOI: 10.1039/C5RA21626E.

[55] Mobin, M.; Aslam, R.; Aslam, J. Non toxic biodegradable cationic gemini surfactants as novel corrosion inhibitor for mild steel in hydrochloric acid medium and synergistic effect of sodium salicylate: Experimental and theoretical approach. Materials Chemistry and Physics. 2017, 191, 151– 167, DOI: 10.1016/j.matchemphys.2017.01.037

[56] Kaczerewska, O.; Leiva-Garcia, R.; Akid, R.; Brycki, B.; Kowalczyk, I.; Pospieszny, T. Effectiveness of O-bridged cationic gemini surfactants as corrosion inhibitors for stainless steel in 3 M HCl: Experimental and theoretical studies. Journal of Molecular Liquids, 2018, 249, 1113– 1124, DOI: 10.1016/ j.molliq.2017.11.142

[57] El-Lateef, H. M. A.; Soliman, K. A.; Tantawy, A. H. Novel synthesized Schiff Base-based cationic gemini surfactants: Electrochemical investigation, theoretical modeling and applicability as biodegradable inhibitors for mild steel against acidic corrosion. Journal of Molecular Liquids, 2017, 232, 478– 498, DOI: 10.1016/ j.molliq.2017.02.105