

INHIBITION OF CORROSION OF MILD STEEL IN H_2SO_4 SOLUTION BY SULFACHLOROPYRIDAZINE: SYNERGISM BY CATIONS AND HALIDES.

O. A. Hazazi

Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University,
 Makkah Al-Mukarramah, Saudi Arabia Kingdom
 Email: oahazazi@hotmail.com

Abstract- The synergism between sulfachloropyridazine (SCP), halides and/or copper ions on the inhibition of the corrosion of mild steel in 0.5 M H_2SO_4 solution has been studied using potentiodynamic measurements and electrochemical impedance spectroscopy (EIS). It has been found that the corrosion inhibition of mild steel by SCP is enhanced in the presence of halides and/or copper ions. SCP alone preferentially inhibits the anodic branch while Cu^{2+} + SCP inhibits the anodic branch and promote the cathodic one. However, the overall effect is that the inhibition efficiency in the latter case is larger than the former. In the presence of SCP + Cu^{2+} + halides, the inhibition efficiency is the largest and the promotion of the cathodic current by Cu^{2+} is overweighed by adding halides. Thus adding both Cu^{2+} and halides to SCP significantly inhibit the anodic branch while keeping the effect on the cathodic branch negligible. Experimental results fits with Langmuir isotherm.

Keywords - Environmentally corrosion inhibitor; Langmuir isotherm; Mild steel; Synergism; sulfachloropyridazine

I. INTRODUCTION

Deterioration of materials due to corrosion waste resources, decrease productivity, damage environment and in the worst cases personal might be injured, even lives lost [1]. The production efficiency and life time of the equipment in addition to products poisoning are another examples of the bad impact of the formation of scale as a result of corrosion. Using acids in pickling, cleaning, descaling, to remove undesirable scales and corrosion products is one of the remedial solutions [2, 3]. However acids should be mixed with corrosion inhibitors to reduce the further dissolution of metals in such harsh media. Utilizing organic inhibitors has been a subject of interest for long time [4-8]. The inhibition efficiency of these inhibitors are inherently related to the presence of at least one functional group (reaction center) which acts as a center for the establishment of the adsorption process [9-11].

Recently many organic inhibitors has been reported as toxic and thus much interest has been paid to finding an environmentally corrosion inhibitors [12-26]. On the other hand several studies have been reported on the joint adsorption of organic inhibitors with anions and/or cations on the surface of corroded metal [27-34]. Such joint adsorption follows the formation of donor-acceptor surface complex between free or π -electron of an organic inhibitor and vacant d-orbital of a metal [35].

Inhibition efficiency of a corrosion inhibitor could be increased via the enhanced adsorption or the complexation with cations on the surface of the corroded metal. Such way of inhibition is called synergism in which a small

concentration of an inhibitor exerts a significant inhibition efficiency in the presence of a secondary cheap species. This process is controlled by several factors including for example the potential of zero charge of the corroded metals [23] and the relative inhibition efficiency of the complex formed compared with the individual substituents.

II. EXPERIMENTAL

Electrochemical measurements were performed on mild steel of the following composition (wt. %): 0.07% C, 0.29% Mn, 0.07% Si, 0.012% S, 0.021% P and the remainder iron. Samples of 0.5 cm² were used. Sulfachloropyridazine (SCP) of structure shown in Fig. 1, copper salt and sodium halides were obtained from Sigma-Aldrich and used as received.

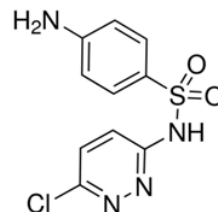


Fig. 1 Structure of sulfachloropyridazine

The solution of 0.5 M H_2SO_4 was prepared by dilution of AR grade 98% H_2SO_4 . Stock solutions of sodium halides were prepared in 0.5 M H_2SO_4 and the desired concentrations were obtained by appropriate dilution.

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Electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and a Hg/Hg₂SO₄/SO₄²⁻ coupled to a fine Luggin capillary as the reference electrode (RE). In order to minimize the ohmic contribution, the Luggin capillary was kept close enough to the working electrode (WE) which was fitted into a glass tube of proper internal diameter by using epoxy resins. The WE surface area of 0.5 cm² was abraded with emery paper down to 2000 on test face, rinsed with distilled water, degreased with acetone, and dried with a cold air stream. Before measurements the electrode was immersed in the test solution at open circuit potential (OCP) for 20 min at 25 °C or until the steady state is obtained. All electrochemical measurements were carried out using PGSTAT30 potentiostat/galvanostat. The potential of potentiodynamic polarization curves was done from a potential of -250 mV vs. OCP, to 250 mV vs. OCP at a scan rate of 2 mV/s. Current densities were calculated on the basis of the apparent geometrical surface area of the electrode. The measurements were repeated at least three times to test the reproducibility of the results. The open circuit potentials (OCP) of samples in H₂SO₄ solution was measured against standard Ag/AgCl electrode as a reference electrode for 60 min.

currents, i.e., SCP preferentially inhibit the anodic branch. Also the corrosion potential shifted to anodic direction. However, the potential shift is not enough for the inhibitor to be nominated as an anodic inhibitor. The effect of the inhibitor concentration on the Tafel slopes is negligible indicating that the inhibitor exerts its action via simple blocking, and that the adsorption of the inhibitor does not change the mechanism [36].

The protection efficiency is given by:

$$\% P = \left[1 - \frac{i_{corr1}}{i_{corr2}} \right] 100 \quad (1)$$

where, i_{corr1} and i_{corr2} are corrosion current densities in the absence and presence of inhibitor, respectively. Values of the protection efficiencies obtained in the presence of different concentrations are given also in Table 1. The maximum inhibition efficiency (ca. 75 %) obtained in the presence of 60 μM SCP. Under the present conditions SCP is positively charged as pK_{a1} and pK_{a2} of SCP equal 1.90 and 5.40, respectively [37]. Based on this the corrosion

Table 1. Polarization data for mild steel in 0.5 M H₂SO₄ in the absence and presence of SCP.

System	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (μA/cm ²)	θ	% P
Blank	-458	92	83	199	--	--
1x10 ⁻⁵ M SCP	-440	93	81	105	0.47	47
3x10 ⁻⁵ M SCP	-425	95	79	68	0.65	65
6x10 ⁻⁵ M SCP	-418	96	76	50	0.75	75

III.RESULTS AND DISCUSSION

Figure 2 shows the polarization curves of mild steel obtained in 0.5 M H₂SO₄ in the absence and presence of various concentrations of SCP at 25 °C. Electrochemical parameters extracted from this figure are given in Table 1. As can be seen the effect of SCP on the cathodic branch is negligible, while the effect on the anodic branch is significant; the anodic branch bodily shifted to lower

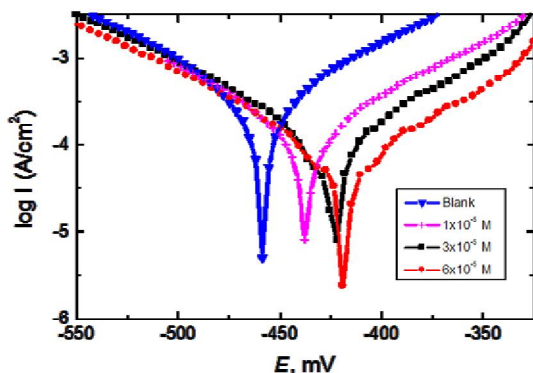


Fig. 2 Potentiodynamic polarization curves obtained at mild steel electrode in 0.5 M H₂SO₄ in the absence and presence of sulfachloropyridazine at 25 °C.

inhibition could be enhanced by adding halides to SCP solutions where the pre-adsorption of halide enhances the adsorption of positively charged SCP under the present conditions. On the other hand it has been reported that SCP form complexes with copper ions [38]. This is utilized here

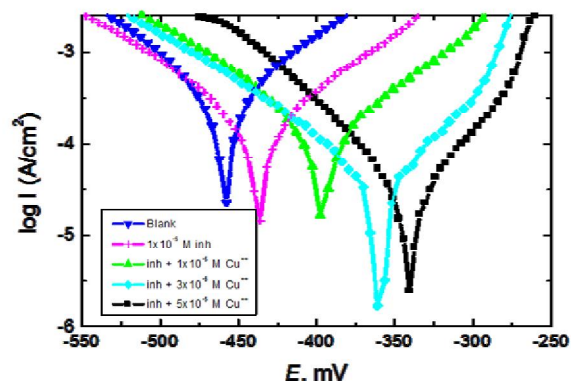


Fig. 3 Potentiodynamic polarization curves obtained at mild steel electrode in 0.5 M H₂SO₄ containing 1.0 x10⁻⁵ M SCP and different concentrations of copper ions at 25 °C.

in the possible enhancing of the inhibition efficiency of SCP via the complexation with copper ions.

Fig. 3 shows the polarization curves obtained at mild steel in 0.5 M H₂SO₄ in the absence and presence of constant concentration of SCP and different concentrations of copper ions. Electrochemical parameters obtained from this figure is given in Table 2. Inspection of Figure 3 and Table 2 reveals the significant increase in the inhibition efficiency

83 % in the presence of 10 μM SCP + 10 μM Cu²⁺ + 30 μM Cl⁻. It is noteworthy to mention that such large inhibition efficiency is attained while keeping the cathodic branch current is little bit larger than the blank response. The maximum shift in the corrosion potential equals 99 mV, and the mixture could be assigned as a mixed type inhibitor, similar to the above case.

Table 2. Polarization data for mild steel in 0.5 M H₂SO₄ in the absence and presence of sulfachloropyridazine (SCP) with

System	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	θ	% P
Blank	-458	92	83	199	--	--
1x10 ⁻⁵ M inh	-440	93	81	105	0.47	47
inh + 1x10 ⁻⁵ M Cu ⁺⁺	-397	97	80	57	0.71	71
inh + 3x10 ⁻⁵ M Cu ⁺⁺	-362	102	86	45	0.77	77
inh + 5x10 ⁻⁵ M Cu ⁺⁺	-341	106	88	31	0.84	84

upon adding copper ions to SCP; for instance, while the inhibition efficiency in the presence of 10 μM SCP equals 47 %, it increases to 84 % upon adding 50 μM Cu²⁺ to the 10 mM SCP, i.e. the inhibition efficiency is almost the double of that in the absence of copper ions. It is noteworthy to mention that even though the inhibition efficiency increases (as a reflection of the whole process) the individual current of the cathodic branch is increased in the presence of SCP + Cu²⁺ compared with SCP alone. It has been reported that copper retard the hydrogen evolution as the exchange current densities of hydrogen evolution at copper and iron are of the same order [39]. It is noteworthy to mention that E_{corr} is shifted regularly in the anodic direction upon increasing the concentration of the copper ions; it shifts from -458 mV (obtained in blank solution) to -341 mV (obtained in the presence of 10 μM SCP + 50 μM Cu²⁺), i.e. the shift in the corrosion potential is 117 mV. Thus in the present case the 10 μM SCP + 50 μM Cu²⁺ mixture could be considered as an anodic inhibitor blend [24].

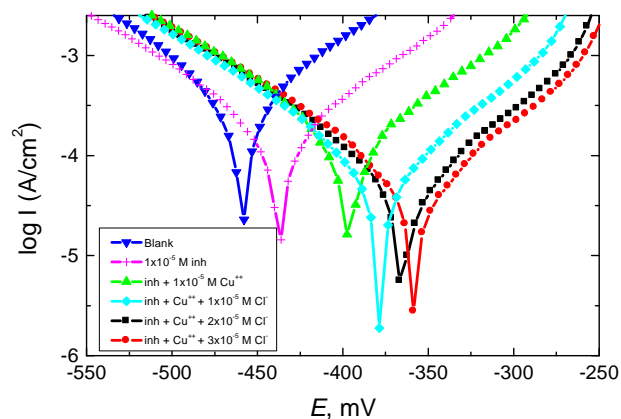


Fig. 4 Potentiodynamic polarization curves obtained at mild steel in 0.5 M H₂SO₄ (Blank) in the absence and presence of sulfachloropyridazine with copper ion and chloride at 25 °C

Table 3. Polarization data for mild steel in 0.5 M H₂SO₄ in the absence and presence of sulfachloropyridazine (SCP) with constant concentrations of copper ion and different concentration of chloride.

System	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	θ	% P
Blank	-458	92	83	199	--	--
1x10 ⁻⁵ M inh	-440	93	81	105	0.47	47
inh + 1x10 ⁻⁵ M Cu ⁺⁺	-397	97	80	57	0.71	71
inh + Cu ⁺⁺ + 1x10 ⁻⁵ M Cl ⁻	-381	97	80	47	0.76	76
inh + Cu ⁺⁺ + 2x10 ⁻⁵ M Cl ⁻	-368	95	81	38	0.81	81
inh + Cu ⁺⁺ + 3x10 ⁻⁵ M Cl ⁻	-359	97	79	35	0.83	83

Because of the significant increase in the current of the cathodic branch as a result of the increase of copper ion concentration, low concentration of copper (10 μM) was selected and then the effect of increasing the concentration of the chloride was examined and the results are shown in Fig. 4. Electrochemical parameters extracted from this figure is given in Table 3. Interestingly the inhibition efficiency increased from 47 % in the presence of 10 μM SCP only, to

For further insight into the corrosion inhibition process the corrosion behavior of mild steel in 0.5 M H₂SO₄ the electrochemical impedance spectroscopy (EIS) at 298 K after 30 min of immersion are conducted both in the presence of constant concentration of Cu²⁺ and different concentrations of SCP and shown in Fig. 5. The charge-transfer resistance (R_t) values are calculated from the difference in the impedance at

lower and higher frequencies [40]. Then the double layer capacitance (C_{dl}) is calculated using Eq. 2 ;

$$C_{dl} = \left[\frac{1}{2\pi f_{max} R_{ct}} \right] 100 \quad (2)$$

where, f_{max} is the frequency at which the imaginary component of the impedance is maximal (Z_{max}). The inhibition efficiency is calculated from the following equation;

$$\% P = \left[\frac{(1/R_t) - (1/R_{t/inh})}{(1/R_c)} \right] 100 \quad (3)$$

where, R_t and $R_{t/inh}$ are the charge transfer-resistance values in the absence and presence of inhibitor, respectively. As can be seen from this figure, all the Nyquist plots contain slightly depressed semicircles with the center under the real axis. This implies that corrosion of the mild steel in 0.5 M H_2SO_4 solution mainly controlled by a charge-transfer process [41]. Parameters extracted from Fig. 5 are given in Table 4.

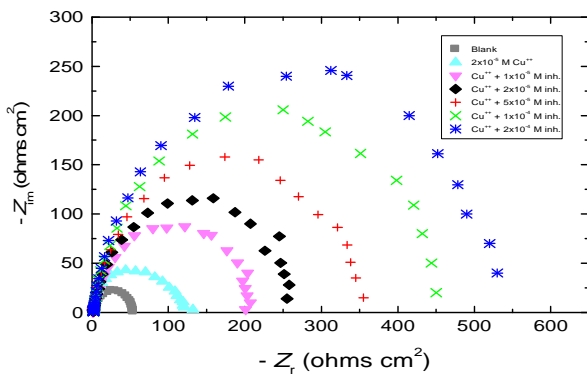


Fig. 5 Nyquist plots obtained at mild steel in 0.5 M H_2SO_4 in the presence of constant concentration of Cu^{2+} and different concentrations of SCP

The deviation from pure semi-circle behavior known as frequency depression happens due to roughness and inhomogeneity of the surface during corrosion [22]. The polarization resistance in the presence of Cu^{2+} increased. On adding SCP the diameters of semicircles significantly increase with the increase in concentration. This is attributed to the increase in substrate impedance with the increase in inhibitor concentrations. This could be explained based on the formation of Cu-SCP complex on the electrode surface. The inhibition efficiency is increased to 90 % in the presence of 200 μ M SCP + 20 μ M Cu^{2+} .

Table 4. Effect of [inh] on the polarization resistance and protection efficiency for corrosion of mild steel in 0.5 M H_2SO_4 (blank) and after addition of 2×10^{-5} M Cu^{2+} at 25 °C.

System	R_{ct} (Ω)	% P
Blank	52	--
2×10^{-5} M Cu^{2+}	120	57
$Cu^{2+} + 1 \times 10^{-5}$ M Inh.	204	74
$Cu^{2+} + 2 \times 10^{-5}$ M Inh.	261	80
$Cu^{2+} + 5 \times 10^{-5}$ M Inh.	357	85
$Cu^{2+} + 1 \times 10^{-4}$ M Inh.	455	89
$Cu^{2+} + 2 \times 10^{-4}$ M Inh.	541	90

Fig. 6 shows the impedance plots obtained at carbon steel in the absence and presence of constant concentration of SCP and Cu^{2+} , 10 μ M each, while increasing the concentration of halides. Parameters extracted from this

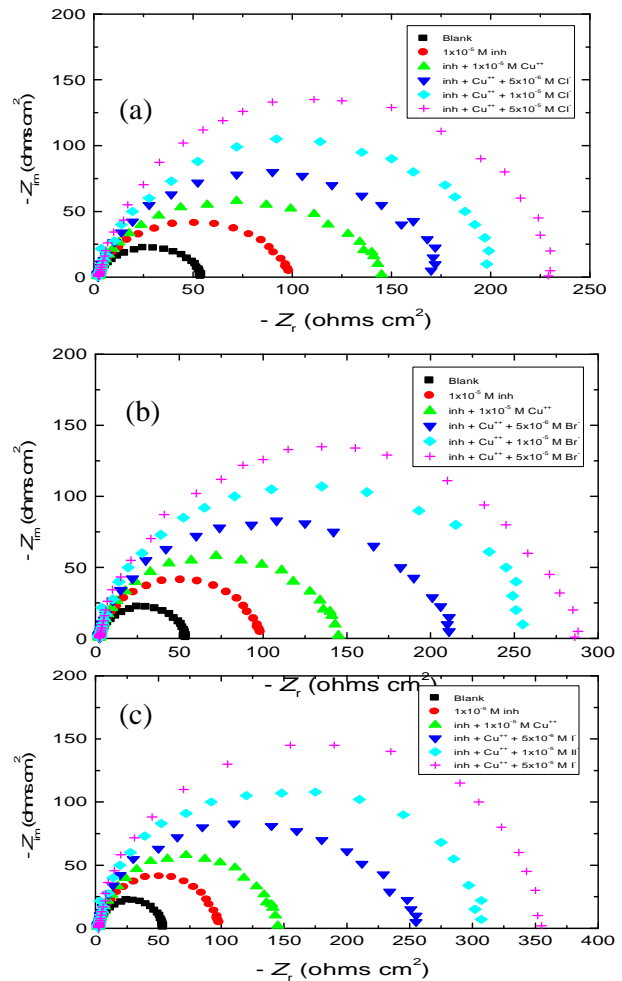
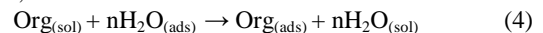


Fig. 6 (a-c). Effect of halide ions on the corrosion of mild steel in 0.5 M H_2SO_4 (blank) in the presence of sulfachloropyridazine and copper ion at 25 °C.

figure are given in Table 5. It is clear that the semi-circle radius increase upon adding halides to H_2SO_4 solution containing 10 μ M SCP + 10 μ M Cu^{2+} which is reflected on the increase in the inhibition efficiency. However the increase in the inhibition efficiency does not depend on the type of halide as the difference in the inhibition efficiency in the presence of any of the added halides is not that large.

Adsorption Isotherm

The substitutional adsorption of an inhibitor to the adsorbed water molecules ($H_2O_{(ads)}$) is represented by the following equation;



where, $Org_{(sol)}$ and $Org_{(ads)}$ are the organic molecules in the aqueous solution and the adsorbed one, n is

the number of water molecules replaced by one inhibitor molecule. The basic information on the interaction between

Table 5. Effect of halide ion concentration on the polarization resistance and protection efficiency for corrosion of mild steel in 0.5 M H₂SO₄ (blank) in presence of sulfachloropyridazine at 25 °C.

System	R_{ct} (Ω)	% P
Blank	52	--
1x10 ⁻⁵ M inh	100	48
inh + 1x10 ⁻⁵ M Cu ⁺⁺	144	64
inh + Cu ⁺⁺ + 5x10 ⁻⁶ M Cl ⁻	173	69
inh + Cu ⁺⁺ + 1x10 ⁻⁵ M Cl ⁻	198	74
inh + Cu ⁺⁺ + 5x10 ⁻⁵ M Cl ⁻	229	77
inh + Cu ⁺⁺ + 5x10 ⁻⁶ M Br ⁻	210	75
inh + Cu ⁺⁺ + 1x10 ⁻⁵ M Br ⁻	257	80
inh + Cu ⁺⁺ + 5x10 ⁻⁵ M Br ⁻	286	82
inh + Cu ⁺⁺ + 5x10 ⁻⁶ M I ⁻	252	79
inh + Cu ⁺⁺ + 1x10 ⁻⁵ M I ⁻	308	83
inh + Cu ⁺⁺ + 5x10 ⁻⁵ M I ⁻	355	85

the inhibitor and the mild steel surface could be extracted from the so-called adsorption isotherms. Adsorption isotherms provide useful insights into the mechanism of corrosion inhibition. Fitting of the experimental data to various isotherms including Langmuir, Temkin, and Flory–Huggins isotherms has been examined, and it has been found that the experimental results in this study for SCP and SCP/copper ions systems accord with Langmuir isotherm, given by Eq. 5 [42], and the plots are presented in Fig. 7 for SCP and SCP/Cu²⁺.

Table 6. The parameters of the linear regression obtained from the Langmuir adsorption isotherm.

	Slope	Intercept	R	K_{ads}	ΔG_{ads} , kJ mol ⁻¹
Inh	1.0912	2.1 x 10 ⁻⁵	0.9901	4.76 x 10 ⁴	36.635
Inh + Cu(II)	1.1121	0.2 x 10 ⁻⁵	0.9991	5.00 x 10 ⁵	42.462

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (5)$$

where, K is the equilibrium constant for adsorption process which reflects the extent of interaction between the inhibitor and the metal surface and C is the concentration of the inhibitor. Consequently inhibitor exerts its action via the formation of monolayer, and there is no interaction between the inhibitor molecules [43]. The parameters derived from Langmuir, i.e. K and change in free energy of adsorption ΔG_{ads}^0 are given in Table 6. The large value of K reflects the stronger ability of adsorption of the inhibitor on the metal surface. ΔG_{ads}^0 was calculated using Eq. 6 [44];

$$\Delta G_{ads}^0 = -RT \ln(55.5K_{ads}) \quad (6)$$

where, R is molar gas constant (8.314 J K⁻¹), T is temperature in Kelvin and value 55.5 is the concentration of water in mol dm³ in solution.

The large negative value of ΔG_{ads}^0 indicates the strong adsorption of the inhibitor. Generally speaking, the energy values of $\Delta G_{ads}^0 \leq -20$ kJ mol⁻¹ are associated with an electrostatic interaction between charged inhibitor molecules and charged metal surface, i.e., physisorption; while those ≥ -40 kJ mol⁻¹ involve charge sharing or transfer from the

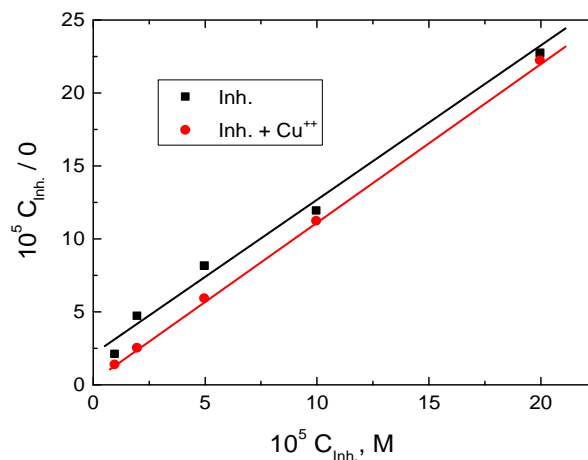


Fig. 7 Langmuir isotherm for mild steel in 0.5M H₂SO₄ containing Inh. and (Inh + Cu²⁺) at 25 °C.

inhibitor molecules to the metal surface to form a coordinate type bond, i.e. chemisorption. Thus in the present case (ΔG_{ads}^0 ca. 40 kJ mol⁻¹) chemisorption is the most probable mode with a small contribution of the physical mode, i.e., charge sharing between the inhibitor and the metal surface forming co-ordinate covalent bond [45].

IV. CONCLUSIONS

The synergistic corrosion inhibition of SCP by halides and/or copper ions has been studied in 0.5 M H₂SO₄ solution using potentiodynamic measurements and electrochemical impedance spectroscopy (EIS). Both halides and copper ions enhanced the corrosion inhibition of mild steel by SCP with preferential effect on the anodic branch. Adsorption of SCP in the absence and presence of copper ions fits with Langmuir isotherm.

REFERENCES

- [1] Y. Zhang, M. Nie, . Wang, Y. Zhu, F. Shi , J. Yua and Baorong Hou, " Effect of molecular structure of aniline–formaldehyde copolymers on corrosion inhibition of mild steel in hydrochloric acid solution" *J. Haz. Mat.* 289 (2015) 130–139.
- [2] P. Mourya, S. Banerjee and M.M. Singh, "Corrosion inhibition of mild steel in acidic solution by *Tagetes erecta* (Marigold flower) extract as a green inhibitor", *Corr. Sci.* 85 (2014) 352–363.
- [3] F. Bentiss, M. Lagrenee and M. Traisnel and J. C. Hornez, "The corrosion inhibition of mild steel in acidic media by a new triazole derivative", *Corr. Sci.* 41 (1999) 789–803.
- [4] S.A. AbdEl-Maksoud and A.S. Fouda, "Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium", *Mater. Chem. Phys.* 93 (2005) 84–90.
- [5] H. Keles, M. Keles, I. Dehri and O. Serindag, " The inhibitive effect of 6-amino-m-cresol and its Schiff base on the corrosion of mild steel in 0.5 M HCl medium", *Mater. Chem. Phys.* 112 (2008) 173–179.
- [6] H. Wang, H. Fan and J. Zheng, " Corrosion inhibition of mild steel in hydrochloric acid solution by a mercaptotriazole Compound" *Mater. Chem. Phys.* 77 (2003) 655–661.
- [7] M. Abdallah, " Ethoxylated fatty alcohols as corrosion inhibitors for dissolution of zinc in hydrochloric acid", *Corros. Sci.* 45 (2003) 2705–2716.
- [8] M. Lagrenee, B. Memari, M. Bouanis, M. Traisnel and F. Bentiss, "Study of the mechanism and inhibiting efficiency of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole on mild steel corrosion in acidic media", *Corr. Sci.* 44 (2002) 573–588.
- [9] M.A. Hegazy, M. Abdallah, M. K. Awad and M. Rezk, Three novel di-quaternary ammonium salts as corrosion inhibitors for API X65 steel pipeline in acidic solution, Part I: Experimental results, *Corros. Sci.* 81 (2014) 54–64.
- [10] G.I. Ostapenko, P.A. Gloukhov and A.S. Bunev, " Investigation of 2-cyclohexenylcyclohexanone as steel corrosion inhibitor and surfactant in hydrochloric acid", *Corr. Sci.* 82 (2014) 265–270.
- [11] M. Özcan, D. Toffoli, H. Üstünel and T. Dehri, "Insights into surface-adsorbate interactions in corrosion inhibition processes at the molecular level", *Corr. Sci.* 80 (2014) 482–486.
- [12] M. Bobina, A. Kellenberger, J. P. Millet, C. Muntean and N. Vaszilcsin, "Corrosion resistance of carbon steel in weak acid solutions in the presence of L-histidine as corrosion inhibitor", *Corros. Sci.* 69 (2013) 389–395.
- [13] I. B. Obot, Z.M. Gasem and S.A. Umoren, "Molecular level understanding of the mechanism of aloes leaves extract inhibition of low carbon steel corrosion: a DFT approach", *Int. J. Electrochem. Sci.* 9 (2014) 510–522.
- [14] P.B. Raja, A.K. Qureshi, A.A. Rahim, H. Osman and K. Awang, "Neolamarckia cadamba alkaloids as eco-friendly corrosion inhibitors for mild steel in 1 M HCl media", *Corr. Sci.* 69 (2013) 292–301.
- [15] M.M. Fares, A.K. Maayta and M.M. Al-Qudah, "Pectin as promising green corrosion inhibitor of aluminum in hydrochloric acid solution", *Corr. Sci.* 60 (2012) 112–117.
- [16] H. Bentrab, Y. Rahali and A. Chala, "Gum Arabic as an eco-friendly inhibitor for API 5L X42 pipeline steel in HCl medium", *Corr. Sci.* 82 (2014) 426–431.
- [17] M.A. Abu-Dalo, A.A. Othman and N.A.F. Al-Rawashdeh, "Exudate gum from acacia trees as green corrosion inhibitor for mild steel in acidic media", *Int. J. Electrochem. Sci.* 7 (2012) 9303–9324.
- [18] S. Banerjee, V. Srivastava and M.M. Singh, "Chemically modified natural polysaccharide as green corrosion inhibitor for mild steel in acidic medium", *Corr. Sci.* 59 (2012) 35–41.
- [19] P. Roy, A. Pal and D. Sukul, "Origin of the synergistic effect between polysaccharide and thiourea towards adsorption and corrosion inhibition for mild steel in sulphuric acid", *RSC Adv.* 4 (2014) 10607–10613.
- [20] O. A. Hazazi, A. Fawzy and M. I. Awad, "Synergistic effect of halides on the corrosion inhibition of mild steel in H₂SO₄ by a triazole derivative: kinetics and thermodynamic studies", *Int. J. Electrochem. Sci.* 9 (2014) 4086.
- [21] A. Khamis, M. M. Saleh, M. I. Awad and B.E. El-Anadouli "Inhibitory action of quaternary ammonium bromide on mild steel and synergistic effect with other halide ions in 0.5 M H₂SO₄", *J. Adv. Res.*, 5 (2014) 637.
- [22] O. A. Hazazi, A. Fawzy, M. R. Shaaban and M. I. Awad, "Enhanced 4-amino-5-methyl-4H-1,2,4-triazole-3-thiol Inhibition of Corrosion of Mild Steel in 0.5 M H₂SO₄ by Cu(II)" *Int. J. Electrochem. Sci.*, 9 (2014) 1378.
- [23] A. Khamis, M. M. Saleh, M. I. Awad and B.E. El-Anadouli, "Enhancing the inhibition action of cationic surfactant with sodium halides for mild steel in 0.5 M H₂SO₄", *Corr. Sci.*, 74 (2013) 83-91.
- [24] A. Khamis, M. M. Saleh and M. I. Awad, "Synergistic Inhibitor Effect of Cetylpyridinium Chloride and Other Halides on the Corrosion of Mild Steel in 0.5 M H₂SO₄", *Corr. Sci.*, 66 (2013) 343.
- [25] A. Khamis, M. Saleh and M. I. Awad, "The counter ion influence of cationic surfactant and role of chloride ion synergism on corrosion inhibition of mild steel in acidic media", *Int. J. Electrochem. Sci.*, 7 (2012) 10487 - 10500.
- [26] M. I. Awad, "Eco friendly corrosion inhibitors: Inhibitive action of quinine for corrosion of low carbon steel in 1 M HCl", *J. Appl. Electrochem.*, 36 (2006) 1163-1168.
- [27] C. J. Wood, W. J. Marbel, M. Prystupa, M. J. Hudson and D. L. Wilkens, in: *Proc. of 5th Inter. Conf. on Water Chemistry of Nuclear Reactor Systems*, vol. 1, BNES, 1989, pp. 111–120.
- [28] T.M. Angeliu and P. L. Andresen, " Effect of Zinc Additions on Oxide Rupture Strain and Repassivation Kinetics of Iron-Based Alloys in 288°C Water", *Corrosion* 52 (1996) 28–35.
- [29] K. Aramaki, "The effect of modification with hydrogen peroxide on a hydrated cerium (III) oxide layer for protection of zinc against corrosion in 0.5 M NaCl", *Corr. Sci.* 48 (2006) 766–782.
- [30] T. Notoya, V. Oteino-Alego and D. P. Schweinsberg, "The corrosion and polarization behaviour of copper in domestic water in the presence of Ca, Mg and Na-salts of phytic acid", *Corr. Sci.* 37 (1995) 55–65.
- [31] D. M. Drazic and L. Z. Vorkapic, "Inhibitory effects of manganese, cadmium and zinc ions on hydrogen evolution reaction and corrosion of iron in sulphuric acid solutions", *Corr. Sci.* 18 (1978) 907.
- [32] M.S. Abdel Aal and M. H. Wahdan, *Br. Corr. J.* (1998) 25.
- [33] H. Leidheiser, I. Suzuki, " Cobalt and Nickel Cations as Corrosion Inhibitors for Galvanized Steel", *J. Electrochem. Soc.* 128 (1981) 242.
- [34] M.Wahdan, "The synergistic inhibition effect and thermodynamic properties of 2-mercaptobenzimidazol and some selected cations as a mixed inhibitor for pickling of mild steel in acid solution", *Mater. Chem. Phys.* 49 (1997) 135.
- [35] M. Duprat and F. Dabos, in: *Proceedings of the Fifth SEIC*, Ferrara, Italy, 1980, p. 675.
- [36] J. M. West, in " *Electrodeposition and Corrosion Process*", second ed., Van Nostrand-Reinhold, London,1970. p.93.
- [37] Z. Qiang and C. Adams, " Potentiometric determination of acid dissociation constants (pK_a) for human and veterinary antibiotics", *Water Res* 2004, 38, 2874-2890.
- [38] M. S. Iqbal, A. H. Khan and B. A. Looher, "Comparative study of pharmaceutical properties of some new derivatives of sulfamethoxazole", *Pharm Dev Technol.* 15 (2010) 613-618.
- [39] J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandalov and U. Stimming, " Trends in the Exchange Current for Hydrogen Evolution", *J. Electrochem. Soc.*, 152 (2005) J23-J26.
- [40] M. Lebrini, F. Robert and C. Roos, " Inhibition Effect of Alkaloids Extract from *Annona Squamosa* Plant on the Corrosion of C38 Steel in Normal Hydrochloric Acid Medium", *Int J Electrochem Sci* 5 (2010) 1698–1712.
- [41] F. B. Growcoc and R. I. Jasinski, "Time-Resolved Impedance Spectroscopy of Mild Steel in Concentrated Hydrochloric Acid", *J Electrochem Soc* 136 (1989) 2310–2314.
- [42] D. K. Yadav and M. A. Quraishi, " Electrochemical investigation of Substituted Pyranopyrazoles Adsorption on Mild Steel in Acid Solution", *Ind Eng Chem Res* 2012, 51, 8194-8210.
- [43] E. E. Ebenso, I. B. Obot and L. C. Murulana, " Quinoline and its Derivatives as Effective Corrosion Inhibitors for Mild Steel in Acidic Medium ", *Int J Electrochem Sci* 2010, 5, 1574-1586.
- [44] M. Tourabi, K. Nohair, M. Traisnel, C. Jama and F. Bentiss , " Electrochemical and XPS studies of the corrosion inhibition of carbon steel in hydrochloric acid pickling solutions by 3,5-bis(2-thienylmethyl)-4-amino-1,2,4-triazole", *Corros Sci* 2013, 75,123-133.
- [45] G. Moretti, F. Guidi and G. Grion, "Tryptamine as a green iron corrosion inhibitor in 0.5 M deaerated sulphuric acid", *Corr. Sci.* 46 (2004) 387-403.