View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. A. Quraishi, N. K. Gupta, C. Verma, R. Salghi, H. Lgaz and A. K. Mukherjee, *New J. Chem.*, 2017, DOI: 10.1039/C7NJ01431G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

New Phosphonate based corrosion inhibitors for mild steel in hydrochloric acid useful for industrial pickling process: Experimental and Theoretical approach

Neeraj Kumar Gupta¹, Chandrabhan Verma^{1,3}, R. Salghi⁴, H. Lgaz^{4,5}, A.K. Mukherjee¹, M.A. Quraishi^{1,2}*

¹Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi -221005, India.

²Center of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.

³Department of Chemistry, Faculty of Agriculture, Science and Technology, North-West

University, Mafikeng Campus, Private Bag X2046, Mmabatho 2735, South Africa

⁴Laboratory of Applied Chemistry and Environment, ENSA, Universite Ibn Zohr, PO Box 1136, 80000 Agadir, Morocco.

⁵Laboratory of separation methods, Faculty of Science, Ibn Tofail University PO Box 242, Kenitra, Morocco

*Corresponding author:

Ph.no. +91-9307025126; Fax: +91- 0542- 2368428

E-mail: maquraishi.apc@itbhu.ac.in; maquraishi@rediffmail.com

Abstract:

Present work deals with the synthesis and study of inhibition effect of three α -aminophophonates namely, diethyl (((4-chlorophenyl)amino)(phenyl)methyl)phosphonate (APCI-1), diethyl (((4-chlorophenyl)amino)(4-methoxyphenyl)methyl)phosphonate (APCI-2) and diethyl (1-((4-chlorophenyl)amino)-3-phenylallyl)phosphonate (APCI-3) on mild steel corrosion in 1 M hydrochloric acid solution using both experimental and theoretical methods. Weight loss results showed that the inhibition performance of the studied compounds increases with the concentration and the maximum inhibition efficiency were obtained at just 564 X10⁻⁶M

concentration. Among all the three tested inhibitors, APCI-3 showed the best result having inhibition efficiency of 96.90%. The Potentiodynamic polarization study indicates that these α-aminophosphonates act as mixed type inhibitors and predominantly functions as cathodic inhibitor. Adsorption of the tested APCIs on the metallic surface obeyed the El-Awady adsorption isotherm. The adsorption of these compounds on the metallic surface was also supported by the scanning electron microscopy (SEM) and atomic force microscopy (AFM) methods. A good insight about the inhibition mechanism of the tested compounds was derived using the DFT based quantum chemical calculations for their neutral as well as protonated forms. The orientation of inhibitors on the metallic surface and the interaction energies of these molecules were obtained using molecular dynamic simulation studies. Both experimental and theoretical studies suggested that the inhibition efficiency of the tested compounds followed the order APCI-3>APCI-2>APCI-1 and well corroborated each other.

Keywords: α-Aminophophonates; Mild steel corrosion; SEM/AFM; DFT/ MD; El-Awady adsorption isotherm.

1. Introduction

Corrosion is the most damaging and challenging problem all over the world. Each country loses 3-5% of its GDP due to corrosion. According to NACE the annual global cost of corrosion is approximately US \$2.5 trillion, equating 3.4% of the global GDP. In India, the annual corrosion cost is more than US \$100-billion [1,2]. The cost of corrosion can be reduced by 15 to 35% by properly applying the existing methods of corrosion prevention.

The chemical synthesis using one pot multicomponent reactions (MCRs) for variety of purposes are highly desirable owing to the growing interest of green chemistry in all branches of science and technology [3,4]. Recently, MCRs have gained pronounce interest in the field of synthetic organic and medicinal chemistry due to their several fascinating features, such as high selectivity, convergence, atom economy, molecular complexity and versatility [5,6]. The MCRs also associated with high yield, short reaction time, operation simplicity, mild operating condition which attributed to their association with one step nature that results in facile automation, small number of reaction steps, reduced production of waste, simple purification method, fewer number of workup steps and enhance synthetic efficiency [7]. Therefore, the MCRs provides a cheaper and eco friendly way to synthesize various compounds. Moreover, the increasing ecological awareness demands green and sustainable solvents that have very low or

negligible adverse effect on the surrounding environment and living being. Towards utilization of green and sustainable solvents, water has gained substantial attention due to its non-flammable, non-toxic, uniquely redox-stable, non-hazardous, free availability and inexpensive nature. It is general statement that "best solvent is no solvent". Recently, chemical synthesis using concept of multicomponent reactions in association with ultrasound (US) and microwave have been considered as most powerful and interesting green and sustainable alternative methods.

Literature survey reveals that previously phosphonates were introduced as scale inhibitors in water treatment and later their good corrosion inhibition behavior was also recognized [8]. And their impact on the environment was reported to be negligible at the concentration level used for corrosion inhibition [9]. However, authors mainly exploited the use of phosphonates as corrosion inhibitor in protective metal phosphonate films [10] or in H_2SO_4 medium [11, 12] and very few literatures are available on the use of phosphonates as corrosion inhibitor for mild steel in HCl medium [13,14]. In view of these observations, it was thought worthwhile to synthesize α -aminophophonates (APCIs) to investigate their effect on the corrosion of mild steel in acidic medium. The APCIs undertaken in the present work were synthesized using one pot multicomponent reaction under ultrasound irradiation and under solvent and catalyst free condition. The criteria behind considering these compounds for the corrosion inhibition test was based on the fact that they contain several heteroatoms (N and O) along with π - electrons of the aromatic rings that can act as adsorption centers during the metal-inhibitor interaction [15]. Novelty of the present study lies on the fact that although there are variety of organic compounds containing nitrogen, oxygen and sulfur which have been successively used as a corrosion inhibitor, but the use of phosphorus containing compounds as corrosion inhibitor is relatively scare. In view of the above fact and considering the green synthesis by MCRs and ultrasound technique, we herein synthesized and studied the inhibition effect of three phosphorus containing compounds for the mild steel in 1M HCl solution using weight loss, electrochemical (PDP, EIS), surface (SEM, AFM), DFT based quantum chemical calculations and molecular dynamic (MD) simulations methods. A good agreement was observed in the results of experimental and theoretical measurements. The investigated APCIs exhibited higher corrosion inhibition efficiency (96.9% at 564 x10⁻⁶M concentration) than that of hexamine, a commonly used inhibitor in steel industries during pickling process which shows 90% efficiency at 714x10⁻⁶M optimum concentration. Moreover hexamine is a toxic inhibitor so its use must be avoided.

2. Experimental:

2.1. Material

All the experiments including weight loss, electrochemical and surface analysis (SEM/AFM) was performed on the mild steel specimens having following composition (wt%): C=0.076, P=0.012, Mn=0.192, Si=0.026, Al=0.023, Cr=0.050 and Fe=99.621. All the mild steel specimens were prepared as per the standard procedures already reported in our previous publications [2,7]. The test solution of 1 M HCl acid was prepared by diluting the analytical reagent (37% HCl, AR grade) grade HCl by double distilled water.

2.2. Synthesis of inhibitor

All the three α -aminophosphonates (APCIs) were synthesized by solvent free and catalyst free reaction by ultrasonic technique which can be represented according to the reaction scheme shown in Fig.1 as described in literature [16]. In the reaction process 4-chloroaniline (1 mmol), substituted benzaldehyde (1 mmol) and triethylphosphite (1.3 mmol) were poured in a beaker and ultrasonicated for 20s. After completion of the reactions, the crude products were purified through recrystallization that resulted yield about 99%.



Fig.1: Synthetic rout for investigated APCIs

The purity of the synthesized inhibitors was confirmed by the thin layer chromatography result performed using Siliaplate TLC plates- Aluminum (Al) Silica. Synthesized compounds were characterized by the infrared (IR) spectra recorded on KBr discs by using Perkin-Elmer (Spectrum 100) Fourier transform (FT-IR) spectrophotometer. The IUPAC names, chemical structures and IR data of synthesized APCIs are reported in Table 1.

Table 1: IUPAC name, molecular structure, molecular formula and analytical data of studied APCIs.

<u>S.</u>	Name of inhibitor	Chemical structure	Analytical data
No.			
1	diethyl (((4- chlorophenyl)amino)(phenyl)methyl)phosp honate (APCI-1)		C ₁₇ H ₂₁ ClNO ₃ P (mol. wt. 353.78); FT-IR (KBr cm ⁻¹): 3470, 3183, 2862, 2448, 2973, 2823, 1628, 1664, 1580, 1130, 1238, 974, 835, 786, 654. ¹ H NMR (CDCl ₃ , TMS, 500 MHz) δ (ppm) 6.5-7.4 (8H, Ar-H and 1H, NH) 4.7 (1H, CH), 3.6-4.1 (4H, P-O-CH ₂ -),
2	diethyl (((4- chlorophenyl)amino)(4- methoxyphenyl)meth yl)phosphonate (APCI-2)		1.1-1.3 (6H, P-O-CH ₂ -CH ₃). $C_{18}H_{23}CINO_4P$ (mol. wt. 383.11); IR (KBr cm ⁻¹): 3563, 3228, 2986, 2854, 1670, 1594, 1474, 1339, 1232, 1160, 948, 827, 792. ¹ H NMR (CDCl ₃ , TMS, 500 MHz) δ (ppm) 6.5-7.3 (8H, Ar-H and 1H, NH) 4.6 (1H, CH), 3.6- 4.1 (4H, P-O-CH ₂ -), 3.7 (3H, O- CH ₃) 1.1-1.3 (6H, P-O-CH ₂ - CH ₃).
3	diethyl (1-((4- chlorophenyl)amino)- 3- phenylallyl)phosphon ate (APCI-3)		C ₁₉ H ₂₃ ClNO ₃ P (mol. wt. 379.82); IR (KBr cm ⁻¹): 3546, 3173, 2948, 2836, 2684, 1728, 1658, 1548, 1418, 1273, 1138, 926, 868, 675. ¹ H NMR (CDCl ₃ , TMS, 500 MHz) δ (ppm) 6.6-7.4 (9H, Ar-H and 1H, NH), 6.2-6.7 (2H, -CH=CH-) 4.1-4.2 (4H, P-O- CH ₂ -), 3.7 (3H, O-CH ₃) 1.31- 1.34 (6H, P-O-CH ₂ -CH ₃).

2.3. Gravimetric Measurements

Gravimetric technique is considered as one of the best method to study the inhibition performance of the inhibitor due to its simplicity and reliability. In the present study, gravimetric experiments have been used to calculate the corrosion inhibition performance of synthesized APCIs by the previously described methods [17]. All the experiments were performed in triplicate and the average value was taken for calculating corrosion rate for greater accuracy. The corrosion rates $C_{\rm R}$ (mg cm⁻² h⁻¹) was calculated by using the following equation:

$$C_{\rm R} = W / At \tag{1}$$

where, W is the average weight loss occurred in the three parallel experiments, A is the total surface area of one mild steel specimen, and t is the immersion time (3 h). From the calculated corrosion rate, the inhibition efficiency η % and surface coverage area (θ) was calculated by following equations:

$$\eta\% = [(C_{\rm R} - C_{\rm R(i)}) / C_{\rm R}] \times 100$$
⁽²⁾

$$\theta = (C_{\rm R} - C_{\rm R(i)}) / C_{\rm R} \tag{3}$$

where C_R and $C_{R(i)}$ represent the corrosion rates for mild steel in absence and presence of APCIs in 1 M HCl solution, respectively.

2.4. Electrochemical measurements

Published on 03 October 2017. Downloaded by University of Newcastle on 03/10/2017 14:39:46.

All the Electrochemical studies were performed by the method already described in the literature [18]. All electrochemical experiments were carried out by using three electrode cell assembly connected to a Potentiostat/Galvanostat G300–45050 (Gamry Instruments, Inc.,U.S.A.). The obtained data was analyzed by Echem Analyst 5.0 software package. Among the three electrode system, mild steel with exposed area of 1 cm² was used as a working electrode, a platinum electrode as an auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. Prior to each electrochemical experiment, the working electrode was allowed to corrode freely for sufficient time so that it can achieve a steady open circuit potential (OCP).

The electrochemical impedance studies (EIS) were carried out for the mild steel specimens in the frequency range of 100 kHz to 0.01 Hz using an AC source with amplitude of 10 mV peak to peak. The polarization resistance was calculated by fitting the appropriate

$$\eta\% = [(R_{\rm p}^{\rm i} - R_{\rm p}^{\rm 0}) / R_{\rm p}^{\rm i}] \times 100 \tag{4}$$

Where R_{p}^{i} and R_{p}^{0} are the polarization resistance values in the presence and absence of APCIs in 1.0 M HCl solution, respectively.

Polarization measurements was carried out by changing the potential of working electrode from -250 mV to +250 mV versus open circuit potential at a scan rate of 1 mV s⁻¹. Then the anodic and cathodic regions were used for extrapolating their linear segments to calculate the corrosion potential value (E_{corr}) and the corrosion current densities (i_{corr}). The calculated i_{corr} value was used to calculate the inhibition efficiency of APCIs using following relation [19]:

$$\eta\% = [(i_{\rm corr}^0 - i_{\rm corr}^i) / i_{\rm corr}^0] \times 100$$
(5)

Where, i_{corr}^0 and i_{corr}^i are the corrosion current densities in absence and presence of APCIs in 1 M HCl solution.

2.5. SEM and AFM Measurements

SEM and AFM studies were conducted to get the insight into the change in surface morphology of the corroding mild steel sample in 1 M HCl solution in the presence (at 564 x10⁻⁶M) and absence of APCIs. Mild steel coupons were immersed in 1 M HCl solution in the absence, and presence of optimum concentration of APCIs for 3h at 350C, and then taken out and cleaned with double distilled water and ethanol, dried at room temperature and finally analyzed by SEM and AFM. The SEM study was performed by Ziess Evo 50XVP instrument using accelerating voltage of 50 kV at 500X magnification. The AFM analysis of mild steel corroded samples were performed by the NT-MDT multimode AFM, Russia, that is controlled by Solver scanning probe microscope controller. A single beam cantilever with resonance frequency between 240–255 kHz having spring constant of 11.5 Nm⁻¹ with NOVA program was used in semi contact mode to interpret the image. The scanning area for analysis was 10 μ m×10 μ m.

2.6. Quantum Chemical Calculations

Density functional theory (DFT) is an ab initio approach very popular for computing the ground state electronic properties of molecules with high accuracy and in very less time as compared to other computational methods [20]. In this present work all DFT calculations were performed by

using Gaussian 09 program package. The molecular structures of all the APCIs (neutral and protonated forms) were geometrically optimized using the Becke three-parameter hybrid functional together with the Lee–Yang–Paar correlation functional (B3LYP) and the 6-31+G (d,p) orbital basis set for all atoms [21].

The electronic parameters for the most stable conformers of the molecules were used to derive all the quantum chemical electronic parameters. The frontier molecular orbital (FMO) energies, i.e. the highest occupied molecular orbital energy (E_{HOMO}) and the lowest unoccupied molecular energy (E_{LUMO}) were calculated and used for the calculation of other important parameters such as the energy gap (ΔE), global hardness (η), softness (σ), global electronegativity (χ), and the fraction of electrons transfer (ΔN) from the inhibitor to the metal atom by the following equations respectively [22,23]:

$$\Delta E = E_{LUMO} - E_{HOMO} \tag{6}$$

$$\eta = \left(E_{LUMO} - E_{HOMO}\right)/2\tag{7}$$

$$\sigma = 1/\eta \tag{8}$$

$$\chi = -\left(E_{LUMO} + E_{HOMO}\right)/2\tag{9}$$

$$\Delta N = (\chi_{Fe} - \chi_{inh}) / 2(\eta_{Fe} + \eta_{inh})$$
⁽¹⁰⁾

Where χ_{Fe} and η_{inh} represent the electronegativity of iron and hardness of inhibitor respectively. The values of χ_{Fe} and η_{inh} is taken as 7eV mol⁻¹ and 0 eV mol⁻¹ respectively considering the bulk Fe atoms according to the Pearson's electronegativity scale [24].

2.7. Molecular Dynamics

Molecular Dynamic (MD) simulations of tested inhibitors were carried out in a simulation box with periodic boundary conditions using Materials Studio 6.0 (from Accelrys Inc.) [25]. The iron crystal was imported and cleaved along (110) plane and a slab of 5 Å was employed. The Fe (110) surface was relaxed by minimizing its energy using smart minimiser method. Then Fe (110) surface was enlarged to a (10×10) super cell in order to provide a large surface to the inhibitors for interaction. A zero thickness vacuum slab was built. A supercell with a size of a = b = 24.82 Å c = 25.14 Å, contains 500 H₂O, 5H₃O⁺, 5Cl⁻ and one molecule of tested inhibitors was created. The simulation was performed in a simulation box ($24.82 \times 24.82 \times 35.69$

New Journal of Chemistry

 $Å^3$) using the discover module having time step of 1 fs and simulation time of 500 ps carried out at 303 K, NVT ensemble (constant number of atoms, constant-volume, constant-temperature) and COMPASS force field [26]. In simulation system, the interactions between inhibitors and Fe (110) surface can be understood by interaction and binding energies calculated using equation (10) and (11) [27]:

$$E_{\text{interaction}} = E_{\text{total}} - (E_{\text{surface+solution}} + E_{\text{inhibitor+solution}}) + E_{\text{solution}}$$
(11)
$$E_{\text{Binding}} = -E_{\text{interaction}}$$
(12)

Where E_{total} represents the total energy of the entire system and $E_{\text{surface+solution}}$ referred to the total energy of Fe (1 1 0) surface and solution without the inhibitor and $E_{\text{inhibitor+solution}}$ represent the total energy of inhibitor and solution; and E_{solution} is the total energy of the solution.

3. Result and Discussion

3.1.Weight loss experiment

3.1.1. Effect of APCIs concentration

The values of percentage inhibition efficiency (% η) of APCIs, corrosion rate (C_R) for mild steel specimen and the surface coverage (θ) by APCIs obtained from weight loss experiments at different concentrations of inhibitors in 1 M HCl solution at 308K are reported in Table 2.

Table 2: The weight log	oss parameters (±SI	D) derived for	Mild Steel in	1 M HCl solution at
different concentration	is of APCIs.			

inhibitor	Conc	$C_{\rm R}(\rm mg~cm^{-2}~h^{-1})$	Surface coverage	η%
	(x10 ⁻⁶ M)		(heta)	
Blank	0.0	7.66		-
	141	3.20	0.583	58.6 ± 0.35
APCI-1	282	1.60	0.791	79.1±0.35
	423	0.86	0.887	88.7±0.75
	564	0.56	0.926	92.6±0.43

Page 10 of 39

View Article Online DOI: 10.1039/C7NJ01431G

	141	2.66	0.52	65.2±0.43
APCI-2	282	1.30	0.830	83.0±0.87
	423	0.66	0.913	91.3±0.75
	564	0.40	0.948	94.8±0.43
	141	2.26	0.704	70.4±0.75
APCI-3	282	0.80	0.896	89.6±0.87
	423	0.43	0.943	94.3±0.75
	564	0.23	0.969	96.9±0.43

New Journal of Chemistry



Fig.2: Variation of corrosion inhibition efficiency with APCIs concentration.

Published on 03 October 2017. Downloaded by University of Newcastle on 03/10/2017 14:39:46.

The variation of inhibition efficiency with the concentration of APCIs is also shown in Fig. 2. It is clear from the data that APCIs inhibits the corrosion at all studied concentrations and their $\eta\%$ increases with concentration and achieved maximum values of 92.60, 94.78 and 96.95% for APCI-1, APCI-2 and APCI-3, respectively at 564 x10⁻⁶M concentration. The

New Journal of Chemistry Accepted Manuscript

enhancement in $\eta\%$ with concentration is due to the increase in surface coverage by inhibitor molecule and therefore isolating the metal surface from the acid solution [28]. However above 564 x10⁻⁶M concentration inhibition efficiency does not increase significantly suggesting that probably the maximum surface coverage was obtained at this value. [29].

3.1.2. Temperature effect

The effect of temperature on the inhibition efficiency of a corrosion inhibitor is an important factor to be considered before using a corrosion inhibitor in any industry. In order to study the inhibition efficiency variation of studied APCIs with temperature and to calculate the activation parameters, weight loss experiments were performed at different temperatures (308-338 K). The variation of corrosion rate of mild steel in 1 M HCl solution with and without optimum concentration of APCIs is given in Table 3 which clearly shows that the corrosion rate is increasing with increase in temperature. This which might be due to the desorption or etching of the inhibitor film present on the metal surface [30]. The desorption of inhibitor film causes exposure of more metal surface to the HCl medium which resulted into higher corrosion rate [31]. Moreover the elevated solution temperature sometime also causes molecular decomposition which further decreases the corrosion inhibition performance [32].

Temperature (K)		Corrosion rate (C _F		
	Blank	APCI-1	APCI-2	APCI-3
308	7.66	0.56	0.40	0.23
318	11.0	1.23	1.03	0.70
328	14.3	2.36	2.06	1.80
338	18.6	4.70	4.63	4.33

Table 3: Variation of corrosion rate with temperature in absence and presence of optimum concentration of APCIs

The apparent activation energy (E_a) of corrosion process and corrosion rate can be related by Arrhenius equation [33] given by:

$$C_{\rm R} = A \exp(-E_{\rm a} / RT) \tag{13}$$

Where, C_R is the corrosion rate, R is the universal gas constant, T is the absolute temperature and A is the pre-exponential factor. The value of E_a were calculated from the slope (Ea/2.303R) of the Arrhenius graph plotted between log C_R versus 1000/T for mild steel in 1 M HCl solution with and without optimum concentration of APCIs which is shown in Fig. 3. The obtained values of E_a are 24.48, 60.60, 69.65, 84.12 kJ mol⁻¹ for blank solution, APCI-1, APCI-2, APCI-3 respectively which clearly shows that the value of E_a for uninhibited solution is less than that of inhibited solution . The significant rise in the E_a value indicates the protective film formation by inhibitor on the metal surface [34]. The adsorbed inhibitor isolates the metal surface from the corrosive environment and thus increases the energy barrier for the charge and mass transfer between metal and solution interface [28]. In the present study APCI-3 has the highest E_a value which confirms the best inhibition performance of APCIs decreases with rise in temperature which shows the physisorptive type of interaction among the adsorbed inhibitor film and the metal surface [35].

Published on 03 October 2017. Downloaded by University of Newcastle on 03/10/2017 14:39:46.



Fig.3: Arrhenius plots of log $C_{\rm R}$ versus 1000/T for mild steel corrosion in 1M HCl solution in absence and presence of APCIs.

3.1.3. Adsorption isotherm and thermodynamic parameters

It is well reported in literature that the adsorption of an organic molecule on the metal surface is the most important step in the corrosion inhibition process [36]. To understand the corrosion inhibition mechanism of inhibitors and to know the type of interaction between inhibitor molecules and the metal surface the adsorption characteristics of the inhibitor was studied by testing several adsorption isotherms including Langmuir, Temkin, Frumkin and and thermodynamic/kinetic model of El-Awady isotherms.



Fig.4: El-Awady adsorption isotherm plot for mild steel in 1 M HCl solution in presence APCIs at 308K.

In this study, the values for degree of surface coverage (θ) were fitted to a series of different stated adsorption isotherms but among them the Langmuir adsorption isotherm gave the best fit with regression coefficient (\mathbb{R}^2) value very close to unity. This indicated a high degree of fitness of the adsorption data to the Langmuir model. Langmuir adsorption isotherm expression is generally represented by [17]

$$K_{ads}C = \theta / (1 - \theta) \tag{14}$$

Where K_{ads} is the adsorption- desorption equilibrium constant, θ is the surface coverage and $C_{(inh)}$ is the APCIs concentration in mg L⁻¹. The Langmuir isotherm plot gave a straight line when

plotted between log ($\theta/1-\theta$) and $C_{(inh)}$ but its slope deviated considerably (1.23 to 1.83) from the unity which indicated that the isotherm could not be strictly applied (Table 4).

Table 4: Adsorption parameters calculated from El-Awady adsorption isotherm for mild steel in presence of APCIs.

Inhibitor	Slope (y)			Intercept (log <i>K</i>)				
Temperature(K)	308	318	328	338	308	318	328	338
APCI-1	1.58	1.47	1.43	1.44	6.23	5.68	5.38	5.15
APCI-2	1.63	1.51	1.39	1.32	6.52	5.90	5.29	4.79
APCI-3	1.83	1.66	1.34	1.23	7.45	6.53	5.19	4.54

In the derivation of Langmuir isotherm equation it is assumed that the adsorbed molecules do not interact with each other, but this is not true in the present case. These adsorbed APCIs may interact with each other by mutual repulsion or attraction and that might be the reason for the deviation of slope from unity [37]. So, the experimental data was fitted for the modified form of Langmuir isotherm known as El-Awady isotherm which is given by [38]

$$\log(\theta / 1 - \theta) = \log K + y \log C$$

(15)

where, y is number of inhibitor molecules occupying one active site, θ is the degree of surface coverage, C is the concentration, K is the constant related to the equilibrium constant of adsorption process as $K_{ads} = K^{1/y}$. The values of y and log K calculated from El-Awady adsorption isotherm plot (Fig.4) is given in Table 4. Values of 1/y less than one imply multilayer adsorption, while 1/y greater than one suggests that a given inhibitor molecule occupies more than one active site. In the present work the values of 1/y for all concentration were found to be less than unity which indicates the presence of physisorption [39]. The calculated value of K_{ads} is reported in Table 5. In general, the value of K_{ads} represents the strength of adsorption of inhibitor molecule on the metal surface [40]. Higher the value of K_{ads} , stronger is the adsorption of inhibitor on metal surface. Stronger adsorption leads to the more surface coverage by inhibitor on the metal surface and hence better inhibition efficiency [36]. Table 5 shows that the APCI-3 has the highest K_{ads} value among all studied APCIs and thus has highest

inhibition efficiency. The K_{ads} values can be related to the standard free energy of adsorption (ΔG^0_{ads}) according to the relation [41,42]:

$$\Delta G_{\rm ads}^{\rm o} = -RT \ln(55.5K_{\rm ads}) \tag{15}$$

where, *R* is the universal gas constant, *T* is the absolute temperature and value 55.5 represent the molar concentration of water in acid solution. The calculated values for the ΔG^0_{ads} are listed in Table 5. The values of ΔG^0_{ads} at 308K were found to be -33.48, -33.89 and -34.19 kJ mol⁻¹ for APCI-1, APCI-2 and APCI-3 respectively. However, these values are negatively less than the threshold value (-40 kJ/mol) expected for the chemisorption but greater than the (-20kJ/mol) assigned for physisorption [43]. Hence the adsorption APCIs on the mild steel specimen in 1 M HCl solution is a case of both physical as well as chemical adsorption [44].

Table 5: The values of K_{ads} and ΔG_{ads}° for mild steel in presence of APCIs in 1M HCl solution at different temperature.

Inhibitor	$K_{\rm ads}(10^3 { m M}^{-1})$			$K_{\rm ads}(10^3{\rm M}^{-1})\qquad -\Delta G^\circ$			$-\Delta G^{\circ}_{ads}$ ($kJ \mathrm{mol}^{-1}$)
Temperature(K)	308	318	328	338	308	318	328	338	
APCI-1	8.56	7.49	5.64	3.75	33.48	33.14	32.41	31.37	
APCI-2	10.05	7.85	6.30	4.28	33.89	33.26	32.68	31.70	
APCI-3	11.31	8.32	7.18	4.88	34.19	33.41	33.03	32.04	

3.2. Electrochemical measurements

3.2.1. Polarization study

Potentiodynamic polarization study was performed in absence and presence of different concentration of the APCIs in order to corroborate the findings of weight loss measurements. Fig. 5 represents the polarization curves for inhibited and uninhibited mild steel specimens in 1M HCl solution at 298K. Several polarization parameters such as anodic and cathodic Tafel slopes (β_a and β_c), corrosion potential (E_{corr}), and corrosion current density (i_{corr}) were calculated by extrapolating the linear portions of the cathodic and anodic polarization curves and listed in Table 6 along with corresponding inhibition efficiencies (η %).



Fig.5: Potentiodynamic polarization plots for mild steel in 1 M HCl solution in the absence and presence of different concentration of APCIs.

From the result it is clear that on increasing the concentration of the inhibitor molecules the corrosion current density decreases which suggest that the inhibition efficiency of the APCIs increases with concentration. It can be also seen from the polarization curves that the inhibitor molecules shifted the both anodic and cathodic domains of the polarization curves towards the

View Article Online DOI: 10.1039/C7NJ01431G

lower corrosion current density without changing the shape of the curves. This finding suggests that studied inhibitor molecules inhibit mild steel corrosion in 1M hydrochloric acid solution by forming a protective film on the metallic surface without changing the corrosion mechanism [45].

Table 6: Tafel Polarization parameters (±SD) for mild steel in 1 M HCl solution in absence and presence of different concentration of APCIs

Inhibitor	Conc.	$E_{\rm corr}$	<i>i</i> _{corr}	β_{a}	-β _c	η(%) from	R_p	η(%)
	(10 ⁻⁶ M)	(mV/	(μAcm^{-2})	(mV/dec)	(mV/dec)	<i>i</i> _{corr} value	(Ωcm^2)	from $R_{\rm p}$
		SCE)						value
Blank		-445	1150±4.3	70.5±0.32	114.6±0.15		9.58	
APCI-1	141	-513	493±1.7	73.2±0.15	181.3±0.36	57.13±0.15	23.34	58.95
	282	-510	246±2.6	64.3±0.36	124.3±0.28	78.60±0.23	42.19	77.29
	423	-495	115±2.6	83.5±0.28	129.1±0.10	90.00±0.23	78.82	87.84
	564	-522	81±1.0	71.2±0.15	158.7±0.10	92.93±0.08	121.3	92.10
APCI-2	141	-515	398±2.0	84.0±0.42	117±0.36	65.39±0.17	25.8	62.86
	282	-518	198±1.7	56.1±0.14	68.1±0.14	82.78±0.15	62.54	84.68
	423	-486	103±1.7	71.5±0.15	144.7±0.10	91.04±0.15	113.3	91.54
	564	-517	61±1.0	103.5±0.28	121.3±0.28	94.69±0.08	186.1	94.24
APCI-3	141	-522	340±2.0	69.0±0.28	109.4±0.42	70.43±0.17	36.95	74.07
	282	-526	132±1.0	107.1±0.36	167.5±0.20	88.52±0.08	91.79	89.56
	423	-539	63±1.7	112.3±0.10	168.0±0.10	94.52±0.15	158.6	93.95
	564	-516	32±1.7	85.7±0.15	161.9±0.10	97.21±0.15	299.2	96.79

Inspection of the results depicted in Table 6 revealed that presence of inhibitors in the corroding solution at their optimum concentration causes substantial decrease in the values of

corrosion current density (i_{corr}) and maximum decrease was obtained in the case of APCI-3. The corrosion inhibition efficiency obtained from i_{corr} values was compared with the values obtained from polarization resistance and it was found that both follows the same trend and showed maximum value for APCI-3. Results also showed that the presence of inhibitors in the corrosive medium does not alter the value of E_{corr} significantly as the maximum change in the values of E_{corr} were 77 mV, 72 mV and 71 mV for APCI-1, APCI-2 and APCI-3, respectively that is less that 85 mV which indicate that APCIs are behaved as mixed type inhibitors [46,47]. However, from the results depicted in Table 6, it is clear that presence of inhibitors cause relatively more change in the β_c values as compared to the β_a values. On the basis of ongoing discussion it can be inferred that investigated compounds acted as mixed type corrosion inhibitor for mild steel in 1M hydrochloric acid solution with some cathodic predominance [48].

3.2.2.Electrochemical impedance spectroscopic study

The Nyquist plots with equivalent circuit used in the present analysis for electrochemical data interpretation and the Bode phase angle plots for inhibited and uninhibited metallic specimens are depicted in Fig. 6, 7 and Fig. 8 respectively. All the calculated EIS parameters such as solution resistance (R_s), polarization resistance (R_p), phase shift (n), double layer capacitance (C_{dl}) and corresponding surface coverage (θ) and inhibition efficiency (η) are listed in Table 7.





Fig.6 : Nyquist plots for mild steel in 1 M HCl solution in the absence and presence of different concentration of APCIs.



Fig.7: Equivalent circuit used to fit the EIS data for mild steel in 1 M HCl solution.

From Fig. 6 it is clear that Nyquist plots for uninhibited and inhibited mild steel specimens gave the similar appearance which suggests that APCIs inhibit corrosion by increasing the polarization resistance without changing the mechanism of corrosion [28]. The Nyquist plots consist of depressed semicircles with the centers under the real axis, which is commonly observed in the case of solid metal electrodes due to frequency dispersion of interfacial impedance. This phenomenon is mainly due to the factors like surface roughness, inhomogeneity of electrode surface, discontinuity in the electrode and the adsorption of inhibitor

and impurities [49]. It is important to mention that in the present investigation, polarization resistance (R_p) was under taken for measurements rather than more commonly used charge transfer resistance (R_{ct}) because Rp represents the all type of resistances associated on the metal/ solution interfaces such as pore resistance (R_r), diffusion resistance (R_d), film resistance (R_f) and charge transfer resistance (R_{ct}) i.e. $R_p = R_{ct} + R_r + R_d + R_f$, that would give more information about the interface [50]. The result showed that the presence of inhibitor molecules at their optimum concentration causes substantial increase in the values of R_p .

Table 7: Electrochemical impedance parameters (±SD) obtained from EIS measurements for mild steel in 1 M HCl solution in absence and presence of optimum concentration of APCIs.

Conc.	R _s	R_p	$C_{ m dl}$	п	$\eta\%$
(10 ⁻⁶ M)	(Ωcm^2)	(Ωcm^2)	$(\mu F cm^{-2})$		
	1.120	9.58±0.15	106.21	0.827±0.001	
141	0.457	23.34±0.33	95.62	0.763±0.004	58.95±0.56
282	0.451	42.19±0.26	93.99	0.721±0.001	77.29±0.14
423	0.899	78.82±0.41	70.69	0.811±0.002	87.84±0.06
564	0.751	121.3±0.51	66.42	0.805±0.001	92.10±0.03
141	1.105	25.8±0.1	88.25	0.829±0.002	62.86±0.14
282	0.500	62.54±0.45	72.21	0.817±0.004	84.68±0.11
423	0.593	113.3±0.37	68.14	0.766±0.001	91.54±0.03
564	1.831	186.1±0.41	55.83	0.806±0.001	94.24±0.06
141	0.655	36.95±0.24	70.67	0.712±0.003	74.07±0.17
282	0.830	91.79±0.26	62.13	0.805±0.001	89.56±0.09
423	1.137	158.6±0.25	52.80	0.817±0.003	93.95±0.01
564	1.107	299.2±1.3	34.44	0.811±0.002	96.79±0.14
	Conc. (10 ⁻⁶ M) 141 282 423 564 141 282 423 564 141 282 423 564 141 282 423 564	Conc. R_s $(10^{-6}M)$ (Ωcm^2) 1.1201.1201410.4572820.4514230.8995640.7511411.1052820.5004230.5935641.8311410.6552820.8304231.1375641.107	Conc. R_s R_p $(10^{-6}M)$ (Ωcm^2) (Ωcm^2) 1.120 9.58 ± 0.15 141 0.457 23.34 ± 0.33 282 0.451 42.19 ± 0.26 423 0.899 78.82 ± 0.41 564 0.751 121.3 ± 0.51 141 1.105 25.8 ± 0.1 282 0.500 62.54 ± 0.45 423 0.593 113.3 ± 0.37 564 1.831 186.1 ± 0.41 141 0.655 36.95 ± 0.24 282 0.830 91.79 ± 0.26 423 1.137 158.6 ± 0.25 564 1.107 299.2 ± 1.3	Conc. R_s R_p C_{dl} $(10^{-6}M)$ (Ωcm^2) (Ωcm^2) $(\mu F cm^{-2})$ 1.120 9.58 ± 0.15 106.21 141 0.457 23.34 ± 0.33 95.62 282 0.451 42.19 ± 0.26 93.99 423 0.899 78.82 ± 0.41 70.69 564 0.751 121.3 ± 0.51 66.42 141 1.105 25.8 ± 0.1 88.25 282 0.500 62.54 ± 0.45 72.21 423 0.593 113.3 ± 0.37 68.14 564 1.831 186.1 ± 0.41 55.83 141 0.655 36.95 ± 0.24 70.67 282 0.830 91.79 ± 0.26 62.13 423 1.137 158.6 ± 0.25 52.80 564 1.107 299.2 ± 1.3 34.44	Conc. R_s R_p C_{dl} n $(10^{-6}M)$ (Ωcm^2) (Ωcm^2) $(\mu F cm^{-2})$ 1.120 9.58 ± 0.15 106.21 0.827 ± 0.001 141 0.457 23.34 ± 0.33 95.62 0.763 ± 0.004 282 0.451 42.19 ± 0.26 93.99 0.721 ± 0.001 423 0.899 78.82 ± 0.41 70.69 0.811 ± 0.002 564 0.751 121.3 ± 0.51 66.42 0.805 ± 0.001 141 1.105 25.8 ± 0.1 88.25 0.829 ± 0.002 282 0.500 62.54 ± 0.45 72.21 0.817 ± 0.004 423 0.593 113.3 ± 0.37 68.14 0.766 ± 0.001 564 1.831 186.1 ± 0.41 55.83 0.806 ± 0.001 141 0.655 36.95 ± 0.24 70.67 0.712 ± 0.003 282 0.830 91.79 ± 0.26 62.13 0.805 ± 0.001 423 1.137 158.6 ± 0.25 52.80 0.817 ± 0.003 564 1.107 299.2 ± 1.3 34.44 0.811 ± 0.002

New Journal of Chemistry

Results depicted in Table 7 showed that presence of inhibitors decreases the values of C_{dl} as compared to the C_{dl} value of blank which is attributed to decrease in local dielectric constant and/or an increase in the electrical double layer thickness [51]. Fig. 8 represents the Bode and phase angle plots for the mild steel in 1M HCl in absence and presence of the optimum concentration of APCIs. It is clear that the Bode phase angle plots have only one maximum i.e. one time constant at the intermediate frequencies. The broadening of this maximum indicates the formation of inhibitor layer on mild steel surface. Moreover the increase in the phase angle values in presence of APCIs reveals their inhibitive action [52].



Fig.8: Bode plots for mild steel in 1 M HCl solution in the absence and presence of APCIs at different concentration.

- 3.3. Surface study
- 3.3.1. SEM analysis

The SEM study was performed on the mild steel specimens taken after 3h immersion time in presence and absence of APCIs and the micrographs obtained are shown in Fig. 9(a-d).



Fig. 9(a-d): SEM image of mild steel surface after 3h immersion (a) without APCIs (b) with APCI-1 (c) with APCI-2 (d) with APCI-3.

Fig. 9(a) represents the micrograph of mild steel specimen immerged in blank solution whereas Fig. 9(b-d) represents mild steel in presence of APCIs. From Fig. 9(a) it can be seen that the surface of mild steel specimen is severely corroded and damaged due to free acid attack. However in Fig. 9(b-d) surface morphology of the specimens are significantly improved and the surface is smoother and contains less number of pits. This study confirms the protective action of mild steel in acid solution by APCIs.

3.3.2. Atomic force microscopy

The AFM study was performed to know the average roughness of mild steel specimen surface in absence and presence of optimum concentration of APCIs after 3h immersion time. Fig. 10(a) represent the 3D micrograph of mild steel surface in dipped in blank solution. The observation of this micrograph shows that the surface of specimen is highly corroded and contains many peaks and valley like areas due to the dissolution of metal in that region. However, in presence of APCIs a relatively smoother and uniform surface morphology was found in Fig. 10(b-d) due to the corrosion inhibition property of the inhibitors [21]. The average surface roughness R_a (the average deviation of all points roughness profile from a mean line over the evaluation length) of mild steel specimen was found to be 389 nm in absence of APCIs, whereas in presence of APCI-1, APCI-2 and APCI-3 the R_a values were 141nm, 127nm and 102nm, respectively.



New Journal of Chemistry Accepted Manuscript







Fig. 10(a-d): 3D AFM image of mild steel surface after 3h immersion (a) without APCI (b) with APCI-1 (c) with APCI-2 (d) with APCI-3.

3.4. Quantum Chemical calculation





Fig. 11: Optimized molecular structure of non-protonated APCI-1, APCI-2 and APCI-3.







Fig. 13: Optimized molecular structure of protonated APCI-1, APCI-2 and APCI-3.



Fig. 14: The frontier molecular orbital HOMO and LUMO of protonated APCI-1, APCI-2 and APCI-3.

Figs. 11-14 represent the fully optimized and frontier molecular electron distribution pictures of neutral as well as protonated forms of studied inhibitors molecules. From the frontier molecular electron distribution pictures for neutral form of the inhibitor molecules it can be seen

that HOMO and LUMO are mainly localized over the p-chlorophenyl ring and diethylphosphonate moieties suggesting that only these part of molecules mainly involve in electron sharing during metal-inhibitor interactions. In contrast, HOMO for protonated form of these inhibitors mainly localized at phenyl ring of the benzaldehyde moiety, while LUMO is mainly concentrated at p-chlorophenyl and diethyl-phosphonate moieties. The common quantum chemical calculation parameters such as energy of highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals, energy band gap (ΔE), global electronegativity (χ), hardness (η), softness (σ), fraction of electron transfer (ΔN) and dipole moment (μ) derived for neutral as well as protonated form of the investigated molecules are presented in Table 8.

Table 8: Quantum chemical parameters derived for neutral and protonated form of the
investigated APCIs

inhibitors		<i>E</i> _{HOMO}	$E_{\rm LUMO}$	ΔE	η	σ	χ	ΔN	μ
		(Hartree)	(Hartree)	(Hartree)					(Debye)
	APCI1	-0.1694	-0.0255	0.1439	0.0719	13.89	0.097	1.110	7.694
Neutral	APCI2	-0.1689	-0.0267	0.1422	0.0711	14.06	0.097	1.120	8.044
	APCI3	-0.1778	-0.0525	0.1101	0.0576	17.34	0.110	1.275	7.443
	APCI1	-0.3781	-0.1686	0.2095	0.1047	9.54	0.273	-0.076	5.523
Protonate	APCI2	-0.3610	-0.1692	0.1918	0.0959	10.31	0.264	-0.040	3.702
d	APCI3	-0.3283	-0.1712	0.1571	0.0785	12.72	0.249	0.047	4.481

According to the concept of electron transfer (and chemical reactivity) a molecule with high value of E_{HOMO} and lower value of E_{LUMO} would be associated with high chemical reactivity and thereby associated high inhibition performance [53,54]. In our present investigation, values of E_{HOMO} increases on going from APCI-1 to APCI-3 suggesting that magnitude of electron transfer from inhibitors to metal surface and therefore inhibition performance increases in the same order. Similarly, value of E_{LUMO} for any chemical species suggests its electron accepting tendency [53]. The values of E_{LUMO} decreases (increases in negative) on going APCI-1 to APCI-3 indicating that tendency of electron acceptation and thereby inhibition performance increases likewise [55]. During metal-inhibitor interactions, a lower value of ΔE (energy band gap) is consisted with high

inhibition efficiency [56]. In our case, values of ΔE well established the experimental order of inhibition efficiency. In the present study values of E_{HOMO} , E_{LUMO} and ΔE for neutral as well as protonated form of inhibitor molecules were consistent with the exponentially determined inhibition efficiency order. Applying the Pearson electronegativity concept, it can be postulated that a chemical species with high value of global electronegativity should be associated with lower chemical reactivity and inhibition efficiency [57]. In our present case values of global electronegativity did not follow any regular trend for neutral form of the inhibitor molecules. However, for protonated form of the inhibition molecules, values of electronegativities were accordance to the experimentally determined efficiency order. Besides, more commonly used energies parameters (E_{HOMO} , E_{LUMO} and ΔE) chemical reactivity and the inhibition efficiency of any chemical species can be predicted depending upon the value of its global softness (σ) and hardness (η). Generally, a chemical species with higher value of softness and lower value of hardness is comprised with strong metal-inhibitor interaction (high efficiency) [20]. In present study values of softness followed the order: APCI-3 (17.34) > APCI-2 (14.06) > APCI-1 (13.89), which is just accordance to the order of inhibition efficiency derived from weight loss and electrochemical methods, while the values of global hardness follow just inverse order. The values of global hardness and softness were well agreed with the experimental results for neural as well as protonated forms. Relative inhibition performance of structurally similar molecules can also be predicted based on values of their fraction of electron transfer which is a direct measure of electron transfer from inhibitor to metal. Obviously, an organic inhibitor with higher value of ΔN would be associated with higher inhibition efficiency as compared of the organic molecule having lower value of ΔN [57]. In present study, values of ΔN are increasing on going APCI-1 to APCI-3, indicating that magnitude of electron transfer (donation) followed the trend: APCI-3 (1.275) > APCI-2 (1.120) > APCI-1 (1.110), which is consisted with the experimentally determined inhibition efficiency. The values of dipole moment have been derived for neutral as well as protonated form of inhibitor molecules and are listed in Table 8. Generally, value of dipole moment is a measure of polarizability of any organic molecule on the metallic surface during interactions between them. A molecule with high value of dipole moment is more polarizable and covers larger surface area and thereby should act as better corrosion inhibition as compared to the organic molecule with lower value of dipole moment. Both positive and

negative trends of inhibition efficiency have been reported with the values of dipole moment [53]. In our present study values of dipole moments did not show any regular trend.

3.5. Molecular dynamics simulation

For the past years there has been a rapid rise in the use of MD simulations for understanding the interaction between corrosion inhibitor-metals surface [58–60]. Thus in this study, MD simulations were made to study the adsorption behavior of four phosphonate derivatives on Fe (110) surface. For this purpose, a system containing 500 water molecules, $5H_3O^+$, $5 Cl^-$ and one molecule of tested APCIs was constructed to simulate the actual aggressive medium. After 500,000 steps, the system reaches equilibrium which explain that both the temperature and energy reach balance[61]. From the final configurations of tested inhibitors (Fig. 15-16), it is clear that the phosphonate molecules move to the Fe (110) surface to almost parallel or flat disposition. In this instance, the interaction and binding energies of the adsorption of APCIs on Fe (110) are calculated and summarized in Table 9.

Table 9. Selected energy parameters obtained from MD simulations for adsorption of APCI	s on
Fe (110) surface	

System	E _{Interaction} (kJ/mol)	E _{Binding} (kJ/mol)
Fe + APCI-1 +500H ₂ O + $5H_3O^+ + 5Cl^-$	-743.67	743.67
Fe + APCI-2 +500H ₂ O + $5H_3O^+$ + $5Cl^-$	-805.01	805.01
Fe + APCI-3 +500H ₂ O + $5H_3O^+$ + $5Cl^-$	-877.11	877.11

The higher positive values of binding energies are attributed to an effective adsorption and consequently the formation of adsorbed layer of phosphonate derivatives on Fe (110) surface [62]. In the same case, the higher negative values of interaction energies indicate that there is a strong interaction between tested inhibitors and metallic surface [63]. Based on these insights, we can draw a conclusion that the phosphonates tested in this study can provide an effective protection of steel.



Fig. 15: Side views of the final adsorption of the APCIs on the Fe (110) surface in solution.



Fig. 16: Top views of the final adsorption of the APCIs on the Fe (110) surface in solution.

Fig. 17 presents the radial distribution function (RDF) curves of C, N, O, Cl and P of **APCI-3** and Fe atoms. The radial distribution function (or pair correlation function) g(r) can be computed through a structural analysis of the MD simulations results [64]. The RDF is widely used as useful method to estimate the bond length. The peak within 3.5 Å, it's an indication of small bond length which indicates the chemisorption, while the peak outside 3.5 Å shows the physical interactions [65].



Fig. 17: Radial distribution functions of APCI-3 adsorbed on a Fe (110) surface.

From the equilibrium configuration of the APCI-3 molecule, it can be concluded that the most significant interactions (chemisorption) with Fe atoms are having C, O and Cl with the peak distance less than 3.5 whereas the interactions of Van der Waals force or Coulomb force can be occurs between phosphorus and nitrogen atoms and Fe atoms [65].

4. Conclusions

The inhibition effect of three α -aminophophonates namely, diethyl (((4-chlorophenyl)amino)(phenyl)methyl)phosphonate (APCI-1), diethyl (((4-chlorophenyl)amino)(4-methoxyphenyl)methyl)phosphonate (APCI-2) and diethyl (1-((4-chlorophenyl)amino)-3-phenylallyl)phosphonate (APCI-3) on mild steel corrosion in 1M hydrochloric acid solution was studied using experimental and theoretical methods. From the obtained results following conclusions were drawn:

- 1. All the studied compounds acted as good corrosion inhibitor and their inhibition efficiency increases with the increase in concentration and maximum efficiency was obtained at an optimum concentration of 564×10^{-6} M.
- The inhibition efficiencies of the investigated compounds followed the order: APCI-3 (96.9%) > APCI-2 (94.8%) > APCI-1 (92.6%).
- Potentiodynamic polarization study revealed that the studied inhibitors behaved as mixed type inhibitor by decreasing both anodic and cathodic corrosion densities and maximum decrease was observed by APCI-3.
- EIS measurements showed that investigated inhibitor molecules inhibit corrosion by adsorbing on the metal surface and forming the protective film over the metal/ electrolyte interfaces.
- 5. Adsorption of the tested compounds over the metallic surface obeyed the El-Awady adsorption isotherm.
- 6. The substantial improvement in the surface morphologies of the inhibited metallic specimens found after SEM and AFM analysis suggested that the investigated molecules adsorbed over the metal surface and protect it from corrosion by forming inhibitor film.
- DFT based parameters revealed that tested compounds have strong tendency of adsorption and thereby act as good corrosion inhibitors for mild steel corrosion in 1M hydrochloric acid solution.

8. MD study reveals that all the investigated inhibitor molecules strongly adsorbed over the metallic surface nearly by flat or parallel orientation and thereby protect the larger surface area. The values of $E_{\text{interaction}}$ were followed the order: APCI-3 (-877.11 kJ/mol) > APCI-2 (-805.01 kJ/mol) > APCI-1 (-743.67 kJ/mol), which is in good agreement to the experimental results.

Acknowledgment

Gupta and Verma, gratefully acknowledged Ministry of Human Resource Development (MHRD), New Delhi (India) for support.

References

Published on 03 October 2017. Downloaded by University of Newcastle on 03/10/2017 14:39:46

- 1. http://insights.globalspec.com/article/2340/annual-global-cost-of-corrosion-2-5-trillion.
- 2. C. Verma, E.E. Ebenso, M.A. Quraishi, J. Mol. Liq. 233 (2017) 403.
- 3. A. Domling, Chem. Rev. 106 (2006) 17.
- 4. D. Tejedor, F.G. Tellado, Chem. Soc. Rev. 36 (2007) 484.
- 5. C. Beattie, M. North, P. Villuendas, Molecules 16 (2011) 3420.
- 6. M.M. Hooper, Brenton DeBoef, J. Chem. Educ. 86 (2009) 1077.
- C. Verma, M.A. Quraishi, E.E. Ebenso, I.B. Obot, A. El Assyry, J. Mol. Liq. 219 (2016) 647.
- 8. H. S. Awad, S. Turgoose, Corrosion, 60 (2004) 1168.
- R. Laamari, J. Benzakour, F. Berrekhis, A. Abouelfida, A. Derja, D. Villemin, Arab. J. Chem. 4 (2011) 271.
- 10. K. D. Demadis, C. Mantzaridis, P. Lykoudis, Ind. Eng. Chem. Res. 45 (2006) 7795.
- Y. Kharbach, A. Haoudi, M.K. Skalli, Y. Kandri Rodi, A. Aouniti, B. Hammouti, O. Senhaji, A. Zarrouk, J. Mater. Environ. Sci. 6 (2015) 2906.
- Bouklah, O. Krim, M. Messali, B. Hammouti, A. Elidrissi, I Warad, Der Pharma Chemica, 3 (2011) 283.
- M. Benabdellah, A. Dafali, B. Hammaouti, A. Aouniti, M. Rhomari, A. Raada, O. Senhaji, J.J. Robin, Chem. Eng. Comm., 194 (2007) 1328.
- M. Yadav, D. Sharma, S. Kumar, S. Kumar, I. Bahadur, E. E. Ebenso, Int. J. Electrochem. Sci.,9 (2014) 6580.
- 15. N.A. Negm, E.A. Badr, I.A. Aiad, M.F. Zaki, M.M. Said, Corros. Sci. 65 (2012) 77.
- B. Dar, A. Singh, A. Sahu, P. Patidar, A. Chakraborty, M. Sharma, B. Singh, Tetrahedron Lett. 53 (2012) 5497.
- 17. N.K. Gupta, C. Verma, M.A. Quraishi, A.K. Mukherjee, J. Mol. Liq. 215 (2016) 47.
- 18. C. Verma, M.A. Quraishi, N.K. Gupta, Ain Shams Eng. J. (2016) xxx, xxx-xxx. http://dx.doi.org/10.1016/j.asej.2016.07.003
- M. Muralisankar, R. Sreedharan, S. Sujith, N.S.P. Bhuvanesh, A. Sreekanth, J. Alloys Compd. 695 (2017) 171.
- 20. S. K. Saha, P. Banerjee, RSC Adv. 5 (2015) 71120.
- 21. C. Verma, M. A. Quraishi, L. O. Olasunkanmi, E.E. Ebenso, RSC Adv. 5 (2015) 85417.

- 22. C. Verma, M.A. Quraishi, A. Singh, J. Taiwan Inst. Chem. Eng. 000(2015)1.
- 23. I. Ahamad, R. Prasad, M.A. Quraishi, Corros. Sci. 52 (2010) 3033.
- 24. R. G. Pearson, Inorg. Chem. 27 (1988) 734.
- 25. Materials Studio, Revision 6.0, Accelrys Inc., San Diego, USA, 2013.
- 26. H. Sun, J. Phys. Chem. B. 102 (1998) 7338.
- 27. Z. Zhang, N.C. Tian, X.D. Huang, W. Shang, L. Wu, RSC Adv. 6 (2016) 22250.
- 28. N.K. Gupta, M. A. Quraishi, C. Verma, A. K. Mukherjee, RSC Adv. 6 (2016) 102076.
- 29. C. Verma, M.A. Quraishi, Ain Shams Eng. J. 7 (2016) 1.
- 30. I. Ahamad, M.A. Quraishi, Corros. Sci. 52 (2010) 651.
- 31. J. Alijourani, K. Raeissi, M.A. Golozar, Corros. Sci. 51 (2009)1836.
- C. Verma, M. A. Quraishi, K. Kluza, M. Makowska-Janusik, L.O. Olasunkanmi, E.E. Ebenso, Sci. Rep. 7 (2017) 44432.
- 33. C. Verma, M.A. Quraishi, A. Singh, J. Taiwan Inst. Chem. Eng. 49 (2015) 229.
- 34. N.O. Eddy, H. Momoh-Yahaya, E.E. Oguzie, J. Adv. Res. 6 (2015) 203.
- 35. M.A. Deyab, J Ind. Eng. Chem. 22 (2015) 384.
- 36. P.B. Raja, A.K. Qureshi, A.A. Rahim, H. Osman, K. Awang, Corros. Sci. 69 (2013) 292.
- 37. R. Karthikaiselvi, S. Subhashini, J. Assoc. Arab Univ. Basic Appl. Sci. 16 (2014) 74.
- 38. A. A. EI-Awady, B. A. Abd-EI-Nabey, S. G. Aziz, J. Electrochem. Soc. 139 (1992) 2049.
- 39. A.F.S.A. Rahiman, S. Sethumanickam, Arab. J. Chem. 10 (2017) 3358.
- 40. N.A. Odewunmi, S.A. Umoren, Z.M. Gasem, J. Ind. Eng. Chem. 21 (2015) 239.
- 41. A. Singh, Y. Lin, W. Liu, S. Yu, J. Pan, C. Ren, D. Kuanhai, J. Ind. Eng. Chem. 20 (2014) 4276.
- S. Issaadi, T. Douadi, A. Zouaoui, S. Chafaa, M.A. Khan, G. Bouet, Corros. Sci. 53 (2011) 1484.
- 43. N.A. Negm, E.A. Badr, I.A. Aiad, M.F. Zaki, M.M. Said, Corros. Sci. 65 (2012) 77.
- 44. M.M. Solomon, S.A. Umoren, A.U. Israel, E.E. Ebenso, J. Mater. Eng. Perform. 24 (2015) 4206.
- 45. El-Sayed, M. Sherif, J. Ind. Eng. Chem. 19 (2013) 1884.
- 46. I.B. Obot, S.A. Umoren, Z.M. Gasem, R. Suleiman, B. El Ali, J. Ind. Eng. Chem. 21 (2015) 1328.

- 47. S. A. Umoren, I.B. Obot, A. Madhankumar, Z.M. Gasem, Carbohydr. Polym. 124 (2015) 280.
- 48. M.M. Solomon, S. A. Umoren, J. Colloid Interface Sci. 462 (2016) 29.
- K. Ramya, R. Mohan, K.K. Anupama, A. Joseph, Mater. Chem. Phys. 149-150 (2015) 632.
- 50. J. Haque, V. Srivastava, C. Verma, M.A. Quraishi, J. Mol. Liq. 225 (2017) 848.
- 51. M.A. Deyab, J. Ind. Eng. Chem. 22 (2015) 384.
- 52. G. Sı gırcık, T. Tüken, M. Erbil, App. Surf. Sci. 324 (2015) 232.
- 53. A. Ehsani, M.G. Mahjani, R. Moshrefi, H. Mostaanzadeh, J.S. Shayeh, RSC Adv. 4 (2014) 2003.
- 54. S.K. Saha, A. Dutta, P. Ghosh, D. Sukul, P. Banerjee, Phys. Chem. Chem. Phys. 17 (2015) 5679.
- 55. R. Tamilarasan, A. Sreekanth, RSC Adv. 3 (2013) 23681.
- 56. S. John, M. Kuruvilla, A. Joseph, RSC Adv. 3 (2013) 8929.
- J. Haque, K.R. Ansari, V. Srivastava, M.A. Quraishi, I.B. Obot, J. Ind. Eng. Chem. 49 (2017) 176.
- S. Kaya, L. Guo, C. Kaya, B. Tüzün, I.B. Obot, R. Touir, N. Islam, J. Taiwan Inst. Chem. Eng. 65 (2016) 522.
- 59. L.H. Madkour, S. Kaya, C. Kaya, L. Guo, J. Taiwan Inst. Chem. Eng. 68 (2016) 461.
- 60. H. Lgaz, R. Salghi, S. Jodeh, B. Hammouti, J. Mol. Liq. 225 (2017) 271-280.
- 61. S.K. Saha, M. Murmu, N.C. Murmu, P. Banerjee, J. Mol. Liq. 224 (2016) 629.
- 62. L.O. Olasunkanmi, I.B. Obot, E.E. Ebenso, RSC Adv. 6 (2016) 86782.
- 63. A. Kokalj, Corros. Sci. 70 (2013) 294.

- 64. H. Lgaz, R. Salghi, S. Jodeh, B. Hammouti, J. Mol. Liq. 225 (2017) 271.
- S.-W. Xie, Z. Liu, G.-C. Han, W. Li, J. Liu, Z. Chen, Comput. Theor. Chem. 1063 (2015)
 50.

New Journal of Chemistry Accepted Manuscript



Phosphorus containing compounds have been evaluated by experimental and theoretical techniques and more than 96% corrosion inhibition efficiency was observed at 200ppm concentration