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Homo-dinuclear VO^{2+} and Ni^{2+} dihydrazone complexes: Synthesis, characterization, catalytic activity and CO_2 -corrosion inhibition under sustainable conditions



^a Department of Chemistry, College of Science, King Faisal University, P.O. Box 380 Al Hofuf, Al Ahsa 31982, Saudi Arabia

^b Chemistry Department, Faculty of Science, Sohag University, Sohag 82534, Egypt

^c Chemistry Department, Faculty of Science, Benha University, 13518 Benha, Egypt

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ABSTRACT

 $\rm VO^{2+}$ and $\rm Ni^{2+}$ complexes (VOPHL and NiPHL) were prepared by complexation of terephthaloyl salicylidene dihydrazone (H₂PHL) with VO²⁺ or Ni²⁺ ions. The chemical structures were estimated by various spectroscopic methods. Their sustainable corrosion inhibition on mild steel in NaCl solutions saturated with CO₂ was investigated using potentiodynamic polarization (PDP), open circuit potential and electrochemical impedance spectroscopy (EIS) methods. H₂PHL, NiPHL and VOPHL showed maximum capacity within 89.57, 97.25 and 98.22%, respectively. The PDP study refers to that they could act as mixed-type inhibitors *i.e.* retarded both cathodic and anodic reactions. Metal complexes displayed better inhibition than their coordinated ligand. H₂PHL and its M-complexes adsorbed on C-steel surface *via* chemical adsorption with obeying the Langmuir model. The post-exposure investigation, for the inhibited and uninhibited C-steel surface, was elucidated using SEM /EDS. The homogeneous catalytic behavior of NiPHL and VOPHL was studied in the (ep)oxidation of unsaturated cycloalkene (1,2-cyclohexene) and Suzuki-Miyaura cross-coupling. VOPHL shows better catalytic potential in (ep)oxidation processes. NiPHL has higher catalytic efficiency towards cross-couplings. The aqueous hydrolysis of epoxy selective product could be reduced in low temperature of the (ep)oxidation processes. DFT studies were performed on H₂PHL, NiPHL and VOPHL. Electronic representatives E_{LUMO} , E_{HOMO} , energy gap (ΔE), hardness, softness and electronegativity were computed. Theoretical values are in good accordance with corrosive and catalytic experimental results.

1. Introduction

Aroyl salicylediene dihydrazones, as di-Schiff base derivatives, behave as multi-functional O,*N*-donor chelates with strong hetero-donor centers [1,2], which are involved in the synthesis of many high stable transition metal complexes. Regarding their enumerated coordination features, they could behave as mono-, bi- or polyhomo-nuclear chelating pincer ligands within chelating bridging and/or oxobridging bonds in the complexation with metal ion [3]. Due to the amazing facile tautomeric behavior (keto-enol tautomers) [4], they exhibit alternative potential donor centers, as multidentate chelating centers towards low and high oxidation states of various metal ions [5–7].

Mild steel alloys are used in a wide zone of different applicable industries, *e.g.* kitchen tools, structural components and as materials for pipelines in the gas and oil manufacture [8]. With regards to implementations in industrial pipes, the main corrosion agent is carbon dioxide (CO_2), which considered as sweet corrosion, *i.e.* soft corrosion

of mild steel. Sweet corrosion has brought much interest to researchers since 1949 because oil wells ordinarily contain carbon dioxide [9]. Sweet corrosion is caused by the presence of carbon dioxide (CO₂) dissolved in water to form carbonic acid (H₂CO₃), which predominantly causes severe corrosion of mild steel. The corrosive nature of CO₂ could be related to the fact that CO₂ increment the electrochemical cathodic reduction, which is generated by H⁺ and H₂CO₃ [10]. Problems arising from carbon dioxide corrosion have led to the development of different methods for corrosion control.

The use of inhibitors has been known as a very functional and most economical option for preventing CO_2 corrosion [11,12]. There are two major forms of inhibitors, inorganic and organic ones; recently, inorganic inhibitors became exceedingly applied in industries. Oxidizing inhibitors (inorganic) including nitrates and chromates were common in the previous phase of corrosion inhibition investigations. A problem usually associated with inorganic corrosion inhibitors, such as chromates and nitrates, and organic corrosion inhibitors, such as azoles or

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^{*} Corresponding authors at: Department of Chemistry, College of Science, King Faisal University, P.O. Box 380 Al Hofuf, Al Ahsa 31982, Saudi Arabia. *E-mail addresses:* madam@kfu.edu.sa (M.S.S. Adam), hmahmed@kfu.edu.sa (H.M. Abd El-Lateef).

thiourea derivatives is their toxicity [13]. Therefore, the exploration of more efficient inhibitors with environment-friendly features becomes a stringent problem; it has attracted enormous attention [14,15].

Organic molecules that contain heteroatoms such as N, S, O and P, polar groups and π -electron have been mentioned to exhibit good protection capacity. These compounds could be adsorbed on the surface of the electrode forming a bond between π -electron cloud and metal and/or the lone pair electrons of heteroatoms, thereby minimizing the corrosion rate in the aggressive environments [16,17].

The ability of dihydrazone chelating agents (as Schiff base derivatives) to form stable packed neatly pincer chelates with metal ion provides more inhibiting compound classes, *i.e.* dihydrazone ligands and their metal-complexes. The complexation atmosphere of multidonating ligands with various valent metals ions, *e.g.* dihydrazone, could play an essential action in the electro-catalytic reduction processes with redox behavior. Some recent studies referred to that, the metal-complexes show higher inhibition capacity than their corresponding ligands [18].

Phthalolsalicylediene dihydrazone derivatives and their transition metal complexes have many utilities in analytical and medicinal chemistry [19,20]. Their metal pincer chelates were explored as high reactive catalysts in electron transfer and oxygen transfer processes, as well as homogeneous/heterogeneous catalytic oxidation systems [20–22]. Consequently, many fundamental researches highlighted on metal-ar-oyldihydrazones as catalysts for various organic processes [21,22].

Investigation of oxide-metal pincer chelates, as homogeneous catalysts, in the cross-coupling systems, *e.g.* Suzuki-Miyaura reactions need more progress in literatures [23]. On the other hand, Ni-species are well known as highly effective catalysts for most of cross-couplings [24,25]. Ni-pincer chelates display an effective role as homogeneous catalysts for cross-coupling processes of different organometallics and organohalides [26]. Oppositely, $V^{IV}O$ -species exhibited excellent catalytic potential compared [22,27–31] to Ni^{II}-chelates [32] in the oxidation systems of alkenes, alkanes [33], alcohols [34] and Sulfides [35]. Density Functional Theory (DFT) is a prominent process considering the prediction of any chemical progresses. It is highly applicable for corrosion protection systems [36–39]. DFT calculations were improved to support a deeper understanding of the corrosion inhibiting potential of the studying materials, as well as their catalytic proposes [31,35].

It worth to report that aroyl dihydrazones are slightly soluble in most polar and less polar organic solvents [40]. Hence, incorporating of polar *p*-sodium sulfonate group to the organic framework develops its solubility in water and is of interest substantially in many organic catalytic systems [32,41]. Here, it motivates us to synthesize aroyl dihydrazone derivatives in presence of *p*-sodium sulfonate substituent. The different aspects ligand reacted with low and high velants of Ni²⁺ and VO²⁺ ions to form high stable M – complexes. The complexes are applied as homogeneous catalysts in the oxidation of 1,2-cyclohexene and Suzuki–Miyaura cross-coupling under substantial conditions, moreover, as CO₂-corrosive inhibiting reagents.

2. Experimental

2.1. Reagents and methodology

Chemical compounds and reagents are marketably presented from Merck, Sigma-Aldrich and Acros. They applied in all chemical proposes without additional treatments. A GMBH VarioEl model V2.3 Carbon, Hydrogen and Nitrogen apparatus was operated to evaluate the ratio percentages of Carbon, Hydrogen and Nitrogen atoms in their compounds. NMR spectroscopy was estimated by a Bruker ARX400 multinuclear NMR spectrometer at for hydrogen nuclei at frequencies 400.1 and for carbon nuclei at frequencies = 100.6 MHz at 25 °C. Values of chemical shifts, δ , of ¹H and ¹³C nuclei and the coupling constant values between H nuclei, J_{HH} , are determined and given in ppm, respectively, for the ligand H₂PHL. Using JASCO machine as UV–Vis. spectrophotometer (model V-570) with

a 10 mm silica cells in a thermostatted cell holder in order to evaluate the electronic absorption transitions of H2PHL, NiPHL and VOPHL and referenced in the given solvent, water. Shimadzu FTIR-8101 Fourier Transform Infrared spectrophotometer was involved to measure the stretching vibrational diagnostic bands of the studied compounds in the region from 4000 to $400 \,\mathrm{cm}^{-1}$. Thermogravimetric analysis was accomplished by Shimadzu TGA-50H thermal analyzer with flow of an inert carrier gas, nitrogen gas, with flow rate 20 cm³ min⁻¹ and heating rate 10 °C min⁻¹ from 30 to 400 °C. Mass spectra were measured in m/z using waters Qtof Micro YA263 mass spectrometer for the current complexes. A Jenway conductivity meter model 4320 was applied to measure conductivities of H₂PHL, NiPHL and VOPHL in DMSO and DMF using an epoxy bodied conductivity cell (consisting of two electrodes, shiny) at 25 °C (the temperature was held by using a HAAKE model F3-k ultrathermostat with \pm 0.2 °C). The cell constant calibration was carried out from 0.01 to 19.99. Magnetic susceptibility of the studied pincer chelates were measured by Gouy's balance. The calibration was achieved by Pascal's contents and Hg[Co(SCN)₄] in order to get the diamagnetic correction. Values of pH were determined using Metrohm 695 pH/ion meter to \pm 0.005 units at 25 °C in an ultrathermostat (HAAKE model F3-k) error range \pm 0.2 °C. A Thermo Scientific 9100 machine was used to estimate the melting or decomposition point of the studied compounds.

2.2. Preparation of H_2 PHL (N,N-bis(4-sodium sulfonate-2hydroxybenzylidene)terephthalohydrazide)

Terephthaloldihydrazide is the permanent reagent to synthesize the different aspects of ligand H₂PHL, which was prepared with respect to the reported method [4]. The preparation of terephthaloyl salicylidene dihydrazone and its derivatives carried out by a common condensation of salicylaldehyde derivatives with benzene-1,4-dicarbohydrazide [42]. With modification, 4.48 g (20.0 mmol) of *p*-sodium sulfonate-salicy-laldehyde in 60 mL of H₂O was added leisurely to an aqueous media of 1.94 g of trerphethalyldihydrazide (10.0 mmol, 60 mL). The mixture of the components was kept with reflux for 3 h under stirring (100 °C). The reaction completion was controlled by TLC to give pale yellow coloring of the required ligand. The mixed ethanol/water solvents were taken away by slow evaporation with a good amount of the rest, which collected and washed with cooled ethanol. Then, it was dried in an oven and it was quite pure for further workup.

¹H NMR of diketone form (DMSO-*d*₆, 400.1 MHz): δ 6.89 (d, ³*J* = 8.3 Hz, 2H), 7.58 (d, ³*J* = 8.0 Hz, 2H), 7.85 (s, 2H), 8.11 (s, 4H), 8.72 (s, 2H), 11.28 (br s, 2H, NH) and 12.20 ppm (s, 2H, -CH = N-). Distinguished ¹H NMR of the tautomers (dienole and keto-enole forms): 6.79 (d, ³*J* = 8.1 Hz), 7.65 (d, ³*J* = 7.9 Hz), 7.97 (s), 7.99 (d, ³*J* = 8.1 Hz, 2H) and 9.00 ppm (s).

¹³C NMR (100.6 MHz, DMSO- d_6 , dept-135): δ 116.06 (CH), 118.08 (C_q), 127.19 (CH), 128.03 (CH), 128.32 (CH), 129.51 (CH), 140.97 (C_q), 148.97 (CH), 158.05 (C_q) and 162.64 ppm (CH, CH = N). (more details of NMR spectra are shown in the Supplementary Materials in Figs. S1-S3).

2.3. Metal-complexes preparation (NiPHL and VOPHL)

In water (50 mL), H₂PHL (3.03 g, 5.0 mmol) was poured gently to an aqueous atmosphere, 60 mL, of vanadyl acetylacetonate, VO(acac)₂ (from Acros, 99%), or nickel acetate tetrahydrate or Ni (OOCCH₃)₂·4H₂O (from Merck, 98%) (2.65 g or 2.48 g, 10.0 mmol, respectively). The resulted mixed ethanol/water solutions were warmed up to 80 °C and kept under stirring within 3 h. The color of the reaction contents was turned gradually into the corresponding coloring of the desired dinuclear chelating complex. After cooling down, the solvents were extracted in vacuum and the rest was collected and washed by cooled ethanol and dried in vacuum. The crystalline shape of the complexes was obtained by recrystallization in 30 mL H₂O and then dried in oven.

2.4. Corrosion inhibition measurements

The chemical composition of applicable M-steel for corrosion processes is sulfur 0.04%, carbon 0.15%, manganese 0.70%, silicon 0.19%, chromium 0.011%, nickel 0.011% and balance iron. The aggressive solution of 3.5% NaCl (from Acros, 99.5%) was stirred by magnetic stirring for 30 min in 1000 mL cell before starting of the corrosion experiments. The cell was placed on a heater at 50 °C for 1 h under CO₂ atmosphere with a pressure of 0.9 bars with saturation of the solution with CO₂.

Corrosion measurements were carried out using a Gamry electrochemical cell connected to three electrodes in Gamry Instrument Potentiostat/Galvanostat. A platinum sheet (with a 1.0 cm^2 surface area), saturated calomel electrode (SCE) and M – steel were utilized as a counter, reference and working electrodes, respectively. Experimental procedures of open circuit potential, EIS and PDP measurements were similar as described in our previous reports [8,32,35]. The inhibitor concentration ranges used was 0.001 to 0.1 mM.

2.5. Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDS) studies

Pre-cleaned M-steel substrates were completely immersed in the corrosive medium (CO₂-3.5% NaCl solution) in the absence and presence of 0.1 mM of H₂PHL and VOPHL for 42 h in order to relatively examine their morphologies. After 48 h of immersion, each M-steel substrate was twice washing with H₂O prior air-drying. The M-steel surface morphologies in the inhibited and uninhibited solutions were investigated and recorded with a JEOL model 5300 SEM-EDS by applying a playback voltage of 5.0 kV.

2.6. Catalytic potential of NiPHL and VOPHL

1,2-Cyclohexene (from Acros, 99%) (1.0 mmol) (ep)oxidation processes was imitated by an aqueous hydrogen peroxide (from Merck, 30% in water, 3.5 mmol) or tert-butyl hydroperoxide (TBHP) (from Acros, 70% in water, 1.7 mmol) as an external oxidizing agent. The reaction was catalyzed by either NiPHL or VOPHL (0.02 mmol) in various reaction media, 10 mL of acetonitrile (from Merck, \geq 99.9%) or H₂O and in free solvent media at 25 or 85 °C to the optimized time. The catalytic reaction was achieved with a 250 mL two-necked round flask contacted with a condenser of water circulation. The control of the (ep) oxidation reaction was detected kinetically with withdrawing 1.0 mL of the reaction mixture at exact time intervals. The samples (1.0 mL) were treated with 3.0 mL of acetonitrile, 0.02 g of manganese dioxide and 0.02 g anhydrous MgSO₄ to destroy the excess amount of oxidant and to extract the presented water from the samples, and then to dissolve and dilute the sample contents in acetonitrile. The samples were filtrated out by celite. In the case of using water, water was removed totally and the reaction products were extracted by acetonitrile and diluted. The injected filtrate samples were subjected to the GC-MS for analysis with 1 μL using auto-sampler.

Analogously, Suzuki-Miyaura cross-coupling reactions carried out in two necked glass round flask with circulated condenser of water contained phenylboronic acid (from Acros, 98+%) (1.0 mmol), the complex catalyst (NiPHL or VOPHL, 0.02 mmol) in 10 mL of water and in presence of potassium bicarbonate (from Merck, 99.5%) (2.0 mmol). The catalytic process was started by adding bromobenzene (form Acros 99%) or (chlorobenzene Acros 99.5%) (1.2 mmol) under reflux for 4 h at 100 °C in a thermostated oil bath.

(Ep)oxidation products percentages of 1,2-cyclohexene or the C–C Suzuki-Miyaura cross-coupling products were estimated and resolved with Shimadzu Gas Chromatography mass spectrometer (GC–MS-QP2010 SE), having Rxi-5 Sil MS capillary column (30 m length \times 0.25 mm ID \times 025 um film thickness). The injecting system carried out at 25 °C. The oven temperature of GC was started at 40 °C and fixed for

60 s. The rate of the temperature increase was 10 °C min⁻¹ up to 200 °C. The operating inlet was accomplished within the mode of splitless at 200 °C was the mass spectra temperature of transfer line. Helium is acting as the carrier gas with a purity of 99.999% with a flowing rate of 1 mL min⁻¹. Evaluation of yield percentages of the target products was analyzed by Lab solution software.

2.7. Computational methods

Gaussian 09 revision c.01 [43] was exercised for the DFT calculations (Density functional theory) of H₂PHL, NiPHL and VOPHL. Their chemical structures were optimized within the gas and water phases using B3LYP and 6–31 g(d,p) for C, H, O, N, Na and S atoms. The SDD basis set with effective core potential was activated to the additional Ni and V ions. By applying the model CPCM (an abbreviation of the conductor-like polarizable continuum) was helpful to obtain the optimized molecular geometries in the water phase at the level of the B3LYP. Various indices were derived for the studied reagents. The values of frontier molecular orbitals according to Koopman theorem could be associated with the ionization potential (*I*) and the electron affinity (*A*). Magnitudes of *I* and *A* could be used to derive global harness (η), softness (σ), electronegativity (χ) and fraction of electron transfer (Δ N) for the present molecules [32,35].

DFT could be used to deduce E_{HOMO} and E_{LUMO} , which are the abbreviations of the highest occupied and lowest unoccupied molecular orbitals energies, respectively. χ_{Fe} and χ_{inh} could be deduced from DFT studies, which represent the electronegativity of Fe and the studied molecules [32], respectively. Moreover, η_{Fe} and η_{inh} represent the hardness of Fe and the inhibitor molecule, which could be evaluated. The derived magnitudes of $\chi_{Fe} = 7.0 \text{ eV mol}^{-1}$ and $\eta_{Fe} = 0 \text{ eV mol}^{-1}$ were utilized for the calculation of the ΔN [35].

3. Results and discussion

3.1. Synthetic and characteristic tools of H₂PHL, NiPHL and VOPHL

Phthalolsalicylediene dihydrazone [4] is commonly considered as a low soluble ligand in most polar and less polar solvents, however, the attached *p*-sodium sulfonate group in the condensed salicylaldehyde improved its ligand solubility in water and other solvents of high polarity, *e.g.* acetonitrile. Condensation of 1 equivalent of phthaloldihydrazide with 2 equivalents of salicylaldehyde is a highly famous reaction, which took place in polar organic solvent solution [5,21,22,40]. Similarly, 1 equivalent of phthaloldihydrazide with 2 equivalents of *p*sodium sulfonate salicylaldehyde afforded high yielding amount of H₂PHL under sustainable conditions, as a different aspects ligand (Table 1). The chemical structure of H₂PHL was confirmed NMR, Ultraviolet–Visible and IR spectra, EA and conductance measurement (Tables 1 and 2).

The significant ¹H and ¹³C NMR spectral scans of H₂PHL are reinforced in the Supplementary Materials (Figs. S1-S4). Two broad resonating singlet signals at 11.28 and 12.20 ppm are referring to the presence of -CH = N- and -NH protons, respectively. The rest of the signals are found in the aromatic area, which refers to the protons of the aromatic system from 6.90 to 8.72 ppm. As elucidated in literatures the tautomeric character of the aroyl salicylediene dihydrazones [4,21,22], *i.e.* diketone, keto-enol and dienol forms, H₂PHL behaves similarly, as remarked in the NMR spectra. The substantial tautomer is the diketone form, as observed in Fig. 1, which shows side small resonating signals of the other tautomers (keto-enol and dienol forms) in ¹HNMR spectra, Scheme 1. In ¹³C NMR spectra, the most significant resonating signal is at 162.64 ppm for the azo-methine group (-CH = N-).

Analogously to the reported M – complexes synthesis [4,5,21,22,40], 1 equivalent of H₂PHL reacted to 2 equivalents of nickel acetate hexahydrate or vanadyl acetylacetonate to produce two new dihomonuclear Ni- and VO-complexes, NiPHL and VOPHL with good yields (81 and

Elemental analyses, color, melting point, molecular electronic spectra of H₂PHL, NiPHL and VOPHL at concentration 1.0×10^{-5} mol dm⁻³ in an aqueous media at 25 °C and molar conductivities, Λ_m , NiPHL and VOPHL at concentrations = 1.0×10^{-3} mol dm⁻³ in DMSO and DMF at 25 °C.

Comp.	MW (g mol^{-1})	CHN analysis f	ound %, (calc.	%)	m.p. (°C)	UV–Visible	spectra		$Λ_m$ (Ω ⁻¹ ·cm	² ·mol ^{−1})	Yield (%)	Color
		С	Н	Ν	_	λ_{max} (nm)	$\epsilon \text{ (mol}^{-1}\text{cm}^{-1}\text{)}$	Assign.	DMSO	DMF	_	
H ₂ PHL	C ₂₂ H ₁₆ N ₄ Na ₂ O ₁₆ S ₂ 606.49	43.11 (43.57	2.93 (2.66)	8.96 (9.29)	288	331 297 284 227	5592 6218 7994 10,592	$\begin{array}{c} CT \\ n \rightarrow \pi^{*} \\ \pi \rightarrow \pi^{*} \\ \pi \rightarrow \pi^{*} \end{array}$	149	159	89	Yellow
NiPHL	C ₂₂ H ₁₆ N ₄ Na ₂ Ni ₂ O ₁₂ S ₂ 755.87	35.21 (34.96)	2.34 (213)	7.08 (7.41)	> 300	396 318 245	6475 5096 9217	$\begin{array}{c} ML\text{-}CT \\ n \rightarrow \pi^* \\ \pi \rightarrow \pi^* \end{array}$	153	166	81	Green
VOPHL	$\begin{array}{l} C_{22}H_{20}N_4Na_2O_{16}S_2V_2\\ 808.48 \end{array}$	32.28 (32.69)	2.82 (2.49)	6.57 (6.93)	> 300	406 328 246 223	4369 5201 9455 12,074	$\begin{array}{l} ML\text{-}CT\\ n \rightarrow \pi^{*}\\ \pi \rightarrow \pi^{*}\\ \pi \rightarrow \pi^{*} \end{array}$	144	158	76	Brown

vbr = very broad band

Table 2

Characteristic values of infrared spectrum and magnetic moments (µ) for H_2PHL, NiPHL and VOPHL at 25 $^\circ C.$

Group	Compound Wave length (\bar{v} , cm ⁻¹)						
	H ₂ PHL	NiPHL	VOPHL				
O-H _(water)			3389				
N-H	3215	3193	3110				
O-H _(phenolic)	3413						
C-H _{ar}	3036	3048	3061				
C-O	1352	1303	1257				
C=O _(keto)	1701						
	1679						
C=N _(azomethine)	1647	1597	1661				
	1619						
C-N _(azomethine)	1089	1034	1041				
S-O-	1146	1157	1148				
S=O	1479	1375	1373				
M-O		889	853				
M-N		600	751				
M = O			938				
μ (B.M.)	-	3.19	2.42				



Fig. 1. ¹H NMR signals in the aromatic region of H₂PHL tautomers.



Scheme 1. tautomeric behavior of H₂PHL.

76%), respectively. The tentative chemical structure of the M-com-plexes was approximated by IR, Ultraviolet–Visible and mass spectroscopies, EA (elemental analyses), TGA (thermogravimetric analyses), conductance measurements and magnetic susceptibility (Tables 1 and 2).

H₂PHL and its Ni- and VO-complexes show high air stability in the solid phase, which decomposed in temperature at 288 for H₂PHL and above 300 °C for NiPHL and VOPHL (Table 1). Moreover, the wide pH stability range (1.7–9.9) of the ligand and its Ni- and VO-complexes in the standard universal buffer solutions [40] illustrated high stability of the current compounds. The carbon, hydrogen and nitrogen percentages in the chemical structure of H₂PHL, NiPHL and VOPHL are agreed with calculated magnitudes with acceptable small variation (\pm 0.4%), Table 1. H₂PHL, NiPHL and VOPHL are fairly soluble in water and in strong coordinated featured organic solvents, *e.g.* DMSO and DMF. They are sparingly soluble in acetone, acetonitrile and ethanol.

The multi-dentate donor centers in H₂PHL, as two potential tridentate coordinating pincer, relieved H₂PHL molecule to coordinate with two metal ions giving dihomonuclear complexes, simultaneously, as shown in Scheme 2 [21,22,44]. The metal ion forces H₂PHL to coordinate within the dienolic form and then deprotonate the phenolic –OH group in the reaction media (Scheme 2). Acid hydrazide Schiff bases usually caused aerial oxidation of the vanadyl ions from V^{IV} to V^V, when they mixed together in alcoholic media [22,45,46]. Here, VO²⁺ ions did not undergo such a probability of oxidation because the reaction did not take place in an alcoholic solution but in an aqueous media.

In the aqueous media, H₂PHL, NiPHL and VOPHL showed the diversity of the considerable molecular electronic transitions by the Ultraviolet–Visible spectral scans. The highest absorption wavelength, λ_{max} (nm) for each transition is applied to calculate the molar



Scheme 2. Synthetic routes for NiPHL and VOPHL.

absorptivity, e, mol⁻¹ cm⁻¹, and listed in Table 1. In the uncolored area, H₂PHL had two energy transitions of $\pi \rightarrow \pi^*$ bands, which assigned by two absorption bands at 227 and 284 nm. Both bands were influenced by the complexation to Ni²⁺ and VO²⁺ ions to appear as one band at 245 for NiPHL and two bands at 223 and 246 nm for VOPHL, which resulted from the intra ligand spin-allowance [47]. Particularly, the $n \rightarrow \pi^*$ transition gave a notable band at 297 nm, which also shifted in NiPHL and VOPHL to be 318 and 328 nm, respectively. Additionally, an absorption band was detected for H₂PHL at 331 nm at the visible area, which could be attributable for the ligand charge transfer (Fig. 2). The strong remarkable broad band in the visible region for both NiPHL and VOPHL manifested at 396 and 406 nm, respectively, were probably due to the metal to ligand charge transfer (M–LCT) [4,22].

The most characteristic IR spectral data of H₂PHL could merit to distinguish the coordinated function group, which binds to Ni²⁺ and VO²⁺ ions in NIPHL and VOPHL, respectively, as listed in Table 2 and in Fig. S5-S7 in the supporting materials. The OH phenolic stretching broad band –OH of H_2 PHL was confirmed at 3215 cm⁻¹. Due to the deprotonated complex formation via anionic oxygen of the --OH phenolic group to Ni²⁺ or VO²⁺ ion, the characteristic band was disappeared, as observed elsewhere [22,40]. The presented water molecules in the coordinated sphere to the central metal ion to complete the coordination number of Ni^{2+} and VO^{2+} ions could be detected by weak broad vibrational bands at 3193 and 3110 cm⁻¹, respectively Table 2. Strong observable shifts of the diagnostic azo-methine band (Schiff base group) $\bar{\nu}_{(azo-methine)}$ of H_2PHL was detected from 1647 to 1597 and 1599 cm⁻¹ in NiPHL and VOPHL, respectively. Such a shift was certainly resulted from the binding of $-CH = N - \text{group to } VO^{2+}$ or Ni^{2+} ion via nitrogen atom lone pair. The assigned vibrational bands of C=O $\bar{\nu}_{(C=O)}$ of the diketone tautomer at 1701 and 1679 cm⁻¹ in H₂PHL



Fig. 2. Molecular spectral scans of H₂PHL, NiPHL and VOPHL in the UV–Vis. region at [Compound] = 1.0×10^{-5} mol dm⁻³ and 25 °C in water.

were expectedly disappeared after binding to Ni²⁺ and VO²⁺ ions. Both Ni²⁺ and VO²⁺ ions forced the ligand to coordinate within the dienolic tautomer, as reported for Schiff base tautomers by Shul'pin *et al* [9]. The outstanding stretching absorption bands at 1146 and 1479 cm⁻¹ were characterized for the polar groups of S–O and S=O bonds, respectively [32]. Those bands were influenced also by the complexation to Ni²⁺ and VO²⁺ ions to be 1157 and 1148 cm⁻¹ for the anionic S–O bond and 1375 and 1373 cm⁻¹ for S=O bond, respectively. Moreover, additional weak spectral bands in NiPHL and VOPHL were assigned at 889 and 853 cm⁻¹ for the new coordination bonding M–O and at 600 and 751 cm⁻¹ for the M–N binding, respectively. Furthermore, the stretching band of the oxovanadium double bond V = O could be observed at 938 cm⁻¹ in VOPHL [35].

Mass spectrometric scans of H₂PHL, NiPHL and VOPHL are presented in Figs. S8-S10 (in the Supplementary Materials). H₂PHL shows specific peaks for $[L + Na^+]$ at 628.3, 629.2, 630.2 and 631.1 *m/z* and characteristic peaks for [L + 1] at 606.1 and 607.0 *m/z*. The suitable base peaks of the suggested structure of the M – complexes with the presence of Na⁺ ion have appeared at 778.29 and 813.70 *m/z* for NiPHL and VOPHL, respectively. There are also observed peaks corresponded to [M + 1] at 755.86 and 756.24 *m/z* for NiPHL and 809.56 *m/z* for VOPHL (Scheme 2) [41].

Evaluation of the water molecules in NIPHL and VOPHL could be progressed and analyzed thermogravimetrically. The number of the characteristic water molecules in the coordination sphere in NiPHL and VOPHL was assigned by TGA (as shown in Fig. S11). From the thermograph, it was confirmed a predictable decomposed successive stage from 180 to 230 °C. The calculated mass loss percentage was (Δm_{rel}) 5.0 and 8.7% for NiPHL and VOPHL, respectively, which is convenient with the expected mass loss percentage ($\Delta m_{rel} = 4.7$ and 8.9%, respectively). Those mass losses are due to the number of H₂O molecules as coordinated labile solvent molecules, as two in NiPHL and four in VOPHL [35]. Both complexes did not show in the thermograph any detectable decomposition steps for the H₂O molecules in the solid crystal lattice or any other species in the complex molecules in the range up to 400 °C (Scheme 2).

According to the presence of the polar group (p-Na⁺ SO₃⁻–) in all representatives, the molar conductivities, Λ_m , were measured in dimethylsulfoxide, DMSO, and N,N-dimethylformamide, DMF, and were listed in Table 1. Hence, all compounds exhibited high polarity with high molar conductivity values. The conductivity results show in the given solution of H₂PHL, NiPHL and VOPHL, three ions per molecule, two are free sodium Na⁺ cations and one is the complex anion as disulfonate anion $-SO_3^-$. Both NiPHL and VOPHL demonstrated *para*-



Fig. 3. *E* vs time diagram for M-steel electrode immersed in 3.5% NaCl saturated with CO₂ in the absence and presence of different concentrations of VOPHL at 50 °C.

magnetic properties (Table 2) with respectable data 3.10 and 2.47B.M., respectively. The magnetism could predict the position of Ni^{2+} and V^{4+} ion in tetrahedral and octahedral geometrical chemical structures [48]. Furthermore, magnetic properties refer to that no interaction between central metal ions could be taken place in the solutions [34].

3.2. Inhibition corrosion processes

3.2.1. Open circuit potential-time (E_{ocp} -t) investigations

In order to determine the optimum exposure time for electrochemical measurements (EIS and PDP), Eocp-t investigations were performed. Fig. 3 displays the change of E_{ocp} with time (min) for the M-steel electrode immersed in CO2-3.5% NaCl solution in the absence and presence of various concentrations of VOPHL at 50 °C. In the blank solutions (inhibitor-free), the plot for M-steel started at -708 mV and increased sharply to -691 mV after 9 min. Then, it decreased to $\approx -701 \text{ mV}$ and fixed for 50 min. With various doses of VOPHL inhibitor, the E_{ocp} -time plots were shifted more positively, compared to M-steel in the uninhibited solution. This positive shift in the inhibited solution revealed that the adsorption of inhibiting molecules on the M-steel interface improved the corrosion protection for the long exposure time [49]. All plot for the inhibited systems displayed the same features through the observed period of investigation. Hence, the steady-state value of $E_{\rm ocp}$ accomplished up to 50 min, i.e. 50 min of immersion was the optimal exposure period for all electrochemical probes. At the end of the immersion time, the $E_{\rm ocp}$ values trended to stabilize, referring to that desorption and adsorption of inhibitor molecules reached a dynamic equilibrium.

3.2.2. Potentiodynamic polarization (PDP) studies

PDP plots for M – steel immersed in CO₂-3.5% NaCl solution in the absence and presence of various concentrations of H₂PHL, NiPHL and VOPHL, are shown in Fig. 4a–c, respectively. The polarization plot for M – steel at its optimized dose of inhibitors, *i.e.* 0.1 mM, in CO₂-3.5% NaCl solution represented in Fig. 4d. From Fig. 4a–c, it was explored that both anodic and cathodic reactions were shifted to lower current density, indicating that H₂PHL, NiPHL and VOPHL inhibitors retarded both hydrogen evolution and M – steel dissolution reactions. Moreover, the polarization curves shape in the free solutions and those containing inhibitors (Fig. 4a–c) were comparable, suggesting that H₂PHL, NiPHL and VOPHL prohibited the corrosion of M – steel by covering the active sits on the M – steel interface without altering the corrosion mechanism [50]. The polarization parameters of the corrosion current density

 $(J_{\rm corr})$, anodic $(\beta_{\rm a})$ and cathodic Tafel $(\beta_{\rm c})$ of the slopes and the corrosion potential $(E_{\rm corr})$ were calculated by Tafel fitting lines and listed in Table 3. The protection efficiencies $(E_{\rm p}/\%)$ were estimated from the $J_{\rm corr}$ values within Eq. (1):

$$E_p / \% = \frac{J_{corr}^0 - J_{corr}^i}{J_{corr}^0} \times 100 = \theta \times 100$$
(1)

where, J_{corr}^{i} and J_{corr}^{0} are J_{corr} (polarization parameters) in the inhibited and uninhibited solutions, respectively, which recorded in Table 3. The Tafel slopes values of β_c and β_a changed partially with enhancing of the inhibitor concentrations. Furthermore, the β_c and β_a in the solution within the current inhibitors were slightly higher than those of their absence (blank CO₂-saturated brine), as reported elsewhere [32–34]. The difference in the Tafel slopes values with alternative inhibitors doses assigned more evident for β_c than β_a . Those observations concluded suggestively more inhibitive performance of H₂PHL, NiPHL and VOPHL on the cathodic reaction than that on the anodic one [51].

Generally, if the $E_{\rm corr}$ shift is > 85 mV versus $E_{\rm corr}$ in the presence of a blank solution, the inhibitor is classified as anodic or cathodic type, and if the $E_{\rm corr}$ shift < 85 mV, it could be classified as a mixed-type inhibitor [51]. Here, the maximum change in $E_{\rm corr}$ was found to be 44, 14 and 23 mV for H₂PHL, NiPHL and VOPHL, respectively, elucidating that H₂PHL and its Ni- and VO-complexes acted as mixed-type inhibitors. The little shift in $E_{\rm corr}$ value was attributable for the active positions blocking on the metal surface by the adsorption of inhibitor species [51]. Consequently, the inhibitors prohibited both the cathodic (hydrogen evolution) anodic (M – steel dissolution) reactions.

The values of $J_{\rm corr}$ decreased with increment in inhibitor concentrations leading to an increase in % E_p . This indicated that the prepared inhibitors could reduce the corrosion rate. The % E_p magnitudes of H₂PHL, NiPHL and VOPHL increased from 60.47, 69.04 and 72.72% at 0.001 mM up to 89.57, 97.25 and 98.22% at 0.1 mM, respectively. Further progress in the inhibitor concentration did not display any significant more impact on % E_p .

The increase in % $E_{\rm p}$ with increasing of the inhibitor dose could be due to an increase in the number of adsorbed inhibitor species on the surface of M-steel. The inhibitor species that adsorbed on the active areas on the electrode interface incremented with increasing inhibitor concentration, leading to an increase in surface coverage (θ), and accordingly, % $E_{\rm p}$. Based on the average values of % $E_{\rm p}$ within the concentration range examined in this investigation was ordered as followed VOPHL > NiPHL > H₂PHL.

3.2.3. Electrochemical impedance spectroscopy (EIS)

Regarding the EIS method for the characteristics of the metal surface of the electrode reactions, Nyquist plots for M-steel in CO₂-3.5% NaCl solution in the absence and presence of various concentrations of H₂PHL, NiPHL or VOPHL are depicted in Fig. 5a-c. At the optimal dose of H₂PHL, NiPHL or VOPHL (0.1 mM) in CO₂-3.5% NaCl solution is presented in Fig. 5d. The Nyquist diagrams exemplified a one-time constant (a single-semicircle), which incremented with increasing the doses of the H₂PHL, NiPHL or VOPHL. Additionally, the expansion of the Nyquist diagram diameters with increasing of H₂PHL, NiPHL or VOPHL doses could prove the formation of a covering film of the inhibitor on the steel/solution interface [52]. The capacitive loops depressed may be due to the ingrained M-steel surface disparity compatible with dispersion impacts. The potential of unchanged corrosion mechanisms in the solutions containing inhibitor molecules could also be the reason behind owning Nyquist plots "such as arch" shapes [53]. From the Nyquist diagram, the charge transfer resistance (R_{ct}) could be measured as the distinction in the resistance between external Helmholtz-plane and the steel/solution interface [54]. According to the formed preservative layer of the current inhibitors on the M-steel substrate, the resistance should not display only R_{ct} but also other distinguished ones. Hence, the variation in the real impedance between



Fig. 4. Potentiodynamic Polarization plots of M – steel in CO₂-saturated brine in the absence and presence of different concentration of (a) H₂PHL, (b) NiPHL and (c) VOPHL (d) in the presence of optimum concentration of 0.1 mM of H₂PHL, NiPHL and VOPHL at 50 °C.

Table 3

Corrosion parameters for $M - st$	teel in CO ₂ -saturated brine	the absence and presence of	the H ₂ PHL and its comp	lex inhibitors from polariza	ation measurements at 50 °C.
The second secon		· · · · · · · · · · · · · · · · · · ·	2 1	· · · · · · · · · · · · · · · · · · ·	

Inhibitors code	$C_{\rm inh}/\rm{mM}$	$J_{\rm corr}/\mu{\rm Acm}^{-2}$	$E_{\rm corr}/{\rm mV}$ (SCE)	$eta_{ m a}/ m mV$ dec $^{-1}$	- β_c/mV dec $^{-1}$	θ	$I_{\rm PDP}/\%$
Blank	0.0	36.5 ± 2.5	-703	88 ± 8	170 ± 14	-	-
H ₂ HPL	0.001	14.42 ± 1.2	-734	90 ± 10	197 ± 16	0.604	60.47
	0.005	12.27 ± 1.01	-738	96 ± 7	192 ± 12	0.663	66.38
	0.010	7.65 ± 0.51	-731	94 ± 9	180 ± 11	0.790	79.04
	0.050	5.24 ± 0.45	-735	93 ± 5	186 ± 10	0.856	85.62
	0.100	3.81 ± 0.23	-747	97 ± 10	189 ± 15	0.895	89.57
NiHPL	0.001	11.30 ± 1.1	-707	95 ± 11	187 ± 17	0.690	69.04
	0.005	8.22 ± 0.67	-689	93 ± 13	182 ± 15	0.774	77.48
	0.010	3.90 ± 0.37	-701	90 ± 7	192 ± 13	0.893	89.31
	0.050	1.99 ± 0.20	-710	96 ± 8	189 ± 12	0.945	94.54
	0.100	1.00 ± 0.08	-719	92 ± 12	199 ± 16	0.972	97.25
VOPHL	0.001	9.96 ± 0.76	- 699	91 ± 9	186 ± 15	0.727	72.70
	0.005	6.49 ± 0.59	-690	94 ± 13	188 ± 14	0.822	82.21
	0.010	2.85 ± 0.31	-680	89 ± 6	195 ± 13	0.921	92.19
	0.050	1.39 ± 0.11	-701	91 ± 7	197. ± 15	0.961	96.18
	0.100	0.64 ± 0.04	-698	93 ± 11	194 ± 13	0.982	98.22

the higher and lower frequencies is taken as polarization resistance (R_p) . It was consisted of the sum of all steel/corrosive media interface resistances including diffusion resistance (R_d) , accumulation resistance (R_a) and R_{ct} with addition to the solutions film resistance (R_f) in the inhibited media $(R_p = R_a + R_{ct} + R_d$ in uninhibited solution; $R_p = R_a + R_{ct} + R_d + R_f$ in the inhibited solution) [55].

The derived Nyquist diagrams were fitted by Z-view software to obtain the appropriate equivalent circuit as shown in Fig. 6a and b in the blank (free inhibitor) and inhibited medium, respectively. The corresponding equivalent circuit (EQC) was used to analyze the EIS findings is presented in Fig. 6a and b (inset). From EQC, R_s is the medium resistance and constant phase element (CPE) in parallel to R_p .



Fig. 5. Nyquist plots of M-steel in CO₂-saturated brine in the absence and presence of different concentration of (a) H₂PHL, (b) NiPHL, (c) VOPHL and (d) in the presence of optimum concentration of 0.1 mM of H₂PHL, NiPHL and VOPHL at 50 °C.

Additionally, the capacitance part of the adsorbed inhibitor in the inhibited solutions is represented as C_{inh} . A comparable EQC for steel corrosion was proposed in the literature [56]. All semi-circles showed a slightly depressed nature with a center under the real axis, related to the dispersion in frequency due to various physical phenomena, including roughness and in-homogeneity of the electrode during corrosion processes [56–58]. Therefore, in order to account for the impacts of coarseness and other in-homogeneities of steel surface punctually, CPE is used instead of a true capacitor, which calculated from Eq. (2) [32]:

$$Z_{CPE} = \left(\frac{1}{Y_0}\right) [(i\omega)_n]^{-1}$$
⁽²⁾

where, Y_0 is represented as admittance (CPE constant), *i* is the imaginary number, ω is the frequency angular and *n* is the phase shift, which is a measurement for surface in-homogeneity. Generally, the high value of *n* is a commitment to lower surface roughness. From Table 4, the high values of *n* (0.8457 to 0.8947) for the solution containing inhibitors could be compared to that of the blank solution (free inhibitor, n = 0.7911). Hence, the surface of M-steel is smoother within H₂PHL, NiPHL or VOPHL in the inhibiting solution, referring to the formation of a covering layer of the current represents on the M-steel surface. Y_0 is related to the double-layer capacitance (C_{dl}), which deduced by Eq. (3) [32]:

$$C_{dl} = Y_0(\omega_{max})^{n-1} = Y_0(2\pi f_{max})^{n-1}$$
(3)

where, ω_{max} is the frequency angular at the ultimate value of the imaginary part. R_{p} could be represented as R_{p}^{i} in the inhibited solution

and as R_P^u is the uninhibited solution (blank solution). The inhibition power I_{EIS} (%) and surface coverage (θ) could be estimated from Eq. (4):

$$I_{EIS} / \% = \left(1 - \frac{R_P^u}{R_P^i}\right) \times 100 = \theta \times 100$$
(4)

The calculated EIS parameters, $R_{\rm p}$, θ , $C_{\rm dl}$, Y_0 and $I_{\rm EIS}/\%$, are derived from the EQC model and compiled in Table 4. The values of $R_{\rm P}$, closely associated with $I_{\rm EIS}$ /%, in the inhibited solutions containing H₂PHL, NiPHL or VOPHL, were permanently greater than those values in the CO₂-saturated 3.5% NaCl free inhibitor solution. Moreover, the R_P values incremented as a function of inhibitor dose with lowering in the corrosion rate of M-steel could within H₂PHL, NiPHL or VOPHL. The R_{ct} values of H₂PHL, NiPHL and VOPHL were evaluated as 5.07, 6.16 and 8.47 k Ω cm², respectively, and the I_{EIS} /% values were determined as 56.4, 64.06 and 73.9%, respectively for only 0.001 mM. However, the corresponding $I_{EIS}/\%$ with a higher concentration (0.1 mM) of H₂PHL, NiPHL or VOPHL increased up to 88.41, 91.6 and 93.71%, respectively. In contrast, the addition of H₂PHL, NiPHL and VOPHL to the corrosive system resulted in an obvious decrease in the values of C_{dl} , which agreed with the consequence of their adsorption on the M-steel surface [59]. In this regard, the adsorption of H₂PHL, NiPHL or VOPHL on the metal surface would lead to a decrease in local-dielectric constant and/or an increase of the adsorbed film-thickness. The later was due to the fact that H₂O molecules on the M-steel surface were progressively replaced by the adsorbed H₂PHL, NiPHL or VOPHL molecules with a lower dielectric constant [60].

Therefore, the variation in C_{dl} and R_{ct} as a function of [inhibitor] further emphasized that H₂PHL, NiPHL or VOPHL molecules could form



Fig. 6. Comparison of empirical EIS results (black points) measured for M-steel substrates immersed in CO₂-saturated brine and the simulated (red line) for some of the data shown in Fig. 4 (a) the uninhibited solution and (b) inhibited solution in the presence of 0.1 mM VOPHL. Inset equivalent electric circuit used in the fitting of EIS in blank (inset a) and inhibited (inset b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a protective film via adsorbing at the steel/solution interface and prohibited the M- steel surface against the aggressive media attack [61].

The Bode plots for M-steel in CO₂-3.5% NaCl solution without and with H₂PHL, NiPHL or VOPHL are depicted in Fig. 7 (I-a, I-b, I-c), respectively. In such diagrams, the impedance values in inhibited solutions were higher than those in the uninhibited solution, and they augmented with the increment inhibitor doses. By contrast, Fig. 7 (II-a, II-b, II-c) presented the phase angle (log f vs. phase angle) plots of M-steel in CO2-saturated brine in the absence and presence of different concentrations of H₂PHL, NiPHL or VOPHL, respectively, at 50 °C. From Fig. 7 (II-a, II-b, II-c), the aberration from the ideal capacitive behavior (-90°) is more evident in the case of M-steel corrosion in the blank solution as compared to the inhibited medium containing inhibitors. Consequently, the uninhibited M-steel surface is rougher (more corroded) than that with the inhibited one. Moreover, the value of phase angle (°) in the inhibited solutions increased with increasing its doses indicating that the surface smoothness subsequently inhibition capacity increased in the same order. Consequently, H₂PHL, NiPHL or VOPHL could be adsorbed on the steel/medium interfaces and thereby the surface morphology of the M-steel became smoother especially at

higher H₂PHL, NiPHL or VOPHL dose (0.1 mM) [62].

The inhibition capacities, which observed from EIS investigation, are consistent with the derived findings from the PDP method. As predictable, NiPHL and VOPHL showed higher inhibition capacity more than their chelating ligand, H₂PHL. The high inhibition capacity of NiPHL and VOPHL might be related to the more active centers for the following order: VOPHL > NiPHL > H₂PHL.

3.2.4. Adsorption considerations

The adsorption behavior of H_2 PHL, NiPHL or VOPHL was examined by subjecting the potentiodynamic polarization within different adsorption models including Freundlich, Langmuir, Temkin and Frumkin models. The Langmuir model was exhibited by the most convenient isotherm to fit the findings obtained by PDP and was estimated by Eq. (5) [63]:

$$C_{inh}/\theta = C_{inh} + 1/K_{ads}$$
⁽⁵⁾

where, K_{ads} represents the equilibrium adsorption constant, θ is the surface coverage (calculated acceding to Eq. (1)), and C_{inh} is the concentration of H₂PHL or NiPHL or VOPHL inhibitors. Representative Langmuir isotherm plots C_{inh} versus C_{inh}/θ are displayed in Fig. 8a-c for H₂PHL, NiPHL and VOPHL, reactively. The values of correlation coefficient (R^2) were derived as 0.9979, 0.9999 and 0.9996 for H₂PHL, NiPHL and VOPHL, respectively, closer to unity. On the other hand, the plot slopes were near unity, i.e. 1.10 (H₂PHL), 1.02 (NiPHL) and 1.01 (VOPHL) (Table 5). These results inferred the conformity of the findings to the linearized Langmuir adsorption model. The K_{ads} values of H₂PHL, NiPHL and VOPHL were calculated from the intercept of C_{inh} versus $C_{\rm inh}/\theta$ plot and are shown in Table 5. The high $K_{\rm ads}$ values (Table 5) obtained for the current inhibitors generally implied that the replacement of H₂O molecules from the M-steel surface by the inhibitor species, and consequently the studied ligand and its complexes adsorb mightily on the M-steel surface with appreciated inhibitive capability [64]. The K_{ads} values followed the order of VOPHL > NiPHL > H₂PHL, indicating that VOPHL possessed the powerful adsorption ability on the metal surface and thence offered the superior inhibition performance more than NiPHL and H₂PHL.

To specify the nature of adsorption, chemi- or physico-sorption, the standard free energy of adsorption (ΔG_{ads}^{o}) was estimated for the Langmuir adsorption model by Eq. (6) [65]:

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

where, the value of 55.5 is [H₂O] in mol/L. According to the literature [66], the value of $\Delta G_{ads}^o \geq -20 \text{ kJ/mol}$ was taken to indicate physisorption. When ΔG_{ads}^o value is $\leq -40 \text{ kJ/mol}$, it would be compatible with chemisorption including charge sharing from H₂PHL, NiPHL and VOPHL to the metal surface forming co-ordinate bond [66]. The obtained values of ΔG_{ads}^o in the presence of H₂PHL, NiPHL or VOPHL are -46.62, -47.77 or $-48.52 \text{ kJ} \text{ mol}^{-1}$, respectively. So, the adsorption of H₂PHL, NiPHL or VOPHL on the M-steel surface at the studied temperature is fundamentally through chemical adsorption.

3.2.5. Corrosion inhibition mechanism of studied inhibitors in CO_2 -environments

For the M-steel corrosion mechanism in CO₂-solutions, there are two impacts of carbon dioxide have been previously reported [67]: (i) more intensive cathodic hydrogen evolution would be predictable from the acidic solution, this influence is commitment to the H₂CO₃ buffering characteristics [68], and (ii) at the anodic steel surface, carbonate films would be formed, which is related with the low solubility of FeCO₃ [69]. CO₂ gas dissolves in H₂O and forms H₂CO₃, *via* hydration as displayed in Eqs. 7–11:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$$
 (7)

$$CO_{2(aq)} + H_2 O \rightleftharpoons H_2 CO_{3(aq)}$$
(8)

Inhibitors code	C_{inh} mM	$R_{\rm s}/{\rm k}\Omega~{\rm cm}^2$	$R_{\rm P}/{\rm k}\Omega~{\rm cm}^2$	C_{dl} /F cm ⁻² ×10 ⁻⁸	$Q_{\rm CPE}$		θ	$I_{\rm EIS}/\%$
					$Y_0/\mu\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	n		
Blank	0.0	0.001	2.21 ± 0.21	324.5	2.978	0.7911	_	-
H ₂ PHL	0.001	0.016	5.07 ± 0.45	157.6	0.730	0.8745	0.564	56.41
-	0.005	0.007	6.37 ± 0.52	130.1	0.445	0.8841	0.653	65.30
	0.010	0.017	9.39 ± 1.1	100.4	0.302	0.8745	0.764	76.464
	0.050	0.020	13.65 ± 1.2	82.7	0.159	0.8942	0.838	83.80
	0.100	0.029	19.08 ± 1.5	45.9	0.088	0.8947	0.884	88.41
NiPHL	0.001	0.013	6.15 ± 0.56	170.6	0.945	0.8553	0.640	64.06
	0.005	0.027	8.51 ± 0.76	137.4	0.570	0.8457	0.740	74.03
	0.010	0.043	12.53 ± 1.1	105.8	0.392	0.8649	0.823	82.36
	0.050	0.060	17.17 ± 1.6	92.2	0.195	0.8745	0.871	87.12
	0.100	0.052	26.33 ± 2.0	47.4	0.106	0.8844	0.916	91.60
VOPHL	0.001	0.011	8.47 ± 0.71	199.8	1.230	0.8467	0.739	73.90
	0.005	0.015	12.18 ± 0.98	143.3	0.748	0.8553	0.818	81.85
	0.010	0.065	16.69 ± 1.4	109.4	0.516	0.8649	0.867	86.75
	0.050	0.089	25.10 ± 2.1	93.2	0.266	0.8745	0.911	91.19
	0.100	0.112	35.16 ± 3.2	52.3	0.142	0.8841	0.937	93.71

EIS parameters for the M-steel corrosion in CO_2 -saturated brine in the absence and presence of the H₂PHL and its complex inhibitors from polarization measurements at 50 °C.

The H_2CO_3 then dissociates into HCO_3^- and CO_3^{-2-} in two processes as:

 $H_2CO_{3(aq)} \rightleftharpoons H^+ + HCO_3^-$ (9)

 $\mathrm{HCO}_{3}^{-} \rightleftharpoons \mathrm{H}^{+} + \mathrm{CO}_{3}^{2-} \tag{10}$

The anodic dissolution for Fe in H_2CO_3 gives Fe²⁺ ions [70]:

 $Fe \rightleftharpoons Fe^{2+} + 2e -$ (11)

Accordingly, CO_2 -corrosion led to the formation of a FeCO₃ as a corrosion product, which could form a covering or a non-protective scale within precipitation depending on the conditions of the corrosive medium. FeCO₃ formation could be discussed by Eq. (12) [70]:

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \tag{12}$$

The mechanism of corrosion inhibition is a complicated process and relies on the formation of adsorbed/preservative film on the electrode surface. The adsorption process depends upon numerous factors: blend of the inhibitor in the metal surface layer, the interaction between substrate and inhibitor species, electrode potentials, inhibitor dose, chemical reactions, temperature and features of the corresponding surface. Considering the abovementioned results, the increased corrosion rates of mild steel in CO2 saturated NaCl solutions were due to the increased iron dissolution rate with increasing of cathodic limiting currents, which resulted from the buffering of dissolved CO2 and H₂CO₃. The adsorption of H₂PHL, NiPHL or VOPHL on the steel surface could take place immediately. H₂PHL, NiPHL or VOPHL species were capable of adsorbing on the surface of the metal, via O-, N-, S-atoms and imine group (—C=N—) groups and the π -electron donating density of aromatic rings. SEM/EDAX outcomes indicated the formation of a covering film layer on the electrode surface in the inhibiting medium.

VOPHL was found to give the highest inhibition capacity than NiPHL. This could be explained as the based type of central metal ion, *i.e.* VO^{2+} and Ni^{2+} in their complexes. In VOPHL, vanadium ion with high oxidation state 4+, compared to that low oxidation state of Ni^{2+} ion, enhanced its electrophilic attack towards Fe-electrode [32,33,35]. Additionally, the attached high electronegative oxygen with a double bond to V^{4+} ion, as oxovanadium(IV) ion, could improve the electrophilic character of V^{4+} ion. Hence, the high electron density on Fe steel could attract V^{4+} ion more than that Ni^{2+} ion to be adsorbed on its surface. The inhibition mechanism of both NiPHL and VOPHL is agreed with their theoretical calculations, as seen below.

3.2.6. Surface analysis observation (SEM and EDS)

Fig. 9 (I) dissipated the surface microscopic observation by SEM of the M-steel substrates after exposure in CO_2 -3.5% NaCl solution for

48 h in the inhibited solution in the absence (a) and the presence (b and c) of 0.1 mM of H₂PHL and VOPHL, respectively. The surface morphology of the M-steel in blank medium (Fig. 9 I-a) was very rough and damaged as the substrate corrodes because of the aggressive ions action in the studied corrosive environments (CO₂-saturated 3.5% NaCl). Moreover, some pits could also be observed on the steel surface (white arrows) in addition to some corrosion products/aggregates scattered distributed on all the surface of the metal substrate. The presence of H₂PHL or VOPHL as a corrosive inhibitor provided a smoother, cleaner and less corroded metal surface. The surface smoothness indicated strong adsorption of H₂PHL or VOPHL on the metal surface. In the solution containing VOPHL (Fig. 9 I-c), the metallic surface appeared to be higher smooth than in the presence of H₂PHL (Fig. 9 I-b), demonstrating the higher inhibition capacity of complex molecule inhibitor compared to that of the free ligand.

In order to get more knowledge about the M-steel composition in the uninhibited and inhibited solutions, EDS examinations were performed. The EDS analyses are presented in Fig. 9 (II), in which the atomic content elements (%) on M-steel surface in the uninhibited and inhibited medium. The EDS spectra of M-steel substrate in CO2-saturated brine free inhibitor contains (Fig. 9 II-a) the peaks corresponding to C, O, Cl, S, Si, Cr, Mn, Ni and Fe, indicating that the metal surface is covering with the corrosion products probably to Fe₂O₃, FeCl₃ and/or FeCO₃, as reported previously [67-70]. Whereas, in inhibited medium containing H₂PHL or VOPHL (Figs. 9 II-b, 7 II-c), the EDS analysis showed additional peaks on the metal surface for Ni and V, corroborating the existence of the inhibitor layer on the electrode surface. The Fe (%) for M-steel after immersion in CO2-3.5% NaCl solution is 81.32% and those for M-steel exposed to CO2-3.5% NaCl solution containing 0.1 mM of H2PHL or VOPHL is 77.56 or 75.78%, respectively. The decreased of iron percentage in the case of inhibited M-steel as compared with uninhibited M-steel (in blank solution) could be due to the adsorbed inhibitor layer formed on the M-steel surface.

3.3. Catalytic potential

3.3.1. (Ep)oxidation systems

Deu to the importance of olefins (ep)oxidation processes catalyzed by transition metal complexes of various oxidation states [27,71–73], the reactivity of NiPHL and VOPHL as homogeneous catalysts for the 1,2-cyclohexene (ep)oxidation by 30% aqueous H_2O_2 or (70%) *tert*butyl hydroperoxide (TBHP) was investigated in various reaction atmosphere, *i.e.* acetonitrile, H_2O or solvent-free system. The yield percentages of the epoxy selective product were evaluated by GC–MS (gas



Fig. 7. (I) Bode plot (log f vs. log|Z|) and (II) phase angle (log f vs. phase angle) plots of M – steel in CO₂-saturated brine in the absence and presence of different concentration of (a) H₂PHL, (b) NiPHL and (c) VOPHL at 50 °C.

chromatography-mass spectra) and tabulated in Table 6 (Scheme 3). Particularly, the highest yield percentages of the (ep)oxidation of 1,2cyclohexene were recorded at the optimized time with the detection of other side unwelcomed products [28]. 1,2-Cyclohexanediol is the most detected side unwanted product in such 1,2-cyclohexene (ep)oxidation beside the favored selective product, *i.e.* epoxy-1,2-cyclohexane (Scheme 2). The catalytic activity of NiPHL and VOPHL was highly influenced by reaction media by the yield amount of the chemoselectivity (Table 6). Acetonitrile is still the optimal catalytic media for the (ep)oxidation system. With NiPHL and VOPHL, the processes afforded the highest yield



Fig. 8. Langmuir adsorption model of (a) H_2 PHL, (b) NiPHL and (c) VOPHL on the M-steel surface in in CO₂-sturated NaCl at 50 °C.

Adsorption parameters for H_2 PHL, NiPHL and VOPHL inhibitors calculated from adsorption model of Langmuir for M-steel in CO $_2$ -saturated 3.5% NaCl solution at 50 °C.

Inhibitors	Slope values	K _{ads} mol ⁻¹ L	Correlation coefficient (R^2)	ΔG^o_{ads} kJ mol ⁻¹
H2PHL	1.10	$\begin{array}{c} 6.25 \times 10^{5} \\ 9.61 \times 10^{5} \\ 12.65 \times 10^{5} \end{array}$	0.9997	- 46.62
NiPHL	1.02		0.9999	- 47.77
VOPHL	1.01		0.9999	- 48.52

percentages of the epoxy-product in acetonitrile, as not eco-friendly solvent, which agreed with other reported results previously [32–35]. NiPHL afforded 85 and 83% with H_2O_2 or TBHP in acetonitrile, respectively, whereas, with VOPHL, the yield was increased to be 92 and 94% with H_2O_2 or TBHP in acetonitrile, respectively at 85 °C. Under sustainable conditions, *i.e.* water, or in solvent-free conditions, both catalysts did not predict high catalytic potential for the (ep)oxidation system compared to that in acetonitrile at 25 or 85 °C. Furthermore, as observed by us recently, VO^{2+} species is more reactive than that Ni^{2+} one as catalyst for such (ep)oxidation processes [34].

Homogeneity of the catalytic system has a substantial role to enhance the effectivity of the current complex catalysts. For that, the probed processes in acetonitrile cause all reaction components are

almost miscible more than those in H₂O or under solvent-free media [34]. The optimal reactivity of NiPHL consumed a longer time compared to that of VOPHL in different conditions of the catalytic processes with less chemoselective percentages [29], as seen in Table 6. Oxy highvalent of $O = V^{4+}$ ions has easy reversible electrochemical behavior, more Lewis acid character and more valid oxidation states interchange compared to that of Ni²⁺ ion as low valent ions in their complex catalysts [74], gave favored to VO^{2+} than Ni^{2+} with the essential aspects for the higher catalytic efficiency of VOPHL more than that of NiPHL [34]. In another word, the oxidation of NiPHL catalysts could more difficult than that of VOPHL. VOPHL could be easily oxidized form V (IV) to V(V) species within the electron transfer process [72] by the applicable oxidizing agent, i.e.H2O2, in the catalytic mechanism [31,34]. Furthermore, the high ability of the VO^{2+} -species to be converted to oxo/peroxo-intermediate species within the oxygen transfer process could take place [32,33]. The less probability of the above processes of electron and oxygen transfers in the catalytic cycles could reduce the catalytic potential of NiPHL compared to that of VOPHL. The catalytic behavior of NiPHL and VOPHL is convenient with the theoretical calculations, as reported below.

Newly, at room temperature, the catalytic processes produced appreciable yield amounts of 1,2-epoxy cyclohexane with both H₂O₂ and TBHP catalyzed by NiPHL or VOPHL in all applied media conditions. Most reported literatures of the catalytic activity of VO-complexes exhibited, that the highest catalytic potential of monohomonuclear complexes explored at high temperatures, e.g. 70, 80 and 100 °C [30,31,34,35]. The homodinuclear catalysts, as NiPHL and VOPHL, enhance their catalytic potential to the extent that they have good catalytic reactivity for the conversion of 1,2-cyclohexene to 1,2-epoxy cyclohexane at room temperature, compared to the reported monohomo-nuclear catalysts. This could be due to the presence of two central metal ions in the complex molecule, which probably enhances their catalytic potential with high vield amounts of the regarded product, remarkably [31,33]. From Table 6, at room temperature, NiPHL afforded 80, 78 and 75%, using H₂O₂ and 77, 75 and 71% using TBHP of the wanted product in acetonitrile, H₂O and under solvent-free media, respectively. In addition, with VOPHL, the yield percentages of the target product were 88, 82 and 84% using H₂O₂, and 89, 79 and 84% using TBHP in acetonitrile, H₂O and under solvent-free media, respectively. In acetonitrile and under solvent-free conditions, the yield products decreased with decreasing of the reaction temperature from 85 °C to 25 °C. In particular, it is highly observed experimentally that the catalytic processes in water were amended when the reaction temperature reduced from 85 °C to 25 °C, as remarked in Table 6. Conclusively, the aqueous hydrolysis of 1,2-peoxy cyclohexane could not progress or enhanced furtherly, and increased the amount of the most unflavored side product, via the formation of 1,2cyclohexanediol. But, the target product percentages increased at low temperature, i.e. 25 °C in the catalytic system (Scheme 3), as novel surprised and fruitful results. In another word, the low applied temperature of the catalytic processes could reduce the reactivity of the formed chemoselective product towards aqueous hydrolysis in an aqueous media as the eco-friendly atmosphere and so could reduce the unflavored side product, 1,2-cyclohexanediol.

3.3.2. Suzuki-Miyaura reactions

To the best of our back knowledge in literatures, the catalytic efficiency of VO-complex catalysts was recognized and studied recently [23,33,74]. It motivated us here to probe the catalytic potential of VOPHL, as well as, NiPHL in a standard Suzuki-Miyaura cross coupling of phenylboronic acid with 2-bromopyridine and 2-chloropyridine, as 2-halopyridine, in presence of K₂CO₃, as a base. At the optimized catalytic reaction time, *i.e.* after 4 h at 100 °C, which monitored by GC–MS, NiPHL afforded an appreciable catalytic potential with a good yield of the biaryl products under sustainable conditions (87 and 79% for bromopyridine and chloropyridine, respectively). VOPHL afforded moderate to low yield percentages of C–C products under sustainable



Fig. 9. (I) SEM micrographs and (II) EDS analysis of M – steel surface in CO_2 -sturated NaCl (a) blank solution, (b) in the presence of 0.1 mM H₂PHL and (c) in the presence of 0.1 mM VOPHL after immersion time 48 h.

The optimized	(ep)oxidation	conditions of 1	.2-cvclohexene	catalyzed by	NiPHL and VOPHL	using an aqueous	H ₂ O ₂ or TBHP.
	(1)		, , , , , , , ,			0 1	2-2-

Complex	Time (h)	Temp. (°C)	Yield using H ₂ O ₂	(%) ^b		Yield using TBH	2 (%) ^b	
Ĩ		I CO	Acetonitrile	Water	Solvent free	Acetonitrile	Water	Solvent free
NiPHL VOPHL	6 3 4	25 85 25	80 85 88	78 69 82 74	75 82 84	77 83 89	75 68 79 73	71 79 84

^a1,2-cyclohexene (1.0 mmol), an aqueous H_2O_2 (30%) (3.00 mmol) or TBHP (70%) (1.70 mmol) and catalyst complexes (0.02 mmol) in 10 mL given solvent at room temperature or 85 °C at the optimal reaction time.

^b Yield percentages of 1,2-epoxy cyclohexane detected by GC-Mass.



Scheme 3. Catalytic (ep)oxidation of 1,2-cyclohexene by NiPHL and VOPHL using an aqueous H_2O_2 or TBHP.

conditions (62 and 55% with bromopyridine and chloropyridine, respectively), as shown in Table 7 (TOFs and TONs values). Potassium carbonate is the most favored base for the C–C coupling system, which resulted from the high interaction between the catalyst with water and the base to progress the catalytic potential of VOPHL and NiPHL [74,75]. It is obvious, that the immiscibility and solubility of the reactants under the sustainable conditions, *i.e.* in water, which reduce the reactivity of the high soluble complex catalysts with the reactants (phenylboronic acid with 2-halopyridine) [76–78].

NiPHL is more reactive than VOPHL as a homogeneous catalyst for the C–C cross-couplings. The higher reactivity of NiPHL could be due to the high ability of Ni²⁺ ion in its complex catalyst in the catalytic cycle to be reduced to Ni⁰ [79,80]. Such reduction of VO²⁺ ion in its complex could be more difficult compared to that low valent Ni²⁺ ion within oxidative addition and reductive elimination mechanism [81,82]. The oxovanadium(IV) ion with the high electronegativity of the attached oxygen could strongly prevent the formation of the active complex catalyst intermediate with lower valent of the central metal ion, as possible for Ni²⁺ / Ni⁰ in NiPHL. The theoretical studies below provide the expected catalytic potential of NiPHL and VOPHL.

3.4. DFT calculations

The optimized molecular structures, HOMOs, LUMOs and MEP (molecular electrostatic potential) maps of studying reagents are presented in Fig. 10 and the computed DFT index is shown in Table 8. HOMO is related to the electron-donating power of a representative reacting compound molecule [83] and LUMO is linked with the electron-accepting ability [32,35]. The high value of E_{HOMO} and low value of E_{LUMO} could be correlated with the strong metal-chelating bonding and high protection ability [84]. The difference between the HOMO and LUMO energies gave the energy gap (ΔE). VOPHL has a smaller ΔE than that of NiPHL or H₂PHL, which related to good inhibition efficiency and (ep)oxidation reactivity of VOPHL, NiPHL and H₂PHL (for corrosion inhibition only).

From the density of electron distribution, the negatively charged areas were found on the oxygen atoms in > C=O and $-SO_3$ groups.

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This could be attached with benzoyl hydrazone moiety, while the electron density of the LUMO was mainly located over the entire molecule except — SO_3Na group. The HOMO and LUMO for NiPHL molecule showed a partial change in the electron distribution. For the VOPHL molecule, the shapes of the HOMO and LUMO were the same indicating the easily electron transfer probability from the HOMO to the LUMO with bonding formation between the studied reagents [85].

Molecular electrostatic potential (MEP) is a visual method that allows us to distinguish the location of the electron density (Fig. 10). The negatively charged areas are the oxygen atoms in > C=0 and $-SO_3$ groups, the nitrogen atom in -C=N- of NiPHL and VOPHL and, additionally, the oxygen atoms in V = O of VOPHL. These electron rich areas could be the preferred sites for adsorption to steel surfaces. The attached oxygen atom (V = O) could improve the reactivity of VOPHL as a catalyst for the (ep)oxidation processes.

The global electronegativities magnitudes for the studied compounds were also computed. The molecule that possesses the lowest χ related to higher electron-donating, whereas, the smaller value of χ for VOPHL indicates that it has a high ability for the electron transfer. Therefore, VOPHL acts as a good corrosive inhibitor and (ep)oxidation catalyst compared to that of NiPHL and H₂PHL (as corrosive inhibitor only). As mentioned above, the (ep)oxidation progresses need for an essential step of the electron transfer, which agreed with the theoretical expectations of the global electronegativities magnitudes (χ).

The global electronegativities magnitudes for the studied compounds were also computed. The molecule that possesses the lowest χ related to higher electron-donating, whereas, the smaller value of χ for VOPHL indicates that it has a high ability for the electron transfer. Therefore, VOPHL acts as a good corrosive inhibitor and (ep)oxidation catalyst compared to that of NiPHL and H₂PHL (as corrosive inhibitor only). The global hardness (η) and softness (σ) values were also derived for the H₂PHL, NiPHL and VOPHL molecules (Table 8). In regards to the principle of maximum hardness (PMH) [86], the chemical hardness could be considered as a measure of the molecule stability. Hence, the molecules with large chemical hardness values are very stable and they are not effective in the corrosion processes of metals nor as catalysts for both the (ep)oxidation and C-C cross-couplings systems. On the other hand, softness is a measure of polarizabilities of molecules, as well as, the soft molecules could have high reactivity towards corrosion and catalysis. Results showed that VOPHL has a lower value of η and higher value of σ as compared to the NiPHL and H₂PHL that suggested that VOPHL is more reactive and relatively more potent corrosive inhibitor and as (ep)oxidation catalyst than that of NiPHL and H₂PHL (in the corrosion processes only). The better corrosion inhibitor and (ep)oxidation catalysis possesses a high value of the dipole moment [34]. Here, VOPHL has a higher value of dipole moment as compared to that of

Table 7

Suzuki-Miyaura C-C coupling reactions of phenylbronic acid and aryl halide catalyzed by NiPHL and

VOPHL. B(OH) ₂ +	$X \longrightarrow N^{or} \xrightarrow{VOPHL} K_2CO_3 \xrightarrow{H_2O} N^{or}$	
Aryl halide	Catalyst	Yield (%) ^b
2-Bromopyridine	NiPHL	87
2-Chloropyridine	NiPHL	79
2-Bromopyridine	VOPHL	62
2-Chloropyridine	VOPHL	55

^aPhenylbronic acid (1.0 mmol), aryl halide (1.1 mmol), base (K_2CO_3 , 2.0 mmol), water (10 mL) and catalyst (0.20 mmol) in 10 mL H₂O, at 100 °C for 4 h.

^cTON (turnover number) is the ratio of mmoles of product to mmoles of catalyst.

^dThe TOF (turnover frequency) (TON/h) is mmol (mmol catalyst)⁻¹h⁻¹.

^b The yield percentages of the C-C product analyzed by GC-MS.



Fig. 10. Frontier molecular orbital (HOMOs and LUMOs) and molecular electrostatic potential (MEP) of the studying reagents.

Table 8	
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Quantum parameters of inhibitor molecules in gas	s and water phases.
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Compound	HPHL		NiPHL		VOPHL	
	gas	water	gas	water	gas	water
$\begin{array}{c} E_{HOMO} \; (eV) \\ E_{LUMO} \; (eV) \\ \Delta E \; (eV) \\ (eV) \\ H \; (eV) \\ \sigma \; (eV^{-1}) \\ \Delta N \; (e) \\ \mu \; (Debye) \end{array}$	-5.90 -2.20 3.70 4.05 1.85 0.54 -0.79 9.89	-6.07 -2.17 3.90 4.12 1.95 0.51 -0.74 11.89	-5.33 -1.94 3.39 3.64 1.70 0.59 -0.99 10.98	-5.65 -1.88 3.77 3.76 1.89 0.53 -0.86 16.26	- 3.85 - 1.63 2.22 2.74 1.11 0.90 - 1.92 13.94	-4.14 -1.63 2.51 2.89 1.25 0.80 -1.64 18.75

NiPHL and H₂PHL. Consequently, VOPHL has better tendency of polarization. From Table 10, the fraction of electron transfer (Δ N) values for the studying molecules. The high value of Δ N for VOPHL refers to that it is more favored electron donor, so, more favored corrosion inhibiting reagent and more effective catalyst for the (ep)oxidation processes compared to that of NiPHL and H₂PHL (as corrosive inhibitor).

Obviously, those results are considerably oppositely directed to the C–C cross-coupling reactions. The ΔN values aid to explain why NIPHL

has more reactive potential as a catalyst for the C–C cross-couplings regarding that of VOPHL. The most effective step in the catalytic process is the formation of the active catalyst within the reduction of the metal ion to a lower oxidation state [82]. So, NiPHL is an effective catalyst for C–C cross-couplings more than VOPHL.

Mulliken atomic charges are descriptor that determines the local reactivity of the represent molecule. The various atomic charges of H₂PHL, NiPHL and VOPHL are shown in Fig. 11. Atoms that carry a higher negative charge act as electron donors. So, oxygen atoms in three studied molecules are active sites capable of delivering electrons as they interact with the metal surface. While, the sulfur atoms of H₂PHL, NiPHL and VOPHL in addition to vanadium atoms in case of VOPHL molecule carry a high density of positive charges. This shows that these atoms are considered electron acceptor active sites.

4. Conclusion

New sustainable di-Schiff base ligand H₂PHL, derived from terephthaloyl salicylidene dihydrazone, and its VO(II) and Ni(II) complexes have been prepared with full characterization by different spectral tools. H₂PHL formed complexes with VO²⁺ and Ni²⁺ ions with 1: 2 equimolar amounts affording homodinuclear complexes, NiPHL



Fig. 11. Mulliken atomic charges of H₂PHL, NiPHL and VOPHL.

and VOPHL, respectively. In the corrosion inhibition studies, H₂PHL, NiPHL and VOPHL indicated fundamental protection action for M- steel in CO₂-3.5% NaCl solution. PDP measurements show that H₂PHL,

NiPHL or VOPHL acts as mixed-type inhibitors and could efficiently prevent both cathodic and anodic reactions through the chemical adsorption on the surface of carbon steel which obeys a Langmuir model. Results showed that NiPHL and VOPHL show better inhibition performance as compared to their corresponding ligand H₂PHL. The maximum inhibition protection value for H₂PHL, NiPHL or VOPHL is 89.57, 97.25 or 98.22% at 0.1 mM, respectively. Surface analyses (SEM/EDS) confirmed the formation of a protective layer on the M-steel surface of the inhibiting reagent. Homogeneously, the catalytic potential of NiPHL and VOPHL was investigated in the (ep)oxidation of 1,2-cyclohexene under sustainable conditions, VOPHL showed higher catalytic reactivity towards such oxidation processes more than that NiPHL, at low and high reaction temperatures. The central metal ion plays a major role to improve their catalytic potentials, V^{4+} could be easily oxidized to V^{5+} , whereas. Ni²⁺ could not easily oxidize to Ni³⁺ ion. Aqueous hydrolysis of epoxy-cyclohexane could be reduced to low amount percentages in low temperature of the (ep)oxidation processes of 1,2-cyclohexene under sustainable conditions. In the Suzuki-Miyaura cross-coupling of phenylboronic acid and aryl halides under sustainable conditions, NiPHL is more effective than VOPHL is a homogeneous catalyst. Theoretical results are convenient with the considered experimental inhibition potentials and catalytic reactivity of represented compounds. The future perspective suggested more research on VO²⁺-chelating complexes of various ligand backbone as catalysts for cross-coupling systems. Both VO²⁺- and Ni²⁺-chelates could be applied as corrosion inhibitors industrially due to their cheap cost preparation and high reactivity.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Appendix A. Supplementary data

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