Corrosion Inhibition of Carbon Steel in Acidic Environment by Imidazolium Ionic Liquids Containing Vinyl-Hexafluorophosphate as Anion

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Five imidazolium-type ionic liquids, containing both N1-unsatured chain and N3-long alkyl saturated chain as cations and hexafluorophosphate as anion (VImC_xPF₆, x=4, 8, 12, 18 and 22), were evaluated as corrosion inhibitors for carbon steel SAE 1018 in 1.0 M H₂SO₄ solution. The compounds presented relatively high inhibition efficiencies (~81-96%) at 100 ppm as confirmed by weight loss tests and polarization curves. Synthesized inhibitors obeyed Langmuir adsorption and behaved as mixed type inhibitors, displaying physical and chemical adsorption depending on the length of the carbon chain link to N3. Mössbauer analysis of corrosion products mainly determined the presence szomolnokite (FeSO₄ H₂O), whose content increased with aliphatic chain length suggesting that corrosion inhibition occurred by iron sulfate formation. The most effective compound (VImC₁₂PF₆) was the only that displayed the presence of alpha iron, iron hydroxide and rozenite (FeSO₄ 4H₂O) as corrosion products.

Keywords: vinylimidazolium, hexfluorophosphate; ionic liquid; inhibitor efficiency; carbon steel; acidic medium, Mössbauer spectroscopy

1. INTRODUCTION

One of the most economical and practical preventive maintenance methods for minimizing and controlling corrosion in product pipelines, vessels, etc., is to treat the corrosive environment with chemical inhibitors [1,2]. The chemical corrosion inhibitors (CIs) allow decreasing the rate of corrosion process. In the oil and chemical industry, inhibitors have always been considered to be the first line of defense against corrosion [3], especially in acidic media [4-6]. The addition of chemical

inhibitors can effectively protect the metal from acid attack; as a result, there have been developed different families of chemical compounds as inhibitors. Among this class of organic compounds are fatty amides [7,8], pyridines [9-11], imidazolines [12-14], 1,3-azoles [15-17] and other groups. Nevertheless, the environmental protection standards, cost, toxicity and availability of corrosion inhibitors require continuous efforts to develop new chemicals.

Ionic liquids (ILs) have been studied by the research community during the last two decades because of their remarkable physical and chemical properties [18,19]. ILs have low vapor pressure, high thermal and chemical stability, low flammability and are capable of working as catalyst. Moreover, they are an excellent alternative to several volatile organic solvents and welcome environmentally friendly technologies [20-22]. Because ILs are non-corrosive chemical compounds, they have been investigated in electrochemical applications such as batteries [23], light emitting electrochemical cells [24] and fuel cells [25]. On the other hand, there are very few studies involving ionic liquids as corrosion inhibitors for acid environments. Zhang and Hua studied different ILs containing alkyl methylimidazolium as cation and either chloride or hydrogensulfate as anion, which have shown good properties as CIs for carbon steel in aqueous 1 M HCl [26,27]. Ashassi-Sorkhabi and Es'haghi studied 1-butyl-3-methylimidazolium bromide as CI for carbon steel corrosion in aqueous hydrochloric acid, which showed good inhibitor properties [28].

In this work, five imidazolium-type ionic liquids, containing both N1-unsatured and N3-long alkyl saturated chains as cations together with hexafluorophosphate as anion, were synthesized and evaluated as CIs for acidic environment. Weight loss tests and electrochemical polarization curves were applied to test the inhibitory properties of these compounds in AISI 1018 carbon steel immersed in $1.0 \text{ M H}_2\text{SO}_4$. The synthesized compounds displayed inhibitory properties dependent on the chain length linked to N3.

2. EXPERIMENTAL WORK

2.1 Materials

Analytical grade chemicals and triple-distilled water were used to prepare the test solution. The corrosive medium was an aqueous aerated solution 1.0 M H₂SO₄. The concentrations of the inhibitors employed were 10, 25, 50 and 100 ppm. The experiments were performed by triplicate and the average value of the weight loss and electrochemical tests were reported. For each test, freshly prepared solutions and a cleaned set of electrodes were used. In weight and electrochemical tests three sizes of specimens were used, which were made of carbon steel SAE 1018 with the following composition in wt %: C-0.17, Mn-0.40, P-0.040, S-0.050, Fe balanced. The metallic coupons for the weight loss tests have dimensions of 1 cm x 1 cm x 0.025 cm, and the working electrodes for the electrochemical tests have a surface area of 0.312 cm^2 . Before each experiment the electrode was first mechanically abraded with various grades of grinding paper (up to 1200 grit) and then polished with alumina powder (0.05 μ m). At the end they were cleaned with double distilled water and ethanol.

2.2 Measurements and Equipments.

The compounds were synthesized and characterized by ¹H and ¹³C NMR and IR spectroscopy. Melting points were measured in a Fisher Scientific apparatus equipped with a 300°C thermometer. ¹H (300 MHz) and ¹³C (75.4 MHz) NMR spectra were acquired with JEOL Eclipse-300 equipment in DMSO- d_6 , CDCl₃ or Acetone- d_6 at room temperature. Chemical shifts (δ) were reported in ppm. The microwave-assisted reactions were performed using a controllable single-mode microwave reactor, CEM Discovery, designed for synthetic use. The reactor is equipped with a magnetic stirrer and devices to control pressure, temperature (on-line IR detector) and power.

Samples of carbon steel SAE 1018 with dimensions of 5 cm x 2.54 cm x 2.54 cm were exposed to 1000 mL of 1.0 M H₂SO₄ for 90 days at room temperature with and without corrosion inhibitor; the corrosion products were then brushed from steel surface to collect a few milligrams for analysis X-ray patterns and Mössbauer spectra. A Siemens D500 diffractometer equipped with a copper anode X-ray tube to obtain the X-ray patterns was used. The K α (1.5405 Å) radiation was selected with a diffracted beam monochromator covering a diffraction angle range of $2\theta = 4$ -70 in 0.02° increments. Mössbauer spectra were taken at 27°C with conventional spectrometer operated in transmission geometry in triangular mode. The source was ⁵⁷Co in Rh matrix with an activity of about 925 MBq (25 mCi). The velocity scale and all the data are referred to metallic α -Fe absorber at 20°C. The absorption spectra were fitted using the NORMOS-SITE program [29].

2.3 Synthesis of Compounds.

A fraction of 0.03 mol of 1-vinyl-3-alkylimidazolium bromide was obtained according to the reported procedure [30]. This compound was dissolved in 30 mL of water and 0.033 mol of potassium hexafluorophosphate was added to the solution; the mixture was kept at room temperature for 4 h with magnetic stirring. After reaction completion, the ionic liquid product was separated as a phase under the solution. The residual starting materials were removed by washing with water (3 x 50 mL) and the product was dried under vacuum.

1-Vinyl-3-butylimidazolium hexafluorophosphate (VImC₄PF₆)

The product was isolated as a white solid. M.P. 71-72°C. ¹H NMR (DMSO- d_6) δ 0.92 (t, J = 7.4 Hz, 3H), 1.32 (sx, J = 7.4 Hz, 2H), 1.82 (qi, J = 7.4 Hz, 2H), 4.20 (t, J = 7.4 Hz, 2H), 5.44 (dd, $J_I =$ 8.8 Hz, $J_2 =$ 2.5 Hz, 1H), 5.96 (dd, $J_I =$ 15.4 Hz, $J_2 =$ 2.5 Hz, 1H), 7.25 (dd, $J_I =$ 15.4 Hz, $J_2 =$ 8.5 Hz, 1H), 7.90 (d, J = 1.4 Hz, 1H), 8.14 (d, J = 1.4 Hz, 1H), 9.45 (s, 1H) ppm. ¹³C NMR (DMSO- d_6) δ 12.94, 18.57, 30.80, 48.86, 108.65, 119.12, 123.03, 128.66, 135.02 ppm. IR (500–4000 cm⁻¹, KBr pellet): v 3172, 2962, 2881, 1666, 1577, 1552, 1465, 1375, 1178, 962, 933, 844, 746, 557 cm⁻¹.

1-Vinyl-3-octylimidazolium hexafluorophosphate (VImC₈PF₆)

The product was obtained as a yellow viscose liquid. ¹H NMR (DMSO- d_6) δ 0.87 (t, J = 7.1 Hz, 3H), 1.27 (m, 10H), 1.84 (qi, J = 7.1 Hz, 2H), 4.19 (t, J = 7.1 Hz, 2H), 5.44 (dd, $J_I = 8.5$ Hz, $J_2 = 2.5$ Hz, 1H), 5.96 (dd, $J_I = 15.7$ Hz, $J_2 = 2.2$ Hz, 1H), 7.26 (dd, $J_I = 15.7$ Hz, $J_2 = 8.8$ Hz, 1H), 7.89 (d,

J = 1.6 Hz, 1H), 8.14 (d, J = 1.6 Hz, 1H), 9.45 (s, 1H) ppm. ¹³C NMR (DMSO- d_6) δ 13.58, 21.75, 25.28, 28.06, 28.14, 28.82, 30.88, 49.14, 108.62, 119.10, 123.03, 128.68, 135.03 ppm. IR (500–4000 cm⁻¹, KBr pellet): *v* 3162, 2929, 2858, 1654, 1554, 1467, 1376, 1172, 836, 557 cm⁻¹.

1-Vinyl-3-dodecylimidazolium hexafluorophosphate (VIm $C_{12}PF_6$)

The product was isolated as a white powder. M.P. 70-71°C. ¹H NMR (DMSO- d_6) δ 0.86 (t, J = 6.9 Hz, 3H), 1.25 (m, 18H), 1.83 (qi, J = 7.1 Hz, 2H), 4.19 (t, J = 7.1 Hz, 2H), 5.44 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.2$ Hz, 1H), 5.96 (dd, $J_1 = 15.7$ Hz, $J_2 = 2.2$ Hz, 1H), 7.26 (dd, $J_1 = 15.7$ Hz, $J_2 = 8.8$ Hz, 1H), 7.89 (d, J = 1.6 Hz, 1H), 8.15 (d, J = 1.6 Hz, 1H), 9.45 (s, 1H) ppm. ¹³C NMR (DMSO- d_6) δ 13.59, 21.77, 25.27, 28.09, 28.40, 28.50, 28.64, 28.72 (2C), 28.82, 31.00, 49.13, 108.60, 119.09, 123.02, 128.66, 135.02 ppm. IR (500–4000 cm⁻¹, KBr pellet): *v* 3178, 2921, 2852, 1662, 1554, 1467, 1178, 860, 819, 746, 557 cm⁻¹.

1-Vinyl-3-octadecylimidazolium hexafluorophosphate (VImC₁₈PF₆)

The product was isolated as a white powder. M.P. 94-95 °C. ¹H NMR (CDCl₃) δ 0.88 (t, J = 6.9 Hz, 3H), 1.25 (m, 30H), 1.88 (m, 2H), 4.20 (t, J = 7.4 Hz, 2H), 5.40 (dd, $J_1 = 8.5$ Hz, $J_2 = 3.0$ Hz, 1H), 5.80 (dd, $J_1 = 15.4$ Hz, $J_2 = 3.0$ Hz, 1H), 7.07 (dd, $J_1 = 15.7$ Hz, $J_2 = 8.8$ Hz, 1H), 7.38 (s, 1H), 7.59 (s, 1H), 8.76 (s, 1H) ppm. ¹³C NMR (CDCl₃) δ 14.30, 22.89, 26.39, 29.15, 29.57, 29.75, 29.93 (9C), 30.07, 32.13, 50.77, 110.45, 119.66, 123.12, 128.21, 134.22 ppm. IR (500–4000 cm⁻¹, KBr pellet): v3475, 3396, 3133, 3087, 2917, 2848, 1648, 1552, 1465, 1172, 815, 719 cm⁻¹.

1-Vinyl-3-undodecylimidazolium hexafluorophosphate (VImC₂₂PF₆)

The product was obtained as a white powder. M.P. 100-101°C. ¹H NMR (CD₃COCD₃) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.28 (m, 38H), 1.98 (m, 2H), 4.42 (t, *J* = 7.1 Hz, 2H), 5.49 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.8 Hz, 1H), 5.99 (dd, *J*₁ = 15.7 Hz, *J*₂ = 2.8 Hz, 1H), 7.38 (dd, *J*₁ = 15.6 Hz, *J*₂ = 8.8 Hz, 1H), 7.91 (d, *J* = 1.6 Hz, 1H), 8.13 (d, *J* = 1.6 Hz, 1H), 9.33 (s, 1H) ppm. ¹³C NMR (CD₃COCD₃) δ 14.43, 23.41, 26.93, 30.18, 30.48 (15C), 30.68, 32.73, 51.14, 109.95, 120.63, 124.47, 129.84, 136.06 ppm. IR (500–4000 cm⁻¹, KBr pellet): *v* 3469, 3401, 3133, 3085, 2917, 2850, 1648, 1550, 1465, 1174, 719 cm⁻¹.

2.4 Weight loss tests

Weight loss measurements were performed at 25°C and 40°C for 6 h by placing the carbon steel coupons into the acid solution (100 mL) with and without different amounts of inhibitor. At the end of the testing period, the specimens were cleaned according to ASTM G01 [31] and finally its weight loss were recorded. The corrosion rate (v_{corr} , mm/year), inhibition efficiency (IE_w , %) and surface coverage (θ) were determined by the following equations.

$$v_{corr} = \frac{8.76 \times 10^4 W}{ATD} \tag{1}$$

$$\theta = \frac{v_{corr,o} - v_{corr,i}}{v_{corr,o}} \tag{2}$$

$$(IE_w, \%) = \frac{v_{corr,o} - v_{corr,i}}{v_{corr,o}} \times 100$$
(3)

Where W is the weight loss (g), D is the steel density (g cm⁻³), A is the coupon area (cm²), T is the exposure time (h), and $v_{corr,o}$ and $v_{corr,i}$ are the weight loss values in the absence and presence of inhibitors, respectively.

2.5 Electrochemical tests

Electrochemical measurements were performed in a conventional three-electrode glass cell. Electrode potentials were measured against a saturated calomel electrode (SCE), the counter electrode was a mesh of Pt (purity 99.9%) and the working electrode was made of carbon steel SAE 1018 (0.312 cm²).

The SCE was connected to a Luggin capillary, the tip of which was placed very close to the surface of the working electrode to minimize IR drop. Tests were performed at 25±1°C and thermostatically controlled.

Electrochemical testing was performed in a potentiostat/galvanostat PGSTAT302N controlled by a PC through the general purpose electrochemical system (GPES); the software provided by AUTOLAB. The specimen was immersed in the test solution for 40 minutes at the open circuit potential (E_{ocp}) to reach a steady-state condition.

The polarization resistance measurements (R_p) were then performed in the potential range of $\pm 20 \text{ mV}$ versus E_{ocp} at a scan rate of 1.0 mVs⁻¹. This was followed by the cathodic and anodic polarization curves in the potential range of -250 mV to E_{ocp} , and from E_{ocp} to +250 mV at the same scan rate [32,33]. The inhibition efficiencies were determined from the measured polarization resistance values as:

$$(IE_{Rp}, \%) = \frac{R_p^i - R_p^o}{R_p^i} \times 100$$
(4)

Where R_p^o and R_p^i are the polarization resistances in the absence and presence of inhibitor, respectively.

Corrosion current densities (i_{corr}) obtained by Tafel extrapolations were used to determine the inhibition efficiencies using the equation:

$$(IE_T\%) = \frac{i_{corr}^o - i_{corr}^i}{i_{corr}^o} \times 100$$
⁽⁵⁾

Where i_{corr}^{i} and i_{corr}^{o} are the corrosion current densities values with and without inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1 Weight loss tests

The corrosion rate of carbon steel exposed to $1.0 \text{ M H}_2\text{SO}_4$ at 25 and 40°C as a function of CI concentration is shown in Figs. 1 and 2. In these figures, it is observed that at 25 and 40°C, the corrosion rate of carbon steel decreased as the concentration of CI was increased.



Figure 1. Corrosion rate of carbon steel 1018 in 1.0 M H₂SO₄ solution at 25°C in the presence of inhibitors.



Figure 2. Corrosion rate of carbon steel 1018 in 1.0 M H₂SO₄ solution at 40°C in the presence of inhibitors.

This behavior could be attributed to an increase in molecular adsorption of $VImC_xPF_6$ (where x= 4, 8, 12, 18 and 22) compounds at the metal/solution interface on increasing its concentration.

Namely, as concentration is increased a large shift of water molecules and sulfated ions by inhibitor molecules occurred on the active sites of steel immersed in the aggressive environment. The values of v_{corr} and of $IE_w(\%)$ obtained from weight loss tests at different concentrations of VImC_xPF₆ and test temperatures are summarized in Table 1.

Compounds		T= 25°C, 6 h		T= 40°C, 6 h	
	Concentration	v _{corr}	$IE_{w}(\%)$	v_{corr} (mm/y)	IE_{w} (%)
	(ppm/M)	(mm/y)			
Blank	-	681	-	1956	-
VImC ₄ PF ₆	10/2.65 x 10 ⁻⁵	300	56	685	65
	25/6.63 x 10 ⁻⁵	184	73	528	73
	50/1.33 x 10 ⁻⁴	143	79	333	83
	100/2.65 x 10 ⁻⁴	136	80	293	85
VImC ₈ PF ₆	10/2.23 x 10 ⁻⁵	184	73	411	79
	25/5.57 x 10 ⁻⁵	157	77	372	81
	50/1.11 x 10 ⁻⁴	123	82	293	85
	100/2.23 x 10 ⁻⁴	102	85	235	88
VImC ₁₂ PF ₆	10/1.92 x 10 ⁻⁵	102	85	196	90
	25/4.81 x 10 ⁻⁵	75	89	137	93
	50/9.61 x 10 ⁻⁵	68	90	137	93
	100/1.92 x 10 ⁻⁴	34	95	59	97
VImC ₁₈ PF ₆	10/1.59 x 10 ⁻⁵	143	79	254	87
	25/3.98 x 10 ⁻⁵	102	85	137	93
	50/7.97 x 10 ⁻⁵	82	88	98	95
	100/1.59 x 10 ⁻⁴	61	91	98	95
VImC ₂₂ PF ₆	$10/1.43 \times 10^{-5}$	164	76	391	80
	25/3.58 x 10 ⁻⁵	116	83	293	85
	50/7.15 x 10 ⁻⁵	95	86	215	89
	100/1.43 x 10 ⁻⁴	82	88	176	91

Table 1. Inhibitor efficiencies of carbon steel in 1.0 M H₂SO₄ containing different concentrations of ionic liquids.

The v_{corr} of steel decreased with CI concentration at 25 and 40°C, The v_{corr} of steel decreased when the CI decreased in both cases, at 25 and 40°C, the highest corrosion rates were obtained with the VImC₁₂PF₆ and the lowest ones with VImC₄PF₆ at the CI evaluated. The compounds, in all cases, presented the lowest v_{corr} at 100 ppm and the highest ones at 10 ppm. The inhibition efficiency for all the compounds increased by increasing inhibition concentration; the maximum inhibition efficiency for each compound was obtained at 100 ppm. In Table 1, it is observed that the most efficient compound was VImC₁₂PF₆ with a maximum efficiency of 95-97% at 100 ppm at temperatures of 25 and 40°C, whereasVImC₄PF₆ was the least efficient 80-85% under the same conditions. The inhibition efficiency for the compounds VImC_xPF₆ increased with temperature. This behavior may be attributable

to the stability of film inhibitor adsorbed on the metal surface, which is likely as these compounds are very stable in acid environments at moderate temperatures. It is important to note that the difference in compounds $VImC_xPF_6$ are only in the alkyl chain size. This variable, N3-long alkyl saturated chain, is therefore responsible of the adsorption ability of each molecule, which isolates the metal surface from the bulk of the corrosive environment.

3.2 Potentiodynamic polarization tests

The values of electrochemical parameters, i.e., corrosion current density (i_{corr}) , corrosion potential (E_{corr}) , Tafel slops (β_c) and inhibitor efficiency $(IE_T, \%)$ obtained as function of VImC_xPF₆ concentrations are given in Table 2.

Table 2. Electrochemical parameters for carbon steel in 1.0 M H_2SO_4 at different concentrations of $VImC_xPF_6$ at 25°C.

Inhibitor	Concentration (ppm)/(M)	-E _{corr} (mV/SCE)	$i_{\rm corr}(\mu {\rm A/cm}^2)$	$-\beta_{\rm C}({\rm mVdec}^{-1})$	$IE_{T}(\%)$
Blank	-	497	1314	125	
VImC ₄ PF ₆	10/2.65 x 10 ⁻⁵	497	415	132	68
	25/6.63 x 10 ⁻⁵	497	203	119	84
	50/1.33 x 10 ⁻⁴	481	186	119	85
	100/2.65 x 10 ⁻⁴	488	185	112	85
VImC ₈ PF ₆	10/2.23 x 10 ⁻⁵	489	234	123	82
	25/5.57 x 10 ⁻⁵	492	208	117	84
	50/1.11 x 10 ⁻⁴	499	185	124	86
	100/2.23 x 10 ⁻⁴	493	131	127	90
VImC ₁₂ PF ₆	10/1.92 x 10 ⁻⁵	508	125	119	90
	25/4.81 x 10 ⁻⁵	492	128	131	90
	50/9.61 x 10 ⁻⁵	489	114	130	91
	100/1.92 x 10 ⁻⁴	467	52	133	96
VImC ₁₈ PF ₆	10/1.59 x 10 ⁻⁵	498	217	131	83
	25/3.98 x 10 ⁻⁵	498	137	122	90
	50/7.97 x 10 ⁻⁵	487	85	124	94
	100/1.59 x 10 ⁻⁴	467	69	107	95
VImC ₂₂ PF ₆	10/1.43 x 10 ⁻⁵	504	208	120	84
	25/3.58 x 10 ⁻⁵	499	131	110	90
	50/7.15 x 10 ⁻⁵	498	83	108	94
	100/1.43 x 10 ⁻⁴	492	52	104	96



Figure 3. Potentiodynamic polarization curves for carbon steel 1018 in 1.0 M H₂SO₄ solution after adding different concentrations of inhibitor VImC₄PF₆.



Figure 4. Potentiodynamic polarization curves for carbon steel 1018 in 1.0 M H₂SO₄ solution after adding different concentrations of inhibitor VImC₁₂PF₆.



Figure 5. Potentiodynamic polarization curves for carbon steel 1018 in 1.0 M H₂SO₄ solution after adding different concentrations of inhibitor VImC₂₂PF₆.

The inhibitor efficiency was determined by equation (5), in which i_{corr} was obtained by extrapolating the Tafel's slopes to the corresponding free corrosion potential [34]. Figs. 3-5 show the influence of VImC_xPF₆ (x= 4, 12 and 22) on the cathodic and anodic potentiodynamic polarization curves of carbon steel 1018 in 1.0 M H₂SO₄; similar curves were obtained for compounds VImC_xPF₆ (x = 8 and 18). In these figures, it is clear that both anodic metal dissolution and cathodic reduction reactions were inhibited, when the VImC_xPF₆ compound was added to the acid solution; inhibition was magnified as CI concentration was increased. The presence of VImC_xPF₆ induced a shift in the corrosion potential in the cathodic (11 mV) and anodic (30 mV) directions, when compared with that of the blank in 1.0 M H₂SO₄.

A few researchers have reported the classification of inhibitor type as a function of the change in the electrode potential compared to the open circuit potential [35,36]. An inhibitor can be designed as cathodic or anodic if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the blank. Accordingly, the compounds $VImC_xPF_6$ tested in 1 M H₂SO₄ are of the mixed type. Figs. 3-5 show that the cathodic branch displays a typical Tafel behavior. This behavior is necessary to make an accurate evaluation of corrosion rate [37]. In contrast, the anodic branch displayed two inflections (Fig. 3-5); the first located within E_{corr} to +74 mV and the second from +74 mV to +130 mV. $VImC_xPF_6$ affected therefore the anodic reaction at potential lower than E_{corr} at +74 mV due to compound adsorption. Whereas the second inflection is probably ascribed to metal dissolution along with the desorption of low solubility sulfate-type corrosion products of low solubility of iron sulphate type such as melanterite, rozenite, szomolnokite, besides oxydroxides (i.e. goetite) and metal impurities. These processes are developed on steel surface because the desorption rate of $VImC_xPF_6$ is faster than that of molecular adsorption.

Table 3. Electrochemical parameters for carbon steel in 1.0 M H₂SO₄ obtained from polarization resistance tests.

Inhibitor	Inhibitor	$Rp (\Omega cm^2)$	$-E_{corr}$	IE _{Rp} , %
	(ppm/M)		(III V/LSC)	
	-	98	491	-
VImC ₄ PF ₆	10/2.65 x 10 ⁻⁵	253	490	61
	25/6.63 x 10 ⁻⁵	445	494	78
	50/1.33 x 10 ⁻⁴	499	488	80
	100/2.65 x 10 ⁻⁴	506	491	81
VImC ₈ PF ₆	10/2.23 x 10 ⁻⁵	481	495	80
	25/5.57 x 10 ⁻⁵	522	500	81
	50/1.11 x 10 ⁻⁴	538	501	82
	100/2.23 x 10 ⁻⁴	650	495	85
VImC ₁₂ PF ₆	10/1.92 x 10 ⁻⁵	690	502	86
	25/4.81 x 10 ⁻⁵	710	492	86
	50/9.61 x 10 ⁻⁵	790	485	88
	100/1.92 x 10 ⁻⁴	1032	474	91
VImC ₁₈ PF ₆	10/1.59 x 10 ⁻⁵	450	497	78
	25/3.98 x 10 ⁻⁵	713	495	86
	50/7.97 x 10 ⁻⁵	789	489	88
	100/1.59 x 10 ⁻⁴	935	466	90
VImC ₂₂ PF ₆	10/1.43 x 10 ⁻⁵	534	501	82
	25/3.58 x 10 ⁻⁵	675	509	85
	50/7.15 x 10 ⁻⁵	810	503	88
	$100/1.43 \times 10^{-4}$	1045	499	91

The corrosion mechanism of carbon steel in diluted sulfuric acid has been described by the following reactions [38, 39].

$$Fe + H^{+} + e^{-} \Rightarrow FeH$$
 (6)

$$FeH + FeH \implies 2Fe + H_2$$
(7)

 $(OH^{\mbox{-}})_{ads}$ ions can be formed from the adsorbed water.

 $(H_2O)_{ads} \Rightarrow (OH^{-})_{ads} + H^{+}(aq)$ (8)

$$Fe + (OH^{-})_{ads} \Leftrightarrow Fe(OH)_{ads} + e^{-}$$
(9)

$$Fe(OH)_{ads} \Longrightarrow FeOH^+ + e^-$$
(10)

$$FeOH^{+} + H^{+} \Leftrightarrow Fe^{2+} + H_2O$$
(11)

However, the corrosion mechanism of steel in the presence of inhibitor changes as follows:

$$Fe + Inh \Leftrightarrow Fe(Inh)_{ads} \Leftrightarrow Fe^{n+} + ne^{-} + Inh$$
 (12)

The inhibition mechanism (6-12) may apply also for the case of $VImC_xPF_6$ on the anodic sites. However, we think that the mechanism in the anodic and cathodic is more complex as discussed in 3.6. The cathodic branch displayed parallel lines with a nearly constant cathodic slope (βc), which is not modified by the addition of $VImC_xPF_6$ in the corrosive environment, so that it appears they do not modify hydrogen reduction mechanism and therefore reaction on the steel surface is controlled by activation [40,41].

Inhibitor efficiency derived from weight loss tests was confirmed by polarization curves; $VImC_{12}PF_6$, was the most efficient compound while $VImC_4PF_6$ was the least effective; the order of inhibitor efficiency of compounds evaluated as corrosion inhibitors is as follows: $VImC_4PF_6$ < $VImC_8PF_6$ < $VImC_{12}PF_6$ > $VImC_{18}PF_6$ > $VImC_{22}PF_6$. These results are very important because they confirm that the length of hydrophilic chain play an important role in corrosion inhibition.

Table 3 provides the polarization resistances (R_p) of carbon steel in the aggressive environment as a function of inhibitor concentration; they were calculated from the slope of electrode potential and current density equations [42]. It is observed that the polarization resistance increased with the increase of inhibitor concentration; the relative high values of R_p indicated that an inhibition process is occurring on the metal surface. As a result, there is a decrease in active sites and a drop in corrosion current as a lower dissolution rate of the metallic material takes place. The values obtained of the inhibition efficiency by polarization resistances are lower than those determined from the polarization curves in approximately 6 %, but the trend is similar in both cases. The inhibition process of these compounds was proposed as a result of a blocking mechanism of the actives sites on steel surface, which may happen by chemical and/or physical adsorption.

3.3 Adsorption isotherm

The adsorption of inhibitor molecules on the corroding surfaces generally does not reach the real equilibrium and tends to a steady state. It is therefore reasonable to consider quasi-equilibrium adsorption in thermodynamic by using the appropriate adsorption isotherm.

Corrosion inhibition of carbon steel in sulfuric acid solution can be explained in terms of molecular adsorption, which is influenced by the chemical structure and charge distribution of inhibitor, the nature and surface charge of metal and the type of aggressive media [39]. The process of

inhibitor adsorption on metal surface can be described by different isotherms, from which Langmuir is the simplest and it is based on the assumption that all adsorption sites are equivalent and the particle binding occurs independently from nearby sites being occupied or not [43, 44]. In order to obtain adsorption isotherm, the surface coverage values (θ) for the inhibitors were obtained from the weight loss measurements at different concentrations of VImC_xPF₆ in 1.0 M H₂SO₄ solution at 25 and 40°C (Table 1), based on the following models.

Temkin isotherm
$$k_{ads}C = exp(f.\theta)$$
 (13)

Langmuir isotherm
$$k_{ads}C = \frac{\theta}{(1-\theta)}$$
 (14)

Frumkin isotherm
$$k_{ads}C = \frac{\theta}{(1-\theta).\exp(-2f.\theta)}$$
 (15)

Freundluich isotherm
$$k_{ads}C = \theta$$
 (16)

where k_{ads} is the equilibrium constant of the adsorption process, C is the inhibitor concentration and f is the factor of energetic inhomogeneity. The best fitting to the adsorption inhibitor behavior was provided by Langmuir.



Figure 6. Langmuir adsorption isotherms after fitting for $VImC_xPF_6$ inhibitors used for carbon steel in 1.0 M H₂SO₄ at 25°C.

Fig. 6 shows a good fitting between C_{inh}/θ versus C_{inh} , whose correlation factor was close to unit for the VImC_xPF₆ at the temperatures of 25 and 40°C. This allowed establishing that the molecules of corrosion inhibitors VImC_xPF₆ are really adsorbed in the metal/solution interface and protected the steel surface from the corrosive medium. The high value of the adsorption equilibrium constant reflects the high adsorption ability of these types of corrosion inhibitors on steel surface (Table 4). Other works have reported values close to those obtained in this work during the evaluation of corrosion inhibitors in acidic media for carbon steel [39]. The free energy of adsorption (ΔG_{ads}) of inhibitor on steel surface can be determined as:

$$\Delta G_{ads} = -RT \ln(55.5k_{ads}) \tag{17}$$

Compounds	T=	25 °C	T=40 °C		
	$\ln (K_{ads}, mol^{-1})$	$-\Delta G (kJmol^{-1})$	$ln(K_{ads}, mol^{-1})$	$-\Delta G (kJmol^{-1})$	
VImC ₄ PF ₆	11.3	37.9	11.3	37.9	
VImC ₈ PF ₆	11.9	39.5	12.2	40.1	
VImC ₁₂ PF ₆	12.4	40.7	12.8	41.7	
VImC ₁₈ PF ₆	12.6	41.1	13.6	43.8	
VImC ₂₂ PF ₆	12.7	41.4	12.7	41.5	

Table 4. Thermodynamical parameters of $VImC_xPF_6$ adsorbed on carbon steel surface at different temperatures.

The negative values of the free energy of adsorption (Table 4) indicate that adsorption process occurred spontaneously with the formation of a film adsorbed on the steel surface. This may be explained as follows: before the adsorption of inhibitors onto the steel surface, water and contaminants are moving randomly on steel surface; and when inhibitor is added, the molecules are orderly adsorbed onto the steel surface, this originates a decrease in entropy. As a rule, standard free energies of adsorption around -20 kJmol⁻¹ or lower are characteristic of electrostatic interactions between the charged molecules and the charged metal, which indicates that a process of physical adsorption may occur. However, when ΔG_{ads} values are around -40 kJmol⁻¹ or higher chemical adsorption takes place [45]. In this case, VImC₄PF₆ inhibitor has a standard free energy lower than -40 kJmol⁻¹, which suggests that a physical adsorption process is acting on the steel surface, as it is explained in the section of inhibition mechanism. However, the compounds of VImC_xPF₆ (x= 8, 12, 18 and 22) displayed a chemical adsorption on steel, the negative values of ΔG_{ads} along with those of k_{ads} indicated that a spontaneous adsorption process occurred and inhibitors showed a good chemical stability on the metal surface [39, 45].

3.4 Analysis of corrosion products

Figure 7 (a) shows the XRD pattern for the blank material, it displays the presence of different species of goethite (α -FeOOH) (JCPDS No 01-0401, No 81-0464 and No 29-0713). The XRD pattern of the VImC₄PF₆ material (Fig. 7(b)) contains the peaks referred to in the card No. JCPDS No 81-0019, which suggests the presence of szomolnokite (Fe₂SO₄H₂O) phase; the pattern also shows a slight amount of cementite (Fe₃C), as displayed by peaks of low intensity at 2 θ = 19.5 and 22.2° (JCPDS No. 3-989).

The Mössbauer spectra taken at 27°C of the samples of corrosion products are shown in Figs. 8-13 and the parameters involved are reported in Table 5. The spectrum of the blank sample displays (Fig. 8) a broad paramagnetic doublet with IS = 0.290 mm/s and QS = 0.580 mm/s. Mössbauer parameters can be assigned to the presence of superparamagnetic goethite (α -FeOOH), lepidocrocite (γ -FeOOH), akageneite (β -FeOOH) and/or ferrihydrite.



Figure 7. XRD analysis for carbon steel after exposure to acidic environment for (a) blank and (b) inhibited material at 100 ppm $(2.65 \times 10^{-4} \text{ M})$ of VImC₄PF₆.

Sample with compounds	δ mm/s	Δ mm/s	Bhf (Teslas)	Phase	Relative area %
Blank	0.29 ± 0.02	2.72 ± 0.01		(α-FeOOH)	100.0
VImC ₄ PF ₆	0.10 ± 0.01	0.08 ± 0.02	20.6 ± 0.2	Fe ₃ C	12.7
	1.14 ± 0.02	2.72 ± 0.01		FeSO ₄ H ₂ O	80.5
	0.26 ± 0.03	0.38 ± 0.03		Fe(OH) ₃	6.8
VImC ₈ PF ₆	0.10 ± 0.03	0.04 ± 0.05	20.6 ± 0.2	Fe ₃ C	10.8
	1.13 ± 0.02	2.71 ± 0.04		FeSO ₄ H ₂ O	76.8
	0.26 ± 0.02	0.47 ± 0.01		Fe(OH) ₃	12.4
VImC ₁₂ PF ₆	-0.10 ± 0.01	0.0 ± 0.01	33.1 ± 0.8	α-Fe	4.5
	1.14 ± 0.03	3.15 ± 0.04		FeSO ₄ 4H ₂ O	90.5
	0.22 ± 0.03	0.47 ± 0.03		Fe(OH) ₃	5.0
VImC ₁₈ PF ₆	0.08 ± 0.05	0.08 ± 0.02	21.2 ± 0.5	Fe ₃ C	4.5
	1.16 ± 0.03	2.78 ± 0.03		FeSO ₄ H ₂ O	95.5
VImC ₂₂ PF ₆	1.15 ± 0.01	2.74 ± 0.02		FeSO ₄ H ₂ O	95.5
	0.24 ± 0.01	0.47 ± 0.05		$Fe(OH)_3$	4.5

Table 5. Mössbauer parameters obtained at 27°C.

 δ = Chemical Shift relative to α-Fe, Δ = Quadrupole splitting. Bhf = hyperfine magnetic field.

The spectrum of sample of corrosion products with VImC₄PF₆ at 100 ppm (Fig. 9) could be fitted to one magnetic sextet and two doublets; the Mössbauer parameters ($\delta = 0.10$ mm/s, $\Delta = 0.08$ and Bhf = 20.6 T) of this magnetic sextet indicated the presence of cementite (Fe₃C) phase [46].



Figure 8. Mössbauer spectroscopy for carbon steel rust after the exposure of blank material to the acidic environment.



Figure 9. Mössbauer spectrum for carbon steel in 1 M H_2SO_4 and 100 ppm (2.65x10⁻⁴ M) of $VImC_4PF_6$.



Figure 10. Mössbauer spectrum for carbon steel in 1 M H_2SO_4 and 100 ppm (2.23x10⁻⁴ M) of $VImC_8PF_6$.



Figure 11. Mössbauer spectrum for carbon steel in 1 M H_2SO_4 and 100 ppm (1.92x10⁻⁴ M) of $VImC_{12}PF_6$.



Figure 12. Mössbauer spectrum for carbon steel in 1 M H_2SO_4 and 100 ppm (1.59x10⁻⁴ M) of $VImC_{18}PF_6$.



Figure 13. Mössbauer spectrum for carbon steel in 1 M H_2SO_4 and 100 ppm (1.43x10⁻⁴ M) of $VImC_{22}PF_6$.

The first intense doublet with an $\delta = 1.14$ mm/s and $\Delta = 2.72$ mm/s, can be assigned to szomolnokite (FeSO₄H₂O) phase [47]. The second weaker doublet with $\delta = 0.26$ mm/s and $\Delta = 0.47$ mm/s can be ascribed to iron hydroxide (Fe(OH)₃) phase [48]. The Mössbauer spectrum of sample with VImC₈PF₆ at 100 ppm (Fig. 10) could be fitted to one magnetic sextet and two doublets; the Mössbauer parameters ($\delta = 0.10$ mm/s, $\Delta = 0.04$ and Bhf = 20.6 T) of this magnetic sextet indicated the presence of cementite. The first intense doublet with $\delta = 1.13$ mm/s and $\Delta = 2.71$ mm/s can be assigned to the szomolnokite phase; the second weaker doublet with $\delta = 0.26$ mm/s and $\Delta = 0.47$ mm/s was attributed to an iron hydroxide phase. The Mössbauer spectrum of sample with VImC₁₂PF₆ at 100 ppm (Fig.11) could be fitted to one magnetic sextet indicated the presence of metallic α -Fe. The first intense doublet with $\delta = 1.14$ mm/s and $\Delta = 3.15$ mm/s was assigned to the rozenite (FeSO₄4H₂O) phase; and the second weaker doublet ($\delta = 0.22$ mm/s and $\Delta = 0.47$ mm/s) to an iron hydroxide phase.

The Mössbauer spectrum of sample of corrosion products with VImC₁₈PF₆ at 100 ppm (Fig. 12) fitted with one magnetic sextet and one doublet; the parameters ($\delta = 0.08$ mm/s, $\Delta = 0.08$ and Bhf = 21.2 T) of this magnetic sextet indicated the presence of cementite; while the intense doublet with $\delta = 1.16$ mm/s and $\Delta = 2.78$ mm/s can be assigned to the szomolnokite phase. The Mössbauer spectrum of sample with VImC₂₂PF₆ at 100 ppm (Fig. 13) fitted with two doublets; the first intense doublet ($\delta = 1.15$ mm/s and $\Delta = 2.74$ mm/s) was assigned to the szomolnokite phase; whereas the second weaker doublet ($\delta = 0.24$ mm/s and $\Delta = 0.47$ mm/s) was attributed to an iron hydroxide phase.

3.5 Corrosion inhibition mechanism by experimental ionic liquids

The corrosion of 1018 carbon steel in 1.0 M H_2SO_4 was delayed by the presence of different concentrations of 1-vinyl-3-alkylimidazolium hexafluorophosphate derivatives, which were evaluated in this study. The results indicated that the inhibition mechanism (Scheme 1) involved the chemical adsorption on the metal surface and a mixed type inhibitor behavior.



Scheme 1. Corrosion inhibition mechanism and adsorption model of experimental ionic liquids on carbon steel surface in aqueous sulfuric acid medium.

On the cathodic sites the CI seems to work in the following paths: 1) the cationic part is adsorbed on the metallic surface through Van der Waals forces, this way a physical barrier is formed to prevent the adsorption of hydronium ions (H_3O^+) ; later, the chemical adsorption occurred by means of a retro-donation mechanism, in which iron ions and the pair of electrons of the vinyl group interacted. 2) The second possible path of CI is the capture of hydrogen that is formed on the metallic surface. The vinyl group participated in the hydrogenation reaction by taking the hydrogen atoms to form an ethylic group, and changing from an unsaturated to a saturated group.

On the anodic sites, in the absence of CI, metal dissolution occurred and corrosion products such as iron hydroxides (i.e. goethite) evolved. In the presence of CI, the corrosion process is significantly mitigated; this is attributable to the film formation of CI on the hydrated iron sulfate, which is one of the intermediate corrosion products. The long aliphatic chains in the cationic part of CIs that are located randomly supported the formation of highly charged micelles. Additionally, the size of aliphatic chains had an effect on the CI as the inhibitor efficiency was in the order $VImC_4PF_6 < VImC_{22}PF_6 < VImC_{18}PF_6 < VImC_{12}PF_6$, to be the most efficient CI that with 12 carbon atoms. This effect is apparently attributable to a lack of lipophilicity (C4-C8) which restricted

micelle formation; C10-C18 appeared to find an equilibrium of hydro/liphophilicity, while large chain sizes (C18-C22) displayed steric hindrance and as a result either: (1) molecules drastically increased repulsion forces among them, or 2) molecules are folded on themselves preventing micelles formation, these factors contributed to multilayer formation of CI [Fe (H₂O)_xSO₄] $VImC_n^+/SO_4^{2-}/VImC_n^+/PF_6^-$, which are stabilized by Van der Waals forces that restrained iron dissolution.

4. CONCLUSIONS

The five imidazolium-type ionic liquids containing both, N1-unsatured and N3-long alkyl saturated chains (cations), and hexafluophosphate (VImC_xPF₆) as anion, displayed an inhibition efficiency (100 ppm) within 80-97% when tested on carbon steel at 25-40°C in aqueous 1 M H₂SO₄, as confirmed by weight loss and polarization tests. Inhibition efficiency increased with concentration (10-100 ppm) and it was dependent on alkyl chain size linked to N3 (VImC₄PF₆ < VImC₈PF₆ < VImC₁₂PF₆ > VImC₁₂PF₆). It is important to note that VImC₁₂PF₆ with 12 carbon atoms displayed the best performance (95-97%) at 25 and 40°C. These compounds obeyed Langmuir adsorption isotherm and behaved as mixed type inhibitors. Mössbauer analysis of corrosion products determined the presence melanterite, rosenite, szomolnokite and consequently a considerably decrease in sulfur compounds due to FeSO₄H₂O formation is observed as an indication of corrosion inhibition.

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