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Synthesis of Fluconazole and its ionic liquid derivatives, and evaluation of their ability to prevent carbon steel corrosion in hydrochloric acid solution

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Abstract

Fluconazole, an antifungal drug, and its ionic liquid derivatives were successfully prepared and evaluated for corrosion suppression on carbon steel in hydrochloric acid solution using electrochemistry estimations. The chemical configuration and characterizations of fluconazolium ionic liquids were verified using FT-IR and nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR). The results demonstrate that the above additives perform as inhibitors in acidic corrosive environments and exhibit a strong trend in which inhibition capability increased with increasing inhibitor dose. At 100 ppm, polarization data revealed that fluconazole and fluconazolium ionic liquids had relatively high inhibition capacity ((91.26, 98.77, and 98.03%). Fluconazole and its identified ionic liquid derivatives accumulated on the surface of carbon steel using the Langmuir adsorption isotherm concept.

***Keywords*:** Fluconazole; ionic liquid; steel; corrosion; electrochemistry

1- Introduction

Carbon steel is employed in industry sectors for construction because of its ease of accessibility and minimum cost [1]. Its surface is quickly destroyed in the exposure to acids, particularly during the pickling and descaling operations [2-3]. Utilization of organic inhibitors is one of the most widely used strategies for controlling the damage of carbon steel in acid solutions [4-6]. Organic corrosion inhibitors with heter-oatoms, in addition to lone electron pairs and bond funds in their molecules that utilize as adsorption sites, have been studied [7-8]. The chemical layout of the material, the active locations of the inhibitor [9], the molecular dimensions, the nature of the steel top layer [10], the category of connections between the organic compounds and the steel surface [11], the electrochemical potential at the interface [12], the formation of complexes, and the mode of adsorption all influence the inhibitory strengths of these compounds [13-16]. Recent time, scientists have been drawn to the production of new biodegradable and less harmful corrosion inhibitors in order to reduce environmental from the dangerous effects of pollutants use on ecological integrity [17-20]. Anti-bacterial, anti-fungal, surfactants and ionic liquids have recently been discovered as biodegradable, non-toxic corrosion inhibitors [21-24].

The purpose of this study is to explore the inhibitory potential of fluconazole (F1), and its ionic liquid derivatives [1,1'-(2-(2,4-difluorophenyl)-2-hydroxypropane-1,3-diyl)bis(4-decyl-1H-1,2,4-triazol-4-ium) bromide (F2) and 1,1'-(2-(2,4-difluorophenyl)-2-hydroxypropane-1,3-diyl)bis(4-dodecyl-1H-1,2,4-triazol-4-ium) bromide (F3)] for carbons steel corrosion in acid solution. In the fact that Fluconazole is very cheap, easily available, nontoxic and environmental friendly, contains two triazole rings with O, N atoms and double bonds, the molecule is big

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(M.wt = 306) which aid their adsorption onto metal surfaces and preventing corrosion.

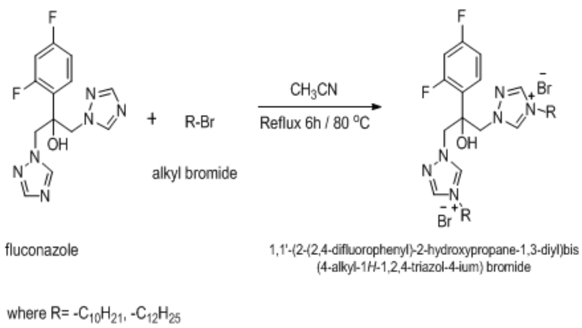
Comparing with other thematically similar research papers [25-27], the main novelty is depend on the prepared new ionic liquid derivatives from fluconazole molecule as used it as an environmental friendly corrosion inhibitors.

2- Experimental

2.1. Preparation and characterizations of ionic liquids

Fluconazoliums, which are quaternization derivatives of two triazolyl rings in Fluconazole (F2 anf F3), are synthesized.

The two ionic liquids were synthesized according to Scheme 1.



Scheme 1 Synthesis of ionic liquids (F2 = R = $C_{10}H_{21}$, F3 =R= $C_{12}H_{25}$).

Nuclear magnetic resonance (^{1}HNMR, and ^{13}C NMR) spectroscopy and FT-IR spectra have both been used to confirm the structures of ionic liquids (AVANCE-II-400-MHz+Bruker-NMR, ANA research center, Zagazig University, Egypt).

2.2. Electrochemical evaluation

An OrigaMaster/ potentiostat/galvanostat was used for the electrochemical experiments. For polarization assessments, a standard three setup was used with a carbon steel anodes (surface area = 0.345 cm^2), a platinum counter wire, and a saturated calomel electrode (SCE) as a reference electrode. A scan rate of 1 mV s^{-1} was used to obtain the polarization curves.

3. Results and discussion

3.1. FT-IR spectra fluconazolium ionic liquids

In Fig 1, fluconazolium ionic liquids' FT-IR spectra are displayed. As shown in Table 1, all of the absorption bands were also seen in the anticipated regions.

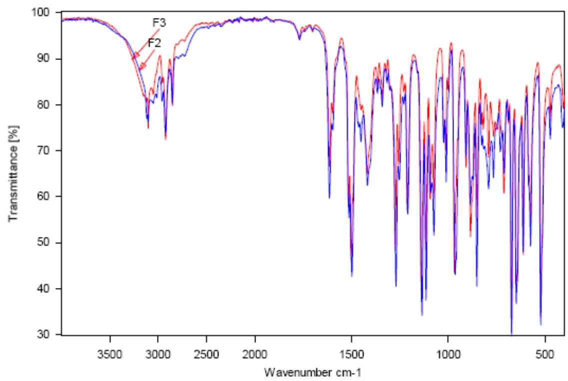


Fig.1 Ionic liquid F2's and F3's FT-IR spectra.

Table 1: FT-IR ionic liquid bands

CPD	Wave No./ (cm^{-1})								
	OH	C-H-aromatic-stretching	CH2	C=N	C-C-aromatic	CH3	C=C aromatic	Triazole ring	C-OH
F2	3118	3078	2961	1615	1466	1367	1352	1271	1075
F3	3104	3052	2924	1614	1503	1420	1304	1275	1075

3.2. ^{1}H NMR spectra of fluconazole and fluconazolium ionic liquids

^{1}H NMR spectra of fluconazole and fluconazolium ionic liquids are shown in Figs. 2, 3 and 4. Table 2 contains all of the ^{1}H NMR records for fluconazoliums and confirms the chemical structures of the synthesized materials (see Fig. 5) [21].

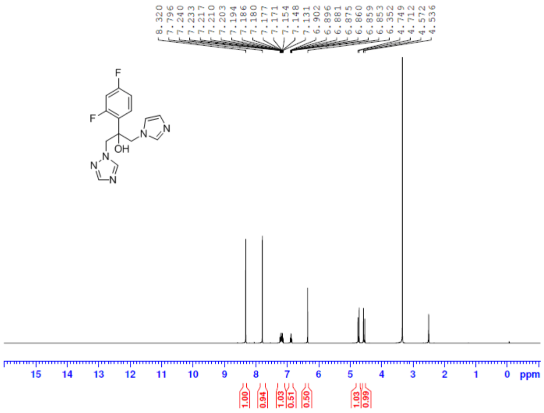


Fig. 2 ^{1}H-NMR for Fluconazole

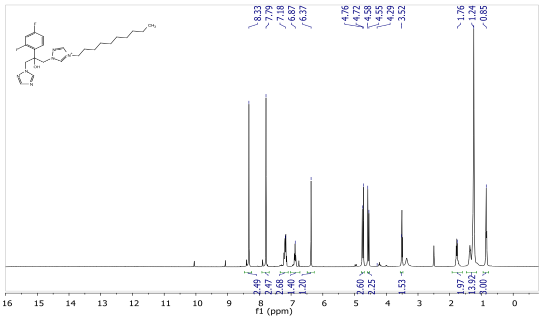


Fig. 3 ^{1}H-NMR for F2

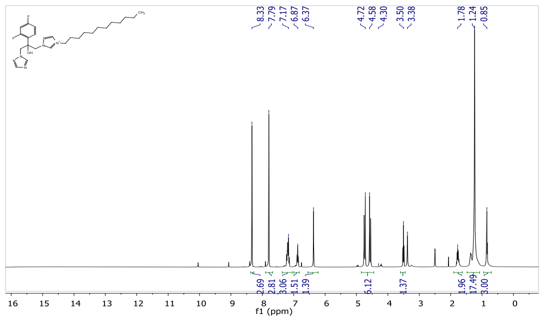


Fig. 4 ^{1}H-NMR for F3

Table 2: ^{1}H NMR records of fluconazole and ionic liquids (F2,F3).

Cpd.	H^a,H^{a^-}	H^b	H^{b^-}	$H^{c,d,e}$	OH	H^f	H^g	H^{g^-}	H^h	H^i	H^j	H^k
F1	8.32	7.79	7.79	7.2	6.35	-	-	-	-	-	-	-
F2	8.33	8.33	7.79	7.18	6.87	6.37	4.72	4,55	3.5	1.76	1.24	0.85
F3	8.33	8.33	7.79	7.17	6.87	6.37	4.72	4.58	3.5	1.78	1.24	0.86

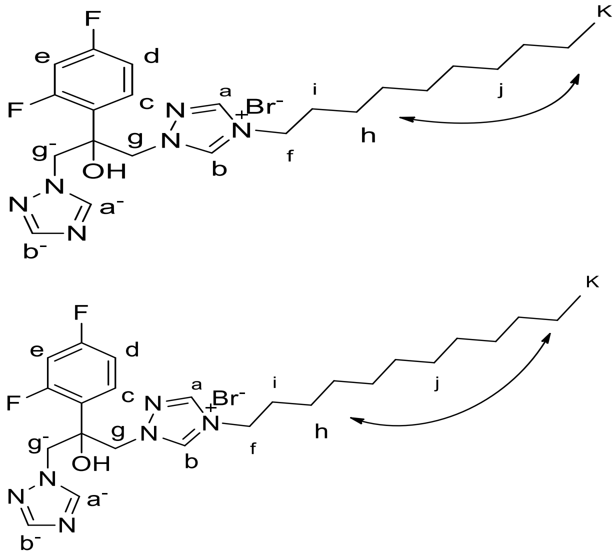


Fig. 5 Structures of F2 and F3 according to ^{1}H-NMR spectroscopy

3.3. ^{13}C-NMR spectra of fluconazole and fluconazolium ionic liquids

The chemical configurations of ionic liquids F2 and F3 are confirmed by ^{13}C-NMR spectra (Table 3 and Figs 6, 7 and 8).

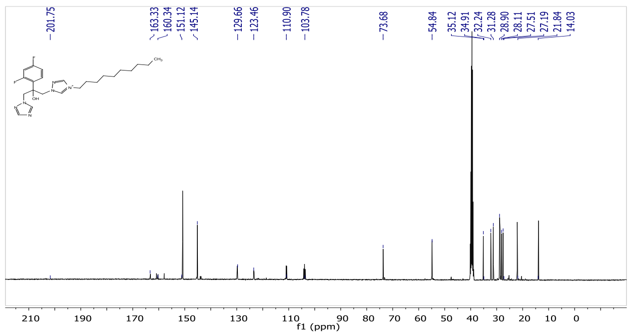


Fig. 6 ^{13}C for compound F2.

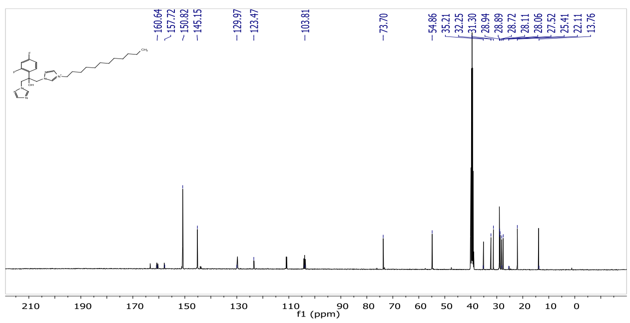


Fig. 7 ^{13}C for compound F3.

Table 3: ^{13}C-NMR values (ppm) for compounds F2 and F3

	F2	F3
C_1	14.03	13.76
C_2	21.84	22.11
C_3	27.19	25.41
C_4	27.51	27.52
C_5	28.11	28.06
C_6	28.9	28.11
C_7	31.28	28.89
C_8	34.24	31.3
C_9	34.91	32.25
C_{10}	35.12	35.21
C_{11}	54.84	54.86
C_{12}	73.68	73.7
C_{13}	103.78	103.81
C_{14}	110.90	111
C_{15}	123.46	123.47
C_{16}	129.66	129.97
C_{17}	145.14	145.15
C_{18}	151.12	150.82
C_{19}	160.34	157.72
C_{20}	163.33	160.64

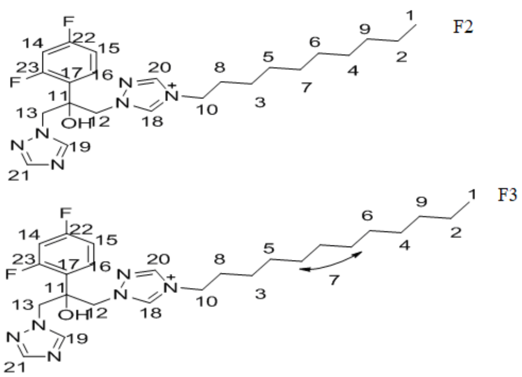


Fig. 8 Structures of F2 and F3 according to ^{13}C-NMR spectroscopy

3.4. Electrochemical tests of fluconazole and fluconazolium ionic liquids

The electrochemical methods of polarization were used to explore the anti-corrosion behavior of fluconazole and fluconazolium ionic liquids on carbon steel in 1 M HCl electrolyte Figs (9-11). Table 4 shows the corrosion current density and potential (j_{corr}, E_{corr}) and Tafel-slopes (βa and βa), and. The following relationship is used to compute the protection efficiency (P_j%) [29]:

$$P_j\% = \frac{j_{corr(0)} - j_{corr}}{j_{corr(0)}} \times 100 \qquad (1)$$

$j_{corr(0)}$ was recorded in the blank solution.

The study concluded that raising the quantity of fluconazole and fluconazolium ionic liquids reduces corrosion rate j_{corr} in HCl acid liquid.

The decline in corrosion rate is caused by the adsorption of F1, F2 and F3 molecules on the carbon steel surface, which slows the oxidation process of the anode while also replacing electrolyte molecules at the interface [30-33].

At 100ppm, fluconazole (F1) and fluconazolium ionic liquids (F2, F3) showed maximum inhibition efficiency (91.26, 98.77, and 98.03%). All inhibitors dramatically change the anodic and cathodic Tafel slopes (βa and βc), indicating that they influence the processes of both cathodic and anodic responses (they are mixed-type inhibitors), with the deviation in Tafel slope values being contributed to a modification in reaction mechanism [34-36].

The inhibitors F1, F2 and F3 fall under the category of a mixed-type inhibitor due to the displacement in E_{corr} being less than 85 mV [37].

Numerous earlier studies have shown conclusively that ionic liquids create their inhibitory activity through the adsorption of their compounds onto metal surfaces [38-41].

The kinds of ionic liquids, the charge distribution through ionic liquid compounds, the character and surface charge of steel, and the kind of corrosive environments all have an impact on the adsorption mechanism. The polarization data showed that the ionic liquids have a primarily anodic inhibitive impact, delaying both anodic (oxidation) and cathodic (reduction) reactions.

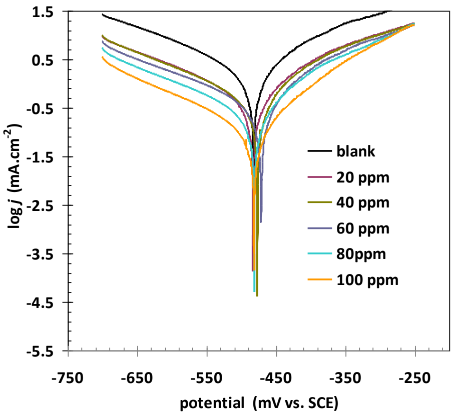


Fig. 9 At 298 K, polarization plots for carbon steel dipped in 1.0 M HCl solution as a function of F1 concentration.

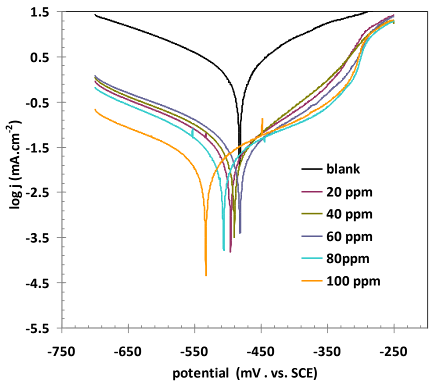


Fig. 10 At 298 K, polarization plots for carbon steel dipped in 1.0 M HCl solution as a function of F2 concentration.

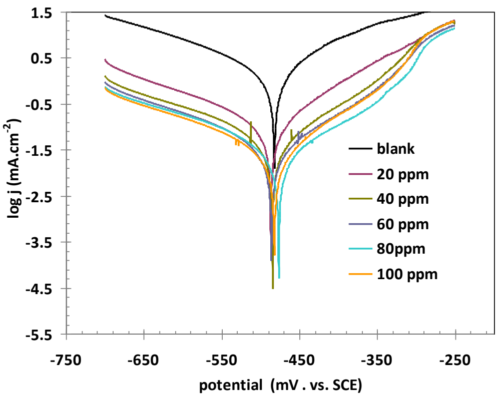


Fig. 11 At 298 K, polarization plots for carbon steel dipped in 1.0 M HCl solution as a function of F3 concentration.

Table 4 Polarization parameters and P_j% of carbon steel dipped in 1.0 M HCl solution as a function of F1 F2 and F3 concentrations.

Cpd.	conc. (ppm)	E_{corr} mV vs. SCE	j_{corr} (µA.cm^{-2})	βa (mV.dec^{-1})	βc (mV.dec^{-1})	P_j%
	1.0 M HCl	-482.0	1119.1	86.4	-115.9	-
F1	20	-483.1	586.8	123.0	123.0	47.56
	40	-476.5	459.2	102.2	102.2	58.96
	60	-471.2	322.0	92.2	92.2	71.22
	80	-480.9	209.9	89.6	89.6	81.24
	100	-481.2	97.8	86.9	86.9	91.26
F2	20	-495.5	21.72	101.2	-98.8	98.06
	40	-490.1	22.16	86.8	-90.4	98.02
	60	-481.5	25.98	112.5	-98.1	97.68
	80	-506.3	26.34	187.7	-133.5	97.65
	100	-533.0	13.77	136.3	-140.1	98.77
F3	20	-486.6	78.50	82	-117.5	92.98
	40	-484.4	39.84	99.4	-124	96.44
	60	-485.0	22.21	90.1	-99.4	98.01
	80	-476.3	22.04	110.5	-116.1	98.03
	100	-482.0	16.29	75.5	-98.7	98.54

4. Conclusion

Following are the conclusions of the studies:

(i) Fluconazolium ionic liquids, F2 and F3, were synthesized through one step reaction with high yield the prepared materials were characterized using ^{1}H-NMR, FT-IR and ^{13}C-NMR.

(ii) Their corrosion inhibition capability on carbon steel was investigated 1.0 M HCl solution using polarization measurement.

(iii) The study concluded that raising the quantity of fluconazole and fluconazolium ionic liquids reduces corrosion rate j_{corr} in HCl acid liquid.

(iv) At 100ppm, fluconazole (F1) and fluconazolium ionic liquids (F2, F3) showed maximum inhibition efficiency (91.26, 98.77, and 98.03%).

(v) This work is critical for readers to gain a better understanding of corrosion protection using ionic liquid as a corrosion inhibitor in acidic media.

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