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# Inhibitory behavior of new ionic liquids against low carbon steel corrosion in a 1 M HCl solution

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#### Abstract

Two new imidazolium-based ionic liquids namely, 1-hexadecyl-3-(4-methylbenzyl)-1H-imidazol-3-ium chloride (IL-CH<sub>3</sub>), and 1-hexadecyl-3-(4-nitrobenzyl)-1*H*-imidazol-3-ium chloride (IL-NO<sub>2</sub>) were synthesized. The inhibitory activity of these compounds against the corrosion of low-carbon steel (LCS) in a 1 M HCl was examined by utilize multiple techniques such as polarization (PP) and electrochemical impedance spectroscopy (EIS). The outcome data displayed that the protection efficiency rises with improving the dose of IL'S (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>). PP data confirm that they are mixed kind inhibitors. Best performances (i.e. 92.9% and 94.5%) were recorded at maximal IL-CH<sub>3</sub> (100 ppm) and IL-NO<sub>2</sub> (100 ppm) doses, respectively. These findings imply that the novel ionic liquids (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) are efficient corrosion inhibitors.

Keywords: carbon steel; acid solution; ionic liquids; Corrosion inhibition

# **1- Introduction**

Carbon steel is the primary metal utilized in the oil and gas manufacturing sectors. Steel corrosion is thus a highly problematic risk factor for developing significant economic and ecological concerns [1-5]. As a result, acid de-scaling and pickling operations are commonly employed in manufacturing processes to eliminate corrosion scales from metal surfaces under harsh conditions, such as strong acidic solutions and high temperatures. In order to prevent corrosion of the steel surface, a special action is therefore required. Varieties of organic molecules were employed in this situation as effective corrosion protections and inhibitors. [6-10]. Regrettably, due to high doses utilized, which could have toxic effects on the surroundings, the utilization of that kind agents is restricted. For minimizing the corrosion of several metallic materials, ionic liquids (ILs) had already

lately been recommended as endorsing compounds in a wide range of applications [11, 12-14]. As shown in a literature review, numerous synthesized ILs were often choose as efficient steel corrosion inhibitors in a variety of electrolyte solutions [15-19]. The main innovation of this work is the layout of two novel ionic liquid additives, 1-hexadecyl-3-(4-methylbenzyl)-1Himidazol-3-ium chloride and 1-hexadecyl-3-(4nitrobenzyl)-1H-imidazol-3-ium chloride (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>).

## 2- Experimental

## 2.1 Synthesis of IL-CH<sub>3</sub>, IL-NO<sub>2</sub>

Synthesis of ILs (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) was carried out according to Scheme 1.

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The purity of prepared IL-CH<sub>3</sub> IL-NO<sub>2</sub> is 99.8%

# 2.2 Anticorrosion efficiency

LCS has been cut into sizes of 1 cm x 1 cm for the electrochemical experiment.

Table 1 lists the LCS's chemical components

chemic	Mn	С	Si	Р	Fe
al					
compon					
ents					
(wt%)	0.349	0.209	0.0035	0.0242	remain
					der

Before each test, the LCS were abraded with a variety of emery papers ranging in grade from 200 to 1800, degreased with acetone, and cleaned with distilled water. A glass unit was used for electrochemical estimations using the Gamry G750 instrument, platinum (Pt), a saturated calomel electrode (SCE), and an LCS plate as the working anode (WE). Assessments of polarization (PP) were made by sweeping the potential at  $E_{OC}$  from –(500) to + (500) mV at a rate of 1.0 mV s<sup>-1</sup>.

Surface cover ( $\theta$ ) and the inhibition efficacy (%IE) were derived using the relation (1)

 $\% IE = \theta \times 100 = (i_{corr(0)} - i_{corr} / i_{corr(0)}) \times 100$  (1)

 $i_{corr(0)}$  = Corrosion current density for blank solution.

 $i_{corr}$  = Corrosion current density when ILs are present.

The EIS assays were made out with a perturbation of 10 mV and a frequency band of 0.2 Hz to 30 kHz.

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Surface coverage ( $\theta$ ) and the%IE were derived from relation (2) [21]:

$$\% IE = \Theta \times 100 = \left[ \left( 1 - \left( R_{\rm ct} / R_{\rm ct} \right) \right] \times 100 \qquad (2)$$

In which  $R_{ct}$  and  $R_{ct}$  are, respectively, the resistance data prior to and after the addition of ILs.

#### 3. Results and discussion

# **3.1 EIS Assessments**

The Nyquist shapes for the corrosion activity of LCS in 1.0 M HCl containing and not containing varying amounts of ILs (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) are shown in Figs. (1-2). Impedance spectrum revealed a single time constant connected to only one capacitive semi-circles, showing that charge transfer was primarily controlling the corrosion activity [22]. The formation of an ILs (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) adsorbed barrier on the top layer of the LCS causes the diameter of Nyquist curves to increase as the ILs (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) dosages rises. Tables (2 and 3) show the EIS, and %IE data. Charge transfer resistance, or R<sub>ct</sub>, increases as the dose of ILs (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) is increased. As ILs (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) molecules replace water and create an inhibitive shield at the LCS, the qualities of  $C_{dl}$  (double layer capacitance) decline [23].



Fig. 1. Nyquist plots for LCS at 25 °C in 1 M HCl without and including IL-CH<sub>3</sub>



IL-CH <sub>3</sub> Conc.	Rs	R <sub>ct</sub>	C <sub>dl</sub>	IE
(ppm)	$(\Omega.cm^2)$	$(\Omega.cm^2)$	μF. cm <sup>-2</sup>	%
Blank	0.89	12.4	112.5	-
20	0.85	49.9	100.4	75.1
40	0.82	58.3	93.6	78.7
60	0.82	63.7	76.4	80.5
80	0.77	74.8	70.6	83.4
100	0.78	89.7	56.9	86.1
120	0.73	79.4	59.8	84.4

Table 2: EIS parameters in 1 M HCl with and without IL-CH<sub>3</sub> at 25 °C for LCS



Fig. 2 Nyquist plots for LCS at 25  $^{\circ}\mathrm{C}$  in 1 M HCl without and including IL-NO\_2

Table 3 EIS parameters in 1 M HCl with and without IL-NO<sub>2</sub> at 25 °C for LCS.

IL-NO <sub>2</sub> Conc.	Rs	Rct	Cdl	IE
(ppm)	$(\Omega.cm^2)$	(Ω.cm <sup>2</sup> )	µF.cm <sup>-2</sup>	%
Blank	0.89	12.4	112.5	-
20	0.87	56.3	97.9	78.5
40	0.87	61.8	78.9	83.9

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60	0.83	72.2	72.8	86.2
80	0.83	77.6	60.5	88.9
100	0.89	152.2	54.8	92.9
120	0.82	149.8	59.9	90.6

The maximum efficiency (86.1% and 92.9%) has been observed at optimum concentrations of IL-CH<sub>3</sub> (100 ppm) and IL-NO<sub>2</sub> (100 ppm), respectively.

### **3.2. PP Measurements**

Figs. (3,4) show the PP graphs of LCS in 1.0 M HCl solution before and after varied IL amounts (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) were added. After having to add ILs (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>), respectively cathodic and anodic sections started moving to the relatively low icorr data, lowering the corrosion rate. The effects of IL concentration (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) on polarization data and (% IE) for LCS corrosion in 1 M HCl at 25°C are shown in Tables (4,5). Corrosion potential (E<sub>corr</sub>) is shifted slightly toward less negative numbers when ILs (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) are added to 1 M HCl, indicating that these ILs (IL-CH<sub>3</sub>, IL-NO<sub>2</sub>) could really be regarded as mixedtype inhibitors [24]. Additionally, this adding doesn't really significantly alter ( $\beta a$  and  $\beta c$ ), indicating that neither the mechanism for liberating hydrogen nor the method by which LCS dissolves are impacted [25]. The maximum efficiency (92.9% and 94.5%) has been observed at optimum concentrations of IL-CH<sub>3</sub> (100 ppm) and IL-NO<sub>2</sub> (100 ppm), respectively.



**Fig. 3.** PP curves for the corrosion of LCS in 1 M HCl solution without and with various concentrations of  $IL-CH_3$  at 25°C.



**Fig. 4.** PP curves for the corrosion of LCS in 1 M HCl solution without and with various concentrations of  $IL-NO_2$  at 25°C.

Table 4 Polarization parameters for LCS in 1 M HCl without and with IL-CH<sub>3</sub> at  $25^{\circ}$ C

IL-CH <sub>3</sub>	Ecorr.	βa	βc	I <sub>corr</sub> .	IE
(ppm)	mV (SCE)	(mV. dec <sup>-1</sup> )	(mV. dec <sup>-1</sup> )	μA cm <sup>-2</sup>	%
Blank	-463	69	108	125.8	-
20	-384	77	124	27.0	78.5
40	-366	72	114	20.2	83.9
60	-343	62	98	17.3	86.2
80	-332	58	102	13.9	88.9
100	-310	88	138	8.9	92.9
120	-352	87	122	11.7	90.6

**Table 5** Polarization parameters for LCS in 1 M HCl without and with IL-NO<sub>2</sub> at 25°C.

IL-NO <sub>2</sub> Conc.	Ecorr.	βa	βc	Icorr.	IE
(ppm)	mV (SCE)	(mV. dec <sup>-1</sup> )	(mV. dec <sup>-1</sup> )	µA cm <sup>-2</sup>	%
Blank	-463	69	108	125.8	-
20	-384	63	98	21.8	82.6
40	-366	84	99	15.9	87.3

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60	-343	75	92	13.0	89.6
80	-332	83	112	7.6	93.9
100	-310	84	125	6.9	94.5
120	-352	85	120	10.6	91.5

Consequently, the main role of ionic liquids is to create a barrier between the LCS surface and the acidic surroundings [26–31]. By stifling both the hydrogen evolving and LCS solubilization responses, ionic liquids could indeed stop LCS corrosion from occurring. IL-CH<sub>3</sub> and IL-NO<sub>3</sub> can remove a considerable number of H<sub>2</sub>O molecules from the LCS surface due to their significantly bigger molecular size and shapes. Adsorption of IL-CH<sub>3</sub> and IL-NO<sub>3</sub> by heteroatoms and  $\pi$ -electrons leading to the establishment of a barrier protection film.

# 4. Conclusions:

Two new imidazolium-based ionic liquids (IL-CH<sub>3</sub> and IL-NO<sub>3</sub>) were synthesized in the current work. The anti-corrosion characteristics of the two ionic liquids (IL-CH<sub>3</sub> and IL-NO<sub>3</sub>) produced was practical investigated. The inhibition optimization obtained from all measured data was in good agreement. Potentiodynamic polarization evaluations revealed that the ionic liquids were mixed suppressors. The EIS study found that by adding the IL-CH<sub>3</sub> and IL-NO<sub>3</sub>, the double-layer capacitances decrease particularly in comparison to the control sample, and the largest charge transfer resistance of IL-CH<sub>3</sub> and IL-NO<sub>3</sub> is a factor of the formation of a dense interfacial film.

#### References

- M.A. Deyab , S.T. Keera, Cyclic voltammetric studies of carbon steel corrosion in chloride -formation water solution and effect of some inorganic salts. Egyptian Journal of Petroleum, 21 (2012) 31-36.
- S.D. Zhua, A.Q. Fu, J. Miao, Z.F. Yin, G.S. Zhou, J.F. Wei, Corrosion of N80 carbon steel in oil field formation water containing CO2 in the absence and presence of acetic acid, J. Corros. Sci. 53 (10) (2011) 3156.
- P.C. Okafor, C.B. Liu, Y.J. Zhu, Y.G. Zheng, Corrosion and corrosion inhibition behavior

of N80 and P110 carbon steels in CO2saturated simulated formation water by rosin amide imidazoline, Ind. Eng. Chem. Res. 50 (12) (2011) 7273.

- H. Li, Y.H. Liu, Y.Z. Wang, J.M. Ma, B.P. Cai, R.J. Ji, Y.Z. Zhang, Corrosion–erosion wear of N80 carbon steel and 316 L stainless steel in saline–quartz slurry, Mater. Corros. 62 (11) (2011) 1051.
- X. Liu, Y.G. Zheng, P.C. Okafor, Carbon dioxide corrosion inhibition of N80 carbon steel in single liquid phase and liquid/particle two-phase flow by hydroxyethyl imidazoline derivatives, Mater. Corros. 60 (7) (2009) 507.
- W. Zhang, H.-J. Li, M. Wang, L.-J. Wang, Y.-C. Wu, Tetrahydroacridines as corrosion inhibitor for X80 steel corrosion in simulated acidic oilfield water, J. Mol. Liq. 2931 (2019), 111478.
- M. Abdallah, I. Zaafarany, J.H. Al-Fahemi, Y. Abdallah, A.S. Fouda, Antibacterial cephalosporin as inhibitors for the corrosion of iron in hydrochloric acid solutions, Int. J. Electrochem. Sci. 7 (2012) 6622,
- K. Palanisamy, P. Kannan, A. Sekar, Evaluation of chromotrope FB dye as corrosion inhibitor using electrochemical and theoretical studies for acid cleaning process of petroleum pipeline, Surf. Interfaces 12 (2018) 50–60.
- M. Vakili Azghandi, A. Davoodi, G.A. Farzi, A. Kosari, Water-base acrylic terpolymer as a corrosion inhibitor for SAE1018 in simulated sour petroleum solution in stagnant and hydrodynamic conditions, Corros. Sci. 64 (2012) 44–54.
- H. Ju, T. Peng, Y. Li, Acridine as effective corrosion inhibitor for hot dipped coatings on steels in diluted HCl solution, Adv. Mater. Res. 79 (82) (2009) 1035
- 11. Lekan Taofeek Popoola, Progress on pharmaceutical drugs, plant extracts and ionic liquids as corrosion inhibitors, Heliyon 5 (2) (2019) e01143, https://doi. org/10.1016/j.heliyon.2019.e01143.
- 12. M.A. Deyab, Ionic liquid as an electrolyte additive for high performance lead-acid batteries, Journal of Power Sources 390 (2018) 176–180.

- Mahtab Hejazifar, Olga Lanaridi, Katharina Bica-Schröder, Ionic liquid based microemulsions: a review, J. Mol. Liq. 303 (2020) 112264, https://doi.org/ 10.1016/j.molliq.2019.112264
- G. Yang, Y. Song, Q. Wang, L. Zhang, L. Deng, Review of ionic liquids containing, polymer/inorganic hybrid electrolytes for lithium metal batteries, Mater. Des. 190 (2020) 108563
- M.T. Zaky, M.I. Nessim, M.A. Deyab, Synthesis of new ionic liquids based on dicationic imidazolium and their anticorrosion performances, J. Mol. Liq. 290 (2019) 111230.
- E. Kowsari, M. Payami, R. Amini, B. Ramezanzadeh, M. Javanbakht, Task-specific ionic liquid as a new green inhibitor of mild steel corrosion, Appl. Surf. Sci. 28915 (2014) 478–486.
- F. El-Taib Heakal, M.A. Deyab, M.M. Osman, M.I. Nessim, A.E. Elkholy, Synthesis and assessment of new cationic Gemini surfactants as inhibitors for carbon steel corrosion in oilfield water, RSC Advances 7 (2017) 47335-47352.
- T. Zhou, J. Yuan, Z. Zhang, X. Xin, G. Xu, The comparison of imidazolium Gemini surfactant [C14-4-C14im]Br 2 and its corresponding monomer as corrosion inhibitors for A3 carbon steel in hydrochloric acid solutions: Experimental and quantum chemical studies, Colloids Surf., A 575 (2019) 57–65.
- Y. Qiang, S. Zhang, L. Guo, X. Zheng, B. Xiang, S. Chen, Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid, Corros. Sci. 119 (2017) 68–78.
- S. S. Abd El-Rehim, H. H. Hassan, M. A. Deyab, A. Abd El Moneim, Experimental and theoretical investigations of adsorption and inhibitive properties of Tween 80 on corrosion of <u>aluminum alloy</u> (A5754) in alkaline media, Z. Phys. Chem. 230 (2016) 67–78.
- M.A. Deyab, Najlae Hamdi, Mohammed Lachkar, B. El Bali, Clay/Phosphate/Epoxy nanocomposites for enhanced coating activity towards corrosion resistance, Progress in Organic Coatings 123 (2018) 232–237.

Egypt. J. Chem. 66, No. 9 (2023)

- M.A. Deyab, G. Mele, Stainless steel bipolar plate coated with polyaniline/Zn-Porphyrin composites coatings for proton exchange membrane fuel cell, Scientific Reports 10 (2020) 3277.
- 23. M.I. Nessim, M.T. Zaky, M.A. Deyab, Three new gemini ionic liquids: Synthesis, characterizations and anticorrosion applications, Journal of Molecular Liquids 266 (2018) 703–710.
- M.A.Deyab, S.S. Abd El-Rehim and S.T.Keera, Study of the effect of association between anionic surfactant and neutral copolymer on the corrosion behaviour of carbon steel in cyclohexane propionic acid. Colloids and Surfaces A: Physicochemical and Engineering Aspects Journal 348 (2009) 170-176.
- 25. M.A. Deyab, Rachid Ouarsal, A. M. Al-Sabagh, Mohammed Lachkar, B. El Bali, Enhancement of corrosion protection performance of epoxy coating by introducing new hydrogenphosphate compound, Progress in Organic Coatings 107 (2017) 37–42.
- Ramazan Solmaz, Investigation of corrosion inhibition mechanism and stability of vitamin B1 on mild steel in 0.5 M HCl solution, Corros. Sci. 81 (2014) 75–84.
- I. Mohammadi, T. Shahrabi, M.Mahdavian, M. Izadi, Sodiumdiethyldithiocarbamate as a novel corrosion inhibitor to mitigate corrosion of 2024-T3 aluminum alloy in 3.5 wt% NaCl solution, J. Mol. Liq. 3071 (2020), 112965.
- E.E.Foad El-Sherbini, S.M.Abd El-Wahab and M.A.Deyab, Electrochemical behavior of tin in sodium borate solutions and the effect of halide ions and some inorganic inhibitors. Corrosion science journal, 48 (2006) 1885-1898.
- 29. H. Huang, F. Bu, Correlations between the inhibition performances and the inhibitor structures of some azoles on the galvanic corrosion of copper coupled with silver in artificial seawater, Corros. Sci. 1651 (2020), 108413.
- 30. M.A.Deyab, H.A.Abo Dief, E.A.Eissa and A.R.Taman, Electrochemical investigations of naphthenic acid corrosion for carbon steel and the inhibitive effect by some ethoxylated fatty acids. Electrochimica Acta journal 52 (2007) 8105-8110.
- 31. M.A.Deyab, The influence of different variables on the electrochemical behavior of mild steel in circulating cooling water containing aggressive anionic species. Journal

of Solid State Electrochemistry 13 (2009) 1737-1742.

Egypt. J. Chem. 66, No. 9. (2023)