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Synthesis of a Non-toxic Organic Ionic Liquid Triazole Derivative: Application in Inhibition against Corrosion Copper in a Neutral Chloride Environment

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ABSTRACT

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Environmentally friendly corrosion inhibitors have gained popularity in recent years due to growing environmental concerns caused by the widespread usage of traditional toxic corrosion inhibitors. These environmentally friendly inhibitors are made from renewable sources, providing both high inhibition efficacy and little to no environmental impact. The aim of the study was to synthesize a novel organic ionic liquid derived from triazole thione and investigate its toxicity and ability to inhibit copper corrosion in a 3% NaCl solution. The inhibitory power of tris(2-hydroxyethyl) ammonium 3-phenyl-5-sulfido-1,5-dihydro-1,2,4-triazol-4-ide (LIPTS) was exploited using electrochemical methods, against the corrosion of copper in a 3% NaCl solution. This study was conducted using stationary techniques, namely polarization and transient curves, particularly electrochemical impedance diagrams. The results obtained showed that this compound has an LD_{50} greater than 4000 mg/Kg, which confirms its ecological nature. Stationary polarization measurements revealed that the product tested as copper corrosion inhibitor acted at low concentrations in the corrosive medium. Its effect was expressed by a displacement of the potential in the anodic direction and a significant decrease in the current density, with the appearance of a plateau of low current density attributed to the formation of a thin film on the metallic surface of the copper. The electrochemical impedance measurements confirm the previous results by revealing the appearance of a low-capacity high-frequency loop corresponding to the presence of a protective film of inhibitor. The inhibitory efficiency is about 98%, indicating the protective effect of this product against copper corrosion in a 3% NaCl solution.

Keywords: Copper, Corrosion, Ionic liquid, Langmuir isotherm, Electrochemistry

Introduction

Corrosion of copper and its alloys is a major problem in many industrial applications, ranging from plumbing fixtures to electronic equipment. Metal structures used in industry are often exposed, depending on favorable conditions (temperature, aggressive ions, pollutants, etc.), to corrosive processes.¹ This is one of the major challenges in industrial processes, resulting in considerable financial losses.^{2,3} For example, exposure of copper and its alloys to seawater deteriorates their structure and promotes accelerated corrosion of metals. In addition to property damage, copper corrosion can lead to environmental problems due to the release of harmful products (corrosion products) into the environment. To solve these problems, several methods have been considered, namely cathodic or anodic protection, painting, and protection by corrosion inhibitors, which is the focus of the present study. However, most of the inhibitors used are chemicals that are hazardous to the environment. It is therefore essential to develop new inhibitors that are environmentally friendly: non-toxic, effective, and durable.

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Considering the toxicity of conventional corrosion inhibitors,^{4,5} in recent years, extensive research has been carried out to find alternative corrosion inhibitors that meet environmental standards. Among these inhibitors are natural products derived from plants (green inhibitors), which constitute a recent approach to preserving the ecosystem and exploiting the properties of these inhibitors against the corrosion of metals and alloys.⁶⁻⁸ However, green inhibitors have drawbacks related to low extraction yield and high cost, in addition to the diversity of extraction by-products. This is why the synthesis of non-toxic organic ionic liquids that could represent effective potential solutions to different types of corrosion has been the focus of this research.⁹ These inhibitors generally attach to the metal surface by chemical or physical adsorption,¹⁰ based on the electrostatic interaction between the metal and the inhibitor,^{11,12} or mixed adsorption. The latter leads to the formation of a uniform film on the metal surface, thereby reducing contact with the corrosive environment or preventing it altogether. The effectiveness of these inhibiting organic compounds is largely based on their ability to form complexes with the metal since they act by adsorption on the metal surface.¹⁴ The π electrons (the electrons of the double bond of the aromatic ring) and the groups containing sulphur, oxygen, and/or nitrogen constitute essential characteristics of this type of inhibitor. Polar functional groups are generally considered the chelation centers for chemical adsorption.

The present study was aimed at synthesizing a new organic ionic liquid derived from triazole thione and investigating its toxicity and inhibiting power against copper corrosion in a 3% NaCl solution.

Materials and Methods

Source of experimental animals

Albino mice of both sexes (weighing between 25 and 30 g) were obtained from a biology laboratory at our university.

Ethical clearance

Ethical clearance for this study was obtained from the Ethics Committee of the Faculty of Science of our university.

Medium and material used

In this study, the material used is a 99.99% copper electrode (Goodfellow). The 3% NaCl corrosive solution used is similar to a marine environment and is made of solid NaCl dissolved in distilled water.

Synthesis of LIPTS inhibitors

The ionic liquid LIPTS, which was tested as a pure copper corrosion inhibitor, was produced in the laboratory in two phases using low-toxicity reagents. All the reagents used in this synthesis are commercial products from the company Sigma Aldrich with a purity of 99%. The first step was to synthesize 3-phenyl 1,2,4-triazole-5-thione by replacing benzoyl chloride with methyl benzoate following the reaction illustrated in Scheme 1.¹⁶ The second step was a reaction of triethanol amine on 3-phenyl 1,2,4-triazole-5-thione in ethanol at reflux for 4 hours. The product obtained is in the form of a liquid after evaporation of the solvent using a rotary evaporator according to the reaction (Scheme 2). NMR is an analytical technique, widely used for the identification of organic products. The NMR spectra obtained were recorded on an AVANCE 300 Bruker NMR device at 300 MHz at the UTRS Analytical Center of CNRST in Rabat, Morocco. The high-yielding ionic liquid, obtained with a yield greater than 90%, was characterized and identified using ¹H and ¹³C NMR.



Scheme 1: Synthesis of 3-phenyl 1,2,4-triazol-5-thione.



LIPTS

Scheme 2: Synthesis of LIPTS

Electrochemical measurement

The electrochemical tests were carried out at ambient temperature, in a cell with three electrodes. The first was the reference electrode of the calomel type saturated with KCl, while the second electrode was the counter electrode, which is a rectangular platinum grid with an area of 8 cm². The third component was a working electrode, which was a cylindrical copper metal with a surface area of 1 cm2 isolated laterally by an epoxy resin. Before any handling, the working electrode was polished with abrasive paper of decreasing grain size (600, 1200, 2000, and 2400). It was then washed and degreased with water and acetone before being dried. Steady and transient electrochemical measurements were performed using a potentiostat (Biologic SP200, France). The scanning speed was 1 mv/s for the plots of the polarization curves and 5 mv/s for the electrochemical impedance diagrams in a frequency domain from 100 KHz to 10 mHz. All these

measurements were taken after stabilization of the corrosion potential for one hour of immersion of the working electrode in the corrosive solution. The inhibitory efficacy (Ei) was determined from the polarization curves according to equation 1.

$E_i = \frac{(\text{Icorr-Icorr(inh)})}{X \ 100}$

(Equation 1)

With Icorr and Icorr (inh) are the copper corrosion current densities in 3% NaCl in the absence of LIPTS and in the absence of LIPTS, respectively.

The surface appearance of the copper electrode with and without inhibitor was characterized by scanning electron microscopy (SEM), which is the most widely used technique for topography at the microscopic scale. This approach works by scanning the surface of a sample with a finely localized electron beam and collecting secondary electrons and backscattered electrons with appropriate detectors. The material analyzed must be conductive to avoid charge phenomena due to electrons: the metallization can be carried out, for example, with carbon for materials with low electronic conduction. The microscope used in this study was the Lecia model Stereo Scan 440 (from the UTRAS Analytic Center, CNRST, Morocco), controlled by LEO software. The secondary electron scanning electron microscope allows the observation of surface morphology (distribution and relief) with a much greater depth of field than in optical microscopy.

Evaluation of LIPTS toxicity using an animal model

The toxicity of LIPTS was evaluated in albino mice of both sexes. The water-soluble product was administered orally in the form of a liquid solution in distilled water. For the determination of the LD_{50} , five groups of animals were chosen, each composed of five males and five females. The doses of product administered to the mice were 1000, 2000, 3000, 4000, 4500, and 5000 mg/kg. Before the injection of the product, the animals fasted for 24 hours. The product was then administered to the experimental population using a gastric tube. After the administration, the mice were observed for a period of 14 days, during which the apparent signs of toxicity, such as weight changes and mortality rates were observed.

Results and Discussion

Toxicity of LIPTS

Acute toxicity refers to toxicity resulting from a single, usually large, absorption of an active substance or product. It is measured by the lethal dose (LD₅₀), which indicates the quantity of the product, that leads to the death of 50% of the animal subjects in the experiment.¹⁷ According to international standards, substances are classified according to their toxicity, based on their LD₅₀ and the dose administered orally, which causes the death of 50% of animals in less than 5 days. There are five classes of toxicity:¹⁸ Class 1: LD₅₀ < 1 mg/kg (the product is extremely toxic); Class 2: 1 mg/kg < LD50 < 500 mg/kg (the product is moderately toxic); Class 3: 50 mg/kg < LD50 < 500 mg/kg (the product is weakly toxic); Class 5: 5000 mg/kg < LD50 < 15000 mg/kg (the product is practically non-toxic).

The present study was conducted on a homogeneous population of animals comprising 10 mice for each dose of LIPTS. The LD₅₀ represents the amount of substance absorbed at one time necessary to cause the death of 50% of the animals in the sample. It is expressed in milligrams of the product tested per kilogram of animal. It is important to note that the LD₅₀ is only valid for a specific species and a given route of administration (respiratory, digestive, or cutaneous) in the body.¹⁹ Although the LD₅₀ may vary from one species to another, its value established in animals provides a numerical estimate of the potential toxicity to humans, since the order of magnitude is generally similar.20 The mortality rate of 50% provides the greatest precision because it is around this percentage that small variations in doses lead to large variations in mortality. The lower the LD₅₀ value, the higher the toxicity of the product.²¹ Thus, the study of acute toxicity offers a first toxicological approach making it possible to identify the main risks associated with the molecule. The toxicologist monitors the groups of animals subjected to experimentation, observes the evolution of their diet, behavior, and weight, and then draws up a mortality report. The choice of the LIPTS ionic liquid was motivated by its excellent anti-corrosion properties on copper and its alloys (for example, metallic archaeological objects). The use of non-toxic products is strongly recommended in museums and the context of interactions with visitors.²²

The toxicity evaluation results (Figure 1) allowed for the tracing of the evolution of the mortality rate in relation to the dose of LIPTS administered. An increase in the amount of product LIPTS delivered resulted in a modest rise in the number of mice that died. This increase reached 40% when the dose of LIPTS was 4000 mg. Subsequently, this rate remained constant even if the dose administered was increased to 5000 mg of product. These observations confirm that the LD_{50} is greater than 4000 mg/kg, which justifies the non-toxicity of the LIPTS inhibitor.

Electrochemical analysis

i) Stationary measurement

The cathodic and anodic traces are represented in Figure 2 after one hour of immersion in a 3% NaCl solution with corrosion potential at different LIPTS concentrations. The analysis of the cathodic domain revealed that, in the absence of an inhibitor, the current density experienced a rapid increase near the corrosion potential, to stabilize and form a current plateau, corresponding to the reduction of oxygen, by the following reaction presented in Equation 2.



Figure 1: Variation in the mortality rate according to the dose administered in LIPTS.

3000

Dose administrée (mg/ kg)

4000

5000

2000

1000



Figure 2: Cathodic and anodic current-voltage curves of copper in 3% NaCl in the presence of different concentrations of LIPTS. *Cu: copper; LIPTS: Inhibitor concentration; I: current density; E: Potential; NaCl: Sodium chloride.

Subsequently, the kinetics of corrosion were controlled by the diffusion process resulting from the reduction of oxygen, which plays an essential role in the corrosion mechanism. This cathodic reaction is the engine of corrosion.^{23,24,25} In the presence of LIPTS, the cathodic polarization curves reveal a shift in corrosion potential towards positive values and a significant decrease in current density, especially with increasing inhibitor concentration. This decrease is observed throughout the cathodic domain. Near Ecorr, the current density decreases from 22.03 μ A.cm⁻² in the absence of an inhibitor to 0.25 $\mu A.\mathrm{cm}^{-2}$ in the presence of 5.10^{-3} M of LIPTS. This explains the protective effect of the product in this potential range. For all concentrations of LIPTS, the variation of the current density on a semi-logarithmic scale presents a linearity by Tafel's law, thus allowing the calculation of current densities by extrapolation of Tafel slopes.²⁶ In the absence of an inhibitor, the current density rapidly increases near the corrosion potential in the anodic range, reflecting the selective dissolution of copper in this medium following the reaction (Equation 3).

Cu \leftrightarrows Cu²⁺ + 2e (Equation 3) The process of anodic dissolution in the presence of chlorides is widely studied and is characterized by the following two reactions, represented in Equations 4 and 5.^{27,28,29}

 $Cu + Cl^{-} \hookrightarrow CuCl + e^{-}$ (Equation 4)

 $CuCl + Cl^{-} \hookrightarrow CuCl^{2-}$ (Equation 5)

At high anode overvoltages, the current density tends to stabilize, forming a current plateau of around 10 mA/cm². This high value indicates the passivation of the metal, suggesting the formation of a layer of corrosion products. The addition of LIPTS inhibitors at different concentrations induces significant modifications of the polarization curves, as well as of the anodic reaction rate. The addition of LIPTS causes a displacement of the corrosion potential towards positive values and a strong decrease in the anodic current density. This decrease is more pronounced with an increase in the concentration of LIPTS. At a concentration of 5.10⁻³M, a current plateau was observed with a value of approximately 0.1 µA/cm². This observation can be explained by the formation of an inhibitory film with a protective character on the metal surface.³⁰ At more positive potentials, the current density increased rapidly and reached the control curve, indicating the deterioration of the film formed by the desorption of the inhibitor from the metal surface.^{31,32} The anodic polarization curves in the presence of different concentrations of LIPTS confirm the improvement of the passive state of the metal by completely modifying the copper dissolution reaction in the 3% NaCl solution.

Table 1 presents the kinetic parameters $(E_{corr}, I_{corr}, B_c, B_a, E[\%])$ of the cathodic and anodic curves. Analysis of these results reveals a shift in corrosion potential towards the anode side and a significant

ii) Adsorption isotherm

The study of the adsorption isotherm makes it possible to better understand the nature of the interactions between the inhibitor and the metal at the interface, and to determine the kinetics of adsorption of the inhibitor on the metal surface. To characterize the mode of adsorption of the LIPTS compound on the surface of pure copper in the 3% NaCl solution, the variation of the concentration as a function of the recovery rate was plotted (Figure 3). The variation of concentration with recovery rate follows the Langmuir isotherm, indicating monolayer adsorption of the inhibitor on the copper surface. The following equations (6 and 7), derived from the potentiodynamic polarization data (Figure 2), were used to plot the curve in Figure 3.^{33,34,35}

$$\frac{\sinh \theta}{\theta} = C \sinh + \frac{1}{\kappa}$$
(Equation 6)
 $K_{ads} = 1/55.5 \exp \left(-\Delta G^{\circ}_{ads}/RT\right)$ (Equation 7)

The different values of ΔG°_{ads} provide indications of the types of adsorptions observed. When the value of ΔG°_{ads} is less than -40 kJ/mol, the inhibitor adsorbed on the surface of the metal undergoes chemical adsorption. When the value of ΔG°_{ads} is between -40 and -20 kJ/mol, the inhibitor molecules adsorb in a mixed manner on the surface of the metal. Finally, when the value of ΔG°_{ads} exceeds -20 kJ/mol, the adsorption of the inhibitor on the surface of the metal is of a physical nature (physisorption).³⁶ Thus, from the results in Figure 3, the LIPTS inhibitor molecules adsorb on the copper surface by mixed adsorption, given that the value of ΔG°_{ads} is approximately -36.76 kJ/mol.

iii) Electrochemical impedance measurements

Concentration effect

To have a better understanding of the occurrence of the copper-copper interaction and the 3% NaCl solution, transient measurements were conducted using electrochemical impedance diagrams. The results of these measurements are shown in Figure 4. After immersion for one hour at an abundant potential, without the inhibitor LIPTS, the electrochemical impedance curves of pure copper in the 3% NaCl solution revealed the appearance of two distinct time constants. The first, located at high frequencies (Rt, Cd), is associated with the transfer of charges accompanying the dissolution of copper, while the second, at low frequencies, is linked to the appearance of a diffusion constant (R_d, T_d).³⁷ The addition of the LIPTS inhibitor at different concentrations in the corrosive medium leads to a capacitive behavior, with a modification of the shape of the electrochemical impedance diagram. This indicates a change in the mechanism of the interfacial corrosion process.



Figure 3: Langmuir adsorption isotherm of LIPTS in 3% NaCl at 298K.

C: Inhibitor concentration; Θ : the recovery rate



Figure 4: Electrochemical impedance of copper in a 3% NaCl solution at different concentrations of LIPTS. LIPTS: Concentration of inhibitor; Cu: Copper; NaCl: Sodium

LIPIS: Concentration of inhibitor; Cu: Copper; NaCl: Sodium chloride; -Zim: Imaginary part; Re: Reel part; Hz: Frequency unit



Figure 5: Electric circuits equivalent to electrochemical impedance in a 3% NaCl solution without (a) and with inhibitor (b).



Figure 6: Electrochemical impedance of copper in a 3% NaCl solution at different immersion times.

* -Zim: Imaginary part; Re: Reel part; Hz: Frequency unit; h: Immersion hour



Figure 7: Evolution of electrochemical impedance of copper in NaCl 3% with 5.10^{-3} M of LIPTS.

* -Zim: Imaginary part; Re: Reel part; Hz: Frequency unit; h: Immersion hour



Figure 8: Scanning electron microscopy of a pure copper electrode before immersion (a); in a 3% NaCl solution; and (b) in the presence of 5.10⁻³M of LIPTS (c)

The diagrams show a significant increase in polarization resistance as a function of inhibitor concentration. However, modeling of electrochemical impedance diagrams using EC-Lab software (software of Biologic SP200, France), with a 2RC circuit in parallel, does not satisfactorily match the experimental results. Therefore, the introduction of a third-time constant was necessary.

Time constants were assigned as described. A contribution to high frequencies ($R_f - C_f$), associated with the dielectric nature of the film formed by the LIPTS inhibitor, reinforced by the corrosion products and the ionic conduction through the pores of the film. The associated capacitances are very low (less than 1µF.cm⁻²), confirming the hypothesis of the formation of a protective film on the surface of metallic copper.^{38,39,40}

A contribution ($R_t - C_d$) at the average frequencies, describes the charge transfer phenomenon at the electrolyte/copper interface at the bottom of the pores. The charge transfer resistance increases with the concentration of inhibitor, reaching a factor of more than 50 times in the presence of 5.10^{-3} M of LIPTS compared to the control sample. This demonstrates the significant effect of this product on reducing charge transfer at the copper/NaCl 3% interface.

At low frequencies, linearity appears for the concentrations of 10^{-3} and 5.10^{-3} M, with a corresponding resistance tending towards infinity, which can be explained by the faradic process (R_F, C_F). The parameter

fitting results for the (R_f,C_f) and (R_t,C_d) pairs, derived from the diagrams in Figure 4, are presented in Table 2.

The inhibition efficiency E% was calculated by the following (Equation 8).

$$E_{i} = \frac{Rt(inh) - Rt(0)}{Rt(inh)} \times 100$$
 (Equation 8)

 $R_t(0)$ and $R_t(inh)$ are the charge transfer resistances in the absence and presence of inhibitors, respectively.

The results presented in Table 2 demonstrate the protective effect of the LIPTS inhibitor on copper in a 3% NaCl solution. This effect is manifested by the formation of a relatively thick inhibitor film, characterized by low capacitance. The torque corresponding to the faradic process is not included in the table because the values of R_F tend towards infinity, which indicates that the inhibitor film formed on the metal surface is reinforced by the corrosion products, making it very resistant.⁴¹ The protective efficacy of the inhibitor is about 98% at a concentration of 5.10^{-3} M, which has been chosen as the optimal concentration for LIPTS. These results agree with those obtained by measurements in a steady state. Figure 5 presents the diagram of the equivalent electrical circuits of the electrochemical impedance diagrams of copper in a 3% NaCl solution in the presence of LIPTS.

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Effect of immersion time

The copper electrode was placed alone in a 3% NaCl solution to test the influence of the variation in immersion time. Electrochemical impedance diagrams are shown in Figure 6. The electrochemical impedance diagrams at different immersion times reveal the same pattern, which indicates the invariability of the corrosion mechanism. These diagrams show a capacitive reaction of copper when it is immersed in a 3% NaCl solution, accompanied by a decrease in polarization resistance with immersion time. After 1 hour, the polarization resistance was 2180 Ω .cm², which was reduced to almost 1500 Ω .cm² after 48 hours of immersion. This reduction is explained by the attack of copper in an aggressive environment, mainly by chlorides, which translates to an acceleration of the corrosion rate of copper. Furthermore, the copper was placed in 3% NaCl in the presence of 5.10⁻³M of the inhibitor at different immersion times. The inhibitory effect of this ionic liquid was evaluated over time, by tracing the evolution of the impedance diagrams present, and the results obtained are presented in Figure 7. In the presence of 5.10⁻³M of LIPTS, the electrochemical impedance diagrams retained the same shape, but a significant increase in polarization resistance was observed. This increase can be explained by the formation of a thick

and compact oxidation film, reinforced by the prolonged immersion time. The low-frequency loop has a linear part, which can be attributed to diffusion through a solid barrier represented by the formed inhibitor film.

Surface analysis

The surface condition of a pure copper electrode with and without LIPTS after 24 h of immersion in the 3% NaCl corrosive solution is represented in Figure 8. Before immersion (Figure 8a), the surface state remains stable with the formation of a red layer of copper oxide. After the immersion (Figure 8b) of the studied electrode in the corrosive solution and in the absence of the inhibitor, the surface state of the copper electrode was attacked at the level of the grain boundaries and the presence of NaCl crystals on the surface, making the surface metallic. In the presence of 5.10^{-3} M of LIPTS, the attack was much less severe compared to that of 3% NaCl without inhibitor. The EDX analysis (Figures 9 and 10) shows the presence of sulfur, which is an essential element of the inhibitor indicating the protective effect of the LIPTS product. Its effect results in the formation of a thin film reinforced by corrosion products.²³

Fab	le	l:	Electroc	hemical	parameters	determined	by	the	Stern-	Geary	relations	hip (derived	from t	he curve	s in	Figure	2.
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Cathodic dom	ain			Anodic dor	Anodic domain						
[LIPTS] (M)	E _{corr} (V _{Ecs})	I _{corr} (µAcm ⁻²)	$\frac{B_c}{(V^{-1})}$	E _{corr} (V _{Ecs})	I _{corr} (μAcm ⁻²)	B _a (V ⁻¹)	E (%)				
0	-0.210	22.83	-175.23	-0.225	22.03	275.36					
10-4	-0.210	4.34	-149.89	-0.212	4.23	185.55	80.98				
5.10-4	-0.157	1.86	-138.67	-0.158	1.47	157.60	91.85				
10-3	-0.119	0.72	-132.84	-0.112	0.66	152.57	97.00				
5.10-3	-0.088	0.25	-129.47	-0.094	0.24	146.24	98.90				

*[LIPTS]: Concentration of inhibitor; E_{corr}: Corrosion potential; Ic_{orr}: Corrosion current; B_c: Cathodic slope; B_a: Anodic slope; E(%): Inhibitory efficacy

 Table 2: Electrochemical parameters obtained from the electrochemical impedance diagram of copper in a 3% NaCl solution at different concentrations of LIPTS.

[LIPTS] (M)	$R_0(\Omega.cm^2)$	$C_{f}(\mu F.cm^{-2})$	$R_{f}(\Omega.cm^{2})$	$C_d(\mu F.cm^{-2})$	$R_t(k\Omega.cm^2)$	E (%)
0	11.24			152	1.21	
10-4	11.36	0.65	2124	72.05	6.32	80.85
5.10-4	10.68	0.34	5120	22.15	21.41	94.34
10 ⁻³	10.24	0.28	6654	16.83	47.75	97.46
5.10-3	10.13	0.19	8646	14.52	73.85	98.36

R₀: Electrolyte resistor; C_f: Film capacity; R_f: Film resistor; C_d: Double layer capacity; R_f: Transfert resistor; E(%): Inhibitory efficacy.







Conclusion

Organic ionic liquids are new compounds with several applications in different fields. The LIPTS product is a triazole derivative, an ionic liquid synthesized in two steps. A toxicity test showed that this product has an LD_{50} greater than 4000 mg/kg, which confirms its nontoxic nature (environmentally friendly). The application of LIPTS as a copper corrosion inhibitor in a 3% NaCl solution revealed that it acts in low concentration by forming an inhibiting film on the metal surface reinforced by the corrosion products. The inhibitory efficacy of around 98% indicates the protective effect of this product.

Conflict of Interest

The authors declare no conflict of interest.

Authors' Declaration

The authors hereby declare that the work presented in this article is original and that any liability for claims relating to the content of this article will be borne by them.

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