



# Task-specific ionic liquid as a new green inhibitor of mild steel corrosion



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## ABSTRACT

The corrosion inhibition effects of an imidazolium-based task specific ionic liquid (TSIL) were investigated on a low carbon steel in 1 M HCl solution. Samples were exposed to 1 M HCl solution without and with different concentrations of TSIL. Weight loss measurements, potentiodynamic polarization test, electrochemical impedance spectroscopy (EIS), scanning electron microscope (SEM), atomic force microscope (AFM) and contact angle measurements were utilized to investigate the inhibition effects of TSIL. The results obtained from the polarization studies revealed that both the anodic and cathodic branches slopes affected in the presence of TSIL. It was shown that TSIL behaved as a mixed type inhibitor with a dominant effect on the anodic reaction rate depression. It was shown that the increase in polarization resistance and the decrease in corrosion current density were more pronounced using 100 mg/L of TSIL after 2 h immersion time. It was also shown that the adsorption of TSIL followed a Langmuir adsorption isotherm.

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## 1. Introduction

Low carbon steel has been extensively used in many different industrial applications due to its excellent mechanical properties [1–4]. Acid solutions are widely used for different applications in industries such as pickling, acid cleaning of boilers, descaling and oil well acidizing [5–7]. Hydrochloric and sulfuric acids are the most common types of corrosive acids used in such industrial operations [2,8]. Acid solutions are very aggressive [9], and the main problem concerning carbon steel applications under different conditions in industry is its low corrosion resistance against acid solutions [2,3,10]. Several methods have been utilized in order to reduce the corrosion rate of low carbon steel in exposure with acidic solutions. One of which is the use of an organic inhibitor [2,3,5,10–13]. Inhibitors are compounds that control, reduce or prevent reactions between a metal and its surroundings when added to the medium in small quantities [14]. The most effective inhibitors are heterocyclic compounds that have  $\pi$  bonds and a phosphorus, sulfur, oxygen or nitrogen heteroatom [6,10,11,15–20]. However, most of the corrosion inhibitors used for the control of steel corrosion in acidic

mediums are heavily toxic and environmentally hazardous materials [18–20]. Therefore, attempts have been carried out to search for eco-friendly corrosion inhibitors for metals in acid solutions. In this regard, many different types of surfactants have been developed.

Surfactants are a group of inhibitors that change the electrochemical behavior of a metal through the hydrophilic head of the molecule [14]. Gemini surfactants are new generation of surfactants that contain two hydrophilic groups and two hydrophobic groups in the molecule, joined together by a rigid, flexible or aliphatic spacer [14,21,22]. These surfactants have a lower critical micelle concentration (CMC), better solubilization and greater efficiency in lowering the surface tension of water [14,23].

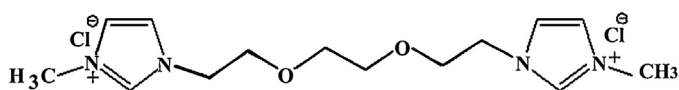
A problem regarding the application of inhibitors in different industries is that most of these compounds are toxic to humans and the environment. Because of this, ionic liquids (ILs) have been developed in recent years [2]. ILs are organic salts that have a melting point below 100 °C. Ionic liquids have a large number of advantageous physicochemical properties such as high ionic conductivity and non-flammability, as well as chemical and thermal stability [5,9,14]. One of the most important characteristics of ILs is their negligible vapor pressure, making ILs eco-friendlier, less hazardous inhibitors of metal corrosion [2]. This does not mean that if ILs released into the environment they will not harm, but because of their negligible vapor pressure, these compounds will not evaporate and will not pollute environment. For example, [bmim][PF<sub>6</sub>]

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**Table 1**  
Elemental composition of the low carbon steel.

Elements	Cu	Mo	Cr	Ni	S	P	V	Mn	C	Fe	Si
wt%	0.02	0.002	0.004	0.015	0.06	0.001	0.005	0.7	0.06	99.12	0.012



**Fig. 1.** The chemical structure of the TSIL.

and [bmim][BF<sub>4</sub>] are the most commonly used ILs. If they are released into water, they decompose and produce hydrofluoric and phosphoric acids which are harmful to the environment [24].

In this study, a task-specific ionic liquid (TSIL) with the molecular structure of a Gemini cationic surfactant was used in order to inhibit the corrosion of low carbon steel in 1 M HCl. Electrochemical and surface characteristic techniques are employed to investigate the inhibition effects of such a surfactant.

## 2. Experimental

### 2.1. Materials and samples preparation

The TSIL was synthesized in our laboratory [25]. The complete <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR spectra and CHN analysis for the c were synthesized and studied in this work is the following:

FIL, {[CH<sub>2</sub>CH<sub>2</sub>]O<sub>2</sub>(mim)<sub>2</sub>}<sub>2</sub>Cl<sub>2</sub>; 1-methyl-3-(2-{2-[2-(1-methyl-1-*H*-imidazol-3-ium-3-yl)ethoxy]ethoxy}-ethyl-1*H*-imidazol-3-ium dichloride: <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, ppm): 2.8 (s, 6H), 3.80 (s, 4H), 4.80 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 4H), 5.10 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 4H), 6.83–7.87 (m, 2H), 7.65 (m, 2H) 9.65 (s, 2H); <sup>13</sup>C NMR (500 MHz, D<sub>2</sub>O, ppm): *d* = 36.1 (2CH<sub>3</sub>), 52.0 (2CH<sub>2</sub>), 62.0 (2CH<sub>2</sub>), 65.0 (2CH<sub>2</sub>), 123.9 (2CH), 126.17 (2CH), 140.6 (2CH); FT-IR (KBr): 3400, 3120, 3072, 2963, 2870, 1630, 1575, 1463, 11,720, 1049, 757, 623. Anal. Calcd. for C<sub>14</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (351.27): C, 47.87; H, 6.89; Cl, 20.19; N, 15.95; O, 9.11 Found: C, 47.67; H, 6.94; Cl, 20.23; N, 16.05; O, 9.12. The chemical structure of the TSIL is shown in Fig. 1.

Hydrochloric acid (37 wt%) was obtained from Merck Co. Distilled water was used for preparing test solutions for all measurements. 1 M HCl solutions containing different concentrations of TSIL were prepared. The corrosion inhibition effects of TSIL were studied in 1 M HCl solution on low carbon steel specimens (20 mm × 20 mm × 1.5 mm). For this purpose, low carbon steel with chemical composition given in Table 1 was obtained from Foolad-mobarakheh Co.

Steel panels were mechanically ground with 400, 600, 800 and 1200 grades of emery paper and degreased with acetone and rinsed with distilled water. Then, they were washed with a 15% (w/v) solution of NaOH (prepared from Merck Co.) and rinsed with distilled water. Finally, samples were immersed in 5% (v/v) HCl, rinsed with distilled water twice and finally dried.

### 2.2. Testing methods

#### 2.2.1. Weight loss measurements

The surface prepared samples were weighed and then immersed in 1 M HCl without and with different concentrations of the TSIL for 1 h. Then, they were washed with acetone and rinsed with distilled water. Finally, the dried samples were weighed again. The corrosion rates of the low carbon steel samples immersed in 1 M HCl were calculated according to Eq. (1) [4,14]:

$$r = \frac{(m_1 - m_2)}{S} \times t \quad (1)$$

The parameters  $m_1$  and  $m_2$  (g) represent the weights of the low carbon steel before and after immersion in the HCl solution, respectively.  $S$  (m<sup>2</sup>) and  $t$  (h) are the surface area of the sheet and the immersion time, respectively. The inhibition efficiency of TSIL was calculated according to Eq. (2).

$$IE\% = 1 - \left( \frac{r_{\text{corr(inh)}}}{r_{\text{corr}}} \right) \quad (2)$$

where  $r_{\text{corr(inh)}}$  and  $r_{\text{corr}}$  (g m<sup>-2</sup> h<sup>-1</sup>) are the corrosion rates of steel in 1 M HCl solutions with and without TSIL, respectively.

### 2.3. Electrochemical measurements

The inhibition effects of TSIL in 1 M HCl solution on the corrosion of low carbon steel were studied by potentiodynamic polarization test and electrochemical impedance spectroscopy (EIS). The measurements were carried out by an IVIUM COPMPACTSTAT in a conventional three electrode cell including low carbon steel sheet as a working electrode, Ag/AgCl, KCl (saturated) as reference electrode and graphite as counter electrode. The area of each electrode exposed to the solution was about 1.0 cm<sup>2</sup>. The rest of working electrode was masked with mixture of beeswax–colophony. The polarization test was done at scan rate and potential range of 1 mV/s and –100 mV to +100 mV (with respect to open circuit potential), respectively. EIS measurements were carried out in frequency region of 10 kHz to 10 mHz (at open circuit potential and perturbation of ±10 mV).

### 2.4. Surface tension measurements

The surface tension values of the HCl solutions with different concentrations of TSIL were measured by a KRUESS PROCESSOR TENSIO METER K14 V3.07 (WilhelmyTechnique). The measurement was done at 25 °C.

### 2.5. AFM and SEM analysis

Surface morphology of the steel panels exposed to the HCl solutions with different concentrations of TSIL and without TSIL was studied by AFM model Ambios and SEM model AIS2100.

### 2.6. Contact angle measurements

An OCA 15 plus type contact angle measuring system was utilized in order to evaluate the static contact angle of the samples using distilled water as the probe liquid at temperature and humidity of 25 ± 2 °C and 30 ± 5%, respectively. A small drop of distilled water (2–3 μl) was applied on the surface of the samples. The shape of droplet was recorded by a Canon type digital camera after 10 s. The images were transmitted to a personal computer for evaluation. Using an image analysis system (G2/G40), the contact angle values were calculated.

## 3. Results and discussion

### 3.1. Critical micelle concentration (CMC) determination

The surface tension method was utilized in order to determine the CMC of the TSIL. The CMC values measured at different

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