



# Ionic liquids based gemini cationic surfactants as corrosion inhibitors for carbon steel in hydrochloric acid solution



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## ABSTRACT

Three ionic liquid based gemini cationic surfactants;  $N^1,N^1,N^1,N^2,N^2,N^2$ -hexadodecylethane-1,2-diaminium bromide (G2IL),  $N^1,N^1,N^1,N^2,N^2,N^2$ -hexadodecylpropane-1,3-diaminium bromide (G3IL) and  $N^1,N^1,N^1,N^2,N^2,N^2$ -hexadodecylhexane-1,6-diaminium bromide (G6IL) were synthesized and their chemical structures were elucidated by using FTIR and  $^1H$ NMR spectroscopic techniques. The physicochemical properties of ionic liquids were measured and discussed. The critical micelle concentration and surface properties were determined from their surface tension measurements. The performance evaluation of the synthesized inhibitors on the carbon steel corrosion in acidic environment (1.0 M HCl) have been investigated at different concentrations by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and weight loss techniques. Potentiodynamic polarization studies indicate that the studied inhibitors are mixed type inhibitors. For all inhibitors, the inhibition efficiency increases with increasing their concentration but decreases with increasing temperature. The adsorption of the ionic liquid surfactants on the metal surface and adsorption process obeys the Langmuir isotherm.

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## 1. Introduction

Inhibitors are compounds that control, reduce or prevent reactions between a metal and its surroundings when added to the medium in small quantities [1–4]. The most effective inhibitors are heterocyclic compounds that have bonds and a phosphorus, sulfur, oxygen or nitrogen heteroatom [5]. However, most of the corrosion inhibitors used for the control of steel corrosion in acidic media are heavily toxic and environmentally hazardous materials [6]. 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 electro-chemical behavior of a metal through the hydrophilic head of the molecule [7]. 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 [8]. These surfactants have a lower critical micelle concentration (CMC), better solubilization and greater efficiency in lowering the surface tension of water [9]. 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 [10]. 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. One of the

most important characteristics of ILs is their negligible vapor pressure, making ILs eco-friendlier, less hazardous inhibitors of metal corrosion. This does not mean that if ILs are released into the environment they will not harm, but because of their negligible vapor pressure, these compounds will not evaporate and will not pollute the environment. Previous studies have demonstrated that imidazole [11], ammonium [12], pyridine [13] and phosphonium [14] have good inhibitory effect on the corrosion behavior of metal in aggressive media. Moreover, there may be a synergistic effect between anion and cation in ionic liquid. Meanwhile, the amount of ionic liquid is tremendous in theory, therefore, ionic liquid is of great potential to be explored as a novel corrosion inhibitor.

Recently, some ionic liquids have been investigated as inhibitors for carbon steel [15] and aluminum [16]. Accordingly, there is a great need to investigate the influence of substituent on the inhibitive performance of ionic liquid. Besides, ionic liquids containing long chain length may exhibit stronger corrosion inhibiting ability because of their good hydrophobicity, but the long alkyl chain also induced poor water-solubility and strong foaming-ability for the ionic liquids, which is detrimental when they used as corrosion inhibitors. Also, several researchers studied the effect of surfactants on corrosion inhibition of carbon steel in acidic media [17–22]. Herein, the potential corrosion inhibition effects of the synthesized gemini surfactant based ionic liquids are reported by potentiodynamic polarization, electrochemical impedance and weight loss measurements. It is also the purpose of this work to test the experimental data obtained from the three techniques with several adsorption isotherms at different temperatures, in order to determine the thermodynamic functions for the adsorption

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process and gain more information about the mode of adsorption of the inhibitor on the surface of the carbon steel.

## 2. Experimental

### 2.1. Synthesis

#### 2.1.1. General procedure for ILs synthesis

The synthesized gemini ionic liquids were obtained by coupling reaction between 1,2-dibromoethane, 1,3-dibromopropane and 1,6-dibromohexane (0.1 mol) and tridodecylamine (0.2 mol) in 50 ml acetone. The reaction mixture was refluxed for 12 h and left for complete precipitation of the gemini compounds. Produced gemini surfactant ionic liquids were filtered off and recrystallized three times from acetone to produce the desired gemini cationic surfactant ionic liquids (G2IL, G3IL and G6IL), Scheme 1 [23]. The structures of the synthesized gemini cationic surfactant-based ionic liquids (G2IL, G3IL and G6IL) were characterized using FTIR and  $^1\text{H}$ NMR as follows:  $N^1,N^1,N^1,N^2,N^2,N^2$ -hexadodecylethane-1,2-diaminium bromide (G2IL), FTIR (KBr):  $\nu = 2940\text{ cm}^{-1}$  ( $\text{CH}_3$ ),  $2850\text{ cm}^{-1}$  ( $\text{CH}_2$ ),  $2260\text{ cm}^{-1}$  ( $-\text{N}^+$ ),  $1420\text{ cm}^{-1}$  ( $\text{CH}_2$ )<sub>n</sub>;  $^1\text{H}$ NMR (500 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 0.85\text{ ppm}$  (t, 3H,  $\text{CH}_3$ ),  $1.31\text{ ppm}$  (m, 2H,  $\text{CH}_2\text{CH}_3$ ),  $1.29\text{ ppm}$  (m, nH,  $\text{CH}_2$ ),  $1.73\text{ ppm}$  (m, 2H,  $\text{CH}_2\text{CH}_2\text{N}^+$ ),  $3.24\text{ ppm}$  (t, 2H,  $\text{CH}_2\text{CH}_2\text{N}^+$ ),  $3.68\text{ ppm}$  (s, 2H,  $\text{N}^+\text{CH}_2\text{N}^+$ ).

$N^1,N^1,N^1,N^2,N^2,N^2$ -hexadodecylpropane-1,3-diaminium bromide (G3IL), FTIR (KBr):  $\nu = 2920\text{ cm}^{-1}$  ( $\text{CH}_3$ ),  $2845\text{ cm}^{-1}$  ( $\text{CH}_2$ ),  $2265\text{ cm}^{-1}$  ( $-\text{N}^+$ ),  $1460\text{ cm}^{-1}$  ( $\text{CH}_2$ )<sub>n</sub>;  $^1\text{H}$ NMR (500 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 0.82\text{ ppm}$  (t, 3 H,  $\text{CH}_3$ ),  $1.21\text{ ppm}$  (m, nH,  $\text{CH}_2$ ),  $1.52\text{ ppm}$  (m, 2H,  $\text{CH}_2\text{CH}_3$ ),

$1.75\text{ ppm}$  (m, 2H,  $\text{CH}_2\text{CH}_2\text{N}^+$ ),  $2.47\text{ ppm}$  (m, 2H,  $\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+$ ),  $3.21\text{ ppm}$  (t, 2H,  $\text{CH}_2\text{CH}_2\text{N}^+$ ),  $3.48\text{ ppm}$  (s, 2H,  $\text{N}^+\text{CH}_2\text{N}^+$ ).

$N^1,N^1,N^1,N^2,N^2,N^2$ -hexadodecylhexane-1,6-diaminium bromide (G6IL), FTIR (KBr):  $\nu = 2930\text{ cm}^{-1}$  ( $\text{CH}_3$ ),  $2815\text{ cm}^{-1}$  ( $\text{CH}_2$ ),  $2266\text{ cm}^{-1}$  ( $-\text{N}^+$ ),  $1444\text{ cm}^{-1}$  ( $\text{CH}_2$ )<sub>n</sub>;  $^1\text{H}$ NMR (500 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 0.80\text{ ppm}$  (t, 3 H,  $\text{CH}_3$ ),  $1.30\text{ ppm}$  (m, 2H,  $\text{CH}_2\text{CH}_3$ ),  $1.25\text{ ppm}$  (m, nH,  $\text{CH}_2$ ),  $1.75\text{ ppm}$  (m, 2H,  $\text{CH}_2\text{CH}_2\text{N}^+$ ),  $1.73\text{ ppm}$  (m, 2H,  $\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+$ ),  $3.20\text{ ppm}$  (t, 2H,  $\text{CH}_2\text{CH}_2\text{N}^+$ ),  $3.8\text{ ppm}$  (s, 2H,  $\text{N}^+\text{CH}_2\text{N}^+$ ).

### 2.2. Solution

The aggressive solution, 1 M HCl was prepared by dilution of analytical grade HCl (37 wt.%) with distilled water. Concentration range of used synthesized inhibitor varied from  $5 \times 10^{-5}$  to  $5 \times 10^{-3}$  M for corrosion measurements. Double distilled water was used for preparing test solutions in all measurements.

### 2.3. Materials and sample preparation

Tridodecylamine (purity > 97%), 1,2-dibromoethane (purity > 98%), 1,3-dibromopropane (purity > 99%) and 1,6-dibromohexane (purity > 98%) which were of analytical grade chemicals were obtained from Aldrich Chemical Company (Germany). All the solvent and reagents were used as received without further purification.

The working electrodes were cut from the carbon steel bar (0.11% C, 0.45% Mn, 0.04% P, 0.05% S, 0.25% Si, and the balance is Fe) and then connected to a copper wire and embedded in epoxy resin. Before measurements, the electrodes were grinded gradually with grit SiC paper (grade 240, 400, 600, 800 and 1200), then degreased in acetone and ultrasonically cleaned in alcohol.

### 2.4. Measurements

#### 2.4.1. Physicochemical properties

Physicochemical properties of the prepared ionic liquids such as melting point, density and viscosity were measured according the following methods:

To measure the density, a standard 5 ml pycnometer was calibrated by using deionized water at 298 K ( $0.9970\text{ g cm}^{-3}$ ) [24,25]. The pycnometer was filled with dried and degassed ionic liquid sample.

The working equation for calibration of pycnometer is

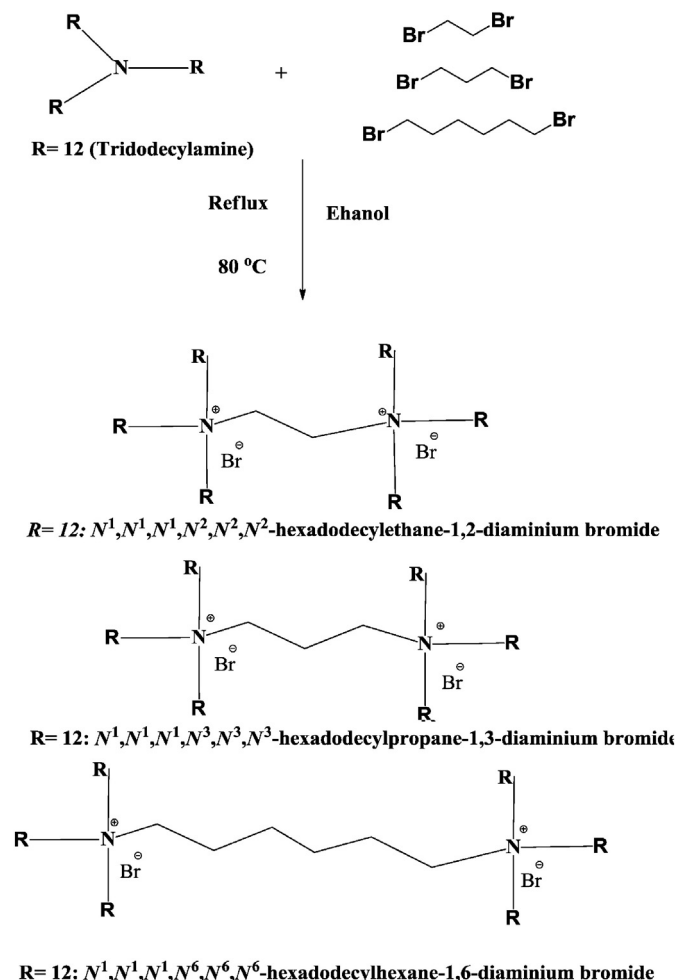
$$V = (m_{(w+e)} - m_e) / \rho_w = m_w / \rho_w \quad (1)$$

where  $m_w = 4.8381\text{ g}$  is water mass filled in the pycnometer, the mass of empty pycnometer  $m_e = 8.8033\text{ g}$   $m_w + e$  is the mass of filled pycnometer,  $\rho_w$  is density of distilled water at 298 K ( $997.04593 \pm 0.00081\text{ kg m}^{-3}$ ). Masses were determined using Sartorius electronic analytical and precision balance (TE214S) with readability of 0.1 mg.

The intrinsic viscosities ( $\eta$ ) of the synthesized gemini ionic liquids was measured in distilled water at temperature range of (50–90 °C) using a capillary viscometer (Übbelohde suspended level type) under thermostated condition at surfactant concentrations  $0.5\text{ g l}^{-1}$  [26].

#### 2.4.2. Surface tension

Surface tension was measured by the platinum ring method using a Kruss K6 tensiometer for aqueous solution of the synthesized gemini cationic surfactants-based ionic liquids with a concentration range of  $1 \times 10^{-2} - 5 \times 10^{-6}$  M at 20, 40 and 60 °C. The solutions were poured into a clean Teflon cup, the solutions were left for 2 h to allow the stabilization and complete adsorption at the solution surface. The surface tension values were measured a minimum of three times and the recorded values were taken as the average of these values. The critical micelle concentration (CMC) was determined from surface tension profile [27,28].



Scheme 1. Synthetic route of the ionic liquid inhibitors.

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