Synthesis, surface properties and inhibition behavior of novel cationic gemini surfactant for corrosion of carbon steel tubes in acidic solution

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ABSTRACT

In the present investigation a novel gemini surfactant namely N,N'-((oxalylbis(oxy))bis(ethane-2,1-diyl))bis(N,N-dimethyldodecan-1-aminium bromide) was synthesized, characterized, and tested as a corrosion inhibitor for carbon steel in 1 M HCl solution. The corrosion inhibition efficiency was determined by using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and weight loss methods. From the results, it was clear that the synthesized inhibitor is a good inhibitor for carbon steel in 1 M HCl solution. The inhibition efficiency increases by increasing the concentration of the inhibitor. Thermodynamic and activation parameters were discussed. The synthesized inhibitor's adsorption was found to follow the Langmuir's adsorption isotherm.

1. Introduction

Corrosion process plays an important role in the field of economics and safety. Various types of steel including carbon steel are used in different industries (chemical and electrochemical industries, nuclear, power, petroleum, and food industry), and also in daily life. However, carbon steel suffers from a certain type of corrosion within some environments. For this cause, the electrochemical properties of carbon steel are the subject of many studies. Hydrochloric acid is widely used as aggressive solution to remove unwanted scale and rust in many industrial processes. Due to the aggressiveness of acids, corrosion can be minimized by addition of corrosion inhibitors in small concentrations [1–7]. Surfactants are among those organic compounds which can be used as corrosion inhibitors in acid solutions [8–10]. The ability of a surfactant to physical (electrostatic) adsorption or chemisorption onto the metal surface was found to be responsible for the corrosion inhibition of the metal surface [11]. Gemini surfactants are a new generation of surfactants that have been paid considerable attention. A gemini surfactant is consists of two hydrophilic groups and two hydrophobic groups that are joined together by a rigid and flexible aromatic or an aliphatic spacer in a molecular structure [12–16]. They are more surface-active and have much lower critical micelle concentration (CMC) values than their monomeric counterparts. Because of their unique physical–chemical properties, gemini surfactants continue to gain widespread interest for various applications [17]. The aim of this work is to study the effect of the prepared surfactant on the corrosion inhibition of carbon steel in 1 M HCl solution using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss methods. In addition, the surface properties of the new gemini surfactant were determined.

2. Experimental methods and materials

2.1. Synthesis of inhibitor

The inhibitor that was used in this work was prepared through two steps. In the first step, we react (4.457 g, 0.05 mol) 2-dimethylaminoethanol with (12.462 g, 0.05 mol) dodecyl bromide. The reactants were allowed to reflux in ethanol at 80 °C for 24 h, and then the reaction mixture was left to cool to room temperature. After that the mixture was washed with diethyl ether and was filtrated by using a filter paper to separate the white precipitate (N-(2-hydroxyethyl)-N,N-dimethyldodecan-1-aminium bromide). In the second step, the gemini surfactant compound was synthesized by a condensation reaction between (6.7674 g, 0.02 mol) N-(2-hydroxyethyl)-N,N-dimethyldodecan-1-aminium bromide and (0.9003 g, 0.01 mol) oxalic acid in toluene as a solvent and p-toluene sulfonic acid as a dehydrating agent at 140 °C for 8 h. The reaction was completed when the water (0.36 g, 0.02 mol) was removed from the reaction system. Furthermore, the reaction mixture was distilled under vacuum to completely remove the solvent. The produced compound was recrystallized twice from ethanol. The chemical structure of the synthesized novel cationic gemini surfactant (Fig. 1), N,N'-((oxalylbis(oxy))bis(ethane-2,1-diyl))bis(N,N-dimethyldodecan-1-aminium bromide) was characterized by FTIR, ^{1}H NMR and Mass spectroscopic analysis.

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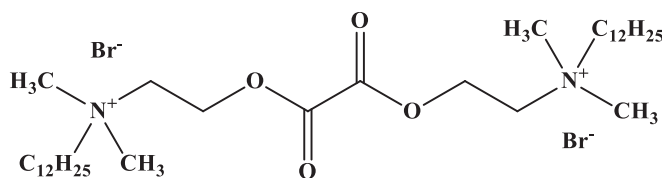
N,N'-((oxalylbis(oxy))bis(ethane-2,1-diyl))bis(N,N-dimethyldodecan-1-aminium bromide)

Fig. 1. The chemical structure of the synthesized cationic gemini surfactant.

2.2. Carbon steel sample

The chemical composition of the working electrode, a steel electrode (API 5L line pipe), was determined using the spectrolab quantometer, as represented in Table 1. The steel electrode was mounted in polyester. It was mechanically ground with 320, 400, 600, 800, 1000 and 1200 emery paper, washed by acetone and bidistilled water, then dried and inserted into the cell.

2.3. Weight loss technique

Steel specimens with dimensions of 3 cm × 6 cm × 0.5 cm were immersed in 1 M HCl in a closed beaker with and without the addition of different concentrations of inhibitor for 24 h at 25–60 °C. Triplicate specimens were exposed for each condition and the average weight losses were reported.

2.4. Electrochemical technique

For electrochemical measurements, a classical three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference was used. Carbon steel rod as a working electrode was pressure fitted into a polytetrafluoroethylene (PTFE) holder exposing only a 0.7 cm^2 surface to the solution. The exposure surface was abraded with different grades of emery paper, degreased with acetone, washed with bidistilled water and then dried. The experiments were done at a constant temperature (within ± 1 °C). EIS measurements were carried out in a frequency range of 100 kHz to 30 MHz with a 10 mV sine wave as the excitation signal at open circuit potential. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically with a scan rate of 0.2 mV s^{-1} from −0.8 to −0.3 V versus SCE. Before each run, the working electrode was immersed in the test solution for 30 min to reach steady state. All potentials were measured against SCE. Measurements were obtained using a Voltalab 40 Potentiostat PGZ 301 combined with corrosion program (Voltamaster 4) [18].

2.5. Surface tension technique

Surface tension was measured with a Du NouyTensiometer (Kruss Type 6) for different concentrations of the synthesized cationic gemini surfactant. Doubly distilled water with a surface tension equal 72 mN m^{-1} at 25 °C was used.

3. Results and discussion

3.1. Confirmation of chemical structure of the prepared inhibitor

The chemical structure of the synthesized cationic gemini surfactant was confirmed by FTIR, ^{1}H NMR and Mass spectroscopy.

3.1.1. FTIR spectra

FTIR spectrum of the synthesized compound showed the following absorption bands at 2923.56 cm^{-1} (C–H stretching), 1738.51 cm^{-1} (C=O stretching), 1464.67 cm^{-1} (C–H bending), 1198.54 cm^{-1} (C–O stretching), 1083.8 cm^{-1} (C–N$^+$), and 515.865 cm^{-1} (C–Br). The FTIR spectrum confirmed the expected functional groups in the synthesized cationic gemini surfactant as shown in Fig. 2.

3.1.2. ^{1}H NMR spectra

The ^{1}H NMR spectra of the synthesized compound showed different bands at δ = 0.8487–0.8762 ppm (t, 6H, NCH$_2$CH$_2$(CH$_2$)$_n$C**H**$_3$); δ = 1.1697–1.3271 ppm (m, 36H, NCH$_2$CH$_2$(C**H**$_2$)$_n$CH$_3$); δ = 1.7276 ppm (m, 4H, NCH$_2$C**H**$_2$(CH$_2$)$_n$CH$_3$); δ = 3.2698 ppm (s, 12H, NC**H**$_3$); δ = 3.4609 ppm (t, 4H, NC**H**$_2$CH$_2$(CH$_2$)$_n$CH$_3$); δ = 3.6473–3.7207 ppm (m, 4H, OCH$_2$C**H**$_2$NCH$_2$C**H**$_2$(CH$_2$)$_n$CH$_3$); δ = 4.5766–4.8151 ppm (m, 4H, OC**H**$_2$CH$_2$NCH$_2$CH$_2$(CH$_2$)$_n$CH$_3$). The data of ^{1}H NMR spectrum confirmed the expected hydrogen proton distribution in the synthesized cationic gemini surfactant as shown in Fig. 3.

3.1.3. Mass spectra

The mass spectrum of the synthesized compound showed that a molecular ion peak m/z 730.05 (4.57%), base peak at m/z 58.04 (100%) **C$_2$H$_2$O$_2$** and other significant peaks are shown at m/z 73.52 (9.27%) **C$_4$H$_{11}$N**, 88.06 (69.04%) **C$_4$H$_{10}$NO** or **[C$_5$H$_{14}$N]$^+$**, 93.92 (7.78%) **CH$_3$Br**, 212.17 (83.60%) **[C$_{14}$H$_{30}$N]$^+$**, 244.26 (12.56%) **C$_{11}$H$_{22}$N$_2$O$_4$**, 382.28 (3.29%) **C$_{21}$H$_{38}$N$_2$O$_4$**, 570.91 (3.07%) **[C$_{34}$H$_{70}$N$_2$O$_4$]$^{2+}$**. The data of Mass spectrum confirmed the chemical structure of the synthesized cationic gemini surfactant as shown in Fig. 4.

3.2. Weight loss measurements

The corrosion rate (k) was calculated from the following equation [19]:

$$k = \frac{\Delta W}{St} \tag{1}$$

where ΔW is the average weight loss of three parallel steel sheets, S is the total area of the specimen and t is the immersion time. The corrosion

Table 1
Chemical composition of carbon steel sample

Element	C	Si	Mn	P	S	Ni	Cr	Al	V	Ti	Cu	Fe
Weight (%)	0.19	0.05	0.94	0.009	0.004	0.014	0.009	0.034	0.016	0.003	0.022	Rest