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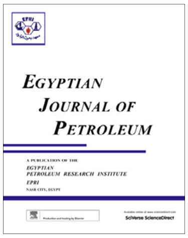
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**FULL LENGTH ARTICLE**

# Novel surfactants incorporated with 1,3,5-triethanolhexahydro-1,3,5-triazine moiety as corrosion inhibitors for carbon steel in hydrochloric acid: Electrochemical and quantum chemical investigations

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**Abstract** The main objective of this work was to examine the corrosion inhibition ability of three novel surfactant molecules synthesized from 1,3,5-triethanolhexahydro-1,3,5-triazine, which named (I, II and III). The chemical structure of these surfactants was confirmed by FT-IR and $^1H$ NMR spectroscopy. Also the surface active properties for the synthesized compounds were calculated. The effect of these surfactants on carbon steel in a solution of 1 M HCl was studied using mass-loss and electrochemical measurements. Protection efficiencies were found to be 93.1%, 90.7%, and 87% for III, II, and I, respectively. The order of increasing inhibition efficiency was correlated with increasing the number of ethylene oxide units. Potentiodynamic polarization curves indicated that the prepared surfactants acted as mixed type inhibitors. Adsorption of the inhibitor obeys the Langmuir isotherm. Quantum chemical calculations based on ab initio method were performed on I, II and III. The molecular structural parameters, such as the frontier molecular orbital energy HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), the charge distribution and the fraction of electrons ($\Delta N$) transfer from inhibitor to carbon steel were calculated and discussed.

## 1. Introduction

Carbon steel is widely used in many industrial applications. In most industrial processes, the acidic solutions are commonly used for the pickling, industrial acid cleaning, acid descaling, oil well acidifying, etc. [1–5]. Carbon steel has remarkable economic and attractive materials for engineering applications owing to its low cost, easy availability and high mechanical

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strength. Corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. Thus, the search for new and efficient corrosion inhibitors has become a necessity to protect metallic materials against corrosion [6]. To be effective, an inhibitor must displace water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction, prevent transportation of water and corrosion active species on the surface [7]. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosion media [8]. To prevent the attack of acid, it is very important to add a corrosion inhibitor to decrease the rate of metal dissolution in such solutions. Thus, many studies concerning the inhibition of carbon steel corrosion using organic substances are conducted in acidic and basic solutions [9–13]. Inhibitors, which reduce corrosion on metallic materials, can be divided into three kinds: (i) inorganic inhibitors, (ii) organic inhibitors and (iii) mixed material inhibitors [14]. Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms. The influence of organic compounds containing nitrogen, such as amines and heterocyclic compounds, on the corrosion of steel in acidic solutions has been investigated by several researchers [15–18]. Surfactants are special type of organic compounds and exhibit unique properties due to their amphiphilic molecule. This is the reason of their wide application in the field of inhibition of metals against corrosion. The surfactant inhibitor has many advantages such as high inhibition efficiency, low price, low toxicity and easy production [19–24]. The adsorption of the surfactant on the metal surface can markedly change the corrosion resisting property of the metal [25,26], So the study of the relationship between the adsorption and corrosion inhibition is of great importance. Quantum chemical calculations have been proved to be a very powerful tool for studying the inhibition mechanism [27,28]. In continuation to our program for the synthesis of new corrosion inhibitors [29–35], the present study aimed to synthesis three nonionic surfactants based on 1,3,5-triethanolhexahydro-1,3,5-triazine. The inhibiting action of the three prepared surfactants (I, II, and III) on the carbon steel in 1 M HCl solution has been investigated. The gravimetric and electrochemical techniques such as potentiodynamic polarization and impedance measurements were used in this study. Theoretical studies on electronic and molecular structures of three surfactants were conducted using quantum chemical calculations. The choice of these compounds was based on molecular structure considerations that, these compounds contain heteroatoms such as N and O, which induce greater adsorption of the inhibitor molecule onto the surface of carbon steel.

## 2. Experimental method

### 2.1. Synthesis of 1,3,5-triethanolhexahydro-1,3,5-triazine

1.47 mol of ethanolamine was added to a stirred solution of 37% aqueous formaldehyde (1.42 mol) at a rate to keep the temperature between 50 and 55 °C. The addition was completed after 3 h, and the reaction stirred for an additional hour. The reaction mixture was then cooled in an ice bath, and potassium hydroxide was added such that the temperature did not exceed 25 °C. The organic layer was separated and subjected to vacuum distillation resulting in the isolation of 1,3,5-triethanolhexahydro-1,3,5-triazine [36]. The mechanism of reactions is illustrated in Scheme 1.

### 2.2. Ethoxylation

The prepared 1,3,5-triethanolhexahydro-1,3,5-triazine was charged in dry and closed vessel, which allowed passing nitrogen and ethylene oxide gases to introduce 6, 10 and 20 units of ethylene oxide beside the three (–$CH_2CH_2O$–) in the original nucleus, compound (4) so that the total ethylene oxide units become 9, 13 and 23. The reaction took place in presence of triethylamine as a catalyst at 80–100 °C [37,38].

### 2.3. Esterification

The prepared ethoxylated derivatives were esterfied with oleic acid in a three-necked flask in the presence of p-toluene sulfonic acid (0.1 wt%) as a catalyst. The reaction mixture was heated at 150 °C with continuous stirring until the theoretical amount of water was collected. The product was purified by washing with a hot solution of supersaturated sodium chloride. The organic layer was separated, dried over anhydrous sodium sulfate, and the solvent was distilled off to give the corresponding esters (final products which abbreviated as I, II and III).

### 2.4. Measurement of surface tension

Equilibrium surface tension measurements were made at 25 °C using the Du Nouy ring method Tensiometer (Kruss Type 6) for different concentrations of the synthesized nonionic surfactants. All solutions were prepared in double distilled water with a surface tension equal 72 mN $m^{-1}$ at 25 °C.

### 2.5. The weight loss measurements

Experiments were performed on carbon steel samples (CS37) having the following chemical composition: 0.11% C, 0.45% Mn, 0.04% P, 0.05% S, 0.25% Si and the reminder is Fe and with an exposed area of $7 \times 3 \times 0.5$ cm. Measurements were carried out in a glass vessel containing 100 ml of 1 M HCl with and without addition of different concentrations of different inhibitors (concentration ranged from $1 \times 10^{-5}$ to $1 \times 10^{-3}$ M) at temperature 25 °C for 24 h immersion time. Solutions were freshly prepared from analytical grade chemical reagents using distilled water.

### 2.6. Electrochemical measurements

The electrochemical measurements were carried out using Volta lab 40 (Tacussel-radiometer PG Z301). In this method, the working electrode was immersed in the test solution for 30 min until the open circuit potential was reached. After that the working electrode was polarized in both cathodic and anodic directions. Standard ASTM glass electrochemical cell was used. Platinum electrode was used as auxiliary electrode. All potentials were measured against a SCE as reference electrode. Potentiodynamic polarization measurements were obtained by