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Three Gemini cationic surfactants based on polyethylene glycol as effective corrosion inhibitor for mild steel in acidic environment

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Abstract Three Gemini quaternary ammonium surfactants based on polyethylene glycol have been prepared and characterized using FTIR and ^{1}HNMR spectra. The effect of ethylene oxide units' number on the steel corrosion in 1.0 M HCl has been estimated using weight loss, polarization and electrochemical impedance spectroscopy. The Gravimetric technique has been done at three different temperatures 25, 40 and 55 °C. The synthesized Gemini cationic surfactants with the higher molecular weight (higher number of ethylene oxide units) showed the higher inhibition efficiency under all conditions. All the prepared Gemini inhibitors showed higher inhibition efficiency upon raising the solution temperature from 25 to 55 °C. The synthesized inhibitor G1500Br showed inhibition efficiency reach to 94% at temperature 55 °C. The Langmuir adsorption isotherm is the best-fitted isotherm concerning the tested Gemini surfactants adsorption onto steel surface. The change in the free energy of adsorption refers to physicochemical adsorption on steel surface. The synthesized materials act as a mixed-type inhibitor based on the potentiodynamic polarization results.

1. Introduction

The mild steel is used in various industrial applications in huge scale. These industrial applications, mainly use acidic solutions in its process like acid pickling, acid cleaning, acid descaling, oil well acidification, petrochemical process and others (Yadav et al., 2014; Abd El-Lateef, 2015; Nam et al., 2014; Mousavi et al., 2012; Singh et al., 2012; Liu et al., 2009; Mohammed et al., 2010), the acidic medium may be naturally present. Hence, all these aggressive mediums can cause a terrible loss in resources and money unless the mild steel has been protected. The acidification process, which enhances the production of oil, requires usage of 15–28% HCl solution. According to these obstacles, the steel corrosion protection is an indispensable process of saving money and resources (Yadav et al., 2015). The organic corrosion inhibitor production has been increased incrementally due to their huge consumption in the protection of metals. The ability of these organic inhibitors to protect the steel depend on their adsorptive ability, which depend on the testing solution and the chemical structure, surface charge and electronic density of the inhibitor (Shaban et al., 2015c; Abd El-Maksoud and

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fouda, 2005; Verma et al., 2015; Karthikaiselvi and Subhashini, 2014). Cationic surfactant corrosion inhibitors are a category of organic inhibitor, which are characterized by their high adsorptive ability where they possess different active site for adsorption in addition to the amphipathic structure which increases their rate of migration to the interface (Migahed et al., 2013; Biswas et al., 2015; Hegazy, 2015; Shaban et al., 2016d,a). The polar head group mainly possesses heteroatoms and conjugated double or triple bond which enhances their interaction with the vacant d-orbital in the corrode steel and blocking the active center by forming a barrier film isolate the steel from further corrosion, hence the corrosion rate decreases (Hegazy and Aiad, 2015; Balbo et al., 2013; Negm et al., 2010; Yakun et al., 2015). The Gemini surfactants are a category of surfactants where they possess two head groups. Many papers studied the steel corrosion in acidic medium using Gemini cationic surfactants (Tawfik et al., 2015; Asefi et al., 2010; Hegazy, 2009).

The current study aimed to prepare Gemini cationic surfactants utilizing polyethylene glycol as ecofriendly materials and studying their protection for steel corrosion in 1.0 M HCl as aggressive medium. The carbon steel corrosion measurements have been obtained using gravimetric and electrochemical techniques. The effect of ethylene oxide units number and solution temperature on the corrosion process have been studied. The adsorption nature of the synthesized materials has been assessed.

2. Experimental method

2.1. Materials

All the specimens used in the study have the composition (in wt.%) 11% C, 0.25% Si, 0.45% Mn, 0.05% S, 0.04% P and the remainder is Fe. The steel specimens were abraded with a variety of emery papers up to 1200 grades mechanically. Then, it was rinsed consecutively in acetone and double-distilled water before weighting and immersing in the uninhibited and inhibited solutions.

Polyethylene glycol with different molecular weights (Mwt = 600, 1000 and 1500), and 2-bromoacetic acid and *N, N*-diethyl aniline were purchased from Merck chemical company (Germany). The corrosive medium was a 1.0 M HCl solution and it was prepared by dilution of concentrated hydrochloric acid (37%, Merck) with double-distilled water and considered as blank solution. Different concentrations of the tested synthesized inhibitor that varied from 5×10^{-5} to 1×10^{-2} M has been used in the corrosion measurements.

2.2. Inhibitor

The used inhibitors were prepared through two steps:

2.2.1. Synthesis of polyethylene glycol bromoesters

The polyethylene glycol bromoester has been prepared throughout esterification between 0.2 mol. From 2-bromoacetic acid and (0.1 mol.) of polyethylene glycol-600, 1000 and 1500 individually in a desired amount of xylene (150 ml) as the solvent. 0.01% *p*-toluene sulfonic acid was inserted to the reaction contents as a dehydrating agent. The product has been obtained completely when the depicted theoretical amount of reaction water has been received in dean–stark system (0.2 mol, 3.6 ml water). The catalyst was removed the reaction mixture using petroleum ether (Shaban et al., 2015a, 2016b; Galal et al., 2012).

2.2.2. Synthesis of Gemini quaternary surfactant based on polyethylene glycols

(0.03 mol) From the synthesized dibromoethanoate polyethylene glycol (the first step) was refluxed with (0.06 mol.) *N*,*N*-diethyl aniline in ethyl alcohol absolute as solvent (120 ml) for 12 h. After solvent evaporation using vacuum evaporator, the product was washed twice using diethyl ether (Negm et al., 2011; Shaban et al., 2015b). The obtained products were labeled as: G600Br, G1000Br and G1500Br as depicted in Scheme 1.

2.3. Electrochemical techniques

They have been carried out with a Voltalab 40 (Potentiostat PGZ 301) conducted with a personal computer at 25 °C and the data analyzed using the volta master 4 software. The working electrode of exposed area 0.7 cm^2, has been created from the same carbon steel specimen used in the gravimetric method and subject to the same treatment before the test. The working electrode was immersed for 1 h at 25 °C in the inhibited solution before each measurement until reach stable potential. Each experiment has been repeated trice to obtain reproducible data. The Tafel curves were obtained by altering the electrode potential automatically from −900 to −200 mV vs. SCE at OCP with a scan rate 2 mV s^{-1}. Impedance spectra have been obtained in the frequency range from 100 kHz to 50 mHz with ten points per decade after reaching a steady state from OCP (30 min. for all experiment (Hegazy et al., 2013; Dobryszycki and Biallozor, 2001).

2.4. Weight loss measurements

The carbon steel sample was cut into specimens with a dimension of 2.5 cm × 2.0 cm × 0.06 cm. Before starting each experiment, the specimen coupon has been abraded with a variety of emery paper from 320 to 1200 and cleaned with distilled water and acetone. The coupon was weighted before and after immersion for 24 h (in the aggressive solution) using an analytical balance. Three different temperatures 25, 40 and 55 °C have been selected to study the effect of temperature on the corrosion process in the presence of the synthesized materials. The experiments were accomplished trice and the average weight loss was obtained (Emregul and Atakol, 2004).

3. Results and discussion

3.1. Structure confirmation

The chemical structures of the synthesized cationic materials (G600Br, G1000Br and G1500Br) were confirmed using FTIR and ^{1}H-NMR spectroscopy.

FTIR spectroscopy has been used to confirm the new formed functional groups, which are characteristic for the synthesized surfactants. Fig. 1. represents the FT-IR absorption

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