



Synthesis, characterization and evaluation of some anionic surfactants with phosphate group as a biodegradable corrosion inhibitor for carbon steel in acidic solution



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ABSTRACT

Novel anionic surfactants with phosphate group were synthesized and characterized by using FTIR and ^1H NMR spectroscopic analyses. The critical micelle concentration (CMC) and degree of dissociation of counter-ions were determined and discussed from conductivity measurements. The biodegradability of these surfactants was determined and discussed. Their corrosion inhibition effect on the carbon steel (CS) in 0.5 M H_2SO_4 solution has been evaluated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and weight loss methods. The inhibition efficiency increases with increasing the inhibitor concentration but decreases with the temperature increasing. The adsorption of inhibitors on the carbon steel surface obeys the Langmuir adsorption isotherm. Polarization curves show that the synthesized inhibitors are mixed-type inhibitors. Thermodynamic parameters of adsorption and kinetic were obtained from weight loss at different temperatures (25–60 °C).

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1. Introduction

The study of steel properties in general and electrochemical specially has received a great attention. In such respect, the corrosion inhibition of steel becomes very interesting and important owing to its wide applicability in industry and domestic life. One of the major consumers of corrosion inhibitors is the oil industry, where corrosion inhibitors are employed to control the corrosion rate of steel alloys in gas and oil well equipment [1–5]. Both general and localized corrosion types are encountered in this industry. The corrosion rate depends on the fluid composition, e.g., oil type, oil/water ratio, water salinity and the acidity of water caused by CO_2 and H_2S . The choice of the inhibitor is based on two considerations. Firstly, it can be synthesized conveniently from relatively cheap raw materials. Secondly, the presence of nitrogen, oxygen, sulfur and multiple bonds in the inhibitor molecule is needed. This leads to increase the adsorption of the compound on the steel surface and to promote effective inhibition [6]. The inhibition of the mild steel corrosion by sodium dodecyl benzene sulfonate (SDBS) in acidic solution was investigated [7]. The obtained results showed that, the presence of SDBS reduce the corrosion rate significantly. This is attributed to the adsorption of anionic SDBS on the positively charged mild steel surface through electrostatic attraction. Anionic surfactant [*p*-myristyloxy

carbonyl methoxy-*p*-sodium carboxylate-azobenzene] was investigated as a corrosion inhibitor for carbon steel in 1 M H_2SO_4 solution and that inhibitor seemed to obey the Langmuir adsorption isotherm equation [1]. Kerkouche et al. studied the effect of sodium dodecyl benzene sulfonate on the corrosion inhibition of Fe–1Ti–20C alloy in 0.5 M H_2SO_4 . It is found that maximum inhibition is observed at a concentration above its critical micelle concentration (CMC) and Temkin adsorption isotherm fits well with the experimental data [8]. The inhibitive effect of some nonionic surfactants on the corrosion of carbon steel in sulfuric acid solution was reported [9,10]. The application of surfactants as corrosion inhibitors for carbon steel dissolution in acidic media has been studied by some authors [11–17]. It was found that these substances have a marked inhibiting efficiency near their critical micelle concentration (CMC) values. The adsorption of a surfactant markedly changes the corrosion resisting property of a metal. However, no substantial information is available on the corrosion inhibition of anionic surfactants with phosphate group in 0.5 M H_2SO_4 solution. In the present work, we are developing novel anionic surfactants with phosphate group and different alkyl chain lengths. The CMC, degree of counter ion dissociation and biodegradability were determined and discussed. Evaluation of these surfactants as corrosion inhibitors for carbon steel in 0.5 M H_2SO_4 solution was studied using weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods. Also, the effect of inhibitor concentration and temperature on the corrosion inhibition was discussed. Adsorption thermodynamic parameters are calculated and discussed in detail.

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2. Experimental method

2.1. Chemicals

Phosphoric acid (85%), and polyethylene glycol-400 were purchased from Merck chemical company (Germany). Octyl ($\geq 99\%$), dodecyl ($\geq 98\%$), hexadecyl ($\geq 95\%$) and octadecyl alcohol ($\geq 95\%$) and sodium hydroxide ($\geq 98\%$) were analytical grade chemicals and obtained from Sigma-Aldrich chemical company (Germany). All the reagents were analytical grade and used as received without further purification.

2.2. Synthesis

The tested inhibitors were synthesized as described in our previous work [18]: Octyl, dodecyl, hexadecyl and octadecyl alcohol (0.5 mol) were esterified separately by phosphoric acid (0.5 mol) in xylene as a solvent and 0.01% *p*-toluene sulfonic acid as a catalyst, until the azeotropic amount of water (0.5 mol, 9 ml) was removed. Subsequent purification was done by means of vacuum distillation to give the alkyl ester of phosphoric acid (yield, 81%) [19]. The produced alkyl ester of phosphoric acid (0.2 mol) and polyethylene glycol-400 (9 U of ethylene glycol per molecule) (0.1 mol) were esterified individually in xylene (50 ml) at 138 °C. The reaction was stopped after the complete removal of the water of the reaction (0.2 mol, 3.6 ml). Then, the reaction mixture was quenched using sodium hydroxide (0.2 mol), and followed by removing all of the volatile material from the resulting solution. The anionic surfactants obtained (yield, 84%) were designated as C8A, C12A, C16A and C18A [20].

Chemical structure of the synthesized inhibitor (Fig. 1) was confirmed by FTIR and ^1H NMR spectroscopy. FTIR analysis was carried

out using ATI Mattson infinity series TM, Bench top 961 controlled by Win First TM V2.01 software. ^1H NMR analysis was measured in DMSO- d_6 using a Joel ECA 500 MHz NMR spectrometer.

2.3. Electrical conductivity measurements (*K*)

Specific conductivity of different aqueous concentrations from the synthesized anionic surfactant was measured with a digital conductivity meter (Cond 3210 SET 1, Probe tetra corn 325, Wissenschaftlich Technische Werkstatern) using a double jacket glass cell. The cell constants were determined using KCl solutions. Measurements were performed in a jacketed cell of knowing cell constant at 25 ± 1 °C. [21].

2.4. Biodegradability

Biodegradability test in river water of the anionic surfactants was determined by the surface tension method using a Dü-Nouy tensiometer (Krüss type K6) [22]. In this method, each surfactant was dissolved in river water by a concentration of 100 ppm and incubated at 38 °C. A sample was withdrawn daily (for 28 days), filtered and the surface tension value was measured. The biodegradation percent (D%) was calculated as follows:

$$D\% = (\gamma_t - \gamma_0) / (\gamma_{bt} - \gamma_0) \times 100 \quad (1)$$

where: γ_t is the surface tension at time *t*, γ_0 is the surface tension at time = 0 (initial surface tension) and γ_{bt} is the surface tension of river water without the addition of surfactants at time *t*.

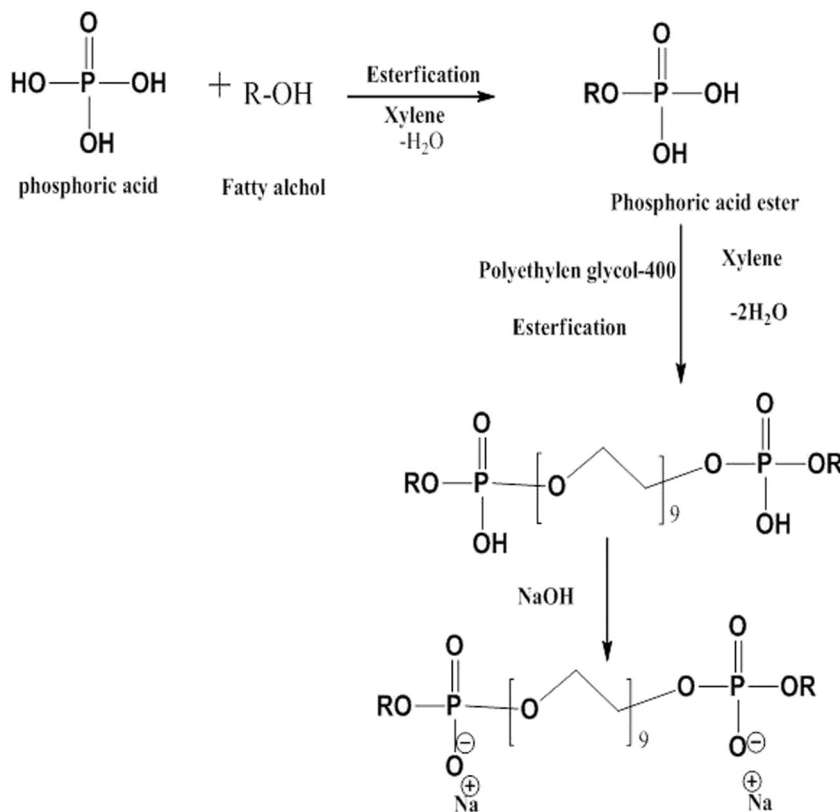


Fig. 1. The chemical structure of the synthesized anionic surfactant inhibitors. when R = 8; sodium 3,6,9,12,15,18,21,24-octaohexacosane-1,26-diyl dioctyl bis(phosphate), (C8A) R = 12; sodium didodecyl 3,6,9,12,15,18,21,24-octaohexacosane-1,26-diyl bis(phosphate), (C12A) R = 16; sodium 3,6,9,12,15,18,21,24-octaohexacosane-1,26-diyl dihexadecyl bis(phosphate), (C16A) R = 18; sodium 3,6,9,12,15,18,21,24-octaohexacosane-1,26-diyl dioctadecyl bis(phosphate), (C18A)

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