



Non toxic biodegradable cationic gemini surfactants as novel corrosion inhibitor for mild steel in hydrochloric acid medium and synergistic effect of sodium salicylate: Experimental and theoretical approach



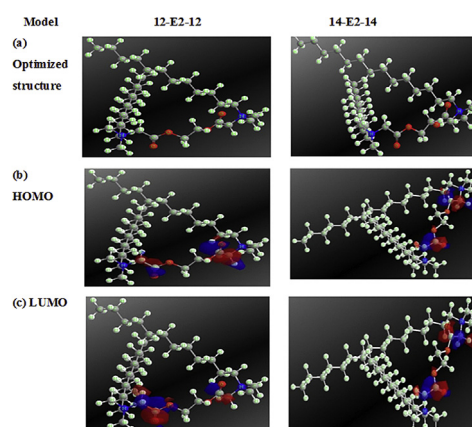
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HIGHLIGHTS

- Environment friendly gemini surfactants were studied as corrosion inhibitor for MS.
- Studied compounds act as good inhibitor for MS corrosion in 1 M HCl at 30–60 °C.
- η of inhibitors is synergistically increased in presence of sodium salicylate.
- The synthesized cationic gemini surfactants act as mixed-type inhibitor.
- Experimentally obtained results are in good agreement with theoretical results.

GRAPHICAL ABSTRACT



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ABSTRACT

Two biodegradable, non toxic cationic gemini surfactants having ester linkage in the spacer namely, $C_mH_{2m+1}(CH_3)_2N^+(CH_2COOCH_2)_2N^+(CH_3)_2C_mH_{2m+1}.2Cl^-$ (m-E2-m, m = 12, 14), were synthesized and characterized using elemental analysis, FT-IR and 1H -NMR. The corrosion inhibition performance of synthesized compounds separately and in combination with sodium salicylate (SS), along with the nature and stability of inhibitive film, for mild steel (MS) in 1 M HCl solution at 30–60 °C was evaluated using weight loss, potentiodynamic polarization, EIS, UV–visible spectroscopy, FTIR, SEM/EDAX, TGA and quantum chemical calculations. Results of the studies confirm m-E2-m as effective corrosion inhibitor for MS in HCl; the inhibition effect being synergistically strengthened in presence of SS. The synthesized compounds act as mixed type inhibitor and adsorb on MS surface in accordance with Langmuir adsorption isotherm. Experimentally measured inhibition efficiencies are correlated with the molecular parameters obtained using PM6 semi-empirical method. Empirical results are in good agreement with the theoretical predictions.

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1. Introduction

Mineral acid solutions e.g., HCl or H₂SO₄ are widely used as pickling acids for removal of unwanted scale such as rust or mill-scale from steel or ferrous alloys surfaces at temperatures up to 60–90 °C. However, pickling acids solutions are highly corrosive and their corrosiveness needs to be suppressed by appending appropriate corrosion inhibitors in small concentrations. Organic compounds containing heteroatom such as N, O, S or P, multiple bonds or aromatic rings have long been used as effective corrosion inhibitors in acid solutions [1–8]. However, most of these organic corrosion inhibitors are hazardous to both environment and human being and need replacement by biodegradable non toxic compounds.

An umpteen number of references are available dealing with the corrosion inhibition studies of conventional surfactants (having one head group and one hydrophobic group) for iron and steel in acidic media [9–15]. In comparison to traditional corrosion inhibitors, surfactants are economical, easy to produce, and possess high inhibition efficiency and low toxicity. The inhibitory effect of the surfactants generally increases with increasing concentration and hydrophobic chain length up to critical micelle concentration (CMC); above CMC the inhibition effect remain almost constant. In the recent decade a new type of surfactants called dimeric or gemini surfactants, with of two amphiphilic moieties joined at the level of, or close to, the head groups by a spacer group, have attracted the attention of various researchers. These surfactant exhibits higher functionalities such as low value of CMC and high value of solubilisation and interfacial activity than their monomeric counterpart [16,17]. These surfactants have attracted considerable interest as corrosion inhibitors for iron and steel in acid media [18–24] and proved to be much superior corrosion inhibitor as compared to the monomeric counterpart and extremely efficient even at very low concentration [25]. However, gemini surfactants are quite stable and non-biodegradable. The non-biodegradable gemini surfactants have been converted into biodegradable eco-friendly compounds by introduction of cleavable ester bond in their chemical structure [26–29].

The aim of the present work is to study the corrosion inhibition effect of two ester bonded cationic gemini surfactants (labelled as m-E2-m; where E2 is the diester group in gemini's spacer part and m = 12, 14 the number of carbon atoms in alkyl tail) for mild steel (MS) in 1 M HCl solutions at 30–60 °C using weight loss, electrochemical techniques and quantum chemical calculations. Further, to maximise the adsorption of studied inhibitors while minimising the aqueous inhibitor concentration, the effect of sodium salicylate (SS) on inhibition effect of m-E2-m has also been examined. The biodegradability test on 12-E2-12 and 14-E2-14 has confirmed that the compound is eco-friendly and its biodegradability is 42% and 39%, respectively after 5 days [30,31]. The haemolytic activity test to evaluate toxicity of 12-E2-12 and 14-E2-14 has revealed their extremely low toxicity (HC₅₀ value: 236.4 µg/ml and HC₅₀ value: 190.5 µg/ml, respectively) compared to conventional surfactant CTAC (HC₅₀ value: 0.00312 µg/ml) [30,31]. The compounds of the type m-E2-m or m-E2-m in combination with SS have yet not been evaluated as corrosion inhibitor.

2. Experimental

2.1. Mild steel specimen

The chemical composition of MS as analyzed by optical emission spectrophotometer (% weight) is 0.061 C, 0.18 Mn, 0.018 P, 0.035 Cr, 0.054 Mo, 0.017 Al, 0.034 V and rest Fe. Prior to each experiment, MS specimen surface was hand polished sequentially with 320,

400, 600 and 1200 grade of SiC papers, rinsed with double distilled water, degreased in ethanol, acetone and finally dried in warm air.

2.2. Test solutions

The corroding medium, 1 M HCl was prepared by dilution of AR 37% HCl by double distilled water with and without m-E2-m surfactants. The concentration range of the m-E2-m inhibitors varies from 1×10^{-5} – 1×10^{-2} mM for corrosion measurements. Freshly prepared solution was prepared for each experiment. SS is analytical and m-E2-m inhibitors used in this investigation were synthesized.

2.3. Synthesis of m-E2-m inhibitors

The m-E2-m inhibitors used in this investigation were synthesized following an earlier prescribed procedure [32,33]. Firstly, ethane-1,2-diyl bis(chloroacetate) was prepared by reaction of chloroacetyl chloride (0.22 mol) with ethylene glycol (0.1 mol). Chloroacetyl chloride was added drop wise and then heated for 8 h at 50 °C in nitrogen atmosphere (Fig. 1.). The reaction mixture was separated by washing with ether and saturated solution of NaCl. The organic phase was dried over magnesium sulphate. In the following step, a mixture of ethane-1,2-diyl bis(chloroacetate) and *N,N*-dimethylalkylamine in the molar ratio of 1:2.1 was added to a round bottomed flask and refluxed in ethyl acetate for 10 h. Thin layer chromatography (TLC) was used to monitor the progress of reaction. Finally, the solvent was removed under vacuum by rotary flash evaporator. The cationic gemini surfactants was obtained as a white crystalline solid. After recrystallization, the purity and chemical structure of both the surfactants was confirmed by elemental analysis, FT-IR and ¹H NMR.

2.4. CMC determination

The CMC of both the surfactants alone and in combination with 0.01 M SS were determined by tensiometry. The surface tension of the solutions was measured as a function of surfactants concentration using a Kruss11 Tensiometer by the platinum ring detachment method. Concentrated stock solution of studied surfactants prepared in double distilled water and 1 M HCl was added in instalments to a known quantity of corrosive medium in a vessel and the readings were taken after thorough mixing and temperature equilibration. The measurement of the surface tension was continued until the attainment of equilibrium values. The particular concentration at which the surface tension vs. concentration plot shows a break corresponds to the CMC (Fig not shown here).

2.5. Weight loss measurements

Rectangular MS specimens of size 2.5 × 2.0 × 0.1 cm were used for weight loss measurements. Specimens were weighed accurately before and after immersion for 6 h at 30–60 °C in 200 ml of 1 M HCl solution without and with different concentrations of synthesized surfactants. The procedure of immersion test and calculation of inhibition efficiency (η_w) of the synthesized surfactants has been described elsewhere [34,35].

2.6. Electrochemical measurements

The electrochemical measurements were performed using a conventional three electrode cell assembly with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and MS specimens as working electrode, using an Auto lab Potentiostat/Galvanostat Model 128N with inbuilt impedance analyzer

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