



A comparative study on the electrochemical behavior of mild steel in sulfamic acid solution in the presence of monomeric and gemini surfactants

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ABSTRACT

The electrochemical behavior of mild steel in sulfamic acid solution in the presence of a gemini cationic surfactant, butanediy-1,4-bis(dodecyldimethylammonium bromide (12-4-12), and its monomeric counterpart, dodecyltrimethylammonium bromide (DTAB), was investigated as a function of the surfactant concentration by means of electrochemical impedance spectroscopy (EIS). The critical micelle concentration (cmc) values of DTAB and 12-4-12 in 1 M sulfamic acid solution, measured by surface tension measurement, were found to be 1.2 and 0.02 mM, respectively. The EIS results revealed a higher charge transfer resistance in 12-4-12 solution compared to that in DTAB solution at the same concentration normalized by the cmc (c/cm_c). The morphology of the steel samples after being exposed to the acidic test solutions was examined by atomic force microscopy (AFM). The AFM micrographs showed a reduction of surface roughness in the presence of the surfactant which is more evident at higher surfactant concentrations. The adsorption of both surfactants in the sulfamic acid solution was studied by Langmuir and Flory-Huggins adsorption isotherms at submicellar concentrations.

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1. Introduction

Acid solutions are generally used for pickling, chemical and electrochemical etching of metals and cleaning of undesirable scales and rusts on steel surface in several industrial sectors such as oil and gas industry [1–3]. Inorganic acid cleaners based on sulfamic acid are extensively used in a large variety of household and industrial applications e.g., multistage flash evaporators (MSF), seawater desalination plants, heat exchangers, cooling tower systems and etc. Sulfamic acid (monoamido sulfuric acid), H_2NSO_3H , is a dry, non-volatile, non-hygroscopic, odorless, and white crystalline solid. The aqueous solutions of sulfamic acid solubilize hard scales and form soluble compounds with most industrial deposits [4–6]. It can be used on mild steel with no problem of pitting or chloride-induced stress corrosion cracking (SCC). Sulfamic acid behaves as a strong acid in aqueous solution but its corrosivity is significantly lower in comparison to other acids such as sulfuric and hydrochloric acids.

It is very important to add corrosion inhibitors to prevent metal dissolution during acid cleaning of equipments, tubes and pipelines made of steels [7,8]. Most well known acid inhibitors are organic compounds containing nitrogen, oxygen and sulfur heteroatoms [8,9]. Among these, cationic surfactants with quaternary ammonium head groups have many advantages such as high inhibition efficiency, low price, and easy production. They can adsorb on metal surface and block the active sites decreasing the corrosion rates [9–12]. In last 20 years, a new generation of surfactants, gemini surfactants, has attracted great interest. This kind of surfactant contains two hydrophilic head groups and two hydrophobic chains in its chemical structure, separated by a rigid or flexible spacer. These surfactants have remarkably lower critical micelle concentration (cmc) and higher surface activity compared to conventional single chain surfactants of equal chain length [13,14].

The adsorption of the cationic gemini surfactants on the metal surface can markedly change the corrosion-resisting property of the metal and understanding the relations between the state of aggregation of surfactant molecules on metal surface and corrosion inhibition is of great importance [15]. Several gemini surfactants have been investigated as corrosion inhibitors for various metals and alloys in acidic media [1,15–24]. It has been reported that corrosion inhibition of cationic surfactants increases with the surfactant concentration up to cmc and remains constant afterwards. Indeed, in the context of corrosion inhibition using surfactants, the

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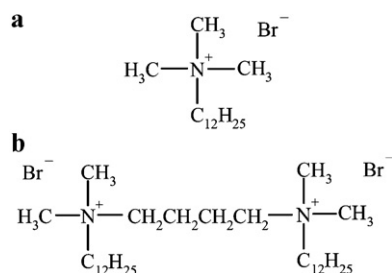


Fig. 1. The chemical structure of the surfactants used. DTAB (a) and 12-4-12 (b).

cmc marks an effective boundary condition below which surfactant adsorption is typically below the monolayer level, and above which adsorption can consist of multiple layers of physically adsorbed surfactant molecules [25]. By increasing the surfactant concentration close to the surface, a micellization process at the surface occurs at concentrations far below the cmc of the surfactant in the bulk [26]. Thus, the hydrophobic tails of adsorbed surfactants act as nucleation sites for the formation of admicelles [27]. At or near the cmc, micelles form in solution leading to dimers, and multiple molecule aggregates formation. At higher concentrations, above the cmc, the surfactants assemble into fully developed aggregate or double and multi layers at the mild steel surface [24,26]. Summarily, in the adsorption of surfactants on oppositely charged surfaces, the first step is direct adsorption mostly via an ion exchange mechanism of individual surfactant. The second step is cooperative adsorption involving hydrophobic interactions between alkyl chains of oncoming surfactants and surfactants adsorbed in the first step. This corresponds to the formation of surface aggregates or admicelles [26].

In this study, the electrochemical behavior of mild steel in sulfamic acid solution in the presence of a gemini cationic surfactant, butanediyl-1,4-bis(dodecyltrimethylammonium bromide (12-4-12), and its monomeric counterpart, dodecyltrimethylammonium bromide (DTAB), was investigated as a function of the surfactant concentration by means of electrochemical impedance spectroscopy (EIS). Surface tension measurement and atomic force microscopy (AFM) were utilized to understand the effect of these two surfactants on the physicochemical properties of sulfamic acid solution and metal surface morphology after being exposed to the solutions. In addition, the adsorption isotherm of the inhibitors was investigated. To the best of our knowledge, this research is the first to study the corrosion inhibition of gemini surfactant in 1 M sulfamic acid solution.

2. Experimental

2.1. Materials

Dodecyltrimethylammonium bromide (DTAB) was purchased from Merck and N,N'-didodecyl-N,N,N',N'-tetramethyl-1,4-butanediylammonium dibromide (12-4-12) was synthesized according to the previous report [28]. The chemical structures of these compounds are shown in Fig. 1.

1 M sulfamic acid solutions containing DTAB and 12-4-12 at eight different concentrations were prepared in fresh distilled water. The concentration range for DTAB and 12-4-12 were 0.06–30.5 mM and 0.001–0.5 mM, respectively. 1 M sulfamic acid solution without any surfactant was considered as the blank solution for all electrochemical tests.

2.2. Surface preparation

The mild steel panels were obtained from Mobarake steel Company. The specimens were abraded using emery paper 600 and 800,

respectively and then degreased using acetone. An area of 1 cm² of each sample was exposed to the electrolytes while other areas of the plate were sealed with a beeswax–colophony mixture.

2.3. Surface tension measurements

The equilibrium surface tension as a function of surfactant concentration was measured with a KRUSS Tensiometer (model K100-MK2) at 20 ± 1 °C. The glassware was cleaned with chromic acid and then pure water carefully. The platinum ring was washed with ethanol and burned 3–4 times before each measurement. The surface tension measurements for each concentration were repeated several times to obtain the maximum deviation of 0.11 and 0.24 mN m⁻¹ for DTAB and 12-4-12, respectively. Doubly distilled water with a surface tension of about 72 mN m⁻¹ was used to prepare all solutions, as no precipitation (or solid particles) of surfactants was observed in the acidic solution at 20 °C.

2.4. Electrochemical impedance spectroscopy

EIS test was implemented on mild steel panels with dimensions of 2 cm × 6 cm and thickness of 2 mm using Ivium Compactstat at open circuit potential within frequency range of 10 mHz–10 kHz with 10 mV perturbations after 6 h [29] immersion in 150 mL acid solutions. Reference and counter electrodes were silver–silver chloride (Ag/AgCl) and graphite, respectively.

2.5. Atomic force microscopy

Prepared mild steel panels with dimensions of 1 cm × 1 cm after 6 h exposure to 150 mL of 1 M sulfamic acid solutions without and with different concentrations of DTAB and 12-4-12 at room temperature were cleaned with distilled water, then dried with a cold air blaster, and were analyzed by means of Atomic Force Microscope (model Veeco) operating in non-contact mode.

3. Results and discussion

3.1. Surface tension measurements

The values of surface tension (γ) were measured in 1 M sulfamic acid solution for various concentrations of the DTAB and 12-4-12 at $T = 293$ K. The relation between surface tension (γ) and concentration (c) for DTAB and 12-4-12 was inspected. Plot of surface tension (γ) versus $\log c$ indicate that by increasing the concentration of these cationic surfactants, surface tension decreases. At a certain concentration known as critical micelle concentration (cmc), the surfactant molecules form micelles. The intercept of two straight lines designates the critical micelle concentration (cmc).

The surface active parameters of surfactants including maximum surface excess concentration (Γ_{\max}), effectiveness (π_{cmc}), head group surface area of the surfactant or minimum area per molecule (A_{\min}) and standard free energy of micellization ($\Delta G_{\text{mic}}^{\circ}$) onto air/solution interface were calculated using the Eqs. (1)–(4) as follows [30–32]:

$$\Gamma_{\max} = \frac{-1}{2.303nRT} \left[\frac{\partial \gamma}{\partial \log c} \right]_T \quad (1)$$

$$\pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} = 20 + nRT\Gamma_{\max} \ln \left(\frac{\text{cmc}}{c_{20}} \right) \quad (2)$$

$$A_{\min} = \frac{1}{(\Gamma_{\max} \times N_A)} \quad (3)$$

$$\Delta G_{\text{mic}}^{\circ} = -2.303RT \log(\text{cmc}) \quad (4)$$

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