



Efficiency of cationic gemini surfactants with 3-azamethylpentamethylene spacer as corrosion inhibitors for stainless steel in hydrochloric acid



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ABSTRACT

The corrosion inhibition efficacy of two cationic gemini surfactants with 3-azamethylpentamethylene spacer on AISI 304 stainless steel in 3 M HCl was investigated by polarisation measurements and electrochemical impedance spectroscopy (EIS). Following corrosion testing, the surface of stainless steel samples was studied by scanning electron microscopy (SEM). The results showed that the effectiveness of corrosion inhibition were up to 95% depending on the C-chain length and the gemini surfactant concentration. The inhibitive action is due to an adsorption of inhibitor molecules onto the metal surface following a Langmuir adsorption isotherm model. The variation in the cathodic and anodic branches reveals that the surfactants tested act as mixed-type inhibitors. The highest inhibition efficiency was reached around the values of the critical micelle concentration. The results obtained from both polarisation and EIS measurements are in a good agreement.

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1. Introduction

Cationic gemini surfactants are an interesting class of chemical compounds. These dimeric surfactants consist of two monomeric moieties linked by a spacer [1], which can be flexible (e.g. polymethylene groups) or rigid (e.g. benzene ring) [2]. Interest in gemini surfactants arises from their superior aggregation, surface and biological properties compared to conventional analogues. Dicationic compounds strongly reduce the surface tension [3], exhibit lower critical micelle concentration (CMC) values [4] and so much higher biological activity [5]. In terms of concentration, they are about one to two orders of magnitude more efficient compared to conventional surfactants [1,6,7]. Moreover, from an environmental point of view, dicationic compounds are less hazardous than monomeric ones [8]. Due to their excellent properties, gemini surfactants can have many potential industrial applications such as cleaning agents and detergents, biocides, preservatives and solubilisation agents in textile dyeing [7,9–14]. They can be also applied in nanotechnology as gene delivery agents and supramolecular solvents [15–17]. Recently, greater attention has been paid to the use of gemini surfactants as corrosion inhibitors (CIs) for metals, especially in acidic environments [18–24]. The mechanism of corrosion inhibition is based

on the adsorption of surfactant molecules onto the metal surface, replacing water molecules and forming a protective film [25,26]. The process is physicochemical. The electrostatic interactions between positively charged nitrogen atoms and negatively charged metal surface are related to physisorption [27]. Chemisorption is connected with donor-acceptor interactions [28]. Adsorption is favourable due to the presence of electron-rich structures such as heteroatoms with unbonded electrons (N, O, S, P) [29,30] and π electrons (benzene rings, multiple bonds) [22,24] as these can share electrons with the free *d*-orbitals of metals [27].

A key parameter for using surfactants as corrosion inhibitors is the critical micelle concentration value (CMC), a value related to the surfactant concentration when molecules start forming aggregates (micelles). Typically at this value, surfactants first adsorb onto an interface (air-water, water-metal surface) and then form micelles or multilayers. The CMC value depends on the chemical structure of the gemini surfactants. Increasing the length of the alkyl chain [31,32], the spacer [33] and the number of quaternary nitrogen atoms [34,35] decrease the CMC values. Also, heteroatoms or multiple bonds change the aggregation properties of the molecules [7,36]. Therefore, the efficacy of corrosion inhibition can be influenced by a reasonable modification of gemini surfactant structure [22].

Corrosion in acidic environments is a serious problem in petrochemical, marine or chemical production [37,38] due to the use of hydrochloric acid solutions [29] for cleaning, pickling, descaling or oil well acidification [26,39]. Every year corrosion results in huge economic

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losses, decreasing operation efficiency and increasing the risk of accidents [40].

Stainless steels are widely used in industry as construction materials for piping, tanks and vessels etc. [25,38], because of their good corrosion resistance due to the presence of a passive layer (mixed oxide layer) on its surface. Despite the good properties of stainless steel, corrosion may occur and the use of protection systems is needed [41]. One option would be the use of cationic gemini surfactants, however, there is a lack of information on their performance as corrosion inhibitors for stainless steels.

Therefore, in this paper, the efficiency of cationic gemini surfactants with a 3-azamethyl pentamethylene spacer as corrosion inhibitors of stainless steel in 3 M hydrochloric acid is studied by electrochemical techniques and surface morphology analysis by scanning electron microscopy (SEM).

2. Materials and experimental techniques

2.1. Cationic surfactants

Gemini surfactants, 3-azamethyl-1,5-pentamethylene-bis(*N*-dodecyl-*N,N*-dimethylammonium bromide) (3N-12) and 3-azamethyl-1,5-pentamethylene-bis(*N*-octadecyl-*N,N*-dimethylammonium bromide) (3N-18) have been prepared by a method previously described in the literature [7,42]. The chemical structure of the synthesised surfactants is presented in Fig. 1.

2.2. Stainless steel

The working electrode was made of stainless steel (AISI 304). The chemical composition of the working electrode in (weight %) being: Cr 17–20, Mn < 2, Ni 8–11, C < 0.08, Fe balance.

2.3. Electrolytes

The test electrolyte, 3 M HCl was prepared by dilution of analytical grade HCl (32%) with deionised water. Solutions with different concentrations of inhibitors were prepared from the stock solution of 3 M HCl. The range of concentrations for the compound with twelve carbon atoms in the alkyl chain was: 0.1–2 mM and for the one with eighteen carbon atoms was 0.005–0.1 mM. The concentration chosen were based upon CMC values of the surfactants previously determined by the authors using conductometry methods [43]: 1.06 mM for 3N-12 and 0.076 mM for 3N-18. All experiments were carried out at room temperature in a naturally aerated test solution.

2.4. Electrochemical methods

Electrochemical tests were carried out using a conventional three-electrode cell with a platinum counter electrode, a saturated calomel electrode (SCE) as a reference electrode and a working electrode of stainless steel AISI 304 plate (2.5 × 2.5 cm). All polarisation curves

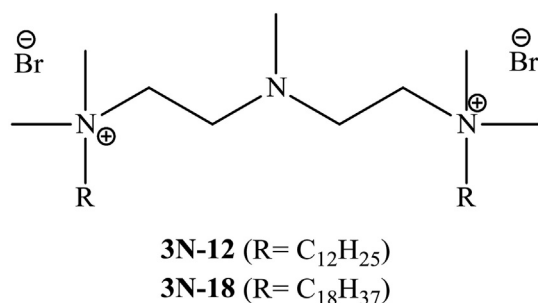


Fig. 1. Structure of the *N*-substituted gemini surfactants.

were recorded using a potentiostat (Versastat™ 4.0). Individual separate anodic and cathodic potentiodynamic polarisation measurements were obtained by changing the electrode potential automatically from (cathodic) OCP to -300 mV vs the OCP and (anodic) OCP to $+300$ mV vs OCP, respectively, with a scan rate 0.5 mV s⁻¹. Linear polarisation resistance measurements (LPR) were obtained by changing the potential from -20 to 20 mV versus the measured OCP with a scan rate of 10 mV min⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a potentiostat (Versastat™ 4.0). Impedance spectra were obtained over a frequency range of 100 kHz to 10 mHz with a 10 mV sine wave as the excitation signal at open circuit potential. SCE and platinum electrodes were used as the reference and counter electrodes respectively.

2.5. Surface morphology

The morphology of the 304 stainless steel surface after the corrosion test was also studied by scanning electron microscopy (SEM) using a FEI Quanta 200 operating at 20 kV and different magnifications.

3. Results and discussion

3.1. Open circuit potential

Open circuit potential measurements were obtained at room temperature for the stainless steel samples in 3 M HCl without (blank) and with the addition of different concentrations of either 3N-12 or 3N-18 gemini surfactants. Fig. 2 shows the trend in the OCP with time. The OCP of the blank solution was -401 mV_{SCE} after 1 h, reaching -355 mV_{SCE} after 24 h. Adding inhibitors shifted the potential towards more positive values than the values for the blank solution. The stainless steel potential in the blank solutions changed from -401 mV_{SCE} to -355 mV_{SCE} after 24 h of immersion. 3N-18 appeared to be the most efficient as the potential increased from -348 mV_{SCE} to -313 mV_{SCE} (after 24 h at 0.01 mM). While 1 mM was the best concentration of 3N-12 which shifted OCP from -352 mV_{SCE} to -330 mV_{SCE}.

3.2. Potentiodynamic polarisation measurements

Figs. 3 and 4 display the potentiodynamic anodic and cathodic polarisation curves of stainless steel in 3 M hydrochloric acid in the presence and absence of the selected inhibitors. It is noticeable that both anodic metal dissolution and cathodic hydrogen evolution reactions were reduced by adding the inhibitors. There is a positive shift for the anodic overvoltage and the cathodic overvoltage compared to

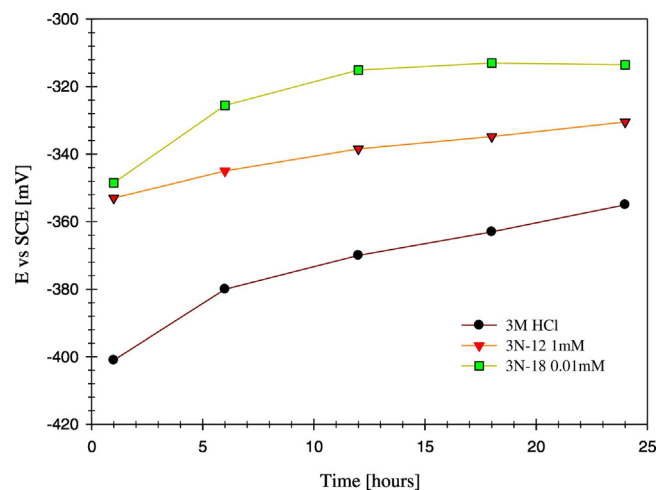


Fig. 2. Open circuit potential-time curves for stainless steel electrode immersed in 3 M HCl in the absence and presence of synthesised cationic surfactants.

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