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PHYSICOCHEMICAL PROBLEMS OF MATERIALS PROTECTION

Non-Gemini Dicationic Surfactants with Alkylthio Group as Corrosion Inhibitor for Mild Steel in HCl Solution

Serkan Öztürk*

Department of Chemistry, Faculty of Science and Arts, Bursa Uludağ University, Bursa, 16059 Turkey

**e-mail: serkanozturk@uludag.edu.tr*

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Abstract—Two non-geminine dicationic surfactants containing long chain-dodecyl and hexadecylthio groups were synthesized and their structures were confirmed by spectroscopic methods (FT-IR and NMR). At different concentrations of synthesized inhibitors (5, 25, 50 and 100 ppm) their effectiveness against corrosion of mild steel was investigated by weight loss method for different immersion times (1–4 day) in 1.0 mol L^{-1} HCl solution. In addition, inhibition efficiencies were investigated in HCl solutions with different concentrations (1.0, 2.0 and 4.0 mol L^{-1}) at 50 ppm inhibitor concentration. While they exhibited good inhibitory properties at all immersion times, they showed the best inhibition activities at 4 days of immersion. In corrosion inhibition tests performed in 2.0 to 4.0 mol L^{-1} HCl solutions, dicationic surfactant containing dodecylthio group showed higher protection. The critical micelle concentrations of the two synthesized compounds and the surface tension at this concentration were determined, and scanning electron microscopy (SEM) images of metal surfaces were obtained to support the corrosion results.

Keywords: synthesis, alkylthio, corrosion inhibitor, weight loss, SEM

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1. INTRODUCTION

Corrosion is the change of physical, chemical and mechanical properties of materials as a result of chemical and electrochemical reactions with the effect of the environment [1]. If the material in question consists of metals and alloys, then the expression metal corrosion can be used and metallic corrosion can also be defined as the state of corrosion of metal or metal alloys by oxidation or other chemical effects. Corrosion is an undesirable event, causing great economic losses to every country. A large part of iron and steel is lost every year as a result of corrosion or becomes unusable. Metal lost as a result of corrosion causes economic losses far above its own cost. On the other hand, corrosion losses affect not only the iron and steel industry, but also the efficiency of all investments made by utilizing this industry, and become a matter of concern to the country's economy. In addition to material losses, corrosion is an event that harms human life and health and causes environmental pollution [1].

In the industry, pickling, which is a highly effective surface cleaning method, is frequently used to clean the rust on the metal surface and the foreign materials on the surface. The most used acids in this cleaning process are HCl and H_2SO_4 solutions [2]. During the cleaning process, metal corrosion occurs as a result of oxidation over time on the metal surface in contact with the acid. In the cathode reaction of metal corrosion in an acidic environment, hydrogen ions from the acid are reduced and H_2 gas is formed. The most widely used method to prevent or reduce metal corrosion that occurs in an acidic environment is the use of inhibitors.

Corrosion inhibitors can control, reduce, or prevent reactions between a metal and its surroundings when added to the medium in small quantities [3]. It is desired that inhibitors that will have an anti-corrosion effect dissolve well enough in the corrosive electrolyte environment, close the active centers forming the relatively unstable points on the material surface, adhere well to the surface and cover it, and cut the contact of the surface or active centers with the solution.

Compounds containing sulfur atoms in their structure have always been an important subject of investigation. In the literature, there are many studies on these sulfur-containing compounds for different fields. The most important of these studies are the anti-tumor [4–6] and anti-HIV [7] studies on these compounds. Apart from these, it has been reported that sulfur-containing compounds are used as corrosion inhibitors in acidic [8–13] and mineral oil [14] environments. In sulfur compounds used as corrosion inhibitors, the sulfur atom presents unshared electron pairs and is adsorbed to the metal by chemical adsorption. With this chemical adsorption, it plays an active

Table 1. Physicochemical properties of the cationic surfactants

Compounds	Chemical formula	MW, g/mole	Yield, %	Melting point, °C
3a	$C_{24}H_{53}Br_2N_3OS$	591.58	73	71–72
3b	$C_{28}H_{61}Br_2N_3OS$	647.68	78	83–84

[a] Value measured at 20°C.
[b] Value measured at critical micelle concentration of the surfactant.

role in the fight against corrosion by supporting the adsorption of the compound on the metal surface.

In this study, it was aimed to synthesize 2 new non-gemini dicationic surfactants containing long chain (C12 and C16) alkylthio groups and to investigate the effectiveness of these compounds against metal corrosion in acidic environment. In addition, the critical micelle concentrations of the two synthesized compounds and the surface tension at this concentration will be determined, and scanning electron microscopy (SEM) images of metal surfaces will be obtained to support the corrosion results.

2. EXPERIMENTAL

2.1. Materials and Instrumentation

Relevant thiol compounds, ethylchloroacetate, 3-dimethylamino-1-propylamine and (2-bromoethyl)trimethyl ammonium bromide reagents used in the synthesis and all solvent chemicals were purchased from Merck and Sigma-Aldrich companies. The FT-IR spectra of the dicationic surfactants synthesized as the final product were obtained with the Perkin Elmer Spectrum 100 (USA) FT-IR spectrophotometer. NMR spectra (^{1}H NMR and ^{13}C NMR) of the same compounds were obtained with Agilent 600 MHz Premium Compact NMR spectrometer in DMSO (Dimethylsulfoxide) solvent. NUVE EV 018 vacuum oven was used to dry the metal coupons until they reach constant weight.

2.2. Synthesis of Compounds

2.2.1. Synthesis of etil-(2-alkylthio)-acetates (1a–1b). 13.67 mmol of the thiol compound and 20.50 mmol of potassium carbonate were mixed in a reaction flask for about 30 minutes. Then, a solution of 13.67 mmol ethylchloroacetate in acetone was slowly added to this mixture. The reaction mixture was refluxed at 100°C overnight. When the reaction was complete, the acetone was evaporated in the evaporator. Purified water was then poured into the reaction mixture and extracted with ethyl acetate. After extraction, the ethyl acetate phase was dried with Na_2SO_4 and the ethyl acetate was evaporated. The yields of **1a–1b** compounds obtained as light yellow oily were calculated as 86 and 91%, respectively.

2.2.2. Synthesis of *N*-[(3-dimethylamino)propyl]-2-alkylthio-acetamides (2a–2b). A solution of 3-dimethylamino-1-propylamine in 20 mL ethanol was added in the same mole number on the related ester compound (**1a–1b**) in the reaction flask. The reaction mixture was refluxed at 150°C for 24 h. When the reaction was finished (control by TLC), the solvent was evaporated and then cooled to room temperature. The yields of the products obtained as white wax after cooling were calculated as 96 and 93%, respectively. Melting points were determined as 33–34 and 39–40°C, respectively.

2.2.3. Synthesis of N^1,N^1,N^1,N^2,N^2-pentamethyl-N^2-(3-(2-(alkythio)acetamido)propyl)ethane-1,2-diaminium dibromide (3a–3b). The corresponding acetamide derivative compound (**2a–2b**) and (2-bromoethyl)trimethyl ammonium bromide reagent in the same mole number were refluxed in 20 mL ethanol solvent for 48 h. At the end of the time, the ethanol was evaporated and the mixture was washed with hot acetone. The small amount of solid reagents remaining without reaction were separated by filtration. Acetone was evaporated to obtain dicationic surfactant products dissolved in hot acetone. Yellow solid wax products (**3a–3b**) were recovered. The yields and melting points of the synthesized products are given in Table 1.

2.3. Corrosion Tests in Acidic Environment

Metal plates prepared from cold rolled steel with low carbon content were used for corrosion tests carried out in acidic environment. This steel material complies with DIN EN 10130 norm [15] and its composition is 0.07% (C), 0.35% (Mn), 0.015% (P), 0.015% (S) and the rest is Fe.

The preparation phase of the corrosion tests based on gravimetric measurements was carried out with the method previously reported in the literature [16]. For this purpose, metal plates cut in 0.1 cm thickness, 2.0 cm width and 5.0 cm length were kept in 15% HCl solution for 5 minutes to remove rust stains and oxide layers. The plates were then cleaned with distilled water. The surface of the dried metal plates was sanded with sandpaper (150) and kept in acetone for a while. The plates removed from the acetone were dried first in the vacuum oven and then in the open air for a short time until they reached constant weight. The mass of the metal plate was weighed before the test.

Before the corrosion tests carried out in acidic aqueous medium, 1.0, 2.0 and 4.0 mol L^{-1} HCl solu-

tions were freshly prepared from 37% concentrated hydrochloric acid. After weighing certain amounts of dicationic surfactants (**3a–3b**) used in the tests, they were dissolved in 100 mL 1.0 mol L^{-1} HCl and placed in 150 mL glass containers with lids. In this way, 5, 25, 50 and 100 ppm solutions of surfactants in acidic medium were prepared. On the other hand, for the control test and comparison, 100 mL of 1.0 mol L^{-1} HCl was placed in another glass container and no inhibitor was added into it. Metal plates weighed before the test were immersed in these prepared acidic solutions. The solutions were kept at room temperature for 1, 2, 3 and 4 days without mixing. After the test periods, the metal plates removed from the corrosive environment were rinsed with distilled water. Afterwards, the plates were cleaned with acetone and dried first in a vacuum oven and then in the open air for a short time, and the final mass of the metal was weighed. The weight loss in metal coupons immersed in each corrosive solution was calculated by taking the difference between the pre-test and post-test metal masses. In addition, the weight loss measurements in 2.0 and 4.0 mol L^{-1} HCl solutions were also performed for the two inhibitors with the concentration of 50 ppm.

2.4. Determination of Critical Micelle Concentration (CMC) of Synthesized İnhibitors

The critical micelle concentration of the synthesized dicationic surfactants was determined using the conductometric method. Conductivity measurements were carried out using OHAUS Starter 3100M brand digital conductivity meter. To measure the specific conductivity in each surfactant, a step-by-step dilution-extraction method was followed. CMC values were determined from the breakpoint on each conductivity curve versus surfactant concentration.

2.5. Surface Tension at Critical Micelle Concentration (γ_{CMC})

Surface tensions of aqueous solutions of dicationic surfactants at critical micelle concentration were measured by capillary rise method [17, 18]. The capillary used for measurement is Na-heparinized micro hematocrit tube (NRIS, Soda Lime glass, diameter = 1.0 mm, length = 75 mm). The corresponding values were measured at 20°C.

2.6. Metal Surface İmage by Scanning Electron Microscope (SEM)

SEM image of the metal surface was taken on metal plates cut into squares with a thickness of 0.1 cm, a width of 2.0 cm, and a length of 2.0 cm. After the corrosion tests carried out in an acidic environment, the metal plates were washed with acetone and dried in a vacuum desiccator, and SEM images of the metal surfaces magnified 1000 times under high vacuum were obtained with a scanning electron microscope device (Carl Zeiss EVO 40).

3. RESULTS AND DISCUSSION

3.1. Chemical Synthesis

The synthesis scheme of organic dicationic surfactants designed and synthesized against metal corrosion in an acidic environment is given in Fig. 1. As can be seen in Fig. 1, the synthesis of organic inhibitors was carried out in 3 steps. In the first step, compounds **1a–1b**, which are the starting products of the reaction series, were synthesized according to the widely known substitution procedure. In the second step, the ester group in compounds **1a–1b** was converted to the amide functional group (**2a–2b**) by reaction with 3-dimethylamino-1-propylamine. In the last step, to synthesize dicationic surfactants, related acetamide derivatives (**2a–2b**) containing long chain thio group were reacted with the same mole number (2-bromoethyl)trimethyl ammonium bromide in ethanol for 48 h. In this third and last step, corrosion inhibitors (**3a–3b**) were obtained as a result of the quaternization reaction.

The confirmations of the compound structures (**3a–3b**) were realized by the FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic methods. The FT-IR, ^{1}H NMR and ^{13}C NMR spectra of compound **3a** are given in Fig. 2.

The FT-IR spectrum of (**3a**) showed absorption bands at 3231 cm^{-1} for the amide –NH– group, at 1642 cm^{-1} for the amide C=O group and at 697 cm^{-1} for the CH_2–S–CH_2 group. Similar adsorption bands were obtained for the other synthesized dicationic surfactant compound. The 1H NMR spectrum of (**3a**) showed a weak triplet at δ = 8.22 ppm for the amide $\underline{H}$NC=O proton, a singlet at 3.30 ppm for the $(C\underline{H}_3)_2$–N^+ protons, a singlet at 2.69 ppm for the +N–$(C\underline{H}_3)_3$ protons, and two peaks at 3.21 and 1.46 ppm for the two protons of methylene groups attached to the sulfur atom, respectively. In the ^{13}C NMR spectrum of (**3a**), peaks for the carbon atoms of ($\underline{C}$=O), [$(\underline{C}H_3)_2N^+$–CH_2–CH_2–$N^+(CH_3)_3$], [N^+–CH_2–CH_2–$N^+(\underline{C}H_3)_3$], (S–$\underline{C}H_2$–CO–NH–CH_2), ($\underline{C}H_2$–S–CH_2–CO–NH) groups are shown at δ = 170.40 ppm, 53.86 ppm, 42.74 ppm, 36.38 ppm and 33.25 ppm, respectively. The same specific peaks for the protons and carbon atoms were also obtained in the NMR spectra of compound **3b**.

3.2. Corrosion Tests in HCl Solutions

Weight loss, percent inhibition efficiencies (η %) and corrosion rate (CR) values determined by gravimetric method in 1.0 mol L^{-1} HCl aqueous solution for different immersion time are given in Tables 2, 3

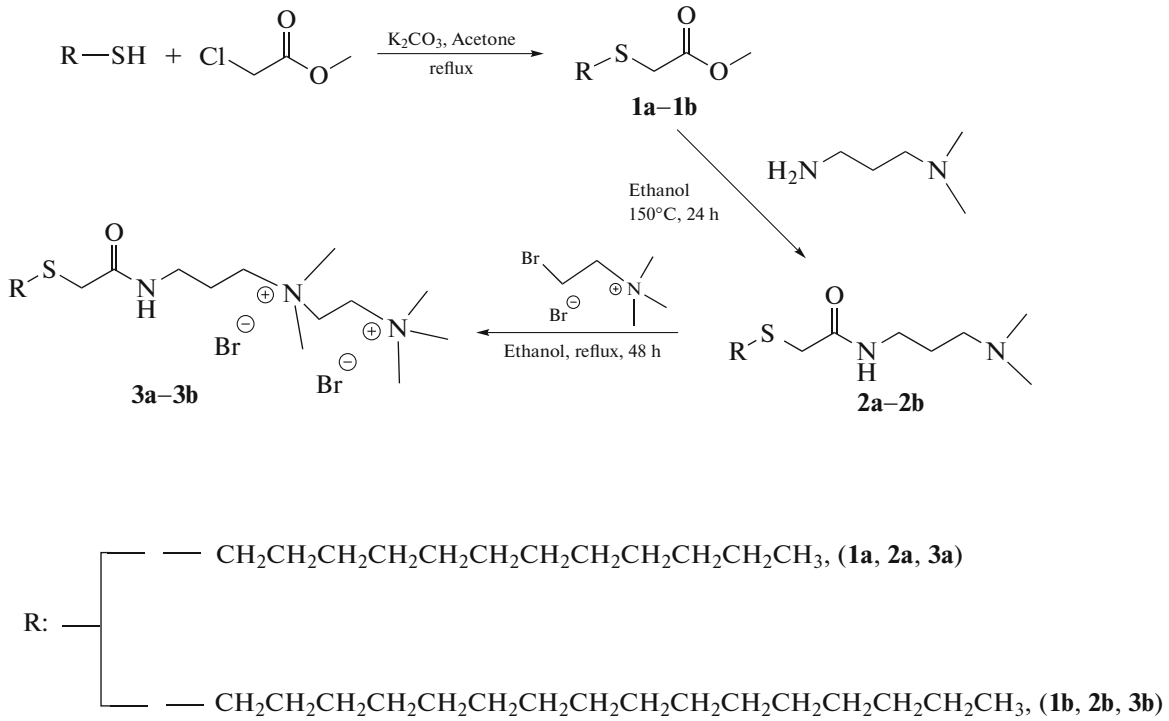


Fig. 1. Synthesis steps of dicationic surfactants.

and 4, respectively. The following equation (Eq. 1) can be used for percent inhibition efficiency:

$$\eta\,\% = \frac{W_o - W}{W} \times 100, \quad (1)$$

where (η %) is the percentage inhibition efficiency, W_o is the weight loss for the coupon in the absence of inhibitor and W is the weight loss in the presence of an inhibitor. Corrosion rate values (mg cm^{-2} day^{-1}) were calculated with the following equation (Eq. (2)):

$$CR = \frac{\Delta W}{At}, \quad (2)$$

where, ΔW is weight loss (mg); A is the area of the coupon (cm^2) and t is immersion time (day). Corrosion tests were carried out at room temperature (25°C) in 1.0 mol L^{-1} HCl solution, at different inhibitor concentrations (5, 25, 50 and 100 ppm) and at different immersion times (1–4 days). Apart from this, corrosion tests were also carried out for 50 ppm concentration of inhibitors in 2.0 and 4.0 mol L^{-1} HCl solutions at room temperature for 1 day. The weight loss and inhibition efficiencies obtained at different acid concentrations are shown in Table 5. In all corrosion tests, inhibitors **(3a–3b)** were dissolved directly in HCl solutions and all calculations were made from the weight loss values.

3.2.1. Effect of the inhibitor concentration, immersion time and HCl concentration on corrosion inhibition efficiency. Inhibitor concentrations studied in corrosion tests were chosen as 5, 25, 50 and 100 ppm. In general, it is known that at inhibitor concentrations lower than the critical micelle concentration (CMC) for surfactants, inhibition efficiencies increase as the concentration increases [19–21]. Inhibition efficiency results are almost unchanged at CMC and above inhibitor concentrations. Considering the weight losses in Table 2 and the inhibition efficiency results in Table 3 for different inhibitor concentrations, it is seen that both dicationic surfactants protect the metal well against corrosion in HCl environment. In particular, for compound **3a**, both high and very close inhibitions were obtained at all studied concentrations. In fact, it was determined that the inhibition percentages decreased slightly at 100 ppm inhibitor concentration. The fact that the weight losses and inhibition efficiency percentages do not change much as the concentration increases, proves that the critical micelle concentration (CMC) of compound **3a** is reached. As can be seen, for compound **3b**, inhibition efficiencies at 5 ppm inhibitor concentration were calculated below 90% (excluding 4 days of immersion) (Table 3). It was observed that the inhibition efficiencies increased as the concentration of the inhibitor **3b** increased. These results constitute evidence that compound **3b** has not yet reached the effective concentration (CMC). In Fig. 3, the efficiency results of the surfactants against inhibitor concentrations can be seen graphically.

It was determined that as the immersion time in 1.0 mol L^{-1} HCl solution increased (1 → 4 days), weight loss and inhibition activities generally

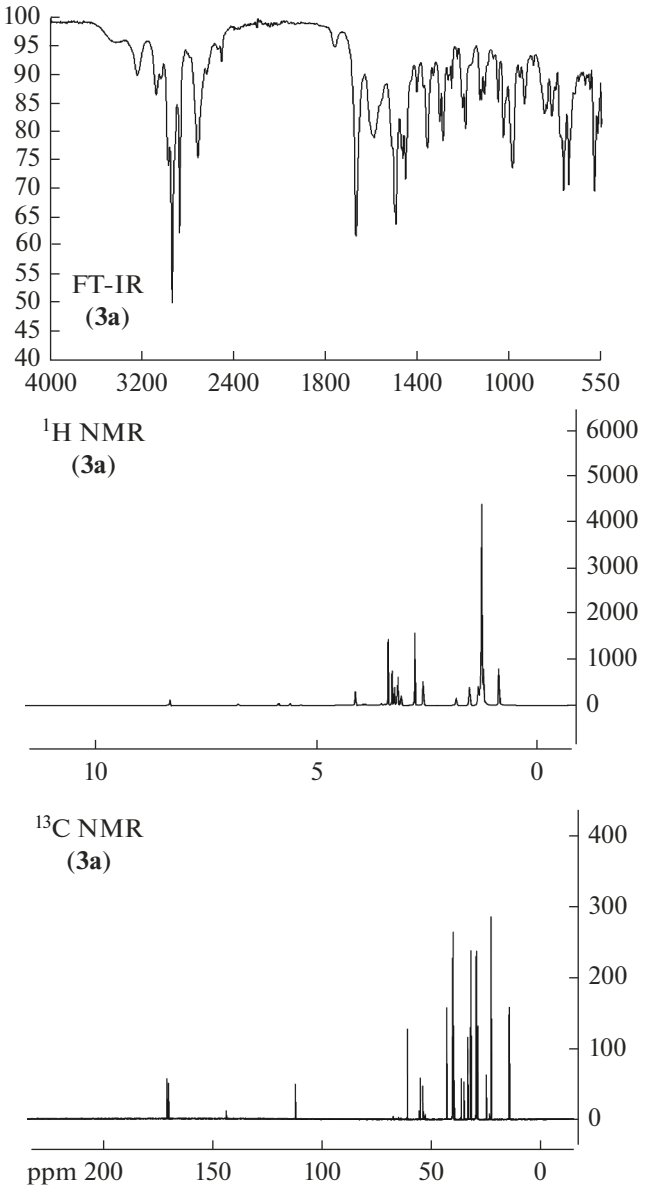


Fig. 2. FT-IR, ^{1}H NMR and ^{13}C NMR spectra of compound **3a**.

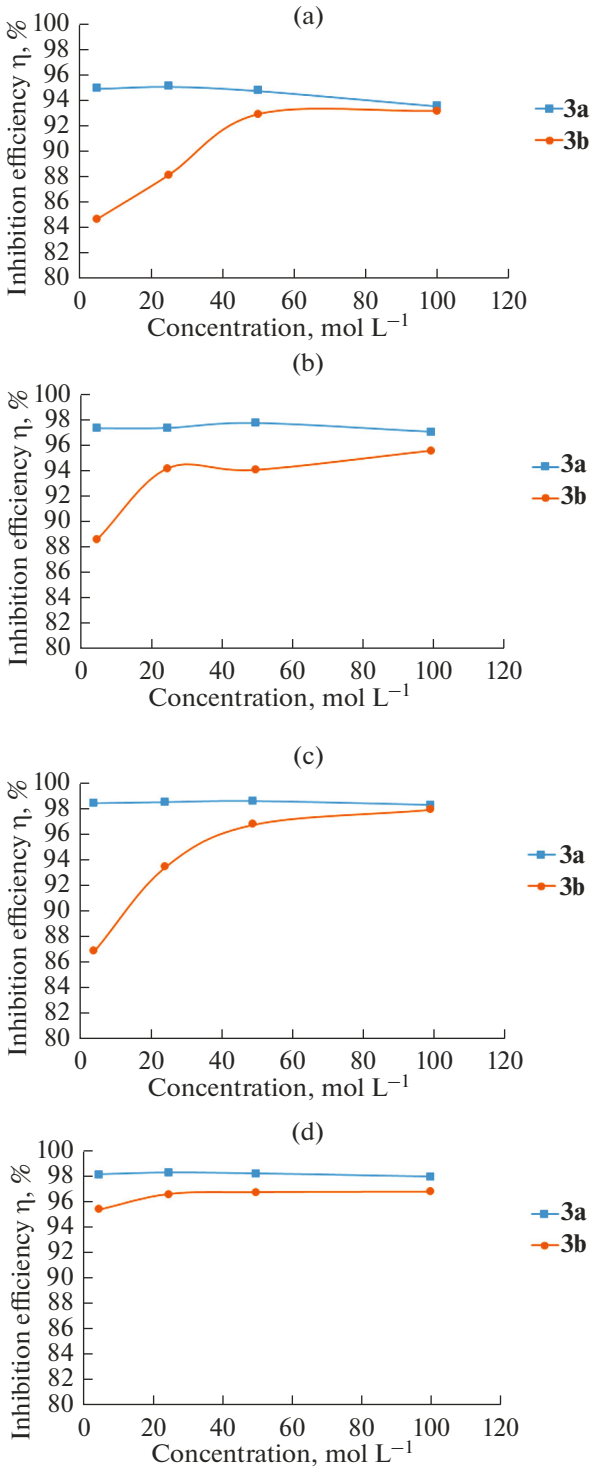


Fig. 3. Plot of inhibition efficiency against inhibitor concentration from the weight loss measurements in 1.0 mol L^{-1} HCl at room temperature after immersion times of (a) 1, (b) 2, (c) 3 and (d) 4 day.

increased. Weight loss in the presence of inhibitor was very low and increased slightly with increasing immersion time. In the corrosive medium without inhibitor, the weight loss was higher and increased a lot with the increase of immersion time. Inhibitors form a protective film on the metal surface and prevent the acidic corrosive medium from reaching the metal surface, thus preventing the oxidation of metal atoms from the surface and causing a small loss of weight. However, in the absence of the inhibitor, the acidic corrosive environment damages the metal surface and allows too many metal atoms to be oxidized, and thus the weight loss was high. In an inhibitor-free medium, the longer the metal surface is exposed to 1.0 mol L^{-1} HCl solution, the greater is the weight loss. This change in weight losses in the media with and without inhibitors, with the increase of immersion time in the corrosive

Table 2. Weight loss of the metal coupons in 1.0 mol L^{-1} HCl medium without and with different concentration of inhibitor for 1–4 days at room temperature

Immersion time, day	Weight loss, mg cm^{-2} [a]								
	without inhibitor	**3a**				**3b**			
		5 ppm	25 ppm	50 ppm	100 ppm	5 ppm	25 ppm	50 ppm	100 ppm
1	12.44	0.64	0.62	0.66	0.81	1.91	1.48	0.89	0.86
2	36.50	1.00	0.99	0.85	1.10	4.16	2.14	2.18	1.63
3	71.14	1.23	1.17	1.10	1.32	9.38	4.75	2.40	1.57
4	83.54	1.47	1.35	1.41	1.63	3.74	2.75	2.63	2.60

[a] Mean of the three measured values.

Table 3. Corrosion inhibition efficiencies (η %) for varying concentrations of compounds **3a–3b** in 1.0 mol L^{-1} HCl medium for 1–4 days at room temperature using weight loss measurements

Immersion time, day	Corrosion inhibiton efficiency η (%) of the inhibitors							
	3a				**3b**			
	5 ppm	25 ppm	50 ppm	100 ppm	5 ppm	25 ppm	50 ppm	100 ppm
1	94.86	95.02	94.69	93.49	84.65	88.10	92.85	93.09
2	97.26	97.29	97.67	96.99	88.60	94.13	94.03	95.53
3	98.27	98.36	98.45	98.14	86.81	93.32	96.63	97.79
4	98.24	98.38	98.31	98.05	95.52	96.71	96.85	96.89

media, also led to a slight increase in the inhibition activities. The change in the corrosion efficiency against the immersion time at 50 ppm inhibitor concentration can be viewed as a graph in Fig. 4.

Corrosion inhibition efficiencies (η %) of 50 ppm concentrated inhibitors, which were immersed in 1.0, 2.0 and 4.0 mol L^{-1} of HCl solutions were given in Table 5. The corrosion tests in varying HCl concentration were investigated at room temparature for 1 day of immersion time. As the HCl concentration increased, the weight loss values increased both in the medium with and without the inhibitor. The increase in weight loss was less in the medium with inhibitor and more in the medium without inhibitor. Exposure to a higher concentration of HCl in an inhibitor-free environment causes more metal atoms to be oxidized from the metal surface, as it will provide a more corrosive environment [16]. Since the corrosion rate is high in an acidic environment, the weight loss increases as the HCl concentration increases. As seen in Table 5, when the media with inhibitor were compared, as the HCl concentration increased, the increase in weight loss for metal in the presence of the inhibitor **3b** was greater than in the inhibitor **3a**. As a matter of fact, while the weight losses of the two inhibitors in metal are close to each other in 1 mol L^{-1} HCl corrosive medium (0.66 mg cm^{-2} for **3a**, 0.89 mg cm^{-2} for **3b**), they are very different from each other in 4.0 mol L^{-1} HCl medium (1.99 mg cm^{-2} for **3a**, 20.71 mg cm^{-2} for **3b**). This situation was also reflected in the results of the

Table 4. Corrosion rate values for varying concentrations of compounds **3a–3b** in 1.0 mol L^{-1} HCl medium for 1–4 days at room temperature

Immersion time, day	Corrosion rate, mg cm^{-2} day^{-1}								
	without inhibitor	**3a**				**3b**			
		5 ppm	25 ppm	50 ppm	100 ppm	5 ppm	25 ppm	50 ppm	100 ppm
1	12.44	0.64	0.62	0.66	0.81	1.91	1.48	0.89	0.86
2	18.25	0.50	0.49	0.43	0.55	2.08	1.07	1.09	0.82
3	23.71	0.41	0.39	0.37	0.44	3.13	1.58	0.80	0.52
4	20.89	0.37	0.34	0.35	0.41	0.94	0.69	0.66	0.65

Table 5. Weight loss and corrosion inhibition efficiencies η (%) of 50 ppm concentrated inhibitors, which were immersed in varying concentrations of HCl solution for 1 day at room temperature

HCl concentration, mol L^{-1}	Weight loss without inhibitor, mg cm^{-2}	3a		3b	
		weight loss with 50 ppm of inhibitor, mg cm^{-2}	inhibition efficiency η, %	weight loss with 50 ppm of inhibitor, mg cm^{-2}	inhibition efficiency η, %
1.0	12.44	0.66	94.69	0.89	92.85
2.0	25.69	0.97	96.22	3.63	85.87
4.0	70.35	1.99	97.17	20.71	70.56

inhibition efficiency. As the concentration of the corrosive acid medium increased, the increase in weight loss for compound **3a** was very low, so the inhibition efficiency gradually increased. However, the opposite was seen for compound **3b**. Because as the HCl concentration increased, the increase in weight loss for the compound **3b** was too high and the inhibition activities gradually decreased. After these results, it was determined that the inhibitor **3a** provided better protection against corrosion with increasing acid concentration. Figure 5, shows the change of corrosion efficiencies against HCl concentration for 50 ppm inhibitor concentration as graphically.

3.2.2. Effect of the inhibitor concentration and immersion time on corrosion rate. Calculated values related to corrosion rate are given in Table 4. Corrosion rate is high in acidic environment. While the metal is oxidized in the anode reaction of corrosion, in the cathode reaction, H^+ ions from the acid are reduced and H_2 gas is released. Cationic surfactants generally reduce the corrosion rate by inhibiting both anode and cathode reactions [22, 23]. Reducing the corrosion rate is due to the adsorption of inhibitor molecules on the metal surface. It is observed that the corrosion rates are low in the inhibitory environment (Table 4). Especially in the acidic medium containing the compound **3a**, the corrosion rates were lower than the compound **3b** and were found to be very close to each other at each inhibitor concentration. It was determined that the corrosion rates were slightly higher in the acidic medium containing compound **3b** and the corrosion rates decreased significantly as the inhibitor concentration increased. Compound **3b** has a longer hydrophobic chain (C16). Increasing the hydrophobic chain length of the corrosion inhibitor needs to significantly reduce the corrosion rate [24]. Whereas, it is concluded that compound **3a** is more effective in reducing the corrosion rate due to lower corrosion rates at each studied concentration. Weight loss and inhibition efficiency values given in Tables 2 and 3, respectively, support this result. This situation can be explained by the decrease in the solubility of the surfactant in the corrosive medium with the increase of the hydrophobic property.

Looking at Table 4, it was observed that corrosion rates were higher in the absence of inhibitors. The highest corrosion rate in the absence of inhibitor was calculated as 23.71 mg cm^{-2} day^{-1} for a 3-day immersion period. Normally, as the immersion time increases, the corrosion rate also increases. However, at the end of the 4th day, since the percentage of increase in mass loss determined for the inhibitor-free medium decreased, the corrosion rate calculated at the end of the same day showed a decrease. In media

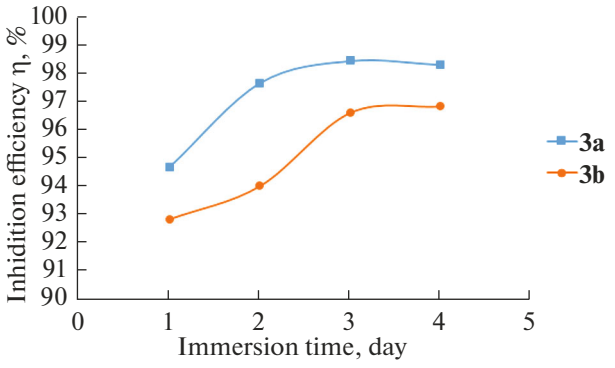


Fig. 4. Graph of corrosion inhibition efficiencies in 1.0 mol L^{-1} HCl solution against immersion time at 50 ppm inhibitor concentration.

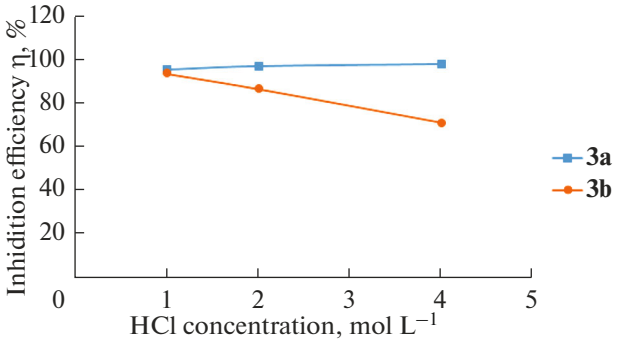


Fig. 5. The change of corrosion efficiencies against HCl concentration for 50 ppm inhibitor concentration.

Table 6. Physicochemical properties of the cationic surfactants

Compounds	CMC, $\times 10^{-4}$ mol L^{-1} [a]	γ_{CMC}, dyn cm^{-1} [a, b]	π_{CMC}, dyn cm^{-1} [a]	ΔG_{mic}, kJ mol^{-1} [a, b]
3a	17.53	19.25	53.55	−15.46
3b	8.63	12.59	60.21	−17.19

[a] Value measured at 20°C.
[b] Value measured at critical micelle concentration of the surfactant.

containing inhibitors, it is observed that the corrosion rate decreases significantly at the studied inhibitor concentrations with the increase of the immersion time. This shows that dicationic surfactants are more effective in reducing the corrosion rate on the metal surface when exposed to 1.0 mol L^{-1} HCl solution for a longer period of time.

3.3. CMC and γ_{CMC} of Inhibitors

The CMC results determined by the conductometric method of the two synthesized surfactants are given in Table 6. The measured conductivities for different concentrations of each surfactant were plotted. Related graphics are given in Fig. 6. As seen in the graphs, the concentrations showed a linear increase with the increase in conductivity. In the concentration-conductivity linear trendline, the concentration at which the slope changes was determined as the critical micelle concentration for the synthesized surfactants [25]. Conductivity measurements were carried out at 20°C. When the critical micelle concentration values in Table 6 are examined, the CMC value of the compound **3a** containing the dodecylthio group was found to be 17.53×10^{-4} mol L^{-1}, and the CMC value of the compound **3b** containing the hexadecylthio group was 8.63×10^{-4} mol L^{-1}. From these results, it can be concluded that the micelles of these cationic surfactants are formed at low concentrations. Compared to **3a** and **3b**, compound **3b** has a greater hydrophobic character because it has a longer carbon chain. Increasing the hydrophobic character of cationic surfactants decreases the critical micelle concentration [26, 27]. This result is logically compatible with the inhibition results given in Table 2, especially for compound **3a**. For compound **3a**, the fact that the inhibition activities are close to each other with the increase in concentration (5 → 100 ppm) indicates that the CMC value has been reached [28]. However, for compound **3b**, an increase was observed in the inhibition efficiency between 5 and 50 ppm, while the inhibition activities were found close to each other between 50 and 100 ppm. It is possible to explain this difference for compound **3b** as its solubility in the corrosive medium is slightly less than that of compound **3a**. Compound **3b** with a lower CMC value has a longer carbon chain, so its solubility in corrosive HCl aqueous solution decreases. As a result of this situation, it is necessary to add more **3b** compounds to the corrosive medium in order to reach the micelle concentration where it is most effective.

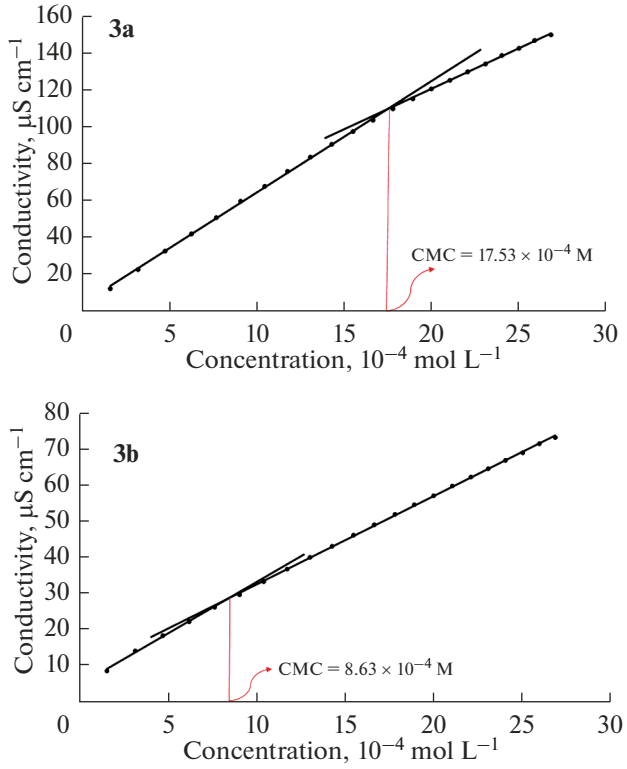


Fig. 6. Graphs of conductivity value measured against concentration.

The surface tensions (γ_{CMC}) of the two synthesized dicationic surfactants, measured by the capillary rise method at critical micelle concentrations, are given in Table 6. Surface tensions were determined to evaluate the surface activity of aqueous dicationic surfactant solutions at critical micelle concentration. Surface tension of **3b** surfactant in CMC was determined to be lower. This result shows that the surfactant compound (**3b**) containing the hexadecylthio group in its structure exhibits better surface activity properties than **3a**. The efficiency in surface tension reduction (π_{CMC}) is the amount of surface pressure reduction achieved in CMC [29]. Activity (π_{CMC}) is an indicator of the maximum reduction in surface tension and can be used to evaluate the effectiveness of surfactant in lowering the

surface tension of water [30]. This value can be calculated with the following equation (Eq. (3)):

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC}, \quad (3)$$

where γ_0 is the surface tension of pure solvent (20°C'de 72.8 dyn cm^{-1}) and γ_{CMC} is the surface tension of solution at the CMC. For compounds synthesized as corrosion inhibitor (**3a–3b**), this value was calculated as 53.55 and 60.21 dyn cm^{-1}, respectively. These results show that the synthesized dicationic surfactants have the potential to reduce the surface tension in the aqueous system. However, it is possible to say that the activity of compound **3b** is more. Because as the γ_{cmc} value decreases, the π_{cmc} value increases, the activity of the surfactant also increases [29]. Although the surface activity of the **3b** compound is higher, the fact that this situation was not reflected in the corrosion inhibition results reveals once again how important the solubility in the corrosive medium is.

The critical micelle concentration is correlated with the Gibbs free energy (ΔG_{mic}) value of micelle formation. The ΔG_{mic} value was calculated with the following equation (Eq. (4)):

$$\Delta G_{mic} = RT \times \ln(\mathrm{CMC}), \quad (4)$$

ΔG_{mic} is the Gibbs free energy of micellization, R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (293 K) and CMC is the critical micelle concetration. The lower the critical micelle concentration of surfactant is, the greater is the tendency of the substance to form micelle. The ΔG_{mic} values in Table 6 confirm this result. The free energy value of the compound **3b** with more hydrophobic character was found to be higher in the negative direction [31]. This result shows that dicationic surfactant with longer carbon chain in its structure has a higher tendency to form micelles.

3.4. SEM Images

The surface images of mild carbon steel immersed for 24 h in 1.0, 2.0 and 4.0 mol L^{-1} HCl aqueous solutions without inhibitor and containing 50 ppm inhibitor are shown in Fig. 7. All the images were taken from the 1000× magnified surface. Figures 7a–7c are SEM images of metal surfaces immersed in 1.0, 2.0 and 4.0 mol L^{-1} aqueous HCl solution without inhibitor, respectively. Figures 7d–7f are images of metal surfaces immersed in 1.0, 2.0 and 4.0 mol L^{-1} HCl solutions containing compound **3a**, respectively, while Figs. 7g–7i are images of metal surfaces immersed in acid solution containing compound **3b**. Deformation and roughness caused by corrosion products are clearly evident on the surfaces of metals (Figs. 7a–7c) immersed in acid solutions without inhibitor. It was observed that the roughness of metal surfaces immersed in acid solutions without inhibitor increased with increasing acid concentration. Looking at Figs. 7d–7f images of metal surfaces immersed in corrosive environments containing **3a** inhibitor, it is seen that corrosion products do not form, the surfaces are smooth and the smoothness is not affected by acid concentration. Scratches on metal surfaces are caused by sanding. In the images in Figs. 7g–7i, it was observed that the smoothness of the metal surfaces immersed in acid solutions containing compound **3b** decreased significantly compared to the metals immersed in acid solutions with compound **3a**; and the rough surface increased as the acid concentration increased. Findings obtained from SEM images of metal surfaces immersed in different HCl concentrations support the results of weight loss and inhibition efficiency given in Table 5. Metals immersed in a corrosive medium containing the **3a** inhibitor have high inhibition efficiency and are very close to each other (see Table 5), which is reflected in the SEM images as a smooth surface. On the other hand, in metals immersed in acid solutions with **3b** inhibitor, the inhibitory efficiency decreased as the acid concentration increased, and this result was obtained in SEM images as the roughness of the metal surfaces increased as the acid concentration increased.

3.5. Corrosion İnhibition Mechanism

The basis of the corrosion inhibition mechanism is the adsorption of dicationic surfactants to the metal surface. Dicationic surfactants containing two positively charged nitrogen atoms are adsorbed on the metal surface by electrostatic interactions (physical adsorption). For this, a dipole is formed between the chloride ions from the acid solution and the positive metal surface [32] and thus the metal surface becomes negative [28]. Then, the dicationic inhibitor may adsorb onto the negatively charged metal surface through electrostatic attraction [19].

Another possible type of adsorption due to the nature of dicationic surfactants is chemical adsorption. Inhibitors have O and S atoms in their structure. As a result of the possible interaction between the unshared electron pairs of these heteroatoms and the vacant *d*-orbitals of the metal surface iron atoms, a coordinate covalent bond is formed and thus the inhibitors are attached to the metal surface by chemical adsorption. On the other hand, the hydrophobic long carbon chain of the surfactants plays also an important role in inhibitory activity. This hydrophobic tail of the dicationic surfactant molecule is oriented perpendicularly to the metal surface. Thus, bilayer or multimolecular layers designated as protective layers are formed via van der Waals forces between the long alkyl chains of the inhibitor molecules. These layers behave as a barrier between the metal and the corrosive medium [28]. It is also known that the inhibitory activity of the surfactant molecules becomes constant when the surfactant concentration reaches critical micelle concentration. At concentrations above the

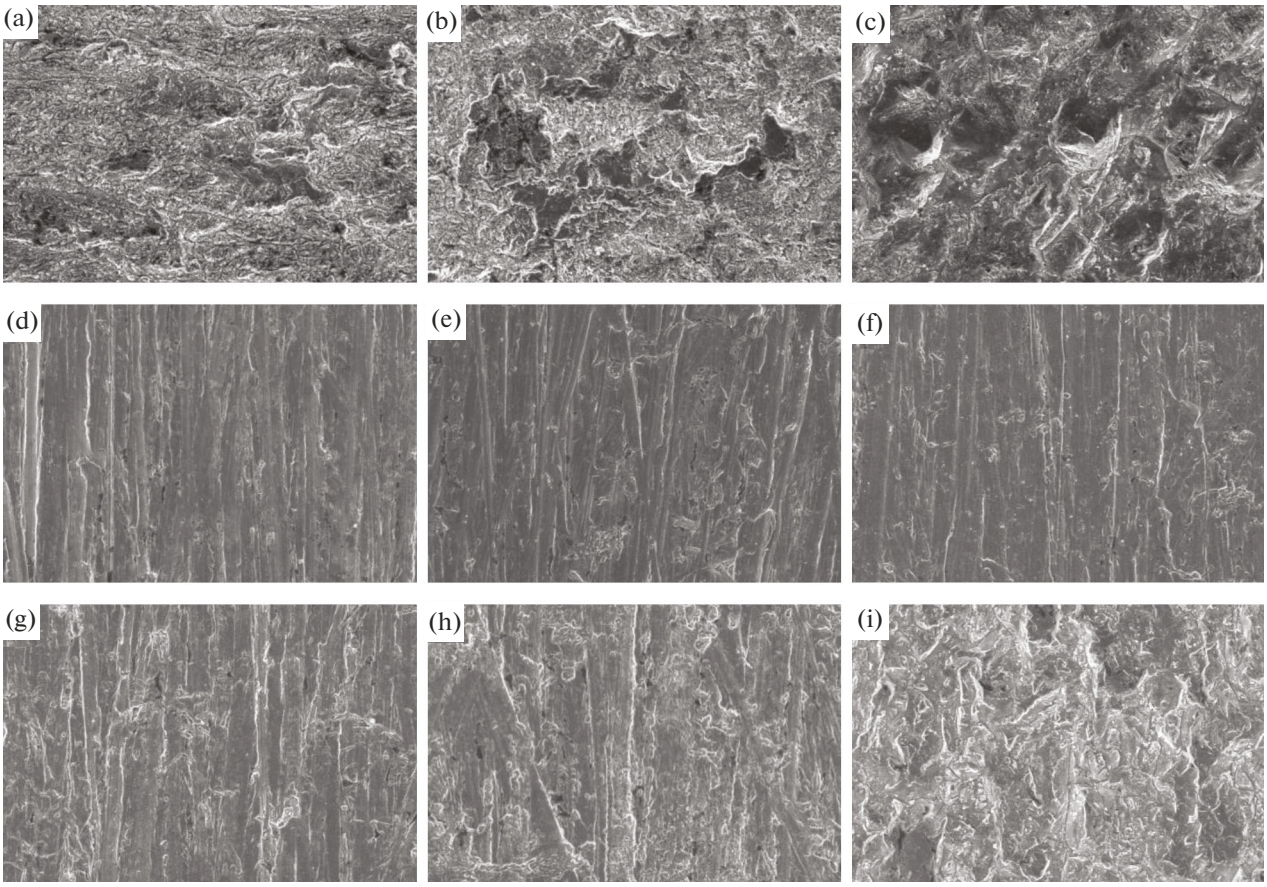


Fig. 7. SEM images of the metal coupon surfaces immersed for 24 h in (a) 1.0 mol L^{-1} HCl without inhibitor, (b) 2.0 mol L^{-1} HCl without inhibitor, (c) 4.0 mol L^{-1} HCl without inhibitor, (d) 1.0 mol L^{-1} HCl with 50 ppm of compound **3a**, (e) 2.0 mol L^{-1} HCl with 50 ppm of compound **3a**, (f) 4.0 mol L^{-1} HCl with 50 ppm of compound **3a**, (g) 1.0 mol L^{-1} HCl with 50 ppm of compound **3b**, (h) 2.0 mol L^{-1} HCl with 50 ppm of compound **3b**, (i) 4.0 mol L^{-1} HCl with 50 ppm of compound **3b**.

CMC, the adsorption density does not change. This situation explains that the inhibitor efficiencies are close to each other at concentrations above the CMC [33]. This result can be seen especially for compound **3a**.

4. CONCLUSIONS

(1) Two new non-Gemini type dicationic active substances were synthesized and both of them showed quite good inhibitory effect in 1.0 mol L^{-1} HCl solution. In particular, even at 5 ppm concentration of compound **3a**, high corrosion inhibition was obtained in 1.0 mol L^{-1} HCl solution.

(2) For each inhibitor concentration studied, there was a slight increase in weight loss of metals immersed in acidic solution with inhibitor as the immersion times increased (1 → 4 days). On the other hand, for metals immersed in an acid solution without inhibitor, the weight loss was higher as the immersion time increased. As a result, the inhibitor efficiencies of dicationic surfactants increased for each inhibitor concentration as the immersion times increased.

(3) Although the inhibitor efficiencies of the two compounds were close to each other at high inhibitor concentrations, the inhibitor efficiency of compound **3a** was found to be higher at low inhibitor concentration (5 ppm). This result indicates that the inhibitor activity of compound **3a** is higher at low inhibitor concentration.

(4) As the concentration of the corrosive HCl solution increased, the inhibitor efficiency of compound **3a** increased, while that of compound **3b** decreased. This result shows that compound **3b** gradually loses its inhibitory activity in high concentration acidic solutions.

(5) Inhibitor efficiencies obtained in different concentration of acidic solution were supported by SEM images.

(6) For compound **3b**, the critical micelle concentration and the surface tension at this concentration were found lower than compound **3a**. The reason for this is that the compound **3b**, which has a longer carbon chain, is more hydrophobic than compound **3a**.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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