

Effect of the hydroxymethyl groups of quaternary ammonium salt cationic surfactants on surface activity and corrosion

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ABSTRACT

Three quaternary ammonium cationic salt surfactants, octadecyl trimethyl ammonium chloride (OTAC), 1-hydroxymethyl-octadecyl trimethyl ammonium chloride (HOTAC), 1,1-dihydroxymethyl-octadecyl trimethyl ammonium chloride (HHOTAC) were purchased to explore the effect of hydroxymethyl groups on hydrophobic parts of surfactants on surface activities, foam properties, and corrosion inhibition. Those parameters including critical micelle concentration (CMC), the surface tension at the CMC (γ_{CMC}), maximum surface excess (Γ_{max}), and minimum surface area (A_{min}) were calculated to evaluate the surface activities of surfactants. The results showed that the surface activity increased with increasing the number of hydroxymethyl groups on hydrophobic parts of surfactants. Foamability and foam stability of three surfactants were evaluated with the Waring blender method. The results indicated that when the temperature was 25°C, foamability and foam stability of the surfactant solution in the absence and presence of NaCl followed the order of HHOTAC > HOTAC > OTAC. In addition, HHOTAC had the highest inhibition efficiency values compared with OTAC and HOTAC, this was attributed to the number of hydroxymethyl groups on hydrophobic parts of surfactants.

Keywords: Quaternary ammonium salt cationic surfactant; Surface tension; Foam properties; Corrosion inhibition

1. Introduction

Surfactant (surface active agent) is an amphiphilic molecule having a hydrophilic head group and one hydrophobic tail group in a single molecule [1,2]. The hydrophobic head group may contain a single chain or up to four chains while the hydrophilic tail group may be a charged or uncharged polar group [3]. Owing to unique amphiphilic structure, surfactants are most widely used in different fields including the printing industry, textile wetting, antimicrobial agents as well as in mining and paper manufacturing [4–6]. Cationic surfactants, in particular, are well known for their antimicrobial activity and are currently employed as disinfectants, antiseptics, preservative agents,

bactericides and antistatic agents for decades [7,8]. The most investigated and commercially-available cationic surfactants are amphiphiles based on quaternary ammonium salts [9]. The positive charges on quaternary ammonium salt cationic surfactants make them adsorbed to the oppositely charged surface, which is an especially significant process in many applications like, emulsifiers, corrosion inhibitors, antistatic agents and so on [10–14]. Owing to traditional quaternary ammonium cationic surfactant with a single chain and single head group, there are obviously limits to improve their different properties. In order to outstanding properties including surface activity, foam property, emulsion stability and corrosion inhibition, the molecular structures of quaternary ammonium salts are modified. The

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experimental results indicate that the properties of surfactants can be improved by altering hydrophilic head groups and hydrophobic tail groups [15].

So far, a large number of studies have focused on the effect of hydroxyethyl groups in hydrophilic parts on the properties of quaternary ammonium cationic surfactants. Sun et al. [16] had prepared a novel quaternary ammonium salt possessing two alkyl chains and a hydroxyethyl group and indicated that the surfactant with the hydroxyethyl group had an outstanding performance on sterilization. Wang et al. [15] had synthesized two cationic quaternary ammonium surfactants with hydroxyethyl groups and investigated the aggregation properties, the conclusion was made that hydroxyethyl groups played an important role on these unique aggregation behaviors. Zhang et al. [17] had characterized a cationic surfactant possessing a Guerbet-type branched tail and hydroxyl-decorated head group and indicated that the introduction of the hydroxylated hydrophilic head was an exceedingly dominant to obtain outstanding performances of the new amphiphilic material. Ivanova et al. [18] studied molecular insights in the temperature effect on adsorption of quaternary ammonium salt cationic surfactants with hydroxyethyl group at the liquid–liquid interface and concluded that hydrogen bonding between water molecules and surfactant heads containing hydroxyethyl group decreased with increasing the temperature, and thus surfactant molecule solubility in water also decreased. Therefore, quaternary ammonium salts cationic surfactant containing hydroxyethyl groups exhibited some outstanding performances. These researchers concentrated mainly on the hydroxyethyl groups of hydrophilic parts, while the studies on hydroxymethyl groups on the hydrophobic parts of surfactants were quite rare. Hence, in this work, octadecyl trimethyl ammonium chloride (OTAC), 1-hydroxymethyl-octadecyl trimethyl ammonium chloride (HOTAC), 1,1-dihydroxymethyl-octadecyl trimethyl

ammonium chloride (HHOTAC) were purchased to study the effect of hydroxymethyl groups on hydrophobic parts to surface activity, foam properties and corrosion inhibition. Various physicochemical parameters such as maximum surface excess (Γ_{\max}), minimum surface area (A_{\min}), corrosion rate (CR) and inhibition efficiency (η) were calculated. In addition, the results were also compared with those of OTAC.

2. Experimental setup

2.1. Materials

Octadecyltrimethyl ammonium chloride (99%), denoted as OTAC for convenience, was obtained from China National Pharmaceutical Group (Beijing). HOTAC and HHOTAC were supplied by the China Research Institute of Daily Chemistry Co., Ltd. The chemical structure, name, molecular weight, and symbols for the studied surfactants are shown in Table 1. Sodium chloride more than 99% purity was supplied from Xian Reagent Co., Ltd., (China). Hydrochloric acid was purchased from Xian Tiancheng Reagent Co., Ltd., (China). The distilled water was used in all experiments.

2.2. Surface tension measurement

The surface tension measures of surfactant solutions were conducted on a tensiometer K12 (Krüss Company, Germany) using the Du Noüy ring method [9]. Three surfactants aqueous solutions with a series of concentrations were prepared at least one day before the measurement [19]. The ring was cleaned by ethanol and distilled water and flamed before the surface tension measurements to obtain the standard surface tension value, which was generally 72.00 mN m⁻¹ at the temperature of 25°C before each

Table 1
Chemical structure, nomenclature, molecular weight, and symbols of the surfactants

Chemical structure	Nomenclature	Molecular weight	Symbol
	Octadecyl trimethyl ammonium chloride	347.5	OTAC
	1-hydroxymethyl-octadecyl trimethyl ammonium chloride	377.5	HOTAC
	1,1-dihydroxymethyl-octadecyl trimethyl ammonium chloride	407.5	HHOTAC

measurement. All experiments were repeated at least three times, the tensiometer sensitivity was 0.5 mN m^{-1} and the reproducibility of the measurements was within $\pm 2\%$ [20].

2.3. Foamability and foam stability measurement

It is well known that the foam was generated by many methods such as the sparge tube technique, gas flow and whipping [21]. However, the standard method to evaluate foamability and foam stability was the Waring blender method [22]. Foamability was an important factor, which demonstrated the difficulty level to generate foam in a surfactant solution and it was expressed by the initial volume (V_0) of foam generated immediately after the mechanical agitation [23]. The foam stability referred to the persistence of foam or the life span of foam after the surfactant produces foam, foam stability was usually expressed in terms of the time ($t_{1/2}$ or half-life) required for the foam volume to collapse to one-half of the initial height [24]. All the measurements were performed at the temperature of 25°C and the values of initial foam volume and half-life time were the averages over three measurements until those values were reproducible [25].

2.4. Bulk foam analysis

100 mL aqueous solutions of three surfactants were prepared and blended at 7,000 rpm for 3 min using the Waring Blender (7012S, Waring Ltd., America). The foam was then poured into a measuring cylinder and the microstructure of foam was measured by the optical microscope, whose light source was the polarized light [26].

2.5. Corrosion inhibition measurement

The inhibiting efficiency of corrosion of the three surfactants as corrosion inhibitors for mild steel specimens in 5% HCl solution was measured to utilize the weight-loss method according to the ASTM Designation G 31–72 [27]. The experimental measurements were performed at a temperature of 50°C . The mild steel specimen done the test had the following chemical composition: C 0.693%, Si 0.043%, Mn 1.050%, P 0.069%, Cr 0.058%, Ni 0.074%, Al 0.036%, S 0.290%, Cu 0.167%, V 0.004%, W 0.001%, Mo 0.0143% and the balance iron. The mild steel specimen surface was abraded with SiC abrasive papers (grade 400 #, 600 #, 1200 #), degreased and cleaned in a beaker with ethanol and acetone, then rinsed with distilled water, and finally dried in warm air [28]. The pre-cleaned and weighed mild steel specimen hanged in beakers containing 250 mL test solution was placed in a thermostatically controlled water bath at 2 h. To calculate the weight loss, the mild steel specimen was retrieved from test solution after 2 h, cleaned with distilled water, air-dried, and finally reweighed utilizing a digital balance (0.0001 g accuracy) [29]. Each experiment was done on triplicate coupons and the average corrosion rate (CR, $\text{g m}^{-2} \text{ h}^{-1}$) and inhibition efficiency (η , %) were calculated according to Eqs. (1) and (2) [30,31].

$$\text{CR} = \frac{W_0 - W_t}{S \cdot t} \quad (1)$$

$$\eta\% = \frac{\text{CR}_{\text{uninhibit}} - \text{CR}_{\text{inhibit}}}{\text{CR}_{\text{uninhibit}}} \times 100 \quad (2)$$

where W_0 and W_t are respectively the mass values of mild steel specimen before and after immersion in the test solution (g), S is the total area of mild steel specimen (m^2), t is the exposure time (h), $\text{CR}_{\text{uninhibit}}$ and $\text{CR}_{\text{inhibit}}$ are the values of corrosion rates in uninhibited and inhibited solutions ($\text{g m}^{-2} \text{ h}^{-1}$).

3. Results and discussion

3.1. Surface tension properties

For it to act as an efficient surfactant, a surfactant must be adsorbed at the interface decreasing the surface tension and must also form aggregates from a certain concentration. Since these properties are heavily affected by the structure, it is fundamental to characterize the potential of the surfactants from an amphiphilic point of view to find structure-activity relationships [32]. Based on the measurement of surface tension of the surfactant solution with a series of concentrations, the surface activity of OTAC, HOTAC, and HHOTAC in the aqueous solution is evaluated at the temperature of 25°C . The variation in the surface tension vs. $-\log C$ is presented in Fig. 1. The critical micelle concentration (CMC) and surface tension at the CMC (γ_{CMC}) are summarized in Table 2. From Fig. 1, it is indicated that the surface tension of three surfactants decreases gradually when the solution concentration increases, the reason is the adsorption of surfactant molecules at the gas-liquid interface. The attractive forces between surfactant and water molecules were much lower than those persisting among water molecules, thereby resulting in surfactant orientation with hydrophobic tail protruding into the gas and hydrophilic head acting as a surface anchor [33,34]. When the surfactant solution concentration is more than CMC, the surface tension shows almost no change with increasing surfactant solution concentrations, which means that the adsorption of surfactant molecules have achieved the saturation at the gas-liquid interface [25].

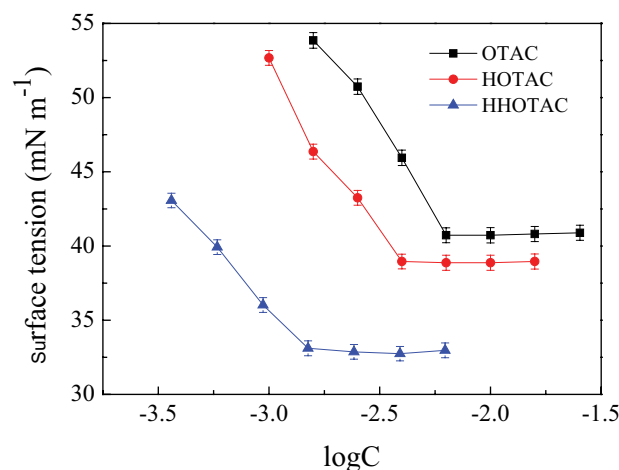


Fig. 1. Surface tension vs. $\log C$ plot for three surfactants at 25°C .

Table 2
Surface properties of different surfactants at 25°C

Surfactants	CMC (mmol L ⁻¹)	γ_{CMC} (mN m ⁻¹)	π_{CMC} (mN m ⁻¹)	Γ_{max} (mol cm ⁻²)	A_{min} (nm ²)
OTAC	15.39	40.15	31.85	0.25	3.05
HOTAC	13.68	38.93	33.07	0.87	2.59
HHOTAC	12.30	34.19	37.81	1.54	2.06

From Table 2, for three surfactants, the rule of γ_{CMC} values is HHOTAC < HOTAC < OTAC, which indicates that the surface activity of quaternary ammonium salts cationic surfactants with hydroxymethyl groups (HOTAC and HHOTAC) is somewhat higher than of OTAC. Therefore, we consider that the number of hydroxymethyl groups plays a key role in surface activity. It can be explained by the fact that the existence of hydroxymethyl groups on hydrophobic parts in the surfactant near head results in the formation of additional hydrogen bonds with the nearest water molecules, which makes that the surfactants containing hydroxymethyl groups display more affinity to the liquid phase [18]. As a result, surfactant molecules can be more closely arranged at the gas–liquid interface. Through the comparison of OTAC, HOTAC, and HHOTAC, it can be concluded that with the increase of a number of hydroxymethyl groups on the hydrophobic parts of surfactants, the CMC values decrease. The conclusion that the more number of hydroxymethyl groups on the hydrophobic parts of surfactants, the stronger the ability to reduce surface tension [15].

From the surface tension curves, the effectiveness of surface tension reduction (Π_{CMC}) that is the difference between the surface tension of distilled water and that at the CMC values, Π_{CMC} values are calculated using Eq. (3) [35] and summarized in Table 2. Analyzing the Π_{CMC} values represented in Table 2 indicates that the main influence factors of Π_{CMC} values are hydroxymethyl groups on the hydrophobic group of surfactants. The larger Π_{CMC} values of HHOTAC prove it has better surface activity.

$$\Pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}} \quad (3)$$

where γ_0 is the surface tension of distilled water with a value of 72.00 mN m⁻¹ at the temperature of 25°C (mN m⁻¹), γ_{CMC} is surface tension at the CMC (mN m⁻¹).

To better demonstrate the accumulation extent of surfactant molecules at the gas–liquid interface, namely the maximum surface excess (Γ_{max}) is introduced here, and its values are obtained by applying the Gibbs adsorption isotherm Eq. (4) [36]. The minimum area (A_{min}) can effectively illustrate the surface area occupied by one surfactant molecule at the gas–liquid interface and it is calculated according to Eq. (5) [37].

$$\Gamma_{\text{max}} = \frac{1}{2.303nRT} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad (4)$$

$$A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}} \quad (5)$$

where Γ_{max} is the saturated adsorption amount ($\mu\text{mol m}^{-2}$), n is a constant dependent on the specific circumstances, which is concerning the number of solute species whose adsorption amount at the interface changes along with the surfactant concentration, R is the universal gas constant (8.314 J K⁻¹ mol⁻¹), T is the absolute temperature (K), and $(\partial \gamma / \partial \log C)_T$ is the slope below the CMC in the surface tension plots. A_{min} is the minimum surface area (nm²), N_A is Avogadro's constant (6.022×10^{23} mol⁻¹).

The Γ_{max} and A_{min} values of OTAC, HOTAC, and HHOTAC are summarized in Table 2. As shown in Table 2, the increase of a number of hydroxymethyl groups leads to increase Γ_{max} values of surfactants molecules at the gas–liquid interface, which indicates that the water molecules exert a high repulsion force on the surfactant molecules, and the later escape to the interface [38]. When the number of hydroxymethyl groups increases, the A_{min} values of surfactants decrease. The reason is that the intermolecular hydrogen bonds can attract the surfactant molecules to arrange more compactly in the gas–liquid interface monolayer [15].

3.2. Foam properties

For it to act as an important medium, the foam has attracted the attention of chemists for a long time by virtue of wide application in many fields including mineral flotation, food industries, detergent, tertiary oil recovery, and etc. [39–41]. Nevertheless, the foam is a metastable system consisting of gas bubbles separated by three-dimensional water channels and goes through undergoes self-destructive processes because of the discharge of liquid, the maturation of Ostwald and the merging of bubbles [42,43]. Hence, it is of great significance to study the foam properties of different surfactants at the external conditions. In general, the foam properties of a surfactant is measured in terms of its foamability, foam stability and size distribution of foam when exposed to different circumstances, in which the foamability and foam stability were very important [44].

In our study, the solution concentration of three surfactants is 0.3 wt.% and the foam properties of OTAC, HOTAC and HHOTAC are measured by the Waring blender method at the temperature of 25°C. Typically, the initial foam volume (V_0) is expressed to foamability, the half-life time ($t_{1/2}$) is expressed to foam stability. In Fig. 2, it is observed that the rule of foamability was HHOTAC > HOTAC > OTAC, so the surfactant HHOTAC has the most prominent foamability by having the greatest initial foam volume in comparison to OTAC and HOTAC. The reason may be explained that the intermolecular hydrogen bonding occurring between the hydroxymethyl groups and water molecules makes the more affinity of HHOTAC molecules to the liquid phase,

which leads to the tighter arrangement of the surfactants molecules at the interface so that the interaction between the hydrophobic groups strong and in turn, the interfacial film becomes tight and the intensity is large, and the foaming is easier [43]. Fig. 2 is the half-life time of three surfactants under the same condition. The half-life time value of HHOTAC containing two hydroxymethyl groups is more than 6.9 min, and the half-life time value of OTAC containing no hydroxymethyl groups OTAC is 5.05 min. Therefore, the foam stability of OTAC, HOTAC, and HHOTAC is greatly influenced by the number of hydroxymethyl groups on the hydrophobic parts of surfactants. When there are hydroxymethyl groups near the hydrophilic parts, the surfactant molecules are tightly arranged in the monolayer, which reduces the gas diffusion between adjacent bubbles [45–47]. Thus, HHOTAC forms more stable foam. Besides, owing to the fact that hydroxymethyl groups in the surfactant near head results in the formation of hydrogen bonds with the nearest water molecules, which indicates that the surfactants with hydroxymethyl groups produced weaker intermolecular cohesion, ultimately leading to the tight and high strength of the foam boundary film. As a result, the foam becomes more difficult to ruptures and is also conducive to the thermodynamic stability of the foam system [48].

Based on the results obtained, it is determined that HHOTAC shows the best performance on foamability and foam stability compared with OTAC and HOTAC. However, the changes in HHOTAC solution concentration has a great influence on foam properties. Hence, it is exceedingly indispensable to investigate foamability and foam stability in the concentrations range of 0.001–0.5 wt.%. From Fig. 3, it can be summarized that the foamability and foam stability of HHOTAC are regular changes with the increase of solution concentration. That is, with increasing concentration, the initial foam volume and half-life time increase when the concentration is less than 0.3 wt.%. Once more than 0.3 wt.%, the initial foam volume and half-life time has no significant increase and maintain at a relatively stable value, which indicates that the adsorption capacity of the surfactant molecules at the gas–liquid interface reaches to saturation. Therefore, when HHOTAC solution concentration is 0.3 wt.%, the initial foam volume and half-life time

are 360 mL and 6.98 min, respectively, which indicates the strongest foamability and foam stability at the concentration of 0.3 wt.% compared to other much higher concentrations. As a result, 0.3 wt.% is fixed for the optimum surfactant concentration for further investigations [49].

3.2.1. Microstructure of foams

In order to further investigate the drainage and coalescence in bulk bubbles generated OTAC, HOTAC, and HHOTAC aqueous solution when the concentration is 0.3 wt.%. The microscope with 40-fold magnification is employed to visualize the microstructure as a function of time.

From Fig. 4, in the initial state, the gas bubbles are observed to be dense in OTAC, HOTAC, and HHOTAC, and these bubbles have good shapes with regular circles or ellipses. But, the contact between bubbles is not close, and the size distribution of bubbles is relatively uniform [23]. It is indicated that these bubbles are comparatively stable in this condition. At 2 min, HOTAC and HHOTAC bubbles have better uniformity than OTAC bubbles. As time passes, in the presence of gravity effect and capillary pressure between spherical bubbles [50], the exceedingly obvious change of foam microstructure is taking place, that is, the big bubbles get even bigger and the small ones disappear gradually result from the drainage and coalescence, ultimately leading to the reduction of bubbles density. The noticeable phenomenon is observed that the bubbles of both OTAC and HOTAC increase rapidly and their distribution are not exceedingly uniform after 5 min, resulting in the remarkable coalescence between bubbles. After 10 min, OTAC gas bubbles show the form of the polyhedron as shown in Fig. 5, which leads to a high development of liquid drainage. Meanwhile, a loose distribution and a remarkable disproportionation are detected in HHOTAC bubbles, where remain relatively sphericity after 10 min [51]. Consequently, HHOTAC foam shows the slowest coalescence in gas bubbles and can develop thicker liquid films as time goes on. The reason is that due to the large density

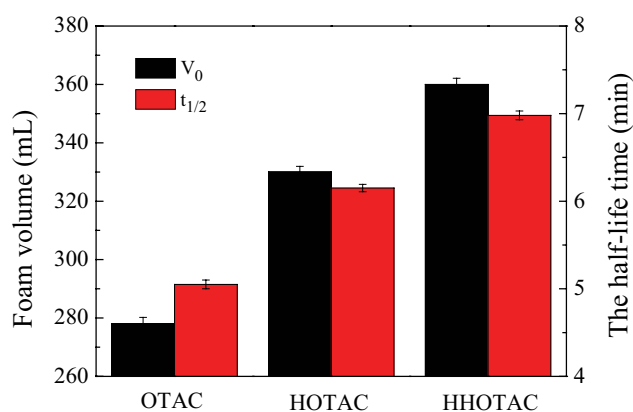


Fig. 2. Initial foam volume and half-life time of three surfactants (0.3 wt.%).

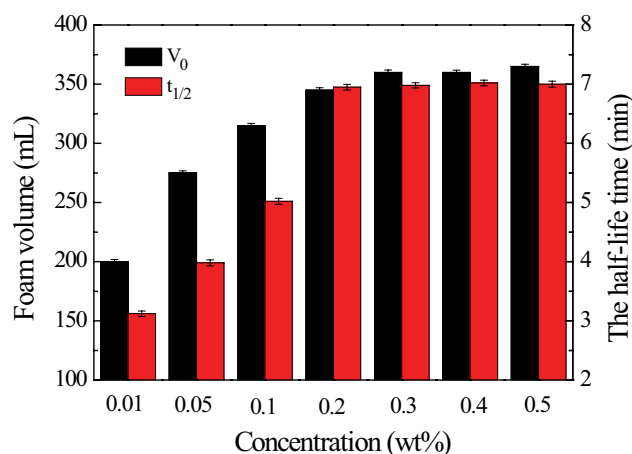


Fig. 3. Initial foam volume and half-life time of HHOTAC at different concentrations.

difference between the gas and liquid phases, the process of film drainage liquid film occurs under the action of gravity, so the liquid film will become thinner. Therefore, this also suggests that the stability degree of three surfactants: HHOTAC > HOTAC > OTAC.

3.2.2. Effect of NaCl concentration on the foam ability

At present, almost all the aqueous foams apply in the petroleum industry are salt-tolerance, which are applicable to the exploitation of oil in underground high-salt environments. So, it is essential to focus on surfactant HHOTAC which has outstanding properties of salt resistance. In the present study, the influence of inorganic (NaCl) on foamability and foam stability are systematically illustrated to further explore the arrangement of the HHOTAC molecules at the gas–liquid interface.

At the fixed surfactant HHOTAC solution concentration of 0.3 wt.%, the variation in the initial foam volume vs. a series of NaCl solutions concentrations is presented in Fig. 6, it is indicated that the initial foam volume displays obvious variation with increasing concentrations of NaCl

solutions at the temperature of 25°C. When the NaCl solution concentration is less than 0.05 mol L⁻¹, the initial foam volume increases rapidly with the concentrations increasing. When the concentration is more than 0.05 mol L⁻¹, the initial foam volume in the NaCl solution shows a slightly declining trend [52]. However, but it is still higher than the initial foam volume of HHOTAC solution without NaCl. The above experiments can be seen that adding NaCl to the surfactant solution, the foamability becomes better. This is ascribed to the counterions (chloride ion) ionized by the NaCl in aqueous solution. From Fig. 7, the existence of counterions near the gas–liquid interface effectively reduces the repulsion between the positively charged head group of HHOTAC, which leads to the tight arrangement of surfactant molecules in the surface adsorption layer. Eventually, the foamability is improved. Fig. 6 is the half-life time values of HHOTAC at a series of inorganic concentrations. It can be seen in Fig. 4 that the change of NaCl solution concentrations has an obvious effect on the half-life time. When the NaCl solution concentration is 0 mol L⁻¹, the half-life time of HHOTAC was 6.98 min. The NaCl solution concentration was 0.15 mol L⁻¹, the half-life time is only 3.61 min. From Fig. 7, with the NaCl solution concentrations increasing, the diffused electric doublet layer is compressed, which weakens the repulsion effect of the charges each other in the solution, thus reducing the thickness of the membrane. As a result, the foam stability becomes worse.

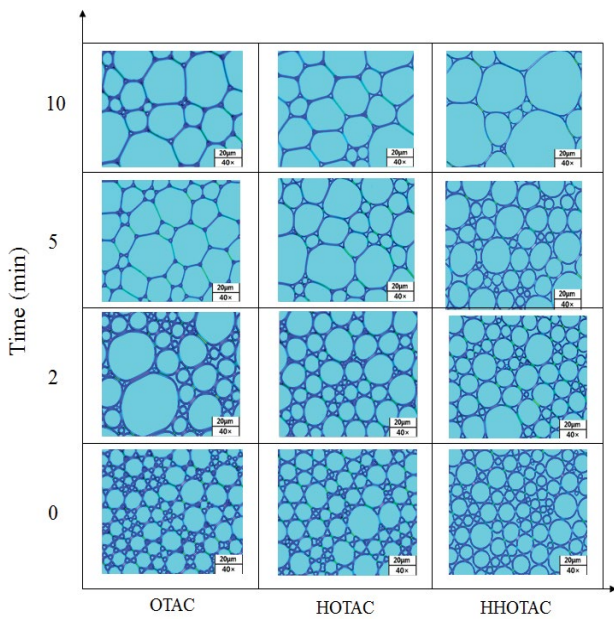


Fig. 4. Microphotographs of foam changes with time.

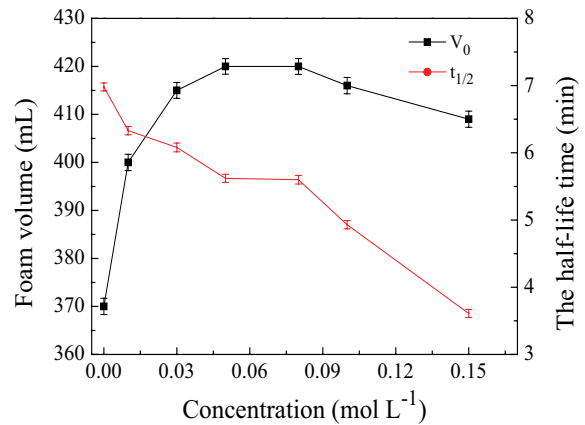


Fig. 6. Initial foam volume vs. NaCl solution concentrations.

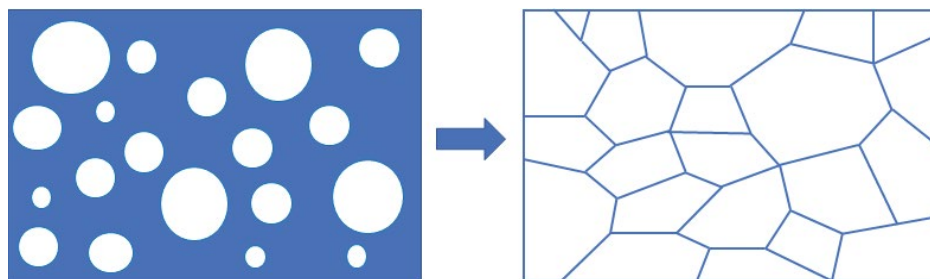


Fig. 5. Diagram of foam morphology in different phases sphericity and polyhedron.

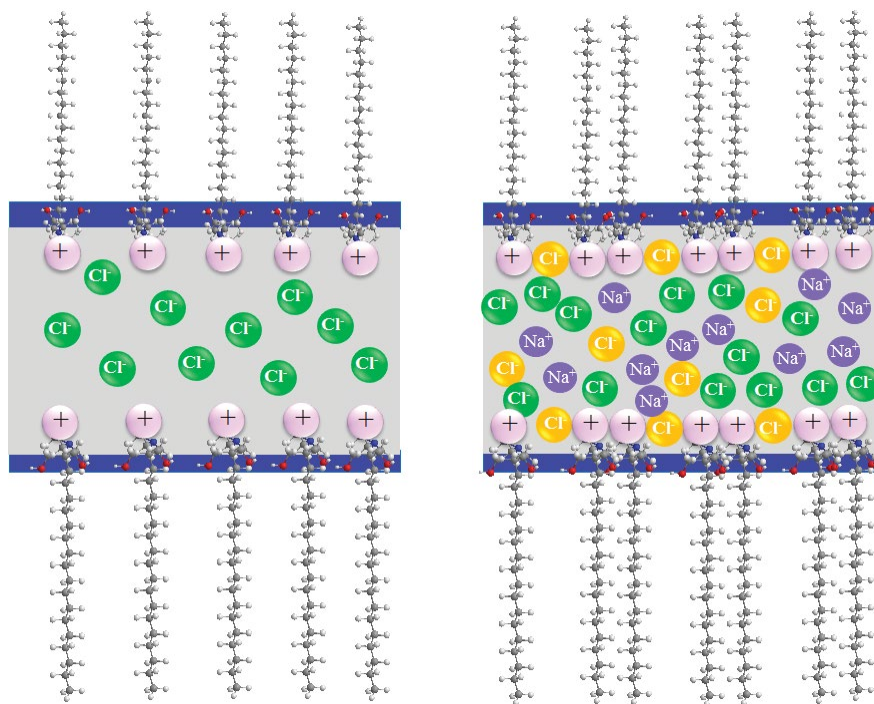


Fig. 7. Structural distribution of HHOTAC in solution in the absence and presence of NaCl.

3.2.3. Corrosion inhibition ability

Carbon steel is widely used as the main alloy in the pharmaceutical industry, petroleum and gas industries, heat exchangers, process vessels, and others [29]. However, the corrosion resistance of carbon steel is limited by its susceptibility in aggressive environments, especially in acid mediums [53]. Due to this fact, many attempts have been made to control this undesirable corrosion and even entire elimination of it [54]. One common solution to reduce corrosion is the addition of some surfactants to the acid corrosive medium to form a protective layer on the metal surface and prevent its oxidation. Among the many surfactants available, quaternary ammonium salts have aroused great interest because of their inhibition efficiency at a lower concentration, since they have positively charged nitrogen atoms on the hydrophilic part can share free electrons with the free d-orbital of metals, and the protective layer formed by the physical or chemical adsorption, ultimately protecting the metal against corrosion [55–57].

The effect of hydroxymethyl groups on the hydrophobic parts of surfactants on the corrosion inhibition of carbon steel in 5% HCl solution at 50°C is investigated. The values of inhibition efficiency (η) and CR of three inhibitors with 10 mg L⁻¹ obtained from the weight loss method are summarized in Table 3. It is clear from the table that the studied surfactants reduce the corrosion of mild steel in HCl medium distinctly, and the rule of inhibition efficiency is HHOTAC > HOTAC > OTAC, which indicates that the number of hydroxymethyl groups on the hydrophobic parts had a significant effect on the inhibition efficiency. As reported in the literature, in a 5% HCl solution, a mild steel surface is positively charged [58]. At first, the Cl⁻ ions

Table 3

Corrosion parameters of mild steel following 2 h in 5% HCl solution in the presence of three inhibitors with 10 mg L⁻¹ at 50°C

Inhibitor	Concentration (mg L ⁻¹)	CR (g m ⁻² h ⁻¹)	η (%)
Blank	0	2.59	–
OTAC	10	0.82	68.29
HOTAC	10	0.69	73.85
HHOTAC	10	0.52	80.09

from HCl solution and Cl⁻ ions from surfactants molecules are adsorbed on the positively charged metal surface thus changing the charge on the solution side of the steel-solution interface from positive to negative. The surfactant molecules containing ammonium groups (A⁺) are electrostatically adsorbed on the metal surface to form a protective film (FeCl⁻ A⁺)_{ads} that protect the metal against corrosion [59]. The adsorption model is shown in Fig. 8. In addition to the electrostatic interaction, the hydroxymethyl groups on the hydrophobic part of HHOTAC can share more free electrons with the free d-orbital of metals, which results in the enhanced adsorption of HHOTAC molecules on the steel surface. Therefore, HHOTAC has the best inhibition efficiency compared with OTAC and HOTAC.

4. Conclusion

In this paper, OTAC, HOTAC, and HHOTAC were purchased to study further the relationship between the structures of surfactants and their surface tension, foam properties, and corrosion inhibition. It is concluded from

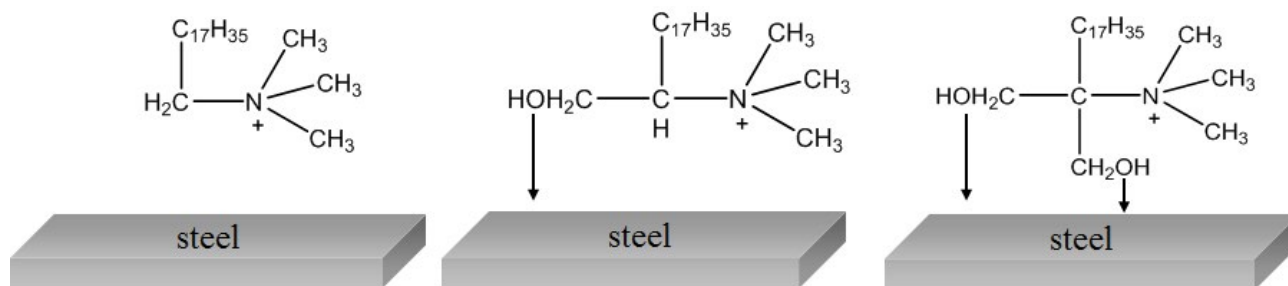


Fig. 8. Adsorption of different surfactants on the steel surface.

the data of CMC, γ_{CMC} , Γ_{max} , and A_{min} that the surface activity increase with increasing the number of hydroxymethyl groups on hydrophobic parts of the surfactant. The experimental results of foam properties showed that HHOTAC solution in the absence and presence of NaCl exhibits the best performances on foamability and foam stability compared with OTAC and HOTAC. In addition, when the temperature is 50°C, the rule of inhibition efficiency with 10 mg L⁻¹ in 5% HCl solution was HHOTAC > HOTAC > OTAC.

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References

- [1] H. Hidaka, T. Oyama, T. Horiuchi, T. Koike, N. Serpone, Photo-induced oxidative synergistic degradation of mixed anionic/cationic surfactant systems in aqueous dispersions. A detailed study of the DBS/HTAB system, *Appl. Catal., B*, 99 (2010) 485–489.
- [2] A.A. Siyal, M.R. Shamsuddin, N.E. Rabat, M. Zulfiqar, Z. Man, A. Low, Fly ash based geopolymer for the adsorption of anionic surfactant from aqueous solution, *J. Cleaner Prod.*, 229 (2019) 232–243.
- [3] A.A. Siyal, M.R. Shamsuddin, A. Low, N.E. Rabat, A review on recent developments in the adsorption of surfactants from wastewater, *J. Environ. Manage.*, 254 (2020) 109797.
- [4] A. Bera, K. Ojha, A. Mandal, T. Kumar, Interfacial tension and phase behavior of surfactant-brine-oil system, *Colloids Surf., A*, 383 (2011) 114–119.
- [5] A. Bera, K. Ojha, A. Mandal, Synergistic effect of mixed surfactant systems on foam behavior and surface tension, *J. Surfactants Deterg.*, 16 (2013) 621–630.
- [6] A. Upadhyaya, E.J. Acosta, J.F. Scamehorn, D.A. Sabatini, Adsorption of anionic–cationic surfactant mixtures on metal oxide surfaces, *J. Surfactants Deterg.*, 10 (2007) 269–77.
- [7] B.E. Brycki, I.H. Kowalczyk, A.M. Szulc, J.A. Brycka, Quaternary alkylammonium salts as cleaning and disinfectant agents, *Tenside Surfactants Deterg.*, 55 (2018) 432–438.
- [8] E. Obłąk, A. Piecuch, J. Rewak-Soroczyńska, E. Paluch, Activity of gemini quaternary ammonium salts against microorganisms, *Appl. Microbiol. Biotechnol.*, 103 (2019) 625–632.
- [9] D.R. Perinelli, D. Petrelli, L.A. Vitali, D. Villasaliu, M. Cespi, G. Giorgioni, E. Elmowafy, G. Bonacucina, G.F. Palmieri, Quaternary ammonium surfactants derived from leucine and methionine: novel challenging surface active molecules with antimicrobial activity, *J. Mol. Liq.*, 283 (2019) 249–256.
- [10] K. Matsuoka, N. Chiba, T. Yoshimura, E. Takeuchi, Effect of double quaternary ammonium groups on micelle formation of partially fluorinated surfactant, *J. Colloid Interface Sci.*, 356 (2011) 624–629.
- [11] B.V.K.J. Schmidt, V. Molinari, D. Esposito, K. Tauer, M. Antonietti, Lignin-based polymeric surfactants for emulsion polymerization, *Polymer*, 112 (2007) 418–426.
- [12] O. Kaczerewska, R. Leiva-Garcia, R. Akid, B. Brycki, Efficiency of cationic gemini surfactants with 3-azamethylpentamethylene spacer as corrosion inhibitors for stainless steel in hydrochloric acid, *J. Mol. Liq.*, 247 (2017) 6–13.
- [13] L.L. Liao, S. Mo, J.L. Lei, H.Q. Luo, N.B. Li, Application of a cosmetic additive as an eco-friendly inhibitor for mild steel corrosion in HCl solution, *J. Colloid Interface Sci.*, 474 (2016) 68–77.
- [14] R. Zhang, J.H. Huo, Z.G. Peng, Q. Feng, J. Zhang, J.X. Wang, Emulsification properties of comb-shaped trimeric nonionic surfactant for high temperature drilling fluids based on water in oil, *Colloids Surf., A*, 520 (2017) 855–863.
- [15] R.T. Wang, Y.L. Li, Q.X. Li, Physicochemical properties of quaternary ammonium surfactants with hydroxyethyl groups, *Tenside Surfactants Deterg.*, 51 (2014) 54–58.
- [16] J.-f. Sun, Q.-x. Li, Y.-l. Li, S.-z. Hou, Synthesis and properties of di-decylmethylhydroxyethylammonium chloride, *Chin. Surfactants Deterg. Cosmet.*, 38 (2008) 83–86.
- [17] Y.J. Zhang, Y.L. Li, Y.B. Song, J. Li, Properties and sodium salicylate induced aggregation behavior of a tail-branched cationic surfactant with a hydroxyl-containing hydrophilic head, *RSC Adv.*, 5 (2015) 105952–105960.
- [18] A.A. Ivanova, A.N. Cheremisin, A. Barifcani, S. Iglauer, C. Phan, Molecular insights in the temperature effect on adsorption of cationic surfactants at liquid/liquid interfaces, *J. Mol. Liq.*, 299 (2019) 112104.
- [19] Y.K. Wang, Y.J. Jiang, T. Geng, H.B. Ju, S.F. Duan, Synthesis, surface/interfacial properties, and biological activity of amide-based Gemini cationic surfactants with hydroxyl in the spacer group, *Colloids Surf., A*, 563 (2019) 1–10.
- [20] N.A. Negm, A.F.M. El Farargy, D.E. Mohammed, H.N. Mohamad, Environmentally friendly nonionic surfactants derived from tannic acid: synthesis, characterization and surface activity, *J. Surfactants Deterg.*, 15 (2012) 433–443.
- [21] Y.J. Sheng, X.J. Wu, S.X. Lu, C.H. Li, Experimental study on foam properties of mixed systems of silicone and hydrocarbon surfactants, *J. Surfactants Deterg.*, 19 (2016) 823–831.
- [22] B.F. Li, H.F. Li, A.Q. Cao, F. Wang, Effect of surfactant concentration on foam texture and flow characteristics in porous media, *Colloids Surf., A*, 560 (2019) 189–197.
- [23] P.S. Piispanen, M. Persson, P. Claesson, T. Norin, Surface properties of surfactants derived from natural products. Part 2: structure/property relationships—foaming, dispersion, and wetting, *J. Surfactants Deterg.*, 7 (2004) 161–167.
- [24] P. Kanokkarn, T. Shiina, M. Santikunaporn, S. Chavadej, Equilibrium and dynamic surface tension in relation to diffusivity and foaming properties: effects of surfactant type and structure, *Colloids Surf., A*, 524 (2017) 135–142.
- [25] C.L. Dai, S.S. Fang, M. Hu, X.J. He, M.W. Zhao, X.P. Wu, S. Yang, Y. Wu, Synthesis, surface adsorption and micelle formation of a class of morpholinium gemini surfactants, *J. Ind. Eng. Chem.*, 54 (2017) 226–233.

- [26] W.-f. Pu, P. Wei, L. Sun, F.-y. Jin, S. Wang, Experimental investigation of viscoelastic polymers for stabilizing foam, *Colloids Surf., A*, 47 (2016) 360–367.
- [27] K. Holmberg, B. Jönsson, B. Kronberg, B. Lindman, *Surfactants and Polymers in Aqueous Solution*, 2nd ed., John Wiley & Sons, Ltd., UK, 2003.
- [28] S. Shahabi, S. Hamidi, J.B. Ghasemi, P. Norouzi, A. Shakeri, Synthesis, experimental, quantum chemical and molecular dynamics study of carbon steel corrosion inhibition effect of two Schiff bases in HCl solution, *J. Mol. Liq.*, 285 (2019) 626–639.
- [29] I. Aiad, S.M. Shaban, A.H. Elged, O.H. Aljoboury, Cationic surfactant based on alignate as green corrosion inhibitors for the mild steel in 1.0 M HCl, *Egypt. J. Chem.*, 27 (2018) 877–885.
- [30] X.H. Li, G. Mu, Tween-40 as corrosion inhibitor for cold rolled steel in sulphuric acid: weight loss study, electrochemical characterization, and AFM, *Appl. Surf. Sci.*, 252 (2005) 1254–1265.
- [31] M. Yadav, S. Kumar, N. Tiwari, I. Bahadur, E.E. Ebenso, Experimental and quantum chemical studies of synthesized triazine derivatives as an efficient corrosion inhibitor for N80 steel in acidic medium, *J. Mol. Liq.*, 212 (2015) 151–167.
- [32] A. Pinazo, R. Pons, M. Bustelo, M.A. Manresa, C. Morán, M. Raluy, L. Pérez, Gemini histidine based surfactants: characterization; surface properties and biological activity, *J. Mol. Liq.*, 289 (2019) 111156.
- [33] N. Pal, N. Saxena, A. Mandal, Synthesis, characterization, and physicochemical properties of a series of quaternary gemini surfactants with different spacer lengths, *Colloid. Polym. Sci.*, 295 (2017) 2261–2277.
- [34] N. Pal, K. Samanta, A. Mandal, A novel family of non-ionic gemini surfactants derived from sunflower oil: synthesis, characterization and physicochemical evaluation, *J. Mol. Liq.*, 275 (2019) 638–653.
- [35] C. Dai, Z. Yang, Y.F. Liu, M.W. Gao, G.C. Zheng, S. Fang, W. Wu, M.W. Zhao, Surface adsorption and micelle formation of surfactant N-alkyl-N-methylmorpholinium bromide in aqueous solutions, *J. Mol. Liq.*, 220 (2016) 442.
- [36] Q. Zhang, Z.N. Gao, F. Xu, S.X. Tai, X.G. Liu, S.B. Mo, F. Niu, Surface tension and aggregation properties of novel cationic Gemini surfactants with diethylammonium headgroups and a diamido spacer, *Langmuir*, 28 (2012) 11979–11987.
- [37] Z.P. Du, E.Z. Li, Y. Cao, X. Li, G.Y. Wang, Synthesis of trisiloxane-tailed surface active ionic liquids and their aggregation behavior in aqueous solution, *Colloids Surf., A*, 441 (2014) 744–751.
- [38] N.A. Negm, M.F. Zaki, M.A.I. Salem, Synthesis and evaluation of 4-diethyl amino benzaldehyde Schiff base cationic amphiphiles as corrosion inhibitors for carbon steel in different acidic media, *J. Surfactants Deterg.*, 12 (2009) 321–329.
- [39] C. Stubenrauch, L.K. Shrestha, D. Varade, I. Johansson, G. Olanya, K. Aramaki, P. Claesson, Aqueous foams stabilized by *n*-dodecyl- β -D-maltoside, hexaethyleneglycol monododecyl ether, and their 1:1 mixture, *Soft Matter*, 5 (2009) 3070–3080.
- [40] J.C.M. Chapelain, S. Faure, D. Beneventi, Clay flotation: effect of TTAB cationic surfactant on foaming and stability of illite clay microaggregates foams, *Ind. Eng. Chem. Res.*, 55 (2016) 2191–2201.
- [41] S.A. Jones, V. van der Bent, R. Farajzadeh, W.R. Rossen, S. Vincent-Bonnieu, Surfactant screening for foam EOR: correlation between bulk and core-flood experiments, *Colloids Surf., A*, 500 (2016) 166–176.
- [42] H.X. Zhao, C.X. He, Y.W. Zhou, J. Yang, C. Luo, B.C. Xu, Study on foaming properties of N-acyl amino acid surfactants: sodium N-acyl glycinate and sodium N-acyl phenylalaninate, *Colloids Surf., A*, 567 (2019) 240–248.
- [43] X.N. Wu, J.X. Zhao, E.J. Li, W.S. Zou, Interfacial dilational viscoelasticity and foam stability in quaternary ammonium gemini surfactant systems: influence of intermolecular hydrogen bonding, *Colloid. Polym. Sci.*, 289 (2011) 1025–1034.
- [44] H.T. Wang, W.B. Guo, C.B. Zheng, D.M. Wang, H.H. Zhan, Effect of temperature on foaming ability and foam stability of typical surfactants used for foaming agent, *J. Surfactants Deterg.*, 20 (2017) 615–622.
- [45] Y. Wang, X.C. Liu, Y. Zhou, J.P. Niu, Influence of hydrocarbon chain branching on foam properties of olefin sulfonate with foamsan, *J. Surfactants Deterg.*, 19 (2016) 1215–1221.
- [46] X.-C. Wang, L. Zhang, Q.-T. Gong, L. Wang, L. Zhang, L. Luo, Z.-Q. Li, S. Zhao, J.-Y. Yu, A study of dynamic interfacial properties as related to foaming properties of sodium 2,5-dialkyl benzene sulfonates, *J. Dispersion Sci. Technol.*, 30 (2009) 346–352.
- [47] S.X. Shi, T.X. Yin, W.G. Shen, Switchable foam control by a new surface-active ionic liquid, *RSC Adv.*, 6 (2016) 93621–93625.
- [48] M. Sreenu, R.B.N. Prasad, P. Sujitha, C.G. Kumar, Synthesis and surface-active properties of sodium *N*-acylphenylalanines and their cytotoxicity, *Ind. Eng. Chem. Res.*, 54 (2015) 2090–2098.
- [49] A.S. Hanamertani, R.M. Pilus, N.A. Manan, M.I.A. Mutalib, The use of ionic liquids as additive to stabilize surfactant foam for mobility control application, *J. Pet. Sci. Eng.*, 167 (2018) 192–201.
- [50] S.I. Karakashev, M.V. Grozdanova, Foams and antifoams, *Adv. Colloid Interface Sci.*, 176 (2012) 1–17.
- [51] W.-f. Pu, P. Wei, L. Sun, F.-y. Jin, S. Wang, Experimental investigation of viscoelastic polymers for stabilizing foam, *J. Ind. Eng. Chem.*, 47 (2017) 360–367.
- [52] Y. Wang, J.J. Ge, G.C. Zhang, Foaming properties of commercial lauramide amide oxide in high-salinity water, *J. Surfactants Deterg.*, 20 (2017) 755–760.
- [53] O. Kaczerewska, R. Leiva-Garcia, R. Akid, B. Brycki, I. Kowalczyk, T. Pospieszny, Effectiveness of O-bridged cationic gemini surfactants as corrosion inhibitors for stainless steel in 3 M HCl: experimental and theoretical studies, *J. Mol. Liq.*, 249 (2018) 1113–1124.
- [54] T.N.J.I. Edison, R. Atchudan, A. Pugazhendhi, Y.R. Lee, M.G. Sethuraman, Corrosion inhibition performance of spermidine on mild steel in acid media, *J. Mol. Liq.*, 264 (2018) 483–489.
- [55] A.M. Badawi, M.A. Hegazy, A.A. El-Sawy, H.M. Ahmed, W.M. Kamel, Novel quaternary ammonium hydroxide cationic surfactants as corrosion inhibitors for carbon steel and as biocides for sulfate reducing bacteria (SRB), *Mater. Chem. Phys.*, 124 (2010) 458–465.
- [56] M.A. Hegazy, E.M.S. Azzam, N.G. Kandil, A.M. Badawi, R.M. Sami, Corrosion inhibition of carbon steel pipelines by some new amphoteric and di-cationic surfactants in acidic solution by chemical and electrochemical methods, *J. Surfactants Deterg.*, 19 (2016) 861–871.
- [57] S.M. Tawfik, Corrosion inhibition efficiency and adsorption behavior of N,N-dimethyl-4-(((1-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)imino)methyl)-N-alkylbenzenaminium bromide surfactant at carbon steel/hydrochloric acid interface, *J. Mol. Liq.*, 207 (2015) 185–194.
- [58] N.K. Allam, Thermodynamic and quantum chemistry characterization of the adsorption of triazole derivatives during Muntz corrosion in acidic and neutral solutions, *Appl. Surf. Sci.*, 253 (2007) 4570–4577.
- [59] Sk.A. Ali, M.T. Saeed, S.U. Rahman, The isoxazolidines: a new class of corrosion inhibitors of mild steel in acidic medium, *Corros. Sci.*, 45 (2003) 253–266.