

Egyptian Petroleum Research Institute
Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp



### FULL LENGTH ARTICLE



# Synthesis, surface properties and biological activity of N,N,N-tris(hydroxymethyl)-2-oxo-2-(2-(2-(alkanoyloxy) ethoxy) ethoxy) ethanaminium chloride surfactants

## Ismail Aiad<sup>a</sup>, M. Abo Riya<sup>b</sup>, Salah M. Tawfik<sup>a,\*</sup>, Mahmoud A. Abousehly<sup>c</sup>

<sup>a</sup> Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

<sup>b</sup> Faculty of Science, Chemistry Department, Benha University, Al Qalyubiyah, Egypt

<sup>c</sup> General Petroleum Company, Cairo, Egypt

Received 19 April 2015; revised 2 July 2015; accepted 7 July 2015 Available online 17 December 2015

#### **KEYWORDS**

Cationic surfactants; Surface; Biological activity; Sulfate reducing bacteria; Emulsification **Abstract** A new series of some cationic surfactants were synthesized namely: 2-(2-(2-(dodecanoy loxy)ethoxy)-N,N,N-tris(hydroxymethyl)-2-oxoethanaminium (DDAC); N,N,N-tris(hydroxymethyl)-2-oxo-2-(2-(2-(tetradecanoyloxy) ethoxy)ethoxy) ethanaminium (TDAC) and N,N,N-tris(hydroxymethyl)-2-oxo-2-(2-(2-(hexadecanoyloxy)ethoxy)ethoxy)ethanaminium (HDAC). The chemical structures of the synthesized cationic surfactants were confirmed using FT-IR and <sup>1</sup>H-NMR spectroscopies. The surface tension of the synthesized cationic surfactants was measured at 25, 40 and 55 °C. The surface parameters were determined from the surface tension measurements. The emulsification power and foaming power measurements showed the applicability of these surfactants in the oil field. The biological activity of the synthesized surfactants was measured against pathogenic bacteria (*Staphylococcus aureus* and *Escherichia coli*) and fungi (*Candida albicans* and *Aspergllus niger*) using inhibition zone diameters. The obtained data revealed that the dodecanoate derivative (DDAC) has more antimicrobial activity against the investigated microorganisms than tetradecanoate and hexadecanoate derivatives (TDAC and HDAC).

© 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of Egyptian Petroleum Research Institute. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/ licenses/by-nc-nd/4.0/).

#### 1. Introduction

\* Corresponding author. Tel.: +20 1273615278.

When increasing the concentration of the solution of single chain surfactant molecules, consisting both hydrophobic and hydrophilic polar heads, to a certain limit, micelles are formed. This limit of concentration is known as "*critical micelle concentration*" and surfactant molecules above in aqueous

http://dx.doi.org/10.1016/j.ejpe.2015.07.020

E-mail address: salahtwfk85@yahoo.com (S.M. Tawfik).

Peer review under responsibility of Egyptian Petroleum Research Institute.

<sup>1110-0621 © 2015</sup> The Authors. Production and hosting by Elsevier B.V. on behalf of Egyptian Petroleum Research Institute. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

solution are known to form various microstructure forms of micelle such as spherical, vesicular and rod-like [1-4]. Several factors affect the microstructure of surfactant micellization such as structure of the surfactants, concentration and temperature [5-8]. Quaternary ammonium salt compounds show germicidal, antibacterial, antifungal and anticancer activities. A series of quaternary ammonium salts with general formula  $R_3N^+X^-$ , which include hetero nitrogen atom was the hetero atom, enhance the biological action [9]. Among the various classes of surfactants the cationic and more especially the quaternary ammonium salts are the most effective antimicrobial agent which kill or inhibit the growth of both Gram-positive and Gram-negative bacteria. In clinical and industrial environments quaternary ammonium compounds are widely used for controlling bacterial growth. The mode of antimicrobial action of quaternary ammonium compounds involves distortion of outer membrane lipid bilayers through association of the positively charged quaternary ammonium with the polar head groups of acidic phospholipids. The hydrophobic tail part interacts with the hydrophobic membrane core [10]. The studied surface activity relationship showed that in addition to the positively charged site, a significant hydrophilic component of the surfactant is used for controlling the biological activity of the cationic surfactant [11]. Several works deal with the synthesis of different cationic surfactant compounds and studied the relationship between surface activity and antimicrobial activity against wide strain of pathogenic bacteria, fungi and yeast [11-14].

Our study aims to synthesize some cationic surfactants (scheme-1) with different hydrocarbon chain lengths and to study the influence their structures on surface tension, interfacial tension, emulsification power, foaming power and thermodynamic parameters of adsorption/micellization. In addition, the antimicrobial activities were measured using well diffusion method.

#### 2. Materials and measurements

#### 2.1. Materials

- Di-ethylene glycol, triethanol amine and chloroacetic acid were purchased from Alfa chemical company.
- Analytical grade Dodecanoic, tetradecanoic, and hexdecanoic acids were obtained from Aldrich chemical company (Germany).
- All the reagents were delivered as analytical grade chemicals and used as obtained without any treatment.

#### 2.2. Synthesis

#### 2.2.1. Synthesis of fatty alkyl di-ethylene glycol esters

Different fatty acids namely Dodecanoic, tetradecanoic, and hexdecanoic acids (0.1 mol.) were esterified separately by di-ethylene glycol (0.1 mol.) in xylene as a solvent and 0.01% p-toluene sulfonic acid as a catalyst, until the azeotropic amount of water (0.1 mol., 1.8 mL) was removed. The solvent was distilled off using rotary evaporator. On the other hand, excess residual materials were vacuum distilled off [15].

#### 2.2.2. Synthesis of chloro acetic acid ester

Alkyl ester of di-ethylene glycol (0.1 mol.) and chloro acetic acid (0.1 mol.) were esterified individually in xylene (250 mL) as the solvent under reflux conditions at 140 °C. The solvent was distilled off under vacuum using rotary evaporator. The synthesized chloroacetic acid esters were showed in Scheme 1 [15].

#### 2.2.3. Synthesis of cationic surfactants

The synthesized cationic surfactants were obtained by the coupling reaction between triethanol amine (0.1 mol.) and the synthesized chloro acetic acid ester (0.1 mol.) in 50 ml acetone. The reaction mixture was refluxed for 12 h and left for complete precipitation of the cationic compounds. The produced quaternary ammonium salts were filtered off and recrystallized three times from acetone to produce the desired cationic surfactants [16]. Scheme 1 shows the synthetic route of the cationic compounds.

#### 2.3. Measurements

#### 2.3.1. Surface tension

Surface tension was measured by the platinum ring method using a Kruss K6 tensiometer. The surface tension measurements were performed for aqueous solution of the synthesized cationic surfactants with a concentration range of 0.01-0.00005 M at 25, 40 and 55 °C. The solutions were poured into a clean Teflon cup, and the solutions were left for 2 h to allow the stabilization and complete adsorption at the solution surface. The surface tension values were recorded as the average of at least three successive readings. The critical micelle concentration (CMC) and surface parameters were determined from surface tension profile [17].

#### 2.3.2. Interfacial tension

The interfacial tension of the synthesized quaternary ammonium salts was measured between aqueous solution of the synthesized surfactants at concentration of 0.1% by weight and light paraffin oil, at 25 °C using the same procedures of the surface tension measurements [18].

#### 2.3.3. Emulsion stability

Emulsification power of the synthesized cationic surfactants was measured by vigorously stirring a mixture of 10 mL (0.1 %) of the synthesized cationic surfactant solutions and 10 mL of light paraffin oil at 25 °C. The time required for separation of 9 mL of pure surfactant solution was expressed as emulsion stability [19].

#### 2.3.4. Foaming power

Foaming power of the synthesized quaternary ammonium salts was measured after shaking 100 mL of 0.1% concentration of the surfactant solution vigorously in a stoppered graduated 250 mL cylinder at 25 °C. Foam production was measured by the foam height (in mL) and foam stability was measured by the time [20].

#### 2.3.5. Biological activity

The antimicrobial activity of the synthesized cationic surfactants was measured against pathogenic bacteria and fungi as



#### Where, n= 3: N,N,N-tris(hydroxymethyl)-2-oxo-2-(2-(2-(dodecanoyloxy) ethoxy)ethoxy) ethanaminium chloride (DDAC)

n= 5: N,N,N-tris(hydroxymethyl)-2-oxo-2-(2-(2-(tetradecanoyloxy) ethoxy)ethoxy) ethanaminium chloride(TDAC)

n= 7: N,N,N-tris(hydroxymethyl)-2-oxo-2-(2-(2- (hexadecanoyloxy) ethoxy) ethoxy) ethanaminium chloride (HDAC)

Scheme 1 Synthesis of cationic surfactants.

well as sulfate reducing bacteria using the agar diffusion technique, 1 mg/ml solution in dimethyl sulfoxide was used. The tested organisms were Gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*) and fungi (*Candida albicans* and *Aspergillus*). The bacteria and fungi were kept on nutrient agar media media were inoculated with different investigated microorganisms. The diameter of the inhibition zones was measured after 24 h of incubation at 30 °C for bacteria and 48 h of incubation at 28 °C for fungi [21].

#### 3. Results and discussion

#### 3.1. Structure

*N*,*N*,*N*-tris(hydroxymethyl)-2-oxo-2-(2-(2-(dodecanoyloxy) ethoxy) ethoxy) ethanaminium chloride (DDAC) 2.65 g (90%); M.p.: 250 °C; <sup>1</sup>H NMR (300 MHz, CDCl3) Table 1, (Fig. 1 as

Table	1	'H-NMR	peaks	of	the	synthesized	cationic
surfacta	ints	•					

Danda	S (nnm)						
Danus	o (ppm)						
	DDAC	TDAC	HDAC				
(t, 3H, C <u>H</u> <sub>3</sub> )	1	0.83	1.01				
(m, 2H, CH2CH3)	1.21	1.22	1.21				
(m, 2H, CH2CH2CO)	2.49	2.5	2.49				
(t, 2H, CH <sub>2</sub> C <u>H</u> <sub>2</sub> CO)	3.18	3.17	3.22				
(m, nH, C <u>H</u> <sub>2</sub> )	3.48	3.49	3.45				
(t, 1H, CH <sub>2</sub> O <u>H</u> )	3.69	3.69	3.68				
(s, 2H, N-C <u>H</u> <sub>2</sub> COO)	3.87	3.78	3.74				
(t, 2H, OC <u>H</u> <sub>2</sub> CH <sub>2</sub> O)	4.01	3.87	3.76				
(d, 2H, N-C <u>H</u> 2OH)	5.45	4.1	5.32				



Figure 1 <sup>1</sup>H-NMR spectrum of the synthesized cationic surfactant (DDAC).



Figure 2 FTIR spectrum of the synthesized cationic surfactant (DDAC).

representative compounds); IR (KBr):  $v = 3357 \text{ cm}^{-1}$  (OH), 2931 cm<sup>-1</sup> (CH<sub>3</sub>), 2845 cm<sup>-1</sup> (CH<sub>2</sub>), 2612 cm<sup>-1</sup>( $-N^+$ ), 1737 cm<sup>-1</sup> (C=O), 1403 cm<sup>-1</sup> (CH<sub>2</sub>)<sub>n</sub>, 1084 cm<sup>-1</sup> (C=O), (Fig. 2 as representative compound); EA: calc. 57.78% C, 9.70% H, 3.21% N, 29.32% O, 8.12% Cl; found 57.37% C, 9.63% H, 3. 19% N, 29.11% O, 8.06% Cl.

N,N,N-tris(hydroxymethyl)-2-oxo-2-(2-(2-(tetradecanoy loxy) ethoxy) ethoxy) ethanaminium chloride (TDAC) 2.15 g (88%);M.p.: 265 °C; <sup>1</sup>H NMR (300 MHz, CDCl3) Table 1; IR (KBr):  $v = 3351 \text{ cm}^{-1}$  (OH), 2931 cm<sup>-1</sup> (CH<sub>3</sub>), 2843 cm<sup>-1</sup> (CH<sub>2</sub>), 2612 cm<sup>-1</sup>( $-N^+$ ),1733 cm<sup>-1</sup> (C=O), 1404 cm<sup>-1</sup> (CH<sub>2</sub>), 1030 cm<sup>-1</sup> (C=O); EA: calc. 63.28% C, 10.62% H, 3.21% N, 29.32% O, 8.12% Cl; found 62.84% C, 10.55% H, 3. 19% N, 29.11% O, 8.06% Cl.

*N*,*N*,*N*-tris(hydroxymethyl)-2-oxo-2-(2-(2-(hexadecanoy loxy) ethoxy) ethoxy)ethanaminium chloride (HDAC) 3.22 g (85%);M.p.: 280 °C; <sup>1</sup>H NMR (300 MHz, CDCl3) Table 1; IR (KBr):  $v = 3331 \text{ cm}^{-1}$  (OH), 2933 cm<sup>-1</sup> (CH<sub>3</sub>), 2840 cm<sup>-1</sup> (CH<sub>2</sub>), 2613 cm<sup>-1</sup>( $-N^+$ ),17378 cm<sup>-1</sup> (C=O), 1403 cm<sup>-1</sup> (CH<sub>2</sub>), 1034 cm<sup>-1</sup> (C=O); EA: calc. 68.78% C, 11.54% H, 3.21% N, 29.32% O, 8.12% Cl; found 68.30% C, 11. 46% H, 3. 19% N, 29.11% O, 8.06% Cl.

## 3.2. Surface activity of the synthesized quaternary ammonium salts

#### 3.2.1. Surface tension and critical micelle concentration (CMC)

Figs. 3–5 represent the variation of surface tension versus -log C of the synthesized quaternary ammonium salts (DDAC, TDAC and HDAC) at 25, 40 and 55 °C. From the surface tension profile, it can be seen that increasing the surfactant concentration shows sharp decrease in the surface tension which indicates the accumulation of the surfactant molecules at the air/solution interface. The curve is then broken at a certain concentration called critical micelle concentration (CMC) [22]. From the surface tension profile the surface tension values decreased gradually with increasing alkyl chain length (hydrophobic chains) from the dodecanoate derivative, DDAC



Figure 3 Surface tension vs. -log concentration of DDAC cationic surfactant at different temperatures.





**Figure 4** Surface tension vs. -log concentration of TDAC cationic surfactant at different temperatures.



**Figure 5** Surface tension vs. -log concentration of HDAC cationic surfactant at different temperatures.

 $(C_{12})$  to tetradecanoate derivative, TDAC  $(C_{14})$  and to hexadecanoate derivative HDAC  $(C_{16})$ .

This could be due to increase the mutual repulsion between hydrophobic chain (nonpolar medium) and the polar medium (water), which leads to the migration of the surfactant molecules toward the air/water interface. Also, the gradual increase of hydrophobic chain lengths in the synthesized cationic surfactant molecules was characterized by a decrease in their CMC values; higher repulsion occurred between the longer hydrophobic chain and the water phase, as a result, the CMC value decreased considerably, Table 2. It was observed that increasing the temperature from 25 to 55 °C leads to a decrease in CMC values. That may be attributed to the hydrogen bond breakdown. As a result, the surfactant molecules separate from the aqueous phase to form the micelles [23].

**Table 2** Critical micelle concentration (CMC), effectiveness ( $\pi_{cmc}$ ), efficiency (Pc<sub>20</sub>), maximum surface excess ( $\Gamma_{max}$ ) and minimum surface area ( $A_{min}$ ) of the synthesized cationic surfactants at 25, 40 and 55 °C.

Compound	<i>T</i> , °C	CMC, mM	$m_{\rm cmc}, mN^{-1}m^{-1}$	Pc <sub>20</sub> , M/L	$\Gamma_{\rm max} \times 10^{-10},$ mol cm <sup>-2</sup>	$A_{\min},$ $\mathrm{nm}^2$
DDAC	25	0.114	42	4.1	1.25	132.87
	40	0.097	43	4.35	0.899	184.61
	55	0.079	44	5.05	0.858	193.45
TDAC	25	0.146	41	4.1	1.721	96.47
	40	0.079	44	4.3	1.295	128.23
	55	0.021	45.5	5.2	0.762	217.69
HDAC	25	0.097	41	3.1	1.6	103.76
	40	0.097	44	3.35	1.15	144.42
	55	0.079	45.5	4	1.097	151.34

3.2.1.1. Effectiveness ( $\pi_{CMC}$ ) and efficiency ( $Pc_{20}$ ). Effectiveness of the synthesized cationic surfactants is determined from the difference between the surface tension of the surfactant solution at the critical micelle concentration ( $\gamma_{CMC}$ ) and the surface tension of the distilled water ( $\gamma_0$ ) as follows and is listed in Table 2.

$$\pi_{\rm CMC} = \gamma_o - \gamma_{\rm CMC}.\tag{1}$$

The lower values of effectiveness belong to the lower surface activity compounds is a series of surfactant, and vice versa. And from the data in Table 2 it is clear that the tetradecanoate and hexadecanoate derivatives (TDAC and HDAC) are more surface active than the dodecanoate derivative (DDAC).

Efficiency,  $PC_{20}$  is the surfactant concentrations that are capable of suppressing the surface tension of the solution by 20 mN/m. The efficiency values of the synthesized cationic surfactants are shown in Table 2. The efficiency,  $PC_{20}$  increases with an increase in the temperature of the solution from 25, 40 to 55 °C. This reflects the negative free energy of adsorption of the prepared surfactants at the aqueous solution/air interface; the efficiency of adsorption is slightly affected by the carbon number.

Increasing the number of methylene groups ( $-CH_2-$ ) along the hydrophobic chains increases the hydrophobicity of the molecules, hence water-hydrophobe interactions increase with a decrease in the surface tension, followed by a decrease in the efficiency Pc<sub>20</sub> (Table 2).

3.2.1.2. Maximum surface excess ( $\Gamma_{max}$ ) and minimum surface area ( $A_{min}$ ). The maximum surface excess of the synthesized cationic surfactants,  $\Gamma_{max}$ , describes the accumulation of surfactant molecules at the air/water interface, and can be calculated according to the Gibbs equation [24]

$$\Gamma_{\max} = 1/2.303 \,\mathrm{nRT} \left( \frac{\partial \gamma}{\partial \log C} \right) \tag{2}$$

where R = gas constant (8.314 J mol<sup>-1</sup> k<sup>-1</sup>) and T = t + 273 (°K). The value of *n* is the number of ionic species whose concentration at the interface varies with the surfactant concentration in the solution.  $\Gamma_{\text{max}}$  values of the synthesized cationic surfactants were calculated at different temperatures and listed in Table 2.

Surfactant compound that lowers the surface pressures is thus present in excess at or near the surface, with an increase in alkyl chain length from dodecanoate derivative to hexadecanoate derivative accompanied by an increase in the surface pressure of the system as an indication for the high accumulation of surfactant molecules at the interface.

The average area occupied by each adsorbed molecule of a surfactant is given by the following equation [25].

$$A_{\min} = 10^{14} / N_A \Gamma_{\max} \tag{3}$$

where N is Avogadro's number.

By inspecting the data in Table 2 the minimum surface per molecule at the aqueous solution/air interface increases with increasing temperature of the measurements which means that the increase of temperature causes a decrease in the number of molecule at the interface the surface area values at the interface of the synthesized cationic surfactant molecules are gradual increased.

#### 3.3. Interfacial tension

The interfacial tension of the synthesized cationic surfactants (DDAC, TDAC and HDAC) was measured between their aqueous solution and light paraffin oil at a concentration of 0.1% at 25 °C. The obtained surface tension values were listed in Table 3, the results revealed that the synthesized cationic compounds showed low interfacial tension values compared to conventional surfactants, which illustrate the high accumulation of surfactant compounds at the interface. The interfacial tension values of the cationic surfactants influenced by their chemical structure at interface (hydrophobic and hydrophilic part) and are ranged between 6 and 13 mNm<sup>-1</sup>. The gradual increase in the alkyl chain length from short chain hydrocarbon (dodecanoate derivative) to long chain hydrocarbon decreases (hexadecanoate) the interfacial tension gradually decreasing from 13 mNm<sup>-1</sup> to 6 mNm<sup>-1</sup>, respectively. The lower interfacial values of the synthesized surfactant are more active and these surfactants can be used in many applications in the petroleum field as corrosion inhibitors and biocides.

#### 3.4. Emulsification power

The emulsification efficiency of the synthesized surfactants was measured as the time required for separation of 9 mL of pure water from the emulsion formed between surfactant solution (0.1% wt) and paraffin oil (10 mL:10 mL). Fig. 6 shows the emulsification power of the synthesized quaternary ammonium salts as a function of time at 25 °C. Increasing the stability of the formed emulsion formed by synthesized surfactants

increases the time required for separation of the pure amount of water, and vice versa, and the emulsifying power depends on the alkyl chain length. The dodecanoate derivative showed moderate emulsion stability (250 s) while the long chain hydrocarbon showed negligible values of emulsification power (tetradecanoate, 30 s and hexadecanoate, 15 s). From the obtained result of emulsification measurements the synthesized surfactants noncable to form emulsion with oil and therefore the synthesized surfactants predicts their applicability in oil field without form stable emulsion with water and caused problems.

#### 3.5. Foaming power

In oil field application the foam causes a very serious problem such as increases pressure of the system and the high pressure fluids may lead to an explosion of the pipes. Therefore foaming power of the synthesized quaternary ammonium salts was measured after shaking 100 mL of 0.1% concentration of the surfactant solution vigorously in a stoppered graduated 250 mL cylinder at 25 °C. The data listed in Table 3, and as seen from foaming power data the synthesized quaternary ammonium salts have negligible tendency toward foam formation, and thus may be used in several applications such as washing machine laundry or additives in oilfield applications.

#### 3.6. Thermodynamic parameters

The standard free energy, entropy and enthalpy of micellization and adsorption for the synthesized quaternary ammonium salts where calculated according to the Gibbs equations at 25, 40 and 55 °C [26], and data are summarized in Table 4:

$$\Delta G_{\rm mic}^{\rm o} = 2.303 \,\rm RT \log CMC \tag{4}$$

$$\Delta G_{\rm ads}^{\rm o} = \Delta G_{\rm mic}^{\rm o} - (0.06\pi_{\rm CMC}A_{\rm min}) \tag{5}$$

$$-\Delta S_{\rm mic}^{\rm o} = \Delta G_{\rm mic}^{\rm o} / \Delta T \tag{6}$$

$$-\Delta S_{\rm ads}^{\rm o} = \Delta G_{\rm ads}^{\rm o} / \Delta T \tag{7}$$

$$\Delta H_{\rm mic}^{\rm o} = \Delta G_{\rm mic}^{\rm o} + T \Delta S^{\rm o} \tag{8}$$

$$\Delta H^{\rm o}_{\rm ads} = \Delta G^{\rm o}_{\rm ads} + T \Delta S^{\rm o} \tag{9}$$



**Figure 6** Effect of hydrophobic chain length of the synthesized cationic surfactant on emulsification power.

**Table 3** Interfacial tension, foam high and foam stability of the synthesized cationic surfactants at 25, 40 and 55 °C.

Surfactants	Interfacial tension, mNm <sup>-1</sup>	Foam high, mL	Foam stability, s
DDAC	13	20	300
TDAC	9	-	-
HDAC	6	_	_

where *R* is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), *T* the absolute temperature,  $\pi_{CMC}$  is the effectiveness and  $A_{min}$  is the minimum surface area.

Negative values of both micellization and adsorption for the synthesized cationic surfactants (DDAC, TDAC and HDAC) indicate that the adsorption and micellization are spontaneous processes. Free energies of adsorption and micellization become more negative with an increase in alkyl chain length. However, the high negativity  $\Delta G_{ads}$  values showed that the process of adsorption is a predominant process than micellization process due to the preference of adsorption governed by the thermodynamic stability of the molecules at the air/water interface. On rising the temperature from 25 to 55 °C the negativity of free energy is increased due to the stability of the adsorbed and micellized surfactant molecules than the freely dispersed in the aqueous phase as shown in Table 3.

Entropy changes of micellization ( $\Delta S_{mic}$ ) are low values which point to the ordering of the synthesized quaternary ammonium salts molecules participated in the micellar phase. Ordering of the molecules evident their compactness at which the hydrophobic alkyl chains are coiled in the micellar core in high compatibility, and the hydrophilic head positive nitrogen group direct to the water phase. That arrangement decreases the repulsion in the surfactant-aqueous phase system and leads to stabilization for the formed micelles.

The sequence of the enthalpy changes ( $\Delta H_{\rm ads/mic}^{\circ}$ ) in Table 4 shows both the micellization and adsorption processes indicate the thermodynamic predominance of the adsorption process than the micellization process for the synthesized surfactants.

#### 3.7. Antimicrobial activity

Quaternary nitrogen compounds act as amphiphilic cations in aqueous solution so many cationic surfactants are used as pesticides and antimicrobial against wide spectrum of organisms as well as for killing sulfate reducing bacteria which can exist in petroleum field and cause many problems such as block out pipe line, produce H<sub>2</sub>S toxic gas, form iron sulfide hard scale and cause microbial corrosion [27-29]. Therefor the microbial activity of the synthesized cationic surfactants was screened against Gram-positive (S. aureus), Gram-negative (E. coli), pathogenic fungi (C. albicans and Asperigllus niger) and sulfate reducing bacteria (Desulfomonas pigra). By analyzing the data in Table 5, it is clear that the antimicrobial activities of the synthesized quaternary ammonium salts were more influenced by the hydrophobic chain length so with an increase in alkyl chain length the antimicrobial activity gradually increased. The hexadecanoate derivatives (HDAC) showed the maximum antimicrobial activities against the investigated Gram-positive and Gram-negative bacteria. These could be due to the relationship between surface activities and antimicrobial activity of the synthesized compounds. Increasing the

Compound	T, °K	$\Delta G_{ m ads},$ kJ/mol	$\Delta G_{ m mic},\  m kJ/mol$	$\Delta S_{\rm ads},$ kJ.mol <sup>-1</sup> K <sup>-1</sup>	$\Delta S_{ m mic},$ kJ.mol <sup>-1</sup> K <sup>-1</sup>	$\Delta H_{ m ads},$ kcal.mol <sup>-1</sup>	$\Delta H_{ m mic},$ kcal.mol <sup>-1</sup>
DDAC	298	-24.89	-22.49	-	-	-	_
	313	-27.26	-24.05	-0.158	-0.104	-	-
	328	-29.01	-25.76	-0.117	-0.114	-67.288	-63.21
TDAC	298	-23.68	-21.88	-	-	-	-
	313	-26.74	-24.58	-0.204	-0.18	-	-
	328	-32.84	-29.37	-0.407	-0.319	-166.2	-134.16
HDAC	298	-24.83	-22.89	-	-	-	-
	313	-26.48	-24.05	-0.11	-0.077	-	-
	328	-28.17	-25.76	-0.113	-0.114	-65.18	-63.21

Table 4 Thermodynamic parameters of adsorption and micellization for the synthesized cationic surfactants at 25, 40 and 55 °C.

Table 5 Antimicrobial activity of the synthesized cationic surfactants against pathogenic bacteria and fungi.

Compounds	Inhibition zone diameter (mm/mg sample)						
	Staphylococcus aureus	Escherichia coli	Candida albicans	Asperigllus niger			
Ampicillin/amphotericin B	20/-	17/-	-/17	-/20			
DDAC	9	13	0	0			
TDAC	10	13	0	0			
HDAC	13	15	0	11			

hydrophobic alkyl chain length increases the adsorption tendency of the synthesized biocide molecules at surfaces of microorganism's membranes, Fig. 7. Hence, the potent action of the tested compounds is increased due to their high population at the cellular membrane [30–36]. The results of the antifungal activity of the synthesized quaternary ammonium salts showed that negative effect against the most pathogenic fungal strain, Table 5. That may be ascribed to the resistivity of the fungi strain to the aggressive environmental components due to the rigidity of their cellular



Figure 7 Structure of the bacterial cell walls.

membranes, so that these fungi have high resistance against synthesized cationic surfactants.

#### 4. Conclusion

The synthesized surfactants showed higher surface activity and their activity was influenced by the chemical structures and hydrophobic chain length. The temperature of the solution causes a significant effect on the thermodynamic parameters of adsorption and micellization. Also, the antimicrobial activity of quaternary salts toward bacteria and fungi were high and depended on the chemical structures of the biocide.

#### References

- [1] F.M. Menger, Angew Chem. Int. Ed. Eng. 30 (1991) 1086–1099.
- [2] J. Appell, G. Port, A. Khatory, F. Kem, S.J. Candau, J. Phys. (Paris) 2 (1992) 1045–1052.
- [3] R. Zana, M. Benrroau, R. Rueff, Langmuir 7 (1991) 1072–1075.
- [4] R. Zana, Y. Talmon, Nature 362 (1993) 228-230.
- [5] P.K. Vinson, J.R. Bellare, H.T. Davis, W.G. Miller, L.E. Scriven, J. Colloid Interface Sci. 142 (1991) 74–91.
- [6] H. Hirata, M. Sato, Y. Sakaiguchi, Y. Katsube, Colloid Polym. Sci. 266 (1988) 862–864.
- [7] D.A. Jaeger, B. Li, T. Clark Jr., Langmuir 12 (1996) 4314– 4316.
- [8] D. Shukla, V.K. Tyagi, J. Oleo. Sci. 55 (2006) 381-390.
- [9] S.M. Tawfik, J. Mol. Liq. 209 (2015) 320-326.
- [10] J. Andrew, B. Mc, G.L. Ruth, E.M. Louiss, C. Carl, G.t. Peter, Appl. Environ. Microbiol. 70 (6) (2004) 3449–3456.
- [11] N.A. Negm, Y.M. Elkholy, F.M. Ghuiba, M.K. Zahran, S.A. Mahmoud, S.M. Tawfik, J. Dispersion Sci. Technol. 32 (2011) 512–518.
- [12] S.M. Shaban, A. Sayed, S.M. Tawfik, A. Abd-Elaal, I. Aiad, J. Ind. Eng. Chem. 19 (2013) 2004–2009.
- [13] N.A. Negm, I. Aiad, S.M. Tawfik, J. Surfactants Deterg. 13 (2010) 503-511.
- [14] I. Aiad, S.M. Tawfik, S.M. Shaban, A. Abd-Elaal, M. El-Shafie, J. Surfactants Deterg. 17 (2014) 391–401.

- [15] G.H. Sayed, F.M. Ghuiba, M.I. Abdou, E.A. Badr, S.M. Tawfik, N.A. Negm, Colloids Surf. A: Physicochem Eng. Aspects 393 (2012) 96–104.
- [16] A. Abd-Elaal, I. Aiad, S.M. Shaban, S.M. Tawfik, A. Sayed, J. Surfactants Deterg. 17 (2014) 483–491.
- [17] S. Chavda, P. Bahadur, V.K. Aswal, J. Surf. Deterg. 14 (2011) 353–362.
- [18] G.H. Sayed, F.M. Ghuiba, M.I. Abdou, E.A. Badr, S.M. Tawfik, N.A. Negm, J. Surf. Deterg. 15 (2012) 735–743.
- [19] A.A. Abd-Elaal, S.M. Tawfik, S.M. Shaban, Appl. Surf. Sci. 342 (2015) 144–153.
- [20] N.A. Negm, S.M. Tawfik, J. Ind. Eng. Chem. 20 (2014) 4463– 4472.
- [21] R.E. Cooper, in: F.W. Kavanagen (Ed.), Analytical Microbiology, vols. I and II, Academic press, New York, 1972.
- [22] E.A.M. Gad, M.M.A. El-Sukkary, D.A. Ismail, J. Am. Oil Chem. Soc. 74 (1997) 43–47.
- [23] W.L.M. Hinze, E.A. Pramouro, Crit. Rev. Anal. Chem. 24 (1993) 133–177.
- [24] S.M. Tawfik, M.F. Zaki, Res. Chem. Intermed. (2014), http:// dx.doi.org/10.1007/s11164-014-1867-3.
- [25] M.J. Rosen, J.H. Mathias, L. Davenport, Langmuir 15 (1999) 7340–7346.
- [26] N.A. Negm, F. Ahmed, S.M. Tawfik, M. Ahmad, H.H. Hefni, A.K. Manal, J. Surfactants Deterg. 16 (2013) 333–342.
- [27] S. Augusta, H.F. Gruber, F. Streichsbier, J. Appl. Polym. Sci. 53 (9) (1994) 1149–1163.
- [28] N. Negm, S.M. Tawfik, Chem. Today J. 30 (6) (2012) 5-8.
- [29] A.M. Badawi, M.A. Mekawi, A.S. Mohamed, M.Z. Mohamed,
- M.M. Khowdairy, J. Surfactants Deterg. 10 (4) (2007) 243–255.
  [30] A. Cukurovali, I. Yilmaz, S. Gur, C. Kazaz, Eur. J. Medic. Chem. 41 (2006) 201–207.
- [31] A. Koch, Clin. Microbiol. Rev. 16 (4) (2003) 673-687.
- [32] N.A. Negm, F.M. Ghuiba, S.A. Mahmoud, S.M. Tawfik, Eng. Life Sci. 11 (2011) 496–510.
- [33] Salah M. Tawfik, J. Ind. Eng. Chem. 28 (2015) 171-183.
- [34] M.F. Zaki, S.M. Tawfik, J. Oleo Sci. 63 (2014) 921-931.
- [35] M.F. Zaki, I.A. Aiad, S.M. Tawfik, J. Ind. Eng. Chem. 21 (2015) 1174–1182.
- [36] S.M. Tawfik, A. Sayed, I. Aiad, J. Surfactants Deterg. 15 (2012), pp. 577–558.