Synthesis and characterization of newly cationic surfactants based on 2-(2-(dimethylamino)ethoxy)ethanol: physiochemical, thermodynamic and evaluation as biocide

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Three newly cationic surfactants based on 2-(2-(dimethyl amino) ethoxy) ethanol were prepared through direct quaternization with different alkyl bromide. The chemical structures of the synthesized surfactants were confirmed by proton nuclear magnetic resonance and Fourier transform infrared spectroscopy. The critical micelle concentrations have been estimated using two different techniques surface tension and conductometric measurements at three different temperatures 25, 45 and 65 °C. The surface parameters were found hydrophilic and temperature dependent. The tail elongation and raising the solution temperature has a reverse effect on the critical micelle concentration. The calculated thermodynamic parameters proved that the synthesized surfactant favor the adsorption at the interfaces than aggregation in micelles. The synthesized surfactant HEDDB has the maximum antibiotic effect against the tested gram positive and negative bacteria and even higher than the used drug. The surfactant HEDHB has higher antifungal activity than the reference drug. The simply synthesized surfactant showed a high effect against sulfate reducing bacteria at low concentration.

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1. Introduction

The surfactants have attracted great interest in both technical applications and fundamental researches. Surfactants are organic compounds have the ability to lower the surface or interfacial tension of the system in which they be dissolved. They comprised of two opposing parts attached together in the same molecule. The tail of surfactant has the ability to dissolve in non-polar media while the head dissolve in polar media. Therefore, the amazing structure of surfactant force them to migrate to the interface or aggregate in micelles in the bulk solution. The mention behavior of surfactant lowers the free energy of the system. The adsorption and the micellization phenomena are responsible for the wide application of surfactants in various fields and fundamental research. In petroleum sectors, the surfactants participate in many applications serving the production of the crude oil like corrosion inhibitors, demulsifier, pour point depressant, biocide and drilling mud [1–8]. Surfactants used in detergent, paints, coating, drug industry [9–13]. The surfactants participate in nanotechnology research as capping agents for controlling size [14–17]. The surfactant can be used as capping agent and reducing agent at the same time as reported by T. Mishra et al. [18]. The similarity in the chemical structure between the surfactants and cell membrane of bacteria facilitates the destructive action of surfactant. The production of crude oil sometimes accompanied by certain types of bacteria called sulfate-reducing bacteria (SRB). The growth of sulfate reducing bacteria cause severe corrosion problems in transfer pipelines and storage tanks and with high growth, it may lead to the souring of the oil well. Therefore, it is necessary to mitigate the sulfate reducing bacteria. The cationic surfactant showed high efficiency in killing the sulfate reducing bacteria, at the same time it participates in the oil production [19–22]. The cationic surfactant is a category of surfactant where the head group carries positive charge [23–25]. Many reports exploited the biological activity of cationic surfactant [26–28]. The presence of some functional groups like NH, OH, SH and halogen in the chemical structure of the surfactant enhance the biological activity and the corrosion inhibition [29,30]. The work aimed to study the physicochemical and thermodynamic parameters of new simply synthesized surfactant in order to manage them is specific application. The adsorption and micellization propensity are the central of various application. The chemical structures of the surfactants were confirmed using FTIR and 1H NMR spectroscopy. The activity against bacteria and fungi were determined. The foaming and emulsification
power have been determined to assess whether they can facilitate oil production or not when they be used as biocide against sulfate reducing bacteria.

2. Materials & experimental

2.1. Materials

2-(2-(dimethylamino)ethoxy)ethanol was used as purchased from Sigma Aldrich chemical company. The octyl bromide, dodecyl bromide and hexadecyl bromide alkylating agents were purchased from a Merck company and used without any purification. All the used organic solvents (ethanol and diethyl ether) were purchased from the Algohhoria Chemical Company. All the mention chemicals and solvents were used without any more purification.

2.2. Synthesis of cationic surfactants

The cationic surfactants were prepared through direct low energy synthetic pathway. The 2-(2-(dimethylamino)ethoxy)ethanol 0.01 mol (1.33 g) was refluxed with 0.01 mol from the alkylating agent separately (octyl bromide (1.93 g), dodecyl bromide (2.49) and hexadecyl bromide (3.05 g) in 100 mL ethyl alcohol as solvent for 15 h). After evaporating the absolute alcohol, the residual was purified with diethyl ether [31]. The short name for the obtained product henceforward are HEDOB, HEDDB and HEDHB for the synthesized cationic surfactant with octyl, dodecyl and hexadecyl alkyl chain respectively. The synthetic pathway is shown in Scheme 1.

2.3. Structure confirmation

The synthetic route of newly cationic surfactants was investigated by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance spectroscopy (1H NMR). The FTIR analysis was carried out in Egyptian Petroleum Research Institute using ATI Mattson Infinity Series™, Bench top 961 controlled by Win First™ V2.01 Software. The 1H NMR was done in National Research Institute using GEMINI 200 (1H 200 MHz) in DMSO-d6.

2.4. Measurements

2.4.1. Surface tension measurements and interfacial tension

The surface tension of the synthesized cationic surfactant aqueous solutions was measured by a platinum ring detachment method using a K6 Krüss (Hamburg, Germany) tensiometer at three different temperatures 25, 45 and 65 ± 0.1 °C. The accuracy of the measurements was ±0.5 mN m⁻¹. The solutions were poured into a clean Teflon cup with a mean diameter of 28 mm. The platinum ring was cleaned before each measurement with diluted chromic acid mixture solution then washed with double distilled water. Each concentration was measured three times and the average was recorded and used without correction. The critical micelle concentration (CMC) was determined from the break point in surface tension (γ) versus [log c] plots [31].

The interfacial tension of the synthesized cationic surfactants was obtained between 0.1% aqueous solutions of surfactants by weight and light paraffin oil at 25 °C using the same procedures of the surface tension measurements [32].

![Scheme 1. Synthetic route of newly cationic surfactants.](image-url)
2.4.2. Foaming power

Foam power was estimated after shaking 100 mL of 0.1% surfactant solution vigorously in a stoppered graduated 250 mL cylinder at room temperature 25 °C. The foam height measured by the initially produced foam height (in mL). The Foam stability was measured by the time required by the produced foam be diminished to the halve of initially produced [33].

2.4.3. Emulsion stability

Emulsion stability was estimated by vigorously stirring a mixture of 10 mL (0.1%) of the synthesized cationic surfactant solutions and 10 mL of paraffin oil at 25 °C. The emulsion stability of the synthesized cationic surfactants was expressed as the time required for separation of 9 mL of pure surfactant solution [34].

2.4.4. Conductivity measurements

The CMCs of the synthesized cationic surfactants have been estimated by conductivity using a digital conductivity meter Cond 3210 SET 1, Probe tetra corn 325 (Wissenschaftlich Technische Werkstattern), having a sensitivity of 1 μS·cm⁻¹. Each surfactant aqueous solution was measured trice and the average was taken. The deionized double distilled water used in the surfactant dilution has a conductivity equal to 1.9 μS·cm⁻¹ [35].

2.4.5. The biological activity evaluation

The antibiotic effect of the synthesized surfactants against pathogenic bacteria (Gram-positive and Gram negative) and fungi has been assessed using filter paper disc agar method [36,37]. The source of micro-organism is Microanalytical Center, Cairo University. The bacteria under evaluation was Escherichia coli and Staphylococcus aureus. The Candida albicans and Aspergillus flavus were used as an example for fungi.

The procedures for the assessment were as follows:

1. The melted agar flask was inoculated with the organism to be tested, and then pour them into a Petri dish.
The antibiotic effect of the synthesized surfactants on the sulfate reducing bacteria (SRB) was assessed using the serial dilution method according to ASTM D4412-84 \[38\]. SRB-contaminated water was supplied from Petro Dara Petroleum Co. (Eastern Desert, Egypt). The contaminated water was subject to growth of $10^7$ bacteria cell/mL. The prepared cationic surfactants were tested as biocide against the SRB by doses of $2.5 \times 10^{-3}$, $1 \times 10^{-3}$, $5 \times 10^{-4}$ and $1 \times 10^{-4}$ M. The system was incubated to contact time of 3.0 h. Each system was cultured in SRB specific media for 21 days at 37–40 °C.

3. Results and discussion

3.1. Structure confirmation

3.1.1. FTIR spectra

The three synthesized surfactants showed nearly the same bands in infrared spectra. Fig. 1 shows the FTIR spectra of the surfactant HEDHB as an example of the synthesized surfactant. Fig. 1 confirms the presence of a stretching vibration band of $–C–H$ aliphatic symmetric and asymmetric at 2852 and 2920 cm$^{-1}$ respectively in addition $–CH_3$ bending at 1398 cm$^{-1}$, $–CH_2$ bending at 1471 cm$^{-1}$. The hydroxyl group appeared at 3376 cm$^{-1}$ while the ether bond and $–CN$ bond at 1131 cm$^{-1}$ and 1081 cm$^{-1}$ respectively. The aromatic proton appeared at 3008 cm$^{-1}$.

3.1.2. $^1H$ NMR spectra

The number and distribution of the prepared cationic surfactant protons were estimated by $^1H$ NMR spectra. Fig. 2 shows the $^1H$ NMR spectra of $N$-(2-(2-hydroxy ethoxy) ethyl)-$N$-dimethyloctan-1-aminium bromide (HEDOB) with signals at: $\delta = 0.79$ (t,3H, $CH_3$ alkyl chain); $\delta = 1.18$ (m,10H, $N^0$-CH$_2$CH$_2$($CH_2$)$_2$CH$_2$); $\delta = 1.59$ (m,2H, $N^0$-CH$_2$CH$_2$($CH_2$)$_2$CH$_2$); $\delta = 2.73$ (m,2H, $N^0$-CH$_2$CH$_2$($CH_2$)$_2$CH$_2$); $\delta = 3.06$ (m,6H, ($CH_2$)$_2$N$^0$CH$_2$CH$_2$($CH_2$)$_2$CH$_2$); $\delta = 3.33$ (t,2H, OCH$_2$CH$_2$N$^0$-CH$_2$CH$_2$($CH_2$)$_2$CH$_2$); $\delta = 3.44$ (t,2H, OCH$_2$CH$_2$N$^0$CH$_2$($CH_2$)$_2$CH$_2$); $\delta = 3.51$ (t,2H, HOCH$_2$CH$_2$OCH$_2$CH$_2$N$^0$); $\delta = 3.77$ (t,2H, t,2H, HOCH$_2$CH$_2$OCH$_2$CH$_2$N$^0$) and $\delta = 4.69$ (t,3H, $t$2H, HOCH$_2$CH$_2$OCH$_2$CH$_2$N$^0$).

3.2. Specific conductivity study

Altering the hydrophobic chain length of the synthesized cationic surfactant containing free hydroxyl group and the raising solution temperature have a great effect on the specific conductivity. The recorded values of the degree of counter ion dissociation ($\alpha$) in Table 1, were obtained through Frahm’s method and equal to the ration between the postmicellar to premicellar region slopes. Data in Table 1 and Fig. 3 showed that the specific conductivity is inversely proportional to the hydrophobicity. Increasing the hydrophobic chain length of the synthesized cationic surfactants is accompanied by decreasing the solution specific conductivity. This behavior ascribed to increasing both the total number of counter ions and the bond strength between the surfactant head and the counter ion. Increasing the hydrophobicity is followed by decreasing the hydration, hence the charge density around the micelle enhanced so the bond between the micelle and the counter ion is strengthened (values of counter ion dissociation decrease). By increasing the hydrophobic chain length, the molecular weight increase, so

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Temp. °C</th>
<th>$\alpha$</th>
<th>$A_{\text{cmc}}$</th>
<th>$A_{\text{a}}$</th>
<th>$\pi$ (mN·m$^{-1}$)</th>
<th>$\Gamma$ (mol·cm$^{-2}$)</th>
<th>$A_{\text{cmc}}/C_{20}$</th>
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<tr>
<td>HEDOB</td>
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<td>0.41</td>
<td>2.73</td>
<td>500.17</td>
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<td>0.20</td>
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<tr>
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<td>0.43</td>
<td>2.73</td>
<td>500.17</td>
<td>0.20</td>
<td>6.31</td>
<td>35.93</td>
</tr>
<tr>
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<td>0.38</td>
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<td>0.20</td>
<td>6.31</td>
<td>35.93</td>
</tr>
</tbody>
</table>

* The values obtained from surface tension measurements.

Table 1: The surface properties of synthesized cationic surfactant at various temperatures.
the number of counter ions decreases [39–43]. The degree of counter ion dissociation values of the synthesized cationic surfactants HEDOB, HEDDB and HEDHB was 0.43, 0.41 and 0.40 at 45 °C respectively.

By inspection data in Table 1, and Fig. 4, it was found that the raising the solution temperature is directly proportional to the specific conductivity of the synthesized cationic surfactant. For example, the degree of counter ion dissociation of the synthesized surfactant HEDHB at temperature 25, 45 and 65 °C was 0.38, 0.40 and 0.41 respectively. This behavior ascribed to increasing the dissociation of the counter ion from the head of synthesized surfactant monomer or their micelle with raising the temperature and this effect is dominant than the columbic attraction force between the head and its counter ion [44–47].

3.3. Critical micelle concentration (CMC) and surface activity

The characteristic CMC of the synthesized cationic surfactant aqueous solution at 25, 45 and 65 °C, was estimated by two different methods; surface tension and conductivity. The CMC corresponds to the intersection point in the specific conductivity-concentration curve obtained from conductivity measurements as exemplified in Figs. 3 and 4.

The abrupt change in the surface tension curves of the synthesized cationic surfactant against their bulk concentration as exemplified in Figs. 5–7, correspond to the CMC. The measured CMC from the conductivity method is slightly higher than that obtained from the surface tension as depicted in Table 1, due to the premicellar region [48–50].

Increasing the hydrophobicity has a decreasing effect on the CMC as obvious in the recorded data (Table 1 & Fig. 8). Increasing the chain length of the synthesized cationic surfactants, increase their affinity to aggregate in clusters, hence the micelle be formed at lower concentrations. The measured CMCs at 25 °C were 3.98, 1.72 and 0.83 mM/L for the synthesized surfactants HEDOB, HEDDB and HEDHB respectively.

Increasing the solution hydrophobicity by increasing the length of the synthesized cationic surfactants destroys the water structure, hence the free energy of surfactant solution increase. The surfactant unimers aggregate together in the micelle form or migrate to the interface to avoid contacting with the polar media, hence the free energy, decrease so the affinity to form the micelle increase (CMC decrease) [51–54].

During the micellization process, the hydration of the hydrophilic head group increase compared to the surfactant unimers. This behavior can be distinguished in Figs. 3 and 4 through increasing the specific conductivity as discussed previously. When micelle starts to be formed, we notice steady in the values of surface tension as shown in Figs. 5–7, due to the micelle be formed in the bulk not surface.

Inspection data in Table 1, and Fig. 8, we reveal that, raising the solution temperature has a decreasing effect on the CMC; for example, the CMC of the synthesized surfactant HEDDB are 1.72, 1.06 and 0.85 mM/L at 25, 45 and 65 °C respectively. This behavior is attributed to the decreasing the hydration around the hydrophilic head and disruption the water structure around the hydrophobic tail. The magnitude of the two opposing behaviors determines whether the CMC increase or decrease over a particular range. As depicted in Table 1, it clarified that the predominant effect is decreasing the hydration around the hydrophilic head group, hence CMC decreased [55–57].

The effectiveness (πCMC) is the difference in the surface tension values of blank water (γ0) and at critical micelle concentration (γCMC) of the synthesized cationic surfactants (Table 1). The effectiveness was calculated using surface tension measurements through the following equation:

\[ \pi_{CMC} = \gamma_0 - \gamma_{CMC} \]  

On inspection the effectiveness values of the synthesized cationic surfactant in Table 1, we reveal that the synthesized surfactant with hydrophobic tail contains sixteen carbon atoms (HEDHB) is the most effective surfactant at the three tested temperatures. The πCMC equal to 35.9, 36.8 and 37.8 mN m\(^{-1}\) for the synthesized cationic surfactants HEDOB, HEDDB and HEDHB at 25 °C respectively. The higher value of effectiveness is indicative of the condensed nature of synthesized cationic surfactants unimers at the aqueous medium/air interface and the lower value refer to that the formed monolayer from the monomers is more expanded [58–59]. The surfactant HEDHB is the most effective one due to it has the higher CMC/πCMC as indicated in Table 1. The CMC/πCMC values of the synthesized surfactants HEDHB were 88.6, 127.6 and 128.8 at 25, 45 and 65 °C, respectively.

The efficiency (C20) values were calculated from surface tension measurements and recorded in Table 1. The C20 represents the concentration of the surfactant required to suppress the surface tension by 20 dyne/cm. Inspecting the data in Table 1, we note that by elevating the solution temperature and increasing the hydrophobicity, the efficiency increase. Raising the aqueous solution temperature from 25 to 65 °C, the hydration around the hydrophilic and hydrophobic decrease. From the behavior of the temperature on the CMC, we can conclude that the effect of decreasing the hydration around the hydrophilic head is the prevailing one, so the rate of migration of the surfactant unimers to surface increase so more reduction in surface tension. The efficiency increase by increasing the hydrophobic chain length as a result of increasing the hydrophobicity, therefore the adsorption at surface increase.
The surface excess ($\Gamma_{\text{max}}$) of the prepared cationic surfactants expressed as the concentration of the surfactant unimers at interface per unit area. The ($\Gamma_{\text{max}}$) calculated from surface tension measurements using Gibb's adsorption equation (Eq. (2)) [60]:

$$\Gamma_{\text{max}} = \frac{1}{2.303 \text{nRT}} \left( \frac{\delta \gamma}{\delta \log c} \right)$$

Where $R$ is the gas constant, $n$ is the number of active species ($n$ equal 2 for cationic surfactant with monovalent counter ion), $(\delta \gamma / \delta \log c)$ is the surface pressure (slope at the premicellar region of surface tension-concentration curve) and $T$ is the absolute temperature.

Maximum surface excess describes the accumulation of prepared cationic surfactants at the interface. Hence increasing the surface pressure gives an indication on the high accumulation of the surfactant monomers at the interface.

Minimum average surface area is the average area (in square angstrom) occupied by each cationic unimer adsorbed at the system interface. $A_{\text{min}}$ values give information about the orientation of the prepared surfactant at the interface [61]. The minimum surface area ($A_{\text{min}}$) calculated from Gibb's adsorption equation (Eq. (3)):

$$A_{\text{min}} = \frac{10^{16} \Gamma_{\text{max}}}{N}$$

Where $N$ is Avogadro's number. The mathematically calculated maximum surface excess and minimum surface area of the prepared cationic surfactant at 25, 45 and 65 °C based on surface tension measurements were recorded in Table 1.

By inspection the $\Gamma_{\text{max}}$ and $A_{\text{min}}$ values in Table 1, we conclude that they are hydrophobic and temperature depended. Raising the solution temperature from 25 to 65 °C, the $\Gamma_{\text{max}}$ decreases. This means that the accumulation of the surfactant unimers decreases at the air-water interface by raising the solution temperature. The $\Gamma_{\text{max}}$ of the synthesized surfactant HEDOB were $0.8 \times 10^{-10}$, $0.67 \times 10^{-10}$ and $0.54 \times 10^{-10}$ mol/cm² at temperature 25, 45 and 65 °C respectively. Increasing the hydrophobic tail of the synthesized surfactant, the accumulation at the air-water interface increase. The $\Gamma_{\text{max}}$ were found to equal to $0.8 \times 10^{-10}$, $0.82 \times 10^{-10}$ and $0.85 \times 10^{-10}$ mol/cm² at 25 °C for the prepared HEDOB, HEDDB and HEDHB cationic surfactant respectively.

The cluster formation arises from two opposing forces. An attractive force arises from the hydrophobic effect of the hydrophobic surfactant tail. The electrostatic repulsive force arises from the interaction between the positively charged head groups. The hydrophobic effect favors the aggregation in micelle and closer packing by breaking down the highly dynamic hydrogen bond between water molecules; thus, the longer hydrophobic tails will induce stronger hydrophobic attraction, which forces the surfactants unimers to aggregates in larger micelle with high accumulation at the interfaces [62–64].
Table 2: Micellization and adsorption thermodynamic parameters of the prepared cationic surfactants.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Temp. (°C)</th>
<th>$\Delta_{mic}^{\text{Go}}$ (kJ·mol$^{-1}$)</th>
<th>$\Delta_{mic}^{\text{H}}$ (kJ·mol$^{-1}$)</th>
<th>$\Delta_{mic}^{\text{S}}$ (kJ·mol$^{-1}$)</th>
<th>$\Delta_{ads}^{\text{H}}$ (kJ·mol$^{-1}$)</th>
<th>$\Delta_{ads}^{\text{S}}$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEDOB</td>
<td>25</td>
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<td>-9.19</td>
<td>-37.78</td>
<td>-42.16</td>
<td>-52.23</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>49.04</td>
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<td>-52.12</td>
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<tr>
<td></td>
<td>65</td>
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<td>-57.95</td>
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<tr>
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<td>-50.29</td>
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<td>15.96</td>
<td>-57.65</td>
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<tr>
<td>HEDHB</td>
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<td>-42.16</td>
<td>-52.23</td>
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<tr>
<td></td>
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<td>-57.54</td>
<td>-64.42</td>
<td>-70.68</td>
<td>-77.94</td>
<td>-85.20</td>
</tr>
</tbody>
</table>

The minimum surface area is related to the accumulation of the surfactants unimers at the interfaces. As depicted in Table 1, the accumulation at the interface increase by increasing the hydrophobic effect and with decreasing the solution temperature. The high accumulation force the surfactant unimers to be dense packing and the surfactants ordered vertically to the interface; hence the $A_{\text{min}}$ decreases [42,63].

3.4. Thermodynamic aspects

The propensity of the synthesized cationic surfactant to adsorb at interfaces or aggregate in micelles in bulk solution is a central to their various useful properties. Hence, their behavior at three different temperatures 25, 45 and 65 °C, was studied thermodynamically using the phase separation model proposed by Zana [65]. The standard free energy of micellization ($\Delta G_{\text{mic}}^{\text{mic}}$), the standard free energy of adsorption ($\Delta G_{\text{ads}}^{\text{ads}}$), micellization entropy ($\Delta S_{\text{mic}}^{\text{mic}}$), adsorption entropy ($\Delta S_{\text{ads}}^{\text{ads}}$), micellarization enthalpy ($\Delta H_{\text{mic}}^{\text{mic}}$) and adsorption enthalpy ($\Delta H_{\text{ads}}^{\text{ads}}$) were calculated by following Eqs. (4)–(9):

$$\Delta G_{\text{mic}}^{\alpha} = (2-\alpha)RT \ln (X_{\text{CMC}})$$  

$$\Delta G_{\text{ads}}^{\alpha} = \Delta G_{\text{mic}}^{\alpha} + 6.023 \times 10^{-2} \left( \frac{C_{\text{mic}}}{\Gamma_{\text{mic}}} \right)$$  

$$\Delta S_{\text{mic}}^{\alpha} = -d(\Delta G_{\text{mic}}^{\alpha}/dT)$$  

$$\Delta S_{\text{ads}}^{\alpha} = -d(\Delta G_{\text{ads}}^{\alpha}/dT)$$  

$$\Delta H_{\text{mic}}^{\alpha} = \Delta G_{\text{mic}}^{\alpha} + T \Delta S_{\text{mic}}^{\alpha}$$  

$$\Delta H_{\text{ads}}^{\alpha} = \Delta G_{\text{ads}}^{\alpha} + T \Delta S_{\text{ads}}^{\alpha}$$

Where $\alpha$ is degree of counter ion dissociation for the synthesized cationic surfactants (conductivity measurements) and $X_{\text{CMC}}$ is the critical micelle concentration in molar fraction (surface tension measurements).

The calculated thermodynamic parameters were depicted in Table 2. The data reveal that both the adsorption and micellization processes are spontaneous as indicated by the negative values of change in free energy of adsorption and micellization. The $\Delta G_{\text{mic}}^{\alpha}$ of the synthesized cationic surfactants HEDOB, HEDDB and HEDHB was $-37.58$, $-41.39$ and $-44.6$ kJ/mol respectively at 25 °C. The $\Delta G_{\text{ads}}^{\alpha}$ of the HEDOB, HEDDB and HEDHB was $-42.07$, $-45.87$ and $-49.04$ kJ/mol respectively at 25 °C. On Comparing between the both values of $\Delta G_{\text{mic}}^{\alpha}$ and $\Delta G_{\text{mic}}^{\alpha}$ for the synthesized cationic surfactants, we conclude that $\Delta G_{\text{mic}}^{\alpha}$ is more negative than that of micellization $\Delta G_{\text{mic}}^{\alpha}$, which show the high adsorptive propensity of the synthesized cationic surfactants at the air-water interface than aggregation in micelles (adsorption is energetically favored than micellization). According to the previous results, we can conclude that the synthesized cationic surfactants tend to adsorb at air-water interface first until surface saturation then it aggregates in micelles in the solution bulk [55–57].

Inspection data in Table 2, we reveal that the change in free energy of adsorption and micellization of synthesized cationic surfactants increase in the negative direction upon raising the solution temperature from 25 to 65 °C. This indicates the higher stability of the adsorbed and aggregated surfactant molecules than the dispersed surfactants unimers in the bulk solution. The $\Delta G_{\text{mic}}^{\alpha}$ of the synthesized surfactants HEDOB increased in the negative direction from $-37.58$ to $-46.42$ kJ/mol upon raising the solution temperature from 25 to 65 °C, while the $\Delta G_{\text{ads}}^{\alpha}$ increased in the negative direction from $-42.07$ to $-52.4$ kJ/mol.

The same trend has been observed upon increasing the hydrophobic character of the synthesized surfactants through increasing the length of the surfactants tails from eight to sixteen carbon atoms. The $\Delta G_{\text{mic}}^{\alpha}$ of the synthesized surfactants increased in the negative direction from $-37.58$ to $-44.60$ kJ/mol upon increasing the hydrophobic chain...
length from eight to sixteen carbon atoms at solution temperature 25 °C, while the ΔΓ_{ads} increased in the negative direction from −42.07 to −49.04 kJ/mol at 25 °C.

Elevating the solution temperature causes a decrease of hydration around the hydrophilic group, so the hydrophobicity of the system increase and accompanied by increasing the energy of the system, so molecules of surfactant tend to adsorb and form micelle to decrease the energy of the system [52–54]. Increasing the chain length of prepared cationic surfactants containing free hydroxyl group were accompanied by increasing the hydrophobicity of the aqueous system; which lead to the destroying the water structure thus increasing the free energy of the system. Thus, the surfactant monomers migrate to surface or ag-gregate in clusters. The migration to surface or aggregation in cluster decreases the energy of the system, so the change in the free energy of the prepared surfactant-solvent system will be decreased and increased in the negative direction. The chemical structure of synthesized cationic surfactants containing free hydroxyl group is the main factor influenc-ing their thermodynamic aspects.

The recorded ΔS_mic and ΔS_{ads} values in Table 2, are positive which refer to the ordering of the surfactant molecules when they aggregate in micelles and/or adsorb at the air-water interface. The ordering of surfactant molecules is evident to their compactness whether they adsorbed at air-water interface or aggregates in micelle where the hydrophilic tail coiled interior the micelle and the head faced to water. This ordering decreases the repulsion in the surfactant-aqueous phase system and leads to more stabilization for the formed micelles and/or adsorbed unimers at the air-water interface. The adsorption entropy change (ΔS_{ads}) is more positive than micellization entropy change (ΔS_mic), which reflect the greater freedom of hydrophobic part through motion to the interface than micelle formation [58–59].

3.5. Foaming power of synthesized surfactants

In some applications like fire extinguishing and metal flotation systems, the foam formation is very important. In other, the foam formation is a very serious matter, which should be prevented like in jet system and high-pressure fluid. The foam can increase the pressure of those systems, causing an exploitation. Inspection data set in Table 3, we reveal that the prepared cationic surfactants with the free hydroxyl group have a low foam height with very low stability except the synthesized surfactant HEDHB, which has foam stability, reach to 240 min. Hence, the synthesized surfactant with eight and twelve carbon atoms can be used in the various applications, which not require the foam forma-tion affinity such as washing machine laundry and additives in oilfield applications as corrosion inhibitors and as a biocide for sulfate reducing bacteria [66].

3.6. Emulsification power

The emulsification affinity is an indicator of the synthesized cationic surfactants ability of to locate at the boundaries between the different phases. The emulsification efficiency was measured by the time required for the separation of 9 mL of pure water from the emulsion system. Increasing the separation time, the stability of the formed emulsion increase and vice versa. Inspection data in Table 3, it can be seen that increasing the emulsion stability depend on the chemical structure of the synthesized cationic surfactants containing free hydroxyl group, where by increasing the hydrophobic character upon increasing the chain length of the prepared surfactant, the emulsion stability increase. These results matched with the obtained Γ_{max} in Table 1. By increasing the length of the hydrophobic chain length, the accumulation of surfactant unimers at the interfaces increase, hence the interfacial tension decrease and the emulsion stability increase. The synthesized surfactants HEDOB and HEDDB exhibit low emulsification power range from 3–4 min. According to this low emul-sification power, these two surfactants can be used in applications as demulsifier, corrosion inhibitors and biocide for sulfate reducing bacteria in oilfield system in which any chemical used should have a demulsifier ability in order to facilities the oil production processes. According the dataset in Table 3, the synthesized surfactant with chain length equal to sixteen carbon atoms (HEDHB) has very high emulsion stability (180 min.). Hence, the surfactants HEDHB can be used in several applications as emulsifier including emulsion paints, textile industry and shampoos [67].

3.7. Interfacial tension

The measured interfacial tension of the synthesized cationic surfactants containing free hydroxyl group with light paraffin oil at 25 °C was depicted in Table 3. The dataset reveals that the synthesized cationic surfactant exhibit low interfacial tension values as an indication for the high accumulation of the surfactants unimers at the water-paraffin oil interface. It was found that increasing the hydrophobic chain length of the synthesized surfactants followed by decreasing the interfacial tension value of water-paraffin oil system at 25 °C. These results are in good agreements with the trend of maximum surface excess depicted in Table 1. The interfacial tension values of the synthesized surfactant HEDOB, HEDDB and HEDHB were 9, 7 and 6 mN/m at 25 °C respectively. The lower values of the interfacial tension reflect the ability of these surfactants to be used as a biocides and corrosion inhibitors [67].

3.8. Antimicrobial activity

The antibiotic and antifungal effect of the synthesized cationic surfactants containing free hydroxyl group were screened against pathogenic Gram-negative bacteria (Escherichia coli), Gram-positive (Staphylococcus aureus) bacteria and fungi (Aspergillus flavus and Candida albicans). The obtained datasets were depicted in Table 4. The synthesized three cationic surfactants with different hydrophobic tail showed high potency action against the tested bacteria and fungi. Inspection data in Table 4, we reveal that the synthesized surfactants have antimicrobial activity higher than the used drug references. Inspection dataset in Table 4, it is clear that the antimicrobial activity of the prepared cationic surfactants (HEDOB, HEDDB and HEDHB) depends on their chemical structures. The synthesized biocide characterized by its amphiphatic structure owing a unique behavior. It can adsorb on the cell wall membrane and aggregate in clusters. The killing action of the biocide depends on the adsorption on the cell wall membrane. The synthesized biocide (surfactants) have different surface parameters depending on their chemical structure; like CMC, maximum surface excess, minimum surface area, the change in free energy of

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Emulsion stability (min)</th>
<th>Interfacial tension (mN/m)</th>
<th>Foaming height (mL)</th>
<th>Foam stability (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEDOB</td>
<td>3</td>
<td>9</td>
<td>10</td>
<td>2.5</td>
</tr>
<tr>
<td>HEDDB</td>
<td>4</td>
<td>7</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>HEDHB</td>
<td>180</td>
<td>6</td>
<td>60</td>
<td>240</td>
</tr>
</tbody>
</table>
micellization and change in free energy of adsorption; which discussed in details. Hence the magnitude of these parameters responsible for the activity as antimicrobial.

Inspection the dataset in Table 4, we reveal that the antibiotic and antifungal effect against bacteria and fungi are hydrophobic dependent. In case of the tested bacteria, the antibiotic effect of the synthesized cationic surfactants gradually increases with increasing the hydrophobic chain length of the surfactants until maximum effect at chain length of twelve carbon atoms (HEDDB) then the activity decrease again. This trend is known by the cut-off effect [68–70]. The antibiotic effect of the synthesized biocides HEDOB, HEDDB and HEDHB against Escherichia coli bacteria was 16, 22 and 20 mm/mg respectively.

Regarding to the tested fungi, the synthesized biocide showed promising high antifungal activity which increases upon increasing the hydrophobic chain of the biocide surfactant. The antifungal activity of the synthesized biocides HEDOB, HEDDB and HEDHB against Aspergillus flavus fungus was 13, 14 and 17 mm/mg respectively.

The cut-off effect depends on the surface parameters of the synthesized surfactants, these parameters are CMC, change in free energy of adsorption, accumulation of the surfactants at the cell wall and the size of diffused surfactant unimers [71–74].

Elongation the tail of the synthesized surfactant accompanied by a decreasing the CMC as depicted in Table 1, hence the biocide surfactant concentration at the cell membrane became lower with higher chain. According to this hypothesis, the antimicrobial activity should be ordered as follows HEDOB > HEDDB > HEDHB. The change in the free energy of adsorption increase with increasing the hydrophobic chain length as indicated in Table 2, hence the rate of migration to the cell wall interface increase. According this parameter, the activity can be ordered as follows HEDHB > HEDDB > HEDOB. Another hypothesis related to a decrease in the perturbation of the membrane at higher alkyl tail, assuming that the longer the chain, the better mimic molecule in the lipid layer, leading to disruption in the membrane. As depicted in Table 1, the maximum accumulation of the synthesized biocide surfactants increase with increasing the hydrophobic chain length, hence the activity predicted to increase. Therefore, the magnitude of all the previous determines the behavior of the antibiotic. From the obtained dataset in Table 4, we can conclude that the synthesized surfactants HEDHB have the optimum antibiotic effect, while the synthesized biocide HEDHB has the maximum antifungal effect against the tested microorganism.

Sulfate Reducing Bacteria (SRB) is one of the problems which obstacle the petroleum industry. The SRB bacteria produce H₂S, which cause souring in the petroleum well and corrosion for the equipment beside its hazard effect on the environment. Therefore, it is necessary to mitigate the SRB bacteria to control the microbial induced corrosion (MIC). The synthesized cationic surfactants were evaluated against Sulfate reducing bacteria using serial dilution method and the obtained results were depicted in Table 5. The contaminated water was supplied from Petro Dara Petroleum Co. (Eastern Desert, Egypt), and subject to growth 10⁷ cells/mL. The synthesized cationic surfactants were evaluated at concentration 2.5 × 10⁻³, 1 × 10⁻³, 5 × 10⁻⁴ and 1 × 10⁻⁴ M as an antibiotic against sulfate reducing bacteria. The prepared biocide showed high potent action against SRB. The synthesized biocide HEDDB has the maximum antibiotic effect against SRB. At concentration 5 × 10⁻⁴ M from the tested biocide HEDOB, HEDDB and HEDHB, the growth of SRB were 10⁴, nil and 10⁵ cells/mL respectively.

The bacterial cell membrane comprised from thick wall containing many layers of peptidoglycan and teichoic acids as exemplified in Fig. 9 [75,76]. The positively charged surfactant adsorbed on lipoteichoic acid layer of the Gram-positive bacteria and on the lipid layer of the Gram-negative bacteria. Therefore, the expected mechanism of the synthesized cationic surfactants depends on their affinity to adsorb on the cell wall membrane through the interaction between the positively head group and lipoteichoic acid layer and lipid layer in Gram-positive and Gram-negative bacteria respectively. The adsorption on the cell wall membrane, facilitate the penetration of the hydrophobic tail and

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Inhibition zone diameter (mm/mg sample)</th>
<th>Ref. inhibition zone diameter (mm/mg sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HEDOB</td>
</tr>
<tr>
<td>Gram reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Escherichia coli</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>Staphylococcus aureus</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>Candida albicans</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Cutanea spilolactis</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 4: The antibiotic effect of the synthesized cationic surfactants against pathogenic bacteria and fungi.
the counter ion and hence disturbing the selective permeability of the membrane leading to the cell death [77–81].

3.8.1. Surface activity — antimicrobial activity relationship

From the obtained dataset in both Tables 3 & 4, it is clear that the chemical structures of the synthesized cationic surfactants containing free hydroxyl group are responsible for the antibiotic and antifungal activity. By increasing the hydrophobic chain length, the antimicrobial activity increase as cleared in Tables 3 & 4. The tested biocides are cationic surfactants, which characterized by their amphipathic structure containing hydrophilic head and a hydrophobic tail. This unique structure responsible for the surfactants surface parameters including the adsorption and micellization. The antimicrobial activity of the biocide depends on their adsorption on cell wall membrane then penetration inside the living cell and disturbing the selective permeability of the membrane. As depicted in Tables 1 & 2, increasing the hydrophobic chain length is accompanied by increasing the adsorption at the interface (\( \Delta G_{\text{ads}} \)) and the accumulation at the interface increase (\( \Gamma_{\text{max}} \)), these two parameters enhance the population of the surfactants unimers at the cell wall membrane and adsorption through the positively charged surfactant head group. The surfactant adsorption at cell wall permit the penetration of the surfactant tail inside the cell beside the counter ion and the free hydroxyl group which bind to ribosomal protein. Hence, the selective permeability of the cell wall membrane destroyed, causing cell death [82].

4. Conclusion

Three newly cationic surfactant containing free hydroxyl group were prepared by a simple and direct method. The chemical structures were confirmed using proton nuclear magnetic resonance and Fourier transform infrared spectroscopy. The surface parameters of the synthesized cationic surfactants are chemical structure dependent. The CMC obtained from both surface tension and conductivity measurements were in good agreement. The thermodynamic aspect showed the propensity of the prepared surfactants to adsorb at the air-water interface then

<table>
<thead>
<tr>
<th>Biocide</th>
<th>Conc. 2.5 ( \times 10^{-3} ) (M)</th>
<th>1 ( \times 10^{-3} ) (M)</th>
<th>5 ( \times 10^{-4} ) (M)</th>
<th>1 ( \times 10^{-4} ) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>( 10^{7} )</td>
<td>10(^3)</td>
<td>10(^4)</td>
<td>10(^5)</td>
</tr>
<tr>
<td>HEDOB</td>
<td>nil</td>
<td>10(^2)</td>
<td>nil</td>
<td>10(^3)</td>
</tr>
<tr>
<td>HEDDB</td>
<td>nil</td>
<td>nil</td>
<td>10(^2)</td>
<td>10(^3)</td>
</tr>
<tr>
<td>HEDHB</td>
<td>nil</td>
<td>10(^2)</td>
<td>10(^3)</td>
<td>10(^5)</td>
</tr>
</tbody>
</table>

Table 5
Biocidal effect of the prepared compounds against sulfate reducing bacteria, SRB.

Fig. 9. The structure of the bacterial cell wall membrane.
aggregation in micelle in bulk solution. The synthesized surfactants HEDOB and HEDDB showed low foaming stability, low interfacial tension and low emulsion stability. Therefore it can be used in emulsion paints, textile industry and shampoos. The synthesized surfactants showed antibiotic and antifungal activity compared to the used references drugs. The synthesized HEDDB surfactant showed highly biocidal activity against the sulfate reducing bacteria present in the petroleum oilfield.

Acknowledgements

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