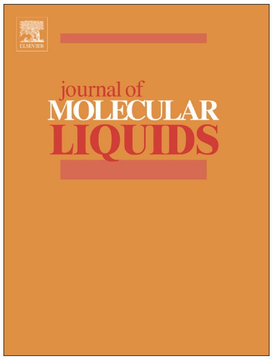

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# Experimental Evaluation of Cationic-Schiff Base Surfactants Based on 5-Chloromethyl Salicylaldehyde for Improving Crude Oil Recovery and Bactericide

**Mohamed A. Betiha[1,2], Samy B. El-Henawy[1], Ahmed M. Al-Sabagh[1], Nabel A. Negm[1,2#], Tahany Mahmoud[1]**

1- Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

2- Egypt Nanotechnology Center, Cairo University, Sheikh Zayed, Egypt

Corresponding author: nabelnegm@hotmail.com

## Abstract

In this study, a new family of cationic and cationic–Schiff Base surfactant was synthesized namely; N-(3-formyl-4-hydroxybenzyl)-N,N-dimethylhexadecan-1-aminium chloride (FHDHAC), (E)-N-(3-((butylimino)methyl)-4-hydroxybenzyl)-N,N-dimethylhexadecan-1-aminium chloride (4-IMHDAC), (E)-N-(3-((hexylimino)methyl)-4-hydroxybenzyl)-N,N-dimethylhexadecan-1-aminium chloride (6-IMHDAC) and (E)-N-(4-hydroxy-3-((octylimino) methyl)benzyl)-N,N-dimethylhexadecan-1-aminium chloride (8-IMHDAC) were prepared from 5-chloromethyl salicylaldehyde compound (5-CMS). The chemical structures of 5-CMS, 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC are characterized using FTIR, $^1$H-NMR instruments. The surface activity measurements of the prepared compounds showed a gradual increase in surface activity by increasing the alkyl chain length. Adsorption and micellization thermodynamic functions revealed the higher tendencies of the different surfactants towards adsorption at the organic/polar phase. The synthesized surfactants were evaluated in the enhanced oil recovery process and showed excellent efficiency (63.98%, 71.25%, and 75.72% for 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC, respectively) during the recovery process near their critical micelle concentrations. The prepared surfactants showed high antimicrobial efficacy against different bacteria and fungi.

**Keywords**: Wettability; cationic–Schiff Base surfactant, interfacial tension; EOR.

## Introduction

Until now, with the entry of other sources of energy, such as solar energy, wind, etc., oil maintains that it is the main source of energy, and the stock of oil is one of the factors that evaluate the economies of some countries. The energies stored naturally inside the oil-bearing formation (gas-drive, water-drive, or gravity drainage) is the main factor facilitating the primary oil recovery. After the deterioration of the natural energies of the reservoirs, the reservoir is injected with water or gas to enhance the production of the reservoir, which is called secondary oil recovery. During this stage, the injected liquid is usually water or gas that is mechanically injected through the injection wells. During this operation, the In general, the second stage does not include adding any chemicals or carrying out chemical reactions inside the reservoir, as this method is considered as mechanical or physical operation in order to enhance production from the oil reservoirs [1]. This stage reaches aging when the ratio of water to the resulting oil is very high. It should be noted that the oil reservoir may maintain a percentage of crude oil that may exceed two-thirds of the crude that has been predicted for the reservoir [2]. The main reason behind the decrease in the production of crude oil from the petroleum reservoir is the increased viscosity of crude oil, in addition to the high interfacial tension (IFT) between the water and the remaining oil. These two factors lead to the emergence of a large capillary force that traps the crude oil inside the capillaries of the reservoir rocks [3]. Therefore, extracting other quantities of the remaining oil after the second stage constitutes a challenge for the industry in the field of oil production, and this challenge calls enhanced chemical recovery of oils.

Chemical floods are one of the most widely used and influencing methods for enhancing oil production after the second stage [4]. Adding alkalis to surfactant causes emulsification of oil droplets and regulates the phase behavior of emulsified oil by increasing the ionic strength to achieve a very low IFT rate through carrying the saponification process [5]. One of the most important advantages of using alkali is the cheapness in addition to reducing the adsorption of surfactants on the solid instead of improving the interfacial activity of the added surfactants [6].

Surface active agents are those that have the ability to form self-assembled molecules in clusters (micelles) and can be adsorbed between various phases interface in the solution [7]. The amphiphilic nature of these molecules is due to they possess a hydrophilic moiety/moieties and a lipophilic moiety/moieties [8]. The surface activities of the cationic and nonionic surfactants were found to increase their interfacial applications especially during emulsification and wettability [9, 10]. The process of increasing the oil extraction by surfactant was classified based on the amount of surfactant concentration in the solution, so it is called micellar flooding if the concentration of surfactant corresponds to critical micelle concentration (CMC) values and if the concentration exceeds the CMC the operation is called surfactant flooding [11]. By using surface flooding, the emulsification process (microemulsions) of the crude oil droplets occurs, and as a result, the entrainment, and coalescence of the crude oil drops with the water occurs as a result of a reduction in the surface tension between the oil and the water. In addition to the previous action, the surfactant had the ability to alter the rock wettability.

Vatanparast et al.[12] discussed the phase behavior of cetyltrimethylammonium bromide (CTAB) and concluded that CTAB improved oil production from a carbonate reservoir and the mixing of CTAB with silica nanoparticle led to more oil recovery. The authors also concluded that the increase in recovered oil was due to a decrease in IFT between oil and water even at high temperatures due to the alteration rock surface by CTAB. Sharma and Mohanty have studied the same compound again for the same purpose with changing conditions of the petroleum reservoir, where they used a solution with a salinity estimated at 600000 ppm and a temperature of 100 °C. The authors reported that the CTAB was unable to reduce the IFT at 100 °C despite its stability or alter the surface of carbonate rocks [13].

To some extent, the authors did not find any publications on the use of Schiff-base and cation surfactant in the operation of improving oil recovery. Therefore, this manuscript is the first report about the use of a single compound carrying a pair of an active group, cationic, and Schiff base combinations. This study aims to prepare a 5-chloromethyl salicylaldehyde compound using zinc chloric as a catalyst and get the benefit from the chloromethyl and aldehydic groups to obtain the cationic and Schiff moieties and determine their surface properties in order to maximize the benefit from them in the field of heavy oil production.

## 2. Experimental Section

### 2.1 Chemicals

Paraformaldehyde (≥99%)**,** salicylaldehyde (≥99%)**,** N,N-dimethyl hexadecyl amine (≥99%), 1-aminobutane (≥99%), 1-aminohexane (≥99%), 1-aminooctane (≥99%), hydrochloric acid (36.5%), sodium chloride (90%) were obtained from Sigma Aldrich (Egypt). Diethyl ether (≥99.0%), toluene (≥99.5%), methanol (anhydrous, 99.8%), and ethanol (96.0-97.2%) were purchased from ADWIC Chemicals Company, Egypt. Prior to solvent use, the solvents were distilled, followed by the drying over A4–molecular sieve. The crude oil was donated by Egypt's Petroleum company, and its basic analysis of the crude oil and brine analysis was given in ***Table 1***.

### 2.2 Synthesis of cationic surfactants

#### 2.2.1 Preparation of 5-Chloromethyl-2-hydroxybenzaldehyde (5-CMS)

Hydrochloric acid (150 mL, 37 wt.%) and 133.066 mmol of paraformaldehyde (10.8 mL, 37 wt.%) were charged into 250 mL-two neck flask. The solution was further purged with HCl gas produced from the reaction between concentrated sulfuric acid and sodium chloride. After 30 min, 15 mL (141.39 mmol) of salicylaldehyde was added drop-wise. The solution was left to stir for 24 h at the same condition until precipitation of a solid adduct. The solid was dissolved in an appropriate volume of diethyl ether, and then water was added to obtain two separate layers. The organic layer was extracted, and diethyl ether was evaporated to obtain the pure product of 5-chloromethyl-2-hydroxybenzaldehyde. The product was further washed with (150 mL diethyl ether/200 mL water) several times till the pH of the medium remained at 6.9. Finally, diethyl ether was vacuum evaporated to obtain crystallized 5-chloromethyl-2-hydroxybenzaldehyde (Yield: 62.9 %, 15.24 g).

### 2.2.2 Preparation of 3N-(3-formyl-4-hydroxybenzyl)-N,N-dimethylhexadecan-1-aminium chloride (FHDHAC)

Equimolar amounts (10 mmol, 1.7 g) of **5–CMS** and N, N-dimethyl hexadecyl amine (11 mmol, 2.96461 g) were dissolved in the appropriate volume of toluene, and the mixture was stirred for 3 h at 75 °C. A rotary evaporator then removed the solvent, and the product was washed three times with diethyl ether, followed by vacuum drying at 40 °C to obtain the desired product (3-(3-formyl-4-hydroxybenzyl)-N,N,N-dimethyl hexadecyl ammonium chloride, (**FHDHAC**).

### 2.2.3 Preparation of Schiff Base based on cation surfactants (4-IMHDAC, 6-IMHDAC, and 8-IMHDAC)

FHDHAC (10 mmol), 1-aminobutane (0.8 mmol), trimethylamine (0.2 mL), and 30 mL of dry ethanol were charged in a 100 mL flask, and the temperature of the mixture was raised the to 70 °C for 6 h. The yellow product of the reaction was distilled to remove ethanol and washed several times with ethanol to afford (E)-N-(3-((butylimino)methyl)-4-hydroxybenzyl)-N,N-dimethylhexadecan-1-aminium chloride, (8.9 mmol, 4-IMHDAC). The reaction was repeated by replacing 1-aminobutane by 1-aminohexane or 1-aminooctane to obtain: (E)-N-(3-((hexylimino)methyl)-4-hydroxybenzyl)-N,N-dimethylhexadecan-1-aminium chloride (6-IMHDAC) and (E)-N-(4-hydroxy-3-((octylimino)methyl)benzyl)-N,N-dimethylhexadecan-1-aminium chloride (8-IMHDAC), respectively ***(Scheme 1)***.

### 2.3. Measurements

To perform transform infrared spectroscopy (FTIR), 0.25 mg of samples 5-CMS, FHDHAC, 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC are well-dried and ground with KBR powder (300 mg) and analyzed on a Thermo iS50-FT-IRNICOLET 6700 instruments (resolution: 4 $cm^{-1}$ with 512 scans). To determine the structure of compounds, Bruker Nuclear Magnetic Resonance Spectroscopy using DMSO-*d6* as a solvent.

### 2.3.1 Surface tension ($\gamma$) and interfacial tension ($\gamma_{IFT}$) measurements

The surface tension values ($\gamma$) of the 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants at serial concentrations started with initial concentration of 0.01 mM were measured using Attension Theta High-pressure chamber (Biolin Company, Finland) (accuracy ±0.01 mN/m) using pendant drop technique at 25 and 50 $^{o}$C. The surface was bound to the downward shape according to ***Equation 1***:

$$\gamma = \frac{\Delta\rho g R_0}{\beta} \quad (1)$$

Where the symbols $\gamma$**,** $\Delta\rho$, $g$, $R_0$ and $\beta$ surface tension, density, gravitational constant, radius of the drop curvature, and factor based on the drop shape, respectively. $\boldsymbol{\beta}$ equals to 3 according the equation of Young-Laplace symbolized in ***Figure 1***.

The pendant drop method was applied for measuring the interfacial tension values ($\gamma_{IFT}$) of 0.01g/mL surfactants solutions through a time range of 1 minute until the readings were stabilized at 25 and 50 $^{o}$C. Attention Theta has intended in a way that could be analyzed $\gamma_{IFT}$ and contact angle using an online image capturing system, which enables the recording of data periodically as desired. In general, the $\gamma_{IFT}$ measurement was accomplished by injecting a drop of surfactant solution from the hocked needle into a solid bulk phase under the required pressure and temperature (ASTM ISO 19403-4).

### 2.3.2 Contact angle and Wettability measurement

Prior to performing analysis, the flat rocks were surface-cleaned using Soxhlet extractor filled with toluene as a solvent, dried under vacuum at 112 °C for 12 h. Then, the flat rock is immersed in brine for 12 h, and after that, the flat rock is submerged in the crude oil that will be used in the flooding test to achieve the oil-wet rock samples. The contact angle between the oil-wet rock and distilled water and different 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants solutions were identified by Sessile Method using Attention Theta high-pressure chamber ( (ASTM ISO 19403-5) at 25, 50 °C.

### 2.3.3 Kraft point

Kraft temperature ($K_T$) was determined by heating surfactants solutions (4-IMHDAC, 6-IMHDAC, and 8-IMHDAC) (1 wt.%) to obtain clear using the visual observation method, and the temperature was obtained for an average of three readings [14].

### 2.3.4 Antimicrobial activities

The 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants were tested for their potency as antimicrobial agents using the agar diffusion technique [15]. The 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants were assessed at 5000 ppm against *Staphylococcus aureus* ATCC 35556, and *Bacillus subtilis* ATCC 6633 as an example of a Gram-positive bacteria, and *Pseudomonas aeruginosa* ATCC 10145, *Escherichia coli* ATCC 23282 as an example for

Gram-negative bacteria. *Candida albicans* IMRU 3669 and *Aspergillus niger* ATCC 16404 are also considered as an example of yeast and filamentous fungus.

The different microorganisms were cultivated in their growing media (bacteria and yeast: nutrient agar, fungus: Czapek's Dox agar). Erythromycin and Metronidazole (commercial medicinal drugs) were used as controls bacteria and yeast, and fungus, respectively. All examinations were executed in triplicates, and data were their averages.

### Core flooding experiments

A distinction was made between the different 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants on their ability to enhance oil recovery after the exhaust of secondary oil recovery (water flooding), thereby increasing the oil proceeds tertiary recovery. An instrument has been designed to simulate the oil production system from wells, consisting of the core holder that contains silica as an oil-bearing material. A pump whose goal is to displace the crude oil and surfactant solution at the desired rate or quantity, cylinders for the crude oil, brine and surfactant solution, and cylinders to measure the volume of the resulting oil. The simulated rock's core holder is characterized by a porous volume of 102.4 cm$^3$, the total volume of the reservoir is 496 cm$^3$, and the crude oil residue after exhausting the second stage is 71 cm$^3$. While conducting the flooding process with the 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants, it should focus on using the optimum concentration of the surfactants. To optimize the concentration of the surfactant, three concentrations of best surfactant will be used, 1 g/L, 2 g/L, and 4 g/L, respectively, at 50 °C. The injection of the surfactant rate into the core holder was at 1 mL/min. The slug is allowed to remain in the core holder for two hours to cause a change in the wetness of the rocks that can be studied.

## 3. Result and discussion

### 3.1.1 FTIR spectroscopy

The 5-CMS compound shows the absorption bands at 3200-3500 cm$^{-1}$ assigned for the starching vibration of hydroxyl groups, low intense bands at 2823 and 2920 cm$^{-1}$ correspond to sym- and asymmetrical vibration of C–H bonds, sharp 1730 cm$^{-1}$ band for the two carbonyl groups, 1350 cm$^{-1}$ apportioned for C-Cl bond [16], 850-720 cm$^{-1}$ bands for the phenyl group [17, 18] ***(Figure 2)***. FGDHAC compound shows similar absorption bands as 5-CMS compound. The disappearance of the 1350 cm$^{-1}$ band was recorded due to the incorporation of the C–Cl bond in the reaction. Also, with a minor decrease in the intensity of the 1730 cm$^{-1}$ absorption band of the carbonyl group due to the incorporation of one carbonyl group in 5-CMS in the reaction and only one group is remained. Otherwise, the main bands were remained unchanged ***(Figure 2)***. The 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC compounds show similar absorption bands as FHDHAC compound with the diminished of the band at 1730 cm$^{-1}$ and the appearance of the new absorption band at 1640 cm$^{-1}$ due to mainly the formation of imine group, –C=N–.  Moreover, it is possible to see the aromatic stretching band (=C-H at 3026 cm$^{-1}$, and –C=C–at 1580 cm$^{-1}$), and the aliphatic bending bands (-CH$_2$ at 1377 cm$^{-1}$, and CH$_3$ at 1463 cm$^{-1}$) in addition to C-N vibration at 1073 cm$^{-1}$ ***(Figure 2)***.

### 3.1.2 $^1$H-NMR spectroscopy

The 5-CMS compound displays the following signals at 4.64 ppm (s, 2H, Cl–C$\boldsymbol{H_2}$-Ar), 6.92-7.64 ppm (dd, 3H, $\boldsymbol{H}$–Ar), 10.24 ppm (s, 1H, O=C$\boldsymbol{H}$-Ar) ***(Figure 3)***. The FGDHAC compound shows the following signals at 0.96 ppm (t, 3H, –C$\boldsymbol{H_3}$), 1.29 ppm (m, 26 H, –C$\boldsymbol{H_2}$–), 1.73 ppm (t, 2 H, –C$\boldsymbol{H_2}$-CH$_2$ N$^+$(CH$_3$)$_2$–), 3.24 ppm (t, 2 H, -C$\boldsymbol{H_2}$–N$^+$(CH$_3$)$_2$–), 3.3 ppm (s, 6H, (C$\boldsymbol{H_3}$)$_2$N$^+$–), 4.5 ppm (s, 2H, $^+$N-C$\boldsymbol{H_2}$-Ar), 5.0 ppm (s, 1H, $\boldsymbol{H}$O-Ar), 6.80-7.44 ppm (dd, 3H, $\boldsymbol{H}$-Ar), 10.24 ppm (O=C$\boldsymbol{H}$-Ar) ***(Figure 3)***. The 4-IMHDAC compound showed the following signals at 0.86 ppm (t, 6H, -C$\boldsymbol{H_3}$), 1.26 ppm (m, 28 H, -C$\boldsymbol{H_2}$-), 1.72 ppm (m, 2 H, –C$\boldsymbol{H_2}$–CH$_2$N=C-), 1.85 ppm (-C$\boldsymbol{H_2}$–CH$_2$N$^+$(CH$_3$)$_2$–), 3.2 ppm (–C$\boldsymbol{H_2}$-N$^+$(CH$_3$)$_2$–), 3.31 ppm (s, 6H, –N$^+$(C$\boldsymbol{H_3}$)$_2$–), 3.61 ppm (t, 2H, –C$\boldsymbol{H_2}$–N=C–), 4.5 ppm ((CH$_3$)$_2$N$^+$–C$\boldsymbol{H_2}$-Ar), 4.9 ppm (s, 1H, $\boldsymbol{H}$O-Ar), 6.74 ppm, 7.42 ppm, 7.65 ppm (d, 3H, $\boldsymbol{H}$-Ar), 8.3 ppm (s, 1H, -N=C$\boldsymbol{H}$) ***(Figure 3)***. The 6-IMHDAC compound showed the following signals at 0.86 ppm (t, 6H, –C$\boldsymbol{H_3}$), 1.26 ppm (m, 36H, –C$\boldsymbol{H_2}$–), 1.72 ppm (m, 2H, –C$\boldsymbol{H_2}$–CH$_2$N=C-), 1.85 ppm (-C$\boldsymbol{H_2}$–CH$_2$N$^+$(CH$_3$)$_2$-), 3.2 ppm (–C$\boldsymbol{H_2}$-N$^+$(CH$_3$)$_2$–), 3.31 ppm (s, 6H, –N$^+$(C$\boldsymbol{H_3}$)$_2$–), 3.61 ppm (t, 2H, –C$\boldsymbol{H_2}$-N=C–), 4.5 ppm ((CH$_3$)$_2$N$^+$–C$\boldsymbol{H_2}$-Ar), 4.9 ppm (s, 1H, $\boldsymbol{H}$O–Ar), 6.74 ppm, 7.42 ppm, 7.65 ppm (d, 3H, $\boldsymbol{H}$-Ar), 8.3 ppm (s, 1H, -N=C$\boldsymbol{H}$-) ***(Figure 3)***. The 8-IMHDAC compound showed the following signals at 0.86 ppm (t, 6H, –C$\boldsymbol{H_3}$), 1.26 ppm (m, 42H, –C$\boldsymbol{H_2}$–), 1.72 ppm (m, 2H, –C$\boldsymbol{H_2}$–CH$_2$N=C-), 1.85 ppm (–C$\boldsymbol{H_2}$–CH$_2$N$^+$(CH$_3$)$_2$–), 3.2 ppm (-C$\boldsymbol{H_2}$–N$^+$(CH$_3$)$_2$–), 3.31 ppm (s, 6H, –N$^+$(C$\boldsymbol{H_3}$)$_2$–), 3.61 ppm (t, 2H, –C$\boldsymbol{H_2}$-N=C–), 4.5 ppm ((CH$_3$)$_2$N$^+$–C$\boldsymbol{H_2}$–Ar), 4.9 ppm (s, 1H, $\boldsymbol{H}$O–Ar), 6.74 ppm, 7.42 ppm, 7.65 ppm (d, 3H, $\boldsymbol{H}$-Ar), 8.3 ppm (s, 1H, –N=C$\boldsymbol{H}$–) ***(Figure 3)***.

### 3.2 Surface active properties of the prepared surfactants

The surface properties of the 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants were determined based on the surface tension data obtained from the measurements of the surfactant's solutions surface tension at 25 °C and 50 °C in twice-distilled water. ***Figure 4*** represents the variation in surface tension values obtained for 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants at different temperatures. The concentrations of surfactants at equilibrium, which associated with the stability of these values, were defined for CMC (critical micelle concentration). The CMC and $\gamma_{CMC}$ values were established from the break-point of the profiles, ***Table 2***.

Obviously, there is a gradual decrease in CMC values by increasing the alkyl group chain length attached to the azomethine group (Schiff Base group) of the used surfactants at 25 °C. The lowest CMC value was obtained at 6.73 mM for octyl-chain of 8-IMHDAC surfactant. At 50 °C, the critical micelle concentration values were decreased compared to these obtained at 25 °C. That can be attributed to the increase in the repulsion between the hydrophobic chains and the aqueous phase by the action of heat, which facilitates the reduction of micellization of surfactant molecules. Generally, the surface tension at the micellization was decreased by increasing both of the alkyl chain length and the temperature.

The effectiveness values ($\pi_{CMC}$) are the difference between the surface tension values of the bidistilled water and surfactant solution CMC and $\pi_{CMC}$ was determined for the prepared surfactants using ***Equation 2*** [19]:

$$\pi_{CMC} = \gamma_W - \gamma_S \quad (2)$$

Where $\gamma_W$ and $\gamma_S$ are the water and surfactant surface tension at CMC. By calculating the average $\pi_{CMC}$ values, it was found that $\pi_{CMC}$ of 8-IMHDAC was the highest among the prepared surfactants.

The maximum surface excess concentration ($\Gamma_{max}$) is described as the concentration per area of surfactants molecules at the interface at the equilibrium, and can be achieved by applying ***Equation 3***:

$$\Gamma_{MAX} = -\frac{1}{RT} \times \frac{\delta\gamma}{\delta \ln C} \quad (3)$$

where $\Gamma_{MAX}$ is the excess surface concentration in (mol/cm$^2$), ***T*** (absolute value), ***R*** (universal gas constant, 8.314 J mol$^{-1}$ K$^{-1}$), and $\frac{\delta\gamma}{\delta \ln C}$ is the slope of $\gamma$-ln C profile.

From the obtained data (***Table 2)***, it was established that as the alkyl chains increase, the $\Gamma_{max}$ values considerably decreased. The 8-IMHDAC surfactant had the lowest $\Gamma_{max}$ value ($6.54\text{x}10^{-11}$ mol/cm$^2$) at 25 °C, and this value was decreased to $2.22\text{x}10^{-11}$ mol/cm$^2$ by increasing the temperature up to 50 °C. The average area occupied by surfactant molecules ($A_{min}$) was determined for each 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants in the solution at the equilibrium using ***Equation 4***:

$$A_{min} = \frac{10^{16}}{N_A \Gamma_{max}} \qquad (4)$$

where $\mathbf{N_A}$ is equal $6.023\times10^{23}$ molecule/mole (Avogadro's number).

Also, through ***Table 2***, $A_{min}$ values increases as both hydrophobic chain length and temperature increase due to the decrease in $\Gamma_{max}$ values. The longest $A_{min}$ value was 253.48 $nm^2$ for 8-IMHDAC, whilst the 4-IMHDAC has the smallest area of 177.98 $nm^2$ at the interface at 25 °C. The increase in the temperature of the surfactant solution causes an increase in the repulsion forces of the hydrophobic alkyl groups, and consequently, the micellization increased at lower concentrations, and the area available for each molecule at the interface was increased, as listed in ***Table 2***.

### 3.3 Thermodynamic evaluation of the prepared surfactants

The surface tension data of the prepared cationic-Schiff Base surfactants were used to define the free–energies of both micellization and the adsorption processes at the interfaces and the bulk of the cationic-Schiff Base surfactants solutions at 25 °C and 50 °C. The reduction in surface tension is in regard to the adsorption of the cationic-Schiff Base surfactant molecules at the air-aqueous interface. The adsorption energy of the cationic-Schiff Base surfactant molecules at the equilibrium can be calculated from ***Equation 5***:

$$\Delta G_{ads} = \Delta G_{mic} - (0.6022) \times \pi_{cmc} \times A_{min}) \qquad (5)$$

Furthermore, the free energy of the surfactant's molecules after micellization in the bulk of the solution can be determined from ***Equation 6***:

$$\Delta G_{mic} = RT \ \ln CMC \qquad (6)$$

Where $\Delta G_{ads}$ $\Delta G_{ads}$ and $\Delta G_{mic}$ are the molar Gibbs free energies of adsorption and micellization processes in kJ/mol. The calculated values of $\Delta G_{mic}$ and $\Delta G_{ads}$ for 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants were listed in ***Table 3***.

The data in ***Table 3*** indicated that both $\Delta G_{ads}$ and $\Delta G_{mic}$ values have negative signs, suggesting the spontaneously of the two processes. The spontaneous behavior of these processes comes from the repulsion that occurred between the hydrophobic chains of the cationic-Schiff Base surfactant molecules and the polar aqueous phase. Also, the negativity of the two values is increased by raising the temperature from 25 °C to 50 °C. Furthermore, it is clear that $\Delta G_{ads}$ have more negative values than $\Delta G_{mic}$ values, indicating the higher tendency of the 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants towards adsorption at the aqueous/air interface than the micellization in the solution bulk to form micelles [20]. The preferability of the surfactants molecules towards adsorption and micellization was determined from $\Delta G_{mic}$-$\Delta G_{ads}$ values. Obviously, the $\Delta G_{mic}$-$\Delta G_{ads}$ values were increased by increasing the temperature from 25 °C to 50 °C, indicating the increased adsorption tendency of 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactant molecules in their solutions at higher temperatures.

### 3.4 Wettability alteration using 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants

The wettability of the surfaces is an important property which can be achieved by the surfactants during several applications. The wettability tendencies of the prepared surfactants were evaluated using interfacial tension and contact angle measurements at the crude oil/surfactant solution interface. The alteration of the wettability of reservoir rocks of petroleum wells is an essential requirement during enhanced oil recovery processes (EOR).

### 3.4.1 Interfacial tension ($\gamma_{IFT}$)

The dynamic interfacial tension ($\gamma_{IFT}$) variations of the crude oil/surfactant solutions systems at the CMC of the 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants at 25 °C and 50 °C were represented in ***Figure 5***. It is clear that the dynamic $\gamma_{IFT}$ profiles of the crude oil/surfactants solutions systems reach the equilibrium after 5 to 10 min. The variation in dynamic $\gamma_{IFT}$ involved different patterns; at the initial time (0-1 min), the $\gamma_{IFT}$ values were decreased sharply (i.e., the high slope of 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC is of 0.6514, 0.3714, 0.3514, respectively) indicating the fast adsorption of the cationic–Schiff Base surfactant molecules at the interface. In the second region at (2-4 min), $\gamma_{IFT}$ values were decreased gradually (i.e., medium slope values of 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC is of 0.05, 0.075, 0.07, respectively), indicating the surface equilibrium between adsorption and desorption processes. At the longer time (4-10 min), $\gamma_{IFT}$ values were almost stable (i.e., small slope values of 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC is of 0.0126, 0.0084, 0.0063, respectively) indicating the achievement of equilibrium between the adsorption and desorption of surfactants molecules to- and from the crude oil/solution interface. The main reason for this response is the occurrence of adsorption and desorption of the cationic-Schiff Base surfactant species at the interfacial crude oil/aqueous layer [21, 22]. The primary decrease in $\gamma_{IFT}$ could be attributed to the hydrophobic characters of the different cationic-Schiff Base molecules, which forced the molecules to adsorb at the interface. The adsorption/desorption equilibrium of the cationic-Schiff Base molecules at the interface is started at the second time region while attaining the complete equilibrium has occurred at the final time region after 4 minutes.

The equilibrium $\gamma_{IFT}$ of the studied crude oil/surfactants solutions systems were varied between 0.32 and 0.69 mN/m at 25 °C ***(Table 4)***. Rising the temperature to 50 °C was decreased the interfacial tension values of the different surfactants to much lower magnitude ***(Table 4)***, which can be assigned to the increase of surfactant molecules pumping to the interface as the increase of the repulsion between these molecules and the aqueous medium. Decreasing the crude oil/surfactants solutions interfacial tension values by increasing the temperature to 50 °C indicates the increase in surface wettability by the surfactant's solutions. The high depression of the interfacial tension at the temperature of the crude oil reservoir enables the use of 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC as additives for enhancing crude oil production from exhausted wells.

### 3.4.2 Contact angle (θ)

During enhanced oil recovery processes, contact angle (θ) of the flooding solutions and the rock surface saturated by crude oil plays an important role as that determines the interaction between the rock and flooding solutions in petroleum reservoirs. Reservoir rocks can be classified into three phases: water wet ($\theta < 75^{o}$), oil-wet ($105 < \theta < 180°$) and moderate wet ($75 < \theta < 105°$) as shown in ***Figure 6***.

The effect of the 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants at CMC concentration on the contact angle at 25 and 50 °C was identified by measuring the contact angle (θ) between saturated sand–rock saturated by crude oil and surfactants solutions ***(Table 4)***. The average contact angles of 4-IMHDAC, 6-IMHDAC and 8-IMHDAC surfactants were observed at 30.9°, 29.2°, and 27.1° at 25 °C, and at 23.9°, 19.2°, and 13.5° at 50 °C, respectively. The spreading of crude oil on the surface of the sand rock is increased by increasing the alkyl group chain length of the surfactant, indicating wettability alteration of the rock system from moderate or oil-wet to water-wet [23]. The change in the angle of contact (θ) or the change in the wettability is the result of adsorption of the cationic–Schiff Base molecules on the external and internal surface of the rock [24]. Moreover, increasing of alky group chain length of cationic–Schiff Base surfactant favors the in-situ formation of the surfactant at the crude oil/water interface due to the interaction between the long alkyl chain and the crude oil.

After the formation of the in-situ surfactant, the surfactant moves to the aqueous phase as the action of emulsification. In this case, some of the surfactant molecules are adsorbed on the internal and external surface of rocks, resulting in wettability alteration, which facilitates the desorption of the crude oil from the rocks. The results of the contact angle and interfacial tension measurements of the 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants can explain their mechanism during the enhanced oil recovery process. In the next section, the efficiencies of the 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants during the enhanced oil recovery process of crude oil from exhausted wells will be measured in a simulated flooding system containing similar wells conditions of salinity, temperature, and pressure

### 3.4.3 Enhanced oil recovery

The results of the flooding experiments of crude oil-saturated sandstone were represented in ***Table 5***. The obtained results from the use of 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants at three different concentrations 1, 2, and 4 g/L, which represents the concentration before, at, and higher than the critical micelle concentration values. The cumulative oil recovery (%) obtained by using the 4-IMHDAC, 6-IMHDAC and 8-IMHDAC surfactants at different concentrations showed their high comparative efficiency during the enhanced oil recovery process ***(Table 5)***. At low concentration (1 g/L), the cumulative recovery of 4-IMHDAC was 54.7%, while this value was increased to 68.9% in the case of 8-IMHDAC. By increasing the concentration of the cationic-Schiff Base surfactants in the flooding solutions up to 2 g/L, i.e., near the CMC of the used surfactants, a considerable increase in the cumulative recovery was obtained. Additionally, a further increase in the surfactant concentrations above their CMC values (4 g/L) showed an extreme increase in the cumulative oil recovery (%) to reach 84.5% in the case of 8-IMHDAC flooding solution.

The results of the cumulative oil recovery from sandstone rock revealed several points. First, at flooding solutions with concentrations lower than the CMC values, the efficiency of the recovery was based on the interfacial properties of the different surfactants used during the recovery process. Surfactants with lower interfacial tension values and contact angles were more efficient in the recovery process. That can be attributed to the high ability of these surfactants to be adsorbed at the sandstone/flooding solution interface, which facilitates their diffusion to the rock pores, i.e., increase the wettability, and consequently repels the adhered crude oil droplets from the rock bulk to the solution ***(Figure 7)***. As can be seen from ***Table 4***, the interfacial tension and contact angle values were decreased by increasing the hydrophobic chain length from 4-IMHDAC to 8-IMHDAC, which is in good agreement with the increasing variety of the recovery efficiency. Second, at flooding solutions with concentrations at the CMC (2 g/L), the cumulative recovering efficiency was increased considerably for the used surfactant flooding solutions to reach its maximum at 75.7% for 8-IMHDAC surfactant ***(Table 5)***. Similar behavior was observed for 4-IMHDAC and 6-IMHDAC, as well. Finally, the maximum cumulative enhanced recovery was obtained in the case of flooding solutions containing surfactants at a concentration of 4 g/L (higher than CMC values). It is essential to optimize the concentration of surfactants concentration in the flooding solutions during the recovery process to avoid economic and production problems.

At the three ranges of surfactant concentrations used during the recovery process, the concentration near the CMC values was the most suitable concentration due to two main points. The first is economical; the high concentration of surfactants above CMC results in more adsorption of their molecules at the rock surface and leads to loss of the surfactants, which increase the cost of the process. The second is related to separation efficiency, high stable water/oil emulsions are formed at high surfactant concentrations, and that leads to a complication of crude oil separation process from the obtained emulsion, and the problem of emulsion breaker is raised. Hence, the optimized surfactant concentrations in the flooding solutions were at their CMC values. The temperature is the third parameter, which should be taken into consideration during the enhanced oil recovery process. The viscosity of surfactant/crude oil emulsion was reduced by rising the temperature ***(Figure 8)***, which leads to the increase in the mobility of the displaced fluid (flooding solution), and consequently, higher sweep efficiency was occurred accompanied by the oil recovery process. The most suitable temperature was found to be at 50 °C, which is also the average reservoir's temperature.

### 3.4 Antimicrobial activity

The prepared cationic–Schiff Base surfactants, 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC, were tested against several potent microorganisms, including *Bacillus subtilis* (*B. subtilis*), *Staphylococcus aureus* (*S. aureus*), *Escherichia coli* (*E. coli*), *Pseudomonas aeruginosa candida Albicans* (*P. aeruginosa, C. Albicans*), and *Aspergillus niger* (*A. niger*) by means of inhibition zone diameter procedures, ***(Table 6)***. Inhibition zone diameter results indicated that the cationic Schiff Base surfactants have good antimicrobial activities; furthermore, the antimicrobial activities are depended mainly on the hydrophobicity of the chain length. The obtained results were in agreement with reported findings [8], where the difference in the optimum activity appears towards different types of bacteria resulting from the difference in the chemical structure of the cationic surface. Thereby, the 8-IMHDAC, which has the most extended chain length (8–carbon attached to the azomethine group), has the optimal activity.

### Conclusion

In this study, three positively charged surface-active agents were synthesized, and their chemical structures were elucidated by $^{1}$H-NMR and FTIR. The surface activity measurements of the prepared compounds showed a gradual increase in surface activity by increasing the alkyl chain length. Adsorption and micellization thermodynamic functions revealed the higher tendencies of the different surfactants towards adsorption at the organic/polar phase. The synthesized surfactants were evaluated in the enhanced oil recovery process and showed good efficiency (63.98%, 71.25%, and 75.72% for 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC, respectively) during the recovery process near their critical micelle concentrations. The prepared surfactants showed high antimicrobial efficacy against different bacteria and fungi.

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*CRediT author statement*

***Ahmed M. Al-Sabagh, Nabel A. Negm, Mohamed A. Betiha, Tahany Mahmoud**: Conceptualization, Methodology, Writing - Review & Editing.*

***Mohamed A. Betiha, Tahany Mahmoud**: Conceptualization, Methodology, Writing.*

**Samy B. El-Henawy**: Validation

***Tahany Mahmoud**: Investigation*

Authors of manuscripts confirm that there is no conflict of interest of this study with other studied.

**Scheme 1: Synthesis protocol of the compounds 5-CMS 4-IMHDA, 6-IMHDA and 8-IMHDA.**

**Figure 1: Illustration of the pendant drop method based on optical drop-shape analysis.**

**Figure 2. FTIR of 5-CMS, 4-IMHDA, 6-IMHDA and 8-IMHDA compounds.**

**Figure 3: $^1$H-NMR of 5–CMS, FGDHAC, 4-IMHDAC, 6-IMHDAC and 8-IMHDAC compounds.**

**Figure 4: Surface tension vs. concentration profile of prepared surfactants: A) at 25 $^o$C, and B) at 50 $^o$C.**

**Figure 5: Dynamic interfacial tension values at surfactants solutions-crude oil interface at: A) 25 $^{o}$C and B) 50 $^{o}$C.**

**Figure 6: Different cases of contact angle at a solid liquid interface.**

**Figure 7: Predicted mechanism of enhanced oil recovery using: 4-IMHDAC, 6-IMHDAC and 8-IMHDAC surfactants.**

Figure 8. Variation of viscosity for crudeoil and surfactant (1 g/L)/crude oil emulsion by raising the temperature.

**Table 1: physicochemical properties of crude oil used**

| Experiment | Method | Result |
|---|---|---|
| **Density at 15.56 (°C)** | ISO 3675 | 0.8983 |
| **Specific gravity (g/cm$^3$)** | ASTM D-4052 | 0.8892 |
| **Viscosity (cp)** | ASTM D-4052 | 824.1 |
| **API gravity at 60 (°F)** | ASTM D-4052 | 27.1 |
| **Asphaltene content (wt.%)** | IP-143 | 7.63 |
| **Wax content, wt. %** | UOP-64 | 17.0 |

**Table 2. Surface properties of 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants at 50 °C and 50 °C**

| Surfactant | T, $^o$C | CMC (mmol/L) | $\gamma_{CMC}$ (mN/m) | $\pi_{CMC}$ (mN/m) | $\Gamma_{max}$ (mol/cm$^2$) | $A_{min}$ (nm$^2$) |
|---|---|---|---|---|---|---|
| **4-IMHDAC** | 25 | 8.40 | 31.8 | 40.8 | 9.32x10$^{-11}$ | 177.98 |
| | 50 | 4.21 | 23.1 | 49.5 | 3.77x10$^{-11}$ | 440.26 |
| **6-IMHDAC** | 25 | 7.91 | 27.8 | 44.8 | 9.09x10$^{-11}$ | 182.64 |
| | 50 | 3.97 | 22.8 | 49.8 | 2.81x10$^{-11}$ | 589.08 |
| **8-IMHDAC** | 25 | 6.73 | 26.9 | 45.7 | 6.54x10$^{-11}$ | 253.48 |
| | 50 | 3.38 | 19.9 | 52.7 | 2.22x10$^{-11}$ | 746.88 |

**Table 3. Thermodynamic parameters of 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants at 25 and 50 °C**

| Surfactant | T (°C) | $\Delta G_{mic}$ (KJ/mol) | $\Delta G_{ads}$ (KJ/mol) | $\Delta G_{mic}$-$\Delta G_{ads}$ |
|---|---|---|---|---|
| **4-IMHDAC** | 25 | -11.84 | -16.21 | 4.37 |
| | 50 | -14.68 | -27.81 | 13.12 |
| **6-IMHDAC** | 25 | -11.99 | -16.91 | 4.92 |
| | 50 | -14.85 | -33.97 | 18.69 |
| **8-IMHDAC** | 25 | -12.39 | -19.36 | 6.97 |
| | 50 | -15.28 | -37.24 | 22.39 |

**Table 4. Interfacial tension and contact angle of crude oil/surfactants solutions at 25 °C, and 50 $^o$C**

| Surfactant | Interfacial tension ($\gamma_{IFT}$, mN/m) | | Contact angle ($\theta$, $^o$) | |
|---|---|---|---|---|
| | 25 °C | 50 °C | 25 $^o$C | 50 $^o$C |
| **4-IMHDAC** | 0.72 | 0.18 | 30.9 | 23.9 |
| **6-IMHDAC** | 0.46 | 0.07 | 29.2 | 19.2 |
| **8-IMHDAC** | 0.32 | 0.01 | 27.6 | 13.5 |

**Table 5. The cumulative oil recovery (%) obtained using 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants at different concentrations at 50 $^o$C**

| Surfactant | Conc. 1 g/L | Conc. 2 g/L | Conc. 4 g/L |
|---|---|---|---|
| | Recovery,% | | |

| | | | |
|---|---|---|---|
| **4-IMHDAC** | 54.67 | 63.98 | 81.28 |
| **6-IMHDAC** | 62.93 | 71.25 | 83.55 |
| **8-IMHDAC** | 68.85 | 75.72 | 84.46 |

**Table 6. Antimicrobial activity of 4-IMHDAC, 6-IMHDAC, and 8-IMHDAC surfactants against pathogenic bacteria and fungi**

| **Surfactant** | **Inhibition zone diameter (mm)** | | | | | |
|---|---|---|---|---|---|---|
| | ***B. subtilis*** | ***S. aureus*** | ***E. coli*** | ***P. aeruginosa*** | ***C. albicans*** | ***A. niger*** |
| **4-IMHDAC** | 21 | 28 | 13 | 14 | 26 | 26 |
| **6-IMHDAC** | 19 | 30 | 18 | 19 | 30 | 29 |
| **8-IMHDAC** | 18 | 24 | 14 | 13 | 25 | 20 |
| **Erythromycin** | 32 | 33 | 28 | 28 | --- | --- |
| **Metronidazole** | --- | --- | --- | --- | 29 | 30 |

Three positively charged surface-active agents were synthesized.

Gradual increase in surface activity was increased by increase of chain length.

Adsorption thermodynamic functions showed high tendency towards adsorption.

The surfactants showed good efficiency in oil recovery.

The surfactants showed high antimicrobial efficacy against bacteria and fungi.

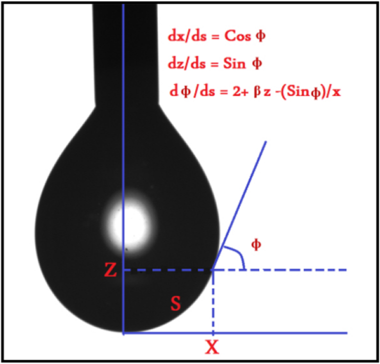


Figure 1

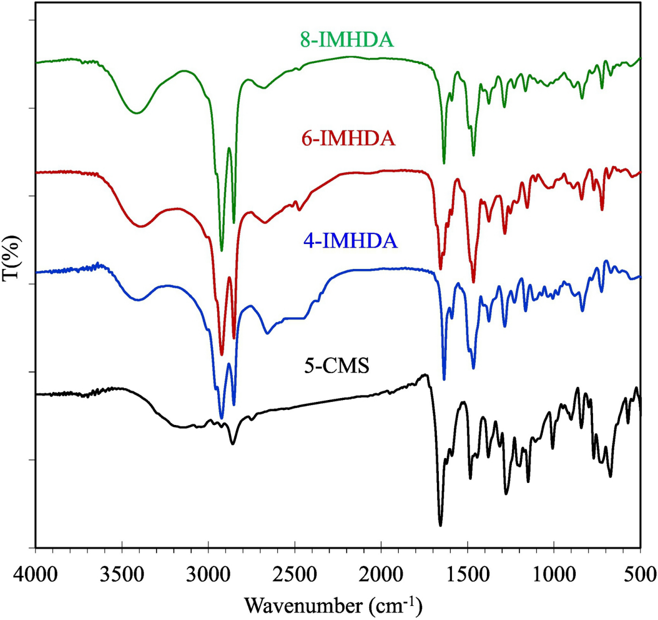
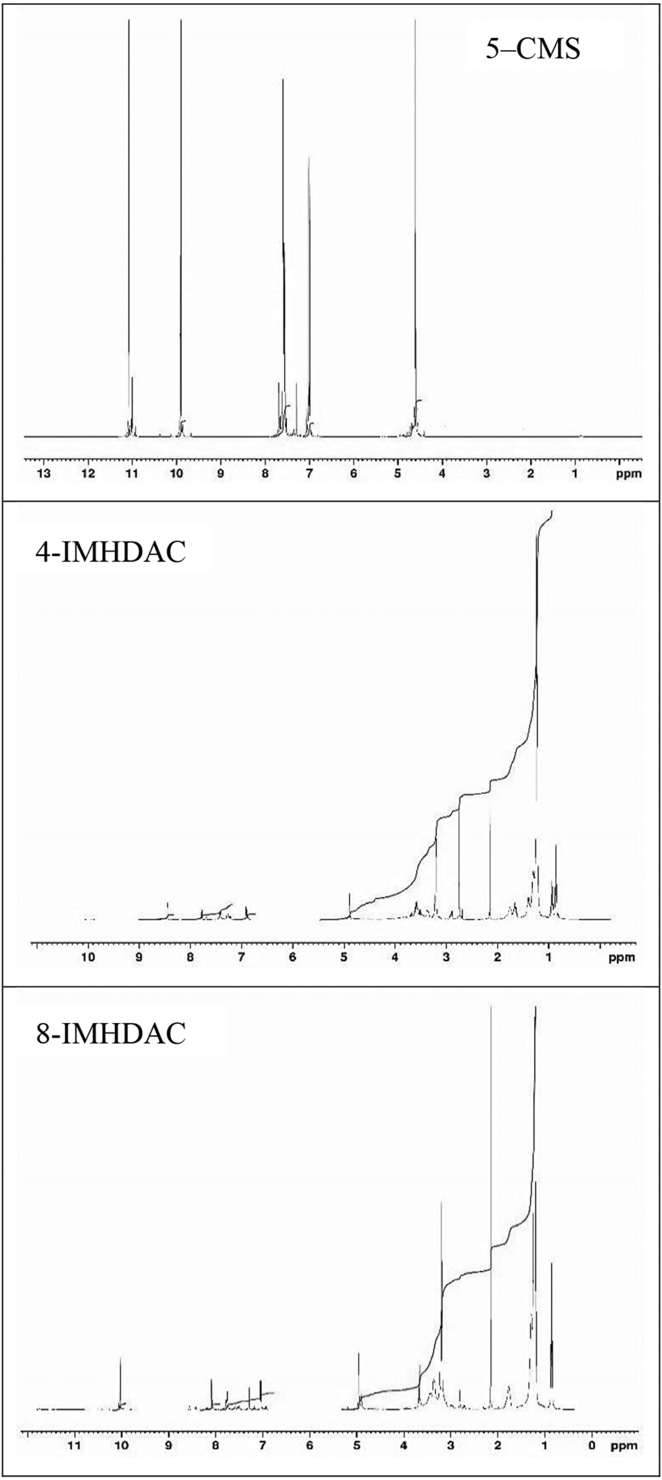

8-IMHDA
6-IMHDA
4-IMHDA
5-CMS
T(%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm$^{-1}$)

Figure 2

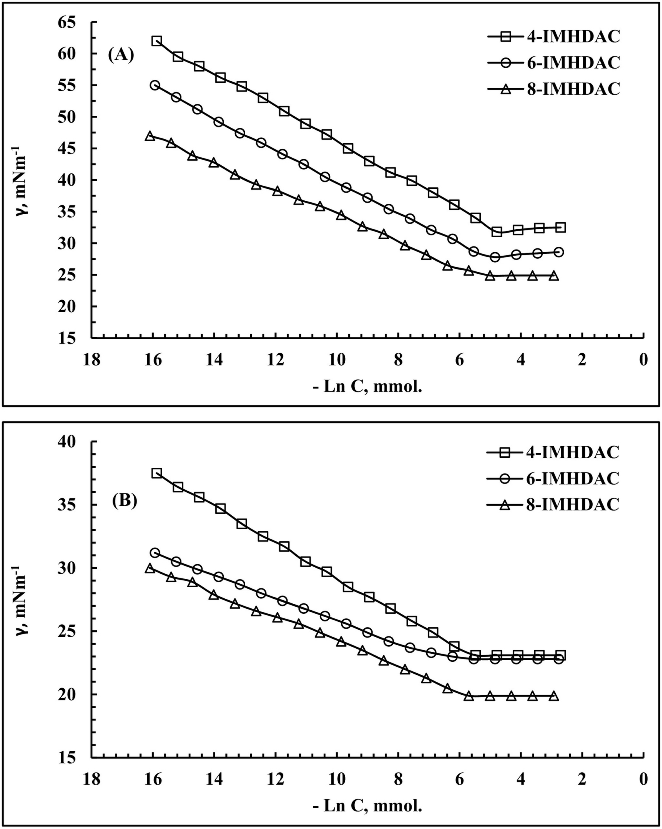


5–CMS

4-IMHDAC

8-IMHDAC

Figure 3



(A)
4-IMHDAC
6-IMHDAC
8-IMHDAC
γ, mNm-1
65
60
55
50
45
40
35
30
25
20
15
18
16
14
12
10
8
6
4
2
0
- Ln C, mmol.
(B)
4-IMHDAC
6-IMHDAC
8-IMHDAC
γ, mNm-1
40
35
30
25
20
15
18
16
14
12
10
8
6
4
2
0
- Ln C, mmol.

Figure 4

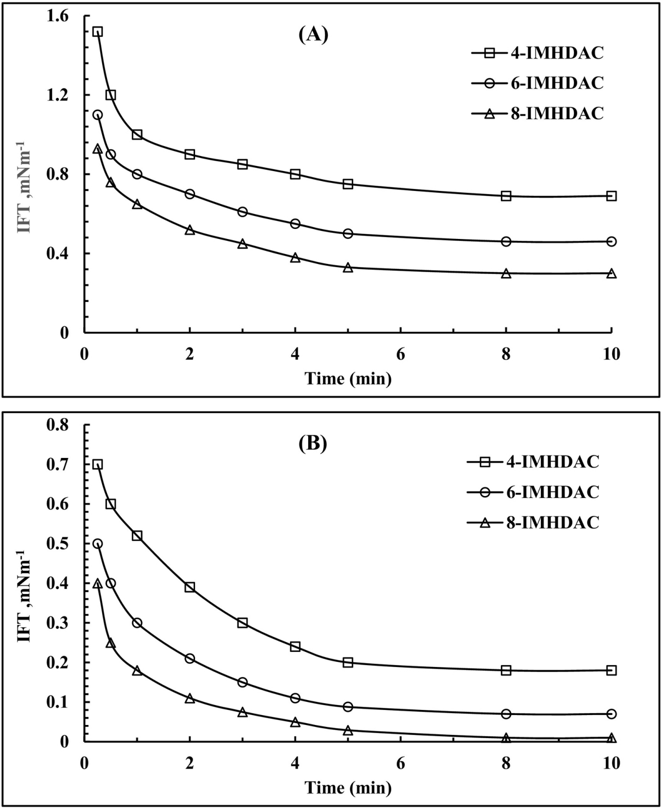

(A)
4-IMHDAC
6-IMHDAC
8-IMHDAC
IFT ,mNm-1
1.6
1.2
0.8
0.4
0
0
2
4
6
8
10
Time (min)
(B)
4-IMHDAC
6-IMHDAC
8-IMHDAC
IFT ,mNm-1
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
10
Time (min)

Figure 5

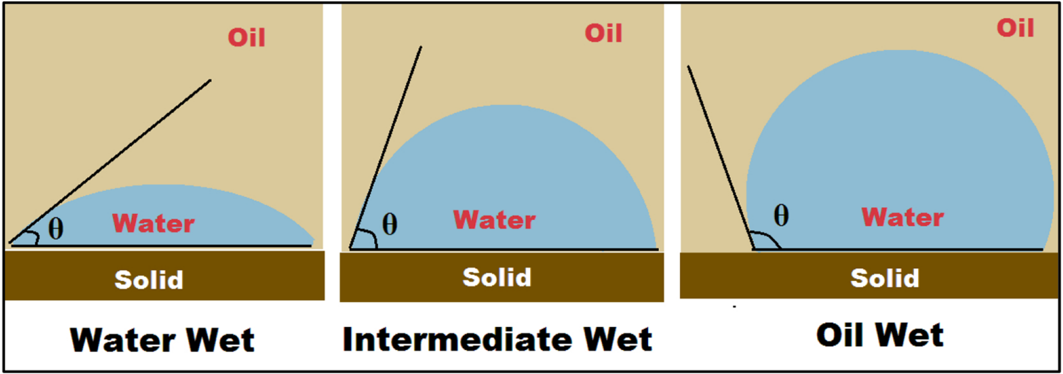

Oil
Water
θ
Solid
Water Wet
Oil
Water
θ
Solid
Intermediate Wet
Oil
θ
Water
Solid
Oil Wet

Figure 6

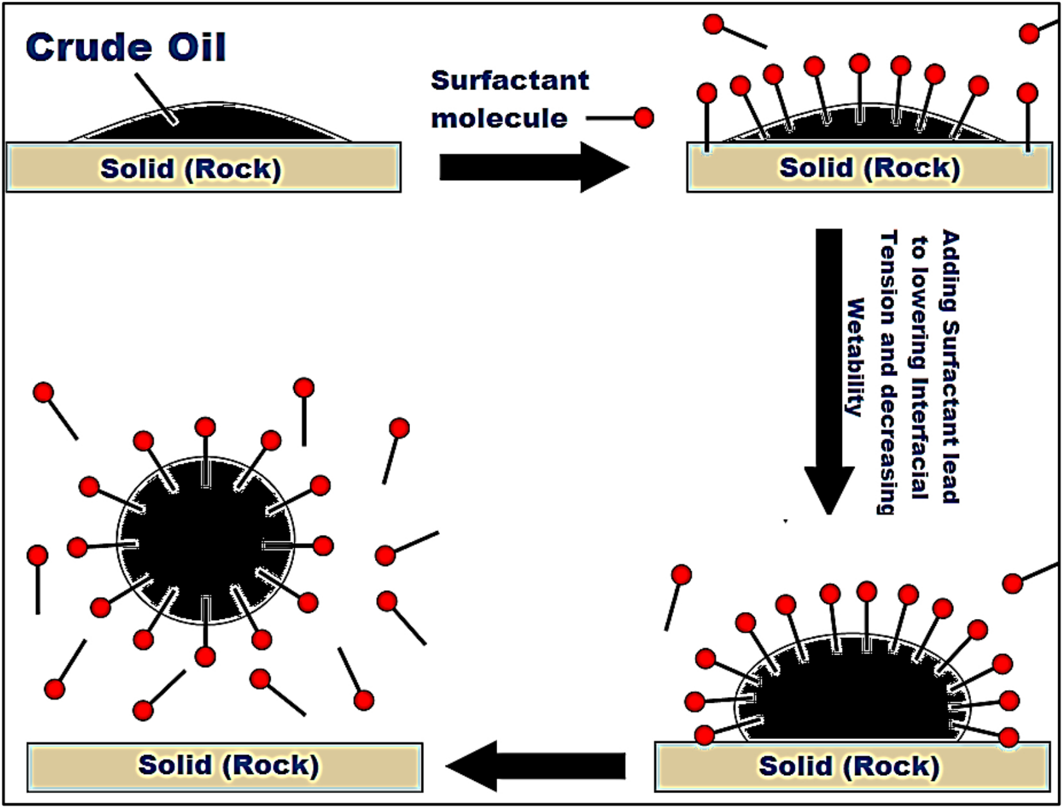

Crude Oil
Surfactant molecule
Solid (Rock)
Solid (Rock)
Adding Surfactant lead to lowering Interfacial Tension and decreasing Wetability
Solid (Rock)
Solid (Rock)

Figure 7

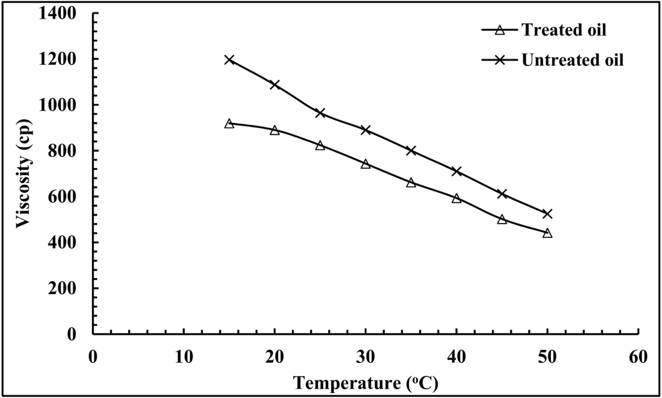

Treated oil
Untreated oil
Viscosity (cp)
1400
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
Temperature (°C)

Figure 8