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Characterization, surface properties and biological activity of new prepared cationic surfactants

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ABSTRACT

Three cationic surfactants were prepared. A condensation reaction between dimethylaminopropylamine (DMAPA) and benzaldehyde was performed. The produced Schiff base was quaternization with three fatty alkyl bromide with different carbon chain length separately to form the desired cationic surfactants. The chemical structure of synthesized cationic surfactants was confirmed by FTIR, ^{1}H NMR and mass spectroscopy. It was found that the chemical structure of prepared compounds has an effect on surface properties, where increasing the hydrophobic chain length decrease the values of CMC, Γ_{max} while A_{min} value was increased. The thermodynamic parameters showed that adsorption and micellization processes are spontaneous. It is clear that the prepared cationic surfactants at first tend to adsorb at surface, then it aggregate to form micelle. The prepared surfactants showed good biological activity against gram positive and negative bacteria and fungi in the following order of II (C12) > I (C10) > III (C16). The serial dilution method was used to evaluate the inhibiting effect of these compounds on the sulfate reducing bacteria growth.

1. Introduction

Surfactants are amphiphile compounds that contain polar or ionic head group and non-polar residues. In the water or similarly strongly hydrogen-bonded solvents, they self-associate at concentrations above the critical micellar concentration (CMC) to form association colloids called micelles. Micelles have interfacial regions containing ionic or polar head groups [1]. Have widespread importance and application such as detergent, paints, coatings formulation, demulsification [2], drilling mud and petrochemical recovery in petroleum industry and due to similarity in chemical structure of quaternary ammonium compounds and cellular constituents eases their destructive action toward microorganisms biocides [3,4].

Because DMAPA contains one primary and one tertiary amine group, it has numerous uses in the production of other chemicals. Final products include agricultural chemicals, anti-static agents, binding agents, carburetor detergents, fabric softeners, flocculants, fungicides, ion exchange resins, phthalocyanine dyes, and water-resistant textile fibers [5]. Derivatives based on DMAPA can be used in fuels as cloud point reducers, dispersants, and stabilizers for prevention of deposits or icing and reduction of octane number requirements. Derivatives are also used as dispersants, anti-oxidants, and corrosion inhibitors for lubricants [6]. Water soluble cationic polyelectrolytes based on DMAPA act as flocculants in removing floating solids and oil from waste water and are used as drilling fluid in the mining industry [7].

The biocidal activity of the cationic surfactants was greatly developed in the last 20 years due to increase of self-immunity for microorganisms toward the conventional biocides [8–11]. So this study aimed to prepare some of cationic surfactants using commercial materials like DMAPA with benzaldehye then studing their surface and thermodynamic properties including, CMC, A_{min}, PC_{20}, Γ_{max}, π_{CMC} ΔG°_{mic} and ΔG°_{ads} then evaluate these cationic surfactants as biocide against fungi and bacteria.

2. Experimental

2.1. Materials

All the reagents were analytical grade and used as received dimethylaminopropylamie (DMAPA), decyl bromide, dodecyl bromide and hexadecyl bromide were purchased from Aldrich Chemicals Co. and the benzaldehyde was purchased from AL-Nasr Chemical Co. Solvents (ethyl alcohol absolute, diethyl ether and acetone) are high grade and purchased from Algomhoria Chemical Co.

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2.2. Instruments

The chemical structure of the synthesized compounds was characterized by:

- FTIR spectra using ATI Mattsonm Infinity series™, Bench top 961 controlled by Win First™ V2.01 software. (Egyptian Petroleum Research Institute).
- ^{1}H NMR was measured in DMSO-d_6 by Spect Varian, GEMINI 200 (^{1}H 200 MHz) (Micro-analytical Center, Cairo University).
- Mass spectra were measured by GC MS-OP1000EX (Micro Analytical Center, Cairo University).
- Tensiometer-K6 processor (krÜSS Company, Germany) using the ring method.

2.3. Synthesis

The desired cationic surfactants were prepared through two steps.

2.3.1. Synthesis of Schiff base compounds

Schiff bases were synthesized throughout condensation reaction of 3-dimethylamino-1-propylamine (DMAPA) with benzaldehyde. Equimolar amounts of amine and aldehydes were refluxed in ethanol at 70 °C for 6 h. The reaction mixture was left to cool and filtered. The products were recrystallized twice from ethanol [12].

2.3.2. Quaternization of prepared Schiff bases

Equimolar of prepared Schiff bases (DMAPAB) were refluxed with different fatty alkyl bromide like decyl bromide, dodecyl bromide and hexadecyl bromide separately in ethyl alcohol absolute as solvent for 45–60 h. The reaction mixture was evaporated under reduced pressure; the solid residue was washed with diethyl ether three times to remove the unreacted materials to give the desired cationic surfactants I, II and III, respectively, as shown in Scheme 1.

2.4. Measurements

2.4.1. Surface tension (γ)

Surface tension of freshly aqueous solutions of synthesized cationic surfactants with concentration range from 1×10^{-2} to 1×10^{-8} M was measured at three different temperatures 25, 40 and 60 °C on Tensiometer-K6 processor. The surface tension of pure water was initially obtained for each experiment for instrument calibration. Between the measurement runs, the ring was initially cleaned with pure water, then acetone. The apparent surface tension values were measured a minimum of 3 times for each sample within 2 min interval between each reading and the recorded values were taken as the average of these values [13]. The CMC values were determined from the abrupt change in the slope of (γ) versus (log c) plots.

2.4.2. Antimicrobial activities

The antimicrobial activities of synthesized compounds were measured against a wide range of organisms comprising bacteria and fungi. The tested bacteria were gram-positive (*Bacillus pumilus* and *Micrococcus luteus*) and gram-negative (*Pseudomonas aeuroginosa* and *Sarcina lutea*), the used fungi were *Candida albicans* and *Penicillium chrysogenum*.

The different species of tested organisms were obtained from the Operation Development Center, Egyptian Petroleum Research Institute, Egypt.

An assay is made to determine the ability of an antibiotic to kill or inhibit the growth of living microorganisms, the technique which used is filter-paper disc-agar diffusion [14] where:

1. Inoculate flask of melted agar medium with the organism to be tested.
2. Pour this inoculated medium into a Petri dish.
3. After the agar has solidified, a multilobed disc that impregnated with different antibiotics laid on top of agar.
4. The antibiotic in each lobe of disc diffuses into medium and if the organism is sensitive to a particular antibiotic, no growth occurs in a large zone surrounding that lobe (clear zone).
5. The diameters of inhibition zones were measured after 24–48 h at 35–37 °C (for bacteria) and 3–4 days at 25–27 °C (for yeast and fungi) of incubation at 28 °C.
6. Measure each clear zone and compare between them to determine the antibiotic which is more inhibitor.

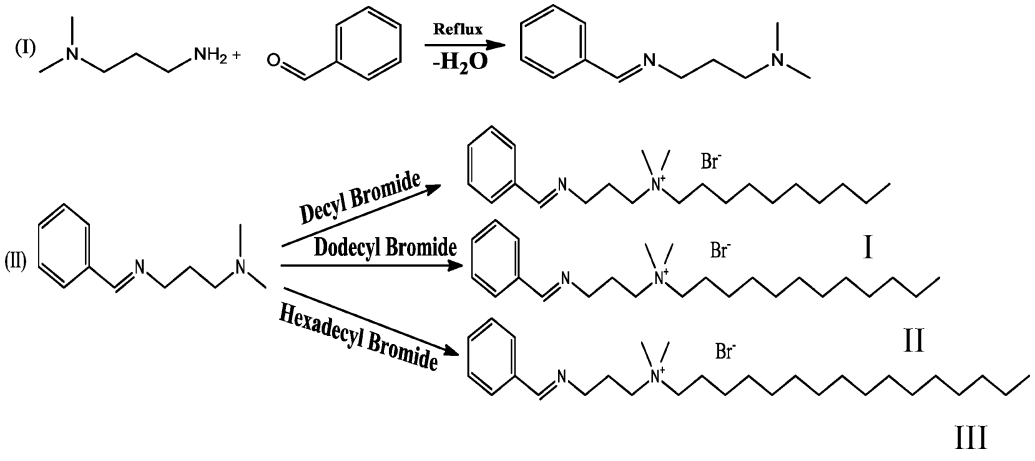
3. Results and discussion

3.1. Chemical structure

The chemical structure of the prepared cationic surfactants was confirmed by the FTIR and ^{1}H NMR spectra.

3.1.1. FTIR spectra

The IR spectra of the synthesized cationic surfactants showed the disappearance of both bands one around 3300 cm^{-1} (corresponding to amino group) and the second around 1730 cm^{-1} (corresponding to carbonyl group) and appearance new band around 1640 cm^{-1} region in all prepared compounds due to mainly



Scheme 1. Scheme preparation of cationic surfactants.