Journal of Industrial and Engineering Chemistry 20 (2014) 4463–4472

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Characterization, surface properties and biological activity of some synthesized anionic surfactants

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ARTICLE INFO

Article history:
Received 13 January 2014
Accepted 6 February 2014
Available online 13 February 2014

Keywords:
Antimicrobial activity
Anionic surfactants
Surface activity
Thermodynamic parameters

ABSTRACT

In this study, esterification reaction between four different fatty alcohols (octyl, dodecyl, hexdecyl and octadecyl alcohol) and phosphoric acid was performed. The produced compound was reacted with polyethylene glycol-400. Then, the reaction product was quenched using sodium hydroxide to form the desired anionic gemini surfactants. The chemical structures of the synthesized surfactants were recognized by FT-IR and ^{1}H NMR spectroscopy. The synthesized surfactants showed higher surface activity. The emulsion stability measurements showed the applicability of these surfactants as emulsifying agents. The foaming power measurements showed the synthesized surfactants have low ability to foam formation. The thermodynamic parameters showed their tendency toward adsorption at the interfaces and also micellization in the bulk of their solutions. The studied surfactants were evaluated as antimicrobial agents against pathogenic bacteria using inhibition zone diameters. The synthesized surfactants showed good antimicrobial activities against the tested microorganisms including Gram positive, Gram negative as well as fungi. The promising inhibition efficiency of these compounds against the pathogenic bacteria facilitates them to be applicable in the petroleum field as new categories of biocides.

1. Introduction

Gemini surfactants, consisting of two monomeric surfactants linked with a spacer, have been synthesized with a view to developing 'next-generation' high quality surfactants. When compared with conventional monomeric surfactants, the corresponding gemini surfactants generally present (i) a significantly lower critical micelle concentration (CMC), (ii) a lower surface tension measured at the CMC, (iii) spontaneous formation of vesicles and/or wormlike micelles even from relatively lower concentrations and (iv) are markably lower Kraft temperature and good water solubility in the case of ionic surfactants [1–3]. These physicochemical properties of gemini surfactants enable us to reduce total consumption of chemicals in industrial products, and therefore, gemini surfactants themselves are deemed to be environmental materials. Never the less, the number of commercially available gemini surfactants is very limited. This is because the synthetic route of gemini surfactants is more complicated than that of monomeric ones, and there by, the synthetic costs are always problematic. In order to use gemini surfactants in a wide variety of applications, gemini surfactants are required to be synthesized with a low-cost synthesis and purification strategy In recent years, a new type of gemini surfactants called "hetero gemini surfactants" has been designed and synthesized [4–16].

Dissymmetric hetero gemini surfactants are classified with three groups: (i) dissymmetric hydrophobic chains with symmetric head groups [11–16]; (ii) symmetric hydrophobic chains with dissymmetric (e.g., anionic, cationic and nonionic) head groups [8,9]; and (iii) dissymmetric hydrophobic chains with dissymmetric head groups [6]. For example, Alami and co-workers have reported oleylnitrile-based nonionic hetero gemini surfactants containing hydroxyl and polyoxyethylene head groups (type iii) [4] and zwitterionic heterogemini surfactants containing anionic phosphodiester and quaternary ammonium head groups (type iii) [6].

In the latter case, greater surface activity (i.e., lower CMC and lower surface tension measured at the CMC) is observed when compared to conventional monomeric and/or gemini surfactants with phosphates head groups [17–22]. Amphiphilic compounds having dimeric moieties are well-known and effective antimicrobial agents. The efficacy of such agents is conditioned by the amphiphilic nature of the surfactant molecule, surface-active

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http://dx.doi.org/10.1016/j.jiec.2014.02.018
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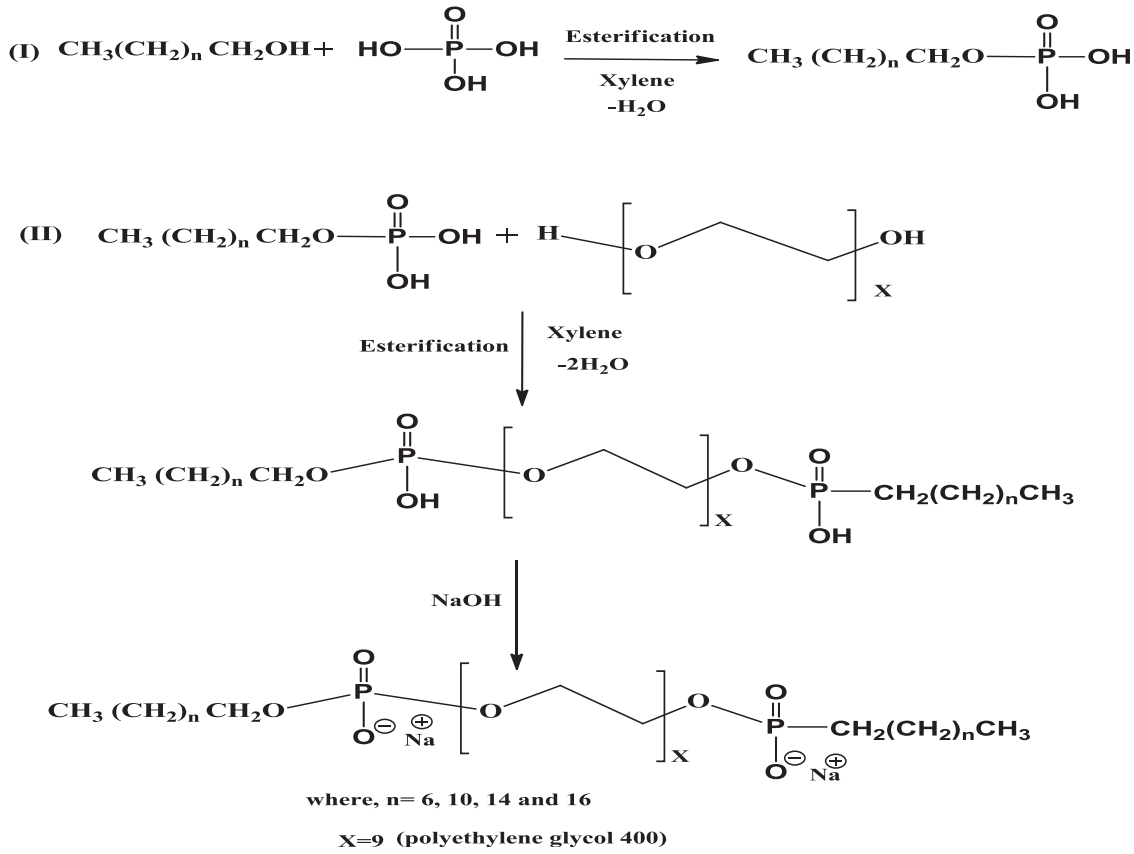

Scheme 1. Synthesis of anionic gemini surfactants.

properties and aggregation patterns. Several contributions have reported synthetic antimicrobial agents having new active moieties. The objective of the present study is twofold: the first is the synthesis of anionic gemini surfactants (Scheme 1) with the variations of hydrocarbon chain length to investigate the influence of the structure on surface tension, interfacial tension, emulsion stability, foaming power and thermodynamic parameters of anionic surfactants. The second goal is to measure the antimicrobial activities of the synthesized surfactants using well diffusion method. The antimicrobial activities of the tested compounds were correlated to their surface activity.

2. Materials and measurements

2.1. Chemicals

Polyethylene glycol-400 and phosphoric acid were purchased from El Goumhoria Trade Pharmaceuticals & Chemicals Company, Cairo, Egypt. Octyl, dodecyl, hexdecyl and octadecyl alcohol and sodium hydroxide were analytical grade chemicals were obtained from Merck chemical company. All the reagents were analytical grade and used as received without further purification.

2.2. Instruments

The chemical structures of the synthesized compounds were characterized by:

1. FT-IR spectra using ATI Mattsonm Infinity series™, Bench top 961 controlled by Win First™ V2.01 software. (Egyptian Petroleum Research Institute.)
2. ^{1}H NMR was measured in DMSO-d_6 by Spect Varian, GEMINI 200 (^{1}H 200 MHz) (Micro-analytical Center, Cairo University).
3. Tensiometer-K6 processor (krÜSS Company, Germany) using the ring method.

2.3. Synthesis

2.3.1. Synthesis of fatty alkyl phosphoric acid esters

Octyl, dodecyl, hexdecyl and octadecyl alcohol (0.5 mol) were esterified separately by phosphoric acid (0.5 mol) in xylene as a solvent and 0.01% p-toluene sulphonic acid as a catalyst, until the azeotropic amount of water (0.5 mol, 9 mL) was removed. Then the solvent was removed using vacuum rotary evaporator. The catalyst was extracted from the reaction medium using petroleum ether. Subsequent purification was done by means of vacuum distillation to remove the excess and residual materials [23].

2.3.2. Synthesis of gemini anionic surfactants

Alkyl ester of phosphoric acid (0.2 mol) and polyethylene glycol-400 (9 U of ethylene glycol per molecule) were esterified individually in xylene (250 mL) as the solvent under reflux conditions at 138 °C. The reaction was stopped after complete removal of the water of the reaction (0.2 mol, 3.6 mL). Then, the reaction mixture was quenched using sodium hydroxide (0.2 mol), and followed by removing all of the volatile material from the resulting solution [24,25]. The anionic gemini surfactants obtained were designated as C8A, C12A, C16A and C18A. Scheme 1 shows the chemical structures of the synthesized compounds.

2.4. Measurements

2.4.1. Surface tension

Surface tension measurements were performed using a Kruss K6 tensiometer by the platinum ring detachment method (±0.5 mN/m). Freshly prepared aqueous solutions of the synthesized