Egyptian Journal of Petroleum (2014) 23, 361–366

HOSTED BY

Egyptian Petroleum Research Institute

Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp
www.sciencedirect.com

FULL LENGTH ARTICLE

Synthesis and evaluation of some derivatives of polysiloxanes

M.M.A. EL-Sukkary [a,*], D.A. Ismail [a], S.M. El Rayes [b], M.A. Saad [b]

[a] Petrochemicals Department, Egyptian Petroleum Research Institute, Cairo, Egypt
[b] Organic Chemistry, Suez Canal University, Ismailia, Egypt

Received 15 September 2013; accepted 19 November 2013
Available online 17 December 2014

KEYWORDS

Glycopolysiloxanes;
Surface active properties;
Polymeric surfactants;
Amphiphilic;
Glyco-polymers

Abstract Silicone surfactants have been widely used in our daily life and many industrial fields on the basis of their unusual properties. Only in the past decades has the use of silicone as a hydrophobic building block for the preparation of surfactants become common. The recent trend to combine silicone, polyoxyalkylene and carbohydrate moieties in the same molecule has resulted in a plethora of new compounds with new properties.

In this article, we report the preparation of a series of "glycopolysiloxanes" surfactants with different molecular weights. They were structurally characterized by IR, ^{1}H NMR and MS.

Specifically, the critical micelle concentration (cmc), effectiveness of surface tension reduction (π_{cmc}), maximum surface excess (Γ_{max}), minimum surface area (A_{min}) and standard free energies of micellization ($\Delta G°_{mic}$) and adsorption ($\Delta G°_{ads}$) have been determined from aqueous surface tension measurements using Du-Nouy Tensiometer (KRUSS K6 type 4851) with a platinum ring. All the surfactants have good surface properties and have low cmc.

The bacteriostatic power of these polymers was tested and compared under the same conditions in aqueous solution against common strains of Gram positive bacteria and strains of Gram negative bacteria.

1. Introduction

Silicone surfactants have been widely used in our daily life and in many industrial fields on the basis of their unusual properties. Only in the past decades has the use of silicone as a hydrophobic building block for the preparation of surfactants become common. The recent trend to combine silicone, polyoxyalkylene and carbohydrate moieties in the same molecule has resulted in a plethora of new compounds with new properties.

Synthetic polymers grafted with sugar (or carbohydrate) groups are receiving growing interest. They are often named "glycopolymers", by analogy with term "glycoconjugates", used for description of the biological molecules in which oligosaccharides are covalently linked to other non-carbohydrate biological molecules, such as proteins (glycoproteins).

The introduction of sugar residues in synthetic polymers can be made in order to imitate these glycoconjugates,

* Corresponding author.
Peer review under responsibility of Egyptian Petroleum Research Institute.

http://dx.doi.org/10.1016/j.ejpe.2014.09.002

prospecting for interesting biological properties for these glycopolymers. For polymers more devoted to industrial applications, the introduction of the less complex sugar group in polymers affords new properties, especially amphilicite, hydrophilicity, solubility in water, super-absorbent properties, biocompatibility, biodegradability and better environmental and toxicological profiles.

In this article, we report the preparation of three "glycopolysiloxanes" surfactants and their study of the surface activities by measuring the equilibrium surface tensions of their dilute aqueous solutions. The parameters studied include CMC (the critical micelle concentration), C_{20} (the surfactant molar concentration required to reduce the surface tension of the solvent by 20 mN m^{-1}), γ_{cmc} (the surface tension at the cmc), Γ_{max} (the maximum surface excess concentration at the air/water interface), A_{min} (the minimum area per surfactant molecule at the air/water interface), cmc/C_{20} ratio (a measure of the factors inhibiting micellization relative to adsorption at the air/water interface), and the thermodynamic parameters $\Delta G°_{mic}$ (the standard free energy of micellization) and $\Delta G°_{ads}$ (the standard free energy of adsorption) [1].

2. Experimental procedures

2.1. Materials

2.1.1. Synthesis of glucose grafted polysiloxanes (GPS)

In 500 ml four neck round-bottom flask 20 g of aminopropylpolysiloxane with different siloxanes length compound **1** (A1, A2, A3) in 100 ml dimethyl formamide (DMF)–isopropanol were added and heated to 60 °C under nitrogen purging, for 30 min. In a separate conical flask 80 g of glucose was dissolved in 100 ml of isopropanol and heated to 60 °C, then was added to the aminopropylpolysiloxane solution slowly, 10 ml every 5 min, after 60 min of addition the solution became homogenous. The reaction was monitored using Perkin Elmer FT-IR by observing the disappearance of the two stretching peaks of the amin group at 3400 cm^{-1} and the presence of a new peak at 3550 cm^{-1} and one peak for N—H at 3400 cm^{-1} [2]. The reaction held 2 h refluxing under nitrogen purging, the solution color will change from colorless to yellow color. The glycopolysiloxane derivatives were extracted by evaporation and condensation of the isopropanol and the DMF respectively for further usage and a yellow powder of the glycopolysiloxane was separated [3].

2.2. Structure confirmation

2.2.1. Infrared spectrum

Infrared spectra were measured on a Perkin–Elmer-1430 infrared spectrometer using KBr for disk formation.

The reaction was monitored by observing the disappearance of the two stretching peaks of the amin group at 3400 cm^{-1} and the presence of a new peak at 3550 cm^{-1} and one peak for N—H at 3400 cm^{-1} [2].

2.2.2. Nuclear magnetic resonance spectra

The ^{1}NMR spectra were measured on a Varian 300 MHz spectrometer, chemical department, Faculty of science, Cairo University.

2.3. Evaluation of the surface properties of the prepared surfactants

2.3.1. Surface tension and interfacial tension measurements

Surface tension values of the synthesized glycopolysiloxane surfactant solutions (GPS1, GPS2 and GPS3) were measured at 25 °C using Du-Nouy Tensiometer (KRUSS K6 type 4851) with a platinum ring. Apparent surface tensions were measured about 3 times for the sample within 2 min interval between each reading. The obtained data were plotted against −log concentration without any correction, cmc values were determined from the plot of surface tension versus concentration [4].

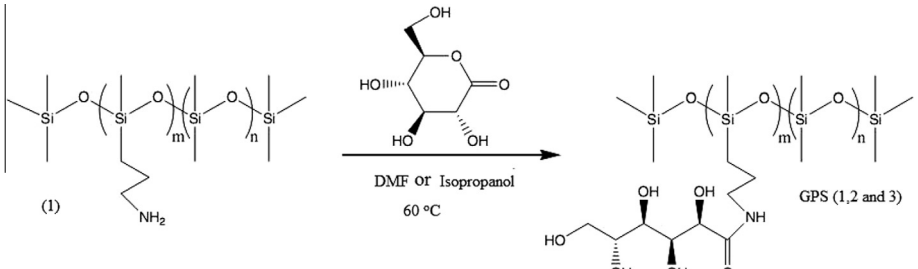
Interfacial tension measurements were made for surfactant–oil system at 25 °C using surfactant solution of concentration 0.1%.

2.3.2. Critical micelle concentration (cmc)

The critical micelle concentration values of the prepared surfactants were determined using the surface tension method [5].

2.3.3. Emulsion stability

The emulsifying property for the prepared surfactants was determined as follows: A surfactant solution (10 ml, 0.1%) was mixed with light paraffin oil (10 ml). The mixture was put in a (100 ml) graduated stopper tube and shook vigorously for 2 min, then the tube was placed up right and the separation of the two layers is observed. The time taken for the separation of (9 ml) of aqueous layer indicates the emulsifying power of the surfactant [6,7].



Scheme 1