

Influence of head-group composition and (chloro)propoxy units disposition consequence on properties of surfactants based on lauric acid, propylene oxide, epichlorohydrin and ethanolamines

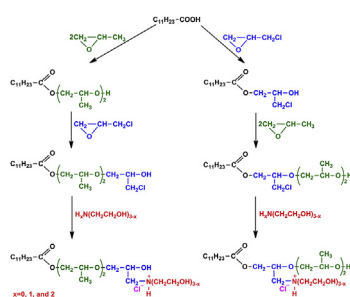
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HIGHLIGHTS

- Nonionic surfactants were synthesized on the basis of LA, OP and EXH.
- Nonionic surfactants were transformed into cationic surfactants.
- Surfactant structure-surface activity relationship was established.
- A very high petroleum-collecting capacity of cationic surfactants was revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

Nonionic surfactants were synthesized by interaction of lauric acid (LA) with propylene oxide (PO) and epichlorohydrin (ECH). The synthesis was conducted in two directions. In the first way, initially, ester of LA with PO was synthesized, then, ECH was added to it. In the second direction, at first, ester of LA with ECH was obtained, then, PO was added. Condensation reactions of both type were carried out at 150–160 °C in the presence of triethyl amine catalyst. Through interaction of (chloro)propoxy derivatives of LA with ethanolamines cationic surfactants were produced. Depending on disposition consequence of ECH and PO units in the head group of the cationic surfactants and the number of ethylol groups linked with the nitrogen atom, the character of the surfactants colloidal-chemical parameters change was established and, with this purpose, electroconductometric and tensiometric measurements were made. When studying petroleum-collecting capacity of the obtained nonionic and cationic surfactants, it was revealed that they are effective for collecting thin petroleum films from the surface of waters having a large range of mineralization.

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1. Introduction

As is known, with variation of surfactants structure their properties change, too. So, colloidal-chemical parameters of surfactants depend on the nature of hydrophilic and hydrophobic groups of them [1,2]. With a change of length of alkyl chain in

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Abbreviations

CMC	Critical micelle concentration
DEA	Diethanolamine
ECH	Epichlorohydrin
LA	Lauric acid
MEA	Monoethanolamine
PO	Propylene oxide
TEA	Triethanolamine

hydrophobic part and with an increase of the number of polar groups in hydrophilic part, the values of critical micelle concentration (CMC), maximum surface excess concentration (Γ_{\max}), surface pressure (π_{CMC}), and other parameters change [3]. Besides, nature of counter-ion and structure of polar group may also be included into the list of the factors influencing properties of surfactants [2,4]. As was mentioned by many authors, cationic surfactants synthesized on the basis of higher alcohols and ECH possess properties intrinsic for liquid crystals [5] as well as anti-corrosive [6] and bactericide capabilities [7]. Surfactants containing 2-hydroxypropoxy group may be obtained from both alcohols and amines. High reactivity of chloropropoxy-group connected to amines enables to produce various (gemini) surfactants containing mono- and dialkyl groups [8].

Zh. Zhi-guo and Y. Hong [9] synthesized novel surfactants entering ethylene oxide (EO) units into derivatives of dodecyl- and tridecyl alcohols containing PO units. They have found out that, with an increase of the number of PO units in the heterochain of the surfactant, CMC decreases but γ_{CMC} rises. Sh. Yada and coworkers [10] have obtained new surfactants incorporating 1, 2 and 3 PO units into the composition of ethoxy-derivatives of C₁₀, C₁₂, C₁₄ and C₁₆ alcohols containing 4, 6 and 8 EO units. It was established that propoxylation of the ethoxylated alcohols brings about lowering CMC and γ_{CMC} . Therefore, consequence of EO and PO units addition significantly influences properties of surfactant. Though, there is some information in the literature about surfactants containing a fragment of higher alcohols, and separately chloropropoxy- [11,12] and propoxy-units [13], there are no publications on the surfactants including simultaneously ECH and PO units.

In the present work, the surfactants having the residue of lauric acid, chloropropoxy- and propoxy-units are synthesized and converted to cationic surfactants using ethanolamines. The character of the surfactants properties variation in dependence of consequence of the epoxide-units disposition and ethanolamine nature is clarified.

2. Experimental

2.1. Chemicals and instruments

¹H NMR and ¹³C NMR spectra were registered on Bruker Avance II+300 (UltraShield™ Magnet) 300.13 MHz and 75.46 MHz spectrometer using deuterated chloroform (CDCl₃) as a solvent. IR spectra were recorded on a model FT-IR, Spectrum BX spectrometer via a use of KBr disks. PO (purity>99%, Alfa Aesar, product of Great Britain), ECH (purity 99%, Alfa Aesar, product of United States), LA (purity 98%, Alfa Aesar GmbH & Co KG, Germany), monoethanolamine-MEA (purity>99% Merck, Germany), diethanolamine-DEA (purity>98.5% Merck, Germany) and triethanolamine-TEA (purity>99% Merck, Germany) were chemicals of analytical grade.

2.2. Synthesis LA-based surfactants containing PO- and ECH-units

The process is carried out in two steps. In the first step, 0.1 mol of LA is charged into an autoclave where, then, triethyl amine catalyst (5% mol of LA) and 0.2 mol PO (or 0.1 of ECH) are added. The interaction of these components is conducted at 150–160 °C during 20–24 h.

In order to remove the amount of unreacted epoxycompound, the reaction mixture was evaporated at 40–50 °C unless a constant mass is attained. According to the determined amount of the reacted PO (or ECH), the conversion of PO (or ECH) and propoxylation degree -n (or chloropropoxylation degree-m) were calculated. In the second step, to the obtained propoxy(or chloropropoxy)-derivative, 0.1 mol of ECH (or 0.2 mol of PO) is added and the condensation is continued under the same conditions. The final product is passed through a microcolumn to remove by-products. The dominant fraction was taken as a main product. The structure of the obtained esters was confirmed by IR- and NMR-spectroscopy methods. (Supplementary Material Figs. 1S–9S).

FTIR spectrum (cm⁻¹) of the C₁₂P₂E (See Step 2 in Scheme 1): 3395 ν (OH), 2923 and 2854 ν (CH), 1734 ν (O–C=O), 1458 and 1377 δ (CH), 1050–1108 (C–O), 752 ν (CH₂Cl), 721 δ (CH₂)_n. ¹H NMR spectrum of the C₁₂P₂E (300.18 MHz, CDCl₃) (δ , ppm): 0.85 (CH₃), 1.1 (CH–CH₃), 1.23 (CH₂ alkyl chain), 1.58 (CH₂–CH₂–COO), 2.26 (CH₂–COO), 3.4–3.6 (CH₂–CH–O), 3.8–4.2 [C(O)–O–CH₂–CH], 5.1 (OH). ¹³C NMR spectrum of the C₁₂P₂E (75.48 MHz, CDCl₃) (δ , ppm): 14.1 (CH₃), 18.8 (CH₃–CH), 22.6 (CH₂–CH₃), 24.9 (CH₂–CH₂–COO), 29.1–29.6 (CH₂)_n, 31.9 (CH₂–CH₂–CH₃), 34.1–34.5 (CH₂–COO), 45.7 (CH₂Cl), 63.2–70.8 (O–CH₂–CH–O), 173.9 (COO).

FTIR spectrum (cm⁻¹) of the C₁₂EP₂ (See Step 2 in Scheme 2): 3389 ν (OH), 2923 and 2854 ν (CH), 1735 ν (O–C=O), 1457 and 1376 δ (CH), 1050–1109 (C–O), 840 ν (CH₂Cl), 721 δ (CH₂)_n. ¹H NMR spectrum of the C₁₂EP₂ (300.18 MHz, CDCl₃) (δ , ppm): 0.84 (CH₃), 1.08 (CH–CH₃), 1.17–1.22 (CH₂ alkyl chain), 1.58–1.59 (CH₂–CH₂–COO), 2.31 (CH₂–COO), 3.4–3.6 (CH₂–CH–O), (CH₂Cl), 3.9–4.1 [C(O)–O–CH₂–CH], 5.0 (OH). ¹³C NMR spectrum of the C₁₂EP₂ (75.49 MHz, CDCl₃) (δ , ppm): 14.1 (CH₃), 16.2–19.2 (CH₃–CH), 22.6 (CH₂–CH₃), 24.9 (CH₂–CH₂–COO), 29.1–29.6 (CH₂)_n, 31.9 (CH₂–CH₂–CH₃), 34.2–34.5 (CH₂–COO), 65.5–71.6 (O–CH₂–CH–O), 174.0 (COO).

2.3. Synthesis of cationic surfactants using chloropropoxy units of the obtained LA-based esters

0.1 mol LA-based surfactant-containing both ECH and PO units is charged into a flask equipped with a magnetic stirrer and a heater. 0.1 mol ethanolamine (MEA, DEA or TEA) is introduced and the interaction is carried out during 6 h. IR- and ¹H NMR-spectra of the cationic surfactant obtained using MEA are given in Figs. 10S and 11S (Supplementary material). FTIR spectrum (cm⁻¹) of the C₁₂P₂EM (See Step 3 in Scheme 1): 3379 ν (OH), 2923 and 2854 ν (CH), 1736 ν (O–C=O), 1457 and 1376 δ (CH), 1074–1108 (C–O), 722 δ (CH₂)_n. ¹H NMR spectrum of the C₁₂P₂EM (300.18 MHz, CDCl₃) (δ , ppm): 0.88 (CH₃), 1.14 (CH–CH₃), 1.25 (CH₂ alkyl chain), 1.6 (CH₂–CH₂–COO), 2.28 (CH₂–COO), 3.4–4.2 (CH₂–CH–O), [C(O)–O–CH₂–CH], (CH₂–CH₂–OH), 5.1 (OH).

2.4. Determination of surface activity of the synthesized surfactants at the water-air border

Surface tension at the water-air border in the presence of the prepared surfactants was measured on a DuNouy ring KSV Sigma 702 tensiometer (Israel). Preparation of the samples and conduction of measurements were made in accordance with the known procedure [14]. The surface tension of the water used for preparing

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