

Surfactants Based on Higher Carboxylic Acids and Epoxy Compounds

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ABSTRACT

Oil-soluble and oil-water-soluble surfactants are of significant scientific and practical interest. These reagents, especially those of non-ionogenic types, are being applied widely in various areas including oil and gas industries. Non-ionogenic surfactants have attracted a special attention because of their high resistance to the action of mineralized media, microorganisms, and shear stress. There is a continued attention in the literature about these types of compounds. Taking into consideration the above mentioned facts, several new representatives of non-ionogenic surfactants have been synthesized. They are based on propylene oxide (PO) and epichlorohydrin (ECH) i.e., epoxy compounds of a large industrial production, and higher carboxylic acids such as pelargonic, palmitic, and stearic acids as well as stearinamide. These derivatives have been synthesized by catalytic method. Their compositions and structures have been identified by physico-chemical methods. It has been shown by stalagmometric measurements that the obtained products possess high surface activity. These surfactants have been characterized by density, refractive index, and solubility in various solvents.

Key Words:

oxypropylation;
chloroxypropylation;
fatty acids;
stearinamide;
surfactants.

INTRODUCTION

Oil-soluble and oil-water-soluble surfactants are of significant scientific and practical interest [1-3]. These reagents, especially those of non-ionogenic type, find a wide application in various parts of economy including oil and gas industries

[4-10]. Non-ionogenic surfactants attract a special attention because of their high resistance to the action of mineralized media, microorganisms, and shear stress. More recent literature also shows that there is a growing interest on the improvements of

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these compounds and their new applications. For instance, some significant studies are being found in the literature about their new applications in chromatography [11-18]. Taking into consideration the above mentioned facts, several new representatives of non-ionogenic surfactants have been synthesized in this study. They are based on propylene oxide (PO) and epichlorohydrin (ECH) i.e., epoxy compounds of a large industrial production, and such higher carboxylic acids as pelargonic acid ($C_8H_{17}COOH$), palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$) as well as stearinamide.

EXPERIMENTAL

PO and ECH were used as industrial products of the factory Organic Synthesis (Sumgait, Azerbaijan). They had a purity of 99.97% and higher. Pelargonic, palmitic, and stearic acids were used as products of Novocherkassk factory of synthetic products (Russia) of a purity 99.5% and higher. Stearinamide used was a product of Shostka factory of chemical products (Ukraine) with a purity of 99.7%.

The oxypropylation and chloroxypropylation reactions of monocarboxylic acids were carried out at 120-140°C for 48-50 h with various initial reactant ratios in an autoclave equipped with regulated heating and mixing systems.

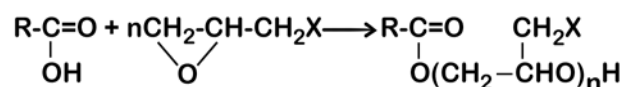
1H NMR Spectra were recorded by the spectrometer Tesla-BS-487C. IR Spectra were recorded by the spectrometer UR-20. The final conversions of PO and ECH as well as the average degrees of oxypropylation and chloroxypropylation were found by gravimetric method.

The surface activities of the synthesized products were estimated according to the values of surface tension of their kerosene solutions in interface with water which were measured by stalagmometric method. The densities of the surfactants were determined by pycno-

metric method. The refractive indexes of the surfactants were found by refractometric method.

RESULTS AND DISCUSSION

The oxypropylation and chloroxypropylation reactions of the indicated acids have been carried out in the presence of a catalyst of basic nature at 140-160°C usually during 14-16 h according to the following scheme:



(Scheme I)

where R is alkyl group and X is H or Cl.

Oxypropylation and Chloroxypropylation of Pelargonic Acid

Pelargonic acid was oxypropylated by catalytic method at the acid to PO molar ratios of 1/1, 1/2, 1/3, 1/4, and 1/5. It has been established that the final conversion of PO decreases as its excess amount in the initial reaction mixture increases (Table 1). The average degree of oxypropylation (few number of PO moles added to 1 mole of acid) was higher at larger molar excess of PO (Table 1).

The obtained products were dark-brown liquids with densities less than 1 g/mL. They were poorly soluble in water and heptane. It has been shown by stalagmometric measurements that the oxypropylated derivatives of pelargonic acid exhibit high surface activity. For example, 0.5 % (by weight) kerosene solution of the product synthesized at the 1/2 molar ratio of acid to PO decreases the surface tension at kerosene-water interface from 41.5 to 21.2 N/m at 22.5°C.

Catalytic chloroxypropylation of pelargonic acid was carried out at the 1/1, 1/2, 1/3, 1/4, and 1/5 molar ratios of acid to ECH as well. It has been found that the

Table 1. Results of study of pelargonic acid oxypropylation.

Factor	Initial molar ratio of pelargonic acid/PO				
	1/1	1/2	1/3	1/4	1/5
Final conversion of PO (%)	100	71.7	40.0	38.8	30.4
Average degree of oxypropylation	1.00	1.42	1.20	1.53	1.52

final conversion of ECH, as a whole, increases as its excess amount in the initial reaction mixture increases (Table 2). As the initial amount of ECH increases, the degree of chloroxypropylation also rises.

As it is concluded from the obtained results, the degrees of chloroxypropylation of pelargonic acid is higher than the degree of oxypropylation.

The final products of pelargonic acid chloroxypropylation were dark-brown liquids with densities higher than 1 g/mL (1.047, 1.123, 1.126, 1.130, and 1.454 g/mL, respectively). They were partially dissolved in water. The refractive indexes (n_D^{20}) were equal to 1.4580, 1.4670, 1.437, 1.457, and 1.4540, respectively. The surface tension values of their 0.5% (by weight) kerosene solutions at interface with water were 13.85, 9.23, 16.62, 14.93, and 15.70 N/m, respectively at 26°C.

Identification of chloroxypropylated pelargonic acid (obtained at molar ratio of 1/3) was made by methods of ^1H NMR and IR spectroscopies. Resonance signals of protons from $-\text{CH}_3$ group (0.84 ppm), $-\text{CH}_2$ group (1.24 ppm), $-\text{CH}_2\text{COO}$ fragment (2.2 ppm), $-\text{OH}$ group (3.16 ppm), $-\text{CH}_2\text{Cl}$ group (3.4 ppm), $-\text{OCH}_2$ group (3.56 ppm) and $-\text{CH}$ group (3.92 ppm) have been appeared in ^1H NMR spectrum recorded in CCl_4 . The absorption bands of $-\text{OH}$ valency vibrations ($3200\text{--}3700\text{ cm}^{-1}$), $-\text{CH}$ valency vibrations ($2900\text{--}3050\text{ cm}^{-1}$), $\text{C}=\text{O}$ valency vibrations ($1760\text{--}1780\text{ cm}^{-1}$), $-\text{CH}$ deformational vibrations ($1450\text{--}1480\text{ cm}^{-1}$), secondary $-\text{OH}$ deformational vibrations (1065 cm^{-1}), $\text{C}-\text{Cl}$ valency vibrations (760 cm^{-1}) and $\text{C}-\text{C}$ valency vibrations (715 cm^{-1}) have been presented in IR spectrum.

Oxypropylation and Chloroxypropylation of Palmitic Acid

Palmitic acid was oxypropylated at the acid/PO molar ratios of 1/1, 1/3, and 1/5. It has been established that the PO conversion and palmitic acid oxypropylation degree values are significantly lower than those in the

case of pelargonic acid. So, the final conversion of PO in the reaction with palmitic acid equals 59.5, 11.03, and $\approx 10\%$, respectively. The values of oxypropylation degree were 0.6, 0.33, and ≈ 0.5 , correspondingly. The final products were dark-brown solids and well-soluble in heptane. At the molar ratio of 1/1 in the absence of catalyst the conversion of PO was 5.8 % with the oxypropylation degree of 0.058.

Chloroxypropylation of palmitic acid was carried out at $130\text{--}140^\circ\text{C}$ and the acid/ECH molar ratio was 1/5. The reaction lasted 48-50 h. The final conversion of ECH and the degree of chloroxypropylation were 14.5 %, and 0.725, respectively. The obtained product was a black resinous substance insoluble in water but well soluble in heptane.

The structure of the product 3-chloro-2-hydroxypropyl palmitate synthesized at the molar ratio of 1/5 was identified by IR spectroscopy. In the IR spectrum, the absorption bands of $-\text{OH}$ valency ($3200\text{--}3600\text{ cm}^{-1}$), $-\text{CH}$ valency ($2800\text{--}3060\text{ cm}^{-1}$), $\text{C}=\text{O}$ valency ($1740\text{--}1790\text{ cm}^{-1}$), $\text{C}-\text{H}$ deformational (1480 cm^{-1}), secondary $-\text{OH}$ deformational (1060 cm^{-1}), $\text{C}-\text{Cl}$ valency (735 cm^{-1}) and $\text{C}-\text{C}$ valency (630 cm^{-1}) vibrations are obtained.

Oxypropylation and Chloroxypropylation of Stearic Acid

Chloroxypropylation of stearic acid was carried out at $120\text{--}140^\circ\text{C}$ and the molar ratios of acid/epoxy compound were 1/1 and 1/5. The regularity concerning with the amounts of PO and ECH added to pelargonic and palmitic acids is confirmed in this case as well, i.e. the amount of the added ECH considerably exceeds the amount of the added PO.

At the equimolar amounts of the reactants the ECH conversion was 88.8% and at the five-fold excess of ECH, its conversion reached 97.4%. The respective chloroxypropylation degrees were equal to 0.89 and 4.87. At the indicated molar ratios the conversions of PO were registered at the level of 50.6 and 26.1%. The

Table 2. Results of study of pelargonic acid chloroxypropylation.

Factor	Initial molar ratio of pelargonic acid/PO				
	1/1	1/2	1/3	1/4	1/5
Final conversion of ECH (%)	79.1	69.9	90.0	93.1	93.7
Average degree of chloroxypropylation	0.80	1.40	2.70	3.72	4.70

degrees of oxypropylation were 0.51 and 1.31.

Oxypropylates of stearic acid are dark-brown solids. The chloroxypropylated derivative of stearic acid, i.e. 3-chloro-2-hydroxypropyl stearate, synthesized at the equimolar ratio of reagents is a dark-brown solid, as well, but the product obtained at the five-fold excess of ECH was a dark-brown oily liquid.

Synthesis of Surfactants Based on Pelargonic and Palmitic Acids Containing Fragments of both PO and ECH

There have been synthesized surface-active products containing the fragments of monocarboxylic acids, PO and ECH simultaneously. As monocarboxylic acids, pelargonic and palmitic acids were used. The reaction scheme for obtaining these surfactants may be described as Scheme II, where R is alkyl group (C_8H_{17} or $C_{15}H_{31}$).

The joint oxypropylation and chloroxypropylation reactions of the indicated acids were carried out in the presence of a base catalyst at 120-160°C during 12-16 h. The molar ratio of acid/PO/ECH were taken as 1/1.5/1.5. The total final conversion of the epoxy compounds was registered as 85.9% in the case of pelargonic acid and 45.8 % in the case of palmitic acid. The average joint oxypropylation and chloroxypropylation degrees of these acids were 2.5-2.6 and 1.3-1.4, respectively.

The final product of the simultaneous interaction of pelargonic acid with PO and ECH was a dark-brown liquid partially miscible with water. Its density at 20°C is 1.045 g/mL. The refractive index at 20°C is 1.444. The surface tension of 0.5% (by weight) kerosene solution at 26°C is 13.85 $\mu\text{N/m}$ which is an indication of high surface activity of this reagent. The composition

and structure of the product synthesized by joint addition of PO and ECH to pelargonic acid were identified by methods of ^1H NMR and IR spectroscopies. In the ^1H NMR spectrum recorded in CCl_4 , the protons resonance signals of $-\text{CH}_3$ (0.84 ppm), $-\text{CH}_2$ (1.26 ppm), $-\text{CH}_2\text{COO}^-$ (2.28 ppm), $-\text{OH}$ (3.2 ppm), CH_2Cl (3.4 ppm), $-\text{OCH}_2^-$ (3.56 ppm), and $-\text{CH}$ (3.88 ppm) groups are noticed. In the IR spectrum recorded from the liquid sample the absorption bands of $-\text{OH}$ valency ($3200\text{--}3700\text{ cm}^{-1}$), $-\text{CH}$ valency ($2900\text{--}3060\text{ cm}^{-1}$), $\text{C}=\text{O}$ valency ($1750\text{--}1790\text{ cm}^{-1}$), C-H deformational (1480 cm^{-1}), secondary $-\text{OH}$ deformational (1065 cm^{-1}), C-Cl valency (750 cm^{-1}), and C-C valency (735 cm^{-1}) vibrations have been presented.

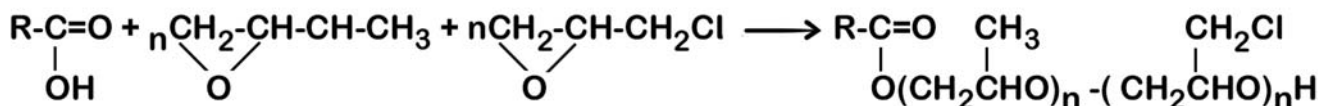
The product of joint addition of PO and ECH to palmitic acid is an amorphous substance of golden colour. It is not soluble in water but partially soluble in heptane.

Oxypropylation and Chloroxypropylation of Stearinamide

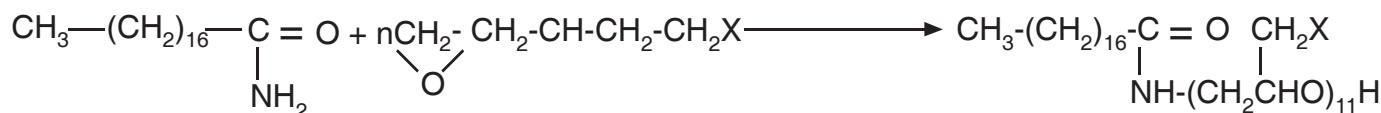
Surface-active substances have been synthesized by catalytic chloroxypropylation of stearinamide as well. Stearinamide was oxypropylated at the 1/5 molar ratio of amide/PO. Chloroxypropylation by ECH was also made at this molar ratio. These reactions were carried out at 140-160°C in heptane medium. The time periods of the reactions was 15-16 h.

The reaction scheme of stearinamide oxypropylation and chloroxypropylation may be represented in the Scheme III, where X is H or Cl.

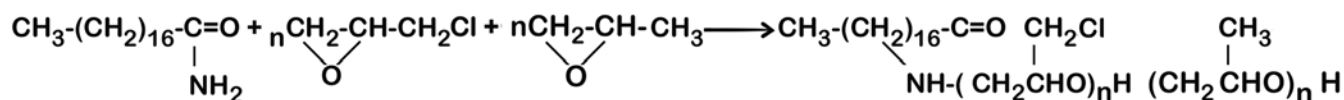
The final conversion of PO is 21.5%. The oxypropylation degree is 1.07. Oxypropylate product of stearinamide is an amorphous substance of yellow-golden colour. It is not practically dissolved in water



(Scheme II)



(Scheme III)



(Scheme IV)

and heptane, nor in acetone, isopropyl alcohol, dimethylsulphoxide, and 1,4-dioxane. It has been established that in the absence of catalyst, oxypropylation of stearinamide proceeds very slowly. In this case the final conversion of PO reaches only 5% and the oxypropylation degree corresponds to 0.25.

In analogy to the results of pelargonic, palmitic and stearic acids (chlor)oxypropylation processes, stearinamide adds ECH at larger amounts than PO. The final conversion of ECH equals 61.9% and the average degree of chloroxypropylation is 3.1. The end product was a dark-brown resinous substance well-soluble in heptane but insoluble in water. Non-catalytic chloroxypropylation of stearinamide occurred slowly up to the final ECH conversion of 23.6%, and the degree of chloroxypropylation reached 1.18.

The surface-active product is catalytically obtained by interaction of stearinamide, PO and ECH at the molar ratios of 1/1.5/1.5 according to the Scheme IV.

The reaction was carried out in heptane medium at 120-160°C. The time of the reaction was 32-36 h. The final total conversion of epoxides was 37.8 %. The average degree of (chlor)oxypropylation is 1.1-1.2. The obtained product was a dark-brown resinous solid soluble in heptane but insoluble in water.

In the scientific-technical literature there are enough references concerning mainly the production and study of the surfactants based on carboxylic acids and ethylene oxide (EO). The compounds synthesized in this study enlarge the list of the surfactance based on PO and ECH, in distinction to EO. These new products permit more hydrophobic surface-active substances having higher solubility in hydrophobic media. Besides, these epoxy compounds may be considered more preferable in comparison with EO due to the familiar difficulties in handling the latter (in gaseous state at room conditions, high explosion and fire hazard, etc).

The above mentioned particularities stipulate the importance of the investigations undertaken in this work.

CONCLUSION

New compounds of high surface-activity were synthesized by way of oxypropylation and chloroxypropylation of pelargonic, palmitic and stearic acids and stearinamide. By this way the possibility of employing fatty acids and amides as new useful surfactants was introduced. The same method maybe applied to other fatty acids or amides in order to obtain additional useful surfactants, especially for oil and gas industries.

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