

FATTY POLYUNSATURATED NONIONIC LIPIDS SUBSTITUTES

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Abstract

Paper aims at analysing the possibility of developing the range of *fat substitutes (F.S.)* as potential ingredients or products (foodstuff additives) with controlled functioning.

The paper focuses on the study of the impact of process parameters on structure, yields and selectivity.

Controlled modification of the *polyoxyethylene chain (n= 3, 9, 18) (PEO)* allows proper of hydrophilia, i.e., of the final *HLB balance* of *F.S.* with favourable impacts on their major colloidal characteristics (dispersants, antifoaming agents, emulsifiers, solubility agents, humectants, etc.).

The lipid fractions obtained and suggested as *F.S.* were purified, chemically and physico – chemically characterised in order to establish use potential in foodstuff processing.

Keywords: alkyl nonionic glycerides, fat substitutes, polyunsaturated lipids, polyethyleneoxy propionic acids, fat mimetics.

1. Introduction

Foodstuff fat substitutes (F.S.) represent an older concern signalled in literature. Their protein, lipid, or glucide natura was forced by foodstuff processing suitability.

Esters, in general, glycerides, in particular, in simple and complex mixtures (*E – 430* → *E – 436*; *E – 471* → *E = 482*) have confirmed ever since the beginnings of food processing their role as basic nutritious principles, and recently they have also confirmed their beneficial effects as *foodstuff additives* (emulsifiers, stabilisers, moisturising agents, sequestrants, etc.).

Even more recently, in the dispute “pro and contra” their role in controlled functional nutrition they have also gained new functional abilities as *fat substitutes (F.S.) of a lipid nature*.

The idea of diversifying was suggested by the encouraging result offered by the

synthesis four decades ago [1-5] of the *β-alkyl (C₁₂ – C₁₈) polyethyleneoxy (n = 3, 9 18) acetic and propionic acids* either by condensing *polyetoxylate (n = 3, 9, 18) high alcohols (C₁₂ – C₁₈)* industrially with monochlor acetic acid, i.e. or by nucleophilous addition in the basic catalysis of the same structures to acrylonitrile followed by partial and total acid hydrolysis [7].

Not only toxicity tests in literature and advanced purity of synthesis products, but also the capacity of adapting in a controlled way the *HLB balance* by controlled modification of *polyoxyethylene chain (PEO)* suggested the idea of getting new glycerides (mono -, di -, and tri -) by direct esterification or transesterification (**Figure 1**).

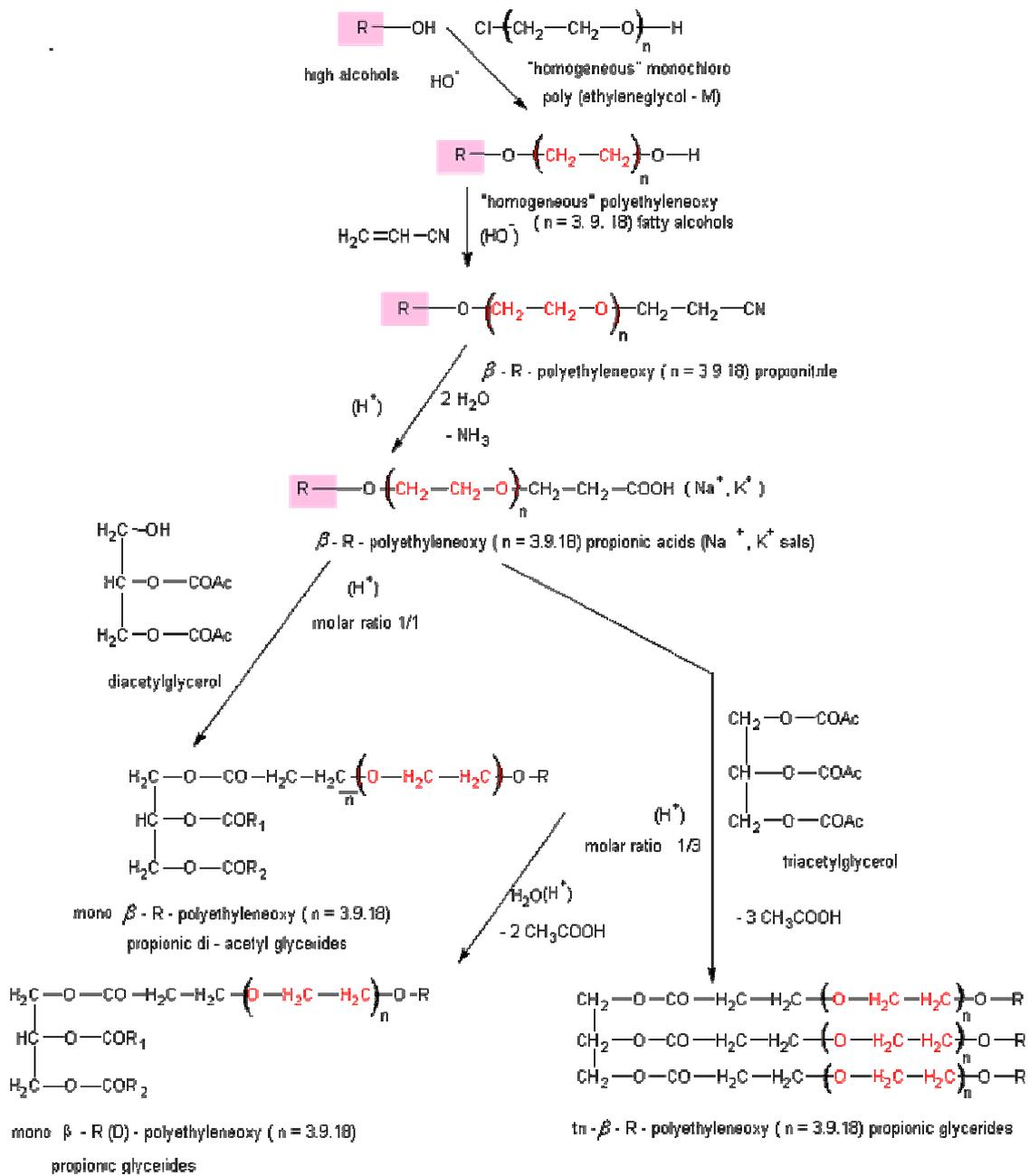


Figure 1 - Processing way in esterification and transesterification of glycerides with β-R-polyethylenoxy (n = 3, 9, 18) propionic acids

Inevitably, the final process product will have the qualities of a complex structure mixture. Chemical and physicochemical characterisation represented an important step in the effort to further define its use value.

Evolution in favour of ester, (glyceride) formation depends on the lowering of water concentration or even on its elimination

from the system. In the case eliminating water is not possible (alcohol miscible with water) the favorizing can be achieved by adding in excess one of the processing components – (anhydrous glycerine, monoacetyl glycerol, diacetyl glycerol).

Eliminating water from the system can be practically achieved in the case of immiscible alcohols and by distillation with an immiscible solvent with or without

alcohol and/or acid recirculation if its volatility allows protecting accessible, working conditions that do not affect the quality of the final chemical processing product. In this study we used glycerol (as alcohol miscible with water).

In the indirect esterification variant, the processed mixture includes "homogeneous" β - alkyl ($C_{12}H_{25}/C_{14}H_{29}$) polyethyleneoxy ($n = 3.9.18$) propionic fatty acids fraction present in the structure of the glyceride. We proceeded to their transesterification in accordance with the adapted classical process scheme (Figure 1). This paper presents the influence of process parameters on the structure, yields, and selectivity of the esterification process itself.

Nonionic lipid fractions obtained proposed as potential *F.S.* were afterwards purified, chemically and physico-chemically characterised in order to establish use potential in foodstuff processing (Figure 2, 3).

Controlled modification of the "homogeneous" polyoxyethylene ($n = 3.9.18$) (PEO) chain allowed proper regulation of hydrophilia of the final *HLB* balance of *F.S.* with favourable consequences on their major colloidal characteristics (dispersants, anti-foaming agents, emulsifiers, mycelial solubility agents, moisturisers, etc.). Foodstuff processing is interested in the large offer of foodstuff additives with controlled *HLB* balances similar to other classical foodstuff additive structures ($E - 431 \rightarrow E - 436$; $E - 430 \rightarrow E - 431$).

2. Materials and Method

3.1 Materials, reagents:

- β - $R(C_{12}H_{25}/C_{14}H_{29})$ polyethyleneoxy ($n = 3.9.18$) propionic acids [8]
- "homogeneous" monochloropoly (ethyleneglycol - 132) ($n = 3$) [8]
- "homogeneous" monochloropoly (ethyleneglycol - 396) ($n = 9$) [8]
- "homogeneous" monochloropoly

(ethyleneglycol - 792) ($n = 18$) [8]

- anhydrous glycerol p.a. (Merck)

- strong mineral acid (H_2SO_4).

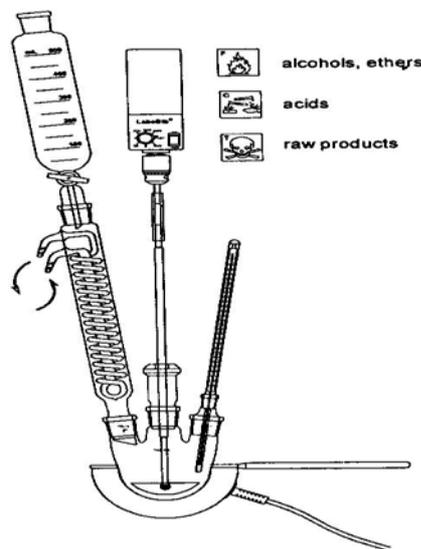


Figure 2 – Esterification and transesterification equipment

3.2 Method

In a three-neck process vessels endowed with efficient stirring, thermometer, and cooler we introduced, 0.1 mols of lipid fraction "homogeneous" β - alkyl ($C_{12}H_{25}/C_{14}H_{29}$) polyethyleneoxy ($n = 3.9.18$) propionic (equivalent molecular weight was assessed from the chromatogram in the gaseous phase) (figure 3). We added under continuous stirring, the acid catalyst (H_2SO_4) of 3 - 5% as compared to the fatty acids under work, and afterwards the β - alkyl [$(C_{12}H_{25}/C_{14}H_{29})$ (7/3)] polyethyleneoxy ($n = 3.9.18$) propionic acids in portions (molar ratio 1/1; 1/3).

We heated mixture between 80 - 160°C and kept stirring for a few hours. The fluid product was darker more or less in relation to work temperature. In some cases there is a stronger change in colour with formation of light brown solid suspensions. We washed the thus obtained (fluid, paste, wax) light brown to dark brown twice with 100 mL of product water at 60 - 70°C by slight

mechanical stirring (to avoid emulsification) after which we collected water residues. The final ester (after purification) was evaluated by current chemical analyses [acid, saponification, ester and iodine value, IR spectra, etc.].

Yields reported to glycerol introduced into the process was between **85 – 95%** (chromatograms in the gaseous phase of

methyl esters) that were compared with their distribution in the initial raw material in the process.

In order to quantitatively evaluate raw products was washed and then it was purified by repeated liquid-liquid extractions.

Table 1 Acid value (calculated and determined) of the β – alkyl $[(C_{12}H_{25}/C_{14}H_{29}) (7/3)]$ – polyethyleneoxy ($n = 0 – 20$) propionic acids

Nr. crt.	(n)	Molecular weight (\bar{M})	Acid value [mg NaOH(KOH)/g acid]			
			as NaOH		as KOH	
			calculated	determined	calculated	determined
1	0	340	117.647	117.10	164.71	165.18
2	3	472	84.746	84.69	118.64	119.10
3	6	604	66.225	65.88	92.72	93.24
4	9	736	54.348	53.93	76.09	75.60
5	12	868	46.083	46.99	64.52	63.84
6	16	1044	38.314	38.95	53.64	52.93
7	20	1220	32.787	33.24	45.91	45.02

Table 2 Dependence of the acid value ($mg\ KOH/g\ product$) in the process of esterification of the β – alkyl $[(C_{12}H_{25}/C_{14}H_{29}) (7/3)]$ polyethyleneoxy ($n = 3, 9, 18$) propionic acids and of their esters in relation to temperatura, in acid catalysis.

Nr. crt.	n	Temperature (°C)	yield (%)
1	0	110	48.18
2	↑ 3	110	↑ 54.32
3	↑ 6	110	↑ 59.05
4	↑ 9	110	↑ 61.09
5	↑↑ 18	110	↑ 71.47
6	9	↑ 130	↑ 64.55
7	9	↑ 150	↑ 69.88
8	9	↑ 160	↑ 72.71

Table 3 Dependence of the acid value ($mg\ KOH/g\ product$) in the process of esterification of the β – alkyl $[(C_{12}H_{25}/C_{14}H_{29}) (7/3)]$ polyethyleneoxy ($n = 3, 9, 18$) propionic acids and of their esters in relation to molar ratio glycerol/acid.

Nr. crt.	n	Ratio glycerol/ propionic acids	Yield (%)
1	9	↑ 1/1	69.04
2	9	↑ 1/1.1	↑ 71.11
3	9	↑ 1/1.3	↑ 75.52
4	9	↑ 1/1.5	↑ 79.67
5	9	↑ 1/2	↑ 81.81
6	↑ 18	↑ 1/1.3	↑ 79.04
7	18	↑ 1/1.5	↑ 82.52
8	18	↑ 1/2	↑ 89.67

Table 4 Dependence of the acid value (*mg KOH/g product*) in the process of esterification of the β – alkyl [(C₁₂H₂₃/C₁₄H₂₉) (7/3)] polyethyleneoxy (*n* = 3, 9, 18) propionic acids and of their esters in relation to time.

Nr. crt.	n	Time (hours)	Yield (%)
1	9	1	71.18
2	9	↑ 1.5	↑ 74.32
3	9	↑ 2	↑ 77.08
4	9	↑ 2.5	↑ 79.05
5	9	↑ 3	↑ 82.49
6	↑ 18	↑ 2	↑ 79.61
7	18	↑ 2.5	↑ 81.82
8	18	↑ 3	↑ 89.93

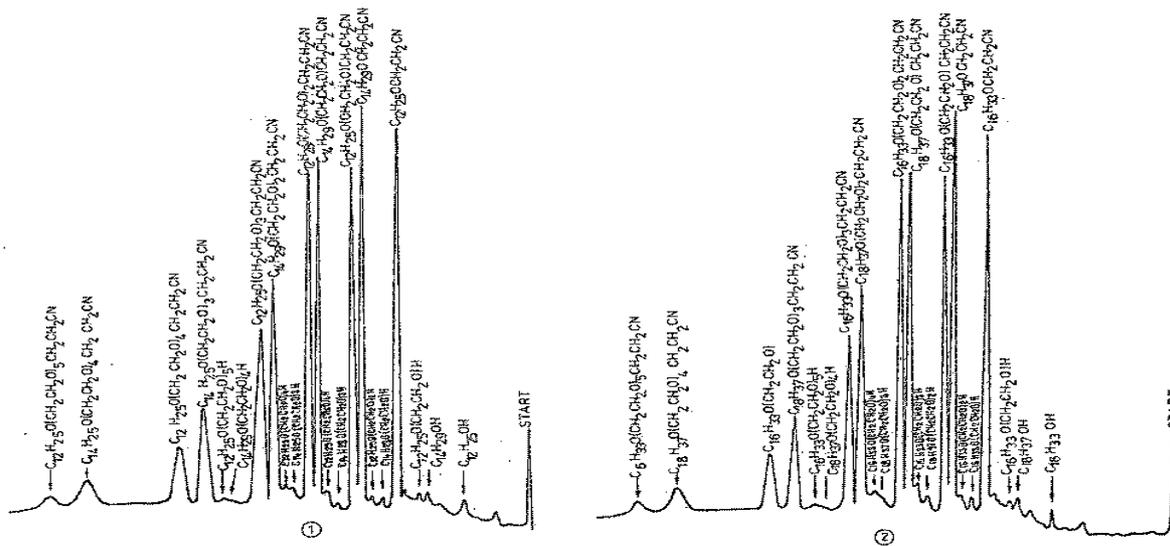


Figure 3 Chromatogram in gaseous phases of β – alkyl (C₁₂ – C₁₄) (1) (C₁₆ – C₁₈) (2) polyethyleneoxy propionitrils (column with Chromosorb W 100 – 120 mesh + 5% silicon oil SE – 30, 1m, N₂ flow 46mL/min., temperature gradient 12°C/min, detector with flame ionization)

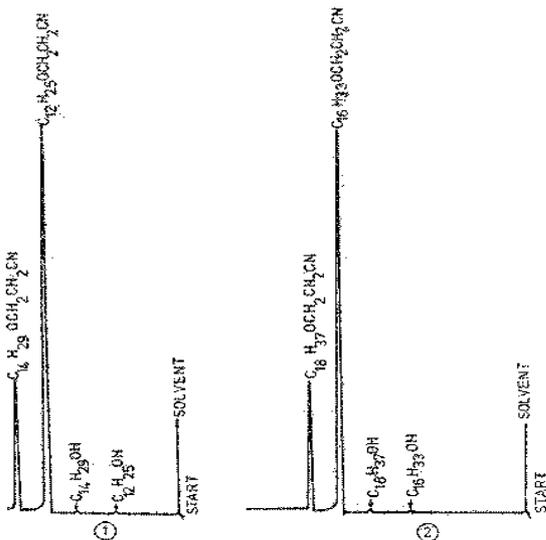


Figure 4 Chromatogram in gaseous phases of β – alkyl (C₁₂ – C₁₈) oxy propionitrils (column with Chromosorb W 100 – 180 mesh + 5% silicon oil SE – 30, 1m length, N₂ flow 46mL/min., temperature gradient 12°C/min., detector with flame ionization)

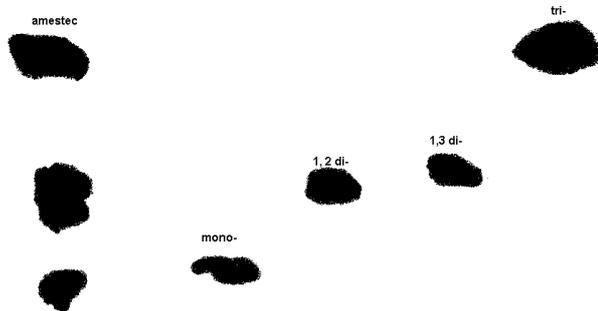


Figure 5 Thin layer chromatogram of mono-, di and tri-glycerides solvent system petroleum ether/ethyl ether (70/30 v/v)

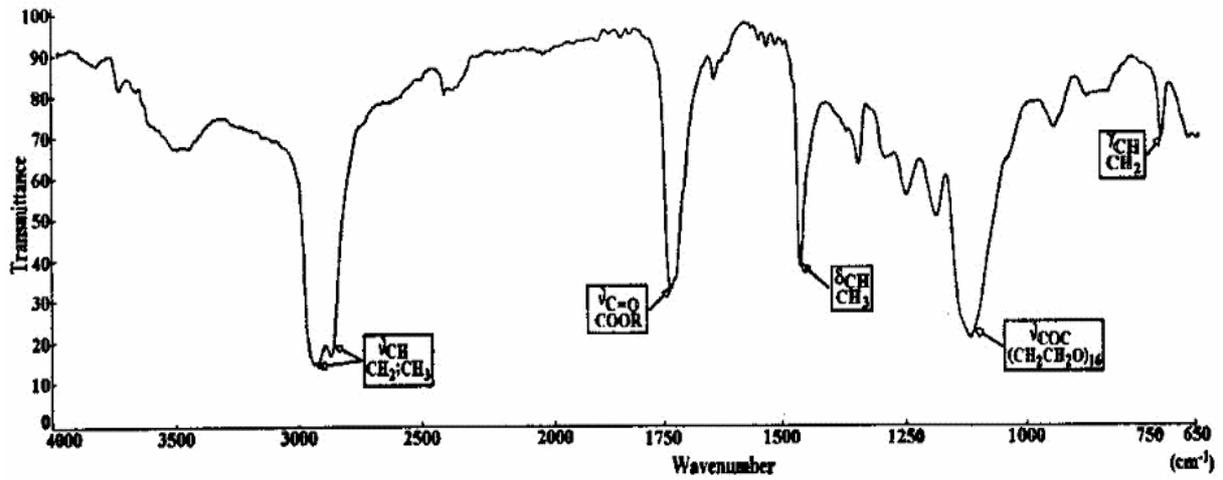


Figure 6 – Infrared absorption spectrum of the β – alkyl ($C_{12} - C_{14}$) / ($C_{16} - C_{18}$) polyethyleneoxy propionic derivatives.

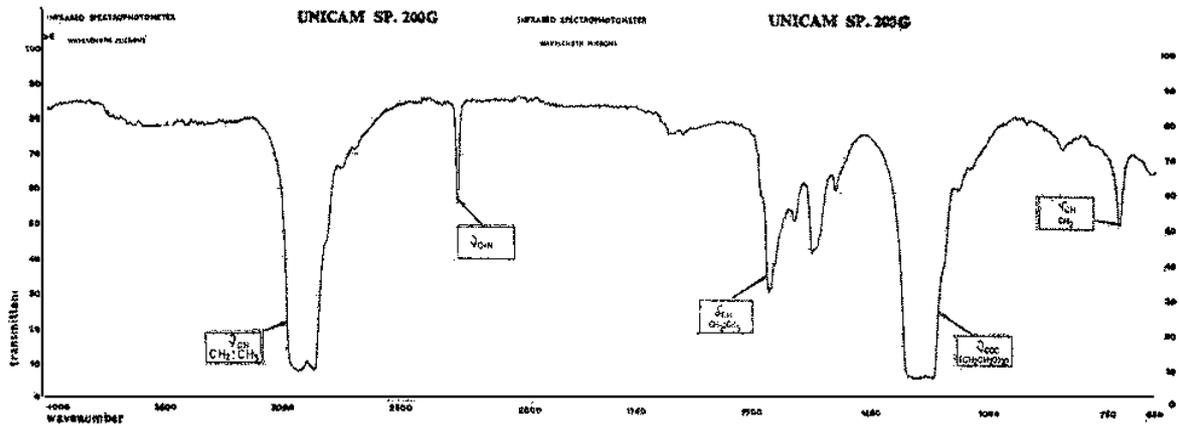


Figure 7 – Infrared absorption spectrum of the β – lauryl/miristyl (7/3) – polyethyleneoxy ($n = 20$) propionitriles (1,7) film on KBr window

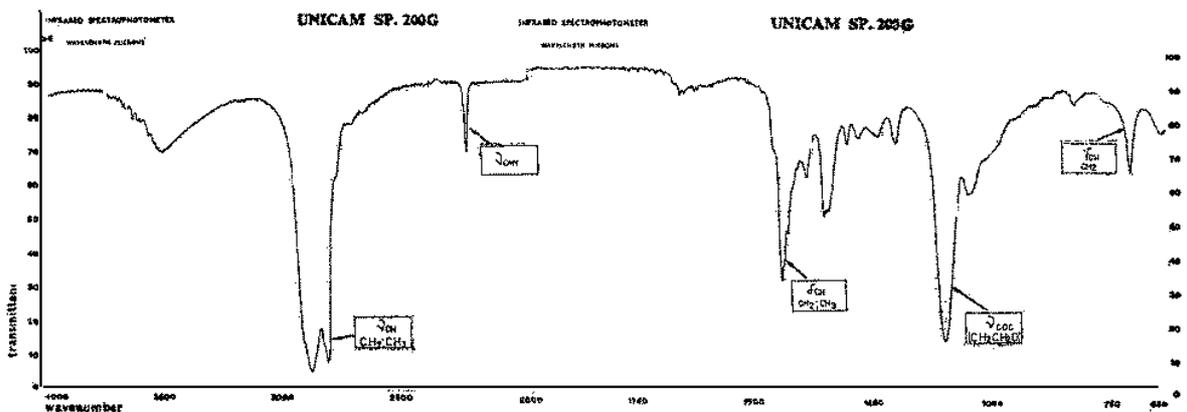


Figure 8 – Infrared absorption spectrum of the β – lauryl/miristyl (7/3) oxy– propionitril (1,1) film on KBr window

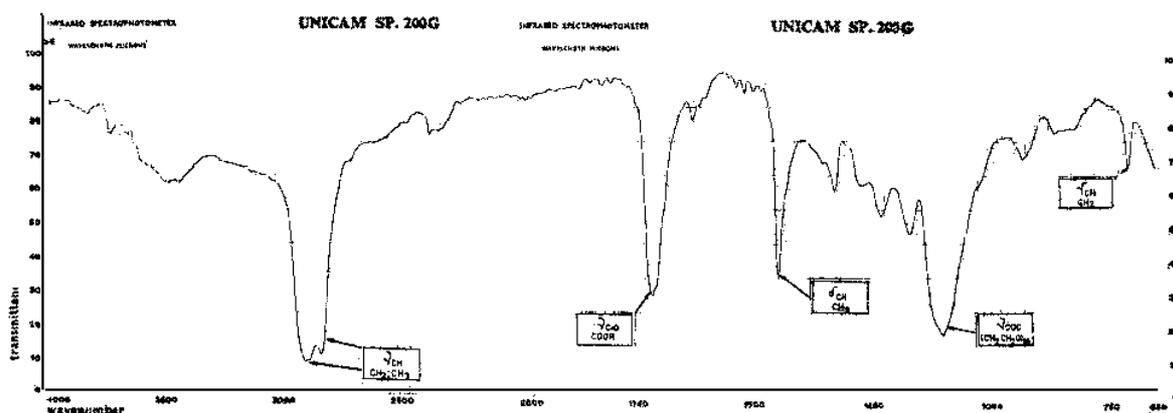


Figure 9 – Infrared absorption spectrum of the β – lauryl/miristyl (7/3) – polyethyleneoxy ($n = 20$) propionitrils methyl ester

3. Results and Discussion

In all cases studied, over 80°C the content in β – alkyl $[(\text{C}_{12}\text{H}_{25}/\text{C}_{14}\text{H}_{29}) (7/3)]$ polyethyleneoxy ($n = 3, 9, 18$) propionitriles decreases steadily no matter the acid catalyser used and one can notice the presence of propionic esters (tables 1–4).

Meanwhile content in ester increases with the decrease of polyoxyethylene chain length in the polyethoxylate high alcohol that has to be introduced.

Analysis of experimental data offered by total acid hydrolysis of β – alkyl $[(\text{C}_{12}\text{H}_{25}/\text{C}_{14}\text{H}_{29}) (7/3)]$ polyethyleneoxy ($n = 3, 9, 18$) propionitriles synthesized [8] shows the incipient presence of the esters ever since this phase (in limited amounts).

This paper did not aim at assessing individual content in mono-, di-, and triglycerides in the processing mixture, nor did it aim at assessing the distribution of β – alkyl $[(\text{C}_{12}\text{H}_{25} / \text{C}_{14}\text{H}_{29}) (7/3)]$ polyethyleneoxy ($n = 3, 9, 18$) propionic acids in relation to hydrophilous chain size in transesterification and esterification of various glycerol hydroxyl groups.

4. Conclusion

This results shall be topic of further papers, in strict relation to the results and to the interest in practically utility in foodstuff

processing together with the study of basic colloidal properties.

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