

Hydrolysis of β -alkyl ($C_{12}H_{25}/C_{18}H_{37}$) polyethyleneoxy ($\bar{n}=3-20$) propionitriles in micellar catalysis conditions (I)

C. Jianu^a, Monica Butnariu^b, Ileana Cocan^a, A. Rinovetz^a, G. Bujancă^a, I. Jianu^a

^a Banat's University of Agricultural Sciences and Veterinary Medicine, Faculty of Food Processing Technology, 300645-Timişoara, Calea Aradului 119, Romania

^b Banat's University of Agricultural Sciences and Veterinary Medicine, Chemistry Department, 300645-Timişoara, Calea Aradului 119, Romania

Abstract

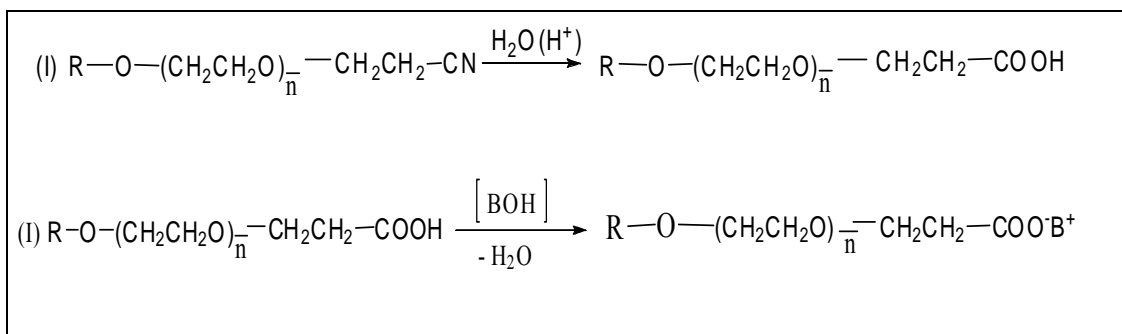
This paper presents the results of total acid hydrolysis of β -alkyl ($C_{12}H_{25}/C_{18}H_{37}$) polyethyleneoxy ($\bar{n}=3-20$) propionitriles (I) in classical heterogeneous system and micellar catalysis conditions with dodecylbenzene sulphonic acid (III) and *p*-toluenesulphonic acid (II). Alkaline (Na, K) and ammonium salts (NH₄; MEA; DEA; TEA) of the β -alkyl $C_{12}H_{25}/C_{18}H_{37}$ polyethyleneoxy ($\bar{n}=3-20$) propionic acids (I) as valuable ionic-anionic surfaceactive components in hygiene receipts are also in agroalimentary processing.

Keywords: total acid hydrolysis, alkyl polyethyleneoxy propionitriles; micellar catalysis; alkyl polyethyleneoxy acids, ionic-anionic colloids.

1. Introduction



β -alkyl ($C_{12}H_{25}/C_{18}H_{37}$) polyethyleneoxy ($\bar{n}=3-20$) propionic (I) acids and their sulfonated derivatives have been noted in literature [1] during these last decades on one hand due to their remarkable basic colloid competences (foaming, wetting - displaying, emulsifying, cleaning, antistatic agents, etc.) and, on the other hand, due to

the low toxicity of the polyoxyethylene chains and to their accelerated biodegradability in the agroalimentary post-processing technological waters. They can be obtained through total acid hydrolysis of the corresponding propionitriles according to the processing route:



where: $R=C_{12}H_{25}/C_{18}H_{37}$; $\bar{n}=3-20$; BOH (neutralizer agent) (sulfonation);

B^+ [cations Na^+ ; K^+ ; NH_4^+ ; monoethanolammonium (*MEA*); diethanolammonium (*DEA*); triethanolammonium (*TEA*)];

$H^+=HCl$; H_2SO_4 ; p-toluenesulphonic acid () (ii) dodecylbenzenesulphonic acid () (iii).

Total acid hydrolysis of propionitriles with low polyethyleneoxy chains ($\bar{n} < 6$) and ($\bar{n} = 0$), respectively, goes on with limited yields in heterogeneous systems due to the low solubility of the processing substratum in water.

Micellar catalysis (MC) is a modern and efficient technique of achieving an advanced contact between a non-electrolytic processing substratum in an organic phase [β -alkylpolyethyleneoxy ($\bar{n} = 3 - 20$) propionitrile] and the acid ionic catalyst in the water phase at interface contact in the heterogeneous hydrolysis system. The transfer of the catalyst from the water phase into the organic one through the micellar ensemble facilitates the „homogenisation” of the system. MC has similarities with different processing systems:

- at the interface;
- in the catalysis, through interphase transfer;
- in the melting (Gordon, J., 1965);
- catalysed by ion-exchanger resins (Regen, S., 1975);
- through extraction with „ion pairs” (Brädström, A., 1969, 1974);
- through encapsulation with hydrophobic „sites” (cyclodextrines) (Breslow, R., 1970).

Phase transfer catalysis has become a self-sufficient procedure as a result of the accumulation, during the last seven decades, of a rich experimental and theoretical material [2-18] though the term

(notion) was initially suggested by (Wittig, G., et al., 1947), and later by (Regen, S., 1979), who studied the hydrolysis 1-Br-adamantine in catalysis through phase and micellar transfer using catalysts such as superficialactive ammonium quaternary salts.

2. Materials and Methods

2.1 Materials (Aldrich – Sigma)

- hydrochloric acid 37% (CAS 7647-01-0);
- sulfuric acid 98% (CAS 7664-93-9);
- dodecylbenzenesulphonic acid sodium salt (CAS 2155-30-0);
- p-toluenesulfonic acid monohydrate 98,5% (CAS 6192-52-5);
- acrylonitrile 99% (inhibited with 35 – 45 ppm hydroquinone monomethyl-ether) (CAS 107-13-1);
- 1 – dodecanol (dodecylalcohol) 98% (CAS 112-53-8);
- 1 – tetradecanol 99% (miristylalcohol) 99% (CAS 112-72-1);
- 1 – hexadecanol 99% (cetylalcohol) 99% (CAS 36653-82-4);
- 1 – octadecanol 99% (stearylalcohol) 99% (CAS 112-63-0);
- iron (II) sulfate heptahydrate 99% (CAS 7782-63-0);
- β -alkyl ($C_{12}H_{25}/C_{18}H_{37}$) polyethyleneoxy ($\bar{n}=3-20$) propionitrile min. 99% (USAB Food additives laboratory);
- β -alkyl ($C_{12}H_{25}/C_{18}H_{37}$) (7/3) polyethyleneoxy ($\bar{n}=3-20$) propionic acids;
- sodium methoxide (powder) (sodium methylate) 95% CAS (124-41-4).

2.2 Methods

Processing β -alkyl ($C_{12}H_{25}/C_{14}H_{29}$; $C_{16}H_{33}/C_{18}H_{37}$) (7/3) – polyethyleneoxy ($\bar{n} = 3 - 20$) propionitriles

In a processing vessel with mechanical stirring, thermometer, dropping funnel, refrigerator, inert atmosphere (30–35°C for

the fraction C_{12} – C_{14} ; 50–55°C for the fraction C_{16} – C_{18}) introduce 0.1 mol high polyethoxylated alcohol fraction $C_{12}H_{25}/C_{14}H_{29}$ and $C_{16}H_{33}/C_{18}H_{37}$, respectively, purified (no water, free polyethyleneglycols, free high alcohols), 0.0025 mol basic catalyst ($CH_3O^-Na^+$), we suspend 0.0025 mol (0.38 g) $FeSO_4$ anhydrous finely divided and add cautiously (30–45 minutes) under continuous stirring 5.83 g (0.11 mol) acrylonitrile, for the temperature of the mixture keep within prescribed values (if necessary, the processing vessel is cooled down in a water-ice bath). We keep in the same conditions for two hours to perfection, neutralise the catalyst with about 4.8 mL of solution CH_3COOH 5%, filter when warm the precipitated salts; if necessary, we purify the light yellowish fluid residue from acrylic oligomers by column elution on silica gel G. Yields compared to the high polyethoxylated alcohol are practically quantitative.

Processing β -alkyl ($C_{12}H_{25}/C_{14}H_{29}$; $C_{16}H_{33}/C_{18}H_{37}$) (7/3)-polyethyleneoxy ($n = 3$ –20) propionic acids.

β -alkyl-polyethyleneoxy-propionic acids were obtained through classical total acid hydrolysis of nitriles and similar β -alkyl-polyethyleneoxy-propionamides.

Total hydrolysis with HCl

In a processing vessel with mechanical stirring, thermometer, ascending refrigerant and dropping funnel introduce 0.1 mol nitriles or amides, cautiously add at 60–70°C (to avoid abundant foaming or overflow of reaction mass), 0.4 mol (14.5 g) chlorhydric acid (40–42 mL concentrated chlorhydric acid) over 30–45 minutes. We complete the process at 90–100°C for other two hours, then the mixture is neutralised with a mixture of finely divided 16 g NaOH or 54 mL NaOH 30% aqueous solution. Precipitated inorganic salts are filtered and water from the product is removed in void (10–20 mm col. Hg).

The fluid residue obtained after concentration is purified through repeated liquid/liquid extractions in the ethylic

ether/water system and then through column elution on ion exchangers. The purity of the β -alkyl-polyethyleneoxy-propionic acids is verified by comparing the theoretical acidity value with the value determined experimentally or by thin layer chromatography separation. Yields compared to nitriles or amides introduced are between 90–95% in micellar catalysis conditions.

Total hydrolysis with paratoluene-sulphonic acid (TS) and dodecylbenzene sulphonic acid (DBSH)

In a processing vase with mechanical stirring, thermometer, ascending refrigerant, and dripping funnel we introduce 0.1 mol nitriles or amides, we add cautiously at 60–70°C, between 0.1–0.4 mol acid catalyst (TS or DBSH) and 2.77 mol (50 mL) water. The process is completed at 90–100°C, for about 2 hours, after which the mixture is salefied with finely divided NaOH and water from the product is removed in the void (10 – 20 mm col. Hg). The residue thus obtained is purified through repeated alcoholic extractions or through ion exchanger elution column. Salefy exhaustively (stoichiometrically) with inorganic or organic bases and determine the β – alkyl – polyethyleneoxy – propionates content through “antagonic titration” with N, N, N – trimethyl – N – benzyl-ammonium chloride solution. Yields compared to nitriles or amides are between 94 – 98%.

3. Results and Discussion

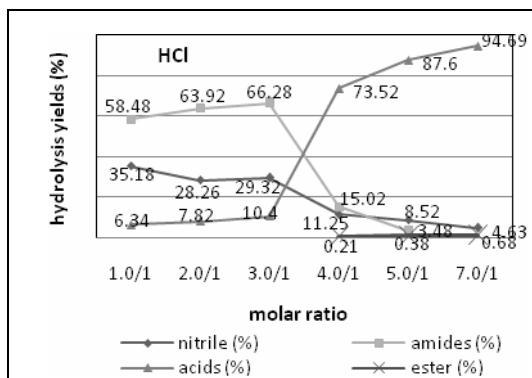
Experimental data analysis (Figures 1-3) shows that:

- in the traditional hydrolysis (heterogeneous system) with HCl the increase of the molar ratio HA/propionitrile favours both total hydrolysis partial hydrolysis (amide formation);
- in the same processing conditions, ester content increases insignificantly but it suggest the possibility of breaking propionitrile links and the condensing of polyethoxylated high alcohols with β -alkyl polyethyleneoxy ($\bar{n}=3$ –20) propionic acids;

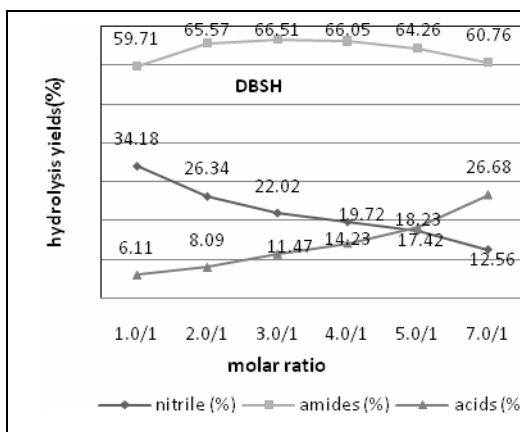
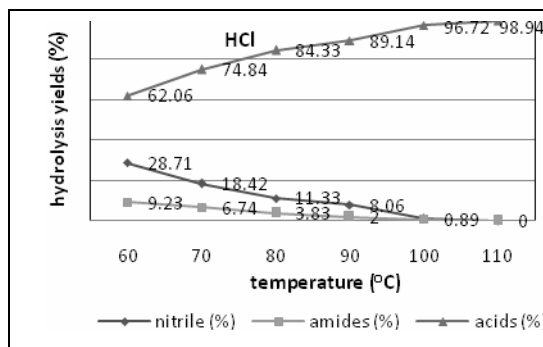
- in micellar catalysis (dodecylbenzenesulphonic (*DBSH*) acid and/or *p* – toluenesulphonic) (*TS*) acid total and partial acid hydrolysis yields suggest the same trends with more propionamide formation;

- the amount of esters formed is practically inexistent, which is justified by the lower acidity constant of these catalysts compared to the *HCl*.

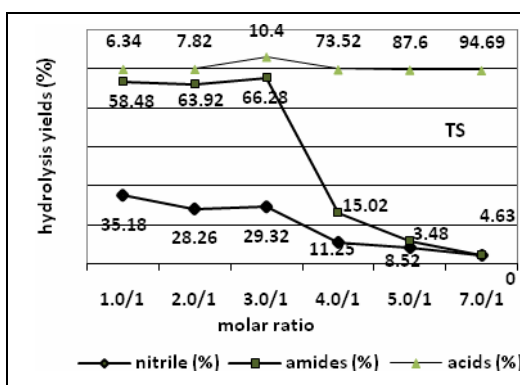
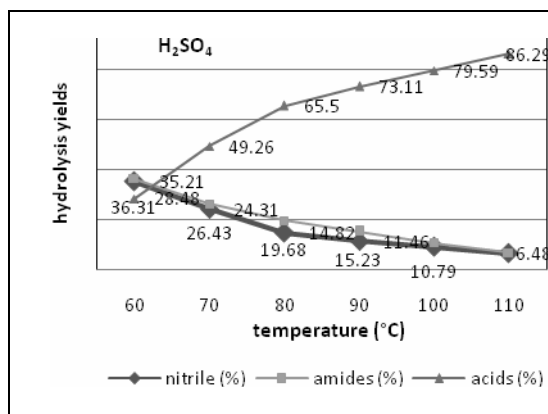
- between the two organic acid catalysts there are no major differences in yield.



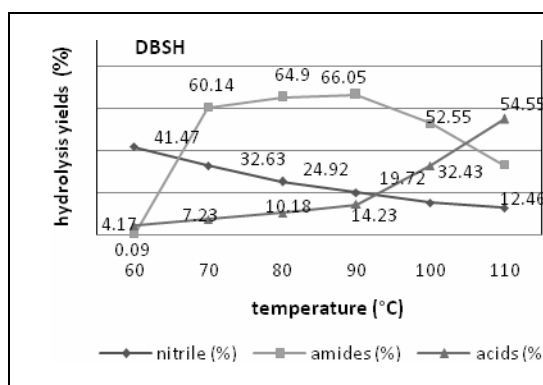
(a)



(b)



(c)



(c)

Figure 1. The dependence on the ratio HA/nitrile of the total acid hydrolysis yield of the β – lauryl/miristyl (7/3) oxypropionitrile, processing time 60 minutes, temperature 90°C, molar ratio water /propionitrile 2/1

Figure 2. The dependence on the temperature of the total acid hydrolysis yield of the β – lauryl/miristyl (7/3) oxypropionitrile, molar ratio HA/nitrile 4/1, processing time 60 minutes, molar ratio water/propionitrile.

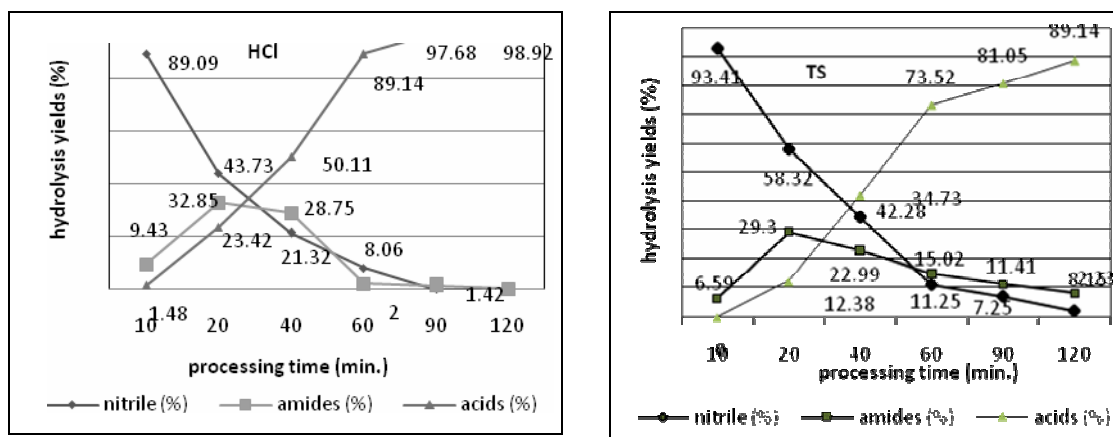


Figure 3. The dependence on the processing time of the total acid hydrolysis yields of the β -lauryl/miristyl (7/3) oxypropionitrile, molar ratio HA/nitrile 4/1, temperature 90°C , molar ratio water/propionitrile 5/1.

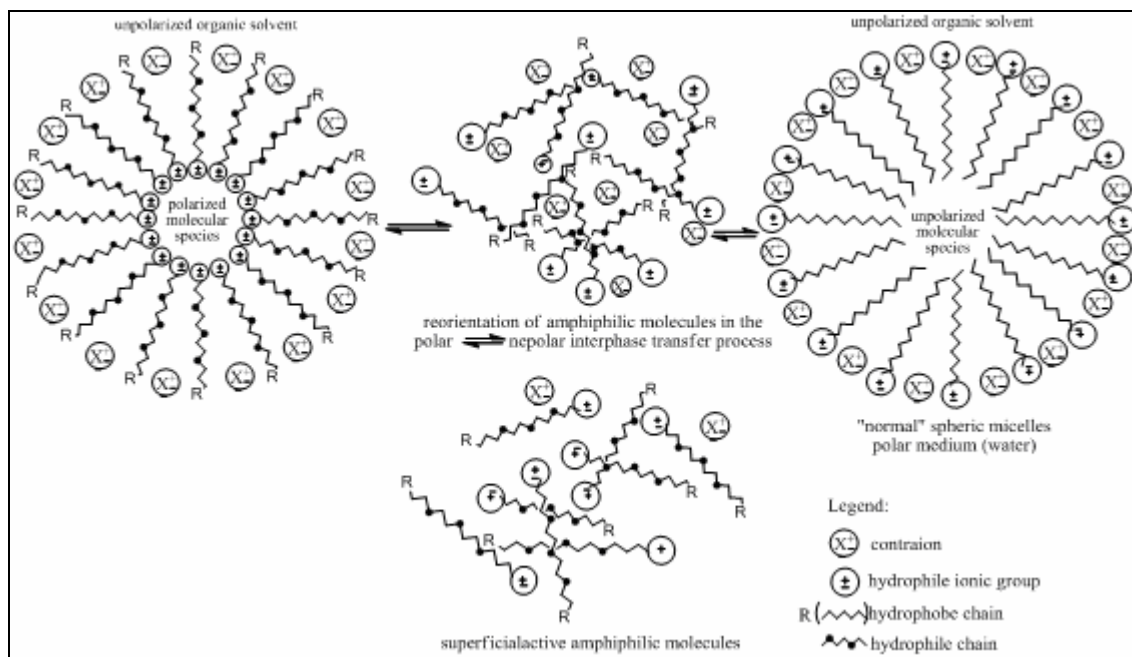


Figure 4 Probable route of the association and micellar solubilisation of some homogeneous diderivatised polyethyleneoxy (PEO) chains with hydrophil group (marginal) in polar (water) and nonpolar (organic solvents) media

In all the cases, over 80°C of the content in β -alkyl polyethyleneoxy propionitrile decreases steadily no matter the acid catalyst used and propionic esters appear. Over 110°C in the presence of chlorhydric acid there are increasing amounts of superior alcohols due to the scission of the ether bridges. The increase of the duration

of the processing favours total acid hydrolysis. At high temperatures (over 80°C) in the presence of chlorhydric acid after about **60 minutes** nitril disappears from the mixture and after another **90 minutes** intermediary propionamides also disappears. In the presence of **TS**, at the same temperature and in the same amount of water there are traces of propionitriles

and propionamides even after **180 minutes** with general conversions (*effects of the micellar catalysis*).

4. Conclusion

Total and partial acid hydrolysis of β -alkyl polyethyleneoxy ($\bar{n}=3-20$) propionitriles in micellar catalysis conditions is probably favoured by the mechanism rendered in **Figure 4** which supposes the presence of the acid organic catalyst at concentrations higher than micellar critical concentration (**CCM**) of each of them.

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