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ASPECTS REGARDING THE SYNTHESIS AND SURFACE PROPERTIES OF SOME GLYCINE BASED SURFACTANTS

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Articolul prezintă datele experimentale privind obţinerea unor surfactanţi pe bază de amino acizi prin condensarea clorurii de lauroil cu glicină şi glicilglicină. Sfârşitul reacţiei a fost determinat prin metoda Sorensen, iar produşii de reacţie au fost caracterizaţi cu ajutorul spectroscopiei FT-IR. A fost investigată activitatea superficială a soluţiilor apoase de lauroil-glicinat de sodiu şi lauroil-glicil-glicinat de sodiu. S-a stabilit, prin tehnica DLS, că sărurile de potasiu şi trietanolamină (TEA) a lauroil-glicil-glicinatului prezintă două generaţii de agregate: o generaţie cu un diametru mai mic de 100 nm, corespunzător agregatelor micelare, şi o generaţie cu agregate mai mari (>300 nm), posibil vezicule.

The article presents experimental data regarding some amino acid based surfactants, obtained by condensation of lauroyl chloride with glycine and glycylglycine. The end of reaction was determined by Sorensen method and reaction products were characterized by means of FT- IR spectroscopy. The surface activity of aqueous solutions of sodium lauroyl-glycinate and sodium lauroyl-glycyl-glycinate was investigated. By DLS technique was established that both potassium and TEA lauroyl- glycyl-glycinate presents two generations of aggregates: one with a diameter bellow 100 nm, corresponding to the micellar aggregates and one with bigger aggregates, possible vesicles (>300 nm).

Keywords: amino acid based surfactants, surface properties, self-assemble

1. Introduction

Surfactants (tensioactive substances) are products with asymmetric molecular structure, whose molecule includes a water soluble group (hydrophilic) and a partially soluble or non-soluble in water group (hydrophobic). Due to their

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abilities to modify the properties of the systems in which they are introduced, surfactants molecules became indispensable in the life of the modern man, being encountered in various domains: starting with personal hygiene products and ending with industrial use.

The present tendencies in the field of surfactants are:

- Passing from petrochemical products (paraffin, olefins, benzene, oxo – alcohols, fatty amines, alkylene oxides, etc.) to renewable raw materials with vegetal or animal sources (fatty acids or fatty alcohols from fats and oils, saccharose, glucose, sorbitol, aminoacids, peptides, protein hydrolizates, cholesterol, sitosterol, campesterol, etc), since the petrochemical raw materials and the aggressive chemical processes for the synthesis of surfactants often lead to products that have a negative impact on the environment (surfactants are known as high water pollutants);
- New fields of applications for surfactants (biology, medicine, nanomedicine, and targeted delivery of drugs or cosmetic active ingredients, use of colloidal systems as synthesis medium for nanoparticles) based on the theoretical knowledge and experimental techniques of study and characterization which are constantly growing.

From the biodegradable and biocompatible surfactants two important classes are remarkable, namely:

- Carbohydrates based surfactants – nonionic surfactant obtained from renewable resources (glucose and fatty alcohols), which have superior detergency, foaming and wetting properties, gentle action on the human skin, and they are highly biodegradable. They are used in detergent formulas for domestic or institutional purpose and in cosmetics industry;
- Protein based surfactants, amphiphilic products which contain an aminoacid or a protein hydrolizate as hydrophilic group and a long hydrocarbon chain as hydrophobic group, used in pharmaceutical and cosmetics industry due their lack of toxicity, gentle action on the skin, good surface activity, and high rate of biodegradability. They are also used in detergent industry due to their capability to improve the fabric touch, to reduce the degradation of fibers like cotton and wool, and due to the anti-pilling and antistatic effects they have on fabrics.

The structure diversity of aminoacids and of the hydrophobic group with long hydrocarbon chain leads to a multitude of derivatives of N - N^{α}- acylates, O^{α}-amidic, O^{α}- esteric, N- alkyilic or bolaamphiphilic [1-5].

The aim of this work is to synthesize glycine based surfactants which exhibit properties of self – assembling into aggregates superior to micelles.

2. Experimental

2.1. Method for the synthesis of lauroyl – glycine and lauroyl – glycylglycine

In a three-necked flask provided with a thermometer, a dropping funnel and a stirrer, 0.05 moles of aminoacid are dissolved in 60 ml of water. A 25% solution of NaOH is added drop wise under permanent stirring. When the mixture is brought to pH 11, 25 ml of acetone are added. The alkaline reaction medium increases the aminic component nucleophilic character, which is higher when it is found on its non – proton form. Over a period of one hour, 0.05 moles of lauroyl chloride are added drop wise to the mixture. During the acyl chloride addition, the mixture temperature is being maintained at 10°C, and more NaOH solution is added if necessary, in order to maintain the mixture pH to 11. After the complete addition of acyl chloride, the mixture is heated to 30-55°C and is maintained at this temperature for 120-180 min. The reaction mixture is then cooled, and the pH is adjusted again to 1.5 by adding 35 % hydrochloric acid. The acylated aminoacid precipitates. Then, the crude reaction product is vacuum filtered and washed with distillated water in order to eliminate the remaining acid (final pH = 7). The filtered product is then oven-dried at a temperature lower than 50°C in order to avoid coloring.

The acylation rate, and the specific reaction conditions for the synthesis of lauroyl – glycine and lauroyl glycylglycine are given in Table 1.

Table 1

Working conditions for the synthesis of glycine based surfactants

Compound	Aminoacid / lauroyl chloride molar ratio	Reaction Medium	LC Adding Temp.,^{0}C	Post-reaction Temp. ^{0}C	Post-reaction Time, min.	Content N_{aminic}, %		Acylation rate AR, %
						initial	final	
Lauroyl-glycine	1:1 (3,75gG +12 ml CL)	water (60 ml)+ acetone (25 ml)	10	30	120	0,75	0,059	92,33
Lauroyl-glycylglycine	1:1 (6,6 g GG+12 ml CL)	water (60 ml)+ acetone (25 ml)	10	55	180	0,32	0,007	97,81

The acylation rate is calculated using the equation (1).

$$AR = \frac{N_{ai} - N_{af}}{N_{ai}} \times 100 \qquad (1)$$

Where N_{ai} is the initial content of aminic nitrogen, and N_{af} is the final content of aminic nitrogen in the reaction mixture.

The infrared spectra were recorded on a FT-IR Perkin –Elmer spectrometer, and the results are given in Table 2.

Table 2

Results of IR spectrometry

Compound name	Characteristic Frequencies, cm^{-1}
Lauroyl- glycine	3320,3079, 2954, 2917, 2848, 1738, 1701, 1641, 1555, 1439, 1405, 1377, 1347, 1302, 1268, 1249, 1132, 1038, 870, 719, 684, 632, 554, 500, 419
Lauroyl -glycylglycine	3303, 3082, 2953, 2917, 2849, 1702, 1637, 1553, 1465, 1418, 1390, 1263, 1194, 1084, 1028, 937, 897, 779, 722, 692, 640, 553, 493, 456, 419

The main characteristic frequencies on the lauroyl – glycine spectrum: 3320 cm^{-1} (NH), 1701 cm^{-1} (C=O), 1641 cm^{-1} (amidic band I), 1555 cm-1 (amidic band II), 719 cm^{-1} ($-(CH2)_n-$, n>3).

The main characteristic frequencies on the lauroyl – glycylglycine spectrum: 3303 cm^{-1} (NH), 1702 cm^{-1} (C=O), 1637 cm^{-1} (amidic band I), 1553 cm^{-1} (amidic band II), 722 cm^{-1} ($-(CH2)_n-$, n>3).

2.2. Surface activity evaluation

The synthesized aminoacid based surfactants are in their acidic form, having free carboxylic groups. Since the surface activity of surfactants is ensured by the presence of both hydrophilic and hydrophobic parts, the aminoacid based surfactants were neutralized with a NaOH solution in order to provide the affinity for water.

The surface activity was evaluated by determining the critical micelle concentration of sodium lauroyl – glycinate and sodium lauroyl glycyl-glycinate aqueous solutions. The determinations were made by means of KSV Sigma 700 automatic tensiometer. The variations of the surface tensions with the concentrations for the two synthesized products are shown in figures 1 and 2.

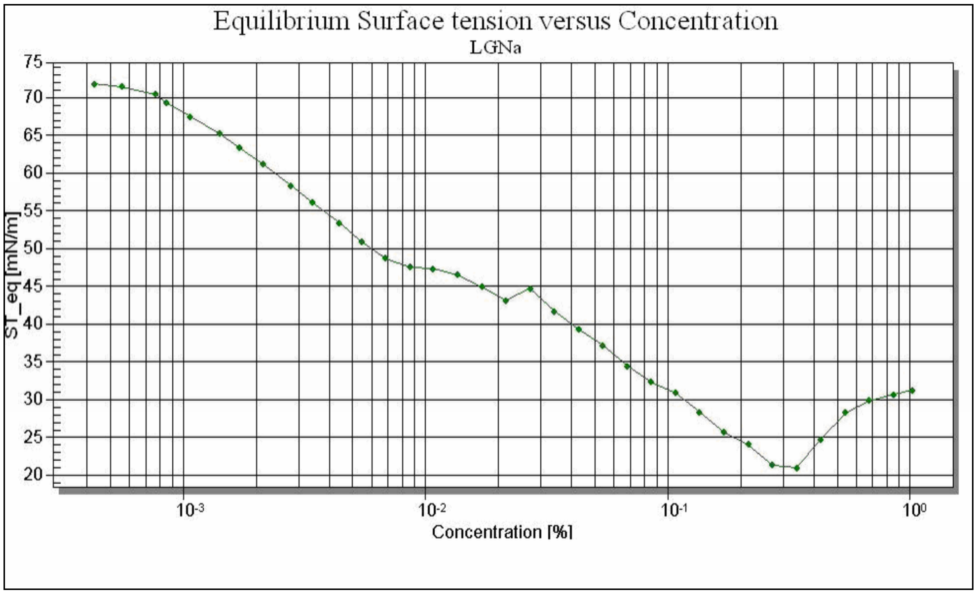

Fig. 1. Equilibrium surface tension versus the concentration of sodium lauroyl - glycinate (Cmc = 0,34% (12 mmol/l), ST = 20,96 mN/m).

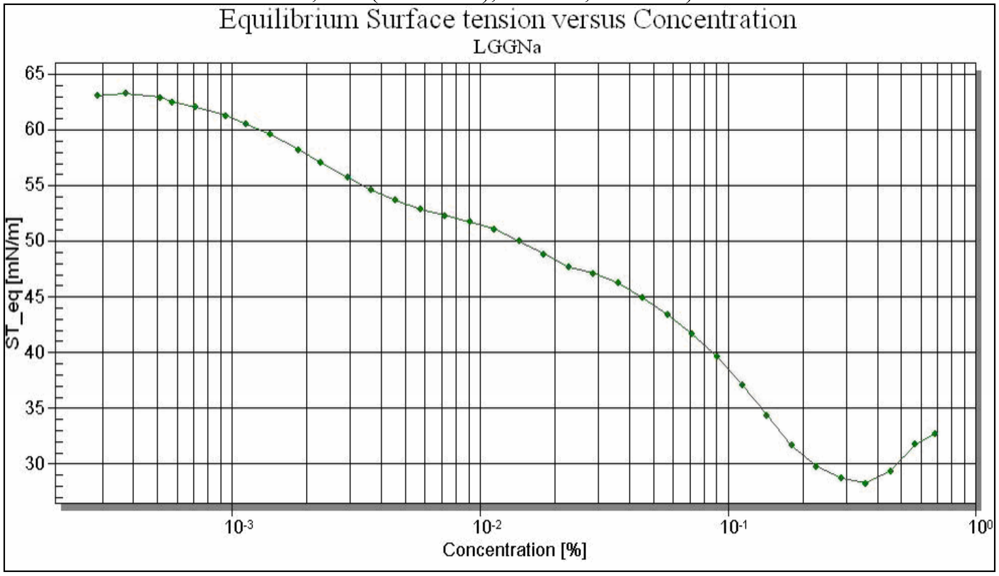

Fig. 2. Equilibrium surface tension versus the concentration of sodium lauroyl - glycylglycinate (Cmc = 0,36% (11 mmol/l), ST = 28,26 mN/m)

It was found that the aqueous solutions of the synthesized products are placed in the domain of the anionic surfactants critical micelle concentrations, and also that at this concentration the products lead to a significant decrease in the surface tension of water.

2.3. Studies regarding the lauroyl – glycyl-glycinate aggregation in aqueous solutions using DLS technique

The particles dimensions were measured using the DLS - Dynamic Light Scattering – technique by means of a Zetasizer Nano instrument. The results for the 0.5% aqueous solutions of potassium lauroyl –glycyl glycinate (LGG-K) and triethanolamine lauroyl –glycyl glycinate (LGG-TEA) are shown in fig.3 and fig.4.

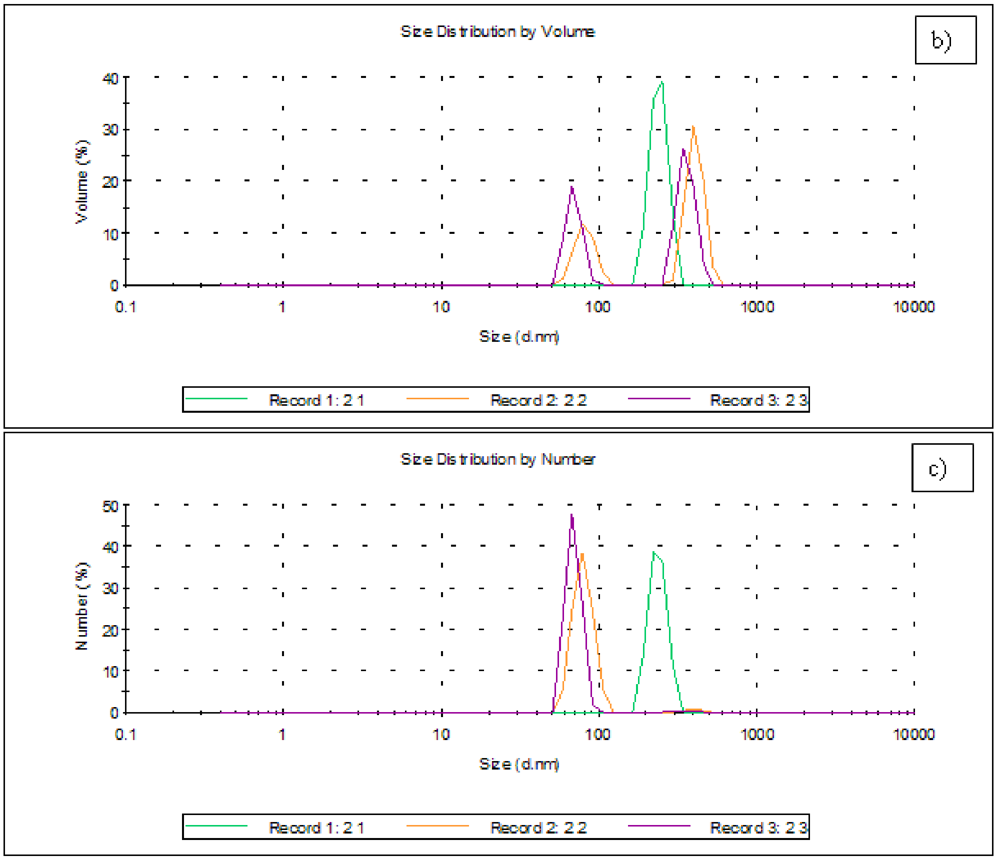

Fig. 3. Intensity (a), volumetric (b) and numeric (c) dimensional distribution of LGG-K particles with no software filtration

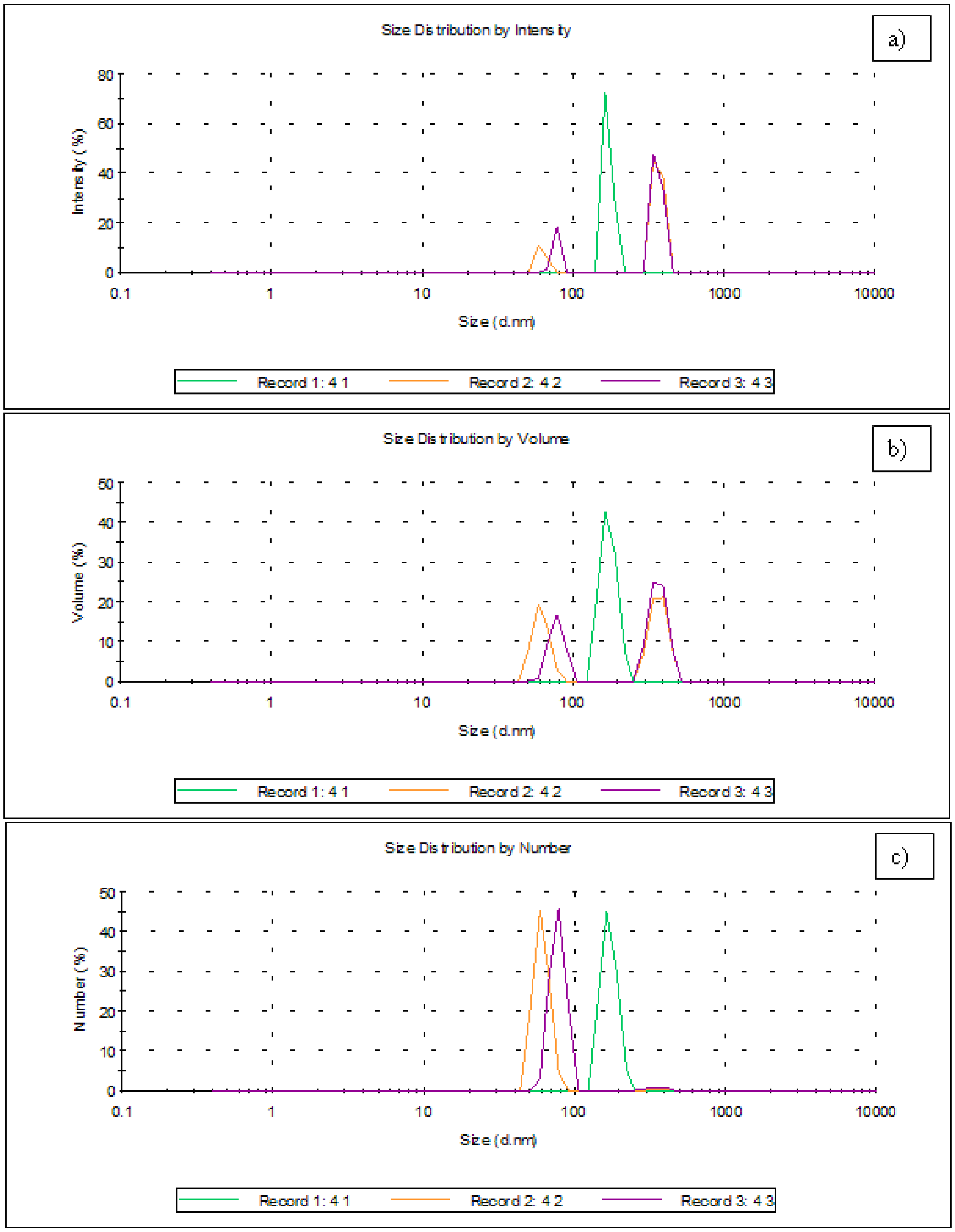

Fig. 4. Intensity (a), volumetric (b) and numeric (c) dimensional distribution of LGG-TEA particles with no software filtration

Two types of aggregates generations are noticeable: one below 100 nm and the other higher than 300 nm. By analyzing the three types of distribution (intensity, volumetric and numeric), it points out that the share of the two types of aggregates is rather equivalent. If it is considered that the average micelle dimension in a surfactant solution is of 50 nm, it can be assumed that the first generation of aggregates is formed by micelles of the potassium or triethanolamine lauroyl glycyl-glycinate, and the second generation is being formed by bigger aggregates (vesicles).

3. Conclusions

The tendency in surfactant industry is to use renewable raw materials instead of petrochemical products.

Two types of aminoacid based surfactants, lauroyl-glycine and lauroyl glycylglycine were synthesized and characterized. The sodium salts of these two surfactants have a good surface activity.

The pursued study emphasized that the potassium lauroyl glycyl-glycinate self-assemblies into micelles and also into bigger aggregates, with dimensions around 340 nm.

REFERENCES

[1] *MaRosa Infante, A. Pinazo, J. Seguer*, Colloids and Surfaces, A: Physicochemical and Engineering Aspects, **vol. 123-124**, 1997, pg.49-70

[2] *Krister Holmberg*, Novel Surfactants - Preparation, Applications, and Biodegradability, Marcel Dekker, New York, 2001

[3] *Jiding Xia*, Protein-Based Surfactants-Synthesis, Physicochemical Properties and Applications, Marcel Dekker, New York, 2003

[4] *M.C. Moran et al*, Green amino acid-based surfactants, Green Chem, **no.6,** 2004, pg.233-240

[5] C. *Boettcher*, B. *Schade, J.-H. Fuhrhop*, Comparative Cryo-Electron Microscopy of Noncovalent N-Dodecanoyl- (D- and L-) serine Assemblies in Vitreous Toluene and Water, Langmuir, **no.17**, 2001, pg. 873−877