



Original Contribution

BIO SURFACTANTS DERIVED FROM 4-AZASEBACIC ACID

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ABSTRACT

Most of ionic surfactants used for a long time have been alkyl and aryl-alkyl sodium sulphates and sulphonates, but these are hardly biologically decomposed. Recently, the strategy of surfactants manufacturing has moved beyond conventional conceptions of amphiphiles made from petroleum. The variety of available bio surfactants includes naturally occurring compounds such as: fatty acids, glycolipids, acyl peptides, phospholipids, proteins and liposaccharides. N-acyl and N-alkyl amino acids can be used as active surface agents, in detergents industry, but also in pharmaceutical industry and cosmetics.

In this paper there is presented the investigation of the most important surfactant properties of some N-acyl and N-alkyl derivatives of 4-azasebacic acid, using the surface tension method. These products have the properties of nonionic detergents and they do not react with hard water ion and foam less than ionic detergents. There were obtained formulations with high amphiphilic power, better than many commercial petrochemical surfactants, with a critical micelle concentration from 6.7 to 9.6 mmol/l, low surface tensions ranging from 21.5 to 30.6 mN/m and foam stability between 25-43% (after 2 h) respectively. Properties of these compounds are superior to fatty acids soaps and they are not toxic for the environmental and present low Kraft points.

Key Words: alkyl and aryl-alkyl sodium sulphates, sulphonates, active surface agents

INTRODUCTION

Most of ionic surfactants used for a long time have been alkyl and aryl-alkyl sodium sulphates and sulphonates, but these are hardly biologically decomposed. Recently, the strategy in surfactant manufacturing has moved beyond conventional conceptions of amphiphiles made from petroleum. The variety of available biosurfactants includes naturally occurring compounds such as fatty acids, glycolipids, acylpeptides, phospholipids, proteins, liposaccharides.

Products which possess a structure compared to that of fatty acids and their derivatives are biodegradable, non-toxic and non-allergenic. Development of novel amphiphiles from sustainable and renewable

materials also will contribute greatly to resource conservation.

Sodium salts of N-acyl aminoacids have been recognized for their surfactant properties. Their properties are also superior to soaps of fatty acids and they present low Kraft points because of peptidic bonds (– CO – NH –). [1], [2], [3].

A synthetic aminoacid with an amfion structure can be also considered

4-azasebacic acid, which is a hydrolysis degradation derivate of N-(β-cianoethyl)-ε-caprolactam. [4]

Generally, N-acylated aminoacids can be used as surfactants, but also they can be used in pharmaceutical and cosmetic industry. [8],[9] Both aminoacids and peptides derived from naturally raw materials can be used for the synthesis of reminded products. [10],[11],[12] Acylation at the nitrogen atom takes place with good yields, without catalysts. Classically N-acylation techniques, with strong alkaline bases solutions, present the great risk of

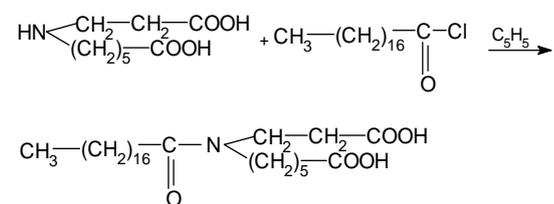
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secondary reactions. [7]

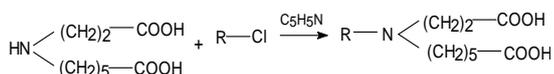
In this paper, there were used N-acylation and N-alkylation derivatives synthesized in presence of anhydrous pyridine; in this way, the secondary hydrolysis reactions were avoided and the yields of the main products obtaining are also greater than in case of traditional methods of N-acylation, in presence of alkaline bases.

EXPERIMENTAL

The synthesis of 4-azasebacic acid has been performed respecting the literature data for working procedure. [1] In our previous work, [13] there were presented comparatively N-acylation syntheses which use anhydrous pyridine and alkaline bases solutions, for some degradation products of N-β-cyanoethyl-ε-caprolactam.



(a)



R: C₁₄H₂₉, C₁₈H₃₇

(b)

Figure 1. N-acylation of 4-azasebacic acid (a)
N-alkylation of 4-azasebacic acid (b)

There have been investigated the most important surfactant properties of these N-acylated and N-alkylation products: surface tension, critical micelle concentration, foaming. Some of these compounds showed high surface activities, better than many commercial products belonging to the class of non ionic detergents.

Surface tensions were measured using a GBX-TEN 089 tensiometer equipped with a Wilhelmy plate.

Solutions of N-acyl and N-alkyl compounds (2.5 g/L) were dissolved in a 0.1

M sodium phosphate buffer solution at pH 7.0. This solution was added to 50 mL of the same phosphate buffer solution. Surface tension was continuously measured and recorded at 20°C until a constant surface tension value was observed. The CMC was obtained at the breaking point of the surface tension curve in relation to the logarithm of the mixture concentration.

Foaming properties were measured using the method described by Padmashree *et al.*: [14] 3 g of surfactants were mixed with 300 mL of water in a graduated 1-L cylinder. The solution was stirred at 1600 r/min. The volume and height of foam were measured 30 s, 1 min., 3 min., 10 min. and 20 min. after stirring. Variation of foam height versus time, at 20°C and 60°C is presented in figures 3,4. The foaming capacity (FC) can be expressed as the percentage of volume according to the following formula: [14]

$$\text{FC} = \left[\frac{\text{Volume after stirring} - \text{Volume before stirring}}{\text{Volume before stirring}} \right] \times 100 \quad (1)$$

The foam volume was recorded at 5, 30, 60 and 120 min after stirring. Foam stability (FS) values, presented in table 2, were calculated using the following formula: [14]

$$\text{FS} = \left(\frac{\text{Foam volume after a time "t"}}{\text{Initial foam volume}} \right) \times 100 \quad (2)$$

Surface tension

Surface tensions of N-acyl and N-alkyl compounds solutions decreased with increasing concentration and then reached clear break points, which were taken as the CMC. Figure 2 shows the relationship between the concentration and the surface tension for these compounds.

Discussion of CMC

A linear decrease in surface tension is observed when the concentration of the mixture is increased for all surfactants up to the CMC, beyond which there is no observable change in surface tension (Figure 2). This behaviour is common to surfactants in solution. Values for CMC and surface tensions at CMC are given in table 1.

The synthesized N-acylated and N-alkylated compounds have CMC comparable to commercial surfactants, ranging from 7.4-

8.8 mmol/l, with a low surface tension ranging from 27.8-28.9 mN/m. CMC are lower than those of many commercial surfactants, making them better detergents.

Discussion of foaming properties

Variation of foam height versus time is presented in figure 3. After N-acylation, these compounds have a foaming capacity comparable to that of commercial surfactants. A second parameter concerns foam stability

over time. Foams are unstable thermodynamic systems. Their stability and their breakdown depend on complex phenomena such as the hydrodynamic drainage of the liquid, the dilution of the aqueous film and the coalescence of bubbles. Table 2 shows the stability of foam formed over a period of time. The foaming stability (FS) of N-acylated and N-alkylated compounds ranges from 19 to 43%, after 2 h.

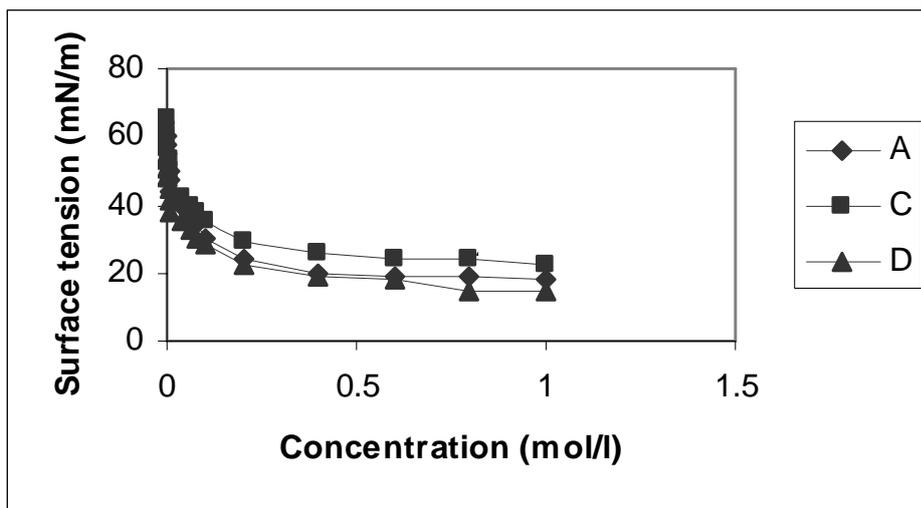


Figure 2. Variation of surface tension in function of concentration, for N-acyl and N-alkyl 4-azasebacic acid derivatives
 A: N- stearoyl 4-azasebacic acid
 C: N- cetyl- 4-azasebacic acid
 D: N- lauryl- 4-azasebacic acid

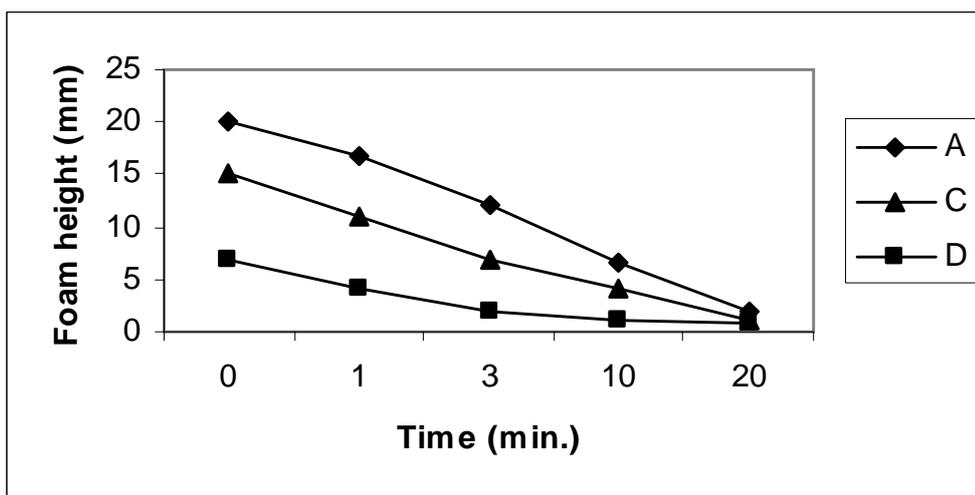


Figure 3. Variation of foam height in function of time, for N-acyl and N-alkyl 4-azasebacic acid derivatives
 A: N- stearoyl 4-azasebacic acid
 C: N- cetyl- 4-azasebacic acid
 D: N- lauryl- 4-azasebacic acid

Table 1. CMC and surface tensions at CMC (γ_{CMC}) for the tensioactive compounds studied

Compound	CMC, mol/l	Surface tension at CMC (γ_{CMC}), mN/m, t= 25°C
N- cetyl-4-azasebatic acid	$8.2 \cdot 10^{-3}$	27.8
N- lauryl-4-azasebatic acid	$7.4 \cdot 10^{-3}$	25.5
N- stearoyl 4-azasebatic acid	$8.8 \cdot 10^{-3}$	28.9

Table 2. Foam stability for the tensioactive compounds studied

Tested tensioactive compound	Foam stability			
	5 min.	30 min.	60 min.	120 min.
N- stearoyl 4-azasebatic acid	67	56	51	43
N- cetyl-4-azasebatic acid	51	42	37	28
N- lauryl-4-azasebatic acid	48	32	27	19

CONCLUSIONS

By N-acylation of some derivatives of 4-azasebatic acid, there were obtained compounds with remarkable surface properties.

There were obtained formulations with high amphiphilic power, better than many commercial petrochemical surfactants, with a critical micelle concentration from 6.7 to 9.6 mmol/l, low surface tensions ranging from 27.8 to 28.9 mN/m and foam stability between 19-43% (after 2 h) respectively.

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