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Synthesis and surfactant properties of N-acylation compounds derived from hydrolysis degradation products of N-(β-cianoethyl)-ε-caprolactam

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N-acyl amino acids can be used as active surface agents in the detergents industry, as well as in the pharmaceutical industry and cosmetics. Properties of these compounds are superior to those of fatty acids soaps and they are not toxic to the environment and have low Kraft points, because of peptide bonds (CO–NH). Acylation at the nitrogen atom can be performed with good yields without catalysts, for strong nucleophilic derivatives.

The synthesis of some derivatives of 4-azasebacic acid, which are hydrolysis degradation products from N-(β-cianoethyl)-ε-caprolactam, has been described and the N-acylation processes for these compounds are also presented. The obtained products have been characterized using various methods: IR, UV-VIS, ^{1}H-NMR, ^{13}C-NMR, elemental analysis, TLC, m.p. (Boethius), and in some cases refractive index. The most important surfactant properties of these N-acylated products were investigated using the surface tension method. The related thermodynamic parameters were also calculated.

Key Words: N-acylation, surfactants, 4-azasebacic acid, N-(β-cianoethyl)-ε-caprolactam, critical micelle concentration, surface tension, foaming

Introduction

Most of the ionic surfactants used for a long time have been alkyl and alkyl-aryl sodium sulfates and sulfonates, but these compounds are not easily biologically decomposed. Recently, the strategy of surfactants manufacturing has moved beyond conventional conceptions of amphiphiles made from petroleum.[1] The variety of available biosurfactants includes naturally occurring compounds such as fatty acids, glycolipids, acyl peptides, phospholipids, proteins, and liposaccharides.[2–4]

Zwitterionic surfactants have attracted the interest of researchers both in industrial applications and within academic fields, owing to their unique properties, such as excellent water solubility, insensitivity to the presence of salts, good biodegradability, biological safety—due to their mildness to the skin and eyes, high foam stability, and a synergistic effect with a wide variety of ionic and nonionic surfactants. Many zwitterionic surfactants have been synthesized and the increasing demand for this kind of surfactant has already enabled them to achieve well above average growth.[4,5] Alkylbetaines and their derivatives represent a class of zwitterionic surfactants with a positive charge on the nitrogen atom and a negative charge on the carboxyl group, which exists as electro-neutral internal salts within a wide pH range.[6–8]

Sodium salts of N-acyl amino acids 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 peptide bonds (−CO–NH−).[9]

4-Azasebacic acid is a synthetic amino acid with an amfion structure and it is a derivate of N-(β-cianoethyl)-ε-caprolactam.[10]

Generally, N-acylated amino acids can be used as surfactants, but also they can be used in the pharmaceutical and cosmetic industries.[8,11] Amino acids and peptides derived from naturally raw materials can be used for the synthesis of reminded products.

In our previous work,[12] the N-acylation processes of some degradation products of N-(β-cyanoethyl)-ε-caprolactam were reported by using anhydrous pyridine and alkaline bases solutions; the secondary hydrolysis reactions were avoided and the yields of the main products were greater for the processes in the presence of pyridine.

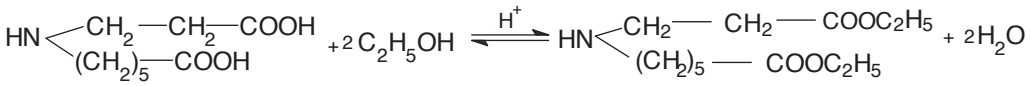
Acylation at the nitrogen atom takes place with good yields, without catalysts. Classically N-acylation techniques, with strong alkaline bases solutions, present the great risk of secondary reactions.[7,11,14,15]

In this paper the synthesis of some derivatives of 4-azasebacic acid and the N-acylation processes were described for these compounds. The resulting products have been characterized by various methods: FTIR, UV-VIS, ^{1}H-NMR, ^{13}C-NMR, elemental analysis, TLC, m.p. (Boethius). and in some cases refractive index measurements. Their surfactant properties such as surface tension, critical micelle concentration, and foaming were investigated and the related thermodynamic parameters were calculated. Some of these compounds showed high surface activities, better than those of many commercial products. The reaction schemes of the synthesized compounds are presented in Figure 1. N-acylated surfactants were prepared according to Figure 1.

Experimental

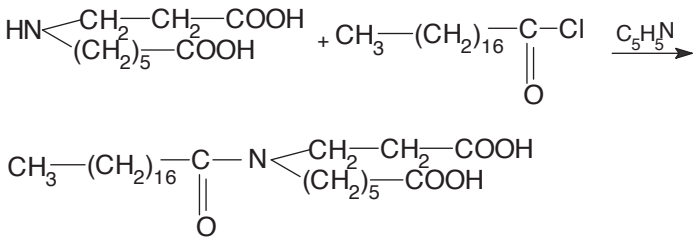
The synthesis of 4-azasebacic acid was performed as described in the literature.[13] This compound, which is a hydrolytic degradation derivative of N-(β-cianoethyl)-ε-caprolactam, was used as raw material for some N-acylation syntheses. All the other chemicals were reagent grade, purchased from Fluka and used without further purification.

Melting points of the obtained products were determined by using a Boetius apparatus KSP II Krüss Optronic.



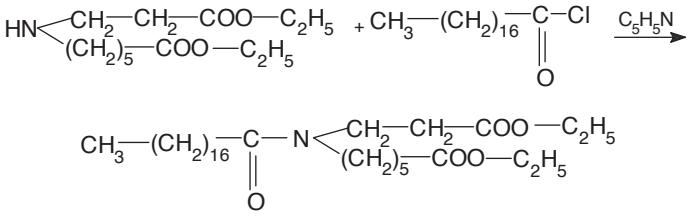
(1)

Diethyl 4 azasebacate



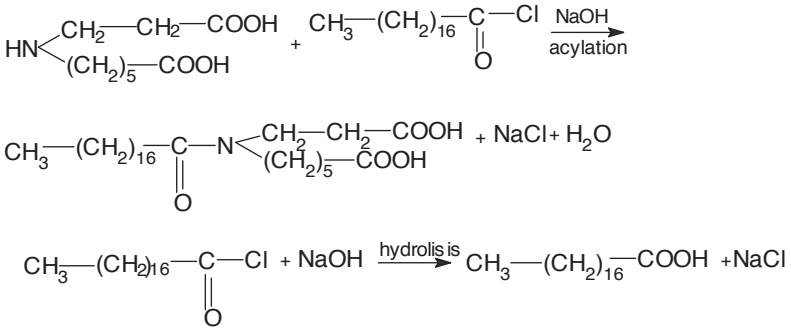
(2)

N-stearoyl 4-azasebacic acid



(3)

N- stearoyl-diethyl 4-azasebacate



Acylation of 4 azasebacic acid in the presence of NaOH 10% solution

Figure 1. The reaction schemes of the synthesized compounds.

Thin layer chromatograms were performed on Merck plates with silica gel, by using as solvent the mixture *sec*-BuOH: HCOOH: H_2O= 75:15:10, usually for 10 h; unitary spots were developed with a UV lamp (λ =254 nm and 365 nm).

Electronic spectra were obtained by using a UV-VIS JASCO-V550 spectrophotometer, with MgO as reference.

FT-IR spectra were recorded in the in domain 4000-400 cm^{-1}, by using a Varian Resolutions Pro 3100 spectrophotometer.

NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300 MHz (^{1}H-NMR) and 75 MHz (^{13}C-NMR), respectively, in $CDCl_3$ and DMSO-d_6, with tetramethylsilane (TMS) as the internal standard.

For elemental analysis a COSTECH ECS 4010 CHNSO analyzer was used.

Refraction index for esters was obtained with an ATAGO refractometer coupled with a digital thermometer.

Surface tension was measured using a GBX-TEN 089 tensiometer equipped with a Wilhelmy plate.

Synthesis of diethyl 4-azasebacate (1)

Gaseous hydrochloric acid was added to a mixture of 4-azasebacic acid (1 mmol) and absolute ethanol (2.5 mmol). This mixture was refluxed at 75 °C for 7 h. Non-reacted ethanol was removed from the reaction product by simple distillation. It was obtained in a yield of 95% to the ester. The purity of the product was verified by thin layer chromatography (TLC), obtaining a unitary spot at $R_f = 0.53$, which is different to the raw materials' values ($R_f = 0.37$ for 4-azasebacic acid and 0.44 for ethanol). The refractive index of the ester was $n_D^{20} = 1.3832$.

The structure of diethyl 4 –azasebacate was confirmed by FTIR, ^{1}H-NMR (see Figure 2), ^{13}C-NMR spectra, and elemental analysis.

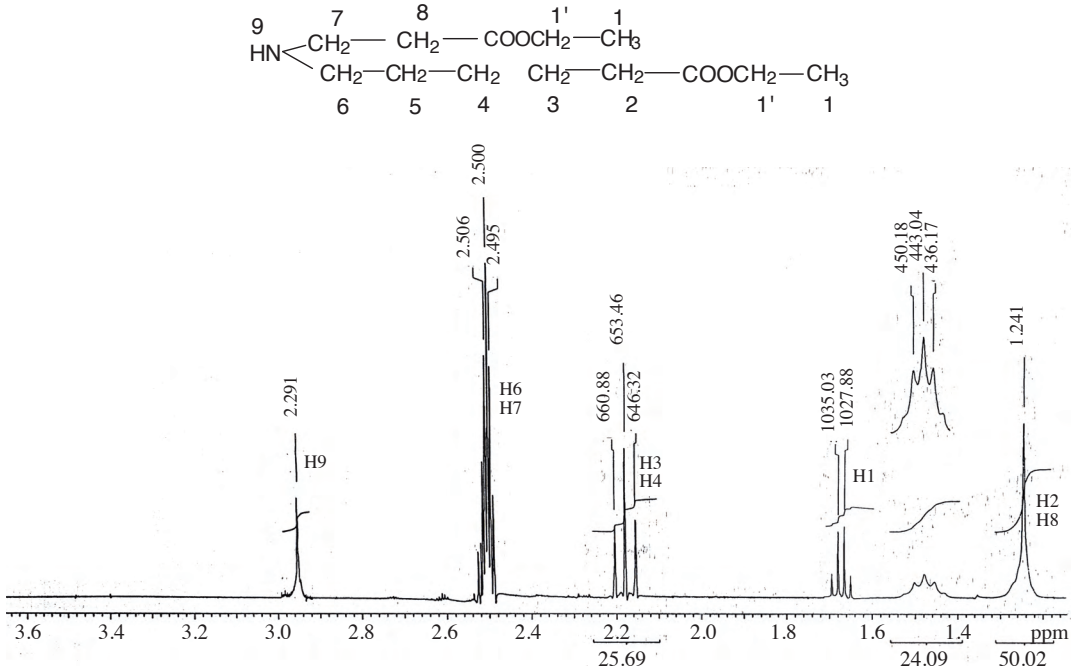


Figure 2. ^{1}H-NMR spectrum of diethyl 4 azasebacate.

IR: 3100-3000 (υ_{N-H}), 2962 and 2834 (υ_{CH3}, υ_{CH2}), 1739 ($\upsilon_{C=O}$), 1487 and 1504 (υ_{C-O}), and 800-770 cm^{-1} ($\delta_{(CH2)n}$).

^{1}**H-NMR:** δ = 1.24 ppm (t, 2H, N-CH_2-C$\underline{H}_2$-COOR, and N-$(CH_2)_4$-C$\underline{H}_2$-COOR), 1.45 (3H, C$\underline{H}_3$-CH_2), 1.671 (2H, CH_3-C$\underline{H}_2$), 2.21 (m, 2H, N-CH_2-CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2COOR), 2.52 (t, 2H, N-C$\underline{H}_2$-CH_2-COOR, and N- C$\underline{H}_2$-$(CH_2)_4$- COOR), 2.97 ppm (1H; H9, $\underline{H}$-N).

^{13}**C-NMR:** δ 13.63 ($\underline{C}H_3$-CH_2), 19.18 (CH_3-$\underline{C}H_2$), 32.61 (HN-CH_2-CH_2-$\underline{C}H_2$-$\underline{C}H_2$-CH_2), 41.68 (HN-CH_2-$\underline{C}H_2$-CH_2- CH_2-CH_2), 57.39 (HN-$\underline{C}H_2$-CH_2-CH_2-CH_2-CH_2), 52.54 (CH_2-$\underline{C}H_2$NH), 64.21 (HN-CH_2- CH_2- CH_2- CH_2-$\underline{C}H_2$), 77.11 ($\underline{C}H_2$-CH_2NH) and 172.8 ppm ($\underline{C}$OO).

UV-VIS: λ = 198 nm (n$\rightarrow \pi^*$ transition, due to the presence of carbonyl –C=O of the esteric group).

Elemental analysis: calc.: C 60.23%, H 9.65%, N 5.40%, O 24.71%; found:

C 59.88%, H 9.23%, N 5.71%, O 24.26%.

The N-acylation of 4-azasebacic acid – in the presence of pyridine (2)

Into a 50 mL round-bottom flask with a stirring bar were placed 4-azasebacic acid (1.2 mmol), stearoyl chloride (1 mmol), and anhydrous pyridine (5 mmol). The mixture was refluxed at 90 °C for 5 h. After cooling, the reaction mixture was treated with a solution of HCl (2N) to decrease the solution pH below pH 3. The precipitate was then filtered, dried, and purified by recrystallization from absolute ethanol. A white powder was obtained, with m.p. 84-85 C (Boetius) and a yield of 95%. TLC chromatogram of the N-acylation product showed a single spot, for R_f = 0.46. The reaction product is soluble in acetone, formic acid, ethanol, *sec* buthanol (by heating), and water (by heating).

IR: 2920 and 2851 (υ_{CH3}, υ_{CH2}), 1659 ($\upsilon_{C=O}$, amide band I), 1547 (υ_{C-O}, amide band II), 1298 (υ_{O-C-N}, amide band III) and 942-887 cm^{-1} ($\delta_{(CH2)n}$).

^{1}**H-NMR** δ (ppm): 0.85 (m, 3H,C$\underline{H}_3$-$(CH_2)_{16}$), 1.23 (m, 32 H, C$\underline{H}_2)_{16}$), 1.47 (2H, N-CH_2-C$\underline{H}_2$-COOH), 2.20 (m, 2H (N-CH_2-CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2)), 2.50 (m, 2H, N-CH_2-C$\underline{H}_2$-CH_2-CH_2-CH_2)), 3.35 (t, 2H, N-CH_2-CH_2-CH_2-CH_2-C$\underline{H}_2$), 4.57 (t, 2H, N-C$\underline{H}_2$-CH_2-CH_2-CH_2-CH_2), 7.53 (t, 2 H, N-C$\underline{H}_2$-CH_2), 12.07 (s, 1H, -COO$\underline{H}$)**;**

^{13}**C-NMR:** δ 13.88 ($\underline{C}H_3$-$(CH_2)_{16}$), 21.75 [($\underline{C}H_2)_{16}$], 31.24 (N-CH_2-$\underline{C}H_2$-CH_2- CH_2-CH_2), 33.64 (N-CH_2-CH_2-$\underline{C}H_2$-$\underline{C}H_2$-CH_2), 43.36 (HN-CH_2-CH_2- CH_2-CH_2-$\underline{C}H_2$), 47.39 (N-$\underline{C}H_2$-CH_2-CH_2-CH_2-CH_2), 63.35 ($\underline{C}H_2$-CH_2N), 49.04 (CH_2-$\underline{C}H_2$N), 128.7 ppm (N-$\underline{C}$O), 175.3 $(CH_2)_2\underline{C}$OOH), 183.4 $(CH_2)_5\underline{C}$OOH).

UV-VIS: λ = 232 nm (n$\rightarrow \pi^*$ transition, due to the presence of the amide carbonyl group –C=O).

Elemental analysis: calc.: C 68.27%, H 11.15%, N 3.06%, O 17.50%; found:

C 69.07%, H 11.53%, N 3.27%, O 17.59%.

The N-acylation of 4-azasebacic acid – in the presence of NaOH 10%

Into a 50 mL round-bottom flask with a stirring bar were placed 4-azasebacic acid (1.2 mmol) and stearoyl chloride (1 mmol); 10 mL of NaOH solution (10%) was added.

This mixture was refluxed at 45 °C for 6 h, at constant stirring. After cooling, the reaction mixture was treated with a solution of HCl (2N) to decrease the solution pH below 3. The precipitate was then filtered, dried, and purified by recrystallization from amyl alcohol to remove traces of fatty acid formed by the secondary

reaction of hydrolysis. A white powder was obtained, with m.p. 75-76 °C (Boetius) and a yield of 78%. TLC chromatogram of the N-acylation product showed one spot, for $R_f = 0.48$. The reaction product is soluble in acetone, formic acid, ethanol, *sec* buthanol (by heating), and water (by heating).

IR: 2950 and 2845 (υ_{CH3}, υ_{CH2}), 1675 ($\upsilon_{C=O}$, amide band I), 1564 (υ_{C-O}, amide band II), 1292 (υ_{O-C-N}, amide band III), and 948-892 cm^{-1} ($\delta_{(CH2)n}$).

^{1}**H-NMR (see Figure 3)**: δ 0.83 (m, 3H,C$\underline{H}_3$-$(CH_2)_{16}$), 1.25 (m, 32 H, C$\underline{H}_2)_{16}$), 2.26 (t,2H,C$\underline{H}_2$-CH_2N), 2.43 (t, 2H, CH_2-C$\underline{H}_2$N), 2.63 (m, N-CH_2-CH_2-CH_2-C$\underline{H}_2$-CH_2), 2.88 (m, N-CH_2-CH_2-C$\underline{H}_2$-CH_2-CH_2), 3.40 (m,2H, N-CH_2-C$\underline{H}_2$-CH_2- CH_2-CH_2), 3.18 (t, 2H, N-CH_2-CH_2-CH_2-CH_2-C$\underline{H}_2$) and 10.18 ppm (-COO$\underline{H}$).

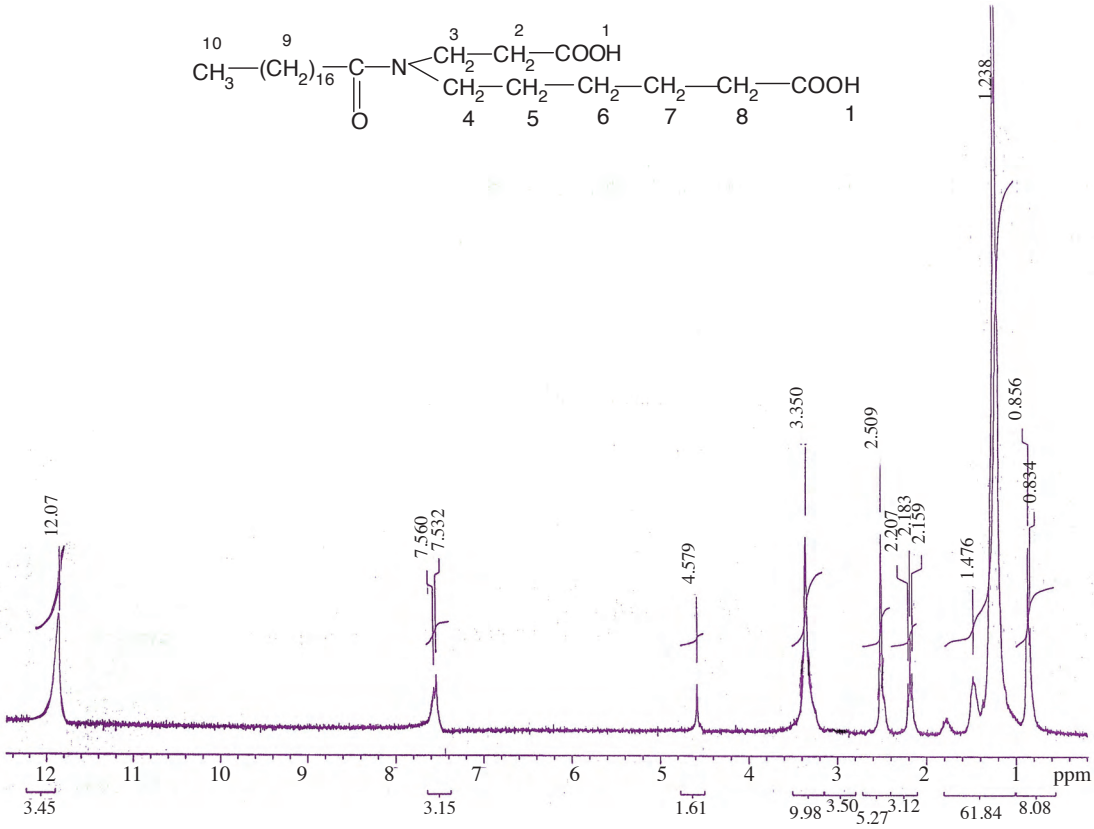


Figure 3. ^{1}H-NMR spectrum of N-stearoyl 4 azasebacic acid.

^{13}**C-NMR**: δ 13.88 ($\underline{C}H_3$-$(CH_2)_{16}$), 21.84 [($\underline{C}H_2)_{16}$], 30.59 (N-CH_2-$\underline{C}H_2$-CH_2-CH_2-CH_2), 32.32 (N-CH_2-CH_2-$\underline{C}H_2$- $\underline{C}H_2$-CH_2), 41.34 (N-CH_2-CH_2-CH_2-$\underline{C}H_2$-CH_2), 46.35 (N-$\underline{C}H_2$-CH_2-CH_2-CH_2-CH_2), 49.88 (CH_2-$\underline{C}H_2$N), 64.05 ($\underline{C}H_2$-CH_2N), 127.37 ppm (N-$\underline{C}$O), 166.8 (($CH_2)_2\underline{C}$OOH), 179.8 (($CH_2)_5\underline{C}$OOH).

UV-VIS: λ = 238 nm (n$\rightarrow \pi^*$ transition, due to the presence of the amide carbonyl group –C=O).

Elemental analysis: calc.: C 68.27%, H 11.15%, N 3.06%, O 17.50%; found:

C 69.13%, H 11.67%, N 3.18%, O 17.86%.

The synthesis of N-stearoyl diethyl-4-azasebacate (3)

Into a 50 mL round-bottom flask with a stirring bar were placed diethyl 4-azasebacate (1 mmol), stearoyl chloride (1 mmol), and anhydrous pyridine (5 mmol). The mixture was refluxed at 90 °C for 5-6 h, at constant stirring. After cooling, the reaction mixture was treated with a solution of HCl (2N) to get a pH < 3. The precipitate was then filtered, dried, and purified by recrystallization from absolute ethanol. The resulting product was obtained in a white powder form with the m.p. to be 78-79 °C and with the yield of 88%. TLC chromatogram of the N-acylation product showed a single spot for $R_f = 0.74$. The reaction product is very soluble in acetone, ethanol, and in water only by heating.

IR: 2914 and 2848 (υ_{CH3}, $\upsilon_{CH2)}$), 1652 and 1738 ($\upsilon_{C=O}$, amide band I and $\upsilon_{C=O}$ esteric), 1550 (υ_{C-O}, amide band II), 1320 (υ_{O-C-N}, amide band III), and 895-759 cm^{-1} ($\delta_{(CH2)n}$).

^{1}**H-NMR (see Figure 4):** δ (ppm): 0.93 (m, 3H,C$\underline{H}_3$-$(CH_2)_{16}$), 1.01 (t, 2H, N-CH_2-C$\underline{H}_2$-COOR and N-$(CH_2)_4$-C$\underline{H}_2$-COOR), 1.23 (m, 32 H, C$\underline{H}_2)_{16}$), 1.63 (q, 2H,CH_3-C$\underline{H}_2$), 2.27 (m, 2H, N-CH_2-CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2COOR), 2.32 (t, 2H, N-C$\underline{H}_2$-CH_2-COOR), 4.10 (m, 2H, N- C$\underline{H}_2$-$(CH_2)_4$- COOR);

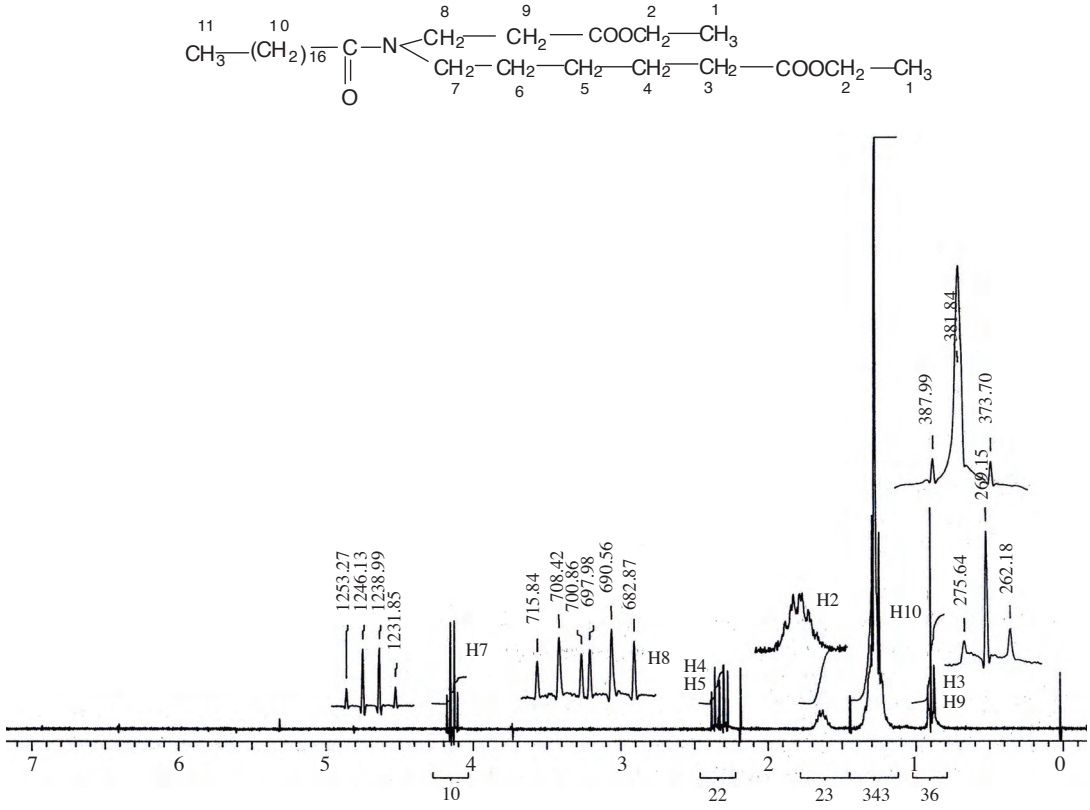


Figure 4. ^{1}H-NMR spectrum of N-stearoyl diethyl 4 azasebacate.

^{13}**C-NMR**: δ 14.57 ($\underline{C}H_3$-CH_2), 19.68 (CH_3-$\underline{C}H_2$), 21.85 ($\underline{C}H_3$-$CH_2)_{16}$), 25.76 [$(\underline{C}H_2)_{16}$], 28.66 (N-CH_2-$\underline{C}H_2$-CH_2-CH_2-CH_2), 33.69 (N-CH_2-CH_2-$\underline{C}H_2$- $\underline{C}H_2$-CH_2), 36.22 ($\underline{C}H_2$-CH_2N), 41.34 (N-CH_2-CH_2-CH_2-CH_2-$\underline{C}H_2$), 46.35 (CH_2-$\underline{C}H_2$N), 49.74 (N-$\underline{C}H_2$-CH_2-CH_2-CH_2-CH_2), 168.7 ppm (N-$\underline{C}$O).

UV-VIS: $\lambda = 230$ nm (n$\rightarrow \pi^*$ transition, due to the presence of the carbonyl amide group –C=O).

Elemental analysis: calc.: C 69.90%, H 11.84%, N 2.71%, O 15.53%; found: C 69.77%, H 11.72%, N 2.59%, O 15.60%.

Surface active behaviors

Solutions of *N*-acyl compounds (2.5 g/L) were dissolved in a sodium phosphate buffer solution (0.1 M) at pH 7.0. This solution was added into 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 by using the method described by Padmashree et al.:[17] 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 the foam height with time, at 20° nd 60 °C is presented in Figures 5 and 6. The foaming capacity (FC) can be expressed as the percentage of volume according to the following formula: [17]

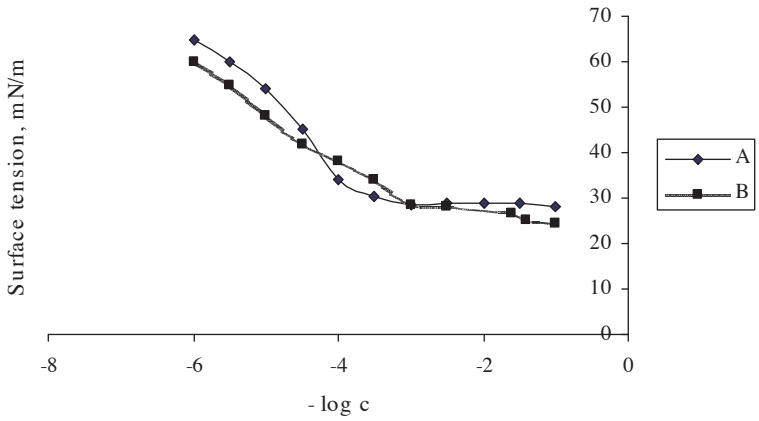


Figure 5. Variation in surface tension with the concentration for *N*−stearoyl 4- azasebacic acid, synthesized in the presence of NaOH 10% (A) and *N*−stearoyl 4-azasebacic acid, synthesized in the presence of pyridine (B).

$$\text{FC} = [(\text{Volume after stirring} - \text{Volume before stirring})/\ \text{Volume before stirring}] \times 100$$

The foam volume was recorded at 5, 30, 60 and 120 min after stirring. Foam stability (FS) values, presented in Table 2, were calculated by using the following formula:[17]

$$\text{FS} = (\text{Foam volume after a time "t"}/\ \text{Initial foam volume}) \times 100$$

Results and discussion

Spectral analysis

The FTIR spectrum of diethyl 4-azasebacate presented important signals of the –N–H group at 2372 cm^{-1} and the signal at 1738 cm^{-1} is characteristic of the – C=O group of dicarboxylic esters (the force constant of the

carbonyl bond is increased by the electron-attracting nature of the adjacent oxygen atom); signals at 1087 and 1044 cm^{-1} correspond to the –C–O– group of esters.[6]

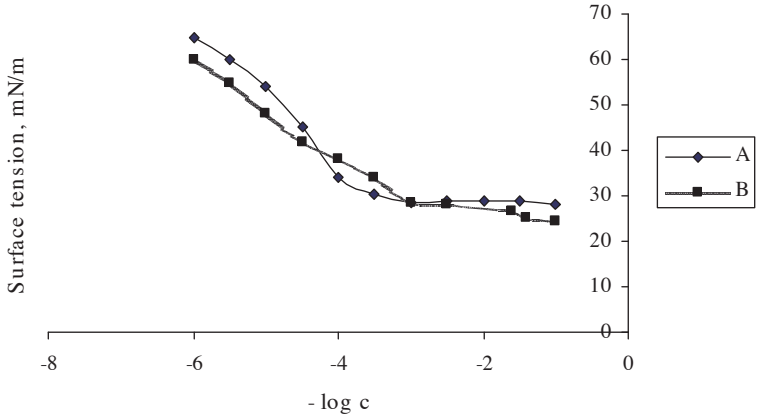


Figure 6. Variation in surface tension with the concentration of $N-$stearoyl 4 azasebacate, synthesized in the presence of pyridine (C).

For the compounds synthesized by N-acylation, there were characteristic bands of amides: a sharp band at 1652-1675 cm^{-1} of the group –C=O ("amide band I"), at 1564-1550 cm^{-1}– "amide band II"; at 1298-1360 cm^{-1} there appeared vibrations of O–C–N, as weak bands of "amide band III". The absorption band of carbonyl amide group –C=O occurs at lower frequencies than normal carbonyl absorption due to the resonance effect.[6] After N-acylation, the bands corresponding to the carbonyl group of 4-azasebacate (at 1738 cm^{-1}) and stearoyl chloride (1780 cm^{-1}) disappeared and an intense absorption band at 1652-1675 cm^{-1} corresponding to the carbonyl stretching of amide band I was observed.

UV-VIS analysis of diethyl 4-azasebacate and of its N-acylation derivatives showed an intense band at 198 nm assigned to the carbonyl esteric group –C=O and medium signals at 230-232 nm, characteristic of the amide carbonyl group.[6,13]

NMR spectra of N-acylation compounds confirmed the structure as the assignments shown in Figures 3 and 4. The ^{1}H-NMR spectrum of diethyl 4-azasebacate presented a broad specific signal of the proton on nitrogen, because the electrical quadrupole moment of the nitrogen nucleus induces a moderately efficient spin relaxation.[6] In this case, coupling of the N<u>H</u> proton to the adjacent protons was observed. Coupling between H-N-C-H takes place through the bonds C-H, C-N, N-H, but coupling between nitrogen and protons on the adjacent carbon is negligible. The position of the specific band at $\approx$ 3 ppm also depends on solvent type and its concentration.

At the frequency of 300 MHz some methylene groups are overlapped, as in case of protons of groups N-CH_2-CH_2-C<u>**H**</u>$_2$-C<u>**H**</u>$_2$-CH_2; they are strongly coupled and they action as a conglomerate of spins.

Methylene protons linked to the carboxylate group –COO are deshielded for the

N-acylation derivatives of diethyl-4-azasebacate. For the N-acylation derivatives, the signal of the –N**H** proton at 2.97 ppm disappeared, because of the amidation process.

Surface tension

Surface tensions of the tested $N-$acylated compounds solutions decreased with the increase in concentration and then they reached clear break points, which were taken as the CMC. Figures 5 and 6 present the relationship between the concentration logarithm 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 (Figures 5 and 6). This behavior is common to all surfactants in solution. The values of CMC and surface tensions at CMC are given in Table 1.

Table 1. Values for CMCs and surface tensions at CMC (γ_{CMC}).

Tested tensioactive compound	CMC, mol/L	ST at CMC (γ_{CMC}), mN/m at 25^{circ}C
$N-$stearoyl 4-azasebacic acid [synthesized in the presence of NaOH (10%)]	9.6×10^{-3}	30.6
$N-$stearoyl 4-azasebacic acid (synthesized in the presence of pyridine)	8.8×10^{-3}	28.8
$N-$stearoyl 4-azasebacate (synthesized in the presence of pyridine)	6.7×10^{-3}	21.5

The N-acylated compounds presented CMC comparable to commercial surfactants, ranging from 6.7 to 9.6 mmol/L, with a low surface tension ranging from 21.5 to 30.6 mN/m. CMCs are lower than those of many commercial surfactants, making them better detergents.

Discussion of foaming properties

The variation in foam height with time is presented in Figures 7 and 8. After

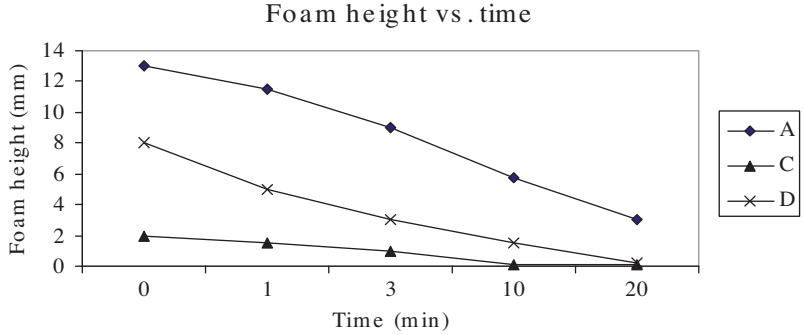


Figure 7. Variation in foam height (mm) with time (min.) for the N-acylated compounds, at 20 $^{\circ}$C, (A) $N-$stearoyl 4-azasebacic acid (synthesized in the presence of NaOH 10%), (C) $N-$stearoyl 4-azasebacic acid (synthesized in the presence of pyridine), (D) $N-$stearoyl 4-azasebacate (synthesized in the presence of pyridine).

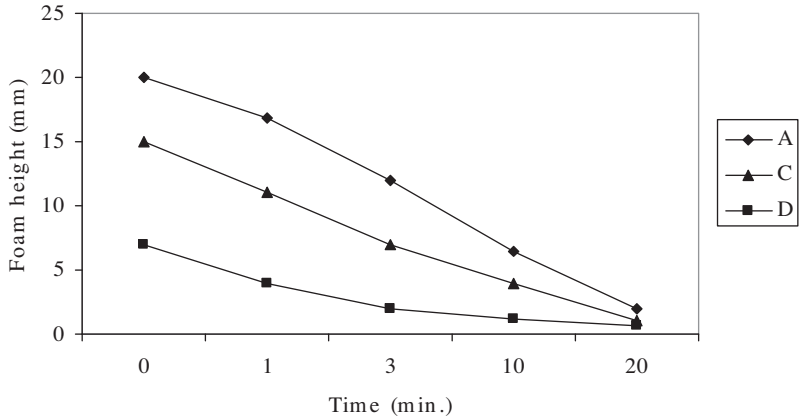


Figure 8. Variation in foam height with time for the N-acylated compounds at 60 $^{\circ}$C (A) $N-$stearoyl 4-azasebacic acid (synthesized in the presence of NaOH 10%), (C) $N-$stearoyl 4-azasebacic acid (synthesized in the presence of pyridine), (D) $N-$stearoyl 4-azasebacate (synthesized in the presence of pyridine).

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 breakdown depend on complex phenomena such as the hydrodynamic drainage of the liquid, the dilution of the aqueous film and the coalescence of bubbles.[15,17] Table 2 shows the stability of foam formed over a period of time. The foaming stability (FS) of the

Table 2. Foam stability for the surface active compounds.

Compound	Foam stability (FS%)			
	5 min	30 min	60 min	120 min
$N-$stearoyl 4-azasebacic acid (synthesized in the presence of NaOH 10%)	67	56	51	45
Nstearoyl 4-azasebacic acid (synthesized in the presence of pyridine)	55	42	37	30
$N-$stearoyl 4-azasebacate (synthesized in the presence of pyridine)	51	36	32	25

N-acylated compounds ranges from 30% to 45% after 2 h.

The maximum surface excess, the area per molecule, and the standard free energy of micelization in aqueous solution were calculated by the Gibbs adsorption equation, using CMC and (γ_{CMC}):[1]

$$\Gamma_{\max} = -1/2.303nRT(d\gamma/dlogC)T \tag{1}$$

$$A_m = (\Gamma_{\max} N_a)^{-1} \tag{2}$$

$$\Delta G^{\circ}_{min} = nRTln(QC_{CMC}) \tag{3}$$

where R is the gas constant, N_a is the Avogadro number, Q is the stoichiometric parameter, $\Gamma_{\max}$ is the maximum surface excess, and A_m is the area per molecule. The calculated results are presented in Table 3.

The values of these parameters demonstrated that zwitterionic surfactants have a formally net charge and they lead to smaller intermolecular repulsions, and thus a more closely adsorption layer at the aqueous-air interface is formed. These compounds tend to form micelles at lower concentrations than ionic surfactants, this being observed by the decreasing of $\Delta G^{\circ}{}_{min}$.

Table 3. Some thermodynamic parameters for compounds tested as surfactants.

Compound	$10^6\Gamma_{max}$ (mol m^{-2})	$10^{20}A_{min}$ (m^2)	$\Delta G^{\circ}{}_{min}$ (kJ mol^{-1})
N−stearoyl 4-azasebacic acid (synthesized in the presence of NaOH 10%)	3.4	52	-24
N−stearoyl 4-azasebacic acid (synthesized in the presence of pyridine)	3.2	54	-26
N−stearoyl 4-azasebacate (synthesized in the presence of pyridine)	2.8	65	-29

Conclusions

The preparation, characterization, and application of some N-acylation derivatives of 4-azasebacic acid have been described. The resulting compounds have been characterized by using IR, UV-VIS, ^{1}H-NMR, and ^{13}C-NMR instrumental analysis methods, elemental analysis, surface tension, TLC, m.p., and refractive index measurements. Some thermodynamic parameters were also calculated. The obtained formulations with high amphiphilic power were better than many commercial petrochemical surfactants, with a critical micelle concentration from 6.7 to 9.6 mmol/L and low surface tensions ranging from 21.5 to 30.6 mN/m and foam stability between 25% and 45% (after 2 h), respectively. The resultant surface active materials are interesting materials for further studies and applications.

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References

1. Liyun, Q.; Yun, F.; Zeyun, W.; Liangyu, J.; Yiyou, W. J. *Surf. Deterg.* **2008,** *11*, 55-59.
2. Bondarev A., Cuiban F., Mihai S., Pântea O., Trîmbitaşu E. *N-acylation of some hydrolysis degradation products of N-(β-cianoethyl)-ε-caprolactam*, Sixth National Conference on Chemistry 16th National Symposium 'Polymers 2008', Sofia, Bulgaria**,** 10-14 September 2008.
3. Fisher, G. H.; *Amino Acids* **2007***, 32*, 1-6.
4. Sánchez, L.; Mitjans, M.; Infante, M. R.; Garcíý, M.; Manresa, M. A.; Vinardell, P. *Amino Acids* **2007**, *32*, 133-136.
5. Nishimura, K.; Tomoda, Y.; Nakamoto, Y.; Kawada, T.; Ishii, Y.; Nagata, Y. *Amino Acids* **2007**, *32*, 59-62.

6. Silverstein, R. M.; Webster F.; Kiemle D. *Spectrometric Identification of Organic Compounds,* John Wiley & Sons, Inc., 2005.
7. Franses, E. I.; Prosser, A. J.; Infante, M.; Perez, L.; Pinazo, A.; *Surfactant Science Series*, **2004**, *117*, 65-92.
8. Laschewski, A.;*enside Surfactants Detergents* **2003**, *40*, 246-249.
9. Popescu, G.; Albu, B.; Nuta, D.; Rata, D.; Aldea, E.; Dinescu, G.; Olteanu, M.; *Bucharest University Bulletin – Chemistry* **2003**, *I-II*, 49 -53.
10. Varade, D.; Mody, S.; Ankleshwaria, H.; Bahadur, P.;*enside Surfactants Detergents* **2003**, *40*, 46-51.
11. Zana, R.;*olloid and Interface Science* **2002**, *97*, 203-205.
12. Greksdova, O.; Oremnsova, J.;*enside Surfactants Detergents* **2002**, *39*, 40-47.
13. Cuiban, F.; Bolocan, I.; Barbu, E.;*rkivoc* **2001**, *N-Substituted derivatives of ε - caprolactam and their thermal and chemical behavior*, In memoriam C.D. Nenitzescu on the occasion of his 100th birthday.
14. Holmberg, K.; *Colloid and Interface Science* **2001**, *6*, 148-151.
15. Berna, J. L.; Battersby, N.; Cavalli, L.; Fletcher, R.; Guldner, A.; Schowanek, D.; Steber, J.;*enside Surfactants Detergents* **2001,** *38*, 86-93.
16. Beller, M.; Eckert, M.; *Angewandte Chemie International Edition* **2000**, *6,* 1010-1027.
17. Padmashree, T. S.; Vijayalakshmi, L; Puttaraj, S. J. *Food Sci. Technol.* **1987**, *24*, 221-225.