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Abstract. The development of green surfactants produced from renewable raw materials at the expense of petrochemical-based surfactants took into account the increasing requirements for environmental protection and the demand of the society for sustainable development. A variety of renewable raw materials such as triglycerides, carbohydrates or amino acids are used in green surfactant synthesis. The natural structure of green surfactants induces low toxicity and high biodegradability. In this work was investigated the behaviour of surfactant systems containing synthesized amino acid-based surfactants (sodium lauroy lglycinate and sodium lauroyl sarcosinate) and amphoteric or nonionic surfactants, highlighting the differences between surfactant systems containing sodium lauroyl glycinate or sodium lauroyl sarcosinate due to nitrogen methylation of the amide nitrogen in the latter. Synergetic behaviour of aqueous surfactant systems were found, leading to improved properties in terms of surface tension and foaming power.

1. Introduction

The multitude of practical applications of surfactants, from household to industrial or special applications, is based on their ability to modify the interfacial and superficial properties of the liquids in which they dissolve. Domestic use of detergents and personal care applications are the largest market segments of surfactants, followed by numerous applications in textile industry, industrial and institutional cleaning, elastomers and plastics, oilfield chemicals, crop protection and food and beverage industry. Despite their numerous benefits, surfactants can affect the environment and human health. Hence, government regulations imposed the shift toward the green surfactants produced from renewable raw materials to the detriment of petrochemical-based surfactants. The transition is slow and is due to the low prices and high performance of synthetic surfactants, compared to more expensive syntheses of green surfactants. Nevertheless, the high biodegradability and low toxicity of modern surfactants together with the effort of scientific community to develop greener routes to create these surfactants are milestones to a future development of green surfactants [1-5].

Both synthetic and green surfactants are used in different products to impart properties such as wetting, emulsification, detergency, solubilisation, dispersion. Amino acid-based surfactants, including N-acyl amino acids are classified as green surfactants, since the hydrophilic group consists of naturally occurring amino acids or protein hydrolysates and the lipophilic tail may originate from vegetable or animal sources [6, 7].

Studies on interactions between sulphate or sulphonate anionic surfactants and amphoteric/nonionic surfactants have highlighted the enhancement of the properties of individual surfactants [8-10], while

studies carried out with mixed surfactant systems containing amino acid based surfactants are few and the investigation of surface properties of such systems is of great interest, due to the above mentioned qualities of green surfactants. In this work was investigated the synergistic effects of adding amphoteric or nonionic surfactants to sodium lauroyl glycinate (NaLGly) and sodium lauroyl sarcosinate (NaLSar) in terms of surface properties.

2. Materials and methods

2.1. Materials
For determination of performance of individual surfactants and their mixtures the following surfactants were used:

Sodium lauroylsarcosinate (NaLSar) from Merck, active matter 95%, molecular weight 293.40.

Sodium lauroylglycinate (NaLGly) prepared by acylation of glycine with lauroyl chloride [11], active matter 94%, molecular weight 279.35.

Lauryl dimethyl amine oxide (AO) from Enaspol, R = C_{12}-C_{14} (even numbered), 30% active matter, molecular weight 229.40.

Cocamidopropylbetaine (CAPB) from Enaspol, 30% active matter, molecular weight 342.52.

Experiments were performed for individual surfactants (NALSar, NaLGly, AO, CAPB) and for mixed surfactant systems NALSar+AO, NALSar +CAPB, NALGly+AO 3:1, NALGly +CAPB with mass ratio 3:1. The surfactant solutions were prepared in distilled water. For viscosity determination the total surfactants concentration for the tested solutions was 10%. More diluted solutions were used for CMC determination (0.5%-5%) and for determination of foaming power the total surfactants concentration for the tested solutions was 0.05%.

2.2. Methods
2.2.1. Surface tension measurements. Surface tension measurements were performed on a KSV tensiometer Sigma 700 model, using the Du Nouy ring method. Aliquots of surfactant stock solution were added in a measured volume (40 mL) by means of an automatic dispenser. The solution was stirred and the surface tension was measured after an equilibration time. Surface tension versus logarithmic surfactant concentration was plotted and the critical micelle concentration (CMC) value was determined by the intersection of baseline with slope.

2.2.2. Measurement of foaming power. For the surfactant solutions used in the study foaming power was evaluated using Ross Miles method. 500 ml of a surfactant solution is allowed to flow into a 1000 mL cylinder from a height of 450 mm onto the surface of 50 ml of the same solution. The volume of foam formed is measured.

2.2.3. Measurement of viscosity. Viscosity of surfactant solutions was determined with a Brookfield viscosimeter. A beaker containing 200 ml sample is placed under the viscometer. A spindle is immersed into the solution up to an immersion mark on the spindle shaft. The spindle type and the speed of rotation are chosen so to give a reading toward full scale.

3. Results and discussions

3.1. Evaluation of surface properties
The studies regarding the surface properties of surfactant mixtures of amino acid-based surfactants with amphoteric or nonionic surfactants were aimed to achieve synergistic effects that allow us to use in an efficient way the amino acid-based surfactants in high foaming and sulphate free formulations. The surfactants used in this study are presented in Figure 1.

Lauryl dimethyl amine oxide (AO) is a versatile surfactant which acts as nonionic surfactant in neutral or alkaline medium, such as that existing in the solutions of anionic surfactants. Cocamidopropyl betaine is a mild amphoteric surfactant which has a negative charge in alkaline products and a positive charge in acidic products.
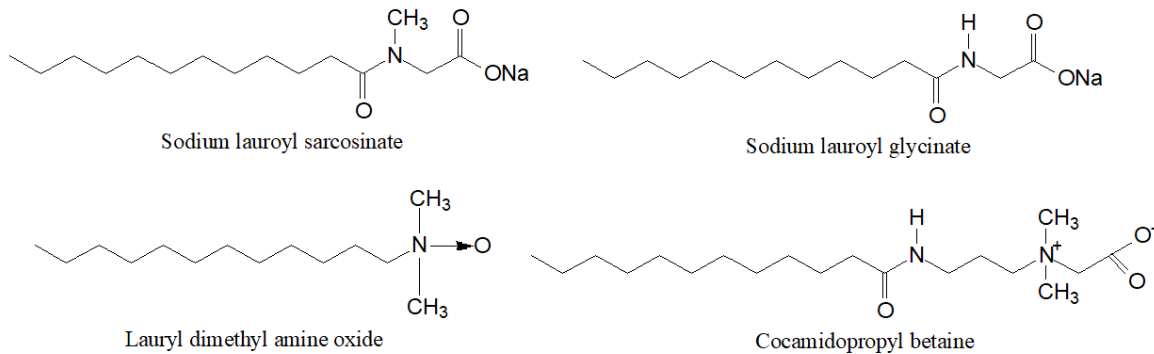
Figure 1. Structure of surfactants.

The surface tension versus surfactant concentration plots for individual and mixed surfactant systems at 298K are shown in Figure 2 and 3.
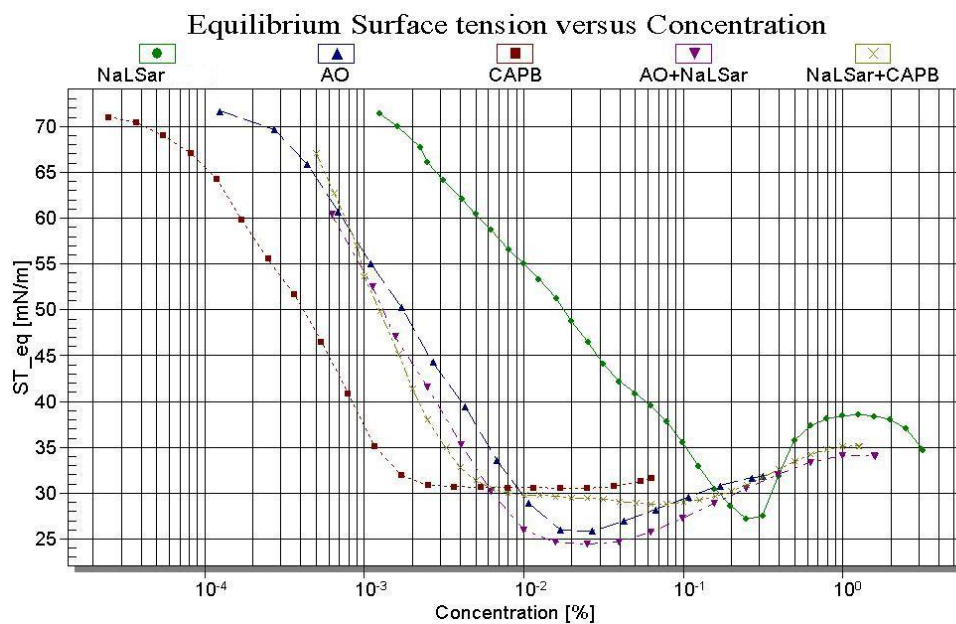

Figure 2. Variation of surface tension with concentration for individual surfactants and mixed surfactant systems containing sodium lauroyl sarcosinate.

The data provided by the determination of CMC enable us to calculate some other surface active parameters such as surface excess concentration Γ_{max}, minimum area per molecule A_{min} and efficiency π [12, 13].

In surfactant solutions the concentration of solute at the air-liquid interface is higher than that in the volume of the solution. This difference of concentration at air liquid interface, the surface excess concentration surface excess concentration Γ_{max} can be calculated using Gibbs adsorption equation:

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{d\gamma}{d\log c}\right) \tag{1}$$

where R is gas constant (8.314×107 ergs mol^{-1} K^{-1}), $d\gamma/dlogc$ is the surface activity indicating the ability of the substance to decrease the surface free energy, actually the slope of the concentration-dependent region from CMC determination, T is temperature in K and n is number of particle furnished by each molecule of the surfactant in solution (for anionic surfactants in which the cation accumulates at the interface, making ion pair with the anionic group, n=2).
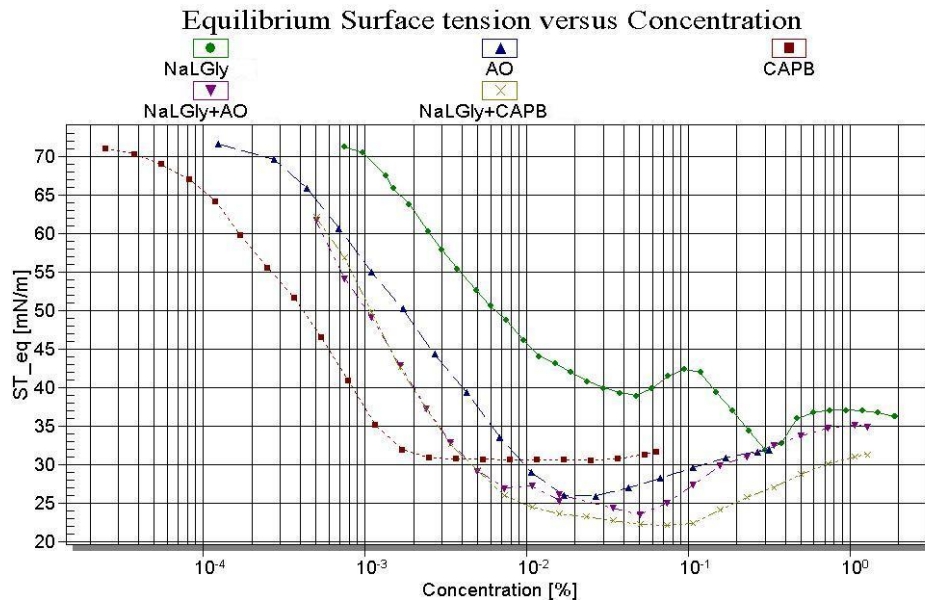

Figure 3. Variation of surface tension with concentration for individual surfactants and mixed surfactant systems containing sodium lauroyl glycinate.

The area per molecule at the air-liquid interface provides the information on the degree of packing of the adsorbed surfactant molecule. For the surface excess concentration, the minimum area per molecule A_{min} can be calculated with the relation:

$$A_{min} = \frac{1}{N\Gamma_{max}}$$

(2)

where N is Avogadro's number.

Efficiency π of a surfactant is given by the difference between the surface tension γ_0 of distilled water (71 mN/m) and surface tension γ at CMC.

$$\pi = \gamma_0 - \gamma$$

(3)

The amino acid-based surfactants included in the study, sodium lauroyl sarcosinate (NaLSar) and sodium lauroyl glycinate (NaLGly) are almost identical anionic surfactants with an amide bond between the hydrophobic tail and the polar headgroup. The difference is that the amide nitrogen in sodium lauroyl sarcosinate is methylated. Intermolecular hydrogen bonding interactions between headgroups can occur only in sodium lauroyl glycinate [14]. This is reflected by the value of A_{min} for NaLGly which is smaller than A_{min} for NaLSar. Also, the CMC value of NaLGly is slightly higher than that of NaLSar, indicating that the aggregate formation is more favored in the case of NaLGly. Considering the fairly close values of surface parameters of the two amino acid-based surfactants, we assume that intermolecular hydrogen bonding does not play a major role in the micellization of studied amino acid-based surfactants [15]. CAPB and AO exhibit lower CMC value because there are no formal coulombic repulsions between the head groups [16].

The surface parameters are presented in Table 1.

Table 1. Surface parameters for single surfactants and mixtures.

Sample	Surfactants and mixtures	CMC (%)	Surface tension (mN/m)	Efficiency	$d\gamma/dlogc$ (mN/m/decade)	10^{10}x Γ_{max} (mol/cm^2)	10^2xA_{min} (nm^2)
1	NaLSar	2.405×10^{-1}	27.33	43.67	-19.87	1.59	104
2	NaLGly	2.879×10^{-1}	32.29	38.71	-25.25	2.02	82
3	AO	1.496×10^{-2}	25.94	45.06	-25.31	4.04	41
4	CAPB	1.819×10^{-3}	30.66	40.34	-28.91	4.62	36
5	NaLSar 75% +AO 25%	1.031×10^{-2}	24.61	46.39	-28.09	4.49	37
6	NaLSar 75% +CAPB 25%	4.658×10^{-3}	29.34	41.66	-35.40	5.66	29
7	NaLGly 75% +AO 25%	7.516×10^{-3}	24.83	46.17	-27.48	4.39	38
8	NaLGly 75% +CAPB 25%	5.918×10^{-3}	22.94	48.06	-37.00	5.91	28

As shown in Figures 2 and 3 and Table 1 the addition of AO or CAPB to the amino acid-based surfactants (samples 5-8) has a major effect in improvement the surface parameters, lowering the CMC value, surface tension and minimum area per molecule. In order to evaluate the interactions between the amino acid-based surfactants and AO or CAPB the ideal CMC values were calculated.

Based on the theoretical work by Clint for ideal mixed micelles, [17] for binary surfactant systems the CMC$_{ideal}$ can be calculated using the following equation:

$$\frac{1}{CMC_{ideal}} = \frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2} \tag{4}$$

where CMC$_1$ and CMC$_2$ are the CMC of the individual surfactants.
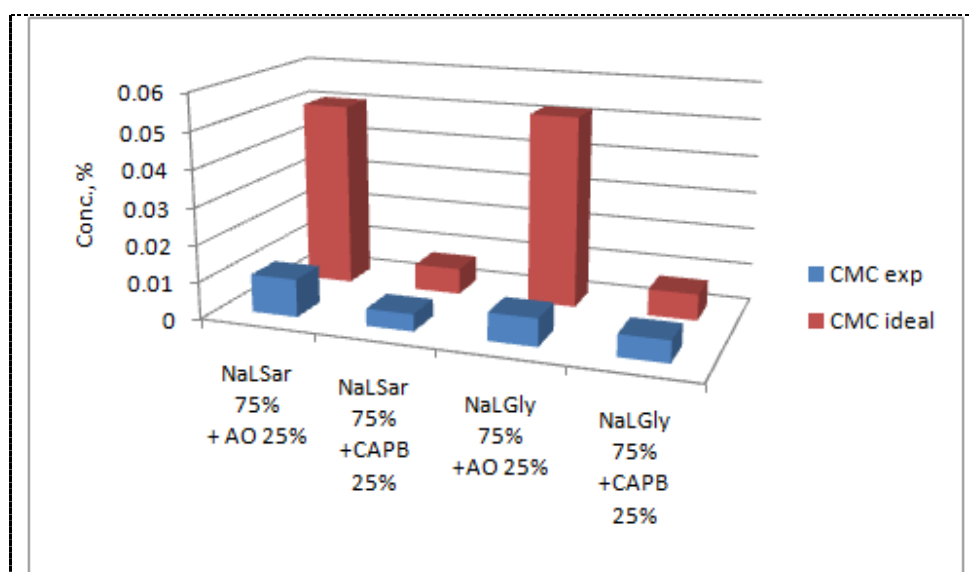

Figure 4. Graphical representations of CMC$_{exp}$ and CMC$_{ideal}$ for mixed surfactant systems.

The experimental CMC values for mixed surfactant systems are lower than those obtained by assuming ideal behaviour, indicating that the interaction is more attractive between the two components in the mixed micelle than the self-interaction of the two components before mixing.

For both systems, with NaLSar and NaLGly, a higher reduction of CMC_{exp} against CMC_{ideal} was observed when AO was used.

The pH of the solutions was 8 at which the AO is nonionic. The coordinate covalent N-O function has high polarity, close to that of quaternary ammonium salts, with the oxygen being a powerful hydrogen bond acceptor [18].

3.2. Evaluation of foaming power

Although it is not an essential attribute of surface activity, the foaming power was studied in order to evaluate the efficacy of surfactant systems for application areas requiring high foaming abilities.

The foaming power of 0.05% aqueous solutions of individual surfactants and mixed surfactants systems are presented in Table 2.

Table 2. Foaming power of individual surfactants and mixtures.

Sample	Surfactants and mixtures	Foam volume in distilled water (cm^3)	Foam volume in hard water (cm^3)
1	NaLSar	0	0
2	NaLGly	0	0
3	AO	355	335
4	CAPB	370	360
5	NaLSar 75% + AO 25%	430	415
6	NaLSar 75% + CAPB 25%	435	420
7	NaLGly 75% + AO 25%	380	135
8	NaLGly 75% + CAPB 25%	395	155

Experiments were performed in distilled water and in hard water 10°dH (178 ppm $CaCO_3$). From the foam volume data it can be seen that they are well correlated with CMC values of individual surfactants or surfactants mixtures.

At the work concentration there is no foam produced by sodium lauroyl sarcosinate or sodium lauroyl glycinate as single surfactants (samples 1 and 2), since the work concentration is below the CMC of either of surfactants.

At the same concentration, AO and CAPB exhibit good foaming properties, since the CMC values are below the work concentration. When mixed surfactant systems are prepared and tested (samples 5-8), the foaming volume is improved, demonstrating that the use of AO or CAPB induce a synergetic effect upon the foaming properties of surfactant systems.

The samples 5 and 7, formulated with AO in distilled water, showed a higher foam volume, which demonstrate once again the synergetic effect of AO on the surface properties of NaLSar and NaLGly. In hard water only the system with NaLSar presents a high foaming power.

3.3. Evaluation of viscosity

The viscosity determinations took place at 25°C, pH=8, the aqueous solution having a 10% total surfactant concentration. The working conditions were 0.5 rot/min using the S62 spindle. The results are shown in Table 3.

No viscosity increase was noted in any of the surfactant mixtures, denoting that other variables may be introduced in order to achieve an important increase in the viscosity of aqueous surfactant solutions.

Table 3. Viscosity of surfactant mixtures.

Sample	Surfactant mixtures	Viscosity (cP)
5	NaLSar 75% + AO 25%	180
6	NaLSar 75% + CAPB 25%	166
7	NaLGly 75% + AO 25%	173
8	NaLGly 75% + CAPB 25%	152

Several studies on the influence of factors such as pH or salinity need to be made in order to optimize the surfactant systems.

4. Conclusions

Through the investigation of the surface tension we were able to determine critical micelle concentration and other surface parameters for individual surfactants NALSar, NaLGly, AO, CAPB and for mixed surfactant systems NALSar+AO, NALSar +CAPB, NALGly+AO 3:1, NALGly +CAPB with mass ratio 3:1. The experimental CMC values obtained of the mixtures are lower than those predicted from Clint's equation. It was observed a higher influence of AO in reducing the CMC value when mixed with either NaLSar or NaLGly, indicating a strong synergistic interaction. Foaming power of mixed surfactant systems is well correlated with CMC values of individual surfactants or surfactants mixtures, demonstrating the synergetic effect of AO on the surface properties of NaLSar and NaLGly. The synergistic effects will allow us to use in an efficient way the amino acid-based surfactants in high foaming and sulphate free formulations with nonionic or amphoteric surfactants..

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