Surface Adsorption in the Mixtures of Sodium Dodecylsulphate and Oxyethylenated Nonylphenol with Different Oxyethylenation Degrees[1]

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The effectiveness of surface adsorption in an aqueous solution of mixtures of surfactants composed of an anionic surfactant, sodium dodecylsulphate, mixed with a nonionic one, polyoxyethylenated nonylphenol, was studied. Their behavior was compared separately. This surface adsorption was characterized by the values of the surface tension at 25°C of the total concentrations below, but near to the critical micelle concentration (CMC) in the mixtures mentioned. These were obtained as a function of different proportions of surfactants in the mixture and different chain lengths of nonionic polyoxyethylenated surfactant. The total surface excess concentrations of the surfactant mixtures and the average of molecular area per surfactant species at the aqueous solution/air interface were calculated. Finally, the values were analyzed vs the above parameters.

KEY WORDS: Mixtures, oxyethylenated nonylphenol, sodium dodecylsulphate, surface adsorption.

Surfactant adsorption in a liquid/air interface up to saturation, related to the relevant area unity, is a useful way to assess its effectiveness. This phenomenon occurs in a different way between an anionic surfactant such as sodium dodecylsulphate and a nonionic one such as oxyethylenated nonylphenol with different oxyethylenation levels, due to their structural differences in relation with the hydrophilic and hydrophobic groups and their different orientation in the superficial interface.

Mixtures of the mentioned surfactants in aqueous solution form mixed micelles with a nonideal thermodynamic behavior (1,2). Both critical micelle concentration (CMC) and the decrease of the surface tension are predictable by application of some of the existing theories (3–6). To complete previous results by the author (7,8), in which different aspects of the physicochemistry of the mixed micelles and the molecular interaction of the above surfactants, considered from the CMC of their mixtures were studied, this paper examines the influence of the indicated mixtures on the respective adsorption in the surface interface up to saturation.

To achieve this goal, the behavior of the surface adsorption in a liquid/air interface of sodium dodecylsulphate and oxyethylenated nonylphenol has been studied. Adsorption is characterized by the variation of the surface tension at concentrations below the CMC, as a function of the mixture ratio and the oxyethylenated chain length of the nonionic surfactant with 5, 10, 15, 20 and 30 mols of the ethylene oxide. The excess surface concentration and the molecular area average in the

liquid/air interface were evaluated separately as to their behavior, with the one of the surfactant components vs the above parameters.

EXPERIMENTAL PROCEDURES

Materials. The anionic surfactant used was sodium dodecylsulphate, pure analytical reagent supplied by Merck (Darmstadt, Germany). The content of anionic active matter was verified by analysis as being higher than 99% (9).

The nonionic surfactants used were oxyethylenated nonylphenols with 5, 10, 15, 20 and 30 mols of ethylene oxide, supplied by Marchon (Barcelona, Spain). Water was extracted by dessication and an average of 0.8% in weight was found between products. The homogeneity of these nonionic products was verified by the graphs of surface tension vs logarithm of concentration; only samples exhibiting sharp breaks have been used. The iodometric titration of the groups of ethylene oxide was found and the average of a few determinations gave these results (7): nonylphenol + 5 m.E.O., 52.18%; nonylphenol + 10 m.E.O., 69.82%; nonylphenol + 15 m.E.O., 75.73%; nonylphenol + 20 m.E.O., 84.94%; and nonylphenol + 30 m.E.O., 92.1%.

The water used in the dissolution of surfactants was bidistilled in the presence of potassium permanganate and the resulting surface tension became 72.09 mNm^{-1} at 25°C.

Apparatus. A Lauda automatic tensiometer incorporating a graphical recorder of the tension and digital control of the temperature has been used for the determination of the surface tensions. Solutions to be measured were thermostated with a $\mp 0.1°C$ variation (10).

Determination of the surface tension. Surface tension was measured by the Wilhelmy method (11), using a 4 cm perimeter platinum plate. Surfactants solutions were measured at equilibrium 24 hr after preparation of the mixture made with the solutions of the components. Determinations were taken at least every 10 min and the constancy of the surface tension vs time was verified in every solution determined. Determinations of surface tensions were made at 25°C.

Surfactants mixtures. Mixtures of surfactants were made with the following anionic–nonionic surfactant ratios: 1:0; 0.98:0.02; 0.9:0.1; 0.75:0.25; 0.6:0.4; 0.5:0.5; 0.4:0.6; 0.25:0.75; 0.1:0.9; and 0:1.

RESULTS AND DISCUSSION

Surfactants show a selective adsorption of their molecules and/or ions in interfaces, as in the case of a liquid/air interface. When the concentration of surfactants are above the CMC, their molecules form molecular and/or ionic aggregates called micelles in the

solution. This CMC value constitutes a division between the lower concentrations formed by the surfactant as a monomer and the higher concentrations formed by colloidal solutions. The graphical representation of the surface tension vs the logarithm of the surfactant concentration (alone or mixed with others) shows a sharp change in the slope at the CMC. In concentrations lower than but close to this CMC, this slope is basically constant, which means that the surface concentration has reached a maximum and constant value. In this range of concentrations, the interface is considered to be saturated by the surfactant and its surface tension decreases until the value of the surface tension corresponding to the CMC is reached. This effect was explained by Van Woorst Vader (12) as due to the increase of the activity of the surfactant inside the dissolution, since the interface is saturated. More recently, Schott (13) has related this phenomenon to the packing density of molecules in the saturated monolayer, which can cause high variations of the surface tension on varying the solution concentration slightly.

The above (practical) phenomenon can be seen in the graphical representation of the results found for the surface tension vs the logarithm of the total concentration of the surfactants, tried with different ratios of sodium dodeylsulphate with oxyethylenated nonylphenol at 5, 10, 15, 20 and 30 m.E.O. (Figs. 1–5). Surfactants alone, without mixing, are included in these Figures. In these graphs, and for every mixture of surfactant, the straight stretch below the CMC was obtained between the surface tension and the logarithm of the concentration to make the study of the surface adsorption easier.

Influence of the molar ratio and the length of the oxyethylenated chain of the nonionic surfactant on the concentration of surface excess. With the results of Figures 1–5, the amount of surfactant adsorbed by unit of surface area was assessed for each ratio of anionic-nonionic surfactant using the Gibbs equation. The Gibbs equation (14), applied to a mixture of surfactant in an aqueous solution, considering constant activity coefficients for both surfactants and the solvent, can be expressed as follows:

$$-d\gamma = RT\Sigma\Gamma_i d \ln C_i \qquad [1]$$

where $d\gamma$ is the change of the surface tension (or interfacial) of the solution; Γ_i, the surface excess of each component of the mixture in the liquid/air interface; and C_i, the molar concentration of each component.

In the case of surfactant mixtures composed by one nonionic (n) and another anionic (Na^+D^-), the expression will be:

$$\Sigma\Gamma_i d \ln C_i = \Gamma d \ln C_n + \Gamma_{Na^+} d \ln C_{Na^+} + \Gamma_{D^-} d \ln C_{D^-} [2]$$

$$C_n = C_t \cdot \alpha \qquad [3]$$

$$C_{Na^+} = C_{D^-} = (1-\alpha) \cdot C_t \qquad [4]$$

where C_n is the molar concentration of the nonionic surfactant; C_t is the total concentration of the mixture; and α, the molar fraction of the nonionic surfactant in the mixture. C_{Na^+} and C_{D^-} are the concentration of the cation and anion, respectively, of the anionic surfactant (1:1).
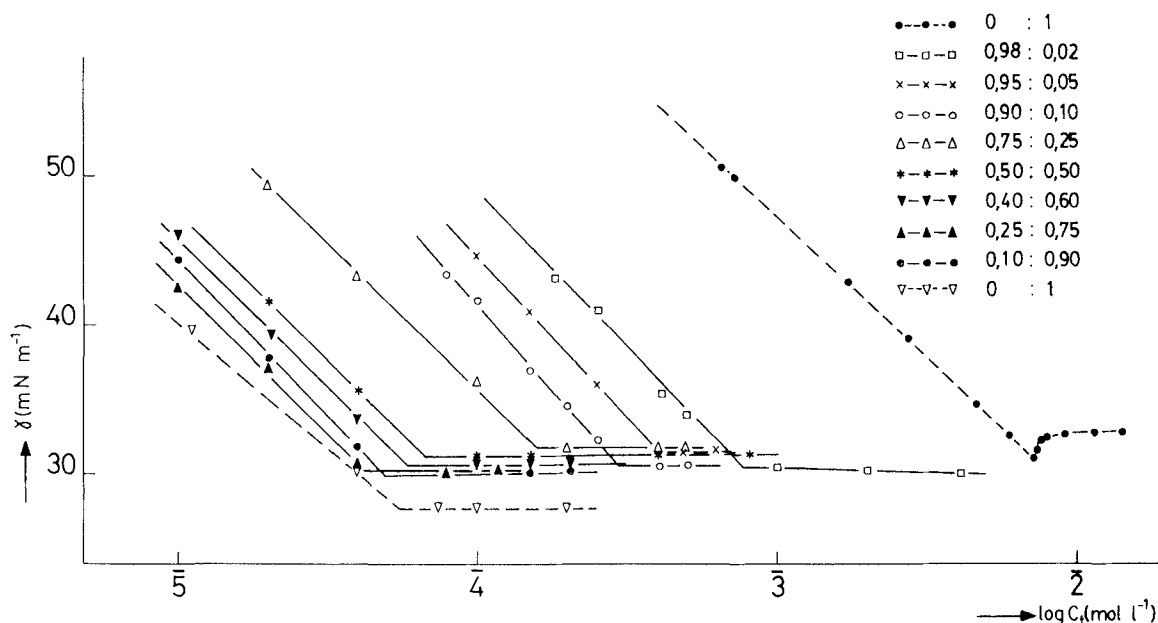

FIG. 1. Variation of the surface tension, at 25°C, vs the logarithm of the total concentration of the surfactants $C_{12}H_{25}OSO_3Na/C_9H_{19}C_6H_4(OC_2H_5)_5OH$ with different ratios of mixture and of these surfactants separately.
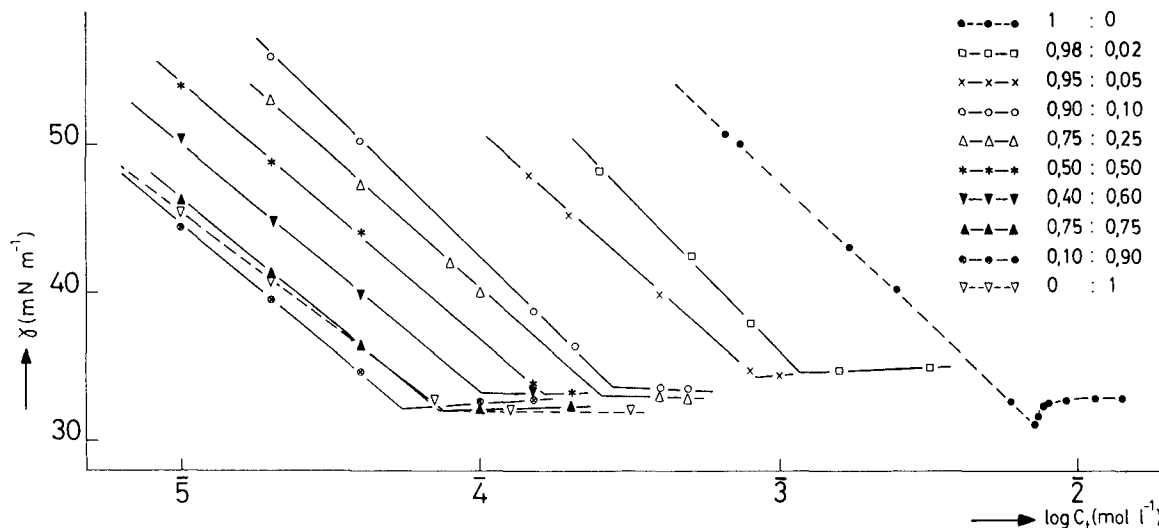
FIG. 2. Variation of the surface tension, at 25°C, vs the logarithm of the total concentration of the surfactants $C_{12}H_{25}OSO_3Na/C_9H_{19}C_6H_4(OC_2H_5)_{10}OH$ with different ratios of mixture and of these surfactants separately.
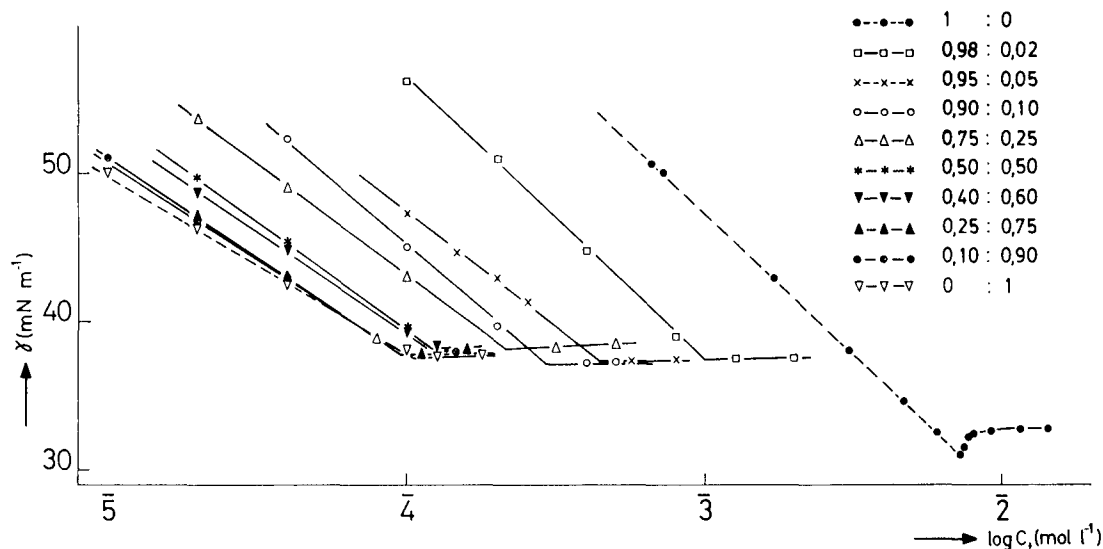

FIG. 3. Variation of the surface tension, at 25°C, vs the logarithm of the total concentration of the surfactants $C_{12}H_{25}OSO_3Na/C_9H_{19}C_6H_4(OC_2H_5)_{15}OH$ with different ratios to mixture and of these surfactants separately.

For α constant, $d \ln C_{Na^+} = d \ln C_{D^-} = d \ln C_n = d \ln C_t$, and considering the molar fraction of the non-ionic surfactant in the mixed micelle (x), deduced for every mixture used in a previous paper by Carrión (7), will be:

$$\Gamma_n = x \cdot \Gamma_t \qquad [5]$$

$$\Gamma_{Na^+} = \Gamma_{D^-} = (1 - x)\Gamma_t \qquad [6]$$

where Γ_n, Γ_{Na^+}, Γ_{D^-} and Γ_t are the surface excess concentration for the nonionic surfactant, the cation and the anion of the anionic surfactant and for the total of the mixture, respectively.

Taking into account these considerations and substituting equations [5] and [6] equation [2], the result will be:

$$\Sigma\Gamma_i^- d \ln C_i = \left[x\Gamma_t + 2(1 - x)\Gamma_t \right] d \ln C_t$$

$$= (2 - x)\Gamma_t d \ln C_t \qquad [7]$$

By placing equation [7] into equation [1], Gibbs equation would adopt the following form:

$$\Gamma_t = \frac{1}{R.T.(2 - x)} \cdot \left(\frac{\partial \gamma}{\partial \ln C_t} \right)_{\alpha, T} \qquad [8]$$

FIG. 4. Variation of the surface tension, at 25°C, vs the logarithm of the total concentration of the surfactants $C_{12}H_{25}OSO_3Na/C_9H_{19}C_6H_4(OC_2H_5)_{20}OH$ with different ratios of mixture and of these surfactants separately.
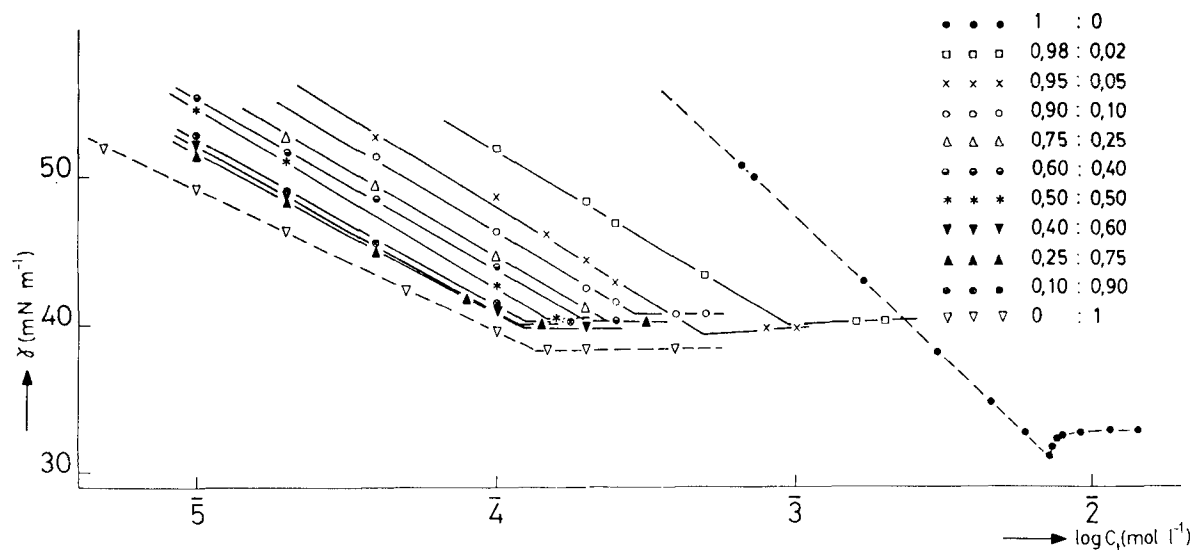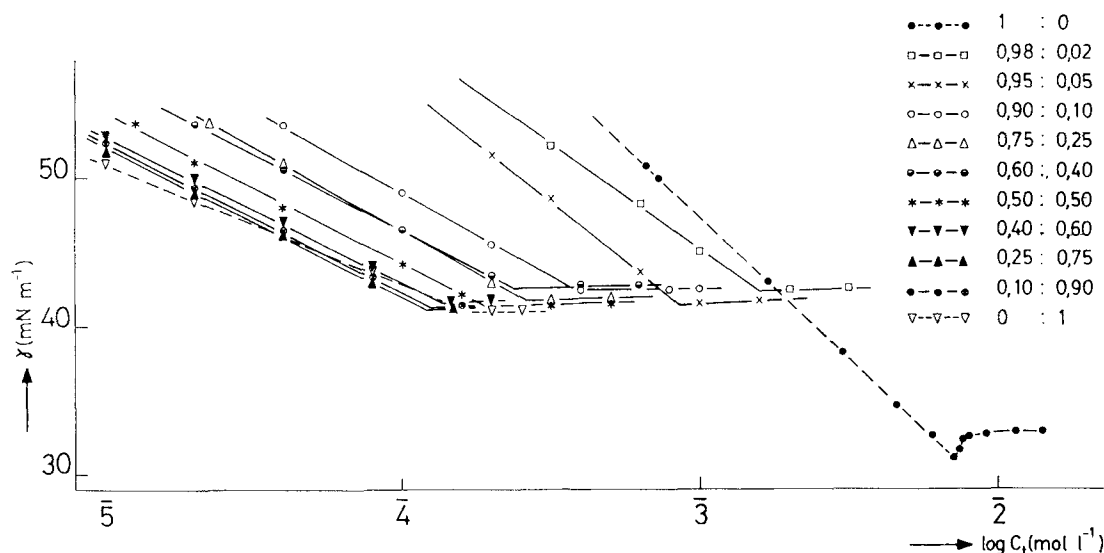

FIG. 5. Variation of the surface tension, at 25°C, vs the logarithm of the total concentration of the surfactants $C_{12}H_{25}OSO_3Na/C_9H_{19}C_6H_4(OC_2H_5)_{30}OH$ with different ratios of mixture and of these surfactants separately.

To assess the surface excess concentration by the Gibbs equation [8] applied to this system, the values "x" molar fraction of the nonionic surfactant in the surface monolayer of the mixture has been considered. These "x" values, shown in Table 1, were deduced from previous results of the molar fraction of the anionic surfactant in the mixed micelle, published by Carrión (7) from the relation (1):

$$\frac{x \cdot \ln \left(C_{12}^M \cdot \alpha/C_1 \cdot X\right)}{(1-X)^2 \cdot \ln \left[C_{12}^M(1-\alpha)/C_2(1-X)\right]} = 1 \qquad [9]$$

where x is the anionic surfactant molar fraction in the mixed micelle; α, the anionic surfactant molar fraction in the solution; C_1, CMC of the anionic surfactant; C_2, CMC of the nonionic surfactant; and C_{12}^M, CMC of the mixtures. Results of the surface excess concentration for each mixture vs the molar fraction of the nonionic surfactant and the length of the oxyethylenated chain are shown in Table 2. Gibbs equation [8] was used to obtain these results.

Table 2 shows the surface excess concentration of the anionic surfactant (sodium dodecylsulphate) separately ($\alpha = 0$) to have a higher value than the one found for the nonionic surfactant without mixing ($\alpha = 1$)

TABLE 1

"x" Values, Molar Fraction of the Nonionic Surfactant in the Surface Monolayer of the Mixture: $C_9H_{19}C_6H_4(OC_2H_4)_n$ $OH/C_{12}H_{25}OSO_3Na$ (7)

α (nonionic)	"n" Oxyethylenated chain length (m.E.O.)				
	5	10	15	20	30
0.02	0.583	0.564	0.522	0.510	0.489
0.05	0.649	0.691	0.583	0.567	0.565
0.10	0.725	0.665	0.628	0.606	0.597
0.25	0.815	0.748	0.724	0.706	0.675
0.40	—	—	—	0.769	0.746
0.50	0.790	0.817	0.780	0.762	0.756
0.60	0.806	0.854	0.804	0.777	0.741
0.75	0.793	0.843	0.822	0.811	0.767
0.90	0.888	0.826	0.895	0.896	0.818

TABLE 2

Surface Excess Concentration of the Mixtures $C_9H_{19}C_6H_4(OC_2H_4)_n/C_{12}H_{25}OSO_3Na$ at 25°C

α (nonionic)	"n" Oxyethylenated chain length (m.E.O.)				
	$(\Gamma_i \cdot 10^6 \text{ mol.m}^{-2})$				
	5	10	15	20	30
0	3.389	3.389	3.389	3.389	3.389
0.02	2.604	2.548	2.267	1.402	1.659
0.05	2.786	2.469	2.156	1.520	1.440
0.10	3.205	2.607	2.208	1.506	1.405
0.25	2.957	2.558	2.056	1.616	1.485
0.40	—	—	—	1.644	1.422
0.50	2.871	2.583	2.100	1.720	1.423
0.60	2.786	2.552	1.988	1.591	1.367
0.75	2.879	2.528	2.028	1.605	1.437
0.90	3.305	2.531	2.052	1.816	1.500
1	2.930	2.680	2.042	1.692	1.400

(oxyethylenated nonylphenol) at the values of both mixtures, which are similar to the nonionic surfactants. If we consider that this surface excess concentration determines the extension of the surfactant adsorption in the aqueous surface, it is easily deduced that the molecule of the anionic surfactant adopts a more perpendicular form to the aqueous surface than the nonionic surfactant, which is more extended along such a surface. This extension of the molecule in the surface interface depends on the nature and length of the hydrated hydrophilic group (oxyethylenated chain) in the case of the nonionic surfactant. Thus, an increase in the length of the oxyethylenated chain of the nonylphenol in the mixture involves a decrease in the surface excess concentration.

Only a small part of the nonionic surfactant in the mixture, like one tried with the lowest α (nonionic) = 0.02, already causes a decrease of the surface excess concentration of the anionic surfactant and similar values as those found for the nonionic surfactant separately. These values kept close to those of the nonionic surfactant on increasing its ratio in the mixture in all the lengths of the oxyethylenated chains tried. This phenomenon is possibly due to the fact that the oxyethylenated chains of the nonionic surfactant surround the polar group of the anionic surface and reduce its repulsive electrostatic force, which promotes the association of the hydrophobic chains of the anionic surfactant. Consequently, the molecular aggregation in the surface monolayer easily take place and their perpendic-

ular position in the superficial saturation on the surface is lost.

Influence of the molar ratio and the length of the oxyethylenated chain of the nonionic surfactant on the area average of the surfactant molecule in the surface interface. Results of the surface excess concentration of each mixture of surfactant (Table 2) have been used to assess the area average of the surfactant molecule in the liquid/air interface (A_m) in nm^2, using the following equation:

$$A_m = \frac{10^{18}}{N \cdot \Gamma_t}$$ [10]

where N is the Avogadro number and Γ_t is the surface excess concentration (mol m^{-2}).

Table 3 shows the results found for the area average per molecule of the surfactant vs the molar fraction of the nonionic surfactant in the mixture and vs the length of the oxyethylenated chain.

Results in Table 3 show that the nonionic surfactant separately, without mixing, gave higher values than the anionic surfactant. With respect to its mixtures, the average per molecule of surfactant increases on increasing the length of the oxyethylenated chain of the nonionic surfactant in all the mixtures of surfactants tried; this also applies to the nonionic surfactant separately, without mixing. This effect is due to a spiral shape in the oxyethylenated chain that can be immersed in the aqueous solution; therefore, its cross-section increases

TABLE 3

Area Average per Molecule (nm^2) in the Surface Interface of the Mixtures of $C_9H_{19}C_6H_4$ $(OC_2H_4)_n$ $OH/C_{12}H_{25}OSO_3Na$ at 25°C

α (nonionic)	"n" Oxyethylenated chain length (m.E.O.)				
	5	10	15	20	30
	Area (nm^2)				
0	0.490	0.490	0.490	0.490	0.490
0.02	0.637	0.652	0.732	1.184	1.001
0.05	0.596	0.672	0.770	1.092	1.153
0.10	0.518	0.637	0.752	1.102	1.181
0.25	0.561	0.649	0.807	0.973	1.118
0.40	—	—	—	1.010	1.167
0.50	0.578	0.643	0.790	0.965	1.167
0.60	0.596	0.651	0.835	1.043	1.214
0.75	0.577	0.657	0.819	1.034	1.155
0.90	0.503	0.656	0.809	0.914	1.107
1	0.567	0.619	0.813	0.981	1.190

with the number of units of ethylene oxide in the chain (16,17).

With regard to the ratio of the nonionic surfactant in the mixture (Table 3) only small amounts — like the molar fraction of the nonionic surfactant of 0.02 — may increase the area average per molecule of the anionic surfactant; this increase is generally similar, as the value of the same nonionic separate surfactant (without mixing), even if the length of the oxyethylenated chain is different. It is also seen in Table 3 that an increase of the ratio of the nonionic surfactant in the mixture does not cause any important variations in the area average per molecule; therefore, the values remain similar to the area average of the nonionic separate surfactant.

The conclusions drawn from the study of the surface adsorption at 25°C of a mixture of sodium dodecylsulphate and oxyethylenated nonylphenol with different levels of oxyethylenation described in this paper are as follows: i) For the range of concentrations, linearity was found to be lower than the CMC with the variation between the surface tension vs the logarithm of the concentration for all the mixtures of anionic surfactant tried. ii) The surface excess concentration of the anionic surfactant was higher than that of the oxyethylenated nonionic surfactant, due to the fact that the latter shows a hydrophilic hydrated group on the surface, causing a decrease of the surface excess on increasing the length of the oxyethylenated chain. iii) A small amount of the nonionic surfactant in the mixture, α (nonionic) = 0.02, caused a decrease of the surface excess concentration of the anionic surfactant and similar values were achieved, as they were in the nonionic ones separately. On increasing the ratio of the nonionic surfactant in the

mixture, the surface excess concentration did not change in all the lengths of the oxyethylenated chain tried. This oxyethylenation surrounded the polar group of the anionic surfactant and reduced its repulsive electrostatic force, which promoted the association of the hydrophobic chain of the anionic surfactant. iv) The area average per molecule of surfactant in the surface interface of the nonionic surfactant was higher than the one of the anionic surfactant. This area average in the mixtures of these surfactants increased on increasing the length of the oxyethylenated chain of the nonionic surfactant, which is due to its spiral shape when immersed in the aqueous solution. v) Small amounts of the nonionic surfactant, α (nonionic) = 0.02, mixed with an anionic surfactant caused an increase of the area average per molecule of the latter. When the ratio of the nonionic surfactant was increased, the area average per molecule did not change at all with the length of the oxyethylenated chain.

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