Surface and thermodynamics properties of commercial fatty-alcohol ethoxylate surfactants

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A R T I C L E   I N F O

A B S T R A C T

The present study provides the surface and thermodynamic properties data of commercial fatty-alcohol ethoxylate surfactants (FAEs) at different temperatures (25–60 °C). These compounds are a mixture of fatty-alcohol ethoxylate oligomers with different degree of ethoxylation (2.6–11) and length of the alkyl chain (C_{10}-C_{18}). In this work, we analyzed determinate the water content by the Karl-Fisher method and measured the surface tension using the Wilhelmy plate method. In addition, we studied the effect of their structural parameters (degree of ethoxylation and length of alkyl chain) and the temperature on the changes of the thermodynamic functions (Gibbs free energy, enthalpy, and entropy) for the processes of adsorption and micellization. It was found an exponential decrease of the critical micellar concentration (CMC) in molar scale with the length alkyl chain of the fatty-alcohol ethoxylate surfactants, and the CMC values and thermodynamic parameters agree with those values found in literature for pure compounds. Moreover, the micellization entropy increases with the degree of ethoxylation of the surfactant.

1. Introduction

The fatty-alcohol ethoxylates (FAEs) are non-ionic surfactants whose hydrophilic part consists in a repetition of "m" units of ethylene oxide (EO) and a hydroxyl group at the end [1], both functional groups (ether and hydroxyl) give them water solubility, but do not ionize. Their hydrophobic tail is a linear alkyl chain (C_nH_{2n+1}-). They are mainly obtained from palm oil and other renewable resources and have an even number of carbon [1].

Fatty-alcohol ethoxylates are one of the most important groups of non-ionic surfactants [2]. They have good detergent and emulsifying properties [3], insensitivity to water hardness, high biodegradability [4], low toxicity compared to alkylphenolethoxylates (APE) [5] and low production cost compared with alkyl polyglucosides (APG). In addition, they can be broadly used as co-surfactant due to their compatibility with other surfactants, such as sodium lauryl ether sulfate, cocoamidopropyl betaine or sodium lauroyl sarcosinate [6–8].

The industrial production of FAEs in carried out by a chain reaction between a primary alcohol and ethylene oxide, which is catalyzed by a base. At the initiation phase, the alcohol loses its labile hydrogen to form an alkoxide and continues with the addition of an ethylene oxide in the propagation phase [9,10]. The termination takes place when the ethylene oxide runs out or the alkoxides are neutralized [11].

Because most FAEs are produced by a base catalyzed addition of ethylene oxide monomers, a statistically polydisperse oligomer distribution is obtained [12,13], and the molar fraction of oligomers with a degree of ethoxylation "m" follows a Poisson distribution [14]. The main impurities of the product are polyethylene glycols (PEGs) (0.05–5 %), ethylene oxide (1–25 ppm) which is removed by low vacuum heating, and 1,4-dioxane which is removed by steam distillation. These impurities are toxic and undesirable if FAEs are included in cosmetic formulations.

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In the production process based on the synthesis of Williamson ethers [15] the fatty-alcohol ethoxylate reacts with monochloroacetic acid in the presence of sodium hydroxide (60–90 °C). In other processes, the fatty ethoxylate alcohol is oxidized with air using a catalyst containing Pd/Pt deposited on active carbon in an alkaline medium between 40 and 100 °C. A product of high purity is obtained with yields close to 100 % [6].

The scientific study of the properties of a pure surfactant is simpler and more rigorous that the determination of the properties of mixtures of oligomers. Consequently, pure FAEs and other similar compounds, such as p,t-Octylphenoxyethoxyethanols (OPE), have been well characterized and studied in literature during the last decades [16–22]. However, studies about properties of mixtures are scarce [4,23–25], which is of particular interest since the production of mixtures of these compounds is much more economically viable than the separate production of each of the compounds and their subsequent mixing. Furthermore, in specific applications, such as detergency, the effect achieved by mixtures is better than that achieved with a pure compound [26,27].

Due to the close relationship between the physical properties of oligomers and the length of the hydrophobic and hydrophilic parts, there is a growing interest in relating the physical characteristics of mixtures with the characteristics of the oligomers and their statistical distribution [28]. For example, the CMC is an essential property of surfactants and can be measured and related with the degree of ethoxylation and length alkyl chain. With an oligomer distribution known, the CMC of the mixture can be estimated using the Clint model [29,30] or the Paul M. Holland model [28,31].

In this work, we studied the essential physical parameters of FAEs (CMC, minimum area per molecule) and the thermodynamics properties of the micellization and adsorption process, and the relationship with their structural parameters.

2. Experimental procedures

2.1. Surfactants

Four fatty-alcohol ethoxylate surfactants were studied, FAE-$C_{10}E_3$, FAE-$C_{10}E_6$, FAE-$C_{12-14}E_{11}$ and FAE-$C_{16-18}E_{11}$. They were supplied by Kao Corporation S.A.U, (Tokyo, Japan). Table 1 shows their INCI name (International Nomenclature of Cosmetics Ingredients) and technical specifications: length alkyl chain (n), degree of ethoxylation (m), average molecular mass (M) [32] and Hydrophilic-Lipophilic Balance (HLB) [25,32], and Fig. S1 in supplementary materials shows their chemical structure. Surfactants solutions were prepared using ultrapure water (resistivity 18.2 MΩ·cm at 25 °C).

2.2. Water content

The water content (w) were determined by the Karl-Fisher method using a compact instrument of volumetric tritation Crison® (Crison Instruments, SA, Barcelona, Spain). The calibration factor (F) were determined by adding a known amount of sodium tartrate dihydrate ($C_4H_4O_6Na_2\cdot2H_2O$, analythical grade) and indicating the amount of water added to the instrument. This method was chosen for its accuracy, sensitivity and selectivity to water. It has been assumed that the surfactants do not contain compounds capable of reducing iodine, neither aldehydes or ketones that could form ketals and acetals with the solvent. Percentages of water content are shown in Table 1 for each surfactant studied.

2.3. Surface tension

Surface tension was determined according to the BS EN 14370:2004 guideline [33] (Wilhelmy Plate Method) using a tensiometer model K11 (Krüss GmbH, Hamburg, Germany) equipped with a 2-cm platinum plate. Surface tension measurements, σ (mN·m^{-1}), were performed in triplicate for ultrapure water (resistivity 18.2 MΩ·cm at 25 °C) and with a minimum of 15 replicates for 100 cm^3 samples of FAEs of increasing concentrations in geometric progression, with a maximum tolerable difference of ± 0.1 mN·m^{-1}. The temperature was controlled within 25 and 60 ± 0.1 °C by circulating temperature-controlled water through a jacketed cell. To prevent the water evaporation, it was used a glass cover provided with a small groove that allows the contact of the plate with the liquid surface.

3. Results and discussion

Fig. 1 shows the surface tension (σ) of aqueous solutions of FAEs at different temperatures vs the log of their bulk phase concentration in mol m^{-3}(log C) and Table 2 shows the CMC determined for the four FAEs and the values of surface pressure (Π).

Critical micelle concentration (CMC) was taken as the concentration at the point of intersection of the two linear portions of the σ-log C plots as is shown Fig. S2 (supplementary materials). The slope of the linear portion of each curve below the CMC was determined by the method of the least mean squares. Although this method offers good results for pure surfactants, for mixtures it shows some difficulties issues due to the absence of an abrupt change in the slope of the two linear portions [29,31]. Surface pressure (Π) was obtained using the Eq. 1, where σ_0 is the surface tension of water and σ the surface tension at the CMC.

$$\Pi = \sigma_0 - \sigma \tag{1}$$

Table 1
Technical specifications of fatty-alcohol ethoxylate surfactants.

Surfactant	INCI	n	m	M, g mol^{-1}	HLB	w, %
FAE-$C_{10}E_3$	Deceth-3	10	2.6	273[a]	9.6[b]	0.42 ± 0.03
FAE-$C_{10}E_6$	Deceth-6	10	6	385[a]	12.7[b]	0.66 ± 0.02
FAE-$C_{12-14}E_{11}$	Laureth-11 + Myreth-11	12/14	11	631[a]	14.4[b]	0.38 ± 0.03
FAE-$C_{16-18}E_{11}$	Ceteareth-11 + Steareth-11	16/18	11	734[c]	13.2[c]	0.84 ± 0.08

INCI: international nomenclature of cosmetics ingredients.
n: alkyl chain length, n-C_iH_{2i+1}-.
m: degree of ethoxylation –(OCH$_2$CH$_2$)$_n$O.
M: average molecular mass.
HLB: Hydrophilic-Lipophilic Balance.
w: water content.
a Determined by Bravo-Rodriguez et al. [32].
b Determined by Jurado et al. [25].
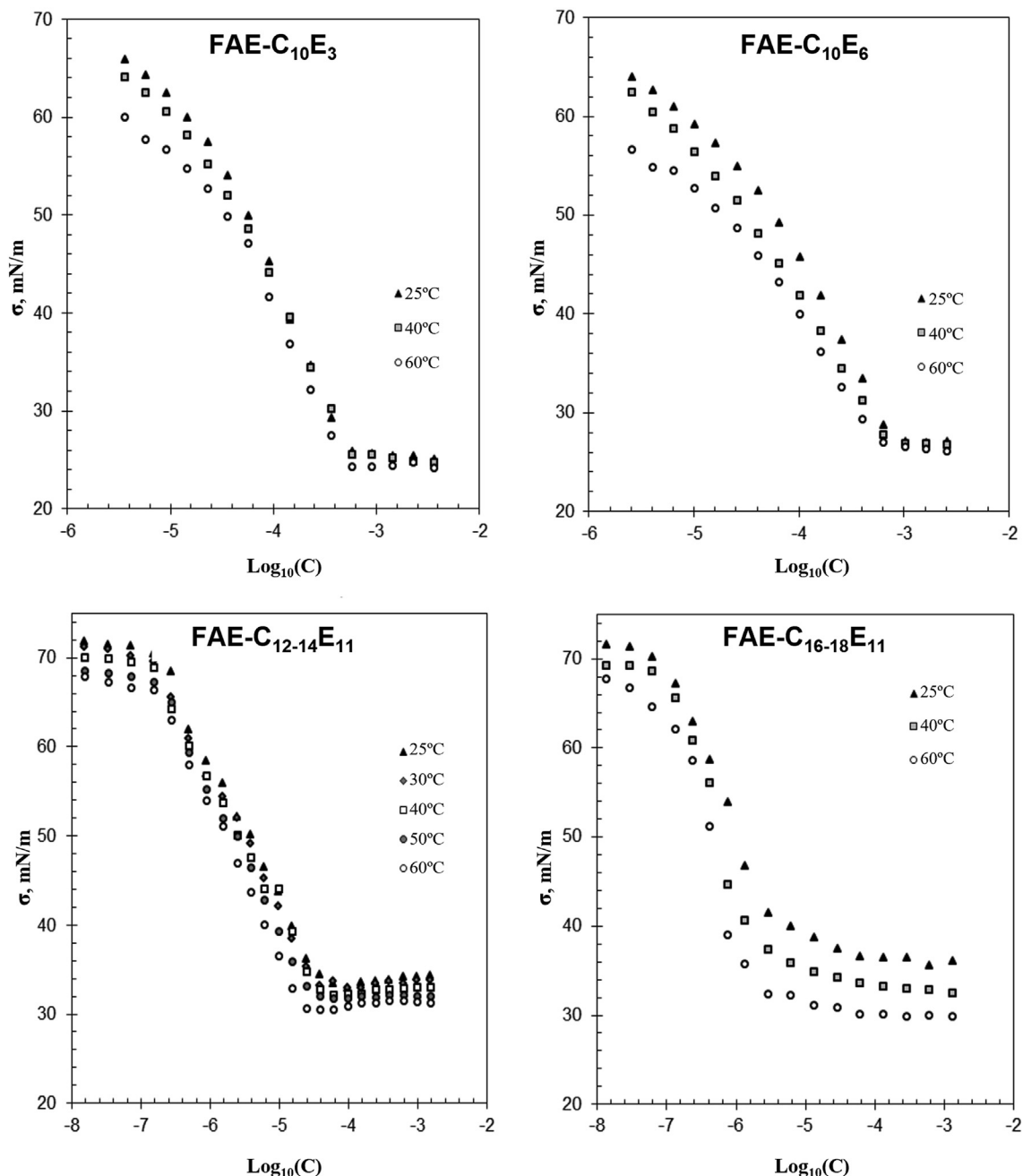c Determined according to Bravo-Rodriguez et al. [32].

Fig. 1. Surface tension vs surfactant concentration at different temperatures.

In case of FAE-$C_{12-14}E_{11}$, it can be seen a slight increase of the surface tension after reaching the critical micelle concentration (CMC), from 0.0409 mM at 25 °C to 0.0217 mM at 60 °C. The increase of the surfactant concentration after the CMC can be explained by the desorption from the interface of the most superficially active compounds (with lower HLB) of the oligomers mixture, and their subsequent solubilization in the micelle. Consequently, there is a decrease in ionic strength which enables lighter packing at interface [16,18]. This phenomenon can appear specially when working with commercial surfactants, which are a mixture of oligomers with variable structural parameters.

As expected, CMC decreases as the temperature is increased. This is due to an increasing destruction of the hydrogen bonds between water molecules and the hydrophilic group of the non-ionic surfactants [34,35]. In addition, results show that the CMC is lower when the length alkyl chain is longer, this can be explained because the increase in length of the alkyl carbon chain increases the degree of van der Waals interactions that can occur between hydrophobic groups. This, in turn, increases the stability in the micelle, which results in a lower critical micelle concentration [18,36,37].

Comparing FAE-$C_{10}E_3$ and FAE-$C_{10}E_6$, both with same length alkyl chain, the CMC is higher for the surfactant with the higher degree of ethoxylation, FAE-$C_{10}E_6$, this is caused by the higher hydrophilic character of the surfactant molecule [16,18,36,37]. This trend cannot be observed in case of FAE-$C_{12-14}E_{11}$ and FAE-$C_{16-18}E_{11}$, for which, despite having a higher degree of ethoxylation (m = 11), they have lower CMC values. Therefore, a higher influence of the length alkyl chain rather than of the degree of ethoxylation on the CMC can be supposed.

Table 2
Critical Micelle Concentration (CMC), surface pressure (Π), maximum surface excess concentration (Γ_{max}) and minimum area occupied per molecule (A_{min}).

	T, °C	CMC, mM	Π, mN m^{-1}	Γ_{max}, mol m$^{-2} \cdot 10^6$	A_{min}, Å^2
FAE-C$_{10}$E$_3$	25	0.6589 ± 0.0162	46.6 ± 0.2	4.440 ± 0.144	37.4 ± 1.2
	40	0.5873 ± 0.0105	44.5 ± 0.4	3.935 ± 0.100	42.2 ± 1.1
	60	0.4930 ± 0.0052	41.7 ± 0.3	3.460 ± 0.074	48.0 ± 1.0
FAE-C$_{10}$E$_6$	25	0.8446 ± 0.0226	44.7 ± 0.1	3.791 ± 0.109	43.8 ± 1.3
	40	0.6978 ± 0.0085	42.4 ± 0.1	3.169 ± 0.047	52.4 ± 0.8
	60	0.5333 ± 0.0184	39.8 ± 0.2	2.878 ± 0.124	57.7 ± 2.5
FAE-C$_{12-14}$E$_{11}$	25	0.0409 ± 0.0012	38.7 ± 0.3	3.410 ± 0.132	48.7 ± 1.9
	30	0.0379 ± 0.0010	38.2 ± 0.2	3.321 ± 0.105	50.0 ± 1.6
	40	0.0330 ± 0.0005	38.1 ± 0.1	3.092 ± 0.057	53.7 ± 1.0
	50	0.0246 ± 0.0005	38.5 ± 0.1	3.139 ± 0.075	52.9 ± 1.3
	60	0.0217 ± 0.0003	37.5 ± 0.1	3.396 ± 0.067	48.9 ± 1.0
FAE-C$_{16-18}$E$_{11}$	25	0.0064 ± 0.0003	36.2 ± 0.1	3.944 ± 0.178	42.1 ± 1.9
	40	0.0041 ± 0.0004	36.7 ± 0.2	5.047 ± 0.558	32.9 ± 3.6
	60	0.0024 ± 0.0001	37.9 ± 0.2	5.392 ± 0.084	30.8 ± 0.5

Maximum surface excess concentrations (Γ_{max}, mol m^{-2}), and minimum area per molecule (A_{min}, Å^2), at the aqueous/air interface were calculated from the following equations [38,39]:

$$\Gamma_{max} = \frac{1}{2.303\nu RT}\left(-\frac{d\sigma}{d\log CMC}\right)_T \quad (2)$$

$$A_{min} = \frac{10^{20}}{N_A \Gamma_{max}} \quad (3)$$

where $(-d\sigma/d\log CMC)_T$ is the slope of the σ-log C plot at constant temperature, R is the gas constant, ν is Gibbs factor which depend on the type of surfactant (non-ionic surfactants ν = 2 [38,39]) and N_A is the Avogadro's number.

Table 2 shows the values obtained, and it can be observed that the maximun surface concentration, Γ_{max}, increases with the length alkyl chain (n) and the minimum area per molecule (A_{min}) decreases inversely according to the Eq. (3).

These results agree with those found by other authors [37] where the slope of the isotherms increases when the length alkyl chain increases, and with the data published by Ueno et al. [40] for the series C_nE_8 with n ranged from 9 to 15. In this case, $(\Delta A_{min}/\Delta n)_{m=8,T=25°C} \approx -4.73$ Å^2. The same trend was observed comparing the values of A_{min} for the surfactants with the same degree of ethoxylation at the same temperature (Table 2), lower values of A_{min} were obtained for FAE-C$_{16-18}$E$_{11}$ compared with FAE-C$_{12-14}$E$_{11}$.

On the other hand, if the degree of ethoxylation is higher the surface adsorption becomes more difficult because of steric reasons, increasing the area occupied by the molecule of surfactant [16,37]. This can be corroborated according with the A_{min} values determined for the FAEs of the same length alkyl chain, at the same temperature, and with different degree of ethoxylation: FAE-C$_{10}$E$_3$ and FAE-C$_{10}$E$_6$.

With the increase of the temperature in the non-ionic surfactant solution, two opposite effects can be expected on the minimum area per molecule (A_{min}): 1) decrease of A_{min} resulting from the increase in the dehydration around the surfactant molecule, and 2) increase of A_{min} due to orientation as a result of the thermal molecular motion [41].

Results in Table 2, show that values of Π and Γ_{max} decreased as temperature increased for both FAE-C$_{10}$E$_3$ and FAE-C$_{10}$E$_6$. Consequently, A_{min} increased with temperature due to the higher thermal agitation of the surfactant molecule on the surface [16]. On the contrary, for FAE-$_{10-18}$E$_{11}$ the values of Π and Γ_{max} increased and A_{min} decreased as the temperature increased. This can be explained because the higher temperature diminished the head size of the FAE molecule, where the dehydration effect exceeded the effect of reorientation of the adsorbed molecules [41]. In case

of FAE-C$_{12-14}$E$_{11}$, A_{min} increased from 25 to 40 °C and diminished from 40 to 60 °C, revealing that at higher temperature the dehydration effect overcame the reorientation effects. In addition, results also shown that a longer alkyl chain on the molecular structure hinders the reorientation of the adsorbed molecules when the temperature increases.

3.1. Change of the micellization state functions

If the model of mass action is applied to calculate the changes on the most important state functions of the micellization process [19,42], the following equations are obtained:

$$\Delta G_{mic}^\circ = RT Ln(x_{CMC}) \quad (4)$$

$$\Delta H_{mic}^\circ = \left[\frac{\partial\left(\Delta G_{mic}^\circ/T\right)}{\partial(1/T)}\right]_P \quad (5)$$

$$\Delta S_{mic}^\circ = \frac{\left(\Delta H_{mic}^\circ - \Delta G_{mic}^\circ\right)}{T} \quad (6)$$

The change on the free energy, ΔG_{mic}°, is calculated using the Eq. (4), where x_{CMC} is the molar fraction of the surfactant in the CMC ($x_{CMC} \approx CMC/55.6$). The standard state considers the surfactant molecules in dissolution [16,39], without aggregation or solvation. Changes in the state functions are referred by mol of surfactant in this standard state.

The enthalpy change, ΔH_{mic}°, was calculated using the Gibbs-Helmholtz equation (Eq. (5)). From the Eqs. (4) and (5), and considering that ΔH_{mic}° is constant in the range of temperature studied, it is inferred that a representation of $Ln(x_{CMC})$ versus the inverse of the absolute temperature should consist of a series of points aligned on a slope line $\Delta H_{mic}^\circ/R$ (Fig. 2).

The entropy change, ΔS_{mic}°, was determined by using the Eq. (6). Values of ΔG_{mic}°, ΔH_{mic}°, and ΔS_{mic}° are shown in Table 3, and Fig. 3 shows the Gibbs isotherm for FAEs at 25 °C, where it is also highlighted the CMC of the surfactants by colored dashed lines.

Values of ΔG_{mic}° are negative, and therefore, the spontaneous aggregation is mainly due to the entropic contribution, being the order of magnitude consistent with the values published by other authors [16,42]. ΔH_{mic}° values were ranged from 6.8 to 23.5 kJ mol^{-1}. This is a weakly endothermic process because it requires the rupture of hydrogen bonds between the oxygen atoms of the hydrophilic part of the FAEs. Values are similar to those published for 2-dodecyloxypoly (ethenoxyethanol), and those found by other author by using different methods [16,42].
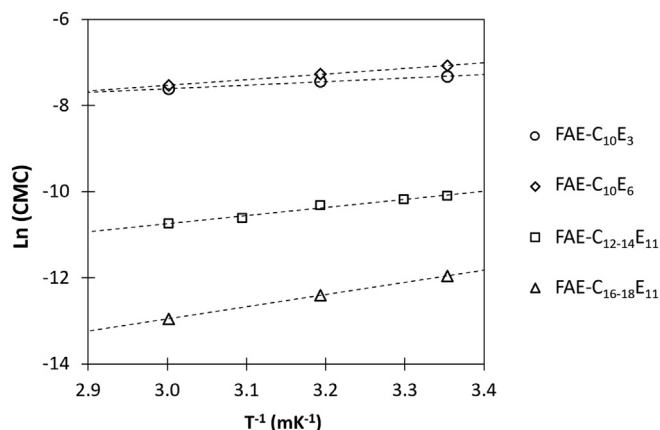
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Fig. 2. Ln(x_{CMC}) vs temperature.

Values of $\Delta H°_{mic}$ increase as the alkyl chain is longer and the degree of ethoxylation is higher. At the initial state, surfactants molecules are in solution and their oxygen atoms are forming hydrogen bonds with the water molecules, whereas in the final state, surfactant molecules are forming aggregates in the aqueous medium. Considering the spherical disposition of micelles, the formation of hydrogen bonds between the molecules of surfactant and the water is limited. Consequently, the aggregation process requires the rupture of the hydrogen bonds and must be endothermic. On the other hand, a higher degree of ethoxylation increases the water solubility, because a higher hydration causes an increase in the energy required to dehydrate the molecule during its incorporation into the aggregate at the micellar concentration [16].

In case of the entropy of micellization, $\Delta S°_{mic}$, results showed an increase with the length of the hydrophobic chain (Table 3) as result of a more favorable micellization process of the surfactant with longer alkyl chain length (less hydrated). Likewise, $\Delta S°_{mic}$ has a slight increase with the degree of ethoxylation, since the desolvation of the oxyethylene units has been stated as the major contributing factor to the positive entropy of micellization in polyoxiethylenated nonionics [16].

Moreover, ΔS_{mic} diminish with the temperature. Eq. (7), ($\Delta S°_{mic}$ dependence with the temperature) can be obtained from Eqs. (4) and (6). Consequently, $\Delta S°_{mic}$ depends on the exo/endo thermic character of the micellization process.

$$\frac{d\Delta S°_{mic}}{dT} = \frac{1}{T}\left(\frac{d\Delta H°_{mic}}{dT}\right) - \frac{\Delta H°_{mic}}{T^2} - R\frac{d(Lnx_{CMC})}{dT} \qquad (7)$$

3.2. Changes of the thermodynamic adsorption functions

Adsorption process takes place at a concentration below the CMC. However, their calculation and discussion are similar to the micellization process:

$$\Delta G°_{ads} = \Delta G°_{mic} - N_A\Pi_{CMC}A_{CMC} \qquad (8)$$

$$\Delta S°_{ads} = \left(\frac{\partial\Delta G°_{ads}}{\partial T}\right) \qquad (9)$$

$$\Delta H°_{ads} = \Delta G°_{ads} + T\Delta S°_{ads} \qquad (10)$$

The free energy of adsorption, ΔG_{ads}, is calculated using Eq. (8), where Π_{CMC} is the surface pressure at the CMC or the maximum surface pressure, and A_{CMC} is the area per molecule at the CMC or the minimum area per molecule. Values of ΔG_{ads} (Table 3) are lower than ΔG_{mic}, because, as it is expected, is a more exergonic process. In this case, the standard state consists in one mol of surfactant adsorbed in a hypothetical monolayer on its minimum surface area, but a zero-surface pressure [16,39,43]. Therefore, $N_A\cdot\Pi\cdot A$ is the work energy to transfer one mol of surfactant form the monolayer to the micelle. This work energy increases slightly with the temperature and markedly with the degree of ethoxylation for the OPEs, according with the results obtained by Rosen et al. for 2-dodecyloxypoly (ethenoxyethanol)s [16].

Change of the entropy of adsorption, ΔS_{ads}, is calculated by the Eq. (8) and Fig. 4. Values of ΔS_{ads} are positive and increase with the degree of ethoxylation. This trend can be observed for the surfactants with the same alkyl chain at the same temperature FAE-$C_{10}E_3$ and FAE-$C_{10}E_6$ (Table 3). According to Rosen et al.[16], changes in the entropy for the OPE should be slightly higher for the same compounds. Our experimental results only corroborate this pattern for FAE-$C_{10}E_3$ and FAE-$C_{10}E_6$.

The enthalpy of adsorption, ΔH_{ads}, has been calculated by applying Eq. (10) (Table 3). As expected, the results show the increase of the ΔH_{ads} with the degree of ethoxylation for FAE-$C_{10}E_3$ and FAE-$C_{10}E_6$ (Table 3), since adsorption at the interface entails a partial dehydration of the chain, which increase with a higher degree of ethoxylation [39]. On the other hand, surfactant having a longer alkyl chain FAE-$C_{12-14}E_{11}$ and FAE-$C_{16-18}E_{11}$ showed lower values of ΔH_{ads}. The increase in the length of the hydrophobic chain enhances the efficiency of adsorption of the surfactant at the interface making it more thermodynamically favourable [39].
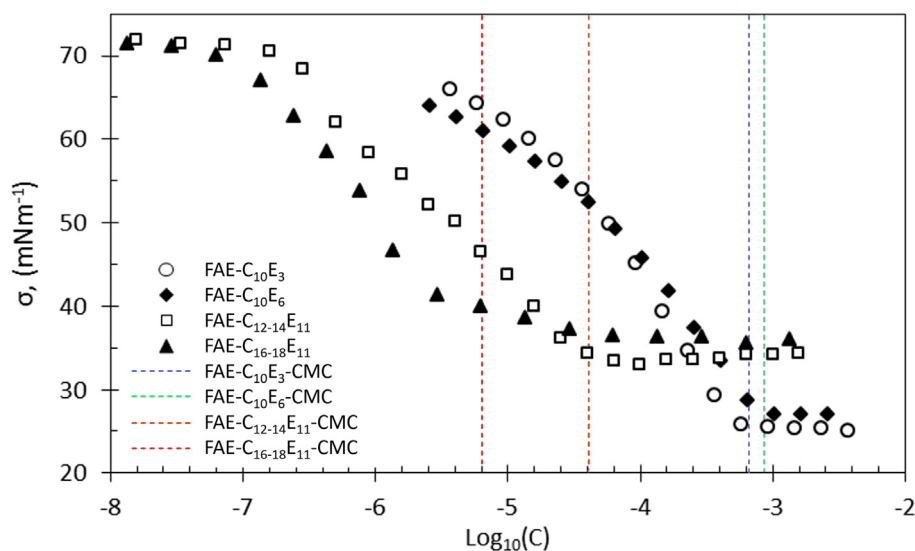
Table 3
Thermodynamic parameters of micellization and adsorption.

	T, °C	Ln(x_{CMC})	$\Delta G°_{mic}$, kJ mol^{-1}	$\Delta H°_{mic}$, kJ mol^{-1}	$\Delta S°_{mic}$, J mol^{-1} K^{-1}	$\Delta G°_{ads}$, kJ mol^{-1}	$\Delta S°_{ads}$, J mol^{-1} K^{-1}	$\Delta H°_{ads}$, kJ mol^{-1}
FAE-$C_{10}E_3$	25	−11.343	−28.118 ± 0.690	6.868 ± 0.169	117.3 ± 0.9	−38.615 ± 1.059	161.5 ± 4.4	11.940 ± 4.740
	40	−11.458	−29.832 ± 0.362			−41.143 ± 0.386		
	60	−11.633	−32.222 ± 0.341			−44.278 ± 0.419		
FAE-$C_{10}E_6$	25	−11.095	−27.502 ± 0.735	10.875 ± 0.291	128.7 ± 1.0	−39.536 ± 1.091	185.1 ± 5.1	15.170 ± 5.432
	40	−11.286	−29.383 ± 0.362			−43.173 ± 0.386		
	60	−11.555	−32.004 ± 1.107			−48.017 ± 1.188		
FAE-$C_{12-14}E_{11}$	25	−14.122	−35.006 ± 1.022	15.664 ± 0.457	169.9 ± 1.5	−46.357 ± 1.555	169.6 ± 5.7	6.735 ± 6.150
	30	−14.198	−35.784 ± 0.950			−47.288 ± 1.005		
	40	−14.336	−37.325 ± 0.548			−49.648 ± 0.588		
	50	−14.631	−39.310 ± 0.840			−51.577 ± 0.867		
	60	−14.756	−40.873 ± 0.653			−51.918 ± 0.687		
FAE-$C_{16-18}E_{11}$	25	−15.971	−39.589 ± 1.675	23.506 ± 0.994	211.6 ± 2.7	−48.768 ± 2.114	152.9 ± 6.6	−0.9085 ± 7.263
	40	−16.421	−42.754 ± 4.508			−50.026 ± 3.159		
	60	−16.967	−46.995 ± 0.495			−54.026 ± 0.524		

Fig. 3. Gibbs isotherms at 25 °C for the FAEs.
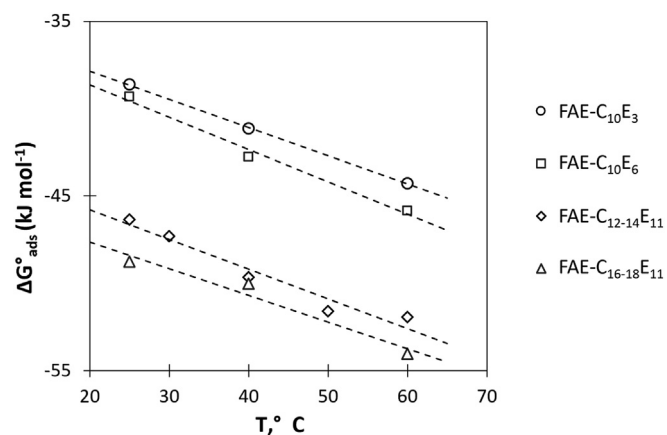

Fig. 4. ΔG°_{ads} vs T for the calculation of ΔS°_{ads}.

4. Conclusions

In this work we studied the effect of the structural parameters and temperature on the surface tension and thermodynamic functions of commercial FAEs. We found that CMC decreases with the increase of the length alkyl chain, and the decrease of the degree of ethoxylation due to the higher hydrophobic character of the surfactant molecule. In addition, the surface excess concentration, Γ_{max}, is higher when the alkyl chain is longer and the minimum area per molecule (A_{min}) decreases inversely. The opposite occurs when the degree of ethoxylation augments. On the other hand, there are two opposite effects on the A_{min} when temperature increase: for FAEs with shorter alkyl chain, A_{min} increases due to a thermal agitation effect, and for the FAE with the longest alkyl chain A_{min} decreases due to a dehydration effect.

Regarding the thermodynamic functions, negative values for ΔG_{mic} confirm the spontaneous aggregation of the molecules. Enthalpy changes of micellization ΔH°_{mic} increase as the alkyl chain is longer and the degree of ethoxylation is higher. Likewise, the ΔS_{mic} increase with the length of the hydrophobic chain and it has a slight increment with the degree of ethoxylation. In case of the energy of absorption, ΔG_{ads}, the values obtained are lower than the energy of micellization ΔG_{mic}, because as it is expected,

is a process more exergonic process. ΔG_{ads} increases slightly with the temperature and markedly with the degree of ethoxylation. Finally, change of the entropy and enthalpy of adsorption (ΔS_{ads} and ΔH_{ads}) showed an increase with the degree of ethoxylation. Data obtained in this study for commercial FAEs surfactants agree with literature data from other authors for pure FAE. Nevertheless, the determination and analysis of surface properties, as CMC becomes more difficult due to the mixtures of the oligomers present in the commercial surfactant.

CRediT authorship contribution statement

José Francisco Rincón-Romero: Investigation, Writing - original draft. **Francisco Ríos:** Data curation, Supervision, Writing - original draft, Writing - review & editing. **Antonia Reyes Requena:** Conceptualization, Supervision. **Germán Luzón-González:** Visualization, Data curation. **Ana Isabel García-López:** Conceptualization, Supervision.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2023.121396.

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