



Original Research Article

Micellar Properties of a Foam Extinguishing Agent Based on Fluorocarbon Non-Ionic and Hydrocarbon Cationic Surfactants in a Mixed System

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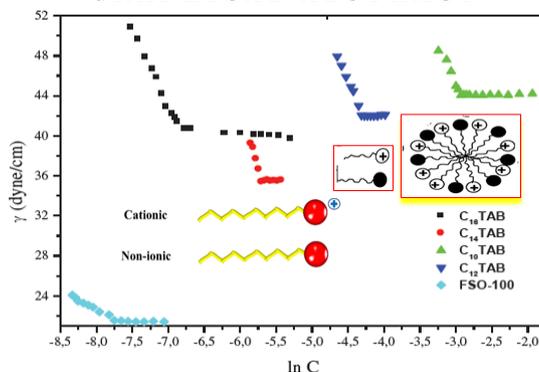
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ABSTRACT

Fluorocarbon surfactant containing perfluorinated is the key component in aqueous film-forming foam extinguishing agent (AFFF), although its environmental concern is becoming more evident. In order to reduce the amount of this fluorinated surfactant while maintaining the micellar and surface properties, mixed systems based on fluorocarbon non-ionic and hydrocarbon cationic surfactants have received more attention with the aim of decreasing the environmental hazard of perfluorinated surfactants. The micellar properties, surface activity, and synergistic behavior of mixture systems of non-ionic fluorocarbon surfactant (undecafluoro-n-pentyl-decaoxyethylene ether (C₅F₁₁EO₁₀)) and three cationic surfactants with different alkyl chain (n-alkyltrimethylammonium bromides: 10 (DTAB), 14 (TTAB) and 16 (CTAB)) are investigated. The effect of cationic chain length on physicochemical and thermodynamic properties are evaluated. Results obtained highlight a remarkable effect of reduction of the critical micellar concentration (CMC) with an increase in length of the chain; this effect is due to high the increase of hydrophobicity with the increase of the chain length. Furthermore, mixed system (C₁₀TAB-C₅F₁₁EO₁₀) has optimal synergy for minimizing surface tension. Also, the case of mixed micelles solutions rich on C₅F₁₁EO₁₀, CMC has less steric hindrance among hydrocarbons and fluorocarbons, which are more or less similar to carbon chains. Finally, the C₅F₁₁EO₁₀ suggests a synergy of CMC reduction with intermediate activity between C₁₆TAB-C₅F₁₁EO₁₀ and the C₁₀TAB-C₅F₁₁EO₁₀. Mixed systems (Foam) containing short-chain fluorotelomers tend to promote fewer toxic alternatives.

GRAPHICAL ABSTRACT



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Introduction

As surfactants are present in liquids and solvents, they strongly influence their surface chemistry. Physicochemical properties of such agents such as viscosity, surface tension, and surface tension of liquids as well as chemical reactions that take place within the solvents are altered by the presence of these agents at a liquid interface [1]. Surfactants are therefore used in a wide range of chemical reactions as catalysts. In a certain reaction state (critical micelle concentration CMC), surfactants form nano-aggregates called micelles when they are sufficiently concentrated. Micelles may be used for solubilization, emulsification, drug delivery, and possibly even for the development of many food and skin care products [2, 3]. Fluorocarbon surfactant (FS) has a hydrophilic head and a fluorinated tail. It is one of the most important special surfactants due to their excellent properties, such as a good stability [4], high surface activity [5], ability to lower the surface tension of water, and synergetic effect [6]. Also, FS is frequently used in industrial applications where traditional surfactants are insufficient [7].

FS is a key ingredient in aqueous film-forming foam extinguishing agent (AFFF) [8]. In fact, fires caused by flammable liquids or gases pose a serious threat to life because they cannot be extinguished easily by water, which can instead cause the fire to spread [9]. AFFFs are effective at suppressing fires because they form an aqueous layer which keeps burning material from contacting oxygen and cools it [9]. Also, because of their outstanding performance as film formers, high surface activity, oleophobicity, and vapor sealants, FS have been widely used as components in many products [10]. FS based on perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have also been widely used in conventional processes of fluoropolymers manufacture [11]. However, these small molecules, containing fluorinated segments, can still contaminate environment due to their great stability and hence make it difficult to degrade in a long-term [12]. It is extremely hard to substitute the fluorocarbon surfactant directly [13]. In recent years, it has become necessary to

reduce the amount of fluorocarbon surfactant by increasing research on surfactant mixtures, while also developing inherently safer alternatives, protecting and enhancing human health as well as the environment. Moreover, the toxicity and adverse effects of fluorinated processing aids on humans and the environment are serious concerns, and it is therefore challenging to develop alternatives that have low environmental effects, are non-accumulative, and degrade rapidly [14]. At the moment, two effective methods reduce the number of carbon atoms in the perfluorocarbon chain to C₈-C₁₀ and branching the perfluorocarbon chain [15-17]. The majority of these studies, however, have focused mostly on theory, with little attention being paid to application performance.

As a result, it was critical to select and prepare fluorocarbon surfactants with excellent performance and low cost in order to make AFFF widely used. The most effective method is to study the mixing of fluorocarbon surfactants and hydrocarbon surfactants in order to reduce the dosage of fluorocarbon surfactants in the actual formulation [18, 19]. Research has recently focused on the mixtures of fluorocarbons and other surfactants in order to develop a chemical substitute for fluorocarbon surfactants [20, 21]. Also, stronger synergistic interaction effect in mixtures has been reported. Thus, the mixed system of fluorocarbon and hydrocarbon surfactants have been extensively used in many industrial fields, such as wetting agents, firefighting and detergents [19, 22].

In this study, we have focused on the effect of chain length of hydrocarbon on the properties of synthetic binary mixture of hydrocarbon-fluorocarbon, including surface properties, aggregation behavior and the micelles shape and size. This study can provide guidance for the scientific application of mixed system of fluorocarbon and hydrocarbon surfactants by optimizing the length of the hydrocarbon surfactant chain which gives the most synergistic effect.

Materials and Methods

Synthesis of mixed surfactant with different chain alkyl

In this study a series of cationic surfactants alkyltrimethylammonium bromides (RTAB) and different alkyl chain length (10, 14 and 16 carbon atoms) were used including Decyltrimethylammonium bromide (DeTAB); tetradecyltrimethylammonium bromide (TTAB; $C_{14}H_{29}N^+(CH_3)_3, Br^-$) and hexadecyltrimethylammonium bromide (CTAB; $C_{16}H_{31}N^+(CH_3)_3, Br^-$), which were purchased from Aldrich with 99% of purity. The FSO100 ($C_5F_{11}-(OCH_2CH_2)_{10}-OH$, (abbreviated $C_5F_{11}EO_{10}$ in what follows) was provided from Zonyl company. Solvent used was deionized water with a surface tension of 69.9 mN/m and a specific conductivity of 3 $\mu S/cm$ at 25 °C. All used surfactants were soluble in aqueous medium at temperatures below 25 °C. Solutions (surfactant/ water) were prepared at room temperature, by mixing stock solutions of C_nTAB (10 mM) and FSO100 ($C_5F_{11}EO_{10}$) (5 mM) in varying proportions. In brief, a volume of 50 ml of mixed system was prepared by mixing two volumes of concentrated solutions of each surfactant (cationic and non-ionic) according to the desired fraction of FSO-100 at each step (0.2, 0.4, 0.6 and 0.8).

For determination of CMC, the measurements were performed on concentrated samples (stock solutions) then diluted successively. Temperature was stabilized at 25 °C during all manipulations using a thermostatic bath.

Method to Surface Tension Measurement

The measurements of surface tension (γ) were carried out using a tensiometer based on Du Noüy method and operates over a range of values ranging from 0 to 90 dyn / cm with accuracy of 0.05 dyn/ cm. The platinum ring is immersed in the solution with an ascending force applied to it. The force required to tearing of the ring is equal to the surface tension that can be read directly on the calibrated device [19, 23].

Theoretical background

Clint Model

For free monomers of an ideal mixtures of two surfactants and assuming a coefficient of unit activity, CMC of mixed surfactants can be predicted using Clint's model, given by following relation (1):

$$\frac{1}{CMC} = \frac{X_1}{CMC_1} + \frac{1-X_1}{CMC_2} \quad (1)$$

CMC_1, CMC_2 are the CMC values of both pure components and X_1 is the molar fraction of surfactant 1 in the mixture.

In addition, according to the ideal state model, the mole fraction of surfactant 1 in the ideal mixed micelle (X_1^m) was estimated using the following formula (2):

$$X_1^m = \frac{X_1 CMC_2}{CMC_1 + X_1(CMC_2 - CMC_1)} \quad (2)$$

Rubingh Model

This descriptive model enables a good understanding of micellar properties and superficial based on parameters as the interaction parameter within the micelles (β^m) through a simplified approach of the mixing non-ideality [24]. As for the activity coefficient, the CMC of the mixture is given by an equation similar to Clint's but incorporating the activity coefficients of surfactants 1 and 2 (f_1, f_2) in the mixed micelle:

$$\frac{1}{CMC} = \frac{X_1}{f_1 CMC_1} + \frac{1-X_1}{f_2 CMC_2} \quad (3)$$

the interaction parameter β is given by:

$$\beta = \frac{\ln\left(\frac{X_1 CMC}{(CMC_1 X_1^m)}\right)}{(1-X_1^m)^2} \quad (4)$$

the mole fractions of the two surfactants in the mixed micelle are calculated by solving the following transcendental equation:

$$\frac{\left(\frac{X_1^m}{1-X_1^m}\right)^2 \ln\left(\frac{X_1 CMC}{X_1^m CMC_1}\right)}{\ln\left(\frac{(1-X_1)CMC}{(1-X_1^m)CMC_2}\right)} = 1 \quad (5)$$

Maeda model

Maeda's model proposed in 1995 [25] has explicitly introduced chain-chain interactions in addition to head-to-head interactions in a mixed ionic/ non-ionic surfactant system. This model is based on the phase separation model; micellization free energy ΔG_{mic} is given by:

$$\Delta G_{mic} = RT(\beta_0 + \beta_1 X_1^m + \beta_2 (X_1^m)^2) \quad (6)$$

$$\beta_0 = \ln \text{CMC}_2 \quad (7)$$

β_2 signifies the head-head electrostatic interaction, it is equivalent to β in the Rubingh theory. It is related to β_1 by:

$$\beta_1 = \ln\left(\frac{\text{cmc}_1}{\text{cmc}_2}\right) - \beta_2 \quad (8)$$

β_1 represents the chain-chain interaction and is associated with the change in the standard free enthalpy, accompanying the replacement of a non-ionic molecule by an ionic molecule.

Results and discussion

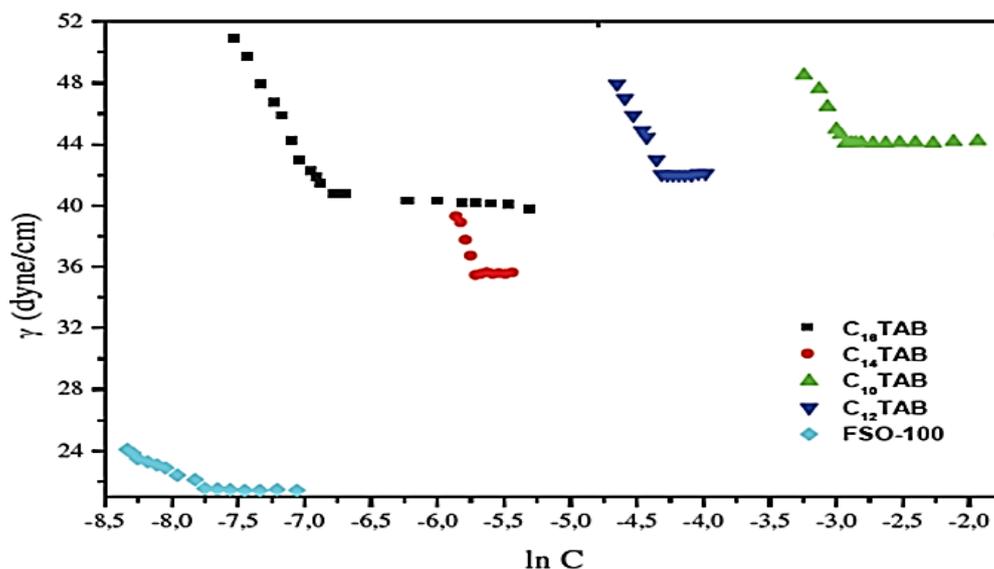


Figure 1: Surface tension as a function of the logarithm of the concentration of different surfactan

Table 1: The CMC values for systems: FSO-100 / HTAB, FSO-100 / TTAB, FSO-100 / DTAB, FSO-100 / DeTAB

X[fso-100]	CMC _(FSO-100/HTAB) mM	CMC _(FSO-100/TTAB) mM	CMC _(FSO100/DeTAB) mM
X=0	1.070	3.356	53.510
X=0.20	0.128	0.390	0.340
X=0.4	0.137	0.250	0.362
X=0.6	0.148	0.240	0.403
X=0.8	0.143	0.180	0.360

Pure surfactants

Figure 1 shows that the nonionic surfactant FSO-100 has less CMC value of γ : 21 dyne/cm. Indeed, the fluorine atoms increase the hydrophobic effect and decrease the CMC, compared with their value for cationic surfactant. Additionally, no charge on the hydrophilic head, reduce electrostatic repulsion and promoted the formation of micellar aggregates at low CMC values. Results based on CMC values (Figure 1) for alkyl ammonium bromides are better and in accordance to other studies.

Mixed systems

Critical micelle concentration CMC

Measurement of surface tension of prepared mixtures of CnTAB/FSO-100 under different molar fraction of 20%, 40%, 60% and 80% of total concentration are represented in Figure 2. The CMC values obtained for all mixtures under different fractions are regrouped in Table 1.

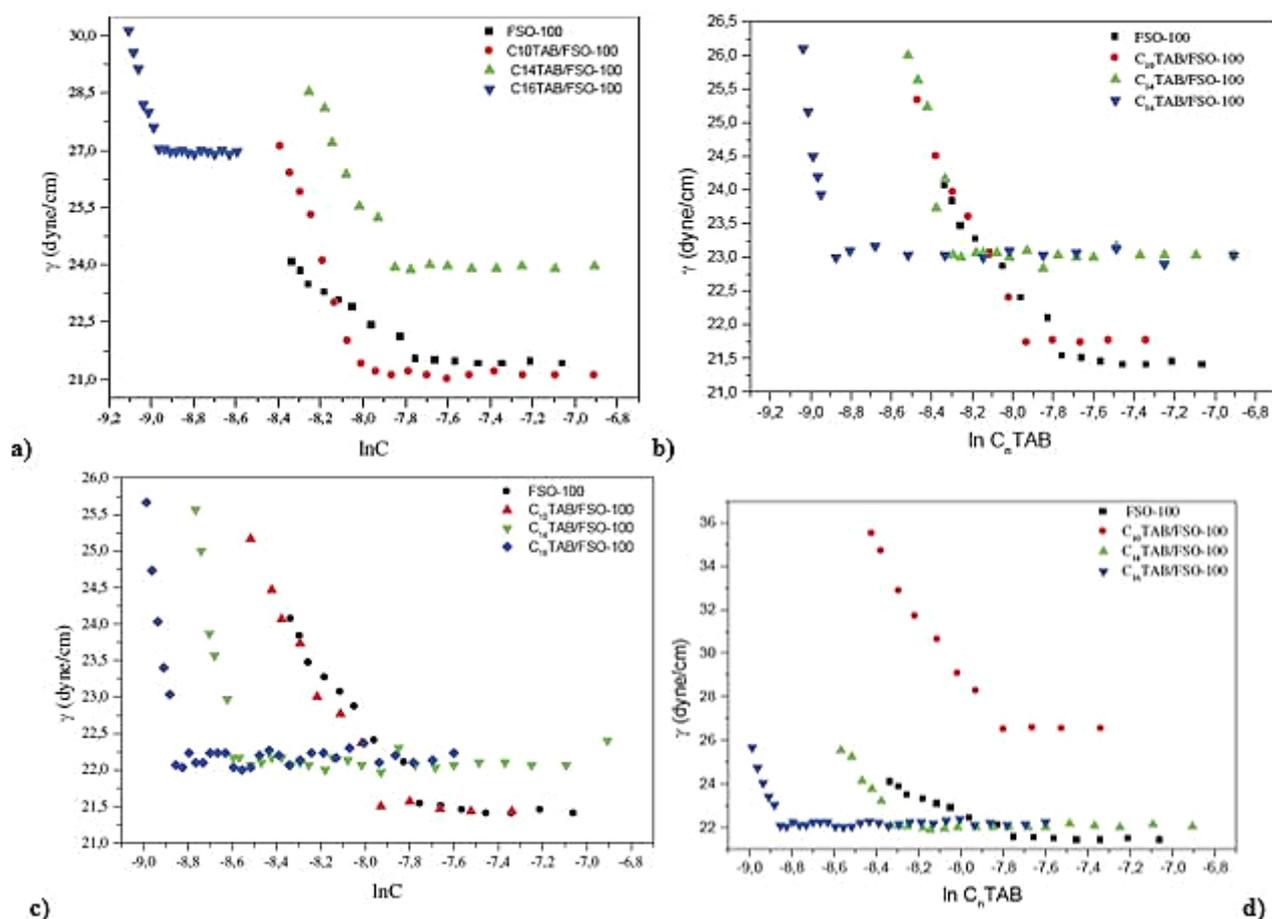


Figure 2: Surface tension as a function of the logarithm of the total surfactant concentration [mM] for pure FSO100 and the 3 systems DeTAB / FSO-100, CTAB / FSO-100, TTAB / FSO-100 with a), cosurfactant molar fractions of 0.20. b) of 0.40, c) of 0.60, d) of 0.80

As shown in Figure 2, the CMC of the different synthesis mixtures is lower than that of pure surfactant, indicating the presence of synergy on micelle formation (type I). Except for the case of a 20 percent ratio, we found a decrease in CMC for FSO-100/CnTAB depending on the length of the hydrocarbon chain of the added cationic surfactant. This decrease in CMC can be explained by the effect of the hydrophobe on molecular aggregation formation. However, for a 20 percent FSO-100 ratio, the CMC of mixture FSO-100/C10TAB is lower than that of mixture FSO-100/C10TAB. It has also been observed that the decrease in CMC values of cationic surfactant (CnTAB) in the presence of non-ionic surfactant may be due to incorporation of the lowest proportion, in this case 20%. Regardless of the length of the CnTAB chain, few enrichments are

observed for the CMC in the rest of the ratios mixture.

Interfacial pressure

Figure 3 shows the variation of superficial pressure π_{CMC} as a function of fluorocarbon surfactant mole fraction $X_{FSO-100}$. π_{CMC} of adsorbed film is defined as the difference between the surface tension of pure water*0 and the surface tension of the solution at CMC:

$$\gamma_{min} (\pi_{CMC} = \gamma_0 - \gamma_{min}).$$

According to the results obtained, cationic FSO-100 is more efficient than pure surfactant CnTAB due to its combination with nonionic FSO-100. The effect is most evident when going from 0 to 20% then remaining relatively constant, especially for C10TAB/FSO-100 where the surface pressure is

optimum at $X_{FSO}=0.2$ as this indicates a synergistic effect.

As shown [Figure 3](#), the data obtained for interfacial pressure indicate a possibility to plot the superficial pressures π_{CMC} versus $X_{FSO-100}$. Also, the π_{CMC} of adsorbed film (formed on the

surface) is defined as the difference between the surface tension of the pure water γ_0 and of the solution CMC:

$$\gamma_{min} (\pi_{CMC} = \gamma_0 - \gamma_{min})$$

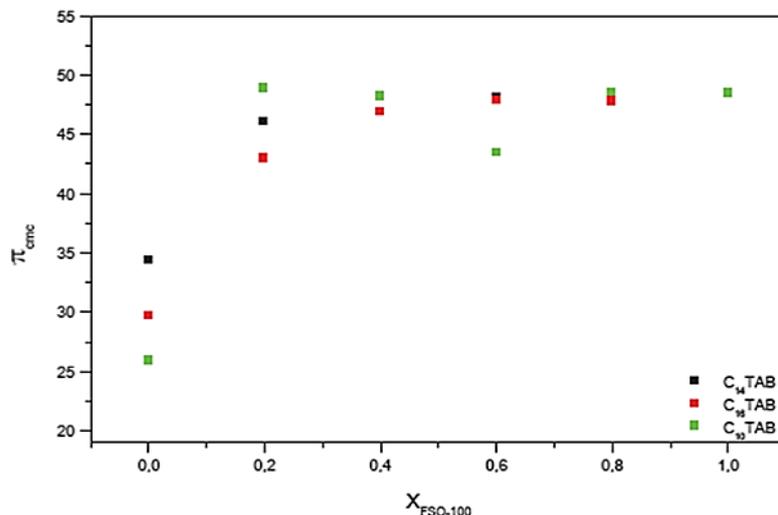


Figure 3: Influence of interfacial pressure of the adsorbed film for the three mixed systems as a function of the FSO-100 proportion

Clint model

The theoretical results obtained of CMC for ideal mixture according to Clint Model, were compared with experimental results of CMC from tensiometer measurements, of three mixtures containing the FSO-100 with 20 to 80% proportion of composition. As shown in [Figure 4](#),

systematic negative deviation from origin is represented by theoretical curve of variation of CMC of $X_{FSO-100}$ for all mixtures with all proportion. This result may be due to a predominant interaction of attractive type in micellar systems between FSO-100 molecules and each cationic surfactants for all proportions and regardless of length of CnTAB chain (type I of synergy) [26].

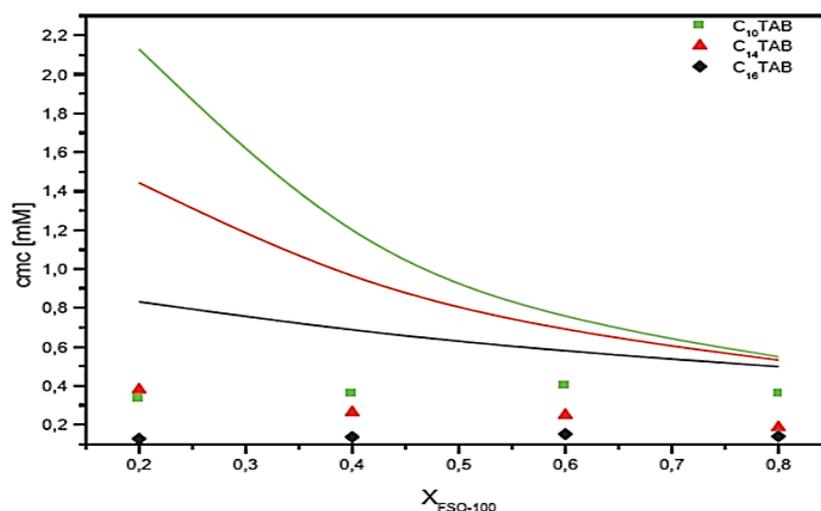


Figure 4: Experimental and theoretical critical micellar concentrations (curves) (Clint model) versus $X_{FSO-100}$ for the three FSO-100 / $C_{16}TAB$ systems, FSO-100 / $C_{14}TAB$ and FSO-100 / $C_{10}TAB$

We observed that the deviation of three systems is important for the lowest value of $X_{FSO-100}$, and

for their highly values close to ideality. [Figure 5](#) shows the variation of micellar composition of

X_{CnTAB} as a function of total CnTAB content using Clint model. Therefore, the results indicate that micelle mixed system of C₁₆TAB/FSO-100 is richer in cationic surfactant, but C₁₀TAB/FSO-100 mix is less rich. These results are valid, hypothesizing an

ideal mixing behaviour. This is not the case for the systems studied here as we have just shown. These data will serve as a baseline for analysing the results on the next section.

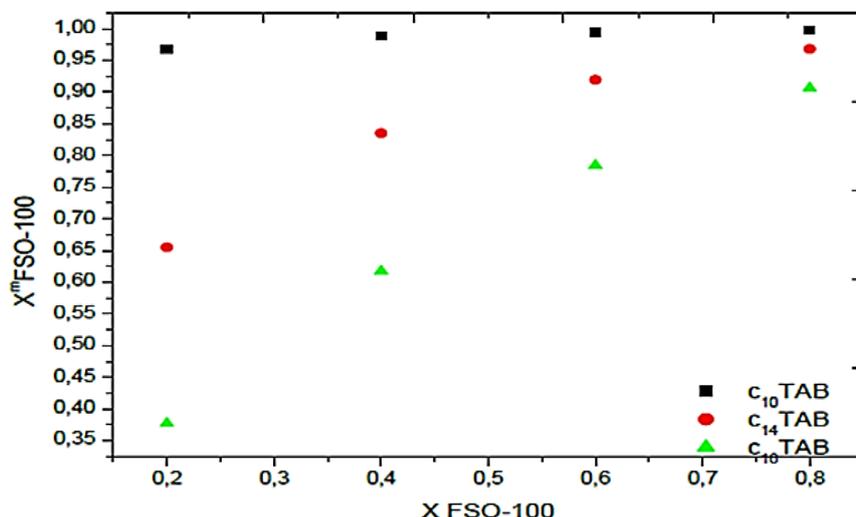


Figure 5: Hypothetical micellar composition in FSO-100 according to the Clint model (ideal mixture)

Rubingh Model

Table 2 groups the different values of β^m , and the enthalpy free of excess micellization for all mixed systems as a function of $X_{\text{FSO-100}}$.

We can see from Figure 6 the variation of β^m according to X_{CnTAB} in all proportions. The negative values of β^m for all mixed systems CnTAB / FSO-100, may be explained by the presence of (9)

interaction with attractive type and synergistic effect for all mixture. These experimental results are consistent with those of Rosen and Col [27], which indicate a synergism type (1), since the following inequalities are verified.

$$\begin{cases} \beta^m < 0 \\ \left| \ln \frac{c_1^0}{c_2^0} \right| < |\beta^m| \end{cases}$$

Table 2: Thermodynamic parameters obtained from the Rubingh model for different values of $X_{\text{FSO-100}}$ for FSO-100 / HTAB systems, FSO-100 / TTAB, FSO-100 / DeTAB

$X_{\text{FSO-100}}$	0.8	0.6	0.4	0.2
X_{DeTAB}^m	0.37	0.30	0.22	0.18
X_{TTAB}^m	0.46	0.40	0.34	0.31
X_{CTAB}^m	0.53	0.47	0.42	0.37
β_{DeTAB}^m	-10.7	-8.7	-7.2	-7.2
β_{TTAB}^m	-5.5	-5.9	-5.6	-7.2
β_{HTAB}^m	-7.6	-6.5	-5.9	-6.6
ΔG_{mic}^E (kJ/mol) DeTAB	-6.1	-3.7	-3.7	-2.6
ΔG_{mic}^E (kJ/mol) TTAB	-3.4	-3.5	-3.1	-3.8
ΔG_{mic}^E (kJ/mol) HTAB	-4.7	-4.0	-3.5	-3.8

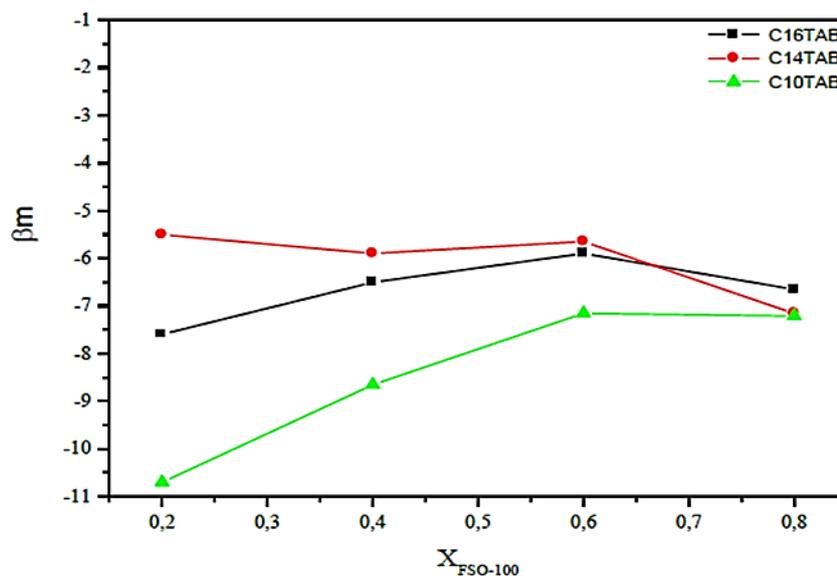


Figure 6: Variation of interaction parameters β^m to X_{CnTAB} according to the model of the regular solution. For the three systems (a) FSO-100 / TTAB (b) FSO-100 / DTAB (c) FSO-100 / DeTAB

In comparison to the $C_{14}TAB$ and $C_{16}TAB$ systems, interactions are increasingly strong for HTAB, except for the 20% case in $CnTAB$. These interactions are expected to be caused by the significant hydrophobic effect present in synergistic interactions in a non-ionic-cationic mixed system. Similar results reported by Basu Ray *et al.* [28], where average interaction for MEGA-10/ $C_{16}TAB$, MEGA-10/ $C_{14}TAB$, and MEGA-10/ $C_{12}TAB$ mixed systems were -1.52, -0.88, and -0.65, respectively; hydrophobic effect is at the origin of this behavior. The deviation from ideality, on the other hand, increases as the length of the hydrophobic chain increases.

In contrast to previous behavior, the $C_{10}TAB$ / FSO-100 system appears with a particular behavior. In fact, strongest interaction was observed for most negative value of β^m (-10.7 for 20% in FSO-100). These values are comparable to those reported for similar systems [25, 29], where similarly the presence of strong attractive interactions entering molecules have been observed. Both surfactants linked with a powerful interactions effect. In particular, with a 20% FSO-100 Type II synergy, the surface tension at the CMC is lower than pure surfactants. Figure 7 shows the variation in X_{CnTAB}^m as a function of X_{CnTAB} .

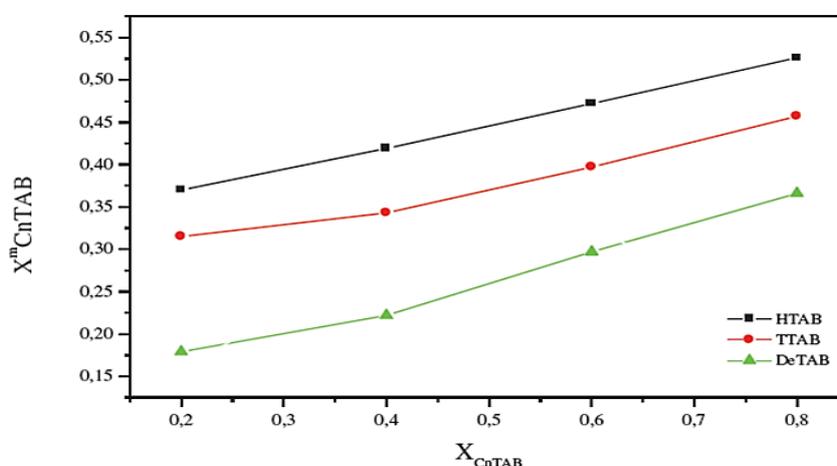


Figure 7: Variation of X_{CnTAB}^m according to the model of the regular solution as function as X_{CnTAB} For the three systems (a) FSO-100 / TTAB (b) FSO-100 / DTAB (c) FSO-100 / DeTAB

As shown in Figure 7, the similar behavior can be observed for three mixed systems examined, and a progressive enrichment of micelle CnTAB with increasing of proportion in CnTAB. we noted for a given percentage, mixed micelle is richer of cationic tension active with increasing of chain length. Moreover, for all mixed systems except in 80% in C16TAB, where it is rich in FSO-100 (XCnTAB), this behavior is due to micellization of non-ionic surfactant as easier (at lower CMC) than that for CnTAB; similar behavior has been observed by Basu Ray *et al.* [30].

The values of excess free enthalpy of mixed micellization ΔG_{mic}^E have negative values as

reported in Figure 8. These results indicate that mixed micellization favors ΔG_{mic}^E compared with each of the two pure components, for all systems and under all proportions.

For the range of 20 to 40% in FSO-100, ΔG_{mic}^E is more negative when increasing the chain length of cationic surfactant (cases of C₁₄TAB and C₁₆TAB). Except for the case of C₁₀TAB, a negative value of ΔG_{mic}^E was observed. Result showed a high synergy for all systems particularly those rich in FSO-100, where spontaneity of formation on mixed micelles increases with the length of hydrocarbonic chain, and the gap height is enriched with FSO-100.

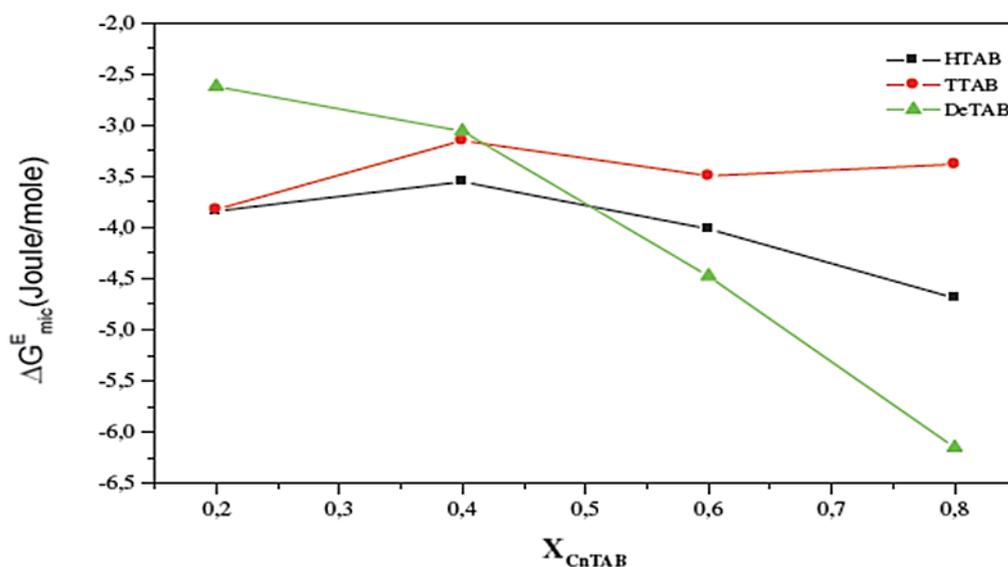


Figure 8: Variation of excess free enthalpy of micellisation of mixtures

The obtained results based on Rubingh Model indicate that aggregates are strongly rich in C₁₀TAB, due to strong attractions inter-molecular. The mixed C₁₄TAB/FSO-100 exhibits similar behavior; however, the mixed C₁₆TAB/FSO-100 with 20%FSO-100 is an ideal mixed surfactant, due to their composition richer on cationic surfactant. Thus, for this fraction, the mixed micelles are enriched in FSO-100. For the other fractions, the behavior is similar to that of the other mixtures.

Figure 9 presents the deviation percent of $X_{FSO-100}^m$ from ideality. we observed an important deviation for the mixture C₁₀TAB/FSO-100 at 20%

and less important one for mixture C₁₆TAB/FSO. For the system with proportion more than 40% in FSO-100, the different deviations meet more or less upward (C₁₄ and C₁₆) or downward (C₁₀).

This behaviour could be related to the CMC values of the pure surfactant, which is very different (case of C₁₀TAB compared with FSO-100), that will cause a very important change in the properties of the mixture. On the other hand, if the CMC of the two pure surfactants have similar values, the non-ideality will be accentuated with the increase of the fraction of the most effective surfactant (FSO-100) [31].

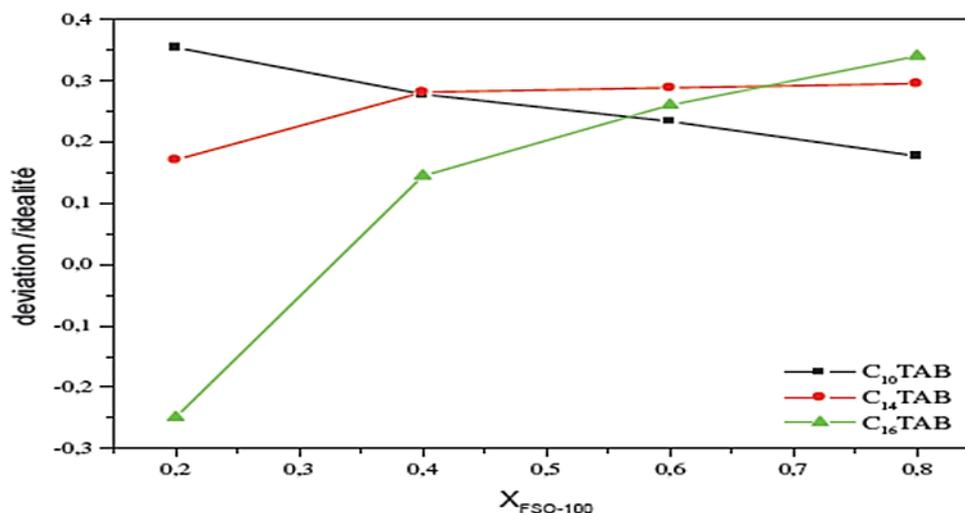


Figure 9: Deviation of micellar composition from ideality as a function of XFSO-100 according to the Rubingh model

Maeda model

The different interaction parameters calculated according to equation (6) for a proportion of 20% FSO-100 are regrouped in Table 3.

Table 3 clearly shows that the value of β_1 is associated with the variation in free enthalpy when an ionic surfactant is replaced by a non-ionic surfactant in the micelle. The most negative value was observed in the case of FSO-100/DeTAB system. This result is in good agreement with

previous observations. In fact, this behavior is related to the greater proximity of hydrocarbon and fluorocarbon chain lengths resulting in increased of insertion of DeTAB chains (14 Å) into FSO-100 (8Å) non-ionic surfactant chains in the mixed micelle.

Thus, high disparity between chain lengths induces weaker attractive interactions, also indicating that steric chain factor plays a major role in mixed micellar formation.

Table 3: The Maeda parameter values for the three FSO-100 / TTAB, FSO-100 / DTAB and FSO-100 / DeTAB systems

	DeTAB/FSO-100	TTAB/FSO-100	HTAB/FSO-100
β_0	-7.73	-7.73	-7.73
β_1	-13.23	-8.08	-7.54
β_2	8.43	6.05	6.65

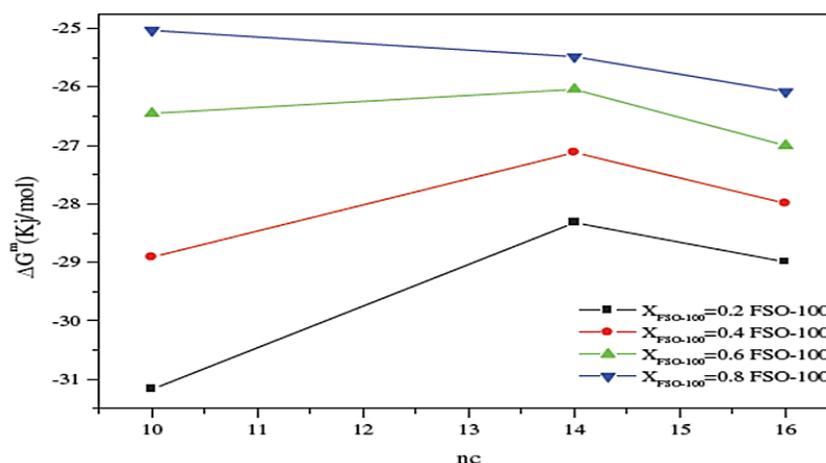


Figure 10: Variation of the free melting enthalpy (according to the Maeda model) according to the length of the chain for the three FSO-100 / TTAB, FSO-100 / DTAB and FSO-100 / DeTAB system

Figure 10 illustrates the variation of ΔG^{mic} based on the length of the cationic surfactant chain at different proportions of CnTAB, for each of three mixtures and at different values of XFSO-100. Negative values of ΔG^{mic} clearly indicate that spontaneity of mixed micellization is most important for the shortest cationic surfactants of FSO-100 mixtures ($X_{\text{FSO-100}} < 50\%$). As we have already mentioned, the opposite results obtained for mixtures richer in FSO-100 with the longest cationic compound show greater spontaneity for the formation of mixed micelles.

Predictions of the micellar form

As is known for surfactants and mixed surfactants, determining the packing of surfactants is more difficult than determining the packing of hard substances due to the soft nature of their boundaries. The basic packing parameter P is widely used to justify the geometrical shape of these structures, which is given as: $P = \frac{v}{al}$; where: l is the length of the hydrophobic chain of the surfactant, a is the area per polar head and v is the volume of the hydrophobic chain [32]. In the case of a mixed system, the effective packing parameters obtained according to the following

equation (10), which has been reported by several recent works [33-35]:

$$P = \frac{(\sum v_i X_i^m)}{(\sum a_i X_i^m) (\sum l_i X_i^m)} \quad (10)$$

where l is the length of the hydrophobic chain, a denotes the surface of the head and v signifies the volume of the hydrophobic chain

Tanford formulas are also used in this work to calculate the lengths and volumes of the chains of all surfactants studied [36]. Polar head sections were deduced directly from tensiometry data from the Gibbs isotherm represented by equation [37].

Based on obtained results data of packing parameter summarized in Table 4, the micellar aggregates of TTAB/FSO-100 and HTAB/FSO-100 mixed systems are spherical shape with diameters of 40 nm, just as the type of geometry observed for pure cationic surfactants. On the other hand, the stacking parameter value of the DeTAB/FSO-100 is greater than 0.3, which indicates their preferred cylindrical shape. This value is indeed intermediary between that of DeTAB (spherical micelles) and that of FSO-100 (vesicular aggregations).

Table 4: Values of the effective packing parameter of mixed systems for different proportions in FSO-100

XFSO-100	DeTAB/FSO-100	TTAB/FSO-100	HTAB/FSO-100
20%	0.36	0.16	0.15
40%	0.36	0.21	0.16
60%	0.36	0.21	0.16
80%	0.36	0.22	0.16

Conclusion

To reduce the dose of fluorinated surfactant, we have improved the properties of surfactant mixtures to be considered as safer alternatives for protecting human health and the environment. A series of experiments on the physico-chemical characterizations of pure hydrocarbon cationic surfactants with different chain lengths, such as (DeTAB), (TTAB), and (HTAB), mixed with non-surfactant fluorinated ionic undecafluoro n-pentyl decaoxyethylene (FSO-100) were carried out in this work. The following are the major findings:

- i. A systematic decrease of CMC for the three mixed systems studied compared with pure surfactants, reflecting an increasing synergistic effect with increasing chain length.
- ii. The mixed micellar system favours excessive incorporation of the CnTAB molecules (C_{10} TAB and C_{14} TAB cases).
- iii. According to Rubingh Model, the interactions between hydrophobic chains are attractive as the chain length decreases. This behaviour shows the existence of a powerful synergistic effect linked to a less steric hindrance between the hydrocarbon

- chains and fluorocarbon of the two surfactants, promoting greater spontaneity of micellar formation. (case of FSO-100/DeTAB system)
- iv. Based on the Clint and Rubingh models, the estimated micellar compositions of FSO-100 at various proportions in FSO-100 were assessed. The largest deviation is for C₁₀TAB/FSO-100 mixture at 20%, but for C₁₆TAB/FSO-100 mixture is less significant.
- v. Synergistic effect identified for C₁₀TAB/FSO-100 and evidence of strong chain interactions in this particular case.
- Finally, the predictions of mixed micellar forms indicate a cylindrical shape in the case of the FSO-100 / C₁₀TAB system and a spherical micellar form in the case of C₁₄TAB / FSO-100 and C₁₆TAB / FSO-100.

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Authors' contributions

All authors contributed toward data analysis, drafting and revising the paper and agreed to responsible for all the aspects of this work.

Conflict of Interest

We have no conflicts of interest to disclose.

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