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The aqueous Triton X-100 - Dodecyltrimethylammonium bromide micellar mixed system. Experimental results and thermodynamic analysis.

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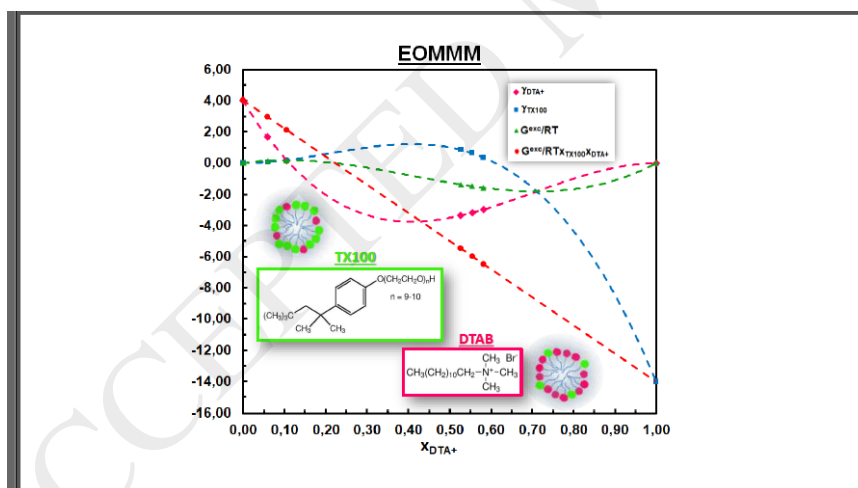
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Graphical abstract



ABSTRACT.

The micellization process of the aqueous mixed system triton X-100 (TX100) – dodecyltrimethylammonium bromide (DTAB) has been studied with a battery of techniques: surface tension, static and dynamic light scattering and ion-selective electrodes. Results have been also analysed with two thermodynamic procedures: the

Regular Solution Theory or Rubingh's model and the recently developed Equation Oriented Mixed Micellization Model (EOMMM). For $\alpha_{\text{DTAB}} \leq 0.40$ (α_{DTAB} : total molar fraction of the system without considering the water), the micelles are predominantly TX100 with scarce solubilized DTA⁺ ions, with TX100 acting as a nearly ideal solvent. In the range $0.50 \leq \alpha_{\text{DTAB}} \leq 0.75$, it seems that none of the components acts as a solvent. Above $\alpha_{\text{DTAB}} \approx 0.75$ there are noticeable changes in the size and electrophoretic mobility of the micelles. These phenomena have been interpreted in the light of the thermodynamic results and literature on some TX100-ionic surfactant mixtures. The case under study is an almost ideal but very asymmetric mixed surfactants system, what is very interesting in view of the very different nature and structures of the components.

Keywords: Triton X-100 – Dodecyltrimethylammonium Bromide – Mixed Micelles – Dynamic Light Scattering – Static Light Scattering – Electrophoretic mobility – Equation Oriented Mixed Micelle Model (EOMMM)

INTRODUCTION.

Molecules that have the property of adsorbing spontaneously onto the interface between two immiscible fluid phases are known as surfactants (surface active) [1,2]. They have two distinct parts on their chemical structure: one with affinity to polar solvents (head group) and the other with affinity to non-polar fluids (hydrophobic tail). At the so called Critical Micelle Concentration (CMC), surfactants self-assemble in bulk through a cooperative process to form aggregates called micelles. This concentration is the most important characteristic of surfactants since it gives rise to abrupt changes in many physical properties such as surface tension, light scattering, conductivity, etc. The measurement of those properties as a function of the surfactant concentration allows the determination of the CMC [1,2].

Surfactant solutions are applied in many technical areas such as enhanced oil recovery, detergency, pharmacy, food, cosmetics, flotation mineral recovery, and pesticides, among others[1,2]. In almost all the applications, surfactant mixtures are commonly used instead of pure surfactants since they have better performance (synergy) [1,3,4]. The mixtures may not only include different surfactants but also surfactants with polymers, polyelectrolytes, proteins, micro and nanoparticles [5,6]. These complex surfactant mixtures allow the design of systems with customized properties. For instance, mixtures of a cationic surfactant with a thermoresponsive anionic polyelectrolyte has been used for

stabilizing liquid foams whose stability responds to an external stimuli [7]. Formulations of mixtures of ionic and nonionic surfactants are frequently employed in detergency. The performance and the applicability of the mixtures of ionic with nonionic surfactants [3,8–13] has improved since the 1960's [8,9]. The inclusion of nonionic surfactants reduces some undesirable interactions between the ionic surfactants and the substrate, such as precipitation with polyvalent cations (mainly Ca^{+2} or Mg^{+2}) or the electrostatic adsorption of cationic surfactants to natural surfaces with negative charge. Cationic surfactants are added to nonionic surfactants due to their biocide properties, i.e. in germicide soaps [14]. Although the synergistic effects of surfactants mixtures have received great attention in view of the rational design of customized mixtures with desirable properties, there is still poor comprehension at a molecular level [14].

The determination of the composition of mixed micelles is a major problem since its value is fixed by the partition equilibria of the species between the aggregates and the surrounding medium. Since the mixed micelles composition is quite difficult to assess experimentally in a direct manner, it has to be estimated on the basis of a given thermodynamic model parameterized with physicochemical properties, mainly the CMC [1]. Among the mixtures composed by ionic and non-ionic surfactants, Carnero-Ruiz and Aguiar [15] have studied three mixed surfactant systems of TX100 (non-ionic surfactant) with cationic surfactants: hexadecyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB). Contrary to the TX100-CTAB and the TX100-TTAB mixed systems, the TX100-DTAB system could not be well modeled by the Regular Solution Theory (RST or Rubingh's procedure) [16]. The system TX100-DTAB differentiates in this and some other characteristics from the systems of TX100 with the other homologues studied in the above referred work, making it appealing for further research.

In the present work, the binary mixture TX100 and DTAB has been studied (see the surfactant structures in the Supplementary Information, SI, in Figure 1 SI). A battery of techniques has been applied: surface tension, static (SLS) and dynamic light scattering (DLS), electrophoretic mobility, and bromide-ion –selective electrode. The mixed micellization thermodynamics has been analyzed using two approaches: the Regular Solution Theory (RST, or Rubingh's approach) [16,17] and the Equation Oriented Mixed Micellization Model (EOMMM)[18]. Both procedures address the interactions in the aggregates and provide the mixed micelle compositions, the Gibbs free energies and the activity coefficients. On the other hand, we have experimentally obtained the composition of the mixed micelles at concentrations of about 10 times the CMC's. Although these values are not strictly comparable with those given by the thermodynamic approaches

which apply at the CMC, they allow us to evaluate the thermodynamic models and interpret the experimental findings.

2. MATERIALS AND METHODS

2.1 Materials

Dodecyltrimethylammonium bromide (DTAB) (>99%) and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100, TX100, $M_w = 647 \text{ gmol}^{-1}$) were obtained from Sigma-Aldrich and used as purchased. Stock solutions of DTAB and TX-100 were prepared using ultra-pure water (Milli-Q, Millipore system). Then, appropriate amounts of stock solutions were mixed and diluted to obtain the desired concentrations and compositions: α_{DTAB} (total mole fraction of DTAB without considering the solvent) = 0 (pure TX100), 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, and 1 (Pure DTAB). That is to say, $\alpha_{\text{DTAB}} + \alpha_{\text{TX100}} = 1$.

For dynamic light scattering experiments, the solutions were filtered three times through 220nm PDVF Millex filters from Millipore and let 24 hours to allow degasification.

2.2 Methods

All measurements were performed at 25.0 ± 0.1 °C.

Surface tension measurements were performed with a manual Krüss Tensiometer with a platinum duNoüy ring.

The refractive index increment at different concentrations was measured with a Phoenix Precision Instruments Co. differential refractometer with a controlled temperature cell jacket. The light source is a mercury lamp with filters to select the wavelength ($\lambda = 546$ nm). The apparatus was calibrated with KCl solutions.

Dynamic light scattering (DLS) and electrophoretic mobility measurements were performed with a Malvern Zeta Ziser Nano ZSP with a He-Ne laser ($\lambda = 633$ nm). Both DLS and electrophoretic mobility measurements were taken for total concentration of surfactant equivalent to ten times the CMC. DLS measurements relates the fluctuations in time of scattered light to the translational diffusion coefficient (D) [19], which can be related to the micelle hydrodynamic diameter, d_h (see details in the SI, point 2.1). The temperature was controlled (± 0.1 °C) using the instrument's own system.

The electrophoretic mobility (u) measurement is based in the laser Doppler velocimetry method with Phase Analysis Light Scattering (PALS) in order to obtain the electrophoretic velocity of the colloidal particles, v , and then the mobility, $u=v/E$ (E is the applied electric field). The zeta potential (ζ) can be calculated using u by means of the Henry equation and von Smoluchowsky approximation, $\zeta = \eta (u/\epsilon)$, where η and ϵ are the solvent viscosity and permittivity respectively. Each mobility value has been obtained as an average of several measurements, according to Malvern's proprietary "Quality Factor" statistical criterion [20]. The total charge of the micelle is obtained with:

$$q = 6\pi\eta Ru \quad (1)$$

R being the radius of the micelles.

The micellar mass was determined by static light scattering (SLS) with a Malvern Autosizer 4700 (laser OBIS Coherent 20 mW, $\lambda = 514$ nm) as a function of concentration and at a scattering angle of 90° , with a pinhole aperture of $300 \mu\text{m}$. The temperature was controlled by the instrument system combined with a Lauda Alpha thermostated circulating water bath. Static light scattering experiments in micelles were interpreted from the Rayleigh's equation applied to particles smaller than light's wavelength [21] (see details in the SI, point 2.2).

Potentiometric measurements were performed with a Metrohm bromide ion-selective electrode, with a saturated calomel electrode as reference. Electric potential was read with a Titrino titrator (Metrohm).

3. THEORETICAL MODELS

Clint's model[22], which bases on a simple phase separation model for micellization, relates the critical micelle concentration of a surfactant mixture, CMC_M , with the mole fractions in the mixture of components (α_i) and the critical micelle concentration of the pure component i , CMC_i :

$$CMC_M = \left[\frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2} \right]^{-1} \quad (2)$$

Here CMC_M is the value expected if the system behaves as ideally. The composition of the mixed micelle for component 1 is $X_1 = \frac{\alpha_1 c - c_1^m}{c - c_1^m - c_2^m}$, where c_i^m is the free monomer concentration of component i . The mole fraction of component 1 in the micelle is defined as $X_1 = n_1/(n_1 + n_2)$, where n_1 and n_2 are the number of molecules of components 1 and 2 in a micelle. Even though the Clint's model for the ideal mixed micelle solutions

represents appropriately very few systems, it is usually employed for analysing the deviation of a mixed system from the ideal behaviour [23].

The Regular Solution Theory (RST) or Rubingh's model[16] is the first model developed for non-ideal systems and is widely employed due to its easy applicability. The non-ideality is contemplated with the intra-micellar activity coefficients γ_i . Thus, the critical micelle concentration of the mixed system (CMC_M) is obtained from the CMC of the pure components (CMC_i and CMC_j) as:

$$CMC_M = \left[\frac{\alpha_i}{\gamma_i CMC_i} + \frac{\alpha_j}{\gamma_j CMC_j} \right]^{-1} \quad (3)$$

For a binary solution, symmetric Margules formulations for the activity coefficients are used as follows:

$$\gamma_{1,M} = \exp(\beta_M X_2^2) \quad ; \quad \gamma_{2,M} = \exp(\beta_M X_1^2) \quad (4)$$

where X_i is the molar fraction of the surfactant i in the micelle (as stated before, the micelles' composition and the total composition of the mixture are not generally equal $\alpha_i \neq X_i$), and β_M is an interaction parameter in $k_B T$ units, k_B and T being the Boltzmann constant and the absolute temperature. From the molecular-thermodynamic theory point of view, the β_M parameter can be calculated as:

$$\beta_M = N_A(W_{11} + W_{22} - W_{12})/RT \quad (5)$$

Here, W_{ij} is the energy of interaction between surfactant molecules i and j in the micelles and R is the gas constant. The parameter β_M is determined from the experimentally obtained CMCs according to:

$$\beta_M = \frac{\ln(\alpha_1 CMC_M / X_1 CMC_1)}{X_2^2} = \frac{\ln(\alpha_2 CMC_M / X_2 CMC_2)}{X_1^2} \quad (6)$$

The system of equations 3 to 6 is solved independently for each mixture (i.e., for each α_{DTAB}) to obtain β_M and X_i . (Only the CMC's and the total system compositions are known).

The parameter β_M quantifies the non-ideality. The larger the negative values of β_M , the stronger the attractive interactions between the surfactants molecules in the micelles. Repulsive interactions yield a positive β_M value, whereas null β_M indicates an ideal mixture. The mixed micelle molar fractions (X_1 and X_2) are obtained by numerically solving equation 7 for each mixture composition (i.e. each α_1). [17]. Frequently, it is not feasible to obtain a solution.

$$\frac{(X_1)^2 \ln\left(\frac{\alpha_1 CMC_M}{X_1 CMC_1}\right)}{(1-X_1)^2 \ln\left(\frac{(1-\alpha_1) CMC_M}{(1-X_1) CMC_2}\right)} = 1 \quad (7)$$

On the other hand, the ideal composition of the mixed micelles can be obtained with the Motomura and Aratono equation[24].

$$X_1^{id} = \frac{\alpha_1 CMC_2}{\alpha_1 CMC_2 + \alpha_2 CMC_1} \quad (8)$$

The RST has been severely criticized [25,26]. Moreover, its extension to multicomponent surfactant mixtures frequently yields unrealistic results [27]. Since it is based on symmetric Margules formulations, it supposes that the energy of introducing a molecule of surfactant 1 in a micelle of pure surfactant 2 is equal to that of introducing a molecule of 2 in a micelle of pure 1, i.e., it assumes that the system is thermodynamically symmetric, what seldom occurs.

The Equation Oriented Mixed Micellization Model (EOMMM) is a new approach based on Equation Oriented Optimization and Margules asymmetric formulations[28] contemplating both symmetric and asymmetric thermodynamic behaviors since the symmetric formulations are a particular case of the asymmetric ones. This method is not restricted by the number of components (it can be easily extended to multicomponent systems) and guarantees the applicability of the Gibbs-Duhem relation[18] (For details see SI). The Equation Oriented Optimization simultaneously solves a system of equations in order to find the minimum/maximum of an objective function subject to a set of constraints. The EOMMM finds the Margules parameters (see SI Point 2.3) and the micelle compositions that globally minimize the total free energy of micellization. It has been recognized as a main drawback that the original RST and its multicomponent extension (MRST) deal with ionic surfactants as non-dissociated components. However, the EOMMM contemplates the dissociation of ionic surfactants through the r parameter and proper expressions for the activities of each component in the micelles. Thus, EOMMM can be employed for non-ionic or ionic surfactants, with or without the presence of supporting electrolyte. The EOMMM eliminates the assumption of interaction symmetry, i.e. the Margules parameters W_{12} and W_{21} are not restricted to be identical. Contrary to the original RST, where the equations are solved for each mixture composition independently, the whole system of equations for all the mixtures is solved simultaneously in order to find the minimum Gibbs free energy of micellization. Thus, the optimum values for the Gibbs excess free energy, the intra-micellar activity coefficients, the Margules parameters and the micelle compositions are obtained. The method is explained in detail in the SI, point 2.3. The pure DTAB micelle ionization degree required

for the application of EOMMM has been taken from literature: average value of 0.260 ± 0.004 [29].

4. RESULTS

In order to experimentally determine the composition of the micelles for each mixture, the micellar mass of the mixed micelles was determined by SLS (see S.I.). As Triton X-100 is a non-ionic surfactant, the charge of the mixed micelles is due to the content of DTA⁺ and Br⁻ ions. A Br⁻ ion selective electrode was used to determine if bromide counterions are condensed on the mixed micelles. When $\alpha_{DTAB} < 0.75$, there is no capture of counterions and then the charge of the micelles is equal to their DTA⁺-ions content, as shown in Figures 2 and 3 of the SI.

The micelles' composition can be estimated using the mass, the hydrodynamic radius and the electrophoretic mobility of the micelles for each mixture composition. The charge of the micelles can be obtained from their electrophoretic mobility. Since micelles are fully ionized, at least it is so for $\alpha_{DTAB} \leq 0.75$, the charge of the micelles (in terms of the elementary charge e) is equal to the number of DTA⁺ ions included in the micelle ($n_{DTA^+} \approx q$). Therefore, the mass of the micelles is obtained as:

$$M_{micelle} = n_{DTA^+}M_{DTA^+} + n_{TX-100}M_{TX-100} \quad (9)$$

where M_i is the molar mass of component i in the mixed micelle. Thus, the molar fraction of DTA⁺ is $X_{DTA^+} = n_{DTA^+}/n$, where n is the aggregation number ($n = n_{DTA^+} + n_{TX100}$).

For $\alpha_{DTAB} > 0.75$, n_{DTA^+} has been estimated using the surface areas and partial molar volumes of the components:

$$V_M = 4\pi(d_h/2)^3/3 = n_{DTA} V_{DTA} + n_{TX100} V_{TX100} \quad (10)$$

$$A_M = 4\pi(d_h/2)^2 = n_{DTA} A_{DTA} + n_{TX100} A_{TX100} \quad (11)$$

where d_h is the hydrodynamic diameter of the micelles, A_M and V_M are the area and volume of a mixed micelle, A_i is the area per polar head group and V_i is the molecular volume of component i . The values here used are $A_{DTA} = 0.375 \text{ nm}^2$, $A_{TX100} = 2.67 \text{ nm}^2$, $V_{DTAB} = 0.162 \text{ nm}^3$ and $V_{TX100} = 4.16 \text{ nm}^3$, all of them were computed using the volume and area of the pure surfactant micelles divided by their aggregation numbers. It must be noted that it has been assumed that the micelles are spherical and that the molecular volumes and areas do not change when passing from pure surfactant to mixed surfactant micelles. It is worth mentioning that TX100 is very hydrated: at $25 \text{ }^\circ\text{C}$ $\delta = 0.3697 \text{ g}_{\text{water}}/\text{g}_{\text{TX100}}$. [30], i.e., it can be estimated from V_{TX100} that about 14 water molecules are included per micelle. The TX100 micellar partial molar volume is $PMV_{TX100} = 587.06$

cm^3/mol [30] which gives a molecular volume of micellised TX100 of 0.8864 nm^3 . The PMV is generally considered as the volume of the molecule although the correct interpretation is that the $\text{PMV}_{\text{TX100}}$ indicates how the inclusion of TX100 molecules affects the total volume of the solution, including structure making and structure breaking effects and electrostriction. For instance, some ions have negative PMV in water. Therefore, the comparison between the $\text{PMV}_{\text{TX100}}$ and the micellised molecular volume computed from the micellar kinetics entity must be done with caution.

The CMC for each mixture composition has been determined by two different methods: surface tension and static light scattering (Figure 4 and 5 in the SI are examples of the experimental results). The experimental values are shown in Table SI-I in the SI. The average CMC for the TX100 is $(2.07 \pm 0.23) \times 10^{-4} \text{ mol.dm}^{-3}$, while the values in literature are $3.1 \times 10^{-4} \text{ mol.dm}^{-3}$ [31], $3.31 \times 10^{-4} \text{ mol.dm}^{-3}$ [15] or $(2.550 \pm 0.015) \times 10^{-4} \text{ mol.dm}^{-3}$ as an average of several literature values [29]. The CMC of DTAB is $0.0144 \text{ mol.dm}^{-3}$ and that of literature is $0.015 \text{ mol.dm}^{-3}$ [15,32] (depending on the experimental method used it can vary between 0.014 and $0.016 \text{ mol.dm}^{-3}$ [33]).

Figure 1 shows the CMC obtained with surface tension and static light scattering measurements as a function of the mole fraction of DTAB for the complete range of compositions, as well as those predicted by the Clint's ideal relation (Equation 2) which are very close to the experimental values.

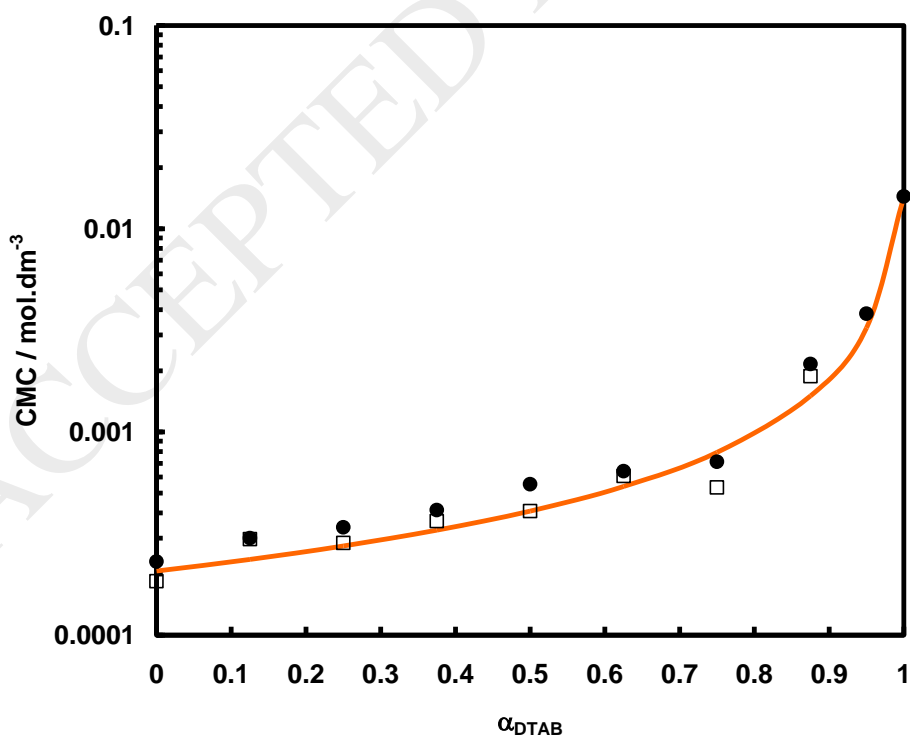


Figure 1. Critical micelle concentration dependence on the mole fraction of DTAB obtained from surface tension (\square) and static light scattering (\bullet) measurements. The continuous red line corresponds to the ideal behaviour predicted by the Clint's model.

Carnero-Ruiz and Aguiar [15] determined from the CMC values of the mixed systems composed of Triton X100 and n-alkyltrimethylammonium bromides that the behaviour of DTAB-TX100 is almost ideal, while TTAB-TX100 and CTAB-TX100 do not behave ideally and have a negative deviation from the values predicted by the Clint's relation.

The mass of the micelles (M) as a function of α_{DTAB} determined by SLS is plotted in Figure 2. An example of the Debye plots can be seen in Figure 6 SI. The values are reported in Table SI-II. We provide some values from literature for comparison: $M = 66700$ Da for pure TX100 micelles in water at 25°C [34]; $M = 58000$ Da[35]; 87930 ± 740 Da as an average of seven values summarized in Robson and Dennis work[36]; for DTAB $M = 20900$ Da[29] or 15500 Da[37].

M decreases when increasing α_{DTAB} (Figure 2), may be as a consequence of the increasing repulsion among the micellised molecules due to the higher content of DTAB. It must be noticed that there is a break at $\alpha_{\text{DTAB}} = 0.5$.

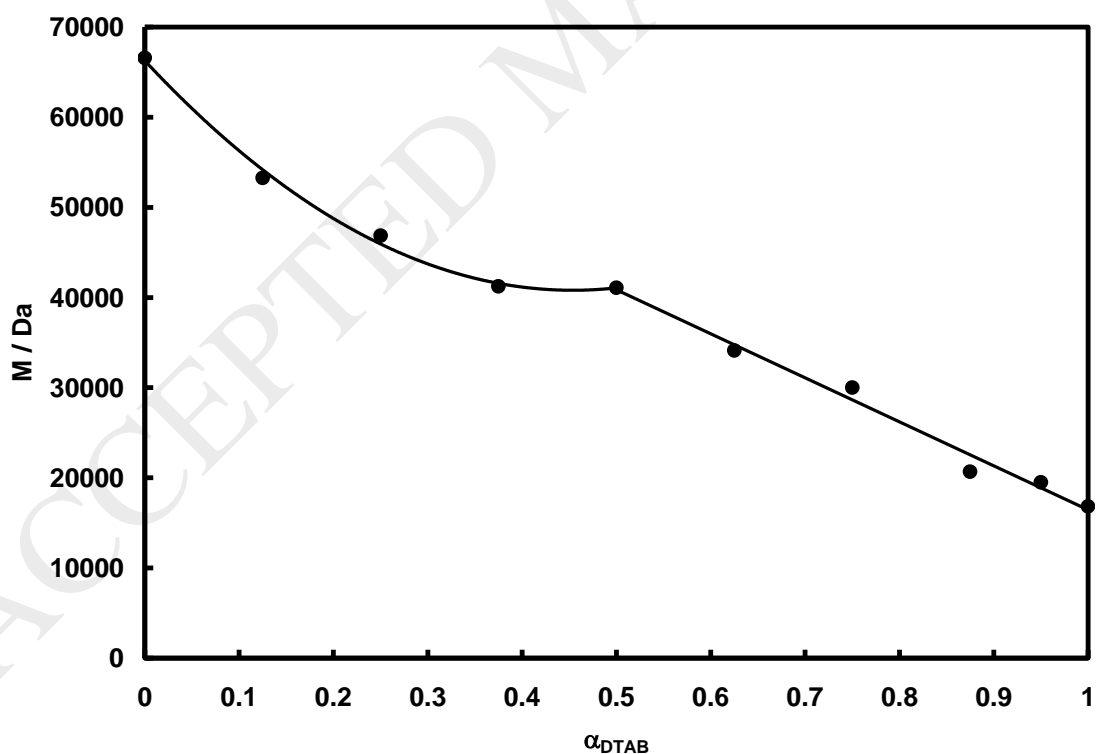


Figure 2: Micelle masses obtained from the Debye's equation versus the mixture composition. Lines are eye guides.

The static light scattering experiments also provide the second virial coefficients (A_2) measured for each mixture, as shown in Figure 3.

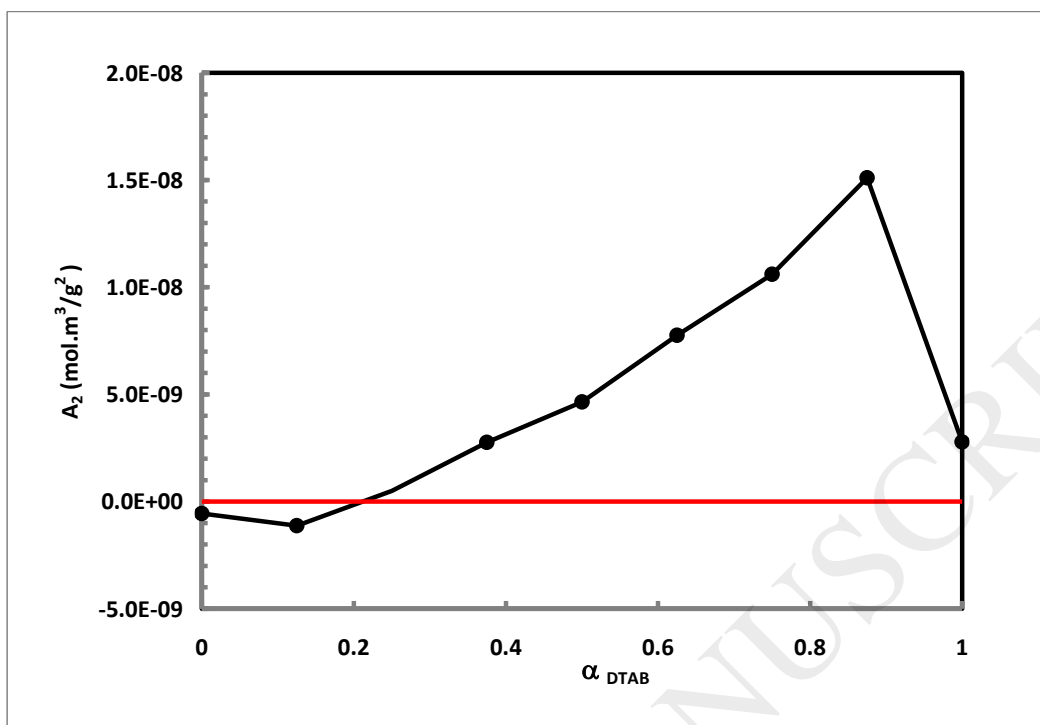


Figure 3: The second virial coefficient from the Debye static light scattering plot, as a function of the overall mixture composition. The red straight line indicates zero.

Figure 4 shows the hydrodynamic diameter of the micelles for different mixtures obtained with dynamic light scattering (DLS). The size of the micelles decreases when increasing the DTAB content, with slope changes at $\alpha_{DTAB} = 0.25$ and 0.85 .

The values for $\alpha_{DTAB} = 0$ and $\alpha_{DTAB} = 1$ are in agreement with literature[38][39]. For $\alpha_{DTAB} = 0$ (pure TX100) Bulavin *et al.*[40] measured by small-angle neutron scattering a constant characteristic diameter of 7.4 nm below $0.0096 \text{ mol.dm}^{-3}$. Mandal *et al.* [30] proposed an oblate ellipsoidal micelle for TX100, with an hydrodynamic radius of 3.962 nm ($d_h = 7.924 \text{ nm}$), a gyration radius $R_G = 3.343 \text{ nm}$ and an equivalent sphere radius $R_o = 3.610 \text{ nm}$. The oblate ellipsoid semiaxes are $a = 5.131 \text{ nm}$ and $b = 1.796 \text{ nm}$.

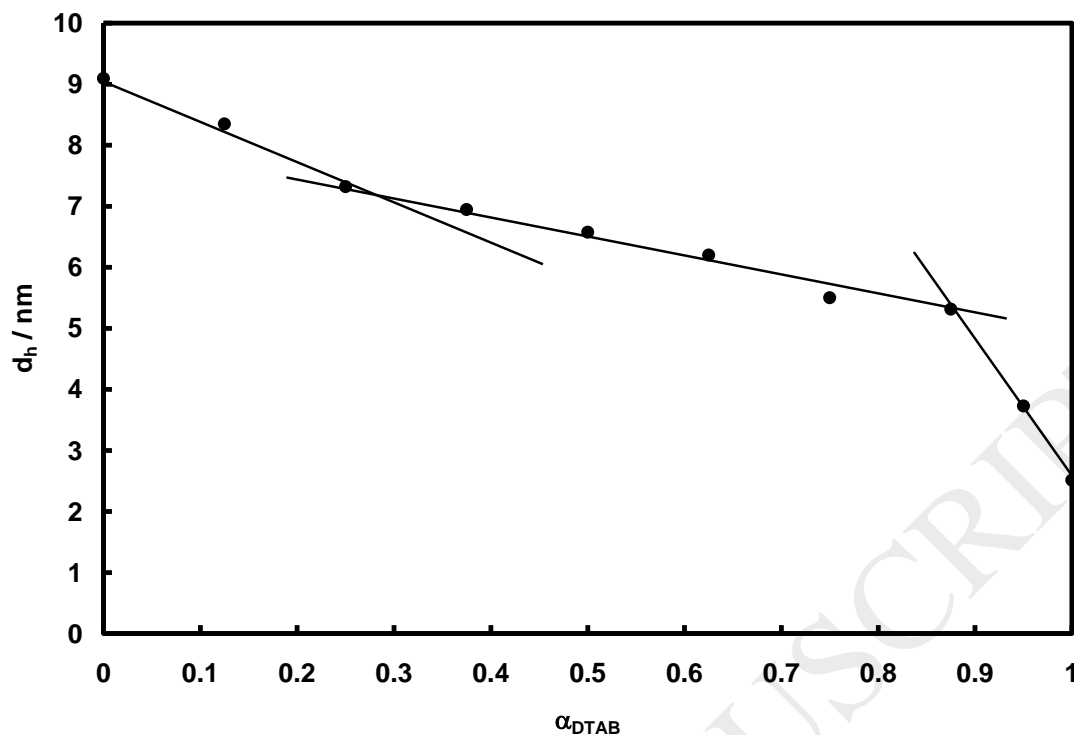


Figure 4 Hydrodynamic diameter of the micelles obtained with DLS as a function of the total molar fraction of DTAB. Lines are eye guides.

Figure 2 SI shows the dependence of the potential (E) of the Br⁻-ion-selective electrode against the saturated calomel electrode (SCE) on the total concentration C for the mixtures having $\alpha_{\text{DTAB}} = 0.25, 0.50,$ and 0.75 . It may be concluded that these mixed micelles do not capture counterions at their surface since there is no break at the CMC for all the systems with $\alpha_{\text{DTAB}} \leq 0.75$. However, for higher DTAB contents micelles capture some counterions (Figure 3 in the SI), although this capture is not so high as in pure DTAB micelles[41].

The micelles do not have bromide ions in their kinetic unit due to their very low surface potential, thus they are completely ionized, at least for $\alpha_{\text{DTAB}} \leq 0.75$.

Fluorescence anisotropy studies on the systems of alkyltrimethylammonium bromides and TX100 provide information about microviscosity inside the aggregates. The structure of the micelles is less tightly packed in mixed aggregates than in the pure TX100 ones[15]. Thus, as the positively charged heads of the DTAB are distanced, the surface charge density is low, causing the counterions to be weakly attached to the micelles. However, it has been previously found for the system DTAB-sodium undecenoate (SUD) that even in micelles negatively charged by the high content of SUD, bromide ions attach

to the micelles' surface [42] (this was also found theoretically [43]). This phenomenon has been attributed to van der Waals adsorption of the Br^- ions to the micelle-solution interface due to their high polarizability. However, in our present case, this may have been hindered by the strongly hydrated polyoxyethylene shell of micelles predominantly formed by TX100.

In Figure 5 the measured micellar electrophoretic mobility (u) is plotted as a function of α_{DTAB} . Both electrophoretic mobility and zeta potential measurements are summarized in Table SI-III and Figure 7 SI. The electrophoretic mobility increases linearly until $\alpha_{\text{DTAB}} = 0.75$, where the slope changes abruptly. This behaviour is similar to that observed in the micelle size vs. α_{DTAB} plot (Figure 4).

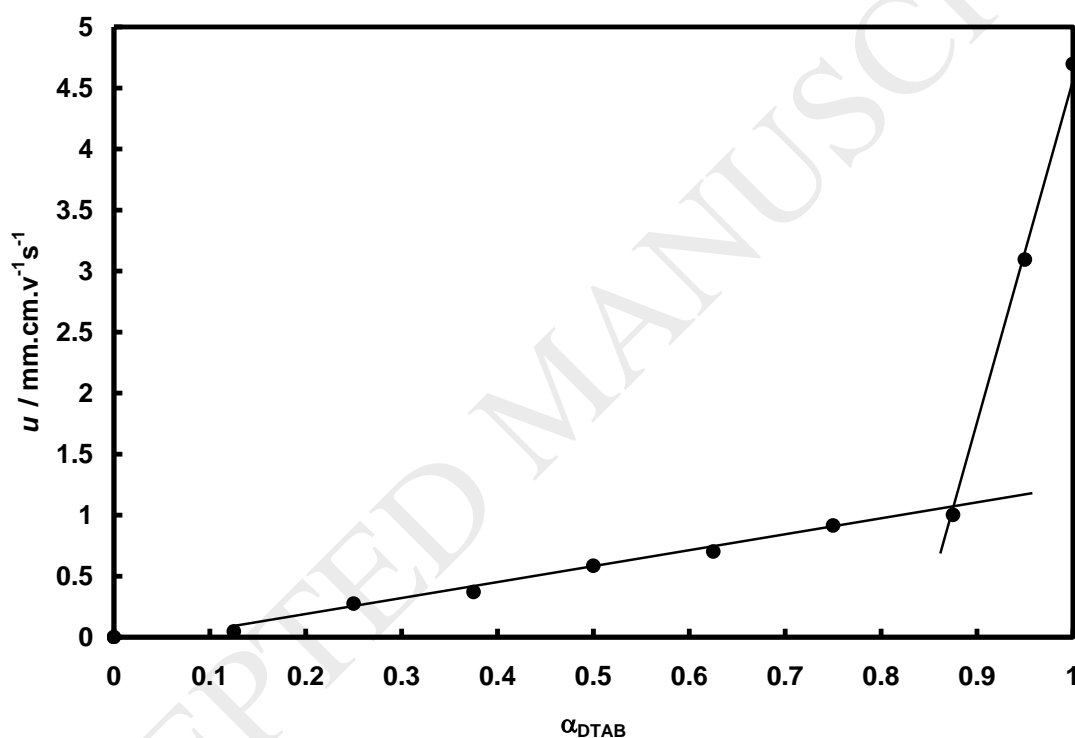


Figure 5 Electrophoretic mobility of mixed micelles vs α_{DTAB} . Lines are eye guides.

The composition of the mixed micelles has been computed using Equation (8) and the results are presented in Table I. However, it must be taken into account that the experimental data in the present work has been obtained in different conditions: the micellar mass has been obtained at the CMC, while the hydrodynamic radius and the zeta potential have been obtained at 10 CMCs. Therefore, cross checking and derivation of conclusions have to be done with caution.

Table I.

Experimental hydrodynamic diameter (d_h), composition (X_{DTAB}) and aggregation number (N_{agg}) of the micelles for the total molar fraction of DTAB in the systems.

α_{DTAB}	X_{DTAB}	N_{agg}	d_H / nm
0	0	103	9,3
0,125	0.003	82	8,3
0,25	0.012	73	5,2
0,50	0.040	65	6,6
0,75	0.072	48	5,5
0,95	0.63	45	3,8

For comparison, we provide some literature values for N_{agg} of TX100 micelles in water: 140 [44], 111 [34] and 135 [45], while for micelles of DTAB the aggregation number ranges between 40 and 73 [33][46][47].

The application of the RST at the CMCs (Equation 7) was only feasible for two mixtures reported in Table II (the model could not be solved numerically for the other mixtures).

Table II

Results of the Rubingh's method: mixed micelles compositions (X_{DTAB}), intra-micellar activity coefficients (γ_{DTAB} and γ_{TX10}); intra-micellar interaction parameter (β_M) and excess Gibbs free energy of micellization (ΔG_{mix}^{exc}).

α_{DTAB}	X_{DTAB}	γ_{DTAB}	γ_{TX100}	β_M	ΔG_{mix}^{exc}
				$k_B T$	RT
0,75	0,173	1,07	0,21	-2,25	-0,322
0,95	0,187	0,98	1,36	0,46	0,07

As already mentioned, the Rubingh's model is gives thermodynamic properties at the CMC and thus they are not strictly comparable with the compositions and data obtained experimentally.

It has been previously found that Rubingh's intramicellar interaction parameter β_M for the DTAB-TX100 system varies along the different mixtures explored while it is almost constant for the TTAB-TX100 and CTAB-TX100 systems [15]. As a consequence, these authors concluded that the RST cannot be applied to the DTAB-TX100 mixtures. However, it is worth noting that in all these systems the β_M values became more negative when decreasing α_{TX100} , a tendency more marked in the DTAB-TX100 system than in the other cationic homologues. As the Rubingh's model assumes that the system has a symmetric thermodynamic behavior, the previous observations gave us the clue that the system DTAB-TX100 is asymmetric [18]. Moreover, Carnero-Ruiz and Aguiar [15] obtained a value of +1.23 for the parameter B_2 when applying the Maeda formulation for the excess free energy of mixing [48]. This parameter is related to the standard free energy upon the replacement of a nonionic monomer with an ionic one (analogue to W_{12} for EOMMM, see below).

Figure 6 shows the results obtained with EOMMM. As suspected, the system is extremely asymmetric (notice the slope of the line $\Delta G_{\text{mix}}^{\text{exc}}/R T X_{TX100} X_{DTA}$). The values of W_{12} and W_{21} are very different. W_{12} represents the energy of introducing a DTAB molecule in a pure Triton X-100 micelle and as it is a positive value ($+4.04k_B T$) there is a repulsive interaction. Conversely, W_{21} is $-14.02k_B T$ meaning a strong attractive interaction when introducing a Triton-X100 molecule in a pure DTAB micelle.

As it can be seen, the excess free energy of mixed micellization is relatively low, as expected from the almost ideal dependence of the CMC on α_{DTAB} .

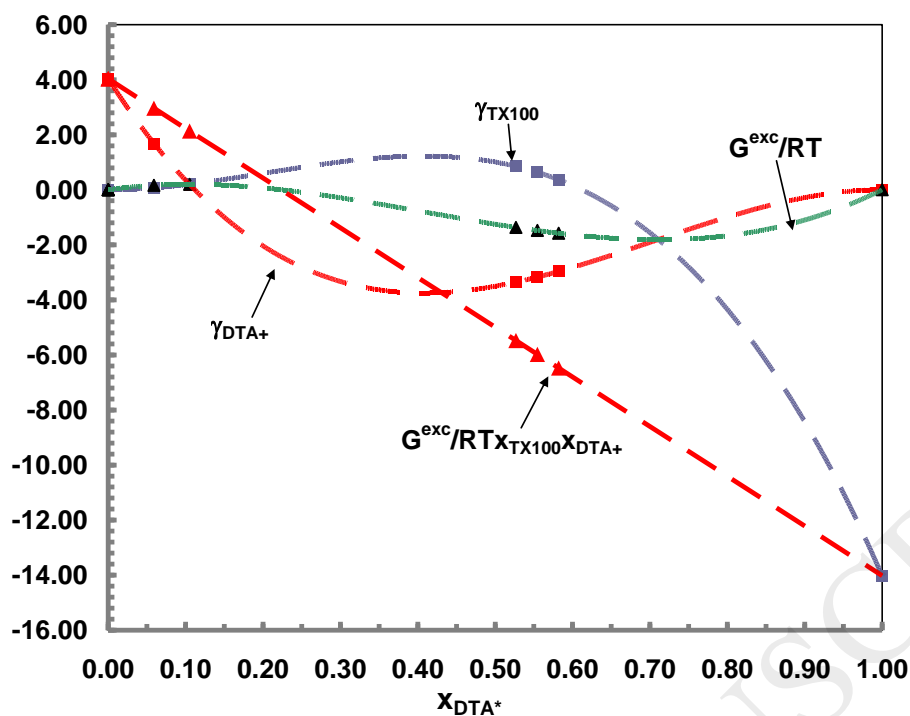


Figure 6: Results obtained with EOMMM for the system DTAB-Triton X-100.

Figure 8 SI shows the CMC values estimated with EOMMM for the different α_{DTAB} which are in good agreement with the experimental and ideal (Clint's relation) ones.

Figure 7 shows the intramicellar activity coefficients and Figure 8 the molar fraction of DTA+ in the micelles (X_{DTA+}) as functions of α_{DTAB} .

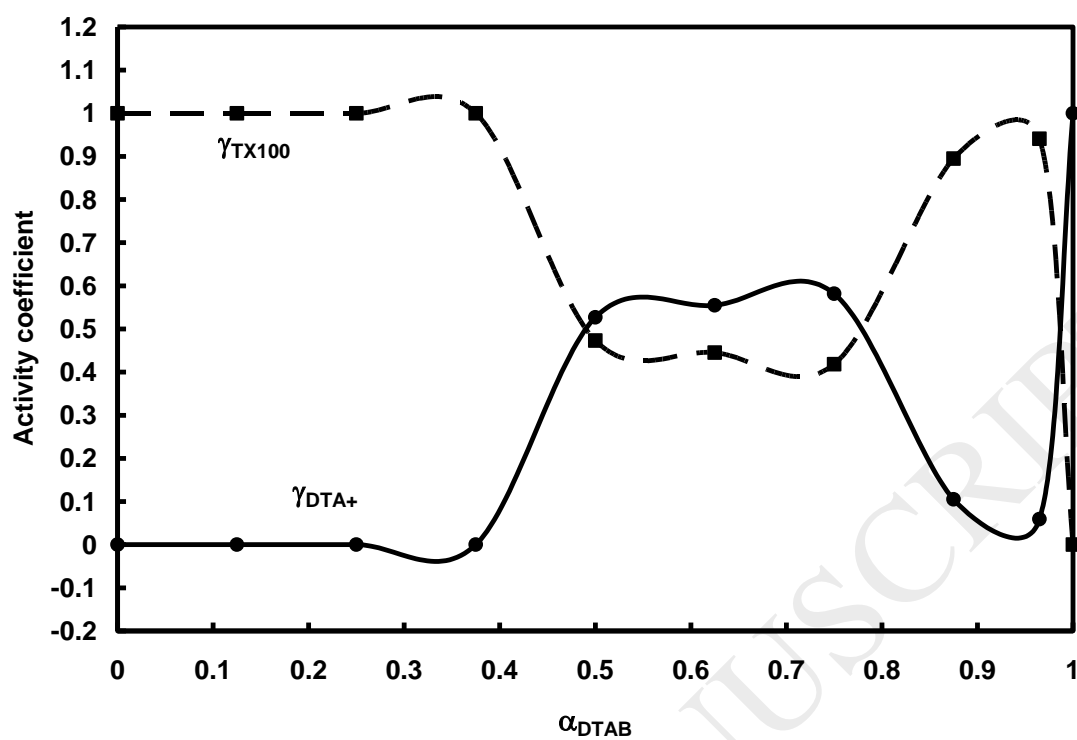


Figure 7. Intracellular activity coefficients of DTA⁺ and Triton X-100 obtained with EOMMM as a function of the mixture composition.

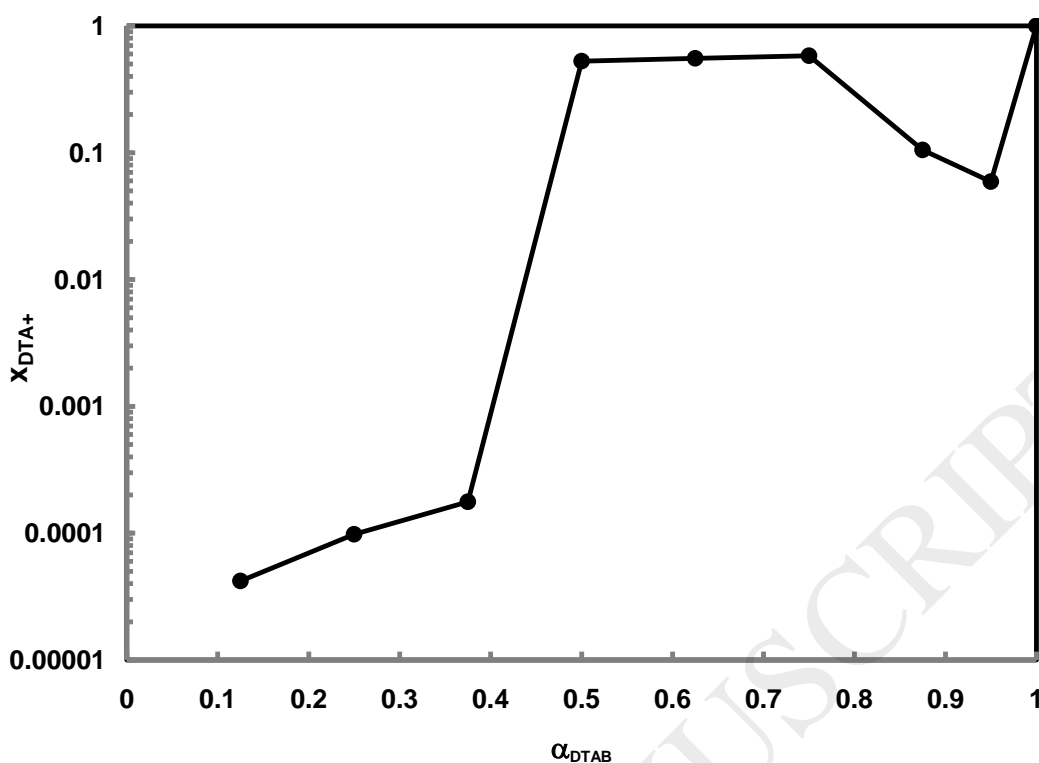


Figure 8: Mixed micelles' composition at the CMC obtained with EOMMM vs. total mole fraction of DTAB in the system.

Carnero-Ruiz and Aguiar[15] did also find that for low values of α_{DTAB} , the content of cationic surfactant in the DTAB-TX100 micelles is also very low, however its inclusion in the aggregates becomes significant when the DTAB content in the mixture increases.

Figure 9 shows the concentration of Triton X-100 at the mixture CMC: $[\text{Triton X-100}] = \alpha_{TX100} \text{CMC}$.

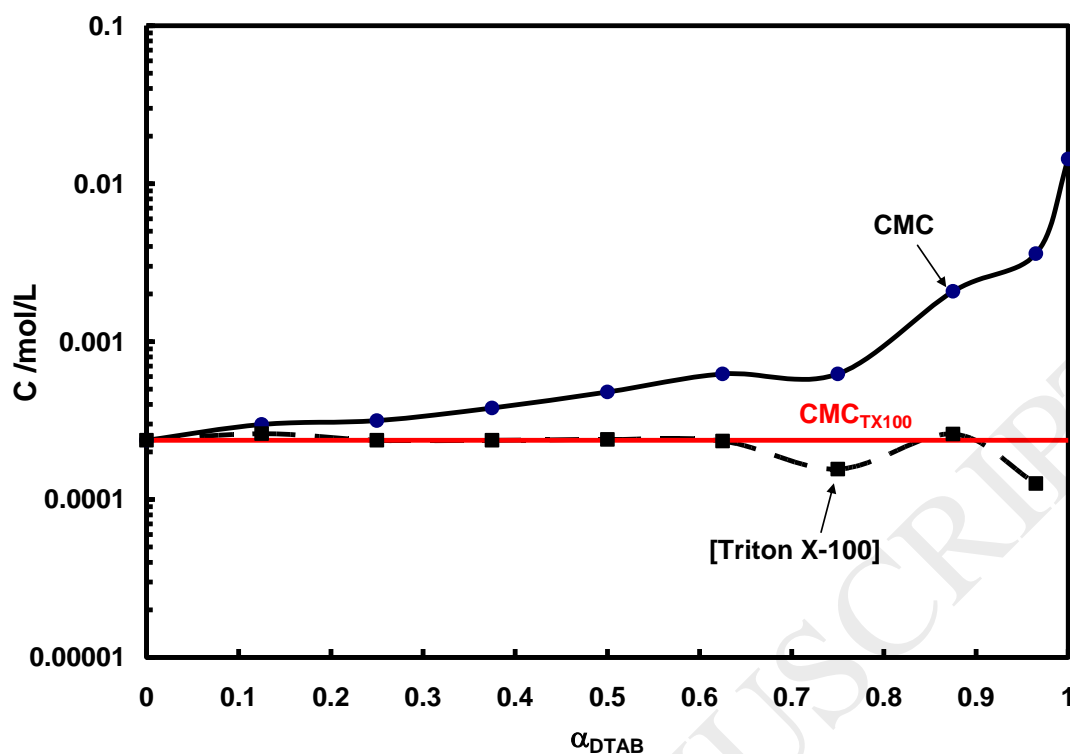


Figure 9: The concentration of Triton X-100 (■) at the mixture CMC (●), and the pure Triton X-100 CMC (----), as a function of the surfactant mixture composition.

5. DISCUSSION

The CMC values determined from surface tension and SLS are in agreement (Figure 1) and the behavior is almost ideal, what is amazing in view of the very different nature of the surfactants. Triton X-100 has a branched hydrophobic chain, a bulky aromatic ring and a highly hydrated polyoxyethylene chain, while DTAB has a straight hydrocarbon chain and a relatively small ionic head group. The very low excess Gibbs free energy of mixed micellization (G^{exc}/RT) (see Figure 6) is consistent with an almost ideal interaction.

On the other hand, the system DTAB-TX100 is very asymmetric (see Figure 6). Thus, it is a very interesting case of an almost ideal but very asymmetric mixed surfactants system. The asymmetric thermodynamic behavior must be the reason for the failure in the application of the Rubingh's procedure which *a priori* assumes that the system is symmetric. When applying the RST, the applicability of the Gibbs-Duhem relation is not guaranteed but it may be satisfied only when a unique value of β_M is obtained for all the compositions. In the present case, it seem impossible to obtain a unique value of β_M or even a reasonable average value if we take into account the very different values of W_{12} and W_{21} ($+4.04k_B T$ and $-14.02k_B T$, respectively). In fact, the only two values obtained

for the intramicellar interaction parameter ($+0.46k_B T$ and $-2.25k_B T$) are too different to make an average with any significance. So, we conclude that the results obtained with the RST are not reliable.

According to the positive value of W_{12} ($+4.04k_B T$), the inclusion of a DTA^+ ion in a pure TX100 micelle is energetically unfavorable as expected from the introduction of a charged entity in a nonionic micelle. Besides, the inclusion of other ionic surfactants increases the inter-head group repulsion, i.e., there is a conflictive micellization with some repulsion between the two components. This may be the reason for the low X_{DTA^+} values for the mixtures with low α_{DTAB} (Figure 8).

It has been found that TX-100 micelles are adequately represented as hard spheres[49] and it has been proposed that there is not a sharp boundary between the hydrophobic interior and the polyoxyethylene chain shell of the TX100 spherical micelles[36][50][51]. Those works have also suggested that the first oxyethylene groups of the alkylphenol and some TX100 molecules are contained in the hydrophobic core.

Pirene fluorescence has been used in alkyltrimethylammonium bromide-TX100 mixed micelles to study the micropolarity of the aggregates[15]. The determinations were made well above the CMC. Pyrene locates near the surface of the hydrocarbon core of the micelles. The micropolarity of the micelles decreases when the DTA^+ content in the aggregates increases, what has been attributed to an increase in the ion-dipole interactions between trimethylammonium and the oxyethylene groups. This in turn causes a partial dehydration of the polyoxyethylenic chains and a reduction in the micelle volume when increasing α_{DTAB} , in agreement with Figure 4 of the present work. The inclusion of cationic surfactants into the mixed micelles produced more crowded aggregates with a more dehydrated structure. The mixed micelles had a less ordered structure than those of pure TX100[15]. Dehydration is an energy consumer process which may contribute to the TX100 micelles reluctance to include DTA^+ ions.

Accordingly Yuan *et al.*[52], the α -methylene group of CTAB is in the near vicinity of the phenoxy ring of TX100. The trimethylammonium group of CTAB locates between the first oxyethylene group next to the phenoxy ring of TX100 and the methyl terminal group of the hydrophobic chain of CTAB is close to those of the nonionic surfactant. CTAB and TX100 are uniformly distributed in the mixed micelles and so the excess entropy of mixed micellization is expected to be near zero (as assumed in the Regular Solution Theory). This may be an explanation for the nearly ideal mixture CMC behavior of the system.

Thus, the hydrophobic core of the pure TX100 micelles is not completely apolar what makes unfavorable the inclusion of the hydrocarbon chain of the DTA^+ ions, a possible explanation of the positive value of W_{12} (repulsive interaction).

On the contrary, the inclusion of a TX100 molecule in a pure DTAB micelle is very favorable as manifested by the negative value of W_{21} . Introducing a bulky, uncharged headgroup between charged groups reduces the mutual electrostatic repulsion energy. In the TX100-CTAB micelles, the trimethylammonium groups are situated facing the aryl groups of TX100, probably interacting with their π -electrons [4]. Similar conclusions have been obtained for TX100-sodium dodecylsulfate (SDS) mixed micelles[53].

The X_{DTAB} values experimentally determined were computed with data of diverse origin and at different surfactant concentrations. The results from DLS and electrophoretic mobility were obtained at 10 CMCs while those obtained with the RST or the EOMMM are at the CMC, so they cannot be compared in a direct manner. It has been observed (from experimental data, not from a model) for other systems that the composition of the micelles may change considerably with the total concentration of the surfactants[4][54]. The following discussion is based only on the results obtained with EOMMM (discarding the results from the RST).

As it can be seen in Figure 4, there is a change at $\alpha_{\text{DTAB}} \approx 0.75$ in the hydrodynamic diameter (d_h), with an abrupt decrease in d_h above this value. There is also a noticeable electrophoretic mobility increase in the same region (Figure 5).

Although Fang *et al.*[4] did not explore the complete phase diagram of the TX100-CTAB system, the behavior of the mixed micelles' diffusion coefficient showed the same tendency as our results: a monotonic decrease indicating a reduction in the micelles' size when the proportion of the ionic surfactant in the overall mixture increases.

The micelles' mass monotonically decreases with α_{DTAB} but there is a slight change at about $\alpha_{\text{DTAB}} \approx 0.5$ (Figure 2). The composition of the micelles does also have a sudden change at $\alpha_{\text{DTAB}} \approx 0.5$ (results from EOMMM in Figure 8).

Figure 7 shows that below $\alpha_{\text{DTAB}} \approx 0.5$, Triton X-100 acts as a solvent: the activity coefficient of TX-100 is almost unity while the activity coefficient of DTA^+ is near zero. Between $\alpha_{\text{DTAB}} \approx 0.5$ and $\alpha_{\text{DTAB}} \approx 0.75$ it seems that both surfactants form a mixture, i.e., a solvent and a solute cannot be identified. Above $\alpha_{\text{DTAB}} \approx 0.75$, there seems to be a different interaction as reflected by the diverse properties here studied, as discussed *ut supra*.

As mentioned above, Robson and Dennis[36] suggested spherical TX100 micelles, having some polyoxyethylene chains immersed into the hydrophobic micelle core. The inclusion of DTA⁺ hydrocarbon tails may change this structure and eventually the mixed micelle core may become fully hydrophobic. This may be what occurs at $\alpha_{DTAB} \approx 0.4$ and may explain the changes observed in Figure 7, where the almost equal activity coefficients indicate mutual solubility of the surfactants.

Figure 9 shows that the mixture CMC remains close to that of the pure TX-100 along the composition range, as it has been found for TX100-CTAB mixtures in which the presence of the cationic surfactant only caused small perturbations to the micellization behaviour of TX100 [4]. Evidently, TX100 micelles act as a rather ideal solvent for DTA⁺ ions (at least up to $\alpha_{DTAB} \approx 0.40$).

The mixed micelles form after the pure nonionic surfactant CMC is reached, i.e., it may be interpreted that, first micelles of Triton X-100 are formed, and then they capture some DTA⁺ ions (see Figure 9). This may be due to the very different CMC values of the pure surfactants and to the energetically unfavorable inclusion of the ionic surfactants in the non-ionic micelles.

Up to this point, it can be concluded that the micelles of Triton X-100 incorporate DTA⁺ ions, but this inclusion is initially difficult, showing some repulsion reflected in the positive W_{12} value. Therefore, the mixed micelles formed have low content of DTA⁺ (Figure 8). The progressive incorporation of DTA⁺ molecules will increase the charge of micelles and reduce their diameter. This also increases the repulsion among micelles. Figure 3 shows the second virial coefficient from the Debye plot of SLS: when the micelles are very rich in Triton X-100 they have small negative A_2 values, indicating an attractive interaction due to van der Waals interactions. The electrostatic repulsion increases when the content of DTA⁺ increases, as well as the positive A_2 values. When $\alpha_{DTAB} = 1$ there is a reduction of A_2 caused by the inclusion of counterions in the micelles' Stern layer and the reduction of the Debye's length caused by the high ionic concentration (the CMC of DTAB is high).

When $\alpha_{DTAB} \geq 0.75$, the DTA⁺ content in the micelles is high enough to capture some counterions, and the Triton X-100 content small enough to allow a reduction of the effective hydrodynamic diameter since, as the nonionic surfactant are not tightly crowded in the micelle, the polyoxyethylene chains may be folded instead of extended to the intermicellar solution, probably helped by the partial dehydration of the polyoxyethylene chains. Similar conclusions have been obtained in the TX100-CTAB mixed system[4]. This way, the electrophoretic mobility increases and the micelles' mass is reduced. In

summary, the nature of the micelles changes along the phase diagram: from micelles predominantly formed by Triton X-100 with some DTA⁺ ions solubilized in them, passing through a transition where micelles have apolar hydrocarbon cores between $\alpha_{DTAB} \approx 0.40$ and 0.75 , to micelles predominantly formed by DTAB with solubilized Triton X-100 at above $\alpha_{DTAB} = 0.75$.

Fang *et al.* [4] found some changes in the TX100-CTAB mixed micelles behaviour above and below about $\alpha_{CTAB} \approx 0.5$, related to changes in the interaction between the components of the system. Unfortunately, the region with $\alpha_{CTAB} > 0.75$ has not been explored by these authors.

Zhang and Dubin[53] found evidence of coexistence of two different mixed micelles in mixtures of TX100-SDS: TX100 rich micelles with some solubilized DS⁻ ions, and SDS rich micelles with some solubilized TX100 molecules. This was justified by the possible existence of energetically equivalent micelles of different composition (due to different forms in which the ΔG_{mic} is affected when one component is included in the micelle of the other component).

Barzikin and Almgren [55] have theoretically demonstrated (on a symmetric thermodynamic behaviour basis) that if the mixed micellization interaction energy is positive (as in mixtures of hydrocarbon and fluorocarbon surfactants), the formation of a two-phase micellar system is possible, i.e., a mixture of coexisting mixed micelles having different composition but with same free energy of micellization. In view of the values of W_{12} and W_{21} in the TX100-DTAB system, this explanation could be valid: in the range $0.5 \leq \alpha_{DTAB} \leq 0.75$ two kinds of micelles could coexist while at higher contents of DTAB, only one of the two kinds of micelles predominates. This is obviously a speculation that cannot be demonstrated by the thermodynamic models here applied (RST and EOMMM) since they are based on the application of the pseudo-phase model with two phases in equilibrium (micelles and monomers' solution).

6. CONCLUSIONS

This article addresses the mixed micelles formed by a non-ionic (TX-100) and a cationic (DTAB) surfactant. The experimental findings have been complemented with the thermodynamic behavior analysis (done with two approaches: RST and EOMMM). The following concluding remarks have been discussed along the article:

- In spite of the very different molecular structures of the components and the very asymmetric thermodynamic interactions, the CMC of the mixtures have a nearly ideal behavior.

- The system is very asymmetric due to the very different structures and nature of the surfactants: the energy of introducing a DTA⁺ ion into a TX100 micelle is positive (meaning certain repulsion), while the introduction of a TX100 molecule in a pure DTAB micelles has a strong negative value (indicating attraction).
- Due to the asymmetric thermodynamic behavior, the RST fails (no feasible solutions are obtained) since the RST assumes symmetry.
- The hydrodynamic diameters and the electrophoretic mobilities have noticeable changes at $\alpha_{DTAB} \approx 0.75$.
- When increasing the DTAB content, the hydrodynamic diameter and the mass of the micelles decrease while the electrophoretic mobility increases as a consequence of the decrease of the size and the increase of the charge of the micelles.
- Below $\alpha_{DTAB} \approx 0.5$ micelles are mainly composed of TX100, thus TX100 acts as a solvent for the DTA⁺ ions. Between $\alpha_{DTAB} \approx 0.5$ and 0.75 no solvent and solute are identifiable inside the micelles but above $\alpha_{DTAB} \approx 0.75$ a change in the aggregates' structure seems to occur. All these transitions are reflected by the different experimental results.
- On the basis of other TX100 mixed systems, it seems feasible that two different kinds of mixed micelles coexist in the range $0.5 \leq \alpha_{DTAB} \leq 0.75$. Future work will be devoted to study structural changes in mixed micelles as a function of the mixture compositions. In order to verify this final statement, we will employ a very sensitive technique, electric birefringence [6], in the hope of discerning whether two different kinds of mixed micelles coexist. Electric birefringence is very sensitive to small changes in the size, shape and surface charge of the colloids, all of which depend in turn on the DTAB content. Particularly we hope that birefringence relaxation experiments will permit us to discern if two kinds of micelles coexist.

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