Catanionic surfactant formation from the interaction of the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) and the ionic liquid 1-butyl-3-methylimidazolium octyl sulfate (bmim-octyl SO₄) in aqueous solution

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ABSTRACT

The interaction between the cationic surfactant Hexadecyltrimethylammonium bromide (CTAB) and the ionic liquid 1-butyl-3-methylimidazolium octyl sulfate (bmim-octylSO₄) in aqueous solution has been investigated at two total concentrations (0.5 and 10 mM) and different CTAB mole fractions (α_{CTAB}).

Samples of different physical appearance were obtained depending on α_{CTAB} suggesting different kind of aggregates. Bluish solutions (α_{CTAB} from 0.1 to 0.6) were assigned to vesicles of the catanionic surfactant formed (CTA-octylSO₄), whereas clear and isotropic solutions ($\alpha_{\text{CTAB}} > 0.6$) corresponded to mixed micelles. Surface tension, electrical conductivity, absorbance and dynamic light scattering (DLS) measurements were performed with the aim of correlating properties changes with the aggregation structures. The critical aggregation concentration (c_{ac}) and the surface tension value at the c_{ac} (γ_{cac}) were much lower for the mixtures than for the individual components. This finding reveals the

exceptional surface activity of these mixtures, attributable to the formation of the CTA-octylSO₄ catanionic surfactant. Once the catanionic surfactant is formed it makes no sense to consider anymore the initial CTAB / bmim-octylSO₄ binary system but a new one composed by CTA-octylSO₄ and the excess of bmim-octylSO₄ or CTAB. On the basis of this consideration the surface activity parameters have been recalculated.

KEY WORDS

Cationic surfactant CTAB; Ionic liquid bmim-octylSO₄; Catanionic surfactant CTA-octylSO₄; Mixed micelles; Vesicles; Synergism

1. Introduction

The interaction between conventional surfactants and ionic liquids (ILs) in aqueous solution can be considered from different points of view depending on the behavior displayed by the IL. In some cases the IL acts as an aqueous cosolvent and modifying some surfactant properties such as the critical micelle concentration (*cmc*) with respect to the value in neat water because of the weaker solvophobic interaction between the alkyl chain of the surfactant and the IL aqueous solution [1-7]. The effect of the ionic liquid on the surfactant properties depends on the IL structure and concentration. Behera and Pandey [1,4,8] reported that at low concentration some ILs act similarly to an electrolyte decreasing the surfactant *cmc* whereas at high concentration they behave as a cosolvent increasing this parameter. In the case of the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) the effect of ILs on the surfactant *cmc* confirms the trend above described [8-13]. However, when IL posses surface activity as reported for long alkyl chain ionic liquids [14-21] and some short alkyl chain ILs [22,23] the ionic liquid / surfactant mixture behaves as a typical binary surfactant system [24-26]. In these binary systems the mixed micelle composition X_1^M as well as the β^M interaction parameter quantifying the synergism can be obtained by applying the equations of the *Regular Solution Theory* [27]. Similar equations derived by Rosen [28] furnish equivalent parameters (X_1^{σ} and β^{σ}) for the mixed monolayer adsorbed at the liquid/air interface. However, for cationic / anionic surfactant systems, the anion-cation pairs formed by electrostatic attraction (catanionic surfactant) can aggregate via hydrophobic interaction leading to spontaneous vesicle formation. From the pioneering studies by Kaler on oppositely charged single tailed

surfactants [29-34] numerous contributions have been reported on the spontaneous vesicle formation and micelle-vesicle transitions produced as a function of the surfactant ratio in the mixture [35-41]. Similar vesicle formation should be expected when a cationic surfactant is mixed with an ionic liquid displaying anionic surfactant-like behavior. In fact there are several examples of catanionic surfactants formed from ionic liquids. They can be obtained by synthesis combining the appropriate cation and anion [42-47] or by mixing the cationic and the anionic compounds in equimolar ratio in aqueous solution [48-51]. In the latter case, in addition to the catanionic surfactant, there will be also in the aqueous solution the salt formed by the respective counterions. In the present study mixtures of the cationic surfactant, CTAB, and the ionic liquid, bmim-octylSO₄, in aqueous solution at different mole fractions will be investigated. Therefore, moreover the catanionic surfactant, CTA-octylSO₄, and the salt resulting from the corresponding counterions, bmim-Br, the excess of one of the components, CTAB or bmim-octylSO₄, will be present in the aqueous solution for non equimolar mixtures.

2. Experimental section

2.1. Materials

Cationic surfactant hexadecyltrimethylammonium bromide (CTAB) was purchased from Sigma. Ionic liquid 1-butyl-3-methylimidazolium octylsulfate (bmim-octylSO₄) was purchased from Fluka. Sodium octylsulfate (octylSO₄Na) was purchased from Fluka. These compounds were used as received. Deionized

water was obtained from a Milli-Q device and filtered through a 0.22 μm membrane.

2.2. Sample preparation

Binary mixtures of CTAB and bmim-octylSO₄ at different CTAB mole fractions (α_{CTAB} ranging from 0.05 to 0.9) were prepared by mixing the appropriated volumes of bulk solutions of CTAB and bmim-octylSO₄ at two total concentrations, 0.5 mM and 10 mM. Samples were allowed to stand for a week to reach steady state.

2.3. Synthesis of salt free CTA-octylSO₄

A sample of 0.448 g of CTAB was mixed with 0.285 g of octylSO₄Na in 25 ml of water. The reaction mixture was stirred vigorously at 60°C for 4 hours. Then, the water was eliminated in a rotary evaporator and the dry residue dissolved in 20 mL of dichloromethane. The organic solution was transferred to a separating funnel and washed with water (4 x 10 mL). The dichloromethane phase was transferred to a round flask and the organic solvent evaporated in a rotary evaporator. A dry residue of 0.440 g of CTA-octylSO₄ was obtained.

2.4. Surface tension measurements

Surface tension measurements were performed at 25°C by means of the Wilhelmy plate method using a Krüss K12 tensiometer. Glass containers and the

platinum plate were cleaned with chromic acid solution and rinsed with deionized water. The plate was flame dried before each measurement. Surface tension was considered to be at equilibrium when the standard deviation of five consecutive determinations did not exceed 0.10 mN/m. From the plots of surface tension vs logarithm of the compound concentration several surface active parameters were determined. The critical aggregation concentration (cac) was obtained by the intersection between the line corresponding to the linear decrease in surface tension and the line of stabilized surface tension. The surfactant effectiveness γ_{cac} (surface tension at the cac) and the surfactant efficiency given by the parameter pC_{20} (-logarithm of the surfactant concentration necessary to decrease by 20 mN/m the surface tension of the pure water) were also obtained from the graph. From the Gibbs equation different parameters related to the surface activity can be estimated. The maximum adsorption at the air-liquid interface (Γ_{max}) was calculated according to: $\Gamma_{max} = -(\Delta\gamma/\Delta\log C) / 2.303 n RT$, being $(\Delta\gamma/\Delta\log C)$ the slope of the linear decrease of γ before the cac , and n the number of species in solution, being $n = 2$ for ionic surfactants. The minimum area (A_{min}) occupied by adsorbed molecule at the air-liquid interface, expressed in $\text{\AA}^2$, are obtained from the equation $A_{min} = 10^{16}/N_A\Gamma_{max}$ where N_A is the Avogadro's number and Γ_{max} the surface excess concentration expressed in $\text{mol}\cdot\text{cm}^{-2}$.

2.5. Conductivity measurements

Electrical conductivity was measured at 25 °C using an Orion Conductivity Cell in conjunction with a Thermo Orion 5 Star multiparameter instrument with a cell constant of 0.475 cm^{-1} .

2.6. Spectrophotometric measurements

Absorbance at 500 nm was measured at 25 °C using a Shimadzu UV240 Spectrophotometer.

2.7. Dynamic Light Scattering measurements

Size measurements were carried out at 25°C using a Malvern Nano SZ instrument. The excitation source was He-Ne laser light of 632 nm. The scattering angle was 173°.

3. Results and discussion

3.1. Phase behavior observed in CTAB and bmim-octylSO₄ mixtures

The mixtures were prepared at 10 mM total concentration because this concentration is about 2-10 times higher than the theoretical *cmc* values, calculated for all the α_{CTAB} range from the individual values reported in literature for CTAB (*cmc* = 0.9 mM) and bmim-octylSO₄ (*cmc* = 30 mM) and the corresponding α_{CTAB} , by means of the Clint equation:

$$\frac{1}{cmc_{calc}} = \frac{\alpha_1}{cmc_1} + \frac{(1-\alpha_1)}{cmc_2} \quad (1)$$

where compound 1 was CTAB and compound 2 was bmim-octylSO₄.

Binary mixtures of CTAB and bmim-octylSO₄ at 10 mM total concentration prepared by mixing appropriate volumes of homogeneous and transparent stock

solutions of each surfactant resulted to be clear and colourless only for $\alpha_{\text{CTAB}} \geq 0.7$. They were bluish for $\alpha_{\text{CTAB}} = 0.1 - 0.3$ and $0.5 - 0.6$ and turbid for $\alpha_{\text{CTAB}} = 0.4$, as it can be seen in Fig. 1.

Fig. 1. Physical appearance of CTAB / bmim-octylSO₄ mixtures at 10 mM total concentration with increasing α_{CTAB} (0.1 to 0.9).

The bluish colour of some compositions suggests the presence of vesicle aggregates as reported for binary mixtures of oppositely charged surfactants [29-41]. The most reasonable hypothesis is that the ionic pair formed by electrostatic attraction between the CTA⁺ cation and the octylSO₄⁻ anion leads to a new compound, the pseudo-double chain catanionic surfactant, CTA-octylSO₄ that aggregates spontaneously in vesicles via hydrophobic interaction. A fact supporting this hypothesis is that when the same study was performed with bmim-methylSO₄ as ionic liquid all the samples were transparent and colourless corresponding to mixed micelles with hydrodynamic radii around 4 nm (the data for this binary system are reported in Supplementary Material). In this case the alkyl chain of the methylSO₄⁻ anion is too short to form a catanionic compound. The formation of vesicles in surfactant-ionic liquid systems has been also reported by other authors [42-51]. Another series of binary mixtures at lower total

concentration (0.5 mM) was also prepared. At this concentration the mixtures resulted to be colourless and transparent for all α_{CTAB} mole ratios.

3.2. Physicochemical properties of the aqueous CTAB / bmim-octylSO₄ mixtures

3.2.1. Absorbance

Absorbance values at 500 nm were determined for the binary mixture samples with different mole fractions (α_{CTAB}) at 0.5 mM and 10 mM total concentration. It can be seen in Fig. 2a that for the 10 mM concentration the shape of the graph agrees with the visual aspect of the samples shown in Fig. 1. The slight rise of absorbance for α_{CTAB} up to 0.3 corresponds to the moderate increase in the bluish colour intensity of samples and for α_{CTAB} 0.5 and 0.6, corresponding to translucent bluish solutions the absorbance follows the same trend. The high absorbance of the mixture at $\alpha_{\text{CTAB}} = 0.4$ reflects the strong turbidity of the sample that results in phase separation over time. Nevertheless the mole fraction at which phase separation takes place not always was the same but highly dependent on the total concentration (results in Supplementary Material). The negligible absorbance values for mixtures with $\alpha_{\text{CTAB}} \geq 0.7$ reflect the total transparency of these samples suggesting a different structure with respect to the bluish samples. At 0.5 mM concentration all the samples were transparent and colourless with negligible absorbance values.

3.2.2. Surface tension

The surface tension values of CTAB / bmim-octylSO₄ mixtures at 0.5 mM and 10 mM concentrations are shown in Fig. 2b for different α_{CTAB} . A dramatic

decrease of the surface tension values is observed for α_{CTAB} from 0 to 0.05. This gives evidence of the strong synergistic effects produced when those compounds are mixed. No appreciable modification of the surface tension for both series can be detected up to $\alpha_{\text{CTAB}} = 0.7$. However, for the mixtures at 10 mM concentration a further increase of α_{CTAB} results in a progressive increase of surface tension. This behaviour could indicate a change in the aggregate structure, as the transparent and colourless visual aspect of these compositions suggested. It can be observed that the surface tension at 10 mM is higher than at 0.5 mM for $\alpha_{\text{CTAB}} = 0.8$ and 0.9. This fact could be understood whether 10 mM were a concentration much higher than the corresponding *cac* of the mixtures (as further confirmed in Section 3.3.). In that case, a change in the structure of the aggregate can occur resulting in a lower monomer adsorption at the interface liquid/air with the corresponding γ increase as a consequence of the new equilibrium aggregate-monomer.

3.2.3. Electrical conductivity

The values of electrical conductivity as a function of the mixture composition at 0.5 mM and 10 mM total concentration are reported in Fig. 2c. The conductivity values obtained for $\alpha_{\text{CTAB}} = 0$ should be attributed to IL monomers because such concentrations are lower than the bmim-octylSO₄ *cmc* (30 mM, see Section 3.3.). The general trend observed at 10 mM concentration for α_{CTAB} from 0 to 0.7 (bluish samples), except for the turbid sample at $\alpha_{\text{CTAB}} = 0.4$, was a moderate progressive conductivity decrease. However, for α_{CTAB} values > 0.7 the conductivity decrease was more dramatic with increasing the CTAB content, suggesting a change in the structure for these transparent and colourless compositions. At 0.5 mM total

concentration very low conductivity values ranging from 30 to 42 $\mu\text{S}/\text{cm}$ were obtained.

Fig. 2. Measurements performed on CTAB / bmim-octylSO₄ mixtures at 0.5 mM and 10 mM total concentrations as a function of the CTAB mole fraction (α_{CTAB}). (a) Absorbance. (b) Surface tension. (c) Electrical conductivity. (d) Aggregate size.

3.2.4. Aggregate size

Dynamic Light Scattering (DLS) measurements were performed to measure the size of the aggregates as a function of the sample composition at 0.5 mM and

10 mM total concentrations (the turbid sample obtained for $\alpha_{\text{CTAB}} = 0.4$ at 10 mM was previously filtered through a 0.4 μm polycarbonate membrane). The results are displayed in Fig. 2d. At 0.5 mM and 10 mM sizes corresponding to vesicle aggregates were obtained for $\alpha_{\text{CTAB}} \leq 0.6$. For $\alpha_{\text{CTAB}} = 0$ no micelles of bmim-octylSO₄ can be formed at 0.5 or 10 mM concentration because the *cmc* value of this compound is 30 mM. For the compositions with $\alpha_{\text{CTAB}} > 0.6$ a dramatic decrease of the radius of the aggregates, from vesicles to typical micelles sizes, was observed. This finding is consistent with the physical appearance of these samples (transparent and colourless) and agrees with data reported by Sarkar [51]. At 0.5 mM concentration similar vesicle radii to the series at 10 mM were obtained for $\alpha_{\text{CTAB}} \leq 0.6$. However, for $\alpha_{\text{CTAB}} \geq 0.7$ aggregates of two different sizes appeared, one population with a radius average of 20-30 nm and the other in the range of 240-280 nm, suggesting the coexistence of micelles and vesicles [56]. However, since the rest of measurements made for $\alpha_{\text{CTAB}} \geq 0.7$ seemed to indicate that they correspond to mixed micelles the possible formation of aggregates of micelles as suggested by Kumar et al. [45] was considered. In this case, the hydrophobic interactions between individual micelles could lead to bigger aggregates. The links between the micelles can be broken by the presence of an electrolyte as NaCl [45]. In the present study a concentration of NaCl as high as 0.2 M was added to the samples to be sure that intermicellar aggregates would not be formed. The salt addition led to a single population of aggregates with micelle size (Fig. 2d).

3.3. Critical aggregation concentration (*cac*) and surface active properties of the CTAB / bmim-octylSO₄ binary system

The critical aggregate concentrations (cac) at which vesicles or micelles are formed were determined from the graphs of surface tension vs logarithm of concentration. For the individual components, CTAB and bmim-octylSO₄, these values resulted to be 0.9 and 30 mM, respectively, and agree with data reported in literature [34, 55,56]. In Fig. 3 some plots $\gamma / \log C$ for different α_{CTAB} are shown, the rest of the graphs are given in Supplementary Material. A dramatic decrease of both critical aggregation concentration (cac) and surface tension at the equilibrium (γ_{cac}) were obtained for the binary solutions in comparison with the individual components even for the lowest α_{CTAB} investigated (0.05), indicating the strong synergism produced when CTAB and bmim-octylSO₄ are mixed.

Fig. 3. Surface tension vs logarithm of concentration for the individual compounds and some of their binary mixtures.

In our study the synergism has been quantified by means of the widely used Rubingh's equations of the Regular Solutions Theory (*RST*) [27] although other authors as Bergstöm [52-54] claim that good agreement between experimental values and those based on the Poisson-Boltzman theory (*PBT*) is obtained. The

main difference between the two theories to explain the large reduction in the cac value when antagonistically charged surfactants are mixed in aqueous solution is that for the *RST* the reason is the attractive interaction between the cationic and anionic surfactant head groups, whereas for *PBT* is due to the increase in entropy when a counterions pair is released from the diffuse layer surrounding the charged aggregate interface to the bulk solution. According to the *RST* the mole fraction of compound 1 in the mixed micelle (X_1^M) can be obtained by solving iteratively the equation:

$$\frac{(X_1^M)^2 \ln(\alpha_1 cmc_{\text{exp}} / X_1^M cmc_1)}{(1 - X_1^M)^2 \ln[(1 - \alpha_1) cmc_{\text{exp}} / (1 - X_1^M) cmc_2]} = 1 \quad (2)$$

And applying this X_1^M value to the following equation, the interaction parameter β^M for the mixed micelle can be obtained:

$$\beta^M = \frac{\ln(\alpha_1 cmc_{\text{exp}} / X_1^M cmc_1)}{(1 - X_1^M)^2} \quad (3)$$

In our study compound 1 is CTAB, compound 2 is bmim-octylSO₄ and cmc is substituted by cac .

Negative values of β^M indicate attractive interactions between the components in the mixed micelle (synergism), positive β^M values indicate repulsive interactions and $\beta^M = 0$ indicates the ideal case of no interaction. However, interactions can not only occur in the bulk solution but also in the liquid/air interface promoting the adsorption of a mixed monolayer. Rosen [28] applied similar equations to calculate the mole fraction of component 1 in the mixed monolayer X_1^σ and the interaction parameter β^σ .

$$\frac{(X_1^\sigma)^2 \ln(\alpha_1 C_{12} / X_1^\sigma C_1)}{(1 - X_1^\sigma)^2 \ln[(1 - \alpha_1) C_{12} / (1 - X_1^\sigma) C_2]} = 1 \quad (4) \quad \beta^\sigma = \frac{\ln(\alpha_1 C_{12} / X_1^\sigma C_1)}{(1 - X_1^\sigma)^2} \quad (5)$$

where C_1 , C_2 and C_{12} are the required concentrations of components 1, 2 and their mixture at α_1 mole fraction, respectively, to decrease the surface tension of the solution (γ) to a fixed value obtained from the plots $\gamma / \log C$ (in our study $\gamma = 45$ mN/m). Negative values of β^σ indicate attractive interactions between the components in the mixed monolayer (synergism), positive β^σ values indicate repulsive interactions and $\beta^\sigma = 0$ indicates the ideal case of no interaction. In Table 1 surface activity parameters (cac , γ_{cac} , pC_{20} , A_{min}) obtained for all the CTAB / bmim-octylSO₄ mixtures studied together with the synergism parameters involving the aggregates (X^M_{CTAB} , β^M) and the monolayer (X^σ_{CTAB} , β^σ) are reported.

Table 1

Surface activity and synergism parameters for the CTAB / bmim-octylSO₄ system at different CTAB mole fractions (α_{CTAB}).

α_{CTAB}	$cac_{exp.}$ (mM)	γ_{cac} (mN/m)	pC_{20}	A_{min} ($\text{\AA}^2$)	X^M_{CTAB}	β^M	X^σ_{CTAB}	β^σ
0	30	31.5	2.56	89.0				
0.05	0.16	28.1	4.79	78.0	0.52	-17.23	0.50	-18.96
0.10	0.08	25.5	4.85	52.7	0.53	-18.65	0.52	-18.71
0.20	0.06	25.9	4.96	56.7	0.52	-18.52	0.54	-18.66
0.30	0.06	25.9	5.05	56.2	0.57	-18.19	0.56	-18.52
0.40	0.06	25.5	5.12	61.0	0.58	-17.79	0.57	-18.42
0.50	0.06	25.1	5.12	60.4	0.59	-17.21	0.58	-18.22
0.60	0.06	25.5	5.15	65.2	0.60	-17.49	0.58	-18.80
0.70	0.06	25.1	5.12	67.0	0.62	-16.87	0.60	-18.58
0.80	0.08	25.5	5.02	64.2	0.63	-16.28	0.61	-18.05
0.90	0.10	25.0	5.00	71.4	0.66	-16.05	0.63	-18.36
1	0.90	36.3	3.92	91.1				

In Fig. 4a experimental and calculated cac values are plotted vs α_{CTAB} . The comparison of experimental and calculated data reveals the strong synergism in the critical aggregation concentration for all CTAB and bmim-octylSO₄ mixtures.

Fig. 4 (a) Theoretical and experimental cac values as a function of the CTAB mole ratio. (b) Surfactant effectiveness (γ_{cac}) and surfactant efficiency (pC_{20}) as a function of the CTAB mole ratio.

In Fig. 4b the surfactant effectiveness (γ_{cac}) and the surfactant efficiency (pC_{20}) are represented as a function of α_{CTAB} . The higher surfactant effectiveness, reflected by the strong γ_{cac} diminution, together with the higher surfactant efficiency, denoted by the high pC_{20} values, for the mixtures respect to the individual components can be observed. It can be observed that the γ_{cac} values reported in Table 1 and Figure 4b are lower than those displayed in Figure 2b at both 0.5 mM and 10 mM concentrations for all α_{CTAB} . As it can be seen in Table 1, very low cac values were obtained for the mixtures specially when comparing these values with the two concentrations used along this work, 0.5 and 10 mM. This fact would allow confirm the hypothesis already mentioned in Section 3.2.2.

about a change in the micellar structure with increasing the concentration, resulting in a diminution of the monomer interfacial adsorption with the consequent surface tension increase. With regard to the area occupied by molecule adsorbed at the interface liquid/air ($A_{\min}$, Table 1), lower values were obtained for the mixtures respect to the individual components, indicating a closer packing between the monomers adsorbed on the monolayer. The negative β^M and β^σ values reported in Table 1 reflect the strong synergism between the cationic surfactant and the ionic liquid both in the aggregates and the monolayer. With regard to the aggregates and monolayer composition (X_{CTAB}^M and X_{CTAB}^σ , respectively), the values change only slightly (from 0.50 to 0.66) with increasing α_{CTAB} in the solution as it can be seen in Fig. 5. These results indicate that the composition of the mixed aggregates and monolayer remains practically constant with the CTAB mole fraction.

Fig. 5. Aggregate (X_{CTAB}^M) and monolayer (X_{CTAB}^σ) composition against the CTAB mole ratio (α_{CTAB}) in the solution.

3.4. Surface activity of synthesized salt free CTA-octylSO₄

In the binary mixtures of CTAB and bmim-octylSO₄ studied, moreover the CTA-octylSO₄ catanionic surfactant, other compounds are present in the aqueous solution. The respective counterions (Br⁻ and bmim⁺) and an excess of bmim-octylSO₄ or CTAB will be also present in the solution depending on the CTAB mole fraction. Since the catanionic surfactant formation involves the electrostatic attraction between a cation CTA⁺ and an anion octylSO₄⁻, the limiting factor in such formation is the lower content of one of the components. To investigate the effect of the other compounds on the surface activity of the catanionic CTA-octylSO₄ in aqueous solution, pure CTA-octylSO₄ was synthesized. Salt (bmim-Br) free CTA-octylSO₄ was prepared as described in Experimental section and its surface activity studied.

Fig. 6. Surface tension vs logarithm of concentration for pure CTA-octylSO₄ and CTA-octylSO₄ plus bmim-Br resulting from the mixture of CTAB and bmim-octylSO₄ at $\alpha_{CTAB} = 0.5$ (a): when total concentration (CTA-octylSO₄ plus bmim-Br) is considered (b): when only the surface active CTA-octylSO₄ concentration is reported in the x-axis.

In Fig. 6a surface tension vs logarithm of total concentration is plotted for the pure CTA-octylSO₄ synthesized as well as for the CTA-octylSO₄ in the presence of the salt, bmim-Br, resulting from the CTAB / bmim-octylSO₄ mixture at $\alpha_{CTAB} = 0.5$. The *cac* obtained for pure CTA-octylSO₄ is 0.042 mM whereas the *cac* for the mixture CTAB and bmim-octylSO₄ at $\alpha_{CTAB} = 0.5$ (leading to CTA-octylSO₄ + bmim-Br) is 0.060 mM (*cac* data from Table 1). However, in the plots $\gamma / \log C$ for the mixtures the concentration to be reported in the x-axis should be only that of the surfactant component, CTA-octylSO₄. The role of the counterions, bmim⁺ and Br⁻, in the aqueous solution is that of an electrolyte, modifying the *cac* of the catanionic surfactant. In Fig. 6b only the concentration of the surface active compound, CTA-octylSO₄, is taken into account. In the latter case, the CTA-octylSO₄ *cac* resulted to be 0.030 mM when bmim-Br is present at equimolar ratio ($\alpha_{CTAB} = 0.5$) in the aqueous solution, instead of 0.042 mM for the pure compound (Table 2).

Table 2

Surface activity parameters of pure CTA-octylSO₄ and CTA-octylSO₄ in the presence of bmim-Br at equimolar ratio.

<i>Compound</i>	<i>cac</i> (mM)	γ_{cac} (mN/m)	pC_{20}	A_{min} (Å ²)
<i>Pure CTA-octylSO₄</i>	0.042	25.0	5.32	65.8
<i>CTA-octylSO₄ (plus bmim-Br)</i>	0.030	25.1	5.42	60.4

3.5. CTAB / bmim-octylSO₄ binary mixtures when catanionic vesicles are formed

Once the catanionic, CTA-octylSO₄, is formed ($\alpha_{\text{CTAB}} \leq 0.6$) has no sense to consider anymore the CTAB and bmim-octylSO₄ binary system, but the right one formed between the catanionic CTA-octylSO₄ and the excess of bmim-octylSO₄ or CTAB (except for $\alpha_{\text{CTAB}} = 0.5$). Naturally, in all these solutions the bmim-Br formed by the respective counterions is also present in the aqueous solution. Since this compound has not surface activity, only the concentration of the surfactant components should be considered to calculate the *cac* of the systems. These recalculated *cac* data are reported in Table 3 together with the synergism parameters (X^M , X^σ , β^M and β^σ) obtained for these systems when applying the equations of the Regular Solutions Theory (Section 3.3.) considering for CTA-octylSO₄ the *cac* value of 0.042 mM.

Table 3

Values of the critical aggregation concentration (*cac*) and synergism parameters for the binary systems of CTA-octylSO₄ and excess of bmim-octylSO₄ or CTAB, together with the *cac* values for the CTAB / bmim-octylSO₄ binary system.

Binary System CTAB / bmim-octylSO ₄		Binary System CTA-octylSO ₄ / Excess of bmim-octylSO ₄ or CTAB					
α_{CTAB}	cac (mM)	α CTA-C ₈ SO ₄	cac (mM)	X^{M} CTA-C ₈ SO ₄	β^{M}	X^{σ} CTA-C ₈ SO ₄	β^{σ}
Binary System CTA-octylSO ₄ / Excess of bmim-octylSO ₄							
0.05	0.16	0.10	0.15	0.71	-8.24	0.67	-10.17
0.10	0.08	0.20	0.07	0.72	-9.57	0.73	-8.30
0.20	0.06	0.40	0.05	0.77	-9.38	0.75	-9.58
0.30	0.06	0.60	0.04	0.81	-8.77	0.78	-9.86
0.40	0.06	0.80	0.03	0.83	-9.65	0.79	-10.70
0.50	0.06	1	0.03	No Excess of bmim-Octyl SO ₄ or CTAB			
Binary System CTA-octylSO ₄ / Excess of CTAB							
0.60	0.06	0.80	0.04	0.81	-4.79	0.74	-7.54

As it can be seen in Table 3, the recalculated cac values are lower than those initially determined. Regarding the synergism between the catanionic compound and the excess of bmim-octylSO₄ or CTAB, less negative β^M and β^σ values than those of the initial CTAB / bmim-octylSO₄ system are obtained (Table 1). That agrees with the lower synergism between a zwitterionic (to which the catanionic surfactant could be compared) and an ionic surfactant respect to cationic / anionic binary surfactant mixtures. On the other hand, for the binary systems of the catanionic CTA-octylSO₄ and the excess of bmim-octylSO₄ or CTAB, the X^M and X^σ values corresponding to vesicle and monolayer compositions, respectively, are higher (Table 3) than those of the CTAB / bmim-octylSO₄ system (Table 1), indicating that the major component in both vesicle and monolayer is the catanionic surfactant.

4. Conclusions

Two different states of aggregation have been characterized as a function of the binary mixture composition for the system formed by the cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), and the surfactant-like ionic liquid, 1-butyl-3-methylimidazolium octyl sulfate (bmim-octyl SO₄), in aqueous solution.

For CTAB mole fractions, α_{CTAB} , higher than 0.6 transparent and colourless solutions with aggregate sizes corresponding to mixed micelles have been found, whereas for $\alpha_{CTAB} \leq 0.6$ bluish solutions with aggregate sizes corresponding to vesicles have been obtained. Values of $\alpha_{CTAB} \leq 0.6$ lead to the formation of the catanionic surfactant, CTA-octyl SO₄. This catanionic compound displays a high surface activity denoted by the low values of critical aggregation concentration (cac) and surface tension at the cac (γ_{cac}), values significantly lower than those of

the individual components. In the range of compositions where the catanionic surfactant CTA-octyl SO₄ is formed, a new binary system consisting of the catanionic surfactant and the excess of bmim-octyl SO₄ or CTAB should be considered. Under this point of view the new surface activity parameters of such system have been reported. This study draws attention on the risk of misinterpretation of the surface activity data in oppositely charged surfactant systems where a catanionic compound can be formed by the appropriate cation and anion combination.

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Appendix A. Supplementary material

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