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Abstract

Hypothesis

Mixtures of the cationic surfactant hexadecyltrimethylammonium bromide (CTA-Br) and the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (bmim-BF₄) in aqueous solutions are expected to behave as typical binary cationic surfactant system taking into account the surface activity displayed by the ionic liquid, instead of considering the IL as a water cosolvent.

Experiments

Surface tension and conductivity measurements have been conducted as a function of the total concentration of the mixtures at different surfactant mole fraction ($\alpha_{\text{CTA-Br}}$) to investigate the surface active properties.

Findings

Turbidity immediately appearing when the compounds are mixed in water suggests the spontaneous formation of the low soluble compound

hexadecyltrimethylammonium tetrafluoroborate (CTA-BF₄), together with the salt formed by the respective counterions bmim⁺ and Br⁻ in solution. For $\alpha_{\text{CTA-Br}} \neq 0.5$, furthermore of the mentioned compounds, the spare bmim-BF₄ (for $\alpha_{\text{CTA-Br}} < 0.5$) or CTA-Br (for $\alpha_{\text{CTA-Br}} > 0.5$), are also present in the aqueous solution. Systems containing excess of bmim-BF₄ show a low critical aggregate concentration (*cac*), but an unexpected high surface tension at *cac* ($\gamma_{\text{cac}} \approx 53\text{-}56$ mN/m), as pure CTA-BF₄. For systems containing excess of CTA-Br, *cac* increases but γ_{cac} decreases up to 36 mN/m. Mixtures of pure CTA-BF₄ and bmim-BF₄ or CTA-Br behave as typical binary surfactant systems.

Key Words

Cationic surfactant, CTAB, ionic liquid, bmim-BF₄, CTA-BF₄, *cac*, surface tension, conductivity, binary systems, synergism

1. Introduction

Some typical properties of ionic liquids (ILs) as high thermal stability, non-flammability, low vapor pressure, low volatility, high solubility power, possible recyclability... have led to consider these compounds as alternative solvents in several industrial applications and basic research [1-5]. The effect of ionic liquids used as dilution media on the critical micelle concentration (*cmc*) of conventional surfactants has been object of numerous studies: When a surfactant is dissolved in a neat ionic liquid, the micellization takes place at a higher concentration than when it is dissolved in neat water [6-14] due to the lower solvophobic interaction between the surfactant alkyl chains and the ionic liquid as compared with the hydrophobic interaction between the surfactant alkyl chains and water.

A different case is when the dilution medium of the surfactant molecules consists of an aqueous solution of an ionic liquid. Numerous studies have been reported [15-29] about the modification of the surfactant micellization in IL / water media. Two opposite behaviors are generally described depending on the IL concentration: At low concentrations, the ionic liquid would behave as an electrolyte decreasing the surfactant *cmc* by reducing the repulsion between the identical charged surfactant ions, whereas at high concentrations IL would behave as a cosolvent increasing the *cmc* because of the lower solvophobicity between surfactant alkyl chains and IL solution respect to surfactant alkyl chains and water, as above mentioned.

Another possible role of an ionic liquid whether it has a long alkyl chain (> C₈) is to behave as a surface active compound when dissolved in water. It has been stated that long-chain ILs display surface activity in water as conventional surfactants do [30-42]. Therefore, when a surface active IL is mixed with a

surfactant in aqueous solution, mixed micelle formation takes place [43-46] as in typical binary surfactant systems.

However, it has been also described that some short alkyl chain ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate (bmim-BF₄), usually considered as water cosolvents, can display surface activity in water [47-50]. In previous studies by the authors on the interaction of surfactants with short alkyl chain ILs [51,52] it was reported that bmim-BF₄ did not only behave as a solvent modifying the *cmc* of the surfactant but as a secondary surfactant. Therefore, the obtained *cmc* or more generally *cac* (critical aggregation concentration) should not be assigned to the individual surfactant but to its mixture with the ionic liquid. In that case the total concentration (surfactant plus surface active ionic liquid) as well as the mole ratio of the mixture of the two surface active compounds should be considered to give a suitable interpretation of the system. Under this point of view, in the present study the interaction between the cationic surfactant hexadecyltrimethylammonium bromide (CTA-Br) and the short alkyl chain ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (bmim-BF₄) at different mole ratios is investigated. The novelty of this work lies in the fact that the interaction of the typical cationic surfactant CTA-Br with the widely used ionic liquid bmim-BF₄ has not been reported. From the above premises it should be expected a moderate synergism in the formation of mixed aggregates between CTA-Br and bmim-BF₄ because of the cationic character of both compounds.

2. Experimental section

2.1. Materials

Cationic surfactant hexadecyltrimethylammonium bromide or cetyltrimethylammonium bromide (CTA-Br) was purchased from Sigma. Ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (bmim-BF₄) was purchased from Fluka. These compounds were used as received. Deionized water was obtained from a Milli-Q device Millipore Synergy UV.

2.2. Sample preparation

Binary mixtures of CTA-Br and bmim-BF₄ at different CTA-Br mole fractions ($\alpha_{\text{CTA-Br}}$ from 0.1 to 0.9) were prepared at a fixed total (CTA-Br + bmim-BF₄) concentration by mixing appropriate volumes of bulk solutions of CTA-Br and bmim-BF₄. For surface tension measurements a total concentration of 2 mM was the maximum initial concentration used given that the binary mixtures at this concentration were already slightly turbid. Binary mixtures of CTA-Br and bmim-BF₄ at different $\alpha_{\text{CTA-Br}}$ were allowed to stand for 24 hours to reach steady state. In the case of binary mixtures of pure CTA-BF₄ with bmim-BF₄ or pure CTA-BF₄ with CTA-Br, at different $\alpha_{\text{CTA-BF}_4}$, samples were prepared at a total concentration of 1 mM because of the lower solubility of such mixtures. The appropriate amount of pure solid CTA-BF₄ was weighted and dissolved in the respective 1 mM solution of bmim-BF₄ or CTA-Br.

2.3. Surface tension measurements

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

2.4. 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.

2.5. Fluorescence measurements.

Steady-state fluorescence measurements were carried out with a Shimadzu RF 540 spectrofluorometer equipped with a thermostated cell holder at 25 °C. Both excitation and emission band slits were fixed at 2 nm. All the data were acquired using quartz cells with 1 cm path length. The fluorescence emission spectra of pyrene dissolved in the CTA-Br / bmim-BF₄ mixtures were recorded from 340 to 450 nm after excitation at 323 nm. The ratio of the first to the three vibronic peaks, *i.e.* I_1/I_3 , can be used to estimate the micropolarity of the aggregates.

2.6. Critical aggregation concentration (*cac*) determination

2.6.1. By surface tension measurements

From the plots of surface tension vs logarithm of the binary mixture concentration the critical aggregation concentration (*cac*) was assigned to the intersection between the line corresponding to the linear decrease in surface tension and the line of stabilized surface tension. Other surface active parameters as surfactant effectiveness γ_{cac} (surface tension at the *cac*) and surfactant efficiency given by the parameter pC_{20} (-logarithm of the surfactant concentration needed to decrease by 20 mN/m the surface tension of pure water) were also determined from these plots. From Gibbs equation other parameters related to the surface activity can be estimated, as the maximum adsorption at the air-liquid interface: $\Gamma_{max} = -(\Delta\gamma/\Delta\log C) / 2.303 n RT$, being $(\Delta\gamma/\Delta\log C)$ the slope of the linear decrease of γ before the *cac*, $R = 8.314 \text{ J}\cdot\text{mol}^{-1} \cdot \text{K}^{-1}$, T the temperature in °K and n the number of species in solution whose interfacial concentration changes with the bulk phase concentration of the surfactant [53]. For single dissociating ionic surfactants in aqueous medium $n = 2$. In the case of binary surfactant systems there are some discrepancies among the appropriate n value to be considered. Rosen et al. [54] calculate n as $n = n_1 \cdot X_1 + n_2 \cdot X_2$ being n_1 and n_2 the number of species of the single surfactants and X_1 and X_2 the mole fractions of the surfactants in the mixed monolayer adsorbed in the interface liquid-air. Some authors consider the addition of the individual n values, reaching values of 4 or even 5 for some surfactant mixtures [55-57] whereas other ones take $n = 2$ [58,59]. On the other hand it has been reported by Eastoe [60,61] and Thomas [62-64] that impurities of divalent cations would diminish n to values lower than 2. In the present study a value of 2

was considered for n . However, being this factor subjected to different interpretations, the value of the slope $\Delta\gamma/\Delta\log C$ is given. Therefore, Γ_{\max} can be recalculated at 25 °C, the temperature of the surface tension measurements, depending on the n value applied to the Gibbs equation. The minimum area (A_{\min}) occupied by adsorbed molecule at the air-liquid interface, expressed in \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 $\text{mol}\cdot\text{cm}^{-2}$.

2.6.2. By conductivity measurements

From the plots of conductivity vs concentration of the binary mixture, the cac was assigned to the concentration at which a change of slope in the linear dependence between conductivity and concentration is produced.

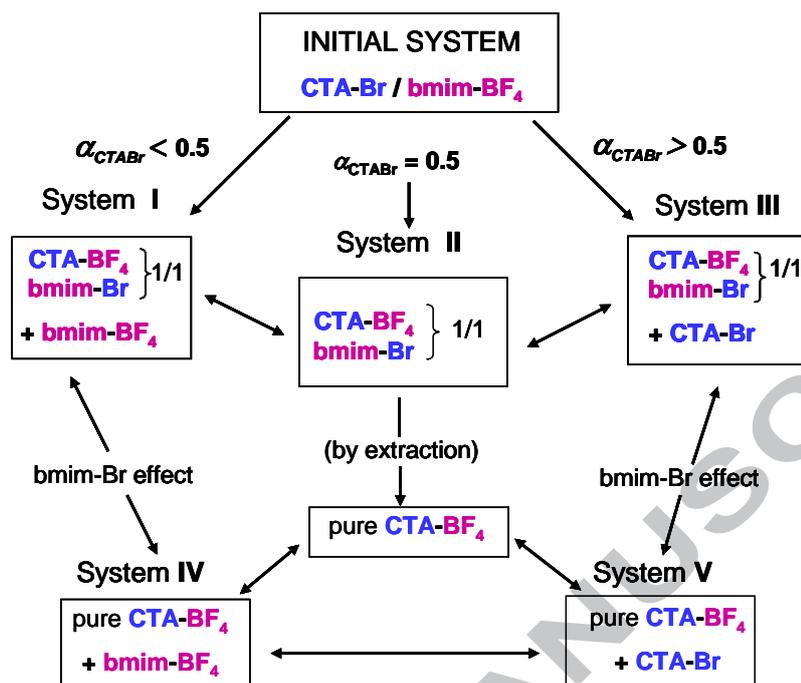
2.7. Isolation of salt free CTA- BF_4

To separate the low water soluble compound, CTA- BF_4 , from the hydrosoluble bmim-Br salt, dichloromethane (DCM) was used. 30 ml of an aqueous solution 50 mM of CTA-Br and 30 ml of an aqueous solution 50 mM of bmim- BF_4 were mixed with 30 ml of dichloromethane (DCM) in a separating funnel. The mixture was vigorously stirred and left to separate for 24 hours. Then the DCM phase was transferred to a flask. Other two fractions of 30 ml of DCM were added to the aqueous solution in the separating funnel and the processes of stirring and phase separation repeated again. The dichloromethane phases (3 x 30 ml) were transferred to the same flask and the aqueous phase (60 ml) containing the bmim-Br was discarded. Afterwards, the DCM phase was poured in the separating funnel and washed with water (2 x 25 ml) to remove any trace of

bmim-Br. Finally, the DCM phase was transferred to an erlenmeyer and dried over anhydrous magnesium sulphate. After removing the organic solvent, salt free CTA-BF₄ was obtained (95 % yield).

3. Results and discussion

A synopsis of the study performed on the CTA-Br / bmim-BF₄ system is shown in Scheme 1. The initial binary system is immediately transformed into System I, System II or System III, depending on the $\alpha_{\text{CTA-Br}}$, because of the spontaneous formation of the low water soluble compound, CTA-BF₄, together with the hydrosoluble salt, bmim-Br, formed by the respective counterions. Given that such compound is formed by the cation CTA⁺ and the anion BF₄⁻, the limiting factor is the lowest mole fraction, $\alpha_{\text{CTA-Br}}$ or $\alpha_{\text{bmim-BF}_4}$. Therefore, except for $\alpha_{\text{CTA-Br}} = 0.5$ (System II), the spare compound bmim-BF₄ (System I) or CTA-Br (System III) not used in the CTA-BF₄ formation is also present in the aqueous solution. On the other hand, CTA-BF₄ was extracted from System II and new systems were prepared by mixing this pure (bmim-Br free) compound with bmim-BF₄ (System IV) or with CTA-Br (System V), allowing the comparison with System I and System III, respectively, to investigate the effect of the bmim-Br salt formed by the counterions of the original system. The surface activity properties of all the systems prepared were determined.



Scheme 1. Synopsis of the study performed on the CTA-Br / bmim-BF₄ system and possibilities of comparison between the different systems in relation to their compositions.

3.1. CTA-Br / bmim-BF₄ binary mixtures at different $\alpha_{\text{CTA-Br}}$ in aqueous solution.

When the 2 mM solutions of CTA-Br and bmim-BF₄ were mixed at different CTA-Br mole fraction, $\alpha_{\text{CTA-Br}}$, mixtures became immediately turbid for any $\alpha_{\text{CTA-Br}}$. The turbidity was due to the exchange between the anions Br⁻ and BF₄⁻ that resulted in the formation of the low soluble compound, CTA-BF₄, together with the salt bmim-Br formed by the respective counterions in a 1/1 ratio. Another system transformation by anion exchange was reported by the authors for the system CTA-Br / bmim-octylSO₄ in aqueous solution [65]. It should be noted that the mixture of CTA-Br and bmim-BF₄ results immediately in one of the three possible systems (I, II, III) displayed in Scheme 1. Although $\alpha_{\text{CTA-Br}}$ is used along the work as reference of the initial binary system, in the new systems the composition would

be better expressed as $\alpha_{\text{CTA-BF}_4}$. In *Supporting Material (T1-SM)* the correspondence between $\alpha_{\text{CTA-Br}}$ and $\alpha_{\text{CTA-BF}_4}$ together with the full composition of samples of the three Systems are reported. The turbid initial samples at 2 mM total concentration became colourless and transparent when subjected to progressive water dilution. When surface tension was registered against logarithm of total concentration, different types of graphs were obtained depending on the $\alpha_{\text{CTA-Br}}$ as illustrated in Fig. 1.

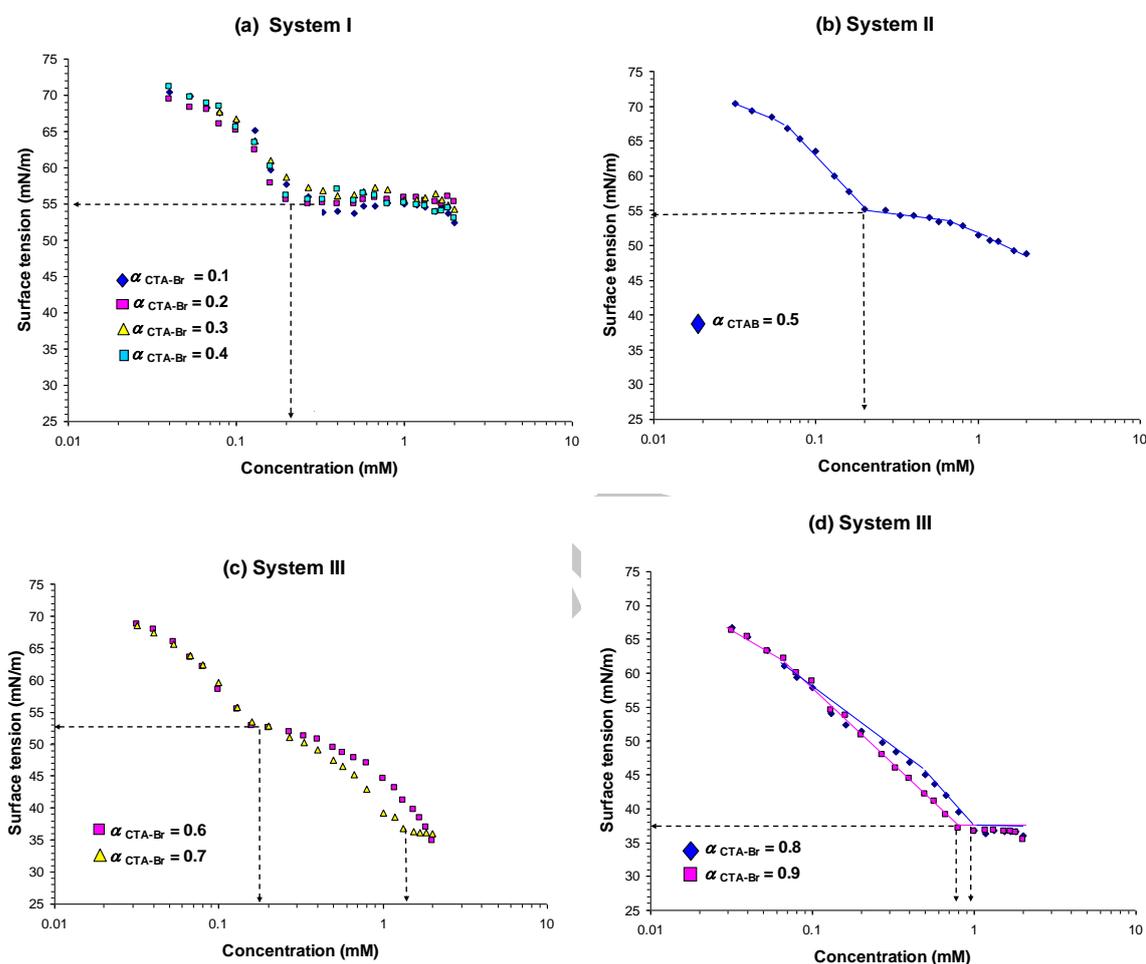


Fig. 1. Surface tension vs logarithm of total concentration for Systems I to III resulting from the binary system CTA-Br / bmim-BF₄ at different α_{CTA-Br} . (a) System I, $\alpha_{CTA-Br} < 0.5$. (b) System II, $\alpha_{CTA-Br} = 0.5$. (c) System III, α_{CTA-Br} 0.6 and 0.7 and (d) System III, α_{CTA-Br} 0.8 and 0.9.

It can be seen in Fig. 1(a) and (b) that for binary mixtures at $\alpha_{CTA-Br} < 0.5$ (System I) and $\alpha_{CTA-Br} = 0.5$ (System II) low cac values ($cac \approx 0.20$ mM) are obtained but associated to high surface tension values at the cac ($\gamma_{cac} \approx 56$ mN/m)

which indicates a very low efficiency in reducing the surface tension of water. The surfactant efficiency is related to the chemical structure of the surfactant, being especially important the characteristics of the hydrophobic chain (nature, number of tails, length, linear or branched...). This parameter is widely reported in numerous studies with the aim of achieving the maximum reduction of the surface tension [66-69]. The very high γ_{cac} values obtained respect to those of the individual components CTA-Br and bmim-BF₄ ($\gamma_{cac} = 36.3$ mN/m and 36.0 mN/m, respectively) seem to confirm that the new systems are very different from the initial CTA-Br / bmim-BF₄, and the peculiar surface activity displayed could be attributed to the new compound CTA-BF₄ because the salt bmim-Br does not display surface activity. The surface activity properties of pure CTA-BF₄ (without bmim-Br present in the aqueous solution) will be further reported in Section 3.2.

In System I, with $\alpha_{CTA-Br} < 0.5$, the other surface active compound is the bmim-BF₄ not used in the CTA-BF₄ formation. However, no significant effect of this compound can be observed on both *cac* and γ_{cac} values when comparing the plots of System I and System II (Fig. 1). An aspect to be considered is that the presence of bmim-Br, whose action as electrolyte leads to a *cac* decrease, could interfere or overlap the possible bmim-BF₄ effect. It should be noted that the concentration of bmim-Br is not constant and it diminishes together with CTA-BF₄ through the dilution. Therefore, the best way to solve these issues would be to determine the surface activity properties of pure CTA-BF₄ (section 3.2.).

In Fig. 1(c), for System III at α_{CTA-Br} 0.6 and 0.7, with a moderate excess of free CTA-Br after the CTA-BF₄ formation, similar *cac* and γ_{cac} values (0.18 mM and ≈ 53 mN/m, respectively) than for Systems I and II are first obtained. However, at higher concentrations than *cac*, surface tension decreases dramatically suggesting

the possibility of another kind of aggregation as was further confirmed by conductivity measurements for $\alpha_{\text{CTA-Br}} = 0.7$. This effect could be promoted by the surfactant CTA-Br which seems to be able to form mixed aggregates with CTA- BF_4 because of a *cmc* value of 0.9 mM. In Fig 1(d), for $\alpha_{\text{CTA-Br}}$ 0.8 and 0.9, when CTA-Br is the predominant component, only an inflexion point appears in the graph at *cac* concentrations around 1 mM and γ_{cac} values of 36 mN/m, compatible with mixed micelles of CTA- BF_4 / CTA-Br.

The aggregation concentration (*cac*) of these systems was also determined by conductivity measurements. An initial concentration higher than 2 mM was used to detect for System III other possible *cac* values at higher concentrations as the plots of surface tension suggested (Fig. 1c) for $\alpha_{\text{CTA-Br}}$ 0.6 and 0.7. In *Supporting Material (F1-SM)* the conductivity graphs are displayed.

“Fluorescence measurements were performed for mixtures of CTA-Br / bmim- BF_4 at some selected $\alpha_{\text{CTA-Br}}$ ratios. The plots (I_1/I_3 vs log C) obtained for $\alpha_{\text{CTA-Br}} < 0.5$, $\alpha_{\text{CTA-Br}} = 0.5$ and $\alpha_{\text{CTA-Br}} > 0.5$ are given in *Supporting Material (Figure S2)*. The differences obtained in the polarity index (I_1/I_3 ratio) suggest a looser packing in the aggregates for $\alpha_{\text{CTA-Br}} \leq 0.5$.”

In Table 1 the self-aggregation (*cac* values) and related surface activity parameters obtained by surface tension and conductivity measurements are reported.

Table 1. Surface activity parameters for Systems I to III resulting from the binary system CTA-Br/bmim-BF₄ at different $\alpha_{\text{CTA-Br}}$ as well as the corresponding $\alpha_{\text{CTA-F4}}$. The values of Γ_{max} and A_{min} were calculated taking $n = 2$ in the Gibbs equation.

System I: CTA-BF ₄ / bmim-Br (1/1) + bmim-BF ₄								
(reference)	$\alpha_{\text{CTA-Br}}$	$\alpha_{\text{CTA-F4}}$	(Conductivity) c_{ac} (mM)	(Surf. tension) c_{ac} (mM)	γ_{cac} (mN/m)	ρC_{20}	$\Gamma_{\text{max}} \times 10^{10}$ (mol/cm ²)	A (Å ²)
	0.1	0.1	0.30	0.32	54.3	-	2.32	71.7
	0.2	0.2	0.12	0.20	55.5	-	2.30	72.2
	0.3	0.3	0.12	0.22	56.8	-	2.44	68.0
	0.4	0.4	0.12	0.21	56.1	-	2.60	64.0
System II: CTA-BF ₄ / bmim-Br (1/1)								
	0.5	0.5	0.14	0.20	55.3	-	2.38	69.8
System III: CTA-BF ₄ / bmim-Br (1/1) + CTA-Br								
	0.6	0.4	0.18	0.18	53.0	3.52	2.36	70.4
			1.9					
	0.7	0.3	0.18	0.18	53.0	3.64	2.52	66.0
			1.7	1.4	36.2		2.32	71.6
	0.8	0.2	1.1	0.95	36.2	3.74	2.55	66.0
	0.9	0.1	1.0	0.80	36.2	3.74	2.20	75.6

A common way to detect a transition between different aggregation structures of a binary system consists in registering the changes in a given property versus the mixture composition at a constant total concentration. In Fig. 2(a) surface tension is plotted as a function of $\alpha_{\text{CTA-Br}}$ at constant total concentrations of 1 and 2 mM. It can be seen that surface tension is practically constant with values ≈ 53 -56 mN/m for $\alpha_{\text{CTA-Br}}$ ranging from 0.1 to 0.4 (System I)

for both concentrations, indicating that no significant change in structure is produced by the presence of bmim-BF₄ in excess. However, a dramatic surface tension decrease is produced for $\alpha_{\text{CTA-Br}} > 0.5$ (System III) when CTA-Br is present in the aqueous solution. When the total concentration is 2 mM the surface tension reach an equilibrium value around 35 mN/m at $\alpha_{\text{CTA-Br}} \geq 0.6$, whereas for 1 mM total concentration the surface tension attain an equilibrium value around 36 mN/m at $\alpha_{\text{CTA-Br}} \geq 0.8$. Therefore, it seems that a structural change is produced for $\alpha_{\text{CTA-Br}} > 0.5$, i.e., in the presence of a CTA-Br excess.

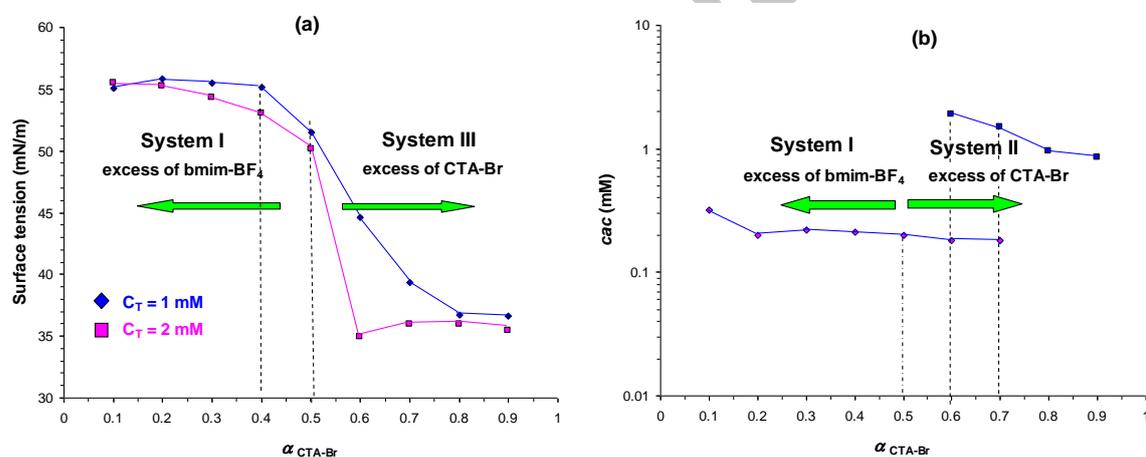


Fig. 2(a) Surface tension as a function of $\alpha_{\text{CTA-Br}}$ for the binary system CTA-Br / bmim-BF₄ at 1 and 2 mM total concentration. **(b)** Critical aggregation concentration (*cac*) as a function of $\alpha_{\text{CTA-Br}}$ for the binary system CTA-Br / bmim-BF₄.

In Fig. 2(b) the *cac* values are displayed as a function of $\alpha_{\text{CTA-Br}}$. The low *cac* value of 0.20 mM seems to be associated to the CTA-BF₄ aggregates, whereas the two *cac* values obtained for $\alpha_{\text{CTA-Br}}$ 0.6 and 0.7 suggest the coexistence between the CTA-BF₄ and others aggregates, probably micellar mixtures of CTA-BF₄ and CTA-Br. At $\alpha_{\text{CTA-Br}} \geq 0.8$ only a *cac* value ≈ 0.8 mM, close to the value of pure CTA-Br, is obtained. Thus, in the case of $\alpha_{\text{CTA-Br}} > 0.5$, when

an excess of CTA-Br exists in the aqueous solution, the formation of mixed aggregates between this cationic surfactant ($cac \approx 0.9$ mM and $\gamma_{cac} \approx 36$ mN/m) and CTA-BF₄ is likely.

3.2. Surface active properties of pure CTA-BF₄.

CTA-BF₄ was extracted from the binary mixture of CTA- BF₄ / bmim-Br obtained from the initial CTA-Br / bmim-BF₄ binary system at $\alpha_{CTA-Br} = 0.5$ (System II). The cac of the isolated CTA-BF₄ was determined by surface tension and conductivity measurements. The results are showed in Fig. 3.

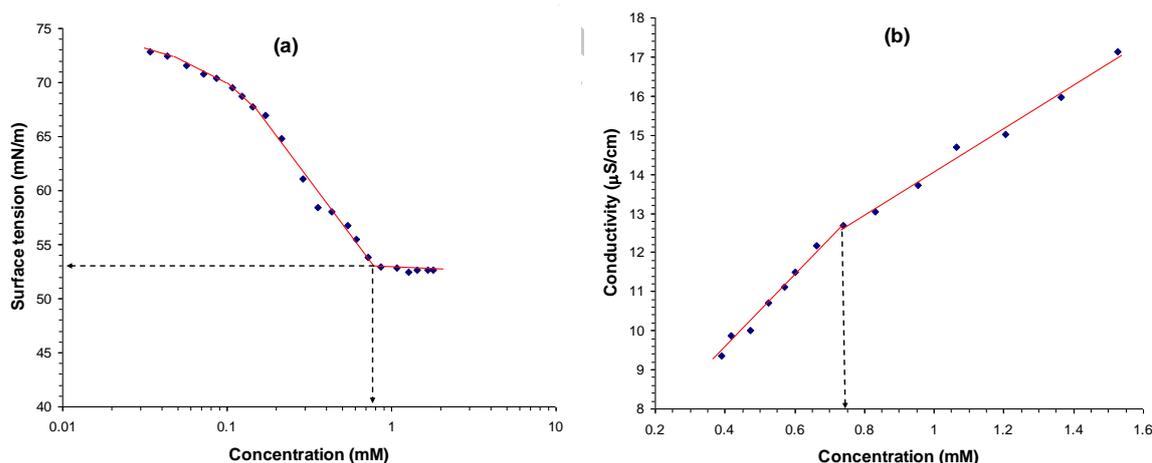


Fig. 3. Critical aggregation concentration (cac) of pure CTA-BF₄ determined by (a) Surface tension and (b) Conductivity.

It can be seen that similar cac values ≈ 0.7 - 0.8 mM are obtained by both techniques. However, the most remarkable feature is the γ_{cac} value ≈ 53 mN/m obtained which suggests the hypothesis that is CTA-BF₄ the responsible of the high γ_{cac} values obtained by Systems I and II. In Table 2 the surface activity parameters of pure CTA-BF₄ are reported together with the parameters obtained

for $\alpha_{\text{CTA-Br}} = 0.5$ (System II) when besides CTA-BF₄, there is bmim-Br in a 1/1 ratio in the aqueous solution.

Table 2. Surface activity parameters determined for pure CTA-BF₄ and System II (CTA-BF₄ + bmim-Br in 1/1 ratio). The values of Γ_{max} and A_{min} were calculated taking $n = 2$ in the Gibbs equation.

Compound	c_{ac} (mM)	γ_{cac} (mN/m)	ρC_{20}	$(\Delta\gamma/\Delta\log C)$	$\Gamma_{\text{max}} \times 10^{10}$ (mol/cm ²)	A (Å ²)
Pure CTA-BF ₄	0.8	53.0	-	- 18.58	1.63	102.0
System II						
{ CTA-BF ₄ (1)	0.2	55.3	-	- 27.14	2.38	69.8
{ bmim-Br (1)						

When comparing both systems, it can be seen (Table 2) that for pure CTA-BF₄ the c_{ac} value (0.8 mM) is higher than the value obtained (0.2 mM) for the initial binary system CTA-Br / bmim-BF₄ at $\alpha_{\text{CTA-Br}} = 0.5$ (System II). This fact confirms the salt effect on reducing the c_{ac} of ionic surfactants, here promoted by bmim-Br. On the other hand, the minimum area occupied by adsorbed CTA-BF₄ molecule (A) increased with respect to System II because of the absence of bmim-Br which is able to reduce the electrostatic repulsion between the CTA⁺ cations.

With regard to the surface tension stabilization, the compound CTA-BF₄ seems to be the responsible of the high γ_{cac} values, as it was before suggested. However, no explanation about the unusual high γ_{cac} value has been found until now. Because of the $\gamma_{\text{cac}} > 52$ mN/m no value of ρC_{20} can be calculated. Given that in Systems I and III, moreover CTA-BF₄, there is bmim-Br salt in the aqueous solution, it would

be interesting to determine the interaction between pure CTA-BF₄ and bmim-BF₄ (System IV) and pure CTA-BF₄ and CTA-Br (System V) in absence of bmim-Br.

3.3. Binary systems of pure CTA-BF₄ / bmim-BF₄ (System IV) and pure CTA-BF₄ / CTA-Br (System V) in aqueous solution.

Binary mixtures of CTA-BF₄ with bmim-BF₄ or with CTA-Br were prepared to give System IV and System V, respectively (See Scheme 1). In these systems there is not bmim-Br in the solution, therefore, the effect of this compound can be illustrated by comparing System IV with System I and System V with System III. Surface tension data vs logarithm of concentration for System IV and System V at different values of $\alpha_{\text{CTA-BF}_4}$ are plotted in Fig. 4.

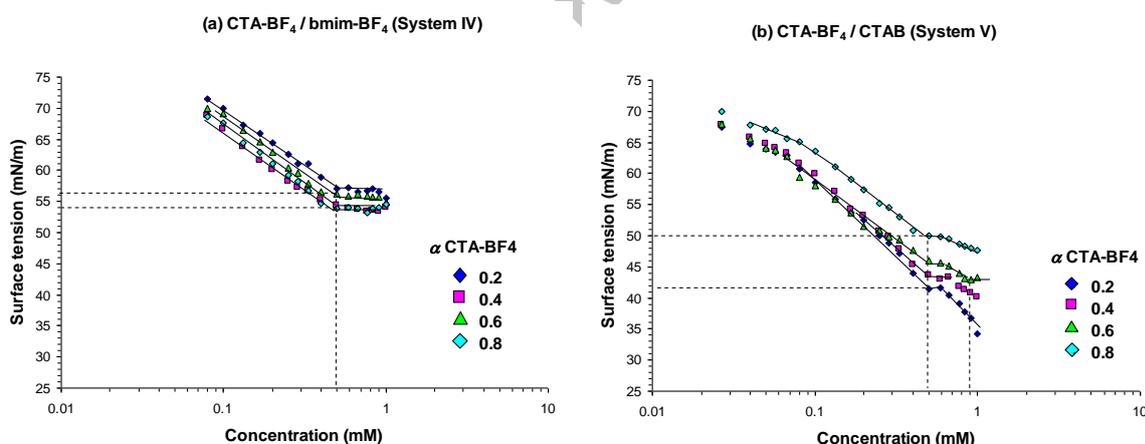


Fig. 4. Surface tension vs logarithm of total concentration at different $\alpha_{\text{CTA-BF}_4}$ for (a) CTA-BF₄ / bmim-BF₄ (System IV) and (b) CTA-BF₄ / CTA-Br (System V).

With respect to the high values of stabilized surface tension, it can be seen in Fig. 4 (a) a similar behavior of these CTA-BF₄ / bmim-BF₄ mixtures (System IV) than for pure CTA-BF₄ (Fig. 4a) and also for System I (Fig. 1a), with $\gamma_{\text{cac}} \geq 53$ mN/m. However, there are clear differences among the *cac* values of pure CTA-

BF_4 (≈ 0.80 mM), System IV (≈ 0.50 mM) and System I (≈ 0.20 mM), attributable to the presence of bmim-BF_4 in System IV or $\text{bmim-Br} + \text{bmim-BF}_4$ in System I. It can be observed the effect of bmim-BF_4 on the CTA- BF_4 *cac* reduction (System IV) suggesting the formation of mixed aggregates between these two compounds. Comparison of Systems IV and I shows the effect of bmim-Br as electrolyte on the *cac* value decrease.

When CTA- BF_4 is mixed with CTA-Br (System V) a progressive surface tension decrease is produced (Fig. 4b) that reaches values in the range 35 to 45 mN/m depending on the $\alpha_{\text{CTA-BF}_4}$ mole fraction. It can be detected a short surface tension plateau around 0.50 mM denoting the aggregates formation (*cac*) and at higher concentrations the surface tension decreases again. These graphs can be compared with those of System III (Fig. 1c), however, in that case, the aggregation is produced at lower concentration because of the salt effect of bmim-Br .

In Table 3 the surface activity parameters for binary mixtures of System IV and System V are reported. It can be seen that although the *cac* values are practically identical, around 0.50 mM, much higher values of surface tension ($\gamma_{\text{cac}} \approx 54\text{-}56$ mN/m) are obtained for System IV where CTA- BF_4 is mixed with bmim-BF_4 . It must be noted that System IV and System V are typical binary surfactant systems, because no other compounds (as bmim-Br) are present in the aqueous solution. Therefore, the *Regular Solution Theory* [70] equations for binary surfactant systems can be applied in such systems. To evaluate the synergism parameters of the binary mixtures, CTA- BF_4 / bmim-BF_4 and CTA- BF_4 / CTA-Br, *cac* values of 850 mM and 0.90 mM were used in the equations for bmim-BF_4 and CTA-Br, respectively.

Table 3. Surface activity parameters obtained for the binary systems CTA-BF₄ / bmim-BF₄ (System IV) and CTA-BF₄ / CTA-Br (System V) in aqueous solution. The values of Γ_{\max} and A_{\min} were calculated taking $n = 2$ in the Gibbs equation.

CTA- BF ₄ / bmim-BF ₄ (System IV)						
$\alpha_{\text{CTA-BF}_4}$	$c_{\text{cac}}^{\text{exp}}$ (mM)	γ_{cac} (mN/m)	ρC_{20}	$(\Delta\gamma/\Delta\log C)$	$\Gamma_{\max} \times 10^{10}$ (mol/cm ²)	A (Å ²)
0.2	0.50	56.8	-	- 18.612	1.63	101.8
0.4	0.50	54.4	-	- 17.98	1.58	105.4
0.6	0.50	56.5	-	- 21.04	1.85	90.0
0.8	0.50	53.9	-	- 20.16	1.77	94.0
CTA- BF ₄ / CTA-Br (System V)						
0.2	0.50	41.4	3.68	-28.04	2.46	67.6
0.4	0.50	43.7	3.66	- 23.25	2.04	81.5
0.6	0.50	46.0	3.72	- 17.81	1.56	106.4
	0.90	43.9				
0.8	0.50	49.9	3.57	- 21.03	1.84	90.1

According to the *Regular Solution Theory* [70] and Rosen [54] equations, the mole composition of the mixed aggregates X^M and mixed monolayers X^σ as well as the corresponding interaction β^M and β^σ parameters can be obtained (*Supporting Material: E1-SM*).

In Fig. 5, as an example, the plots γ vs. $\log C$ for the individual components and their mixture at $\alpha_{\text{CTA-BF}_4} = 0.4$ are shown, illustrating the synergism produced both in the mixed aggregate and mixed monolayer formation for System IV (Fig. 5a) and System V (Fig. 5b). To calculate the synergism parameters corresponding to the mixed monolayer, the required concentration to achieve a constant surface tension value (57 mN/m for System IV and 53 mN/m for System V) is considered.

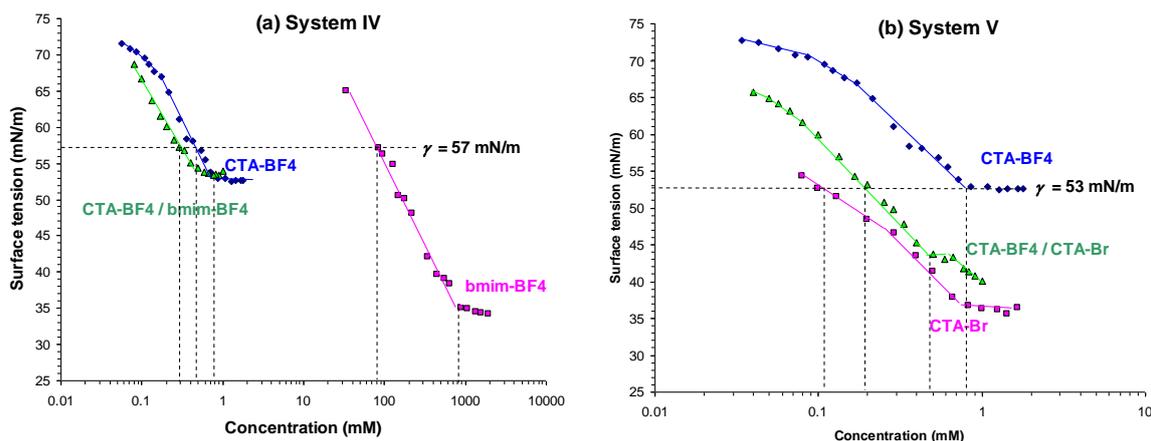


Fig. 5. Plots γ vs. $\log C$ for individual components and their mixture at $\alpha_{\text{CTA-BF}_4} = 0.4$ for (a) System IV and (b) System V.

As it can be seen in Fig. 5(a), both the cac value and the necessary concentration to attain 57 mN/m are lower for the mixture CTA-BF₄ + bmim-BF₄ (System IV) than the corresponding values of the individual components, indicating a strong interaction. Much less interaction is produced in System V (CTA-BF₄ + CTA-Br) as it can be seen in Fig. 5(b), especially with regard to the monolayer formation, given that the mixed concentration necessary to have the selected value of $\gamma = 53$ mN/m is between those of the individual compounds. In *Supporting Material (T2-SM)* the synergism parameters β^M and β^σ as well as the composition of mixed aggregates ($X^M_{\text{CTA-BF}_4}$) and mixed monolayers ($X^\sigma_{\text{CTA-BF}_4}$) are displayed. The very negative values of β^M and β^σ parameters obtained for System IV reflect the strong synergism produced between CTA-BF₄ and bmim-BF₄ in the formation of both the mixed aggregates and monolayers.

In Fig. 6 the mole fractions $X^M_{\text{CTA-BF}_4}$ and $X^\sigma_{\text{CTA-BF}_4}$ are plotted as a function of the $\alpha_{\text{CTA-BF}_4}$ mole fraction in bulk solution for the two systems. The high $X^M_{\text{CTA-BF}_4}$ and $X^\sigma_{\text{CTA-BF}_4}$ values respect to $\alpha_{\text{CTA-BF}_4}$ displayed in Fig. 6(a) for System IV (for

$\alpha_{\text{CTA-BF}_4} < 0.8$) indicate that CTA-BF₄ is the main compound both in the mixed aggregate and monolayer. Being CTA-BF₄ responsible of the high γ_{cac} values (Fig. 5), its predominant presence in the monolayer would explain the high γ_{cac} determined for the system (Table 3). In Fig. 6(b), when CTA-BF₄ is mixed with CTA-Br (System V), the mixed aggregate composition $X^{\text{M}}_{\text{CTA-BF}_4}$ plot shows the typical shape observed in most binary surfactant systems around the theoretical line (1/1) of $\alpha_{\text{CTA-BF}_4} / X^{\text{M}}_{\text{CTA-BF}_4}$ when the $\alpha_{\text{CTA-BF}_4}$ mole fraction in bulk solution increases. With respect to the mixed monolayer composition, the low $X^{\sigma}_{\text{CTA-BF}_4}$ values indicate that the main component in the monolayer is the cationic surfactant CTA-Br. The low surface tension (γ_{cac}) associated to this compound would justify the lower γ_{cac} values obtained for System V (Table 3).

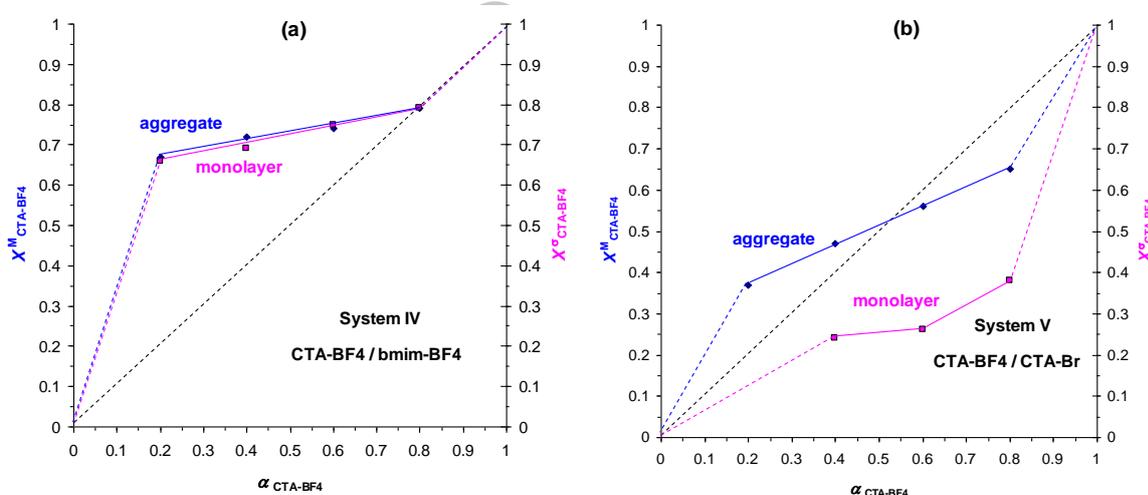


Fig.6. Composition of the mixed aggregates $X^{\text{M}}_{\text{CTA-BF}_4}$ and mixed monolayer $X^{\sigma}_{\text{CTA-BF}_4}$, as a function of the mole fraction in bulk solution, $\alpha_{\text{CTA-BF}_4}$ for (a) System IV (CTA-BF₄ / bmim-BF₄) and (b) System V (CTA-BF₄ / CTA-Br).

4. Conclusions

There are many studies about the surface activity properties of aqueous solutions of binary mixtures between surfactants and short alkyl chain ionic liquids acting as water cosolvents [15,16] and binary systems of surfactants and long-chain ionic liquids acting as surfactants [43,44]. However, the CTA-Br / bmim-BF₄ system here studied behaves in a very different way. The first hypothesis was to consider such mixture as a binary cationic system where a moderate synergism would be expected, because of the surfactant activity reported for the short alkyl chain ionic liquid, bmim-BF₄ [47] in contrast with a previous study of CTA-Br and bmim-octyl sulfate, where a catanionic surfactant was formed [65]. In previous works the surfactant-like behavior of bmim-BF₄ was already studied by the authors in mixtures with conventional nonionic [51] and anionic surfactants [52]. However, the initial hypothesis was discarded when the ionic liquid, bmim-BF₄, was mixed with the cationic surfactant, CTA-Br, because of the immediate and spontaneous formation of the low water soluble compound, CTA-BF₄, together with bmim-Br salt formed by the respective counterions. Once isolated, the peculiar surface activity behavior of pure (bmim-Br free) CTA-BF₄ was evidenced, with a clear and quite low critical aggregation concentration ($cac \approx 0.8$ mM) but with a surprisingly high surface tension at the cac ($\gamma_{cac} \approx 53$ mN/m). This high γ_{cac} value contrasts with the low γ_{cac} values of the individual compounds of the initial system (36.3 mN/m and 36.0 mN/m for CTA-Br and bmim-BF₄, respectively). For CTA-Br / bmim-BF₄ mixtures with a mole fraction in the aqueous solution $\alpha_{CTA-Br} \neq 0.5$, moreover CTA-BF₄ and bmim-Br in ratio 1/1, an excess of the compound do not involved in the CTA-BF₄ formation, i.e., bmim-BF₄ for $\alpha_{CTA-Br} < 0.5$ and CTA-Br for $\alpha_{CTA-Br} > 0.5$, is

also present. For systems with an excess of bmim-BF₄, and independently whether bmim-Br is or not present, there are no significant changes in the surfactant effectiveness of the system revealing the prevailing properties of CTA-BF₄ in these mixtures. The predominant presence of CTA-BF₄ in the mixed monolayer composition could explain the high γ_{cac} values obtained for these systems. On the contrary, the CTA-Br excess in CTA-Br / bmim-BF₄ systems leads to a progressive modification of the *cac* values through the mixture composition, denoting the importance of CTA-Br in the mixed aggregate formation. The major presence of CTA-Br compound in the mixed monolayer would justify the progressive decrease of γ_{cac} up to $\gamma_{cac} \approx 36$ mN/m when the α_{CTA-Br} mole ratio in the aqueous solution increases. The role of bmim-Br in the mixtures is that of an electrolyte, decreasing the *cac* values. In view to future work, it is of interest to investigate in which cases the especial CTA-BF₄ properties would be applied.

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ACCEPTED MANUSCRIPT

Hexadecyltrimethylammonium bromide (CTA-Br) and 1-butyl-3-methylimidazolium tetrafluoroborate (bmim-BF₄) in aqueous solution: an ephemeral binary system

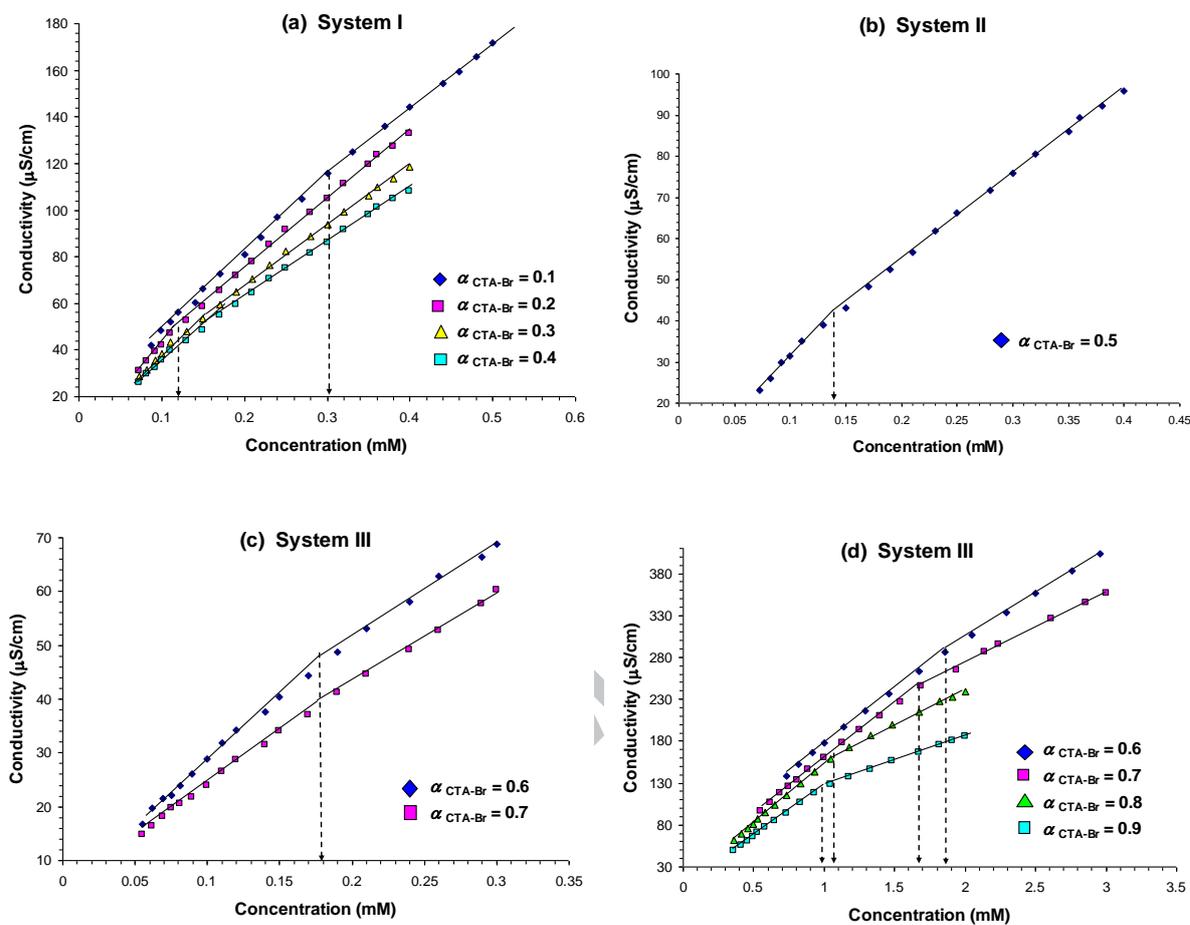
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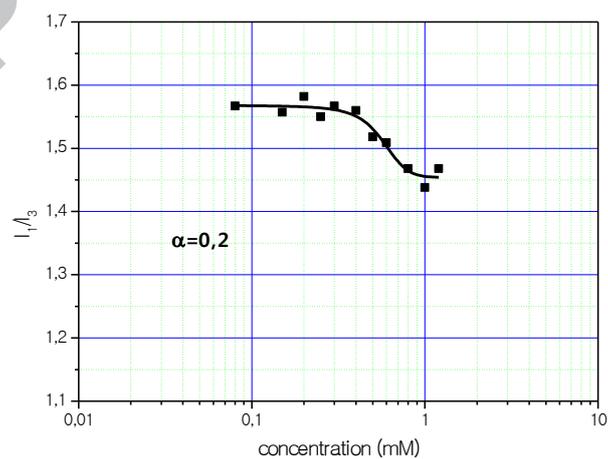
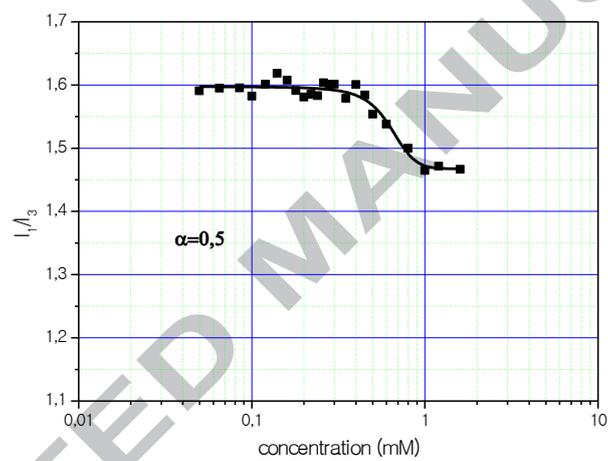
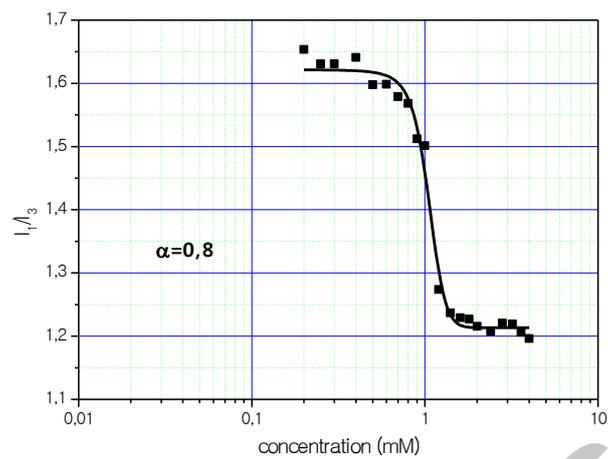
SUPPORTING MATERIAL (SM)

T1-SM. Compositions of Systems I, II and III depending on the $\alpha_{\text{CTA-Br}}$ in the initial system.

	<i>Initial system</i>		<i>Resulting system</i>	
	CTA-Br + bmim-BF ₄ $\alpha_{\text{CTA-Br}}$	<i>New compound</i> CTA-BF ₄ $\alpha_{\text{CTA-BF}_4}$	<i>Counterions salt</i> bmim-Br $\alpha_{\text{bmim-Br}}$	<i>Excess</i> bmim-BF ₄ $\alpha_{\text{bmim-BF}_4}$
System I	0.1	0.1	0.1	0.8
	0.2	0.2	0.2	0.6
	0.3	0.3	0.3	0.4
	0.4	0.4	0.4	0.2
System II	0.5	0.5	0.5	-
				<i>Excess</i> CTA-Br $\alpha_{\text{CTA-Br}}$
System	$\alpha_{\text{CTA-Br}}$	$\alpha_{\text{CTA-BF}_4}$	$\alpha_{\text{bmim-Br}}$	$\alpha_{\text{CTA-Br}}$
III	0.6	0.4	0.4	0.2
	0.7	0.3	0.3	0.4
	0.8	0.2	0.2	0.6
	0.9	0.1	0.1	0.8



F1-SM. Conductivity vs total concentration for Systems I to III resulting from the binary system CTA-Br / bmim-BF₄ at different $\alpha_{\text{CTA-Br}}$. (a) System I, $\alpha_{\text{CTA-Br}} < 0.5$. (b) System II, $\alpha_{\text{CTA-Br}} = 0.5$. (c) System III with $\alpha_{\text{CTA-Br}}$ 0.6 and 0.7 at $c < 0.35$ mM and (d) System III with $\alpha_{\text{CTA-Br}} > 0.5$ at $c > 0.35$ mM.



F2-SM. Fluorescence plots for $\alpha_{\text{CTA-Br}} = 0.8$, $\alpha_{\text{CTA-Br}} = 0.5$ and $\alpha_{\text{CTA-Br}} = 0.2$

E1- SM. Regular Solution Theory (RST) Equations

The mole fraction of compound 1 in the mixed aggregate (X_1^M) can be obtained by solving iteratively the equation:

$$\frac{(X_1^M)^2 \ln(\alpha_1 cac_{\text{exp}} / X_1^M cac_1)}{(1 - X_1^M)^2 \ln[(1 - \alpha_1) cac_{\text{exp}} / (1 - X_1^M) cac_2]} = 1 \quad (1)$$

Applying this X_1^M value to the following equation, the interaction parameter β^M for the mixed aggregate can be obtained:

$$\beta^M = \frac{\ln(\alpha_1 cac_{\text{exp}} / X_1^M cac_1)}{(1 - X_1^M)^2} \quad (2)$$

In our study compound 1 is CTA-BF₄ and compound 2 is bmim-BF₄ or CTA-Br.

The mole fraction of component 1 in the mixed monolayer (X_1^σ) can be obtained by solving iteratively the equation: the interaction parameter β^σ .

$$\frac{(X_1^\sigma)^2 \ln(\alpha_1 C_{12} / X_1^\sigma C_1)}{(1 - X_1^\sigma)^2 \ln[(1 - \alpha_1) C_{12} / (1 - X_1^\sigma) C_2]} = 1 \quad (3)$$

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 γ vs. $\log C$ (in our study $\gamma = 57$ mN/m for System IV or 53 mN/m for System V).

Applying this X_1^M value to the following equation, the interaction parameter β^M for the mixed aggregate can be obtained:

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

T2-SM. Composition of the mixed aggregates ($X^M_{\text{CTA-BF}_4}$) and mixed monolayers ($X^\sigma_{\text{CTA-BF}_4}$), together with the corresponding interaction parameters β^M and β^σ for System IV and System V at different $\alpha_{\text{CTA-BF}_4}$.

CTA-BF ₄ / bmim-BF ₄ (System IV)				
$\alpha_{\text{CTA-BF}_4}$	$X^M_{\text{CTA-BF}_4}$	β^M	$X^\sigma_{\text{CTA-BF}_4}$	β^σ *
0.2	0.67	-14.89	0.66	-9.99
0.4	0.72	-13.05	0.69	-10.48
0.6	0.74	-13.24	0.75	-8.87
0.8	0.79	-11.90	0.78	-9.19

CTA-BF ₄ / CTA-Br (System V)				
$\alpha_{\text{CTA-BF}_4}$	$X^M_{\text{CTA-BF}_4}$	β^M	$X^\sigma_{\text{CTA-BF}_4}$	β^σ **
0.2	0.37	-2.67	(a)	(a)
0.4	0.47	-2.18	0.24	-2.52
0.6	0.56	-2.13	0.26	-1.16
0.8	0.65	-3.08	0.38	-0.81

* for $\gamma = 57$ mN/m; ** for $\gamma = 53$ mN/m: (a): no mathematical solution was found

Graphical abstract

