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## **Pósteres *Posters***

**P01 AGENTES POLIMERICOS PARA LA ANTIRREDEPOSICIÓN DE IMPUREZAS EN EL LAVADO DE TEJIDOS DE FIBRAS SINTÉTICAS**

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**P02 INTERACTION OF NONIONIC SURFACTANTS AND HYDROPHILIC IONIC LIQUIDS IN AQUEOUS SOLUTIONS**

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## INTERACTION OF NONIONIC SURFACTANTS AND HYDROPHILIC IONIC LIQUIDS IN AQUEOUS SOLUTIONS

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### ABSTRACT

The interaction between an ethoxylated nonionic surfactant (C<sub>12-14</sub> EO<sub>8</sub>) and three conventional hydrophilic imidazolium based ionic liquids (bmim-OctylSO<sub>4</sub>, bmim-MethylSO<sub>4</sub>, and bmim-BF<sub>4</sub>) in aqueous solution has been investigated. In most of the reported studies where a surfactant is dissolved in an ionic liquid aqueous solution, conventional ionic liquids are merely considered as solvents. Consequently, the resulting critical micelle concentration (cmc) is considered to be that of the surfactant. However, given that the three ionic liquids selected showed the typical shape of a surface active compound when the surface tension was plotted against concentration, the role of these compounds as "secondary surfactant" and consequently the possibility of mixed micelles formation has been suggested.

### INTRODUCTION

In the last years, the chemical and physical properties of ionic liquids (ILs) have attracted the interest of these compounds in many applications, as organic synthesis, catalysis, chemical separation, electrochemistry, photochemistry, nanomaterials.... One of the most outstanding properties of these compounds is its very low volatility that prevents environmental air pollution and consequently makes them candidates to substitute volatile organic solvents in different application fields. Accordingly with its claimed role of "green solvents", a wide series of studies where different kind of conventional surfactants are dissolved in ionic liquids have been reported. In some of these studies the surfactant is dissolved in the ionic liquid as unique solvent<sup>1-13</sup>. In that case, it has been found that surfactants aggregate in IL media in analogous way as in water, but with two important differences. First, the surface tension of pure ILs ( $\gamma \approx 35-48$  mN/m) is clearly lower than the surface tension of water ( $\gamma \approx 72$  mN/m) and consequently, the diminution of surface tension from the neat ionic liquid to the equilibrium value ( $\gamma_{cmc}$ ) is lower than if the surfactant is dissolved in neat water. The other difference is that the cmc values in ionic liquid are clearly higher than those in water. This fact is attributed to the lower solvophobic interaction between the surfactant alkyl chains in the IL with respect to the hydrophobic interactions between these surfactant alkyl chains in pure water<sup>4-6</sup>.

In other kind of studies, conventional surfactants were dissolved in aqueous ionic liquid solutions<sup>14-23</sup>. That is an interesting case involving three components: surfactant, ionic liquid and water. In the reported studies the attention is focussed on the surfactant, considering that the new cmc obtained is a consequence of the IL effect on the surfactant micellization. However, in the present study we show as other authors, that even for typical short alkyl chain ionic liquids, a process of aggregation in aqueous solution can also take place in some cases<sup>24-33</sup>. For this reason, when a surfactant is dissolved in an aqueous solution containing some of these ILs its

possible role as a “secondary surfactant” should be considered. We claim that these systems should be treated as typical binary surfactant mixtures in aqueous solution and the obtained cmc values for these systems would not correspond solely to the value of the surfactant (modified by the presence of the IL) but to the mixed micelles of surfactant and ionic liquid. Bearing in mind this possibility, in the present work, binary systems consisting of a conventional ethoxylated nonionic surfactant as C<sub>12-14</sub>EO<sub>8</sub> and a common hydrophilic ionic liquid (bmim-Octyl SO<sub>4</sub>, bmim-Methyl SO<sub>4</sub> or bmim-BF<sub>4</sub>) in aqueous solution have been investigated.

## EXPERIMENTAL SECTION

**Materials.** The nonionic surfactant Dehydol PLS 8 corresponding to C<sub>12-14</sub>EO<sub>8</sub> was a gift from Cognis. The ionic liquids bmim-OctylSO<sub>4</sub>, bmim-MethylSO<sub>4</sub> and bmim-BF<sub>4</sub> were purchased from Fluka and used as received without further purification. Deionized water was obtained from a milli-Q device.

**Sample preparation.** In the first series of experiments, aqueous ionic liquid solutions at constant concentrations were prepared and used as surfactant dilution media. From an initial surfactant concentration and through successive dilutions with this ionic liquid solution, decreasing concentrations of surfactant were obtained whereas the ionic liquid concentration remained constant. Consequently, the C<sub>12-14</sub>EO<sub>8</sub> mole fraction  $\alpha_1$  in the mixture decreases progressively through dilution. In the second series of experiments, aqueous C<sub>12-14</sub>EO<sub>8</sub> solutions at constant concentrations were prepared and used as ionic liquid dilution media. In this case,  $\alpha_1$  increases when the ionic liquid is progressively diluted. In the third series of aqueous binary systems, the non-ionic surfactant and ionic liquid were combined together in different mole ratios. Each initial concentrated solution (total concentration including the two components) was diluted progressively with water. Obviously in these cases, the C<sub>12-14</sub>EO<sub>8</sub> mole fraction  $\alpha_1$  is maintained constant through the dilution.

**Surface tension measurements.** The surface tension ( $\gamma$ ) of each solution was measured with a Krüss K12 tensiometer by the Wilhelmy plate method at 25°C. From the plots of surface tension against the logarithm of compound concentration, the critical micelle concentration (cmc), the effectiveness of surface tension reduction ( $\gamma_{cmc}$ ) and the surfactant efficiency given by the parameter  $pC_{20}$  (-logarithm of the necessary concentration to diminish the surface tension of the pure water by 20 unities i.e. 52 mN/m) were determined.

The maximum surface excess concentration ( $\Gamma_m$ ) was obtained from the Gibbs equation:  $\Gamma_m = -(\Delta\gamma/\Delta\log C) / 2.303 n RT$ , being  $(\Delta\gamma/\Delta\log C)$  the slope of the straight line of the graph before the cmc, and  $n$  the number of molecular species in solution ( $n = 1$  for non-ionic surfactants,  $n = 2$  for ionic surfactants, and  $n$  ranging from 1 to 2 in the mixtures). The minimum area per molecule adsorbed at the saturated water/air interface ( $A_m$ ) expressed in Å<sup>2</sup> was obtained from:  $A_m = 10^{16} / N_A \Gamma_m$ , where  $N_A$  is the Avogadro's number and  $\Gamma_m$  the maximum surface excess concentration expressed in mol·cm<sup>-2</sup>.

## RESULTS AND DISCUSSION

### Surface active properties of the individual components

Whereas for long alkyl chain ionic liquids the surfactant behavior has been widely reported<sup>34-45</sup> conventional short chain ILs are mainly considered as solvents.

possible role as a “secondary surfactant” should be considered. We claim that these systems should be treated as typical binary surfactant mixtures in aqueous solution and the obtained cmc values for these systems would not correspond solely to the value of the surfactant (modified by the presence of the IL) but to the mixed micelles of surfactant and ionic liquid. Bearing in mind this possibility, in the present work, binary systems consisting of a conventional ethoxylated nonionic surfactant as C<sub>12-14</sub>EO<sub>8</sub> and a common hydrophilic ionic liquid (bmim-Octyl SO<sub>4</sub>, bmim-Methyl SO<sub>4</sub> or bmim-BF<sub>4</sub>) in aqueous solution have been investigated.

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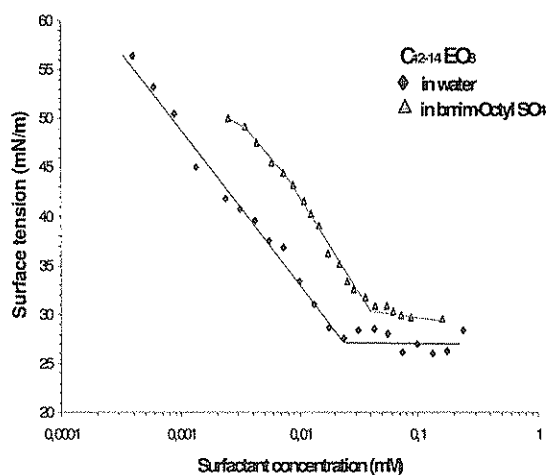
Whereas for long alkyl chain ionic liquids the surfactant behavior has been widely reported<sup>34-45</sup> conventional short chain ILs are mainly considered as solvents.

are considered only as aqueous cosolvents, it would be interesting to consider the ratios between surfactant and ionic liquid in the aqueous solutions. It must be kept in mind that being the ionic liquid concentration constant, the surfactant mole fraction  $\alpha_1$  decreases continuously through dilution. Table 2 shows the cmc values for  $C_{12-14}EO_8$  in pure water and in the different ionic liquid solutions together with the corresponding  $\alpha_1$  mole fractions, calculated at the cmc. The very low  $\alpha_1$  values obtained are consequence of the predominant ionic liquid concentrations in these binary solutions with respect to those of  $C_{12-14}EO_8$  around the cmc. In Table 2 it can be seen that the presence of ionic liquid leads to higher cmc values for  $C_{12-14}EO_8$  with respect to those in pure water. These values increase with the ionic liquid concentration in the aqueous phase, confirming the behavior reported in the literature. The usual explanation is that the solvophobic interaction between the surfactant alkyl chains in the ionic liquid is lower than the hydrophobic interaction between the surfactant alkyl chains in water.

**Table 2.** Values of cmc for  $C_{12-14}EO_8$  dissolved in ionic liquid aqueous solutions and its mole fractions  $\alpha_1$  at the cmc

Dilution media		Nonionic $C_{12-14}EO_8$ dissolved in Aqueous Solutions of IL					
		bmim-OctylSO <sub>4</sub>		bmim-MethylSO <sub>4</sub>		bmim-BF <sub>4</sub>	
IL concent. (mM)	$\gamma$ (mN/m)	cmc (mM)	$C_{12-14}EO_8$ $\alpha_1$	cmc (mM)	$C_{12-14}EO_8$ $\alpha_1$	cmc (mM)	$C_{12-14}EO_8$ $\alpha_1$
0 (water)	72	0.023	1	0.023	1	0.023	1
0.70	60	0.029	$3.98 \times 10^{-2}$	-	-	-	-
1.70	55	0.033	$1.85 \times 10^{-2}$	-	-	-	-
40	60	-	-	0.060	$1.50 \times 10^{-3}$	-	-
50	60	-	-	-	-	0.036	$7.19 \times 10^{-4}$
80	55	-	-	0.080	$7.99 \times 10^{-4}$	-	-
100	55	-	-	-	-	0.073	$7.29 \times 10^{-4}$

In Figure 2 to avoid overlapping, only the case of  $C_{12-14}EO_8$  dissolved in water or in 0.70 mM bmim-OctylSO<sub>4</sub> aqueous solution ( $\gamma = 60$  mN/m) is shown, as an example of the data of Table 2.



**Figure 2.** Surface tension vs logarithm of  $C_{12-14}EO_8$  concentration in water and in 0.70 mM bmim-OctylSO<sub>4</sub> ( $\gamma \approx 60$  mN/m).

The  $C_{12-14}EO_8$  cmc increase with respect to the cmc in water is attributed to the presence of ionic liquid in the aqueous media. In these systems it is generally assumed that the modified cmc values correspond only to the surfactant. However,

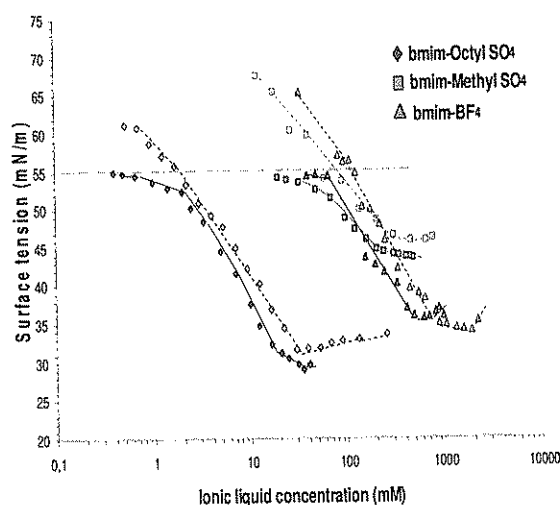
taking into account the “surfactant-like” behavior of the ionic liquids displayed in Figure 1, this assumption should be revised. For this purpose, a second set of experiments were designed.

### Systems with ionic liquids dissolved in C<sub>12-14</sub> EO<sub>8</sub> aqueous solutions

In a new series of experiments, the ionic liquids were diluted with aqueous solutions of C<sub>12-14</sub> EO<sub>8</sub> at constant concentrations. The selected C<sub>12-14</sub> EO<sub>8</sub> concentrations are those giving surface tensions of 45, 50 and 55 mN/m in water solution, respectively. The interest of these experiments lies in the fact that if the nonionic surfactant were the only responsible for the surface activity, keeping this compound at a constant concentration no changes of surface tension denoting surface activity would be expected through ionic liquid dilution. However, when  $\gamma / \log C$  for the ionic liquids was plotted, typical graphs of surface activity appeared. Obviously these surfactant profiles must be attributed to the ionic liquids. Furthermore, the fact that these cmc values are lower than those of the ionic liquids in pure water suggests the possibility of mixed micelle formation between the nonionic surfactant and the ionic liquid. In Table 3 cmc values of ILs in pure water and in C<sub>12-14</sub> EO<sub>8</sub> solutions as well as the C<sub>12-14</sub> EO<sub>8</sub> mole ratios  $\alpha_1$  calculated at the cmc are displayed. In these systems, being constant the surfactant concentration whereas the ionic liquid is progressively diluted,  $\alpha_1$  increases. These  $\alpha_1$  values are extremely low, in the range of  $1 \times 10^{-5}$  to  $1 \times 10^{-6}$  because of the low surfactant concentration.

**Table 3.** Values of cmc for ionic liquids dissolved in C<sub>12-14</sub> EO<sub>8</sub> aqueous solutions and C<sub>12-14</sub> EO<sub>8</sub> mole fractions  $\alpha_1$  at the cmc.

Dilution Media		Ionic Liquids dissolved in Aqueous Solutions of C <sub>12-14</sub> EO <sub>8</sub>					
C <sub>12-14</sub> EO <sub>8</sub>	Aqu. Sol.	bmim-OctylSO <sub>4</sub>		bmim-MethylSO <sub>4</sub>		bmim-BF <sub>4</sub>	
Concent. (mM)	$\gamma$ (mN/m)	cmc (mM)	C <sub>12-14</sub> EO <sub>8</sub> $\alpha_1$	cmc (mM)	C <sub>12-14</sub> EO <sub>8</sub> $\alpha_1$	cmc (mM)	C <sub>12-14</sub> EO <sub>8</sub> $\alpha_1$
0	72	30	0	350	0	850	0
$4.68 \times 10^{-4}$	55	17	$2.75 \times 10^{-5}$	200	$2.34 \times 10^{-6}$	500	$9.36 \times 10^{-7}$
$1.00 \times 10^{-3}$	50	21	$4.76 \times 10^{-5}$	214	$4.67 \times 10^{-6}$	500	$2.00 \times 10^{-6}$
$2.00 \times 10^{-3}$	45	23	$8.69 \times 10^{-5}$	-	-	500	$4.00 \times 10^{-6}$



**Figure 3.** Surface tension vs logarithm of concentration for the ionic liquids in  $4.68 \times 10^{-4}$  mM C<sub>12-14</sub> EO<sub>8</sub> aqueous solution ( $\gamma = 55$  mN/m) and in water (empty symbols).

Figure 3 shows as an example the plots  $\Delta\gamma/\Delta\log C$  for each ionic liquid dissolved in pure water and in a  $4.68 \times 10^{-4}$  mM  $C_{12-14}EO_8$  aqueous solution. The presence of surfactant produces a decrease of the cmc with respect to the cmc value in pure water.

If assuming that mixed micelles are formed, the conventional protocol to study binary systems of surface active compounds in aqueous solution should be applied.

#### Binary systems $C_{12-14}EO_8$ /ionic liquid at constant mole ratios

The general procedure to study binary surfactant systems in aqueous solutions by tensiometry is to plot the surface tension of different solutions in which the two components are mixed at different mole ratios, against the logarithm of the total concentration of both compounds. From these graphs the cmc of the mixed system can be obtained. In the next series of experiments, mixtures of  $C_{12-14}EO_8$  and ionic liquid in a wide range of constant mole fractions including  $\alpha_1$  values as low as those reported in Tables 2 and 3 were prepared. In order to determine whether there is interaction between surfactant and ionic liquid, the experimental cmc values were compared with the theoretical ones corresponding to an ideal behavior according to the Clint equation.<sup>46</sup>

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

Where  $cmc_{calc}$  is the theoretical value for the mixture without interaction,  $cmc_1$  and  $cmc_2$  are the individual cmc values of the components 1 and 2 respectively and  $\alpha_1$  the mole fraction of the first component ( $C_{12-14}EO_8$ ) in the solution.

When the  $cmc_{calc}$  and the  $cmc$  experimental ( $cmc_{exp}$ ) are different, interaction between the two components exists. The mole fraction of compound 1 in the mixed micelle ( $X_1^M$ ) can be obtained by solving iteratively Equation 2 of the Rubingh's Regular Solution Theory<sup>47</sup>.

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

Applying this  $X_1^M$  value to the following Equation 3, the interaction parameter  $\beta^M$  for the mixed micelle can be obtained:

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

Negative values of  $\beta^M$  indicate attractive interactions between the components in the mixed micelle, positive  $\beta^M$  indicates repulsive interactions, and  $\beta^M$  zero indicates the ideal case of no interaction.

In Table 4 the surface active parameters for the three binary systems composed by  $C_{12-14}EO_8$  and bmim-OctylSO<sub>4</sub>, bmim-MethylSO<sub>4</sub> and bmim-BF<sub>4</sub>, respectively, are displayed as a function of the  $C_{12-14}EO_8$  mole fraction  $\alpha_1$ .



Although generally in binary systems the considered values of  $\alpha_1$  move from 0.1 to 0.9 in our case we extended this range to  $\alpha_1$  values as low as the previously calculated in Tables 2 and 3. These low values correspond to those usually found in common applications of dissolutions of a non-ionic surfactant in an aqueous solution of ionic liquid

**Table 4.** Surface active parameters for binary systems  $C_{12-14}EO_8$  / IL as a function of the surfactant mole ratio  $\alpha_1$ .

$\alpha_1$ $C_{12-14}EO_8$	$cmc_{calc}$ (mM)	$cmc_{exp}$ (mM)	$\gamma_{cmc}$ (mN/m)	$pC_{20}$ -	$\Delta\gamma/\Delta \log C$ -	$\Gamma_m \times 10^{-10}$ (mol · cm <sup>-2</sup> )	$A_m$ (Å <sup>2</sup> )
<b>{<math>C_{12-14}EO_8</math> / bmim-Octyl SO<sub>4</sub>}</b>							
0.854	0.028	0.044	29.8	5.52	-19.30	3.38 / <i>n</i>	49 x <i>n</i>
0.483	0.049	0.080	30.1	5.07	-21.84	3.83 / <i>n</i>	43 x <i>n</i>
0.217	0.11	0.23	29.9	4.79	-20.59	3.61 / <i>n</i>	46 x <i>n</i>
$1.43 \times 10^{-5}$	30	22	30.0	2.49	-24.99	4.38 / <i>n</i>	38 x <i>n</i>
<b>{<math>C_{12-14}EO_8</math> / bmim-Methyl SO<sub>4</sub>}</b>							
0.898	0.026	0.044	30.0	5.49	-20.81	3.65 / <i>n</i>	45 x <i>n</i>
0.522	0.044	0.070	30.5	5.05	-27.37	4.80 / <i>n</i>	35 x <i>n</i>
0.236	0.097	0.15	31.5	4.82	-24.42	4.27 / <i>n</i>	39 x <i>n</i>
$3.33 \times 10^{-6}$	333	320	43.4	1.00	-16.72	2.93 / <i>n</i>	57 x <i>n</i>
<b>{<math>C_{12-14}EO_8</math> / bmim-BF<sub>4</sub>}</b>							
0.889	0.026	0.035	31.0	5.38	-24.88	4.36 / <i>n</i>	38 x <i>n</i>
0.495	0.046	0.080	30.5	5.34	-18.53	3.25 / <i>n</i>	51 x <i>n</i>
0.296	0.078	0.135	29.7	5.06	-19.34	3.39 / <i>n</i>	49 x <i>n</i>
$6.46 \times 10^{-5}$	251	240	32.5	1.82	-16.08	2.82 / <i>n</i>	59 x <i>n</i>

The parameters are the calculated cmc ( $cmc_{calc}$ ), experimental cmc ( $cmc_{exp}$ ), surface tension at the cmc ( $\gamma_{cmc}$ ),  $pC_{20}$ , slope of the straight line  $\Delta\gamma/\Delta \log C$ , maximum adsorption at the saturated interface ( $\Gamma_m$ ) and minimum area occupied per molecule at the saturated interface ( $A_m$ ).  $\Gamma_m$  and  $A_m$  are expressed as a function of *n*, the factor of the Gibbs equation related to the number of species in solution. In the case of systems ionic/nonionic *n* should move from 1 (for single nonionic surfactant) to 2 (for single ionic surfactant) but its real value is difficult to be determined. In consequence the factor *n* and indirectly  $\Gamma_m$  and  $A_m$  remain undetermined. On the contrary, the slope  $\Delta\gamma/\Delta \log C$  as a specific characteristic of each system is reported in Table 4.

In general, for all these systems the experimental cmc values are clearly higher than the calculated ones, denoting repulsive interactions between the components in the mixed micelle and consequently  $\beta^M$  should be positive. This is an unusual behavior that has been reported in limited cases<sup>48-50</sup>. However, for  $C_{12-14}EO_8$  mole fractions lower than a given value which depends on each system ( $\alpha_1 < 1.04 \times 10^{-3}$  for bmim-OctylSO<sub>4</sub>,  $\alpha_1 < 1.46 \times 10^{-4}$  for bmim-MethylSO<sub>4</sub> and  $\alpha_1 < 5.55 \times 10^{-4}$  with bmim-BF<sub>4</sub>) a change on the type of interaction between the components is observed. The experimental cmc values are lower than the calculated ones reflecting attractive interactions between surfactant and ionic liquids.

As already mentioned, the usual way to quantify the deviation of experimental  $cmc_{exp}$  from ideal  $cmc_{calc}$  in binary systems of surface active compounds is using the  $\beta^M$  interaction parameter of Rubingh's equation. Accordingly to the behavior observed for these systems, positive  $\beta^M$  should be found for most of mole fractions  $\alpha_1$  and negative  $\beta^M$  only for extremely low  $\alpha_1$ . However, in most cases, it was not possible to

solve Equation 2 to obtain  $X_1^M$  because the iteration process led to values for which the function was not defined. When it was possible, the corresponding  $\beta^M$  values were reported in Table 5. To fill the gaps among the very low  $\alpha_i$  values from Table 4 where the change from repulsive to attractive interactions is produced, we take advantage from the studies described previously when one of the components was kept at constant concentration whereas the other was diluted. If we convert these systems to typical binary systems by considering the total concentration (surfactant plus ionic liquid) and the  $\alpha_i$  calculated at the cmc, we can dispose of new complementary data. In Table 5 these  $\alpha_i$  data with their associated values of  $cmc_{calc}$  and  $cmc_{exp}$ ,  $C_{12-14}EO_8$  mole fraction  $X_1^M$  in the mixed micelle and interaction parameter  $\beta^M$  are reported. When  $cmc_{exp}$  values are clearly higher than the  $cmc_{calc}$  (\*data are taken from Table 4) no values of  $X_1^M$  and  $\beta^M$  can be obtained. For decreasing  $\alpha_i$ ,  $cmc_{exp}$  values became lower than  $cmc_{calc}$  and negative  $\beta^M$  were obtained as a measure of the attractive interaction between the surfactant and the ionic liquid. These results seem to indicate a close correspondence between the cmc data and the interaction parameter  $\beta^M$  within this range of low  $\alpha_i$ .

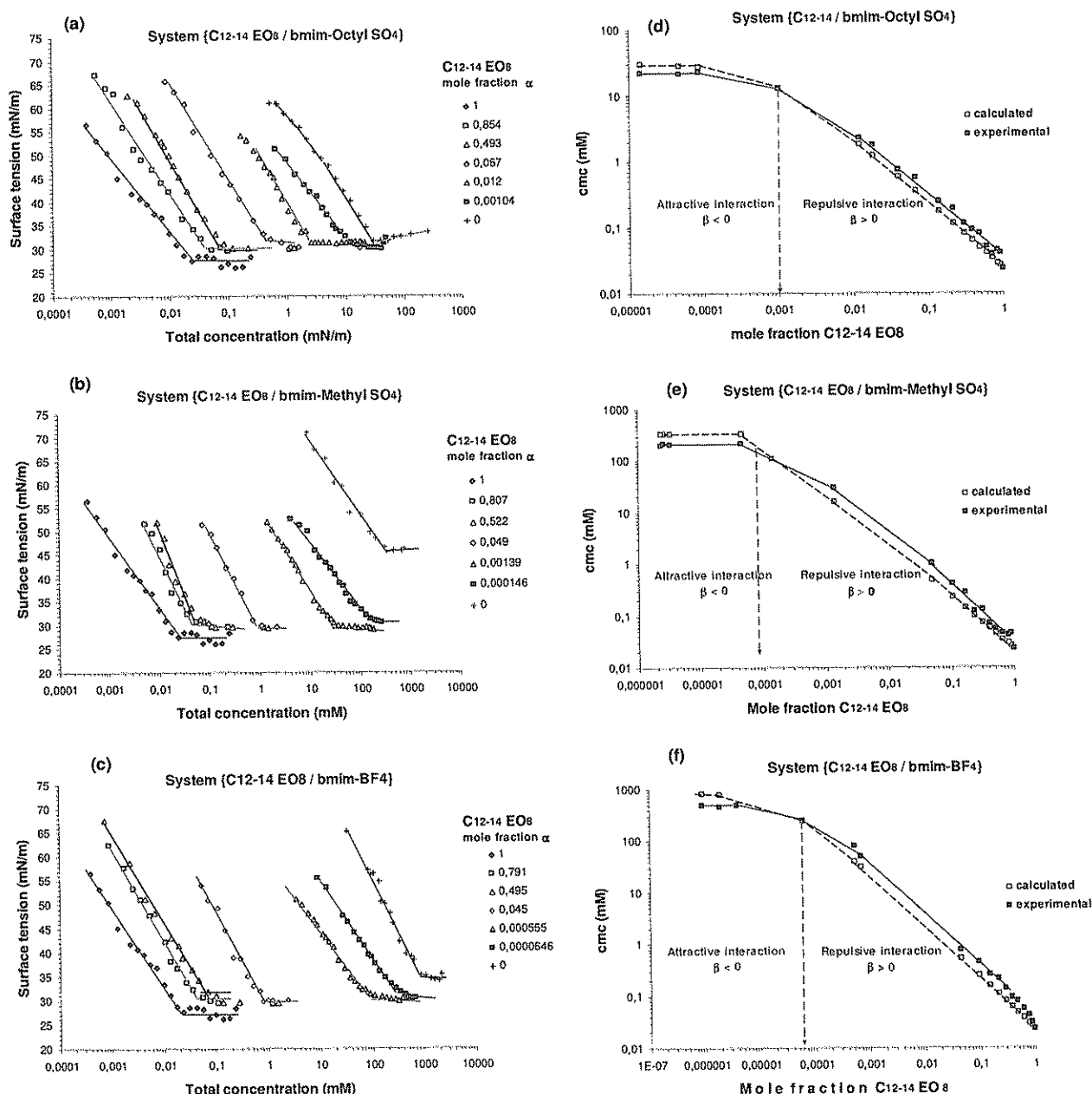
**Table 5.** Extremely low  $\alpha_i$  values with their associated cmc and  $X_1^M$  and  $\beta^M$  (some data of Table 4 are also included) for the three investigated systems.

$\alpha_i$ at cmc $C_{12-14}EO_8$	$cmc_{calc}$ (mM)	$cmc_{exp}$ (mM)	$X_1^M$	$\beta^M$
[ $C_{12-14}EO_8$ / [bmim-Octyl $SO_4$ ]]				
0.0120 *	1.8	2.5	-	-
$1.04 \times 10^{-3*}$	12.7	13	0.579	+ 0.085
$8.69 \times 10^{-5}$	27	23	0.196	- 1.258
$4.76 \times 10^{-5}$	28	21	0.213	- 2.566
$2.75 \times 10^{-5}$	29	17	0.250	- 4.461
$1.43 \times 10^{-5} *$	30	22	0.176	- 3.763
0	30	30	-	-
[ $C_{12-14}EO_8$ / [bmim-Methyl $SO_4$ ]]				
$9.99 \times 10^{-4}$	26.6	80	-	-
$1.46 \times 10^{-4*}$	109	110	0.694	+ 0.065
$4.67 \times 10^{-6}$	327	214	0.252	- 3.142
$3.33 \times 10^{-6*}$	333	210	0.247	- 3.701
$2.63 \times 10^{-6}$	336	214	0.238	- 3.910
$2.34 \times 10^{-6}$	338	200	0.249	- 4.432
0	350	350	-	-
[ $C_{12-14}EO_8$ / [bmim- $BF_4$ ]]				
$7.19 \times 10^{-4}$	31	50	-	-
$5.55 \times 10^{-4} *$	40	60	-	-
$6.46 \times 10^{-5*}$	251	240	0.586	- 1.114
$4.00 \times 10^{-6}$	740	500	0.287	- 2.349
$2.00 \times 10^{-6}$	791	450	0.282	- 3.831
$9.36 \times 10^{-7}$	822	500	0.242	- 4.309
0	850	850	-	-

To explain the change of behavior from repulsive to attractive interaction between the components with decreasing  $\alpha_i$ , the first consideration to keep in mind is the high surface activity of the nonionic surfactant that even at extremely low mole fractions in the aqueous solution (Table 5) attain mole fractions  $X_1^M$  in the mixed micelles higher than 0.200. At these extremely low  $\alpha_i$ , the insertion of non-ionic surfactant monomers between ionic liquid molecules in the micelles produces a decrease of the electrostatic self-repulsion of the ionic liquid leading to mixed micelle formation at

lower cmc than the expected, given rise to negative  $\beta^M$ . When  $\alpha_1$  increases (Table 5) the C<sub>12-14</sub> EO<sub>8</sub> composition in the mixed micelle became predominant ( $X_1^M \approx 0.600-0.700$ ) and in this case, probably the insertion of ionic liquid monomers in the surfactant micelles leads to an electrostatic repulsion that increases the cmc as the slightly positive  $\beta^M$  indicates. We can expect the same behavior for higher  $\alpha_1$  although no values for  $X_1^M$  and  $\beta^M$  can be obtained.

In Figures 4(a-c) to avoid overlapping, only some of the registered plots  $\Delta\gamma/\log C$  (total concentration) for these systems are displayed.



**Figure 4.** Graphs  $\Delta\gamma/\Delta\log C$  for binary mixtures C<sub>12-14</sub> EO<sub>8</sub> / bmim-Octyl SO<sub>4</sub> (a), C<sub>12-14</sub> EO<sub>8</sub> / bmim-Methyl SO<sub>4</sub> (b) and C<sub>12-14</sub> EO<sub>8</sub> / bmim-BF<sub>4</sub> (c). Experimental and calculated cmc values for these binary systems as a function of the C<sub>12-14</sub> EO<sub>8</sub> mole fraction  $\alpha_1$  (d, e, f).

It can be seen that small amounts of nonionic surfactant (very low  $\alpha_1$ ) are sufficient to decrease drastically the initial cmc of the ionic liquids. Moreover, for the C<sub>12-14</sub> EO<sub>8</sub> / bmim-Methyl SO<sub>4</sub> binary system, a drastic diminution of  $\gamma_{cmc}$  from 45.0 mN/m to 32.2 mN/m is produced for a  $\alpha_1$  as low as  $1.46 \times 10^{-4}$ . This abrupt change could be justified by the formation of mixed micelles. It is noteworthy that up to now this possibility has been only considered for long alkyl chain ionic liquids with surfactant properties<sup>32</sup> but not for short alkyl chain ionic liquids, merely considered as cosolvents where the surfactant is dissolved.

In Figures 4 (d-f) experimental and calculated cmc values are plotted as a function of  $\alpha_1$  for all the binary mixtures of the three systems. Given that  $\alpha_1$  and cmc values varied in a range of several orders of magnitude, the graphs were plotted in double logarithmic scale. As can be observed, the change from attractive to repulsive interaction depends on the value of  $\alpha_1$ . In the case of bmim-OctylSO<sub>4</sub> (d), attractive interaction occurs when  $\alpha_1 < 1.00 \times 10^{-3}$  whereas for the systems with bmim-Methyl SO<sub>4</sub> (e) and bmim-BF<sub>4</sub> (f) this occurs when  $\alpha_1 < 1.00 \times 10^{-4}$ .

For higher  $\alpha_1$  repulsive interactions between the components of the binary system are produced given higher  $cmc_{exp}$  values with respect to the  $cmc_{calc}$  although no  $\beta^{M}$  values can be calculated. Accordingly with these results, a decrease or increase in the cmc can be achieved through the adjustment of the mole ratio between the components in the aqueous solution.

Therefore, controlling the experimental conditions of the binary surfactant/ionic liquid systems, the cmc values could be modulated for a specific application.

## CONCLUSIONS

The imidazolium based ionic liquids, bmim-Octyl SO<sub>4</sub>, bmim-Methyl SO<sub>4</sub> and bmim-BF<sub>4</sub> display surface activity in aqueous solution. The differences in such surface activity depend on the nature of the counterion and the best surfactant properties are found for the most hydrophobic anion (Octyl SO<sub>4</sub>). Because of the mentioned surface activity, when these ionic liquids are in aqueous solution with a nonionic surfactant, a typical case of binary surfactant systems should be considered. The differences between the experimental and the calculated cmc values confirm that interaction between both components occurs. A change from attractive to repulsive interaction has been detected for each system depending on the surfactant mole fraction  $\alpha_1$ . For extremely low surfactant mole fractions ( $\alpha_1 < 0.001$  for system C<sub>12-14</sub> EO<sub>8</sub>/bmim-Octyl SO<sub>4</sub> or  $\alpha_1 \leq 0.0001$  for systems C<sub>12-14</sub> EO<sub>8</sub>/bmim-Methyl SO<sub>4</sub> and C<sub>12-14</sub> EO<sub>8</sub>/bmim-BF<sub>4</sub>) experimental cmc values are lower than the calculated ones indicating attractive interactions between surfactant and ionic liquid, i.e. synergism in mixed micelles formation. When the surfactant mole fractions are higher than those indicated for each system, experimental cmc values are higher than the calculated ones, indicating repulsive interactions in mixed micelles formation. Through selecting the appropriate surfactant mole fraction  $\alpha_1$ , a binary nonionic surfactant/ionic liquid system can be tailored for a specific application, depending on whether monomers or micelles are mainly required. The fact that short alkyl chain ionic liquids usually used as cosolvents in aqueous solutions can display surfactant activity introduces a new element to be kept in mind for a better knowledge of surfactants and ionic liquids interactions. Under this approach a new interpretation of some results reported in literature could be made.

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Nuestra actividad está dirigida al estudio de las propiedades físico-químicas y biológicas relacionadas con el comportamiento, distribución y efectos de los tensioactivos y líquidos iónicos en el medio ambiente para el diseño y selección de compuestos que, además de técnicamente eficaces, sean medioambientalmente aceptables e inocuos para el ser humano.

La actividad de nuestro grupo de investigación está orientada al estudio de las propiedades físico-químicas y biológicas de tensioactivos y líquidos iónicos relacionadas con su comportamiento, distribución y efectos en el medio ambiente y tiene como objetivo fundamental la prevención de la contaminación ambiental mediante el diseño y selección de compuestos multifuncionales y eficaces que presenten una baja toxicidad y que al final de su función no persistan en el medio ambiente.

El elevado volumen de producción y uso de los compuestos tensioactivos prioriza la investigación de sus efectos en el medio ambiente. El establecimiento de relaciones entre la estructura molecular del tensioactivo y sus propiedades ecológicas resulta de interés fundamental para el desarrollo de nuevos tensioactivos biocompatibles dado que la protección del medio ambiente es uno de los motores fundamentales del desarrollo e innovación en el sector industrial asociado.

Por otro lado, estas relaciones estructura-actividad pueden aplicarse al diseño y desarrollo de líquidos iónicos (ILs), compuestos de gran interés en el ámbito de la química sostenible dado su enorme potencial industrial como catalizadores y disolventes alternativos a los disolventes orgánicos volátiles. Además, los ILs presentan un gran potencial para mejorar y desarrollar nuevos procesos en química verde puesto que sus propiedades físicas, químicas y biológicas pueden ser moduladas para desempeñar una función particular. Sin embargo, no son fácilmente biodegradables lo que significa que los ILs convencionales pueden acumularse en el medio ambiente, limitación fundamental para su implementación a escala industrial.

Uno de los principales objetivos de nuestro grupo de investigación es desarrollar líquidos iónicos biodegradables como medios de reacción y compuestos multifuncionales en química verde. Para ello se tratará de mejorar la biodegradabilidad de los líquidos iónicos convencionales derivados de imidazolio y piridinio mediante la incorporación de modificaciones estructurales que confieran mayor biodegradabilidad a estos compuestos. La estrategia que se aplicará está basada en los principios para desarrollar tensioactivos biodegradables, tema en el que los autores tienen una amplia experiencia. Las propiedades y características que presenten estos líquidos iónicos determinarán su posible utilización bien como medios de reacción o como compuestos con actividad superficial y antimicrobiana con potenciales aplicaciones farmacéuticas y biológicas (vehiculizadores, conservantes, humectantes, plastificantes, etc.).