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Micellization of sodium laurylethoxysulfate (SLES) and short chain imidazolium ionic liquids in aqueous solution

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ABSTRACT

In the present study the interactions between an anionic surfactant sodium laurylethoxysulfate (SLES) and three short chain imidazolium (1-butyl-3-methylimidazolium) based ionic liquids (bmim-octyl SO_4, bmim-methyl SO_4 and bmim-BF_4) in aqueous solution have been investigated. Generally when a surfactant is dissolved in a hydrophilic ionic liquid aqueous solution the critical micelle concentration (cmc) obtained is attributed to the surfactant because the ionic liquid (IL) is considered to be only a cosolvent. However, some short hydrophilic ionic liquids posses surface activity in aqueous solution and behave like a surfactant. In that case mixed aggregates between surfactant and ionic liquid can be formed. The three SLES/IL systems here studied have been treated as typical binary surfactant mixtures in aqueous solution. Surface tension measurements have revealed that mixed aggregates and monolayers of surfactant and ionic liquid instead of single surfactant are responsible for the surface active properties of these aqueous solutions. From the Regular Solution Theory, negative interaction parameters (β) for mixed aggregates and monolayers have been found for all SLES/IL mole ratios indicating synergism between the anionic surfactant and the ionic liquids.

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1. Introduction

Ionic liquids (ILs), organic salts with a melting point below 100 °C, are compounds that have gained interest both in academic studies and in industrial applications because of their special properties, which can be adjusted by an appropriate combination of the cation and anion. It has been reported, for example, that long alkyl chains attached to the cation lead to compounds displaying surface activity when dissolved in water, denoted by a decrease in the surface tension and the existence of an aggregation concentration, similar to conventional surfactants [1–10]. Short hydrophilic ionic liquids, however, are mainly used as solvents, taking advantage of one of the most noticeable properties of ILs, an extremely low vapour pressure that prevents air pollution and make them potential substitutes for volatile organic solvents. There are numerous studies in which conventional surfactants are dissolved in neat ILs [11–21]. When comparing the plots of surface tension against logarithm of concentration for a surfactant dissolved in ionic liquid or in water, two clear differences can be observed. First, the slope of the linear surface tension decrease in IL is lower than in water because of the lower surface tension of neat IL ($\gamma \approx 35$–45 mN/m) respect to pure water ($\gamma \approx 72$ mN/m). Second, the critical micelle concentration (cmc) of the surfactant in IL is higher than in water. This can be attributed to a lesser solvophobicity of the surfactant alkyl chains in neat ionic liquid than the hydrophobicity of these alkyl chains in water [15–17]. Another possible case is to dissolve the surfactant in an aqueous solution of ionic liquid. Numerous papers have been published on the effect of ionic liquids on surfactant micellization [22–37]. Generally the ionic liquid aqueous solution is considered to be merely a dilution medium that modifies the surfactant activity leading to a new value of its cmc. However, despite their structures, some short hydrophilic ionic liquids show surface activity and behave similar to cationic surfactants [1–4,38–43]. In that case, the critical aggregation concentration (cac) values could be attributed to the mixed aggregates between surfactant and ionic liquid. In the present study the interactions between an anionic surfactant sodium laurylethoxysulfate (SLES) and three ionic liquids containing the same cation (1-butyl-3-methylimidazolium) and different anions (octyl SO_4^-, methyl SO_4^- and BF_4^-) have been investigated in order to know whether these systems can be considered as typical binary surface active agents in aqueous solution. In that case, the Regular Solution Theory equations could be applied to obtain the interaction parameters between the anionic surfactant and the ionic liquids. In a previous study with a nonionic surfactant ($C_{12–14} EO_8$) and the above mentioned hydrophilic ionic liquids [41] this approach was applied and led to an adequate description of the systems.

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2. Experimental section

2.1. Materials

The anionic surfactant sodium laurylethoxysulfate (SLES) (EMAL 227E) was a gift of Kao Corporation S.A. The ionic liquids 1-butyl-3-methylimidazolium octyl sulphate (bmim-octyl SO_4), 1-butyl-3-methylimidazolium methyl sulphate (bmim-methyl SO_4) and 1-butyl-3-methylimidazolium tetrafluoroborate (bmim-BF_4) were purchased from Fluka. All compounds were used as received without further purification. Deionized water was obtained from a Milli-Q Millipore device.

2.2. Sample preparation

In the first series of experiments SLES stock solutions (≈ 1 mM in active matter) were prepared and further diluted with ionic liquid aqueous solution at the required concentration to have a surface tension (γ) of 60 mN/m (0.70 mM for bmim-octyl SO_4, 50 mM for bmim-methyl SO_4 and 60 mM for bmim-BF_4) or 50 mN/m (3.6 mM for bmim-octyl SO_4, 180 mM for bmim-methyl SO_4 and 170 mM for bmim-BF_4). In the second series of experiments concentrated ionic liquid solutions were prepared and further diluted with two different SLES aqueous solutions at the required concentration to have $\gamma = 60$ mN/m (0.008 mM) or $\gamma = 50$ mN/m (0.028 mM). In the third series of experiments, binary mixtures of surfactant and ionic liquid were prepared at SLES mole fractions (α_1) ranging from 0.1 to 0.9 and progressively diluted with water.

2.3. Surface tension measurements

Surface tension (γ) was measured at 25 °C with a Krüss K 12 tensiometer by means of the Wilhelmy plate method. Repeat measurements for each sample were made until the standard deviation of five consecutive measurements did not exceed 0.10 mN/m. The plate and the glass containers were cleaned with sulpho-chromic acid mixture and rinsed thoroughly with deionized water. The plate was flame dried before each measurement. From the plots of surface tension against logarithm of compound concentration, typical surface active parameters were determined. The critical micelle concentration (cmc), or critical aggregation concentration (cac) when expressed in general terms, was obtained by the intersection between the line corresponding to the surface tension linear diminution and the line corresponding to surface tension stabilization. The surfactant effectiveness γ_{cmc} (surface tension at the cmc) 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 pure water, i.e. 52 mN/m) were also obtained from the graph. The Gibbs equation $\Gamma_{max} = \Gamma - \Delta\gamma/\Delta\log C)/2.303\, n\, RT$ was applied to estimate the surface excess concentration Γ_{max} expressed in mol cm^{-2}, being $\Delta\gamma/\Delta\log C$ the slope of the linear surface tension decrease before the cmc and taking $n = 2$ for ionic surfactants. The minimum area (A_{min}) occupied by adsorbed molecule at the air–liquid interface in Å^2 was obtained from the equation $A_{min} = 10^{16}/N_A\Gamma_{max}$, where N_A is the Avogadro's number.

3. Results and discussion

3.1. SLES dissolved in ionic liquid aqueous solutions

The selection of SLES in our study instead of the widely used sodium dodecylsulfate SDS as a typical anionic surfactant was due to the fact that the surface tension minimum appearing around the cmc, even for a very pure SDS compound, because of the presence of dodecanol impurities would modify the shape of the $\gamma/\log C$ curve hindering the right cmc determination. In this first series of experiments we reproduced the typical case of a surfactant dissolved in an aqueous solution of ionic liquid, comparing the cmc of SLES in pure water with the cmc values obtained when SLES was dissolved in each of the three ionic liquid aqueous solutions at two different concentrations. The IL concentrations were those giving surface tension values of 50 and 60 mN/m. The reason to select these relatively high γ values was to have margin enough between the surface tension of SLES solutions at the equilibrium ($\gamma_{cmc} \approx 28$–30 mN/m) and the γ of the dilution media. If SLES was the only surface active compound in the solution, IL would act merely as cosolvent and the cmc value would correspond to SLES modified by the presence of IL in the aqueous media as it is commonly accepted. From that assumption, the corresponding SLES cmc values are reported in Table 1.

Data of Table 1 show that the presence of IL leads to a decrease in the SLES cmc with respect to the value obtained in neat water. It can be seen that the effectiveness of the ionic liquids in reducing the SLES cmc is bmim-BF_4 > bmim-methyl SO_4 > bmim-octyl SO_4. However, taking into account the concentrations required to promote such cmc decrease, bmim-octyl SO_4 is clearly the most efficient IL because of the much lower concentration needed. The reduction in SLES cmc in IL aqueous media is a surprising finding given that the presence of a cosolvent usually leads to an increase in the surfactant cmc [57–61]. That common behavior was reported in a previous study of our group on the micellization of a nonionic surfactant in the presence of the same ILs here investigated [41]. However, in a study on micellization of the anionic surfactant SDS dissolved in aqueous solutions of bmim-BF_4, a dual IL behavior was reported by Behera and Pandey [24]. They found that low bmim-BF_4 content (up to 2% corresponding to ≈ 88 mM) led to a diminution of the cmc, whereas an increase in IL concentration from 10% (≈ 442 mM) to 30% (≈ 1327 mM) produced a noticeable increase in the cmc. Similar behavior was reported by the same authors for a zwitterionic surfactant dissolved in bmim-BF_4 solutions [26]. These authors postulated that at low concentrations bmim-BF_4 behaved as a typical electrolyte, whereas at high concentration its role was as a polar cosolvent. In our study the maximum bmim-BF_4 concentration is 170 mM and our results agree with the trend reported by these authors for low IL concentration range. We have not investigated higher IL concentrations because the γ values associated would be too close to the stabilized surface tension γ_{cmc}. In comparison with SDS used in the above mentioned study [24], the presence of two ethylene oxide (EO) groups in the SLES molecule leads to an increase in the solubility, however, the addition of a oxygen atom between the carbon atom and the sulphur atom in the sulphate head group leads to a diminution in the cmc value by a factor of about eight for every EO unit [63]. With regard to the influence of external additives, electrolytes cause a decrease in the cmc values of both SDS and SLES surfactants because of the diminution of the electrostatic repulsion between the ionic groups whereas for polar cosolvents a cmc increase is expected [57–61]. In Fig. 1, as an example of the cmc decreasing by the ILs presence, plots of $\gamma \log C_{SLES}$ for SLES dissolved in water or in ILs aqueous solutions at the required concentration to have $\gamma = 50$ mN/m are shown (other graphs are reported in Appendix A. Supplementary material).

3.2. Ionic liquids dissolved in SLES aqueous solutions

In this series of experiments concentrated solutions of each ionic liquid were prepared and diluted with aqueous solutions of SLES at constant concentration. The selected SLES concentrations were those giving surface tensions of 60 and 50 mN/m,