Association of imidazolium surfactants with poly(*N*-isopropylacrylamide)

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ABSTRACT

Most investigations about polymer and surfactant interactions are related to standard surfactants, while the scope of literature using imidazolium surfactants is limited. In this work, conductometric and calorimetric techniques have been combined to determine the interaction of poly(*N*-isopropylacrylamide) with two surfactants: 1-tetradecyl-3-methylimidazolium chloride and 1-hexadecyl-3-methylimidazolium chloride. The critical aggregation concentration and the polymer saturation point have been determined as a function of the polymer concentration. To explain the conductivity results, a new model has been proposed that considers the possibility of formation of free micelles before the polymer saturation. This model allows estimating the fraction of surfactant molecules aggregated to the polymer and the ionization degree of them, as well as the fraction of surfactant in the form of free micelles. Isothermal titration calorimetry results reveal that the interaction between the polymer and both surfactants is driven by entropic processes and that the aggregation process is non-cooperative at the initial stages.

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1. Introduction

Ionic liquids (ILs) are organic salts with melting points below 100 °C. ILs have gained the interest of the industrial and academic sectors due to their outstanding properties: ionic conductivity, low vapour pressure, high thermal stability and non-flammability; although the most important characteristic is the possibility of obtaining adjustable physical and chemical properties to satisfy the demands of technical applications by a simple modification of the anion-cation pair [1]. ILs that incorporate in their structure, at least, one hydrophilic headgroup and one long alkyl chain have shown to be surface-active. Therefore, in water, they form micelles at low concentrations and lyotropic liquid crystals at higher concentrations. Quaternary imidazoliums constitute one of the most important families [2] and are potentially better than standard cationic surfactants for a wide range of applications such as oil recovery [3], micellar separation processes [4] or drug delivery [5].

Surfactants and polymers are used together in a wide variety of industrial applications, such as detergents, paints, cosmetics and oil recovery processes. The interaction between polymers and surfactants induces the formation of association structures that modify the solution properties allowing the control of rheology, the surface activity, the micellization process, etc. As a consequence, studies of polymer-surfactant interactions have attracted the attention of researchers from both fundamental and industrial application points of view [6,7].

There are two characteristic concentrations in polymer-surfactant systems: the critical aggregation concentration (*C1*), where the polymer-surfactant interaction begins, and the polymer saturation point (*C2*), where the surfactant molecules saturate the polymer chains and, therefore, additional binding of surfactant molecules cannot occur [7]. These critical concentrations can be easily identified with several instrumental techniques such as surface tension [8], conductometry [8,9], potentiometric measurements [10] or isothermal titration calorimetry [11]. Nevertheless, in spite of the extensive bibliography related to polymer-surfactant interactions, there is not a complete understanding of the mechanisms involved. For instance, it is not known whether free micelles exist before polymer saturation occurs. However, it is usually assumed that free micelles appear after the saturation point [8,12,13] but there is no reason why un-bonded micelles do not exist between *C1* and *C2* [14,15].

The interaction of non-ionic polymers with anionic surfactants is generally stronger than for cationic ones. Nevertheless, it is well known that the interaction with cationic surfactant is enhanced when the polymer bears a hydrophobic group [16]. Poly(N-isopropylacrylamide) (PNIPAM) is a water-soluble polymer of strong interest in the production of smart materials [17]; it exhibits a lower critical solution temperature (LCST) at 32 °C and, due to its isopropyl side group, can be characterized as hydrophobic. Although the interaction of PNIPAM with standard surfactants has been previously investigated [16,18–20], interaction with these imidazolium derivatives has barely been studied and the only work found is related to the effect of decylmethylimidazolium chloride, and other 1-alkyl-3-methylimidazoliums with smaller alkyl chains, on the LCST of PNIPAM [21]. On the other hand, the synthesis of this polymer in the lamellar lyotropic medium formed by 1-tetradecyl-3-methylimidazolium/1-decanol/water has been recently investigated [22]. The aim of this work is to investigate the interaction between PNIPAM and two surfactants, 1-tetradecyl-3-methylimidazolium chloride (TMIC) or 1-hexadecyl-3-methylimidazolium chloride (HMIC), using electrical conductivity and isothermal titration calorimetry. A method to evaluate the presence of free micelles before the polymer saturation is also proposed.

2. Experimental part

2.1. Chemicals

1-Tetradecyl-3-methylimidazolium chloride (TMIC) >98% and 1-hexadecyl-3-methylimidazolium chloride (HMIC) >99% were obtained from IoLiTec and Fusol Material Co. respectively. Both were used without further purification. Poly(N-isopropylacrylamide) (PNIPAM) with molecular weight ~40,000 Da was obtained from Polysciences inc. The intrinsic viscosity of the polymer, determined in water at 20 °C was 0.306 dL/g, which provided a viscous average molecular weight of 4.65×10^4 (Mark Howink parameters [23] $k = 14.5 \times 10^{-4}$ dL/g and $a = 0.50$) and a critical overlapping concentration of $c^* = 3.3$ g/dL. In the experiments, deionized water (Milli-Q) was employed for the sample preparation; the polymer concentration was always below c^*.

2.2. Conductivity experiments

Measurements were carried out with a Metrohm 856 conductivity module using a Metrohm conductometric cell Pt1000. The instrument was calibrated with KCl solutions and the temperature was kept constant to within ± 0.1 °C by passing thermostated water through a jacketed vessel containing the solution.

2.3. Isothermal titration calorimetry (ITC)

The microcalorimeter used was a microCal VP-ITC system. The volume of the calorimetric vessel is 1.4631 mL. The samples were degassed with a MicroCal ThermoVac unit. The titration experiments consist of a series of consecutive additions of concentrated surfactant solution into a polymer water solution contained in the calorimetric vessel. The titrating solution is added to the vessel injecting between 40 and 60 aliquots (2–10 μL) with an automated micro-syringe. Usually 5 to 10 min elapsed between injections for thermal equilibration, and the sample cell was continuously stirred at 307 rpm. As the volume of the titration vessel is small, two experiments were performed for each surfactant; one at high concentration (0.100 M for TMIC and 0.031 M for HMIC) and another at lower concentration (0.0085 M for TMIC and 0.0036 M for HMIC). The entire titration curve was obtained using, as titration agent, the dilution of the highest concentration solution; however, to determine C1 with accuracy, the dilution of the lowest concentration solution was used.

3. Results

3.1. Conductivity measurements

Conductometry is a classical method for studying polymer-surfactant interactions. In Fig. 1 the specific conductance (κ) in the presence of PNIPAM at different fixed polymer concentrations (0.05, 0.10, 0.15 y 0.5 wt%) is plotted versus the surfactant concentration, C_S. The experiments were also conducted in the absence of polymer in order to determine the critical micellar concentration and the results are also included in the figure.

For these surfactants, in the absence of polymer, the experimental points can be fitted with two linear regressions with different slopes. The break point is associated to the CMC and the variation of the slopes before and after the break point can be attributed to the higher mobility of the free surfactant ions and the counterions as compared with the micelles. In the presence of polymer, the plots depict three regions and two break points. As in the absence of polymer, the linear region at low surfactant concentration is related to the presence of surfactant monomers and counterions. Afterwards, the first break point, C1, indicates the beginning of the formation of polymer-bound micelles and is usually referred as the critical aggregation concentration.

For non-ionic polymers the polymer-surfactant interactions can be associated with weaker or stronger hydrophobic interactions. Since PNIPAM incorporates in its structure a pendant isopropyl group, it is feasible for this hydrophobic moiety to be incorporated into the surfactant aggregate. This kind of interactions has been previously reported for the system of PNIPAM and sodium dodecyl sulfate [24,25]. In the region corresponding to intermediate surfactant concentrations, the variation of the conductivity with the surfactant concentration is not linear. A similar behaviour has been found for other polymer–surfactant systems. This can be explained by assuming that polymer-surfactant complexes and free micelles are formed in this region [14,26–28], although it has also been proposed that this may be a consequence of the change in the aggregation number of the polymer-bound micelles [29,30] or in the ionization degree [12]. Finally, the second break, C2, corresponds to the polymer saturation point. At even higher surfactant concentrations, there is again a linear variation of the conductivity, indicating that the concentration of free micelles increases with surfactant content.

The existence of two break points is indicative of polymer-surfactant interactions. For TMIC at the lowest polymer content (0.05 wt%), although the experimental curve suggest that there is a small region of curvature at intermediate surfactant concentrations, the detection of C1 and C2 is beyond the limit of the experimental uncertainties and the intersection between the two lines gives a value similar to the CMC of the system without polymer.

The values of C1 and C2 are presented in Table 1. The strength of the polymer-surfactant interaction can be characterized semi-quantitatively by the C1/CMC ratio [31]. The smaller the value of this ratio is, the stronger the interaction between the polymer and the surfactant. This ratio is in the range 0.60–0.73 for TMIC and 0.64–0.68 for HMIC. These results suggest that there are no strong differences between the interactions of PNIPAM with the two surfactants.

Fig. 2 shows that C1 does not vary significantly, while C2 exhibits a linear dependence with the polymer content. This behaviour is similar to other systems, e.g. ethyl(hydroxyethyl)cellulose–sodium dodecanoate [32] and poly(ethylene oxide)-dodecyl sulfate with different counterions [33]. Nevertheless, the linear fit of C2 does not converge to the CMC in the absence of polymer, as occurs in other systems [34]. The extrapolation gives a value higher than the CMC (see Fig. 2), which suggests that the concentration of free micelles at C2 cannot be disregarded.

In the absence of polymer, the ratio between the slopes of the linear fits above and below the CMC is usually employed to calculate the average ionization degree of the micelles, α_{mic} [35]. However, this is an approximate method that overestimates the degree of counter-ion