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Micelle co-assembly in surfactant/ionic liquid mixtures

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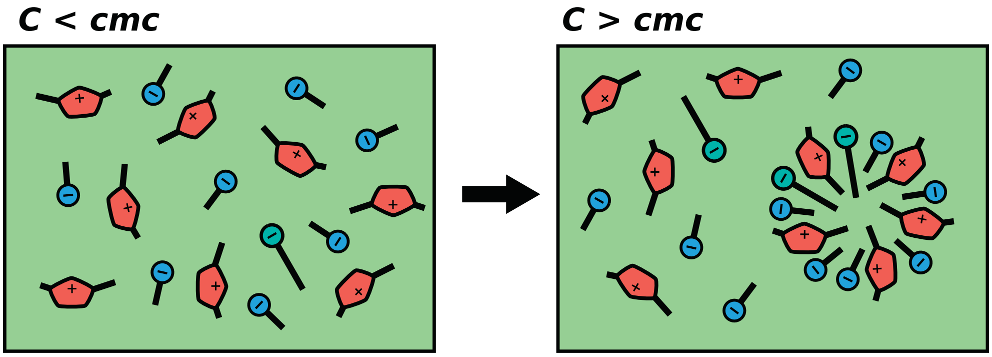
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: The phase behavior of amphiphiles is known to depend on their solvent environment. The organic character of ionic liquids suggested the possibility to tune surfactant aggregation, even in the absence of water, by selection of appropriate ionic liquid chemistry. To that end the behavior of the surfactant sodium dodecylsulfate in a chemically similar imidazolium ionic liquid, 1-ethyl-3-methyl imidazolium ethylsulfate, was explored.

Experiments: The solubility of sodium dodecylsulfate in 1-ethyl-3-methyl imidazolium ethylsulfate was determined, establishing the Krafft temperature. Tensiometry was performed to obtain interfacial properties such as the surface excess and area per molecule. Pulsed-field gradient spin-echo NMR was used to determine the diffusion coefficients of all the major species, including micelles, as a function of surfactant concentration. Importantly, all three methods provided consistent values for the critical micelle concentration.

Findings: Analysis of tensiometry data suggests, and is confirmed by NMR results, that the ionic liquid ions are incorporated along with surfactants into micelles, revealing a complex micellization behavior. In light of these findings past studies with ternary mixtures of surfactants, ionic liquids, and water may merit additional scrutiny. Given the large number of ionic liquids, this work suggests opportunities to further control micelle formation and properties.

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1. Introduction

The phase behavior of amphiphiles within ionic liquids (ILs) is receiving increased attention [1–4]; these systems have many potential applications such as solubilization [5,6], separations [7], and catalysis [8]. Among the key advantages of ionic liquids as sol-

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vents are their negligible vapor pressure and thermostability, and furthermore, IL properties can be varied by the choice of anion and cation chemistry [9]. Ionic liquids themselves may show liquid–crystalline [10] or surface-active behavior depending on the nature and extent of their organic character. For example, several groups have intentionally synthesized ILs with long alkyl chains, and because of their subsequent surface activity at air–water interfaces, they are referred to as "surface active ILs" (SAILs) [11,12] or "ionic-liquid-based surfactants" (ILBSs) [13]. Although SAILs and ILBSs blur the distinction between ionic liquids and ionic surfactants, mixtures of ILs and surfactants nevertheless provide a large experimental space to tune surface activity and self-assembly behavior.

The interfacial and aggregation behavior of surfactants are known to depend on the details of the solvent environment [14]. This dependence has now been demonstrated for several model surfactants in IL-water mixtures [15–18], and in the majority of these cases the IL may be viewed as an additive to what is predominantly an aqueous solvent. By contrast, our group [19] and others [20–22], have shown that surfactant aggregation can occur within neat ILs, that is, even in the absence of water. These findings suggested to us that careful pairings of surfactant and IL chemistry might lead to novel aggregation behavior. In addition to surfactants in neat ILs being simpler than in IL-water mixtures, they are interesting in their own right; for example, such aggregates are preferentially suited to applications under demanding conditions such as high temperature and/or low pressure where the presence of water can be a liability. To that end here we specifically investigate the behavior of a model surfactant, sodium dodecylsulfate, with a chemically similar ionic liquid, 1-ethyl-3-methyl imidazolium ethylsulfate. Detailed analysis of tensiometry and PGSE-NMR data reveals that the ionic liquid plays an important role in the micellization process.

2. Experimental

2.1. Materials and methods

The ionic liquid 1-ethyl-3-methyl imidazolium ethylsulfate $[C_2MIM][C_2SO_4]$, was obtained from Sigma (>95%) and dried by heating at 70 °C under vacuum for 2 days. Sodium dodecylsulfate, SDS, (98+%) was purchased from Fisher and used as received. The purity of the neat ionic liquid and surfactant was assessed by ^{1}H NMR or ^{13}C NMR and did not reveal any impurities. These findings were verified by control experiments using X-ray photoelectron spectroscopy (see Chen et al. [23]).

2.2. Solubility

Clear glass vials containing approximately 1 mL of IL and varying amounts of surfactant were prepared. Samples were heated to 90 °C for 24 h to thermally erase any non-equilibrium structures and were then cooled until the onset of turbidity. The samples were subsequently heated slowly until the onset of transparency, denoted as the melting temperature. The Krafft temperature T_k was taken as the temperature corresponding to a sudden increase in solubility [24].

2.3. Tensiometry

Surface tension was measured by means of the Wilhelmy method using a Micro Trough XS (Kibron, Inc.), and this method is particularly suited to measure interfacial forces in viscous liquid subphases. The surfactant SDS was dissolved directly into $[C_2MIM][C_2SO_4]$ at elevated temperature. Surfactant solutions (300 μL) with different concentrations were applied on an aluminum plate with glass wells. Surface tensions were measured after an equilibration time of 30 min. Temperature was controlled and monitored by using a hotplate placed underneath the multi-well plate and an Omega HH506RA multilogger thermometer probe in the well of interest.

2.4. Pulsed-field gradient spin-echo NMR (PGSE-NMR)

Solutions were prepared by directly dissolving a known amount of surfactant in IL (i.e., SDS in $[C_2MIM][C_2SO_4]$). PGSE-NMR diffusion measurements were carried out on a 400 MHz Bruker NMR spectrometer equipped with a temperature controller. The self-diffusion measurements were performed with a Gaussian-shaped pulsed-field gradient stimulated echo, whose magnitude was 5.35 Gauss/mm. The diffusion time, Δ, between the two pulses was set between 200 and 500 ms, and the gradient pulse duration, δ, was set between 2 and 6 ms, depending on the diffusion coefficient of the mobile species. The diffusion coefficient was determined from the intensity change equation [25]: $I = I_0 \exp\left[-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)\right]$, where I and I_0 are the areas of the signal obtained with or without gradient pulses respectively, D is the diffusion coefficient, γ is the proton gyromagnetic ratio, whose value is given by $2.675 \times 10^8\ \mathrm{T^{-1}\ s^{-1}}$ and g is the magnitude of the two gradient pulses. The diffusion coefficients obtained from proton peaks from the same species are consistent with each other. Due to the overlap of some peaks, we report the diffusion coefficient of $[C_2MIM]^+$ as the average value obtained from H_a, H_b, H_c, H_d, and H_e; the diffusion coefficient of $[C_2SO_4]^-$ as the value obtained from H_h; and the diffusion coefficient of $C_{12}SO_4^-$ as the value obtained from the average of H_C and H_D (see Fig. 3). Diffusion coefficient measurements were repeated at least three times for each concentration.

3. Results and discussion

3.1. Determination of the critical micelle concentration

We first use solubility measurements to determine the Krafft temperature T_k, that is, the minimum temperature needed for micellization. The solubility data in Fig. 1 is determined by heating (as opposed to cooling) the surfactant solutions because it is known that micelles can persist in a supercooled state [24]. From the sharp rise in the solubility data, we identify $T_k \approx 22$ °C.

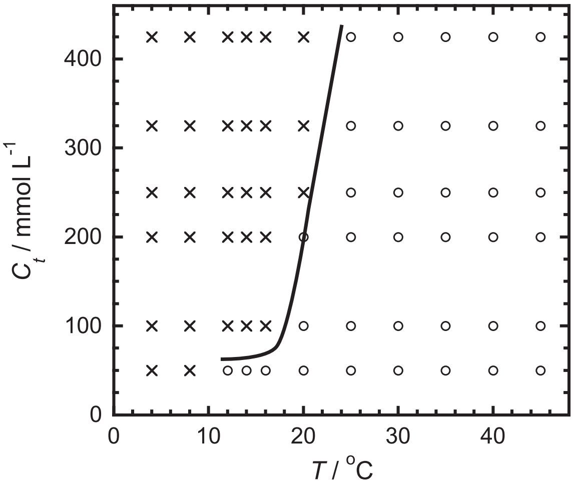

Fig. 1. Solubility behavior of SDS in $[C_2MIM][C_2SO_4]$, with circles denoting the soluble region and crosses denoting the insoluble region. The solid curve is a guide to the eye.

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