

Pre-transitional structuration of aqueous solutions of ionic liquid based catanionics

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Aqueous solutions of three catanionic compounds based on alkyl imidazolium cations ($C_n\text{MIm}$, $n=4, 6$ and 8) and ibuprofenate anion (Ibu) have been studied by small angle neutron scattering on either side of the critical concentration. For comparison sodium ibuprofenate has also been considered. The critical concentration decreases exponentially from 0.1M to 0.004M when the alkyl chain length n increases from 4 to 8 [1] and beyond the systems either micellize ($n=4$ and 6) or phase separate ($n=8$) [2]. The micelles are either spherical ($n=4$) or elongated ($n=6$). Despite this diverse behaviour beyond the transition, the aqueous solutions of all these compounds show the same type of structuration in the pre-transitional range of concentration. Analysis of the structure factor shows that micellization as well as demixing of the catanionic ionic liquids do not proceed through nucleation of dense premicellar aggregates containing few molecules, as usually admitted for the premicellar state, but rather occur within spatially extended concentration fluctuations of small amplitude. The structure factor in the pre-transitional state can be accounted for by a modified Orstein–Zernike equation that includes some ordering within the higher concentration domains. Moreover the ratio χ_T/ξ^2 of the compressibility over the square of the correlation length scales as $C^{-1,4}$, where C is the concentration, for all systems. These results as well as others obtained on more classical surfactants and copolymers are in line with recently proposed scenarii of demixing [3] that have been experimentally observed for crystallization but not for liquid-liquid phase separation.

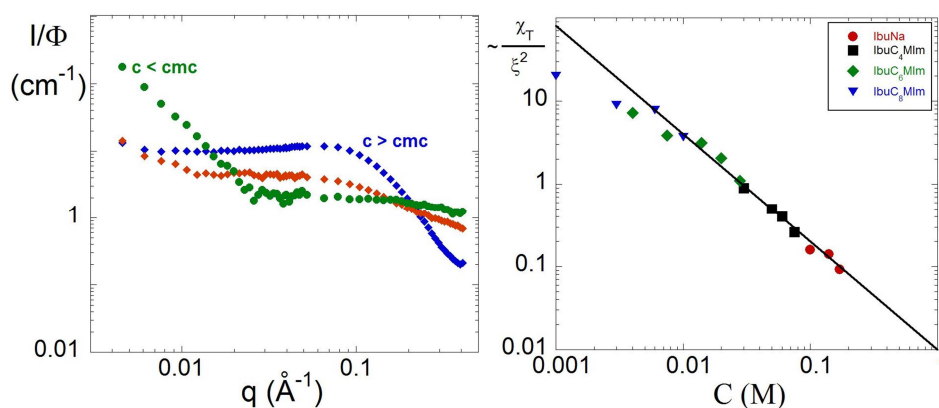


Figure 1 Left: Scattering patterns of IbuC₆MIm on either side of its critical micellization concentration. Right: Master curve characterizing the universal feature of the pre-transitional state of compounds about to micellize or to phase separate.

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