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Effect of surfactant ionicity on critical micelle concentration in aqueous ionic liquid mixtures

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Protic ionic liquids are the largest known solvent class capable of promoting surfactant self-assembly. However, ILs are increasingly used as mixtures with molecular solvents, such as water, to reduce their cost, viscosity and melting point, and the self-assembly promoting properties of these mixtures are largely unknown. Here we investigated the critical micelle concentration (CMC) of ionic and non-ionic amphiphiles in ethylammonium nitrate (EAN)-water mixtures to gain insight into the role of solvent species, and effect of solvent ionicity on the self-assembly process. The amphiphiles used were the cationic cetyltrimethylammonium bromide (CTAB), anionic sodium octanoate sulfate (SOS), and the non-ionic surfactant tetraethylene glycol monododecyl ether (C12E4). Surface tensiometry was used to obtain the CMCs and free energy parameters of micelle formation, and Small angle x-ray scattering (SAXS) was used to characterise the micelle shape and size.

The EAN-water solvents displayed self-assembly results consistent with a salt in water for EAN proportions below 5 mol% across all three surfactants, leading to CMC values lower than the CMC observed in water. A steep incline in the CMC was observed for concentrations between 5 mol% to 50 mol% of EAN for SOS and C12E4. However, CTAB displayed more complex behaviour where the CMC remained below the CMC of water until 33 mol% EAN. Across all surfactants, a plateau in CMC values were observed at very high EAN concentrations, which could indicate that there is a shift in the dominant solvent beyond EAN concentrations of 50 mol%. This study furthers our understanding of PIL solvent behaviour in ternary mixtures with amphiphiles.

Primary authors: KADAOLUWA PATHIRANNAHALAGE, Sachini (RMIT University); GREAVES, Tamar (RMIT University); HASSETT, Michael (RMIT University); CHRISTOFFERSON, Andrew (RMIT University); Dr LE, Tu (RMIT University); Prof. COSTA GOMES, Margarida (ENS de Lyon)

Presenter: KADAOLUWA PATHIRANNAHALAGE, Sachini (RMIT University)

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