

**Liquid Surfactants based on 1-Alkyl-3-Methylimidazolium Alkylsulfonates,
[C_nH_{2n+1}mim][C_mH_{2m+1}SO₃]: Mesomorphism and Self-Aggregation**

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Anion and cation alkyl-chain effects on the self-aggregation of both neat and aqueous solution 1-alkyl-3-methylimidazolium alkylsulfonate salts ([C_nH_{2n+1}mim][C_mH_{2m+1}SO₃]; $n = 8, 10$ or 12 ; $m = 1$ and $n = 4$ or 8 ; $m = 4$ or 8) have been investigated. Some of these ionic liquids constitute a novel family of real double-chain, catanionic surfactants. As pure compounds, their particular propensity for self-aggregation has led to the finding of a liquid crystalline phase in one of its members. Molecular simulations have complemented the pure components study and suggested their self-nanosegregation into well defined non-polar and polar domains in the liquid, non-crystalline phase. As for their aqueous solutions, those salts incorporating intermediate-to-long alkyl chains in both the cation and anion constitute by definition, and have effectively acted as real, pure catanionic surfactants. The latter are rare; they are distinct from both mixed catanionic-anionic surfactants (obtained by mixing two salts) and gemini surfactants (entropically constrained by chains appended to the same polar head group). Specifically, fluorescence spectroscopy and interfacial tension measurements have been used to determine critical micelle concentrations (CMC), surface activity, and, to compare the effects of the alkyl-substitution patterns in both the cation and anion on the surfactant properties of these salts. With relatively small methylsulfonate anions ($n = 8, 10$ and 12 , $m = 1$), the salts behave as conventional single chain cationic surfactants (decrease of the CMC upon increase of the alkyl chain length (n) in the cation). When the amphiphilic character is present in both the cation and anion ($n = 4$ and 8 , $m = 4$ and 8), novel catanionic surfactants with lower CMC values than those of the corresponding cationic analogues, and which exhibited an unanticipated enhanced reduction of surface tension, were obtained. In addition, the thermotropic phase behaviour of [C₈H₁₈mim][C₈H₁₈SO₃] ($n = m = 8$) was investigated using variable temperature X-ray scattering, polarising optical microscopy and differential scanning calorimetry and shows formation of a smectic liquid crystalline phase with a broad temperature range.