**Self-assembled nanostructures in ionic liquids facilitate charge storage at electrified interfaces**

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Driven by the potential applications of ionic liquids (ILs) in many emerging electrochemical technologies, recent research efforts have been directed at understanding the complex ion ordering in these systems, to uncover novel energy storage mechanisms at IL–electrode interfaces. Here, we discover that surface-active ILs (SAILs), which contain amphiphilic structures inducing self-assembly, exhibit enhanced charge storage performance at electrified surfaces. Unlike conventional non-amphiphilic ILs, for which ion distribution is dominated by Coulombic interactions, SAILs exhibit significant and competing van der Waals interactions owing to the non-polar surfactant tails, leading to unusual interfacial ion distributions. bWe reveal that, at an intermediate degree of electrode polarization, SAILs display optimum performance, because the low-charge-density alkyl tails are effectively excluded from the electrode surfaces, whereas the formation of non-polar domains along the surface suppresses undesired overscreening effects. This work represents a crucial step towards understanding the unique interfacial behaviour and electrochemical properties of amphiphilic liquid systems showing long-range ordering, and offers insights into the design principles for high-energy-density electrolytes based on spontaneous self-assembly behaviour.

**Fig. 1 |** Bulk-phase structural and electrochemical characterization of [C4C1Im][AOT]. **a**, Molecular structures of [C4C1Im]+, [BF4]− and [AOT]− (H, white; C, grey; N, blue; S, yellow; O, red; B, pink; F, cyan). Typical distances within the molecular ions are indicated. **b**, SANS profiles of [C4C1Im][BF4] (25 °C) and [C4C1Im][AOT] (25, 50 and 70 °C). Inset: illustration of self-assembly of [C4C1Im][AOT] leading to a repeating nanostructure comprising [AOT]− bilayers (red, cation; blue, anion).

**References**

1. Xianwen Mao, Paul Brown, Ctirad Červinka, Gavin Hazell, Hua Li, Yinying Ren, Di Chen, Rob Atkin, Julian Eastoe, Isabelle Grillo, Agilio Padua, Margarida Costa Gomes, and Alan Hatton "Self-assembled nanostructures in ionic liquids facilitate charge storage at electrified interfaces", *Nature Materials*, **2019**, doi.org/10.1038/s41563-019-0449-6