DOI: 10.1002/ange.201108010

Magnetic Surfactants

Magnetic Control over Liquid Surface Properties with Responsive Surfactants**

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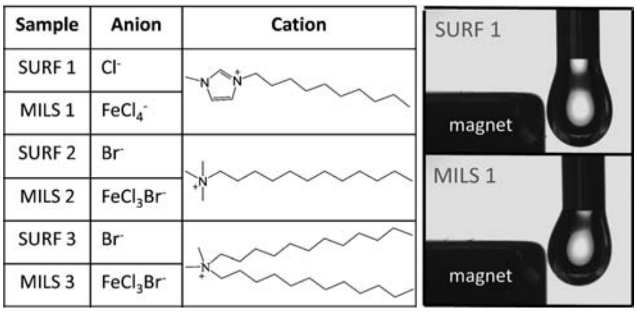
Surfactants responsive to pH,[1] temperature,[2] CO_2,[3] and light[4] are well known. Here we report for the first time ionic liquid surfactants that are magneto-responsive, thus offering the potential to perturb liquid emulsions simply by the application of an external magnetic field. Although ionic liquids (ILs) containing transition metal complexes have been known for some time,[5] it had always been assumed that the metallic centers were isolated, lacking long-range interactions and communication necessary to be magnetically active.[6] Only recently have ionic liquids containing magneto-active metal complex anions, such as 1-methyl-3-butylimidazolium tetrachloroferrate ([bmim]$FeCl_4$),[7] been reported.[7,8] These magnetic ionic liquids (mag-ILs) are especially interesting as they are molecular liquids, rather than typical magnetic fluids (ferrofluids) which comprise magnetic colloidal particles ($\geq$ 10 nm) dispersed in a carrier fluid. The nanoparticle-free mag-ILs are themselves paramagnetic. As such they contain high effective concentrations of metal centers and allow physico-chemical properties (hydrophobicity, electrical conductivity, melting point, etc.) to be controlled by external magnetic fields. Furthermore, because mag-ILs and magnetic ionic liquid surfactants (MILSs) are non-volatile they offer advantages over conventional ferrofluids which often employ flammable organic solvents.



Sample	Anion	Cation
SURF 1	Cl^-	
MILS 1	$FeCl_4^-$	
SURF 2	Br^-	
MILS 2	$FeCl_3Br^-$	
SURF 3	Br^-	
MILS 3	$FeCl_3Br^-$	

Figure 1. Left: Inert (SURFs) and magnetic surfactants (MILSs) studied. Right: Response of liquid droplets to the field from a 0.4 T NdFeB magnet. [SURF 1] = 20 wt%, [MILS 1] = 20 wt%.

Previous work has shown ionic liquids exhibiting magnetic responses.[6,8b] Further examples are introduced here (Figure 1, left), but more significantly these new materials are surface active, which is a fundamental property of colloidal systems. Now, magneto-responsive emulsions become accessible, which to date have only been realized with Pickering emulsions stabilized by magnetic nanoparticles but not for molecular liquids.[9]

Synthesis of the MILSs is readily achieved by mixing an iron trihalide with the appropriate cationic surfactant (see Supporting Information for details). Electrical conductivity measurements of dilute aqueous solutions show that the critical micelle concentrations (cmcs, Table 1) are not greatly affected by the changes in anion alone. At first sight this is surprising as the larger anions ($FeCl_4^-$, $FeCl_3Br^-$) should be less effective at screening cation–cation headgroup repulsions, thus increasing the cmc (surfactants become more hydrophilic). However, the $FeCl_4^-$ and $FeCl_3Br^-$ anions may interact with the hydrophobic moieties, and it is seen that the degree of dissociation, β, increases when exchanging halide for the tetrahalogenferrate(III) anion.

The MILSs investigated here show no saturation magnetization, but do exhibit paramagnetic behavior (see Supporting Information) and the values for magnetic susceptibility, χ, are similar to those reported in the literature (Table 1).[7,14] Effective magnetic moments, μ_{eff}, have also been estimated and are similar to literature values, lying close to the values expected for high-spin d^5 Fe^{III} ions (spin-only value: 5.92 μ_B).[15] The susceptibility χ is significantly higher for MILS 1 than for MILS 2 or MILS 3, perhaps as the increased size and polarizability of the added bromide distorts the perfect tetrahedral geometry resulting in a smaller contact angle of the spins in the complex.[16] It may also be explained in terms of the lower ligand field strength of Br^- with respect

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[**] P.B. thanks HEFCE and the University of Bristol, School of Chemistry for a DTA, PhD scholarship. A.B. and A.M.S. credit funding by ERA NanoSciE+. We also achnowledge STFC for the allocation of beam time, travel, and consumables grants at ILL, and the Krüss Surface Science Centre, Bristol, for facilities for surface tension measurements.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108010.

Table 1: Selected physical properties of SURFs 1–3 and MILSs 1–3.[a]

Compound	M_w [g mol^{-1}]	M.p. [°C]	cmc [mM] ± 0.005	β	X_{mol} [m^3 mol^{-1}]	μ_{eff} [μ_B]
SURF 1	258.61	311[10]	37.0 (39)[11]	0.55	–	–
SURF 2	308.35	246	15.5 (14.5)[12]	0.26 (0.25)[12]	–	–
SURF 3	462.64	162	0.05 (0.07)[13]	0.53[b]	–	–
MILS 1	462.64	−60	40.6	0.73	1.53×10^{-7}[c]	5.38 (5.66)[6][c]
MILS 2	470.55	32	13.6	0.81	1.37×10^{-7}	5.09
MILS 3	624.84	40	0.06	0.87	1.31×10^{-7}	4.99

[a] Bracketed values are derived from the literature. [b] Estimated as 0.5 at low surfactant concentrations.[13] [c] For comparison, C_4 butyl chain [bmim]$FeCl_4$: 1.77×10^{-7} m^3 mol^{-1}, 5.90 μ_B[7]; C_8 octyl chain [omim]$FeCl_4$: 1.76×10^{-7} m^3 mol^{-1}, 5.78 μ_B.[14]

to Cl^-.[14] Surprisingly, even micellar solutions of these MILSs demonstrate a field response (Figure 1, right and Supporting Information), leading to the intriguing possibility of micellar structuring, which would not happen with a normal non-micellizing magnetic IL.

It has been shown that a homogeneous mixture of [bmim]$FeCl_4$ in water could not be separated by a 1 T magnet.[17] However, concentration was spatially varied in the magnetic field gradient, and it is expected that MILSs showing higher magnetic susceptibilities in water could also be made, by altering cation–anion structure (lowering molecular weight of cation or changing the paramagnetic anion), or perhaps further increasing alignment of magnetic moieties by creating non-ionic MILSs. This may then open up the possibility of combining a magnetic field with other separation techniques such as centrifugation, filtration, and adsorption. For example, locally increased concentrations of mag-ILs can increase the efficiency of ultracentrifugation.[18]

Polarizing light microscopy (PLM) textures show that all of the SURFs exhibit transitions from fluid micellar to liquid crystalline phases, understood as arising from a competition between the increase in free energy associated with loss of orientational entropy against excluded volume and other interactions. With no added water pure SURF 1 exhibits a fan-like texture characteristic of a hexagonal phase (or focal conic lamellar phase). The phase progressions of SURF 2 and 3 at 25 °C are consistent with the literature: SURF 2[19] L_1–H_α–crystals; SURF 3[20] isotropic–D_1–D_2 (where L_1 represents a non-birefringent micellar solution, H_α the mosaic texture of a reverse hexagonal phase, D_1 a dilute lamellar phase, and D_2 a collapsed lamellar phase). Mesophase formation is lost on progressing from SURF 1 to MILS 1 and SURF 2 to MILS 2, though dilute isotropic (micellar) phases are still present. This may be explained by increased hydrophobicity of the MILSs: MILS 3, still retains mesophase structures (c.f. discussion below) though less extended than its parent, SURF 3.

Small-angle neutron scattering (SANS) conclusively shows that the SURFs and MILSs aggregate at concentrations in excess of their cmcs (Figure 2 and Supporting Information). Data analyses, through scattering law model fitting, show minor changes in micellar size or shape after exchanging the halide for tetrahalogenferrate(III), and also with concentration. The SANS for SURF 1, SURF 2, MILS 1, and MILS 2 micelles can be fitted using a model for ellipsoidal micelles with principal radii $R_1 = 11$–18 Å and aspect ratios $X = 1.0$–2.4 depending on surfactant and concentration. On the other hand SURF 3 and MILS 3 both show strong Q^{-2} scattering, described by a model of bilayer micellar disks (thickness ca. 22 Å, radius > 900 Å). An interesting feature of the profiles for MILS 1 and MILS 2 is the lack any obvious structure factor, $S(Q)$, indicating only weak electrostatic interactions. This could suggest association of metal halide anions around micelles (or even into the micellar core), thereby compressing the electrical double layer as compared to the regular SURF micelles.

In the absence of an applied field, the MILSs are more effective surfactants than their parent SURFs showing greater surface tension (γ) reduction of water for the same concentration (Figure 3 and Supporting Information). Interestingly,

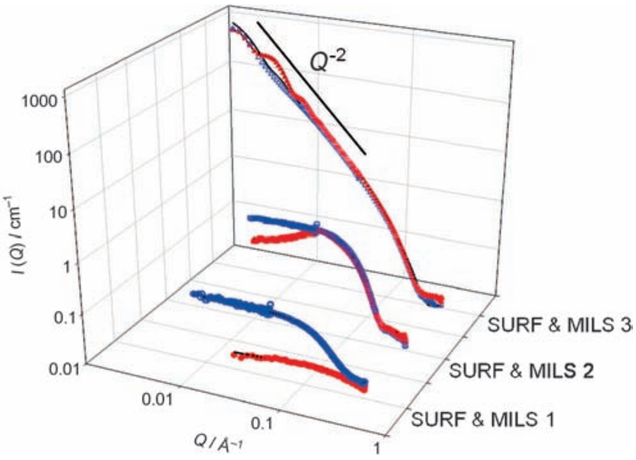

Figure 2. Fitted SANS profiles for SURFs and MILSs at 25 °C. Red ●: SURF 1 (0.04 M), blue ○: MILS 1 (0.04 M); red ■: SURF 2 (0.04 M), blue □: MILS 2 (0.04 M); red ▲: SURF 3 (0.02 M), blue △: MILS 3 (0.02 M). SURF 3 and MILS 3 at 0.02 M due to low solubilities.

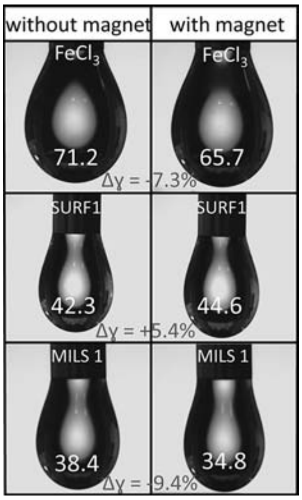

Figure 3. Pendant drop profiles of SURF 1 and MILS 1 with and without a magnet.

the surface properties are magneto-responsive, as placing a magnet (0.4 T) in close proximity (1 mm) to aqueous solutions of the MILS reduces γ even further. The paramagnetic MILS 1 and 2 are bi-functional,

being both intrinsically surface active and also showing a magnetically induced reduction in γ on the order of $-4\ \mathrm{mN\,m^{-1}}$ (possibly due to unpaired electrons aligning with the external field and anion partitioning at the interface). The observed magnetic effect decreases with decreasing MILS concentration. On the contrary, for the inert SURFs γ increased by about $+2\ \mathrm{mN\,m^{-1}}$ in the magnetic field. This is a surprising result, however, recent reports[21] have shown that strong magnets can indeed affect γ for liquid water due to development of hydrogen-bonding and a weakening of van der Waals forces. For pure water saturated with O_2 large effects on contact angle at the solid–liquid interface have been seen in magnetic fields (6 T).[22]

Figure 4 shows a phase-inversion application of MILS 1 (20 wt% in H_2O) in biphasic aqueous surfactant solution–organic solvent (dodecane) systems. Using a vertically applied magnet it is possible to overcome both gravity and the water–oil interfacial tension (ca. $50\ \mathrm{mN\,m^{-1}}$), "levitating" the lower magnetic liquid and pulling some of it through the upper organic solvent. This phase inversion is energetically unfavorable since it both increases water–oil interfacial area, and inverts the liquid phases of different density, but occurs due to lowering of the system magnetic energy.

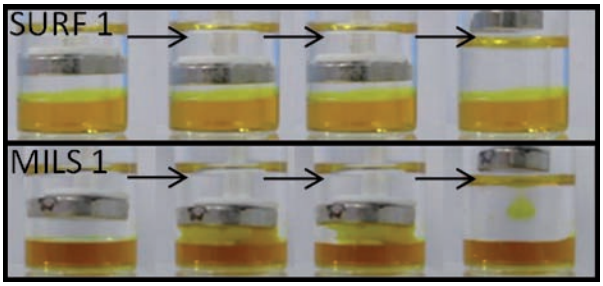

Figure 4. Effect of magnetic field through dodecane on 20 wt% aqueous surfactant solutions. The magnet was smoothly moved up and down by hand, and the entire sequence left to right took ca. 30 s as can be seen in a video provided in the Supporting Information. Top: inert SURF 1; bottom: magnetically active MILS 1. To aid visualization the SURF 1 solution was dyed with trace methyl orange.

Materials combining magneto-responsivity with surface activity offer tantalizing possibilities in potential applications. Traditionally,[23] in order to alter properties of inert surfactant solutions such as cmc, surface tension, aggregate size and shape, or to control phase separation/recovery it has been necessary to perturb the composition, such as with electrolyte or pH, or with external thermodynamic variables (temperature and/or pressure). Disadvantages of these control methods are irreversible changes in system composition, or significant energy inputs. Now, with the magnetic ionic liquid surfactants reported it is possible to control physico-chemical properties non-invasively and reversibly, simply by switching the applied field "on" or "off". Further to this, the potential for controlled orientation of colloidal dispersions, resulting in magnetophoretic effects may also have other applications. These MILSs also have the potential to combine partitioning and enrichment of catalysts induced by internal magnetic field effects (due to faster proton transfer) in photochemical reactions,[24] or allow clean recovery of expensive products and facile recyclability of the solvent medium.

Received: November 14, 2011

Keywords: ionic liquids · magnetic surfactants · micellization · surface tension

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