Experimental Report

13/06/2013

Proposal:	**9-10-1249**	**Council:**	4/2012
Title:	Aggregation of surfactants in magnetic ionic liquids		

This proposal is a new proposal

Research Area: Chemistry

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Samples: [bmim]FeCl4 water surfacants see proposal

Instrument	Req. Days	All. Days	From	To
D22	3	2	27/11/2012	29/11/2012

Abstract:

This proposal aims to explore aggregation behavior of common surfactants in magnetic ionic liquids (MILs) and to investigate the effect of magnetic field on aggregate size, shape and orientation. Such systems are especially significant as until now, with the exception of photosurfactants [1], it has only been possible to affect such behaviour intrusively (e.g. altering pH or temperature). Now, by turning “on” or “off” a magnetic field it may be possible to reversibly control aggregation behaviour, by altering the structure of the underlying solvent medium. This has potential applications spanning emulsions, magnetophoresis and catalysis. The proposal is supported by our recent article (Magnetic Control over Liquid Surface Properties with Responsive Surfactants, Angewandte Chemie, 2012, anie.201108010 accpeted 14-12-11, ref [11] in the list below ILL 9-10-1167). Magnetic surfactants in aqueous media have been studied by us [11], however the related systems which are the subject of this proposal (i.e. normal inert surfactants in a magnetic IL medium) have not been considered until now.

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Small atomic clusters (n = 10-1000 atoms) exhibit hybrid properties between the molecular and bulk solid-state limits[1]. For example, superparamagnetic properties displayed by liquid dispersions of monodomain colloidal particles (ferrofluids) have already lead to new biomedical applications[2,3]. Here, we show for the first time that size effects can be observed in nanoparticle-free ferrofluids through the design of micelles and microemulsions comprising magnetic surfactants[4]. These new systems bridge the gap between molecular nanomagnets (n <30) and magnetic nanoparticles (MNPs n = 100-1000)[5], allowing fine control over cluster size n, whilst also combining magnetic ordering with low-density and electrical insulation. This is a significant step forward since micellar microemulsions have numerous advantages over traditional particulate ferrofluids, including *in situ* tuneability through composition, facile fabrication, monodispersity, good dispersibility and stability, as well as solubilization of hydrophobic additives, essential for drug delivery.

Magnetic surfactants are based on common surfactant ions with metal complexes, and because they contain high effective concentrations of metal centres, their physico-chemical properties (hydrophobicity, electrical conductivity, *etc.*) can be controlled non-invasively and reversibly simply by switching “on” and “off” an external magnetic field. These compounds have been shown to bind to biomolecules and allow magnetic manipulations[6]. They have also been used to generate magnetic emulsions[7], with many suggested applications. This paper is the first report of magnetic microemulsion formation from new anionic magnetic surfactants.

Microemulsions have numerous technological applications[8], in part because of the ability to precisely control size and stability of the nano-domains. Microemulsions made from transition metal-based surfactants have been used as compartmentalized reaction media to prepare sub-micron or nano-sized particles with controlled size and shape, bearing properties relevant for applications such as high density magnetic recording media[9-11]. However, it had always been assumed that the metallic centres were isolated, lacking long range interactions and communication necessary to be magnetically-active and so the intrinsic magnetism of microemulsions has until now been overlooked. This paper describes the first nanoparticle-free ferrofluids based on microemulsions with magnetic surfactants. We have used small-angle neutron scattering (SANS) and SQUID magnetometry to investigate both the bulk “dry” surfactants and microemulsions.

To date the only reported magnetic surfactants have been cationic amphiphiles[4]. Here, magnetic anionic surfactants are reported for the first time, made from the commercially available commodity Aerosol-OT (AOT) (*Supporting information, Figure S1*), and transition *d*- or *f*-block metals; $Co(AOT)_2$, $Mn(AOT)_2$, $Ce(AOT)_3$ and $Ho(AOT)_3$. Common AOT is a known bactericide[12], is already used in pharmaceutical formulations, offers better detergency than cationic surfactants and leads to magnetic surfactants which are less aggressive (lower Lewis acidity) than the cationic analogues. Non-radioactive lanthanides are classified as having low toxicity[13], having uses as catalysts[14,15] and superconductors[15]. Lanthanide anionic surfactants have also been reported for spectroscopic studies because of intrinsic luminescence[16]. Significantly, certain lanthanides have the highest known effective magnetic moments, exhibiting ferro- or antiferromagnetism as well as paramagnetism.

Polarizing light microscopy (PLM) textures show that the magnetic surfactants exhibit a transition from fluid micellar to liquid crystalline phases in water. (*Supporting Information, Figure S3*) and SANS conclusively shows that the compounds aggregate in water above critical micelle concentrations (cmcs) (*Supporting Information, Figure S5*). In a typical organic solvent, heptane, SANS data (Figure 1, *Supporting Information, Table S1*) show only minor changes in micellar size or shape on exchange of the metal ion and also with concentration.

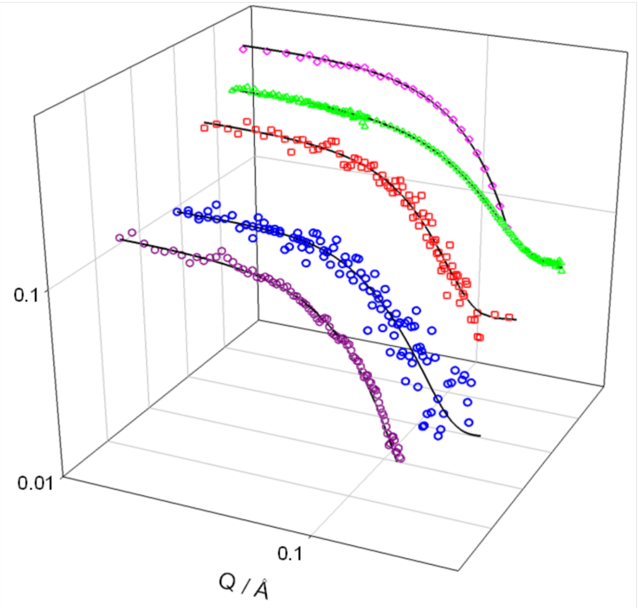

Figure 1: SANS profiles for surfactants in n-d_{-16} heptane at 1.0 wt% at 25 °C. Lines through the data are fits (parameters in *Supporting Information, Table S1*). Co(AOT)$_2$ is at 0. 5 wt% due to phase separation at higher concentrations. Na(AOT) (○), Co(AOT)$_2$ (○), Mn(AOT)$_2$ (□), Ce(AOT)$_3$ (△) Ho(AOT)$_3$ (◊).

SQUID Magnetometry between 5 K and 300 K on the pure surfactants (Figure 2, *Supporting Information, Table S3*) indicates Co, Mn and Ho analogues are paramagnetic over most of the temperature range, with little noticeable deviation between field cooled (FC) and zero field cooled (ZFC) measurements (*Figure S6*). The Co(AOT)$_2$ has a susceptibility χ_mT of 2.16 emu K mol^{-1} Oe^{-1} at room temperature (at field *H* = 0.25 kOe) corresponding to an effective paramagnetic moment μ_{eff} = 4.15 B.M. per Co^{2+} ion, which is consistent with literature for high spin d^7 Co(III) ions (S = 3/2)[17]. Above 20 K the magnetic susceptibility follows the Curie-Weiss law with Weiss temperatures, θ_p, close to -4.7 K. This negative θ_p value together with the reduction of the effective magnetic moment observed on decreasing temperature suggests overall antiferromagnetic behavior at low T. Magnetization as a function *H* (see *Supporting Information, Figure S6a*) at 2.0 K shows reversibility in the entire applied field range studied, $-50 \geq H$ (kOe) ≤ 50. With an increasing magnetic field, a linear dependence in magnetization from 0 to 6 kOe is observed and then the magnetization tends to saturate at around 30 kOe.