Supporting Information

Magnetic emulsions with responsive surfactants

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MagSurf Synthesis

Dodecyltrimethylammonium bromide (99%, DTAB), iron (III) trichloride and gadolinium (III) chloride hexahydrate were purchased from Sigma Aldrich and used without further purification. n-Dodecane (<99%) was purchased from Fluka and purified using fuming sulfuric acid to reach surface chemical purity (Supporting Information). Dodecyltrimethylammonium trichloro-monobromoferrate (DTAF) was synthesized by mixing equimolar amounts of DTAB with iron trichloride in methanol and stirring overnight at room temperature. The solvent was then removed and the product dried at reduced pressure at 80 °C overnight to yield a viscous brown liquid. Dodecyltrimethylammonium trichloromonobromogadolinate DTAG) was synthesized using a similar procedure, yielding a white solid. MagSurfs were characterized by elemental analysis (Table S1), differential scanning calorimetry (DSC), and UV-Vis spectroscopy (Figure S1).

Elemental analysis

Elemental analyses show that all the compounds contain the expected compositions.

Compound	C	H	N
DTAG	31.45 (31.51)	6.39 (5.95)	2.73 (2.45)
DTAF	38.29 (38.31)	7.22 (7.23)	2.98 (2.97)

Table S1 .Elemental analyses, experimental and theoretical (brackets) as % wt.

UV- Visible Spectroscopy

UV-vis absorption spectra of 0.10 M MagSurf acetonitrile solutions were recorded on a Nicolet Eco 300 machine (500 – 900 nm). The spectrum for DTAF shows three bands characteristic of the $[FeCl_3Br]^-$ ion, similar to those for the $[FeBr4]^-$ ion, in agreement with previous literature.[1] There is no absorption in the UV-vis range for $GdCl_3$ or the $[GdCl_3Br]^-$ ion.

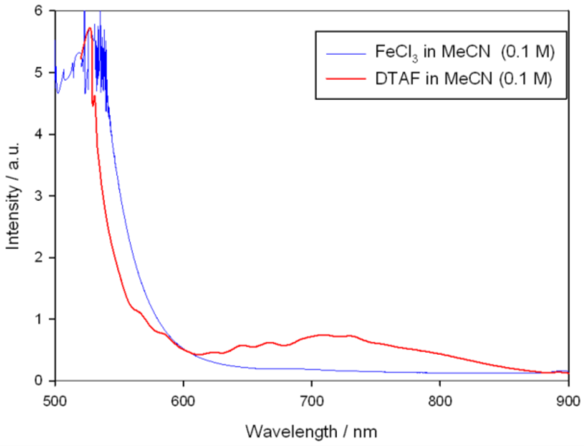

Figure S1. Visible spectra of $FeCl_3$ (starting material) and the MagSurf DTAF at a concentration of 0.10 M in acetonitrile.

Polarizing Light Microscopy (PLM)

A Nikon Optiphot-2 microscope fitted with polarizing filters and a Linkam heating/cooling stage was used. Images were captured on a PC via a video camera and colour processor connected to the microscope. The liquid crystal progression of each surfactant was investigated by the solvent penetration method (i.e. phase cut). A small amount of surfactant was placed on a microscope slide under a cover-slip. The mounted slide was heated until the sample was fluid and optically isotropic. After slow cooling (1.0 ˚C min^{-1}) to 25 ˚C, a drop of water was added to the edge of the cover-slip. As the water penetrated the surfactant, a concentration gradient was established, from water at one side (bottom left Figure S2) to pure surfactant at the other, enabling a range of mesophases to be observed in the field of view.

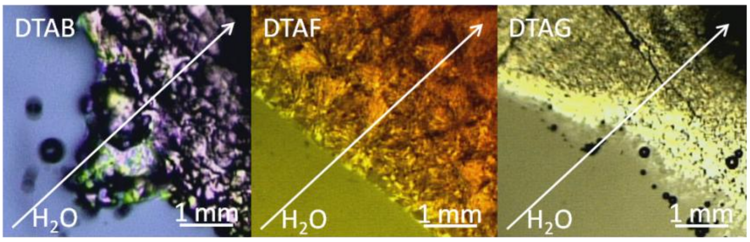

Figure S2. PLM textures showing mesophase formation of surfactants on addition of water at 25 ˚C.

Electrical Conductivity Measurements

Electrical conductivities, κ, were determined using a Jenway Model 4510 Conductivity/TDS conductivity meter with temperature controlled at 25 ˚C ± 0.1 (thermostatic water bath). Critical micelle concentrations (cmcs) were determined as normal, from the break points between the high (low concentration) and lower branches of behaviour. Surfactant ionic dissociation constants (β), were estimated using the ratio of the slopes method.[2]

Compound	**M_w / (g mol^{-1})**	**Mp / ˚C**	**cmc / (mM) ± 0.005**	**β**
DTAG	571.85	-	11.9	0.59
DTAF	470.55	32	13.6 (13.6)	0.81
DTAB	308.35	246	15.5 (14.5)	0.26 (0.25)

Table S2. Selected physical properties of surfactants studied.

Surface Tensiometry Method

Surface tensions between aqueous surfactant solutions and air were performed at 25 ± 1 °C (Figure S3), using a Krüss Drop Shape Analysis DSA1 apparatus. This instrument obtains spatial coordinates of a drop edge (shape and size), which are used to calculate surface tension[3]. Prior to use, the capillary needle (diameter, 1.834 mm) and syringe were rinsed with copious amounts of pure water. Before being mounted on the dosing dispenser, the syringe was rinsed a few times with the surfactant solution to be measured. An aqueous drop was manually formed at the tip of the capillary. Measurements were acquired until steady values of surface tension were reached. Calibration used the surface tension of pure water (Elga, 18 MΩ cm^{-1}).[4]

Measurements of MagSurf aqueous solutions at 0.20 M were taken on the same drop with and without a magnet: NdFeB (N42, 20 mm x 10 mm magnetic field density of 0.44 T on the surface and a gradient of about 36 mT mm^{-2}) and was held in position at an approximate distance of 1 mm from the bottom of the drop surface.

Unpaired electrons in transition metal salts such as $FeCl_3$, $GdCl_3$ and MagSurfs interact weakly with a magnetic field[5] and so a reduction in apparent surface tension should be expected, as the downward magnetic attraction augments gravity. It has also been reported that γ for pure water is affected by a magnetic field due to the development of hydrogen bonding and a weakening of van der Waals forces[6] so the slight increase in γ seen for water was expected.

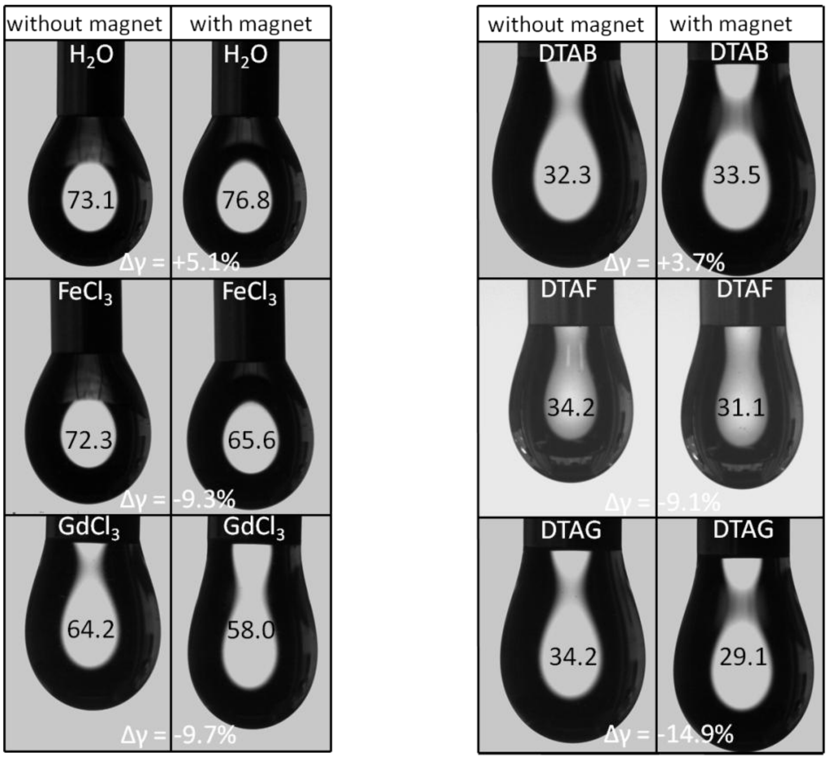

Figure S3. Pendant drop profiles of the surfactants studied with and without a magnet. Units of surface tension are mN m^{-1}.

Emulsion preparation and characterization.

Emulsions were prepared with surface chemically pure n-dodecane, a commercial base oil chosen to represent the chief constituent of engine lube oil[7], pure water and also a set of emulsions were made with brine. For this 20 wt% aqueous (or brine) solutions of the appropriate surfactant were used to make up 10.5 wt% Triton-X100 (Sigma Aldrich) solutions. These mixed surfactant/MagSurf+Triton-X100 solutions were vortexed for 5 minutes, before either base oil (Exxonmobil core 150) or pure n-dodecane was added (7.8 wt% with respect to the final emulsion). The resulting emulsions were voretxed for a further 10 minutes and then sonicated (MSE Soniprep 150 (UK), 23 kHz) five times, each time at full power for four minutes with 30 seconds cooling time between successive sonication. The visual appearances of the water, oil, oil + water bi-phasic system, and the resulting MagSurf emulsions are shown in Figure S5 (Supporting Information).

The emulsion droplet sizes were determined using a Brookhaven Instruments Zeta-PALS Dynamic Light Scattering (DLS) apparatus (Brookhaven Instruments Corporation, Holtsville, NY) with the detector set at 90°. Measurements were taken of the neat emulsions, and then at a series of dilutions with pure water or brine as appropriate. At high concentrations DLS is sensitive to interparticle interactions, in the region of 10 vol% dilution with solvent (water or brine) the DLS particle sizes stabilized to limiting values (Table S3 and S4, Supporting Information).

Sizing for neat mixed micellar solutions not containing oil were also carried out. However, very weak scattered intensities owing to the small sizes (~2 nm) gave rise to unreliable analyses of the correlation functions.

Dodecane Purification

n-Dodecane (Fluka >99%), is known to contain surface-active impurities[8]. Prior to making emulsions, dodecane was purified by washing with fuming sulfuric acid, then neutralising with 10 wt% sodium bicarbonate (aq.). Further washing was done with pure water and the dodecane was dried with calcium chloride. The dodecane was then fractioned under reduced pressure with the middle fraction of the distillate collected for experiments.[9] The cleaned dodecane was assessed for surface chemical purity by interfacial tension $\gamma_{o/w}$ measurements as a function of surface age (protocol outlined below): good agreement of $\gamma_{o/w}$ compared with literature[8] was found.

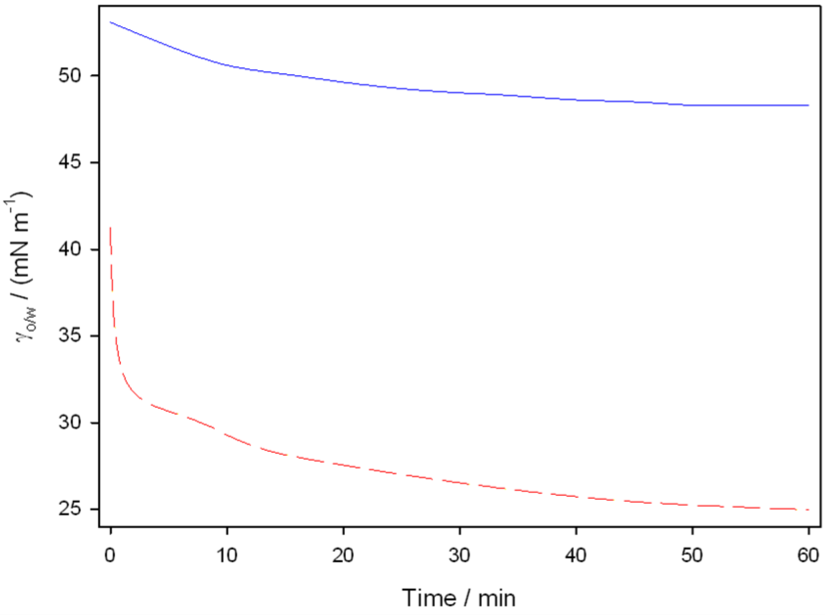

Figure S4. Interfacial tensions as a function of surface age determined by drop shape analysis (see below) for dodecane-water interfaces at 25 ˚C: red-dashed lower curve, as received dodecane; blue upper curve purified dodecane.

To assess the purity of dodecane, interfacial tensions between pure water and either purified or "as purchased" dodecane were performed at 25 ± 1 °C, using a Krüss Drop Shape Analysis DSA1 apparatus. A drop of water was formed at the tip of the capillary, then submerged in a cuvette containing dodecane. Measurements were acquired every 5 minutes for 60 minutes using the automatic fitting function on the DSA1 software.

Emulsion preparation and characterization.

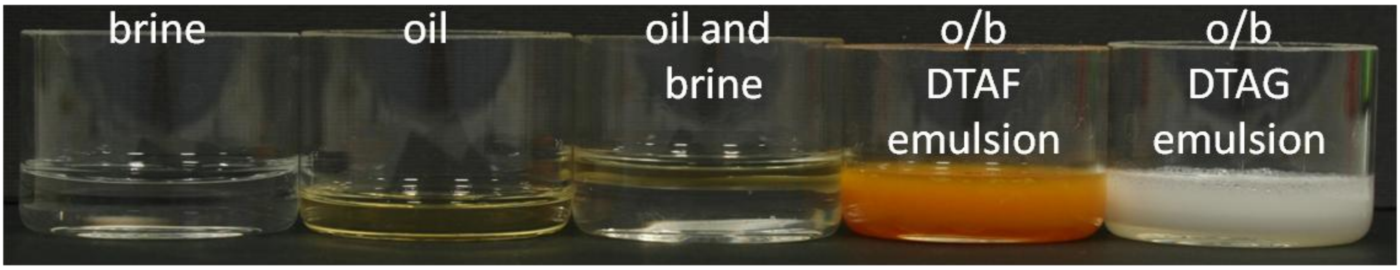

Figure S5. Oil and brine do not mix.

However on adding a surfactant and sonicating, oil in brine (o/b) emulsions form.

Compound	Density / g cm^{-3}	Volume fraction (ϕ)
DTAB / DTAF /DTAG	1.40	0.123
TritonX-100	1.07	0.094
Base oil	0.87*	0.093
dodecane	0.75	0.104
water	1.00	0.690

Table S3. Parameters for emulsion characterization. *At 15 ˚C.

Compound	MagSurf ϕ	100 vol%	50 vol%	25 vol%	10 vol%	5 vol%	1 vol%
DTAG	0.123	21707	159	138	150	154	159
DTAF	0.123	10817	222	172	158	158	136
DTAB	0.123	1308	175	176	220	239	240

Table S4. Apparent emulsion size (nm) for emulsions of lube oil in water as a function of concentration determined by DLS: vol% represents the final volume % of emulsion diluted in water.

Compound	**MagSurf** ϕ	**100 vol%**	**50 vol%**	**25 vol%**	**10 vol%**	**5 vol%**	**1 vol%**
DTAG	0.123	773	93	99	212	232	260
DTAF	0.123	1722	118	75	187	207	209
DTAB	0.123	1307	250	198	184	166	164

Table S5. Apparent emulsion size (nm) for emulsions of dodecane in brine as a function of concentration by DLS: vol% represents the final volume % of emulsion diluted in brine.

Zeta potentials of emulsions

As expected for emulsions stabilized by cationic surfactants, the zeta potentials of the studied emulsions were all determined as positive, between +20 and + 35 mV, hence explaining the observed stabilities.

Effect of a magnetic field on emulsions

Magnified images of Figure 2 (right) in the main paper, showing the effect of a 1T magnet on the magnetic emulsions.

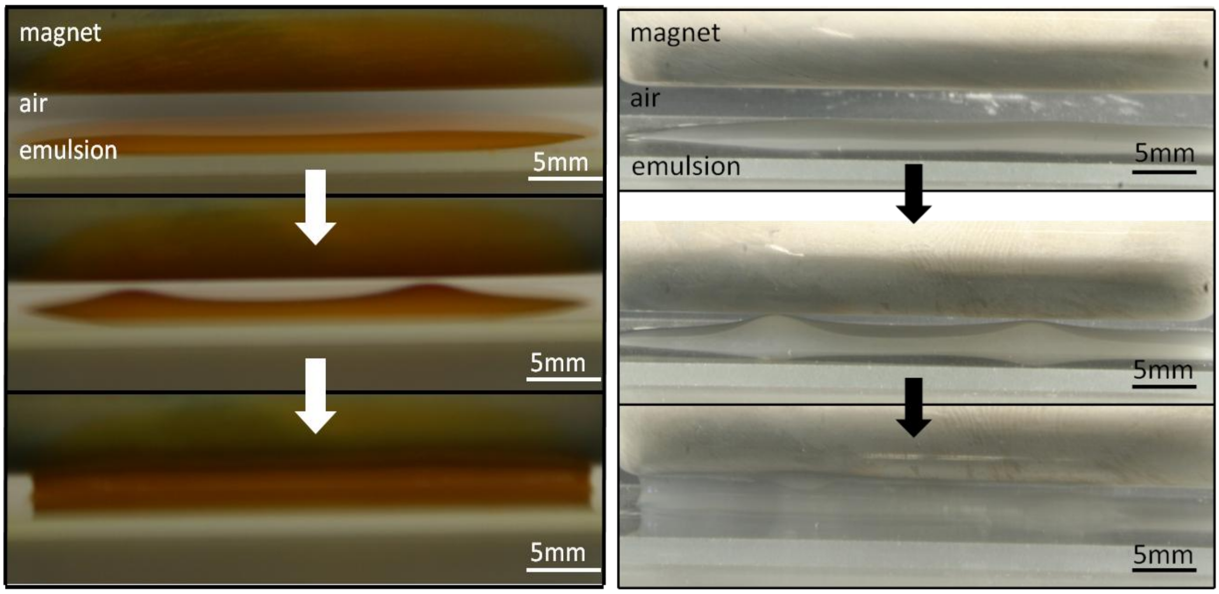

Figure S6: DTAF (left) and DTAG (right) containing emulsions (magnetic surfactant $\phi = 0.123$) attracted to a magnetic field (max = 1 T)

Magnets

The magnets used for Figure 2 in the main paper was a NdFeB (20 mm x 10 mm) with a field density of 0.44 T on the surface, and a gradient of about 36 mT mm^{-2}. And a NdFeB rod magnet (25mm diameter x 50mm) with a maximum field density of ~ 1.0 T, varying along the length. Both magnets were purchased from e-magnets (UK).

Video - link

Figure 2: The interfacial tension of DTAF and DTAG lube oil emulsions (magnetic surfactant $\phi = 0.123$) and dodecane could also be overcome using a magnet. For comparison the system on the left is the non-magnetic DTAB (surfactant $\phi = 0.123$).

Figure 3: The control of a DTAG oil in water emulsion droplet in dodecane.

References

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