SUPPLEMENTARY SECTION

A contrast variation small-angle scattering study of the microstructure of 2,5-dimethyl-7-hydroxy-2,5-diazaheptadecane-toluene-butanol metallomicroemulsions

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Materials

Reagents were used as received from Aldrich, solvents were purified using standard procedures. Mass spectra were obtained in electrospray mode on a Waters Q-tof Micro spectrometer, and 1H NMR spectra were recorded on a Brüker AMX 400 spectrometer and referenced to external TMS.

Synthesis of 2,5-dimethyl-7-hydroxy-2,5-diazaheptadecane (C10)

To a solution of 1,2-epoxydodecane (4.6 g, 25 mmol) in distilled dry ethanol (50 ml) was added N,N,N'-trimethylethlenediamine (3.1 g, 30 mmol, 1.2 equivalents). The reaction mixture was stirred at room temperature for 5 days. Solvent and excess reactant was removed using a rotary evaporator by the addition of small volumes of toluene. The residue was distilled using a short path distillation apparatus (Kugelrohr) to give a pale yellow mobile oil in an 81% yield. 1H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, 3H, 6.6 Hz, $-CH_3$), 1.11 – 1.48 (m, 18H, $-(CH_2)_9-$), 2.16 (s, 6H, NCH_3), 2.24 (s, 3H, NCH_3), 2.18 - 2.27 (m, 3H, HCHN), 2.31 - 2.42 (m, 2H, HCHN), 2.56 (m, 1H, HCHN), 3.53 (m, 1H, CHOH). HR-MS (ESI, MeCN/H_2O) (m/z): calculated for $C_{17}H_{38}N_2O$ + H+ 287.3057, found 287.29.

Sample preparation, microemulsion phase diagram determination

The metal salt - surfactant complexes were formed by dissolving in H_2O (or D_2O) the required mass of ligand and metal salt to produce a 50 mM solution. The solution was vortexed and left to equilibrate for 1/2hr. This stock was separated into 0.8 mL aliquots, to each of which was added further H_2O (or D_2O), toluene (hydrogenous or deuterated) and butanol (hydrogenous or deuterated) as appropriate to form a series of metallomicroemulsion samples. Visual inspection was used to determine the phase boundaries at 25±1 °C.

Pulsed-gradient spin-echo NMR (PGSE-NMR)

Pulsed-gradient spin-echo NMR experiments were carried out on a Bruker AMX360 NMR spectrometer, operating at 360 MHz (^{1}H) and using a stimulated echo-sequence coupled with a 5 mm diffusion probe and a Bruker gradient spectroscopy accessory unit. All experiments were conducted at 25 °C. Temperature stability was maintained by the standard air heating/cooling system of the spectrometer, to an accuracy of ± 0.3 °C. The self-diffusion coefficient D_s was extracted from an analysis of the peak amplitudes according to Equation 1:

$$A(\delta, G, \Delta) = A_o \exp[(-kD_s)] \qquad (1)$$

A is the peak amplitude in the absence (A_o) or presence ($A(\delta, G, \Delta)$) of trapezoidal field gradient pulses of duration δ (400 μs < δ < 2.8 ms), ramp time σ (250 μs), strength G (0.86 T m^{-1}) and separation Δ (140 ms). *k* is given by Equation 2:

$$k = -\gamma^2 G^2 \left(\frac{30\Delta(\delta+\sigma)^2 - \left(10\delta^3 + 30\sigma\delta^2 + 35\sigma^2\delta + 14\delta^3\right)}{30} \right) \qquad (2)$$

where γ is the gyromagnetic ratio.

For molecules in fast exchange, a two-state mobility model may be used to interpret the diffusion data. In this model, the averaged diffusion rate ($\overline{D_s}$) of the species of interest (*e.g.* butanol) is assumed to reside in one of two regions *i.e.* molecularly dispersed (dissolved) in the aqueous phase (D_s^{fast}) or solubilised into the microemulsion droplet (D_s^{slow}), *viz*

$$\overline{D_s} = p_{fast} D_s^{fast} + p_{slow} D_s^{slow} \qquad (3)$$

where *p* is the fraction of time (or equivalently, the concentration) the species spends in the fast (molecularly dispersed) or slow (microemulsion state) environments, *i.e.*

$$1 = p_{fast} + p_{slow} \tag{4}$$

Thus, if one takes the diffusion rate of the slowly diffusing environment to be equal to that determined from the oil component, then the average diffusion rate of the butanol and its rate of diffusion in water in the absence of the surfactant may be used to detemine its partitioning into the microemulsion droplet.

Small-angle X-ray scattering (SAXS)

Small angle X-ray scattering (SAXS) data was collected either on I22 at the Diamond Light Source, Oxfordshire, U.K., or beamline X33 at the European Molecular Biology Laboratory (EMBL) of the Deutsches Elektronen Synchrotron (DESY)Hamburg. The sample to detector distance was 5m, covering a scattering range in Q of 0.007 $Å^{-1}$ to 0.208 $Å^{-1}$. The scattering vector is defined as $Q = (4\pi/\lambda) \sin\theta/2$, where 2θ is the scattering angle and λ is the X-ray wavelength. The samples were mounted in the X-ray beam using 1mm glass capillary tubes and exposed for 30 second duration. The scattering images were collected on a 2D RAPID detector. The beam centre was identified and the isotropic scattering profiles were integrated to one-dimensional linear profiles of intensity vs. scattering vector using the CCP13 software FibreFix.

Phase Diagrams

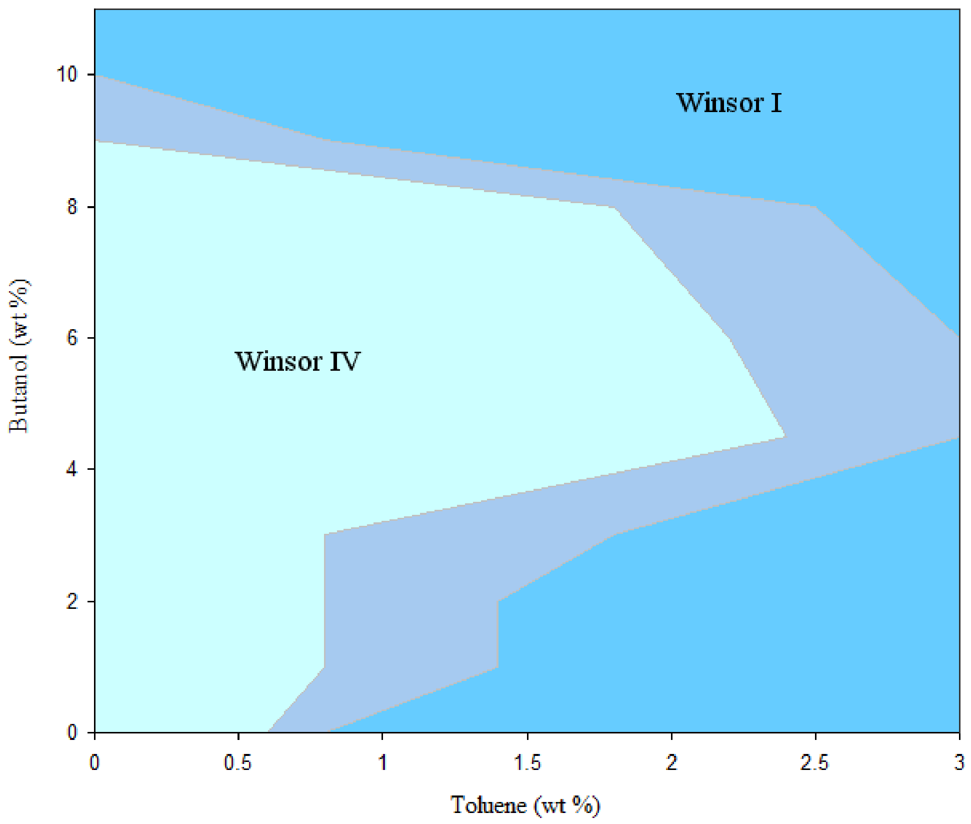

Figure 1S: Phase diagram of an aqueous 25mM $Cu(NO_3)_2$-C_{10} system upon addition of toluene and butanol. The Winsor IV phase is a microemulsion, the grey intermediate phase is an emulsion and the Winsor I phase is an emulsion with excess oil.

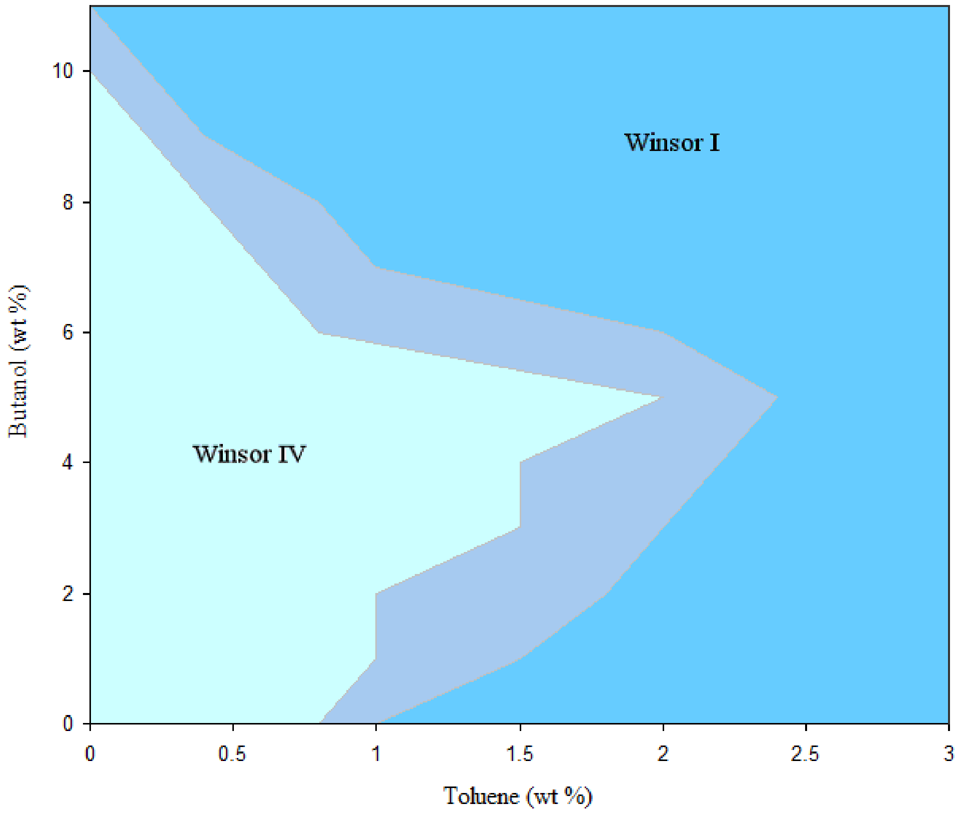

Figure 2S: Phase diagram of an aqueous 25mM $Zn(NO_3)_2$-C_{10} system upon addition of toluene and butanol. The Winsor IV phase is a microemulsion, the grey intermediate phase is an emulsion and the Winsor I phase is an emulsion with excess oil.

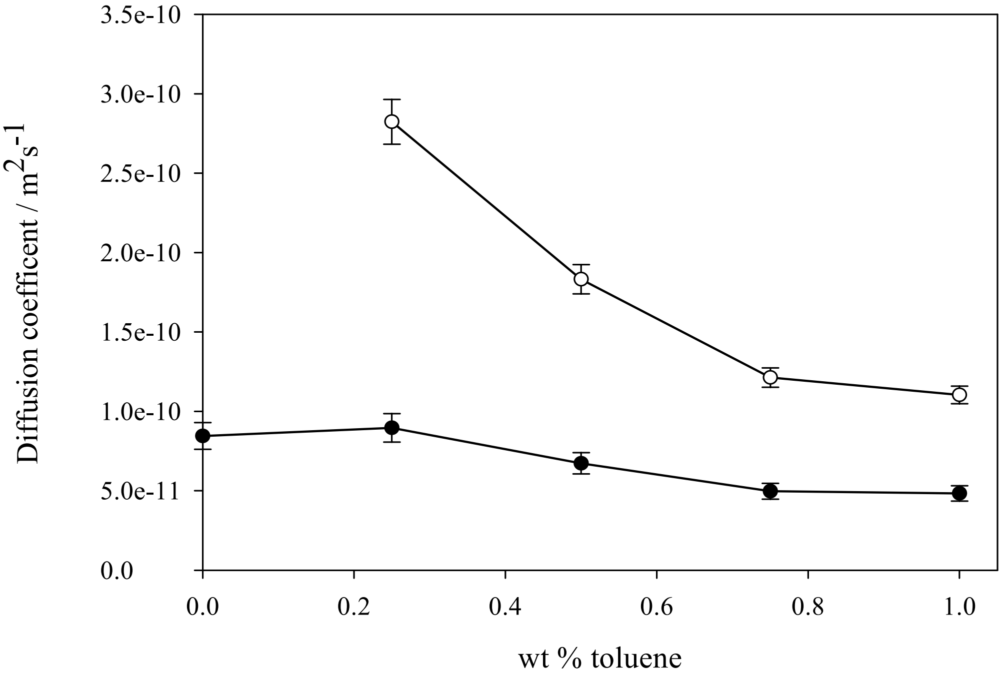

Figure 3S: Diffusion coefficients of $Zn(NO_3)_2$-C_{10} (closed circles) and toluene (open circles) as a function of the weight percentage of toluene added to the system.

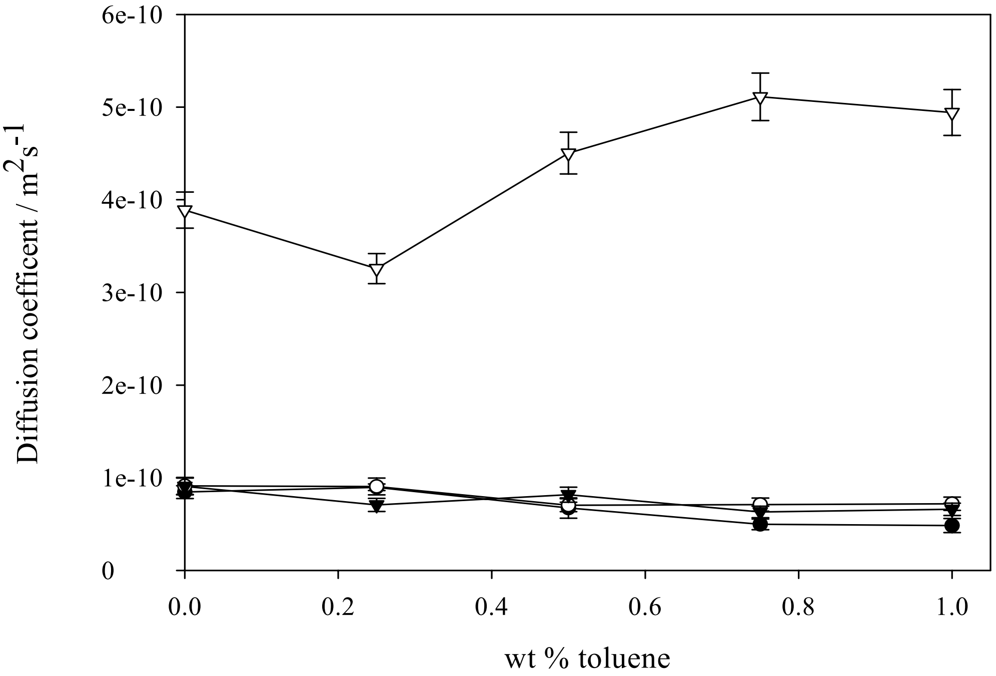

Figure 4S: Diffusion coefficient of $Zn(NO_3)_2$-C_{10} on changes of toluene percentage and in the presence of 0 % BuOH (closed circles), 2.5% BuOH (open circles) and 5% BuOH (closed triangles). Also shown is the BuOH signal at 5% (open triangles).

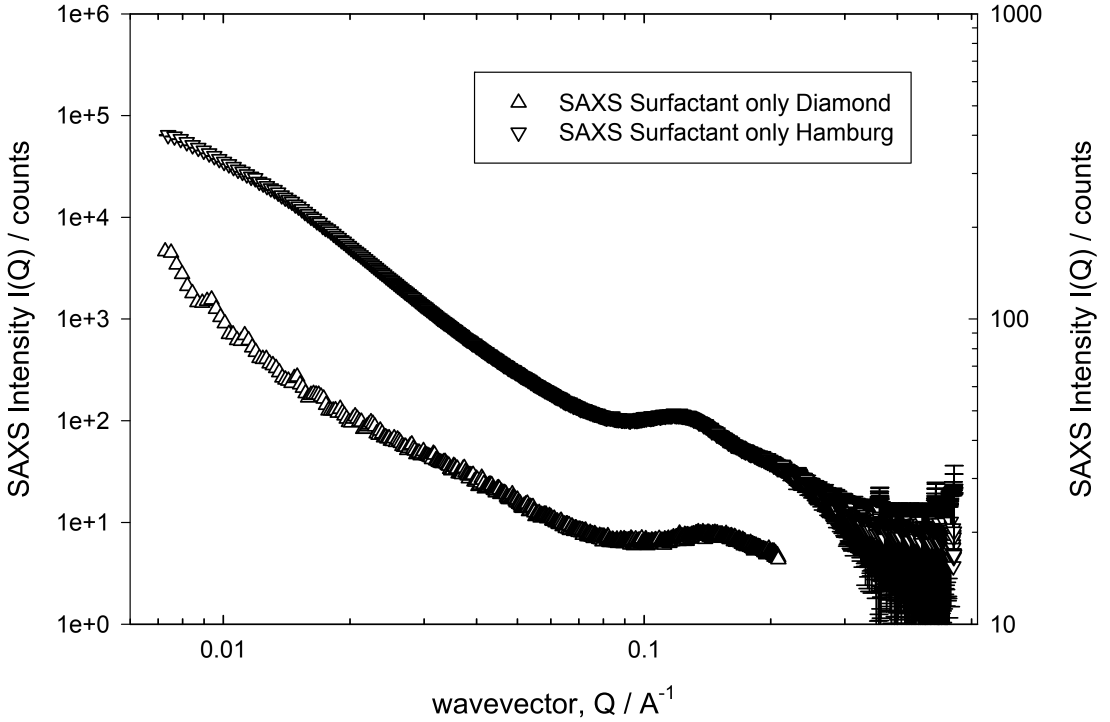

Figure 5S; Comparison of small-angle X-ray scattering from 25mM $Cu(NO_3)_2$-C_{10} in D_2O; Diamond and Hamburg data.

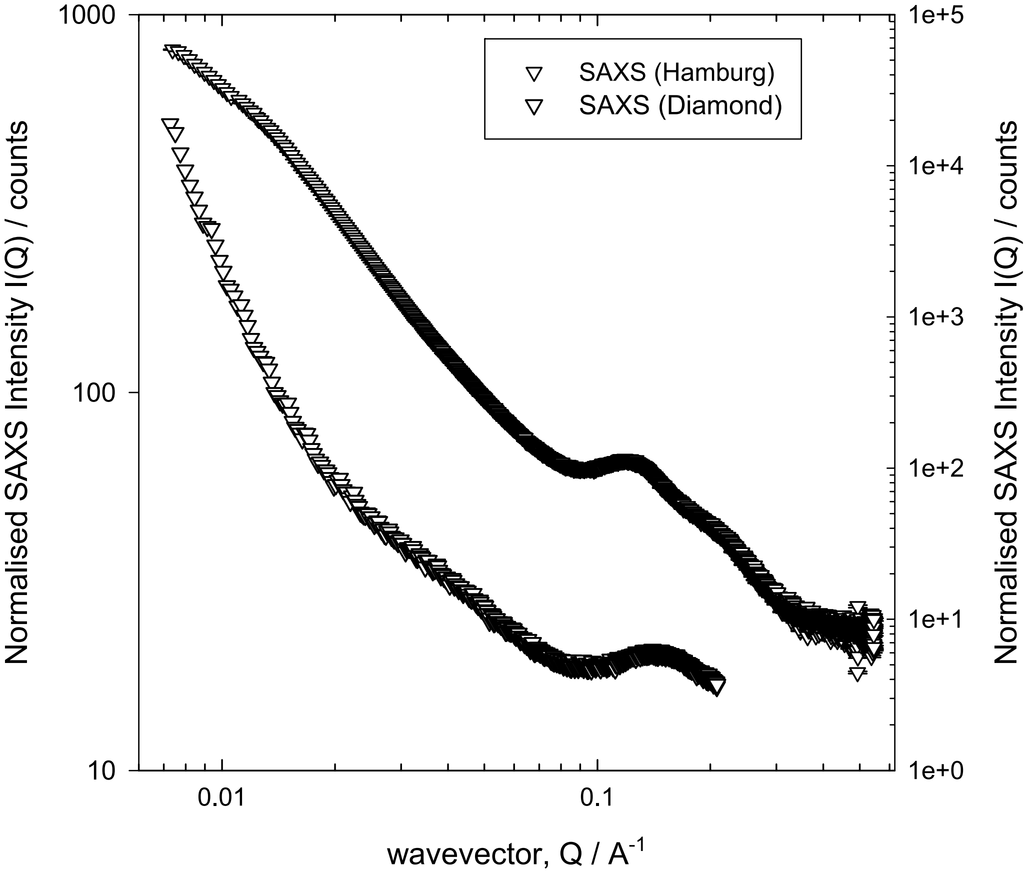

Figure 6S Small-angle X-ray scattering from 25mM $Cu(NO_3)_2$-C_{10} in D_2O with 0.5wt% toluene.

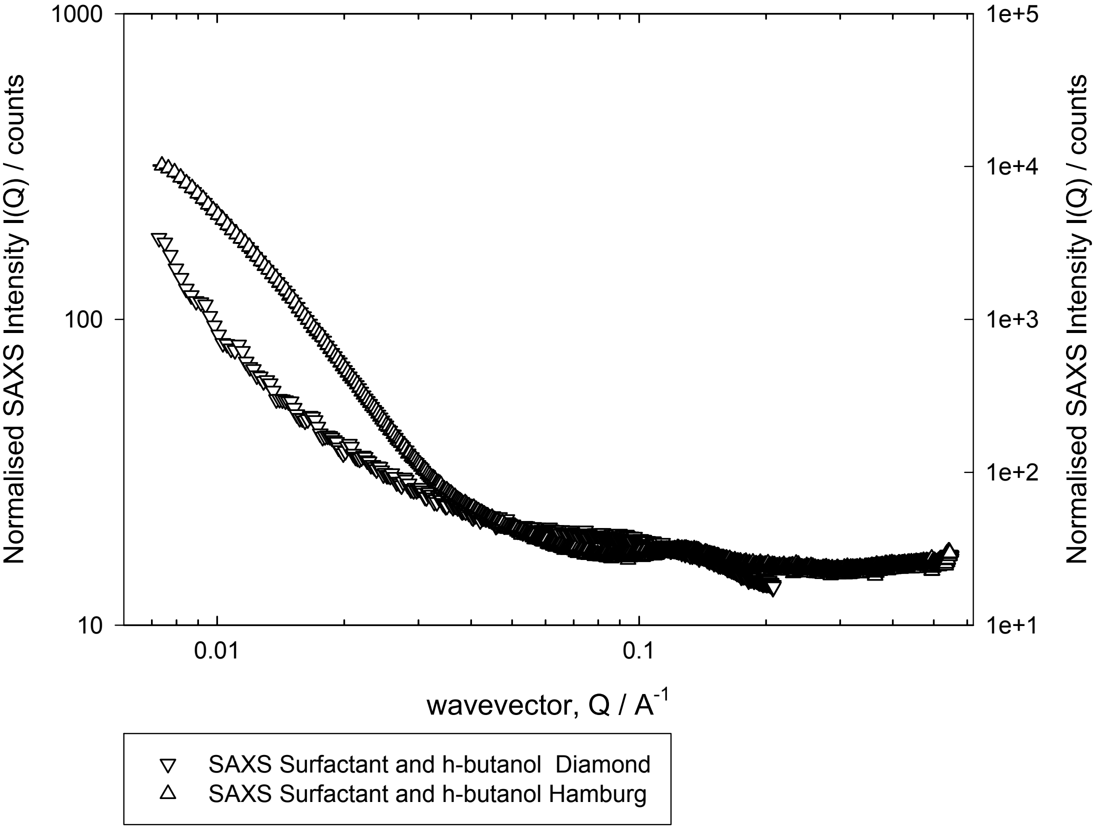

Figure 7S; Small-angle X-ray scattering from 25mM $Cu(NO_3)_2$-C_{10} in D_2O / 5wt% butanol

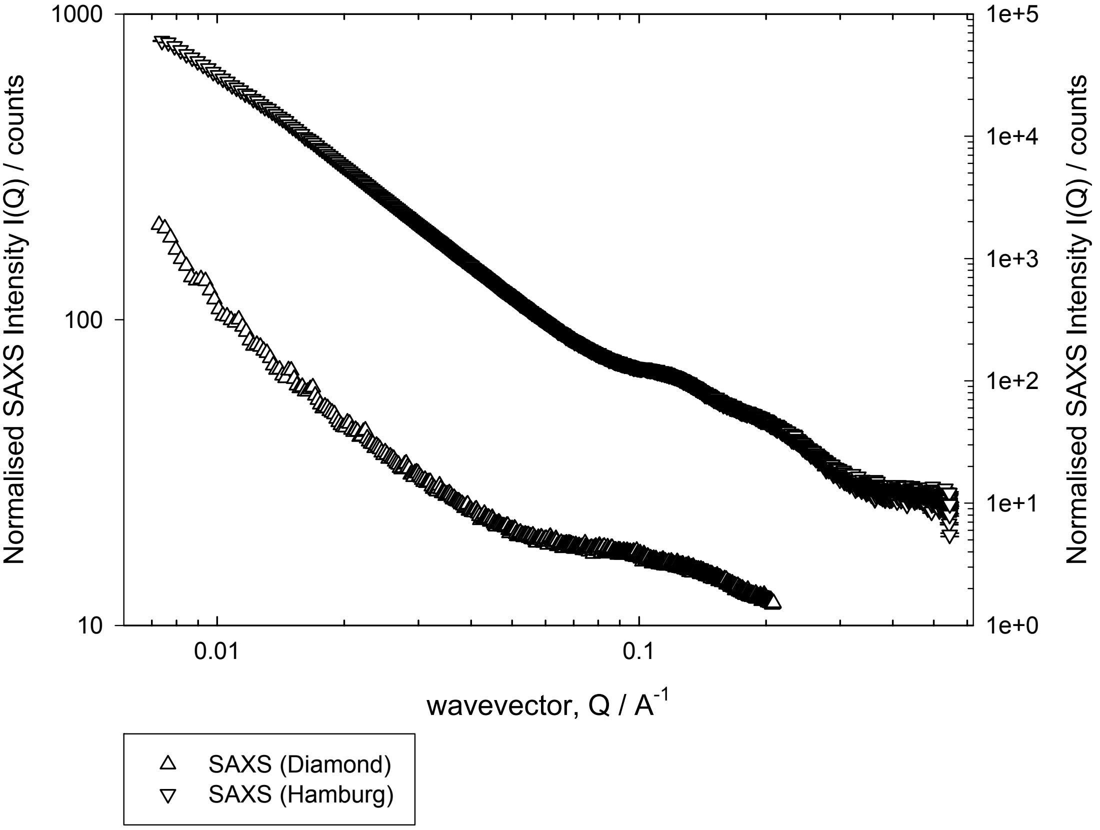

Figure 8S; Small-angle X-ray scattering from 25mM $Cu(NO_3)_2$-C_{10} / 5wt% butanol / 0.5wt% toluene / D_2O.