Experimental report

07/09/2022

Proposal: EASY-398 **Council:** 4/2019

Title: Dynamics in detergentless microemulsions

Research area: Soft condensed matter

This proposal is a new proposal

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Experimental team:

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Samples: octanol

Instrument	Requested days	Allocated days	From	To
IN11	48	48	24/06/2019	26/06/2019

Abstract:

In a previous experiment on IN11C (9-10-1452) we measured the dynamics of some ternary mixtures of water/ethanol/octanol in different. As some structuring can be seen in SANS, we expected to observe a discontinuity in the diffusion coefficient of the components which are involved in the formation of the (comparably) large structures and we intended to treat the binary mixtures as the solvent.
However, no discontinuity in D is observed but rather a continuous transition, which indicates that the structures observed in SANS are only very transient fluctuations. This is an unexpected, yet quite interesting result, but to be able to publish it, we need to measure the unimolecular components as reference, which we initially thought would not be worthwhile.
This should be easily possible in 24h.

NSE Measurements on Ternary MIxixtures

September 7, 2022

1 Abstract

We investigated the coherent and incoherent dynamics of ternary mixtures containing the mostly immiscible compounds water and octanol which are made miscible through the hydrotrope ethanol. Structural investigations had shown that the phase diagram of these mixtures has a zone near the critical point in the single phase region where nanometre sized, so called pre-Ouzo aggregates are formed, while on the octanol rich side of the phase diagram a water network is formed. This report summarises measurements from different experiments on IN11C (9-10-1452, EASY-398), IN15(TEST-2553, TEST-3075, 6-02-612) and WASP (6-02-612). We find that where pre-Ouzo aggregates were observed, the coherent diffusion coefficient decreases at low q regardless of the hydrogenated component while the incoherent diffusion coefficient of ethanol only slightly changes across the phase diagram. The incoherent diffusion coefficient of octanol is strongly decreased in the water rich region of the phase diagram and shows a sudden jump when increasing the octanol content. We interpret these observations as follows: The low coherent diffusion coefficient in the pre-Ouzo region at low q is the dynamic signature of the pre-Ouzo aggregates. The equally low incoherent diffusion coefficient of octanol shows that octanol is frozen in these aggregates, while the only slightly affected incoherent diffusion coefficient of ethanol indicates that ethanol is distributed between the phases and the molecules can change between them relatively easily.

2 Samples

We measured ternaries of water, ethanol, octanol in different contrasts

- P1, octanol contrast: only octanol hydrogenated
- P2: ethanol contrast: only ehtanol hydrogenated
- P3: water contrast: only water hydrogenated, did not do many neutron measurements, as H exchanges anyway

SANS of the data has been measured previously and all samples are more or less on a dilution line shown in fig. 1

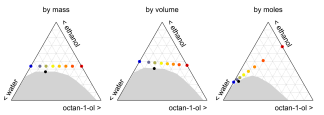

Figure S1: Phase diagram of n-octanol/ethanol/water in mass, volume and mole fractions respectively, indicating the biphasic region by the grey area; the black circle corresponds to the critical point. Mass fractions are calculated with the equivalent masses of the hydrogenated species. The dilution line along which experimental SANS and SAXS spectra have been measured, at constant mass fraction of ethanol, is traced with a color-gradient from blue (water/ethanol, α=0) to red (n-octanol/ethanol, α=1).

Figure 1: From left to right samples DL1-1 (water/ethanol binary) to DL1-8 (ethanol/octanol binary) samples increase in octanol content at constant ethanol mass fraction

3 Fit Function

To fit the data we needed to properly take into account the coherent and incoherent dynamics. Data was denormalised and the q dependent coherent and incoherent intensity was calculated from polarisation according to

$$I_{coh} = I_{up} - I_{down} \tag{1}$$
$$I_{inc} = 1.5 I_{down} \tag{2}$$

where I_{coh} and I_{inc} are the coherent and incoherent intensity and I_{up} and I_{down} are the up and down intensities.

To completely fit the data, it was necessary to take into account a q dependent coherent diffusion coefficient D_{coh} and a q independent incoherent diffusion coefficient D_{inc}. In samples with very weak intensity, fast coherent dynamics become visible, which are described as a q independent relaxation rate Γ_{fast}. The value of Γ_{fast} was fixed at 300 1/ns as determined from an all deuterated sample. On IN11C it was also necessary to allow for a coherent elastic background x_{bkg}, so that the coherent dynamics are given by

$$S_{coh}(q,t) = x_{fast}\exp(-\Gamma_{ast}t) + ((1-x_{fast})(1-x_{bkg})\exp(-D_{coh}q^2 t) + x_{bkg}), \tag{3}$$

the incoherent dynamics are given by

$$S_{dyn}(q,t) = \exp(-D_{inc}q^2 t) \tag{4}$$

and finally the difference between coherent and incoherent intermediate scattering function yields the NSE signal:

$$S(q,t) = I_{coh}(q)S_{coh}(q,t) - 1/3 I_{inc}(q)S_{q,t}(q,t). \tag{5}$$

By using these equations we make two important assumptions: The efficiency of the $\pi/2$ flippers is assumed to be 1 and we assume that there is no such thing as a q

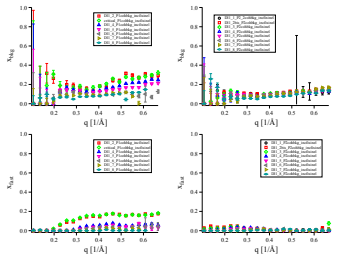

Figure 2: Top: Contribution from coherent elastic background. Bottom: Contribution from fast coherent dynamics in octanol contrast (left) and ethanol contrast (right), both the background contribution and the fast dynamics become significant only for samples with very little hydrogen content.

dependent EISF in our q range, which is probably well justified for IN11C but might become a somewhat dubious assumption for WASP which goes to significantly higher q. Both the contribution from the elastic background and the fast coherent dynamics are negligible in most samples and become noticeable only for samples with very little hydrogen content.

Data from IN15 are at sufficiently low q to simply fit them with a simple exponential to obtain D_{coh}.

4 IN11C

On IN11C we have a complete set of data in octanol contrast P1 and ethanol contrast P2. Coherent and incoherent dynamics are rather similar and we see a jump between sample 3 and 4 in octanol contrast P1, which is probably the signature of a structural change from octanol dispersed in aqueous phase to water dispersed in an octanol phase. While diffusion coefficients in octanol contrast P1 increase when going to a continuous octanol phase, the opposite is true for ethanol contrast P2 where diffusion coefficients decrease with increasing octanol content. There seems to be a minimum for sample DL1-4, which is rather obvious for D_{coh} but not as clear for D_{inc}. The origin of this minimum is not immediately obvious to me. If the transition from a discrete to a percolated octanol phase is between DL1-3 and DL1-4, indeed, it might be a sign that ethanol does take some time to change from one phase to the other. Another interesting

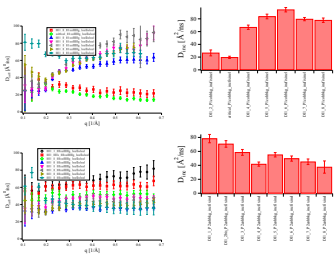

Figure 3: Measurements from IN11C, coherent diffusion coefficients D_{coh} (left) and incoherent diffusion coefficient D_{inc} (right) in octanol contrast P1 (top) and ethanol contrast (bottom); in octanol contrast there is a jump to higher values between sample 3 and 4 in both D_{coh} and D_{inc}; in ethanol contrast there is a more gradual decrease of both diffusion coefficients going from low to high octanol fraction with a minimum at sample DL1-4.

observation is the fact that the diffusion coefficient in the ethanol/octanol binary (DL1-8) is slower in ethanol contrast P2 than in octanol contrast P1. The same holds true for the other samples with high octanol content, where this might be explained by ethanol being trapped in the discrete aqueous phase. This argument does not hold for the binary and it might imply that ethanol is in some way structured in the continuous octanol phase. The results are shown in fig. 3. Interestingly, the selfdiffusion coefficients obtained from Dominik's simulations change continuously and do not reproduce the discontinuities we observe experimentally. The fact that we also see similar effects in discontinuities in NMR gives me faith, that this is an actual result and not just an artefact from fitting.

5 WASP

On WASP we have measured a water rich sample (10 % octanol) which more or less corresponds to DL1-2 and an octanol rich sample (10 % water) corresponding more or less to DL1-7. Both samples were measured in all 3 contrasts, as opposed to IN11C, where water contrast was omitted. We also measured binaries, which behave a little odd. Results are shown in fig. 4. The results from IN11C are essentially reproduced, with the difference that WASP not only extends to much higher q (which will give us

more problems with internal motions which we are not bothered with at 0.6 1/Å) but also yields much better data at low q which was a little fuzzy on IN11C, as we only go up to 1 ns and a lot of the data do not show much of a decay. On WASP, we can nicely see a reduced D_{coh} at low q, which stems from the dynamics of the larger structures that form. The values are in reasonable agreement with values obtained from IN15.

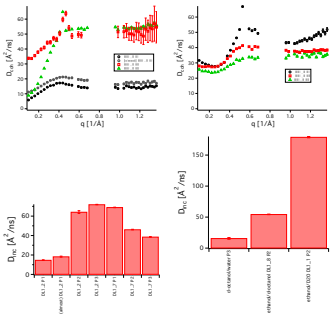

Figure 4: Measurements from WASP, top left: D_{coh} of the water rich sample corresponding to DL1-2 in contrasts indicated in the graph; top righ: D_{coh} of the octanol rich sample corresponding to DL1-7 in contrasts indicated in the graph; bottom left: D_{inc} of ternaries as measured by WASP; bottom right: D_{inc} of binaries as measured by WASP; The coherent diffusion coefficients are in reasonably good agreement with IN11C, except that a decrease at low q in more visibly structured contrasts is more visible with WASP due to its better time range, the D_{inc} are in reasonably good agreement with IN11C, measurements. Only the ethanol/water binary is much faster than what is observed by IN11C, the fits do not look very convincing but it is still strange. [Edit on the question of the water/ethanol binary: The composition between the 2 is not the same, Marie's numbers on that are by mass, this has a higher water ratio and a faster diffusion coefficient is in line with Firoz' NMR measurements] Measurements in water contrast show a high D_{coh} at high q, in the water rich side and a relatively low D_{coh} on the octanol rich side as you would expect for water. The measurements also confirm that D is smaller for ethanol than for octanol on the octanol rich side.

6 IN15

In all fits, D_{inc} was fixed to the value obtained from IN11C or WASP fits. It is not visible enough in the data to make a real difference, so the fits would not converge if you leave it as a free parameter.

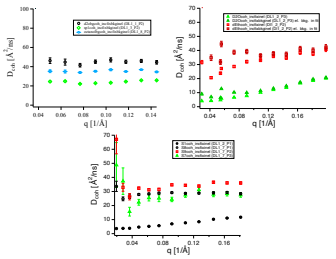

Figure 5: Top Left: D_{coh} of binaries and pre-Ouzo sample in ethanol contrast, no background is subtracted. Values are somewhat lower than what you could expect from IN11C (see fig. 3). Top Right: D_{coh} from water rich sample near the pre-Ouozo zone in etahnol (P2) and water (P3) contrast. All coherent sample is subtracted as background, tried to include or not to include an elastic background in the fit, does not make much of a difference, values are relatively compatible with WASP (see fig. 4, left). Bottom:D_{coh} from IN15; data merge reasonably well with low q part from WASP (compare fig. 4 left for S1 (full black circles) and fig. 4 right for high octanol samples S7, 8, 9) the sequence between P1 and P2 is inverted but the little low q upturn in the WASP data might also be an artefact.