Experimental Report

17/02/2015

Proposal: **9-10-1387** **Council:** 4/2014

Title: Primary Formation Kinetics of Water-rich Non-ionic Microemulsions

This proposal is continuation of: 9-10-1272

Researh Area: Soft condensed matter

Main proposer: **HARBAUER Carola**

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Samples: H2O, D2O, NaCl C6H12, C6D12, non-ionic surfactants

Instrument	Req. Days	All. Days	From	To
D33	3	2	29/11/2014	01/12/2014

Abstract:

Non-equilibrium properties of microemulsions, like the primary microstructure formation mechanism has hardly been investigated. In our previous experiments (9-10-1272), an oil-rich non-ionic microemulsion system of the type D2O - cyclohexane - C10E5 has been studied using the ultra-fast stopped-flow device BioLogic SFM300 at the D33 with a custom made highly temperature stable head piece designed and supplied by us. Here, an unstructured binary solution of cyclohexane/C10E5 and D2O were mixed at different contrasts leading to an oil-rich w/o-microemulsion. The primary formation process of the internal interface was found to be faster than 20 ms and the interfacial composition remains constant over the experimental time course. Throughout the following 180 s the final water-uptake can be resolved and is accompanied by a structural reorganisation. Introducing amphiphilic polymers to the system the reorganisation kinetics are significantly slowed down while speeding up the water-uptake. Nevertheless, no complementary study has been done on the water-rich side. Here a different mixing approach will be chosen in order to achieve a better resolution of the process.

Formation kinetics of ternary microemulsions with various additives along different mixing pathways studied by time-resolved SANS combined with an ultra-fast stopped-flow device

− Report on Experiment No: 9-10-1387 –

Abstract: Nowadays, the equilibrium properties of microemulsions, *e.g.* the phase behaviour [1] and nanostructure [2] are exceedingly well investigated, whereas the non-equilibrium properties remain mostly unexplored. Especially, the mechanism of the primary formation of the microstructure, such as spherical droplets or networks, is not yet fully understood [3]. In our previous experiments (9-10-1272), an oil-rich non-ionic microemulsion system of the type D_2O/NaCl – cyclohexane – $C_{10}E_5$ has been studied using the ultra-fast stopped-flow device BioLogic SFM300 at the D33 with a custom made highly temperature stable head piece designed and supplied by us [4]. Here, an unstructured binary solution of cyclohexane/pentaethyleneglycoldecylether ($C_{10}E_5$) and D_2O were mixed along pathway I at different contrasts (see *Gibbs* phase triangle, figure 1, green line) leading to an oil-rich w/o-microemulsion with water-swollen (inverse) micelles. The primary formation process of the internal interface is faster than 20 ms and the interfacial composition remains constant over the experimental time course. Throughout the following 180 s the final water-uptake can be resolved and is accompanied by a structural reorganisation leading to a more monodisperse unimodal size distribution. These processes are closely related to the interfacial tension and interfacial energy within the system. Furthermore, it was shown before that introducing additives to the system such as symmetric, amphiphilic diblock-copolymers, the reorganisation kinetics are significantly slowed down while speeding up the water-uptake [4]. While now some light has been shed on the formation of oil-rich microemulsions from unstructured precursor solutions, no complementary study has been done on the water-rich side. To complete the picture such measurements were intended by varying the possible mixing pathways. Additionally the influence of the surfactant chain length on the formation kinetics should be investigated by increasing the lengths from $C_{10}E_5 - C_{12}E_6 - C_{14}E_7$. Thereby the bending rigidity should be increased leading to a slower self-organization process. Including anionic surfactants such as sodium dodecyl sulfate (SDS) into the microemulsion, the kinetics should increase due to electrostatic interactions. A systematic study of those parameters and first results will be presented and discussed in detail below.

Time-resolved SANS Experiments: In our previous studies (9-10-1178 and 9-10-1272), we focused on ternary microemulsions with and without symmetric diblock-copolymer additives. In this series of experiments we investigated the droplet size, micelle number density, C_iE_j chain length, asymmetric diblock-copolymer additive, anionic surfactant and waterrich microemulsions. Regarding the system D_2O/NaCl – cyclohexane – $C_{10}E_5$ with a surfactant content $\gamma_b = 0.05$ in the binary unstructured mixture of cyclohexane/$C_{10}E_5$. It will be mixed with D_2O/NaCl in the ratio of 103:10 resulting in an overall water mass fraction of $w_A = 0.11$ ($w_A = m_{D2O}/m_{total}$) (see figure 2). To reach equilibrium ending with water-in-oil micelles, it takes about 15.86 s ± 1.6 s, whereas forming smaller droplets by mixing 143:10 resulting in $w_A = 0.09$ only takes 3.66 s ± 0.3 s. Increasing the micelle number density by increasing γ_b to 0.10 the formation kinetics equilibrates at about 5.44 s ± 0.6 s. It is already known from previous works that the formation process itself includes the uptake of excess water and a reorganization process, simultaneously. To distinguish those, further more detailed analysis is necessary, which is currently ongoing.

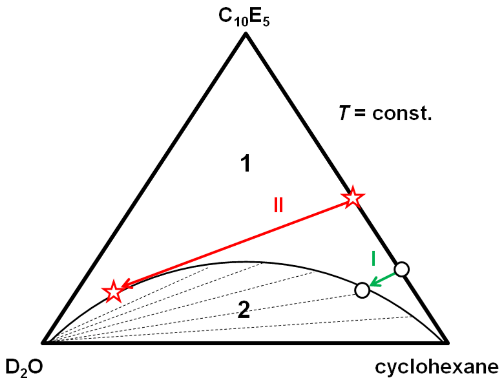

Figure 1: Schematic *Gibbs* triangle with different mixing pathways leading to an oil-rich (I) or water-rich microemulsion (II) starting from a binary unstructured oil/surfactant mixture by adding different amounts of D_2O.

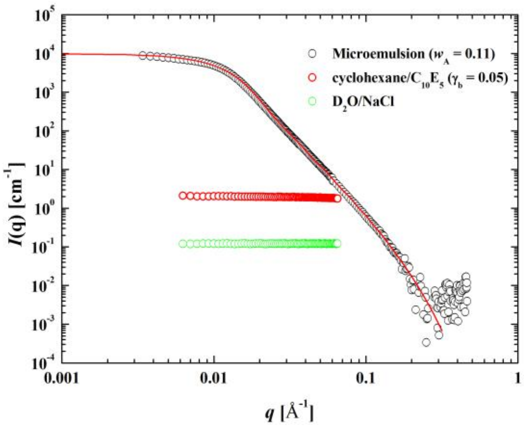

Figure 2: Static SANS curves of the binary stock solution cyclohexane/$C_{10}E_5$ (red circles) and unstructured D_2O/NaCl (green circles). After mixing both solutions in a ratio of 103:10 the micellar microstructure becomes visible (black circles).

In the next step we substituted $C_{10}E_5$ with ionic surfactant SDS as a δ-variation ($\delta = m_{SDS}/(m_{SDS} + m_{C10E5})$). Thereby membrane properties are changed from uncharged to a charged mixed film, leading to higher fluctuations. The binary solution of cyclohexane/$C_{10}E_5$ is mixed with a prestructured stock solution of D_2O/SDS in a respective ratio (see table 1 for details). The compositions, experimental parameters and results are summarized in table 1. It could be observed that adding 5 *wt*-% to the amphiphilic mixture already accelerates the formation kinetics significantly to 0.513 s ± 0.06 s. The double amount of SDS increases it further down to 0.174 s ± 0.03 s.

Table 1: Microemulsion compositions of the type D_2O/NaCl – cyclohexane – $C_{10}E_5$/SDS and their time to equilibrium.

δ	Stock solution D_2O/SDS [*wt*-%]	Mixing ratio	w_A in equilibrium	t_{EQ} [s]
0.00	0.00	103:10	0.11	15.86 s ± 1.60 s
0.05	1.76	101:10	0.11	0.513 s ± 0.06 s
0.10	3.45	100:10	0.11	0.174 s ± 0.03 s

Switching the microemulsion composition from oilrich (water-in-oil) to waterrich (oil-in-water) compositions the analogue experiments were performed as mentioned in the first part. Keeping the dispersed phase at a constant value, two different mixing pathways were used. It could be observed that solving the surfactant within the dispersed phase (cyclohexane) leads to nearly no observable kinetics (see figure 3, left). Whereas solving surfactant within the continuous medium (D_2O) and mixing the microemulsion along the pathway II (see figure 1, red line) does result in resolvable kinetics (see figure 3, right).

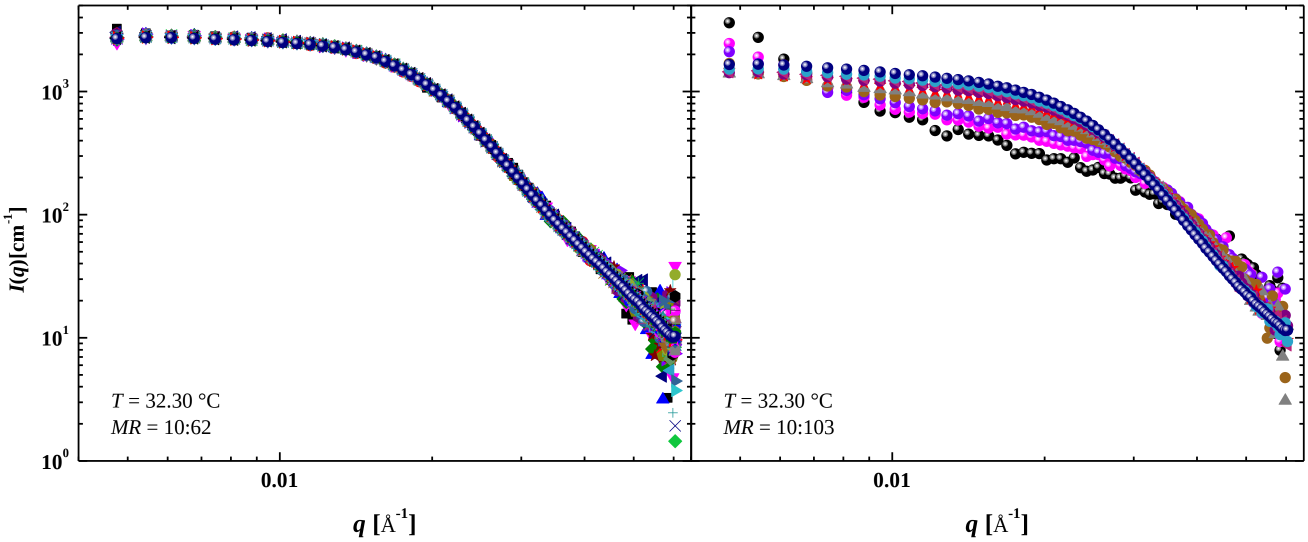

Figure 3: Mixing the same waterrich microemulsion ($\gamma_a = 0.05$, $w_B = 0.065$) along two different pathways. With the surfactant being dissolved in the dispersed oil phase almost no kinetics can be observed (left), being dissolved in the continuous phase does, however (right).

In conclusion, with the cyclohexane already containing $C_{10}E_5$ before the mixing process accelerates it significantly. Increasing the polymer content and the surfactant chain length deccelerates the formation kinetics (data not discussed here). With this knowledge we hope to be able to explain the fundamental question for the primary formation process of microemulsions in more detail to complete the picture (further analysis is currently on going).

Literature: [1] M. Kahlweit, R. Strey, et al., *J Colloid Interf Sci*, 1987, 118, 436-453.
[2] O. Glatter, R. Strey, et. al., *Ber Bunsen Phys Chem*, 1996, 100, 323-335.
[3] M. Gradzielski, *Curr Opin Colloid In*, 2003, 8, 337-345.
[4] H. Klemmer, PhD thesis, *Cuvillier Verlag Göttingen*, ISBN 3954045583, 2013.