Experimental report

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Proposal: 6-02-641 **Council:** 4/2023

Title: How molecular dynamics is coupled to nanostructuration in ultra flexible microemulsions ?

Research area: Soft condensed matter

This proposal is a resubmission of 6-02-630

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Samples: Water
Ethanol
Sodium salicylate
ethyl-hexanol
ethyl acetate

Instrument	Requested days	Allocated days	From	To
IN15	2	2	15/05/2023	17/05/2023

Abstract:

UltraFlexible MicroEmulsions are typically ternary mixtures of common solvents forming "surfactant-free microemulsion". From a structural point of view, such mixtures present nanostructuration that varies between the regions of the phase diagram, forming bicontinuous, water continuous or nanodroplets. This ability for mesostructuration may take its origin in the structure of alcohols, but the influence of molecular diffusivities in the formation and life time of the (dynamical) aggregates, yet, has not been clarified. This is the aim of our current project. Initiated on water/ethanol/octanol solutions, we need to complete our picture with the characterization of two other systems: water/ethanol/ethyl-hexanol to probe the effect of molecular branching and water/sodium salicylate/ethyl acetate where pre-nucleation is observed. We will be able to compare the dynamics in three different situation of aggregates formation: pre-Ouzo region, vicinity of the critical point and pre-nucleation. After our proposal was accepted for WASP (6-02-630) during the last round we re-apply for 2 days on IN15.

Experimental report for experiment 6-02-641

How molecular dynamics is coupled to nanostructuration in ultra flexible microemulsions ?

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The beamtime on WASP was dedicated to the characterization of two different ternary systems: (1) water / ethanol / ethyl-hexanol and (2) water / sodium salicilate / ethyl acetate. This study aims at complementing an earlier work on the model system water / ethanol/ octanol. This system is indeed well known for its organization in metastable droplets in the biphasic region, also known as Ouzo effect, and its pre-Ouzo aggregation area, thermodynamically stable and located in the monophasic region. We have been able to identify the signature of the pre-Ouzo structuration in the octanol dynamics of this system [1]. Here, we complement this study to understand better the origin of the dynamics changes in comparing with a system (1) based on a branched alcohol ethyl-hexanol (EH), and (2) that does not present a pre-Ouzo effet but only critical fluctuation. The Q-range accessible on IN15, as well as the long relaxation times, were necessary to confirm the previous results from WASP.

1. water, ethanol and ethyl-hexanol (EH)

NSE was used to characterize the dynamics of each molecular species, using different contrasts (deuteration of two of the three components) over the nanoscopic scale where pre-Ouzo aggregation takes place. NSE enables to measure separately the coherent and incoherent diffusion coefficients. We found in the octanol system that the coherent one reflects the nanostructuration of the system : in the octanol rich sample, the solution is structured over very small scale and only presents a De-Gennes narrowing effect ; in the water rich side instead, oil aggregates of a few nanometers in size are formed, and this structural organization is reflected in the dynamics : the effective diffusion coefficient presents a q-dependence due to the presence of the aggregates [1].

The EH system presents subtle differences with respect to octanol, due to the different organization of the molecules forming rather rings for EH than chains for 1-octanol. The pre-Ouzo aggregates are more compatible with the ring geometry than with the chains, the dynamics at the supra-molecular scale is therefore less affected. However, a similar slowing down to the octanol system of the dynamics is also observed in the water rich region (samples S4, while S7 presents a flat behaviour). This is illustrated by the figure 1.

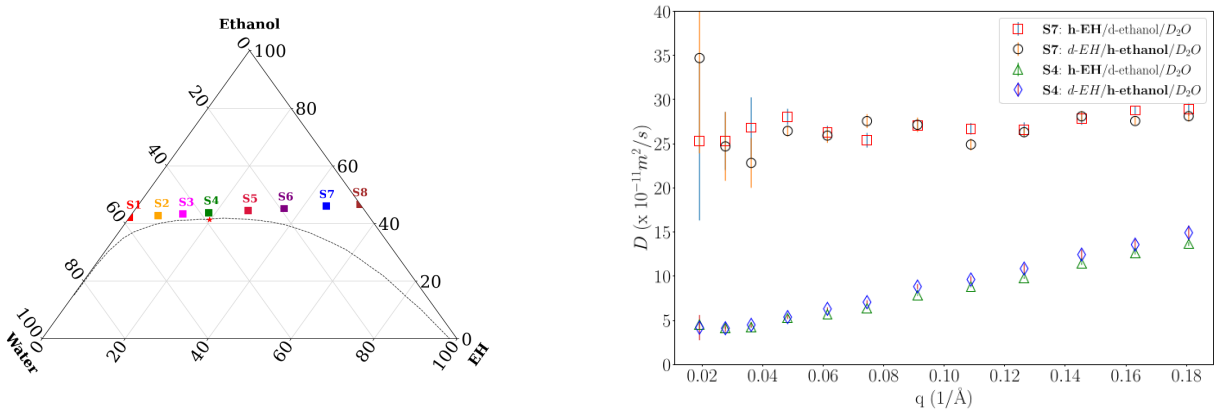

Figure 1. Left : ternary phase diagram of the ternary system water, ethanol and ethyl hexanol. The samples investigated are indicated by the colored squares S1-S8. Right : diffusion coefficient over the measured Q-range, showing a scale dependence in the pre-Ouzo region (sample 2-6) and a flat dependence outside.

2. **water / sodium salicilate / ethyl acetate**

The structure of this mixture containing sodium salicylate acting as an (anionic) hydrotrope has also been very well characterized [2]. It does not present any pre-Ouzo structuration close to the critical point, only Ornstein-Zernike fluctuations are observed like close to any critical point. Moreover, pre-nucleation dynamical aggregates appear close to the solid-liquid binodal similarly to the organization of ionic surfactants.
In this system that does not present any pre-Ouzo organization, no dependence of the diffusion coefficient on the lengthscale is observed, in both constrasts investigated. The figure 2 shows the comparison for the three systems, where the similarity between octanol and ethyl-hexanol is observed in the water rich region, while the ethylacetate mixture close to the critical point exhibits the same trend as the octanol/ethanol/water ternary out of the pre-Ouzo region.
We therefore conclude that the signature in the dynamics arises from the pre-Ouzo agregation and not the critical fluctuations that are also present in the octnol (or ethyl-hexanol) system.

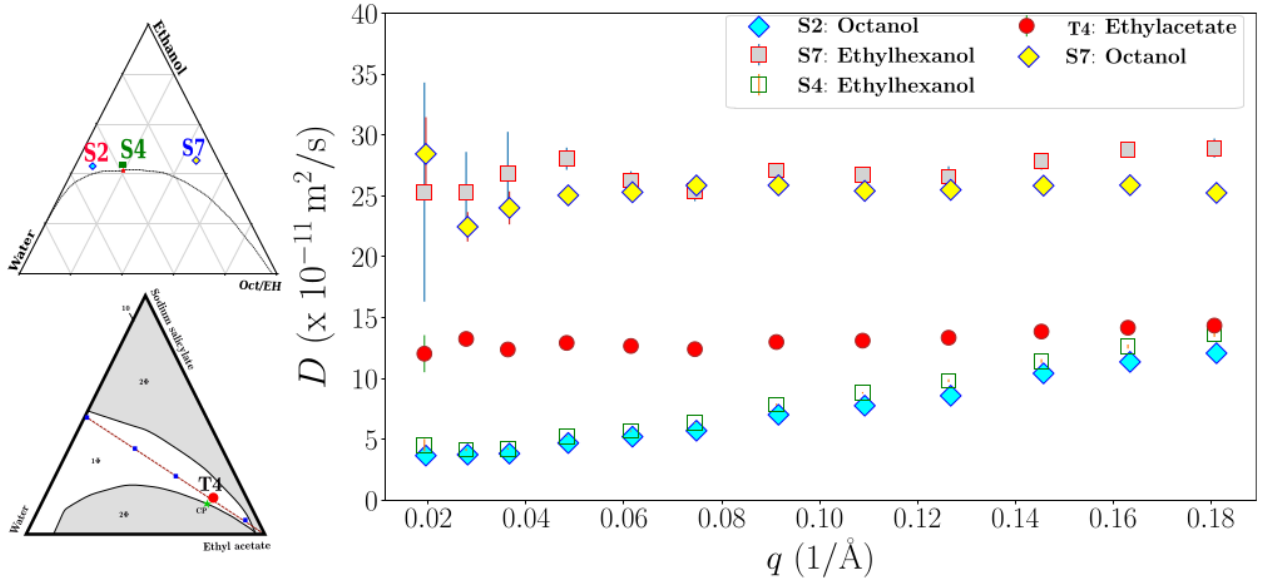

Figure 2 : left : phase diagrams of the water/ethanol/oil system (top) and water/sodium salicilate/ethyl acetate system (top) ; right : diffusion coefficient of the different samples measured on WASP.

References
[1] F. Malayil Kalathil et al., J. Mol. Liquids 432 (2025) 127684.
[2] A. El Maangar et. al., J. Mol. Liquids 310 (2020) 113240.