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Structure and dynamics in Surfactant-free microemulsions

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Ternary mixtures of oil, water and an hydrotrope can lead to complex and usable organization in terms of reactivity or solubility. This is the case of aqueous solutions of ethanol and oil, typically found in all kind of liquors, cosmetics or solvents for liquid-liquid extraction.
The archetypical case of this family is the ternary mixture of water, ethanol and octanol. A rapid dilution of the monoalcohols binary mixture with water takes the system into the biphasic region, where a metastable emulsion of oil droplets forms, known as the « Ouzo » effect. Before reaching this phase, a thermodynamically stable region was also identified close to the critical point and described as pre-Ouzo region [1].
Our work aims at providing a quantitative description of the whole phase diagram of this system from a microscopic point of view. For this purpose, we mainly combined X-ray small angle scattering, quasi-elastic neutron scattering and PFG-NMR. Our investigations enabled us to characterize the organization and the diffusion of each molecular species in the various regions. The main structural parameters describing the different phases could be identified and related with the regimes observed in self and collective diffusion.
The fine tuning of such phases was eventually addressed in exploring temperature effects or subtle chemical substitution on the monoalcohol.

Fig. 1 : phase diagramm (wt.%) of the ternary mixture octanol/ethanol/water. The binary region is colored in grey ; the Widom line starts from the critical point (red dot) and corsses the monophasic region toward the ethanol-water binary line ; the Lifshitz line delimitates the onset of structural organisation ; the minimum hydrotrope concentration (MHC) indicates the minimum quantity of ethanol required to form a monophasic solution as soon as octanol is added to water ; the dynamics was investigated along the blue dotted line.

References

[1] T. Zemb et al., PNAS (2016) 113, 4260–4265
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