Monitoring both, Fat Crystallization and Self-assembly of Sodium Caseinate in Model Emulsions using Synchrotron X-ray Diffraction

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Introduction

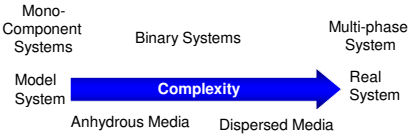
This study deals with oil in water emulsions, which are thermodynamically unstable systems per se. Stabilization of real emulsions is obtained by addition of hydrocolloids, proteins and surfactants in order to increase continuous phase viscosity and stabilize interfaces.

Due to the multiplicity of components, investigations of real emulsions is very difficult. Crystallization of the oil phase even further increases complexity of the study of such emulsions, especially when triglycerides (TAG's) which exhibit a complex polymorphism are involved.

Small and Wide Angle X-ray Diffraction as well as DSC are needed to investigate the thermal properties of emulsified lipids. Indeed several DSC-peaks are observed whilst heating and cooling of the samples. The identification of those thermal events is rather complicated and often quite impossible without the help of techniques that yield information about structures (e.g. X-ray or neutron diffraction, infrared spectroscopy, etc.).

Approach

Both, model and real systems were studied and compared.



Objective

The aim of our work is to investigate and understand TAG crystallization and polymorphism in emulsion. As the physico-chemical properties of TAG's are influenced by both emulsifying proteins and lipid surfactants, it is necessary to control their concentrations in both the continuous and the dispersed phases. Knowing that both concentrations are not easily accessible from non destructive methods we propose here two techniques to monitor them by the means of X-ray scattering at small angles

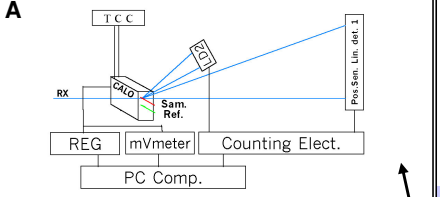


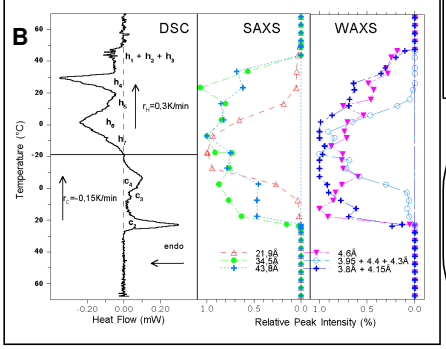
Figure 4 A:

Coupling of SAXS/WAXS and DSC (scheme)

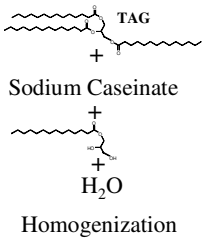
Figure 4 B:

DSC-curves of a TAG-blend are drawn for comparison and clarity next to SAXS and WAXS relative peak intensity plots vs. same T.

The coupling technique allows the attribution of all thermal events to structural changes between three different crystalline species (cf. [1,2]).



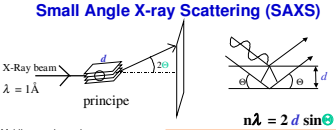
Materials



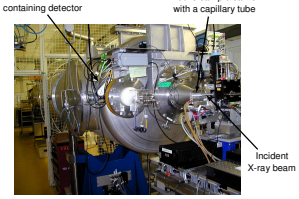
Homogenization

Methods

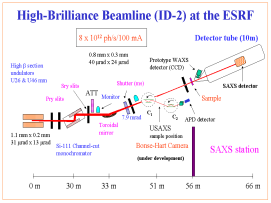
Small Angle X-ray Scattering (SAXS)



ESRF Synchrotron



ID 2 beamline, E.S.R.F., Grenoble, France



Technical description

USAXS measurements at ID02a monitor the self-assembly of sodium caseinate in aqueous solutions as a function of concentration

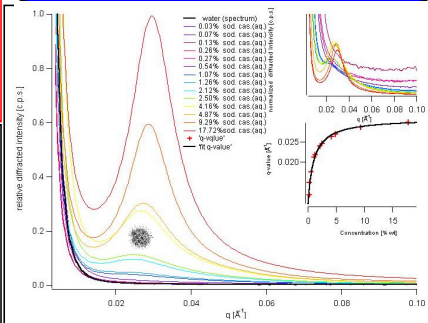


Figure 1: USAXS of aqueous sodium caseinate solutions show micelle formation. ***Insert I:*** USAXS normalized Intensity vs. concentration. ***Insert II***: Peak positions as a function of sodium caseinate concentration (cf. [5,6]).

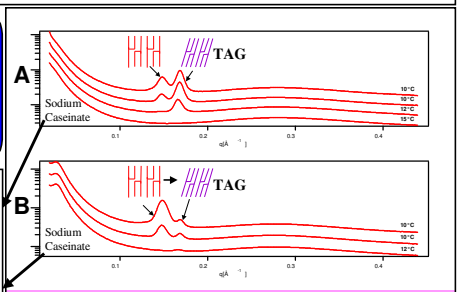
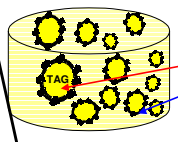


Figure 2: SAXS monitoring of TAG crystallization within droplets of model emulsion containing lipid surfactants (cf. [1]). (A): Emulsion E1 (lower concentration of sodium caseinate) (B): Emulsion E2 (higher concentration of sodium caseinate)

Crystallization in emulsion starts by the formation of a α (rotator) chain packing of TAG. Then a transformation from α to β' is observed. This lateral packing transition is accompanied by longitudinal packing change from untilted to tilted chain position. Data shows that interface composition influences TAG transition and crystallization (cf.[3]).



Conclusion

Coupling of DSC/SAXS/WAXS

USAXS measurements

Synchrotron X-ray diffraction at small and ultra small angle allows precise characterization of crystallization in emulsion as well as the influence of interface composition upon it.

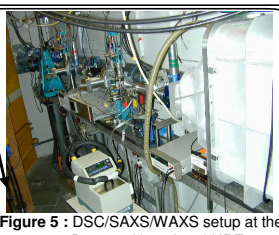


Figure 5 : DSC/SAXS/WAXS setup at the D 22 workbench at LURE

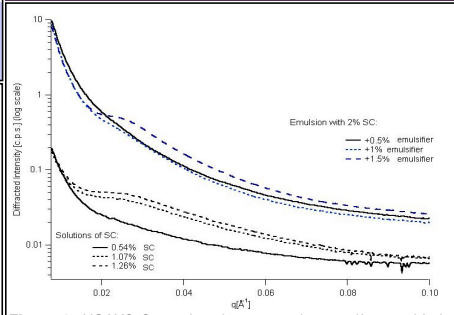


Figure 3: USAXS Scattering due to caseinate self-assembly in model emulsion of different lipid emulsifier concentrations

Bibliography

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[4] M. Cornec, P. J Wilde, and P. A. Gunning , J. Food Sci. 63 (1998) 39;

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