Experimental report

13/02/2019

Proposal: **INTER-372** **Council:** 4/2017

Title: The structure of limoncello

Research area:

This proposal is a new proposal

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Experimental team:

Local contacts: Leonardo CHIAPPISI

Samples: D2O
sugar (saccharose)
ethanol (max 70% in water)
lemon essential oil (<0.3 %)

Instrument	Requested days	Allocated days	From	To
D11	1	1	18/06/2016	19/06/2016

Abstract:

Experimental report for Inter-372:

The structure of limoncello

In the experiment, the structure of samples made of essential oil extracted from citrus zest, deuterated ethanol, sucrose, and heavy water were investigated. The samples were prepared following the traditional recipe for the preparation of the famous Italian liquor, and the composition of the probed samples is shown in Fig. 1.

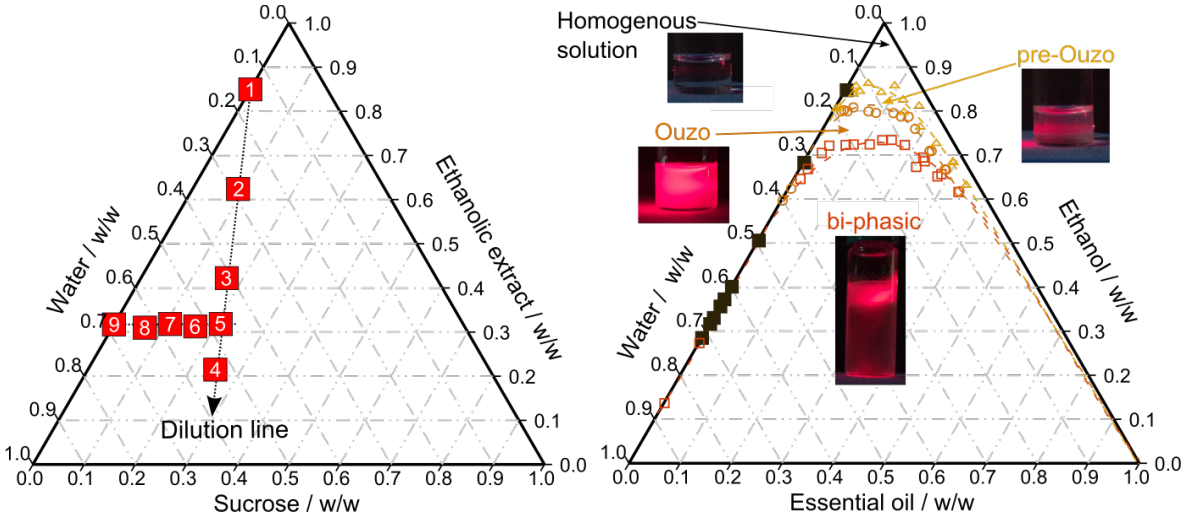

Fig 1: On the right, the ternary diagram reporting the composition of the samples used for the SANS analysis is given. The axes report the relative concentration of water, sucrose, and ethanol/essential oil mixture (~ 0.3 %wt essential oil in d 6 -ethanol). The number within the red square indicates the sample name and the position of the square its composition. Samples 1 to 5 were prepared by dilution of the ethanolic extract with the sucrose syrup; for samples 5 to 9 the amount of sucrose is systematically varied. See experimental section for further details. On the bottom, the phase diagram recorded for mixtures of water, ethanol, and a commercial citrus lemon essential oilextract is given; triangles represent the transition from the homogeneous to the pre-Ouzo region, circles represent the transition to the Ouzo-region, and squares delimit the region where rapid phase separation occurs. Concentrations are given in weight fraction. Lines are only a guide to the eyes. For the sake of comparison, the samplesused for the SANS analysis, are also illustrated as dark squares. These points are compressed onto the left border due to the overall very low content of essential oil in the extract. Pictures of samples prepared inthe four regions of the phase diagrams were taken under laser irradiation (633 nm, <1 mW) to highlight the turbidity of the sample.

The samples were investigated on D11, and an exemplary set of scattering patterns are reported in Fig. 2. The data were analysed with the Porod model and with a model of polydisperse spheres. The obtained radii differ strongly at low water content, while they coincide for high water content. In fact, the difference could be ascribed to the fraction of lemon essential oil which is not participating into the droplet formation, and which leads to an overestimated of the Porod radius. The trend of the radii is shown as a function of the water content of the system in Fig. 3. The study was published in ACS Omega (ACS Omega. 3 (2018) 15407–15415. doi:10.1021/acsomega.8b01858.)

In summary, a structural analysis of real Limoncello samples was performed using SANS, shedding light for the first time on the mesoscopic structure of this very famous Italian liquor. The results

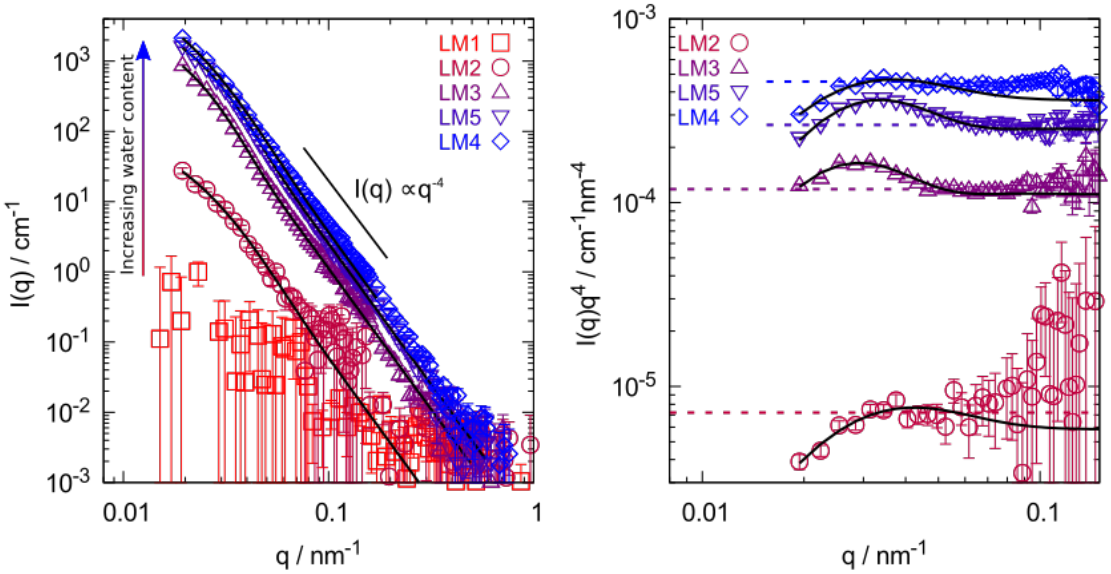

Fig 2: SANS patterns arising from ternary systems prepared by the dilution of the ethanolic extract with a water/sucrose syrup recorded at 298 K. On the top, the coherent scattering intensity is given as a function of the scattering vector. On the bottom, the scattering intensity multiplied with the fourth power of the scattering vector is given. The constant trend represents the Porod region, and the dotted lines indicate the Porod constant.

show that the system is composed of polydisperse oil droplets dispersed in a continuous water/ethanol/sucrose medium. These droplets, whose size of ca. 100 nm shows little variation with temperature and overall composition, are in equilibrium with molecularly dissolved essential oil. To conclude, the work reports the spontaneous formation of 100 nm-sized essential oil droplets in a

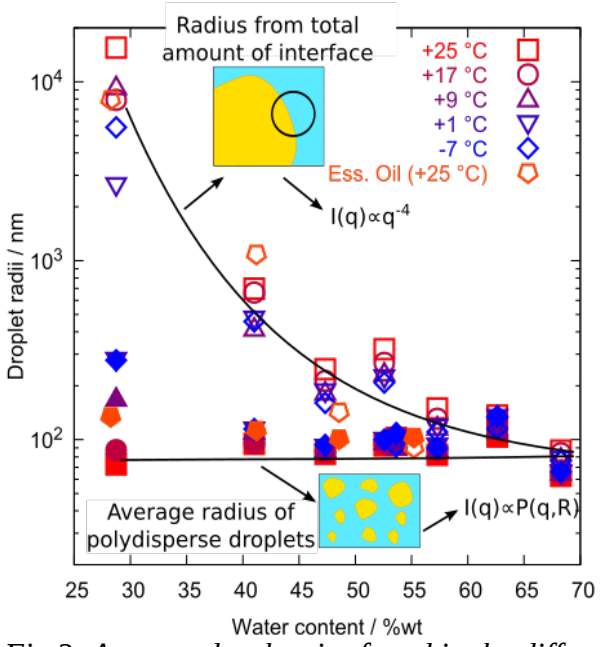

Fig 3: Average droplet size found in the different Limoncello samples by the analysis of the SANS patterns. Empty symbols represent sizes obtained via the Porod analysis under the assumption that the essential oil completely separates into domains dispersed in the water/alcohol/sucrose mixture. Full symbols result from modeling the SANS curves with a polydisperse sphere model, whereby the amount of separated oil was not fixed in the model. Full lines are only a guide for the eye. If a full microphase separation between the oil and the remaining components would take place, the two analyses would lead to the same results.

continuous polar phase, which are stable over a long time range. These findings open two fundamental questions to be addresses in forthcoming studies: what are the physical forces leading to the formation of oil domains with such an exceptional size and what is the mechanism guaranteeing a long term stability to Limoncello systems.