Experimental report

28/07/2022

Proposal:	**9-10-1704**	**Council:**	10/2020
Title:	Testing Different Microemulsion Model Predictions for the Structure Scaling in the Bicontinuous Regime		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: microemulsion

Instrument	Requested days	Allocated days	From	To
D11	1	2	04/06/2021	05/06/2021
			26/08/2021	27/08/2021

Abstract:

The aim of this proposal is testing different theoretical predictions for the structural evolution of bicontinuous microemulsions as a function of the spontaneous curvature of the amphiphilic film. In our experiments we will employ a single-chain (C12E5) and a double-chain (AOT) surfactant for obtaining generally valid results for different types of amphiphilic interfaces. The spontaneous curvature will be varied by changing the temperature and the overall structural constraints by changing the relative oil volume fraction from 25 to 75%. These experiments shall yield a generalized picture of the thermodynamic principles that govern the structure of bicontinuous microemulsions. This will be essential for being able to decide about which structural model is best able to describe this phase region of microemulsions and thereby to develop further our understanding of the principles that govern microemulsion structure and properties.

Experimental Report for Research Proposal 9-10-1704 performed on D11 at ILL

Aim of the proposal

There have been a number of theoretical approaches to describe the structure and properties of microemulsions (thermodynamically stable mixtures of water and oil). However, it is still not really clear, which model describes quantitatively correctly the situation in which one has comparable amounts of oil and water, where bicontinuous or percolated structures are formed. Most scattering experiments in this region have been done for equal amounts of water and oil, where all models yield similar predictions. The standard models such as de Gennes-Taupin[1] or the Cates-Andelmann-Safran-Roux[2] model predict no shift in the peak position when the spontaneous curvature is varied (done by changing the temperature), as area and volume fractions remain constant. In contrast, the DOC model[3] predicts a systematic shift of the peak position. The principle aim of this proposal was to test the predictions of these models experimentally, which has never been done before.

For this purpose, two temperature dependent classical microemulsion systems based on $C_{12}E_5$ and AOT as surfactants were employed. For both systems, the spontaneous curvature was varied by varying the temperature. At the same time, the external structural constraints were varied by varying the oil volume fraction from 25% to 75%.

Experiment

The experimental phase diagrams of the two studied systems $C_{12}E_5$/Octane/D_2O and AOT/Decane/D_2O are shown in Figure 1.

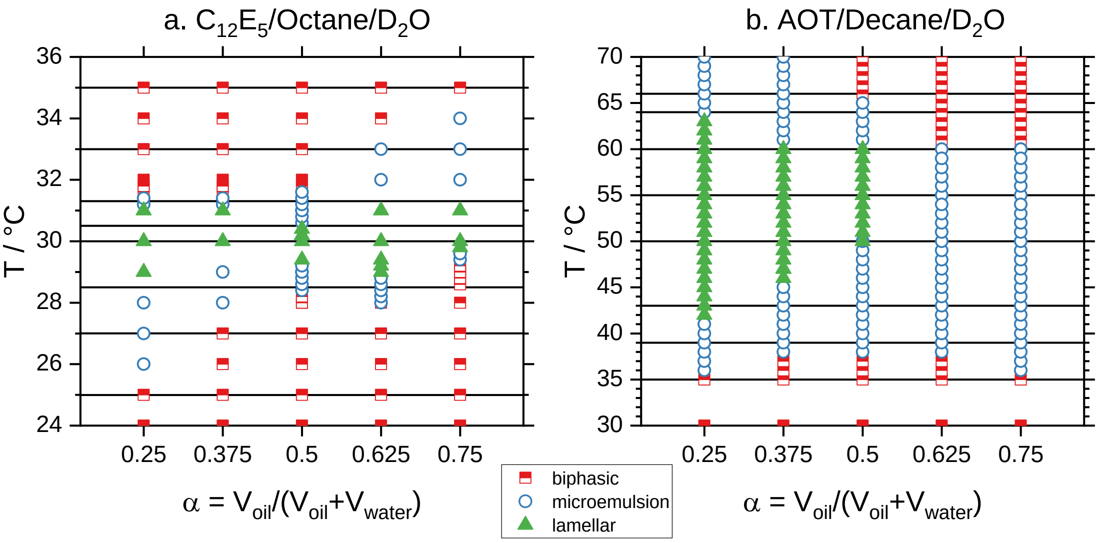

Figure 1: Phase diagrams of the two studied microemulsion systems. The temperatures selected for SANS measurements are shown with horizontal black lines.

SANS measurements were performed at eight temperatures each, which are shown with vertical black lines in Figure 1. The temperatures were set using a Peltier sample changer. For the $C_{12}E_5$ samples, three sample-to-detector distances of 2.53, 13.52 and 38.02 m and collimation lengths of 5.5, 13.5 and 40.5 m were used. For AOT, two sample-to-detector distances of 2.53 and 38.02 m and collimation lengths of 5.5 and 40.5 m were used.

Results

In Figure 2, as an example, the scattering curves for the AOT system are shown. To test the various theoretical predictions the peak locations were determined.

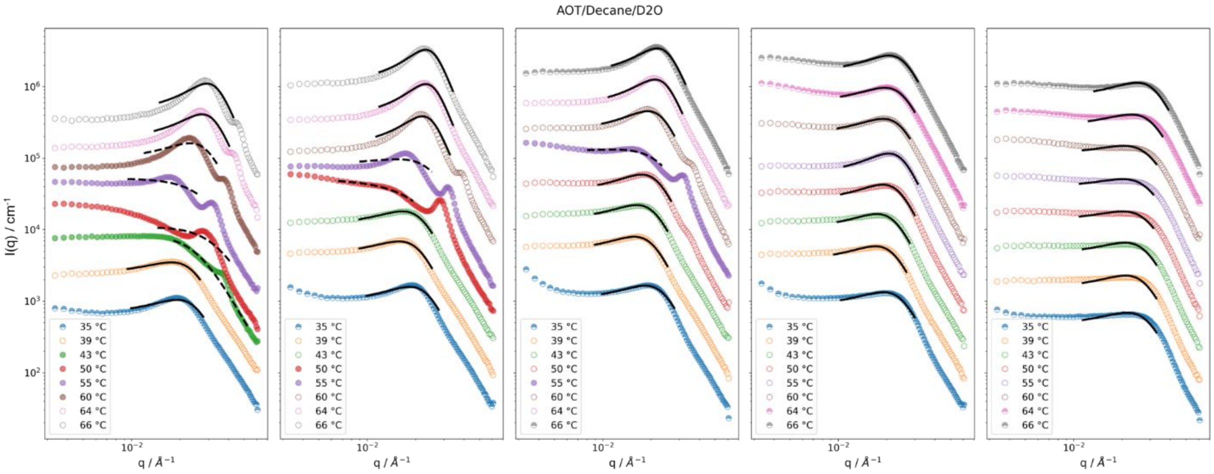

Figure 2: SANS curves for AOT/Decane/D_2O at five different oil volume fractions and eight different temperatures. The black lines indicate a Teubner-Strey (TS) fit.

From the peak location, the spacing D* were calculated by the Bragg equation $D^* = 2\pi/q_{max}$ and is shown in Figure 3 as a function of the oil/water composition of the microemulsion.

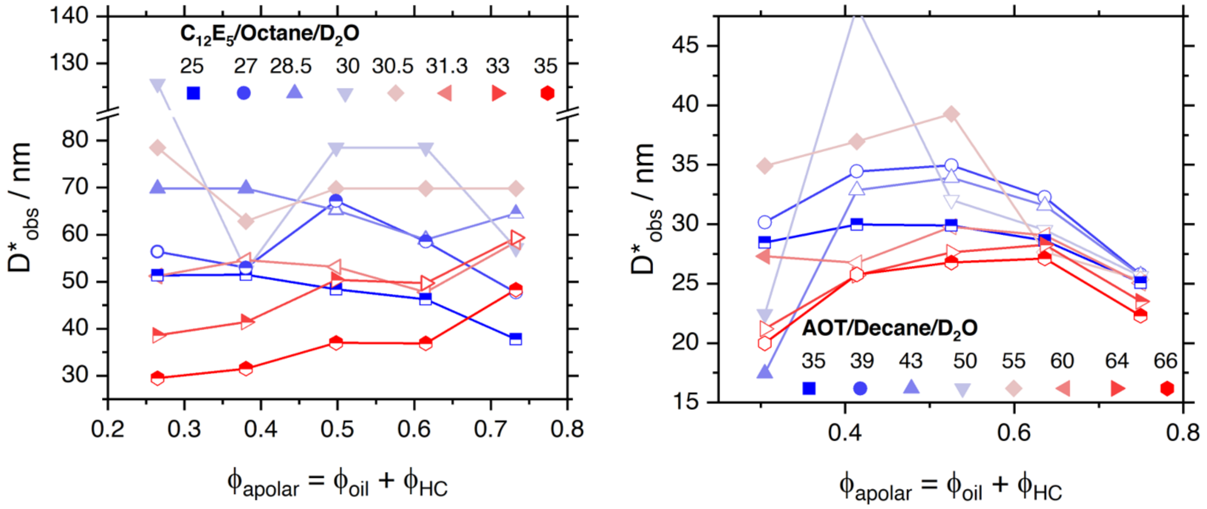

Figure 3: Observed spacing D^* determined from the peak location for the $C_{12}E_5$ and AOT microemulsions.

The high-q scattering was used to determine the specific area per unit volume Σ and by extension the area per surfactant molecule a_0, the results are shown in Figure 4. To compare experimental results to model predictions, a useful form of visualization is to plot the dimensionless quantity $D^*\Sigma$ as a function of the polar/non-polar volume fraction, which is shown in Figure 4.

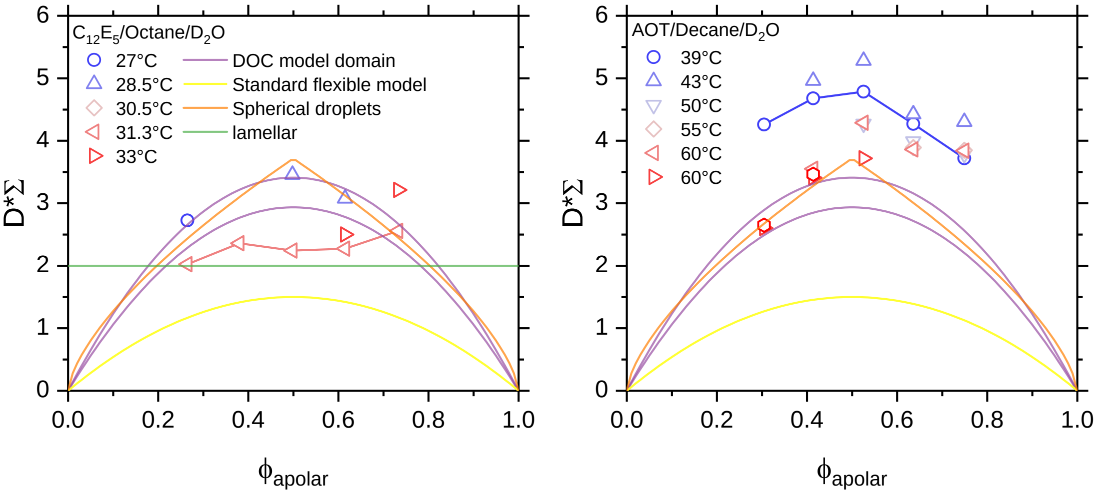

Figure 4: Dimensionless quantity $D^*\Sigma$ for all microemulsion samples and the predicted curves for various models. The temperature which lies fully inside the microemulsion channel is shown with a line.

Figure 4 clearly demonstrates, that none of the standard models can accurately describe the values for $D^*\Sigma$ for all volume fractions. We are currently working on a new theoretical description of the experimental data. This then should give a more detailed insight into the conditions determining the structural properties of microemulsions.

Literature

[1] P.G. de Gennes, C. Taupin, J. Phys. Chem. **1982**, 86, 2294.

[2] M.E. Cates, D. Andelman, S.A. Safran, D. Roux, Langmuir **1988**, 4, 802.

[3] I.S. Barnes, S.T. Hyde, B.W. Ninham, P.J. Derian, M. Drifford, T.N. Zemb, J. Phys. Chem. **1988**, 92, 1988.