Experimental report

06/04/2016

Proposal: **TEST-2537** **Council:** 4/2015

Title: Testing a High Pressure Cell for CO_2 Microemulsions on IN15

Research area:

This proposal is a new proposal

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Local contacts: Ingo HOFFMANN

Samples: H_2O
CO_2
Cyclohexane
Fluorinated surfactant

Instrument	Requested days	Allocated days	From	To
IN15	2	2	04/11/2015	06/11/2015

Abstract:

Testing a High Pressure Cell for CO_2 Microemulsions on IN15

Experimental Report Test-2537

Abstract: Microemulsions with super- or near critical CO_2 have attracted increasing attention due to their potential as a possible replacement for organic solvents. Furthermore, they are also highly interesting from a fundamental point of view since their properties such as bending elasticity constants of the amphiphilic film can strongly be influenced by varying the pressure without changing the components [1]. Fluorinated surfactants, which are known to be efficient in solubilising CO_2 and water are, however, environmentally no longer tolerable. We showed that a partial replacement of CO_2 by cyclohexane enables a reduction of the amount of surfactant needed to formulate a one-phase microemulsion by a factor 2 to 5, depending on the pressure [2]. Thereby, a depletion zone of cyclohexane close to the amphiphilic film forms due to repulsive cyclohexane/fluorinated surfactant interactions. To probe whether this increase of efficiency is connected to an increase of bending rigidity of the amphiphilic film we proposed to perform NSE and SANS measurements of CO_2-microemulsions. During Test-2537 the home-built high-pressure SANS cell has been successfully used to perform a first set of high pressure NSE measurements at IN15 on the microemulsion system brine (1 wt% NaCl) – CO_2 – Zonyl FSO 100/Zonyl FSN 100 The intermediate scattering functions were in a first approach analysed using a single exponential fit obtaining the effective diffusion coefficient D_{eff}. Subsequently, in a preliminary evaluation, the data were described using a double exponential fit [3], which accounts for the diffusional motions (D_0) and peanut-like deformations (modes with $l = 2$) of the droplets. Estimating D_0 from the droplet size and using the average viscosity of brine and CO_2 (Figure 2), we determined $4\kappa - \overline{\kappa} = 4.6 \pm 1.0\ kT$ neglecting the two highest and lowest q-values.

NSE measurements: In order to investigate the bending rigidity of the amphiphilic film of CO_2-microemulsions a test experiment at IN15 (I. Hoffmann) was successfully performed. The home-built high-pressure SANS cell was developed in close collaboration with the IR (R. Schweins and P. Lindner) of the D11-instrument. It is made completely out of non-magnetic substances such as bronze. Screws from stainless steel were exchanged by demagnetized ones. The homogenization of the microemulsion sample was done by glass beads inside the cell and turning the cell upside down. Homogeneity of the sample was ensured by visual inspection through the sapphire windows. The cell was placed on the sample position via an adapter plate. This plate is also used for the SANS experiments and was mounted by the technician of IN15 (C. Gomez). The cell can be mounted by two persons. The fact that the circular entrance window for the neutron beam is small for NSE measurements (diameter 1.7 cm) is mostly compensated by the high scattering contrast (about $\Delta\rho \approx 5 \cdot 10^{-10}$ cm^{-2}). The resolution of the spin-echo spectrometer was determined using a graphite plate directly behind the sapphire window on the detector side. The NSE spectra were recorded at three different detector angles (3.5, 6.5 and 9.5°) and nine different q values of 0.0349 to 0.1429 Å^{-1} and a wavelength of $\lambda = 8$ Å. For the calibration of the data the scattering of D_2O/NaCl (1 wt%) was measured. Raw data evaluation was done using the software available at IN15.

Results: Figure 1 shows the data of the test NSE experiment of the microemulsion system brine (1 wt% NaCl) – CO_2 – Zonyl FSO 100/Zonyl FSN 100 ($w_B = 0.10$, $\gamma_a = 0.08$, $\delta_{FSN} = 0.75$) at $T = 20$ °C and $p = 200$ bar as well as the single exponential fit (dashed lines). Additionally for $q = 0.0483$ and 0.1156 Å the double exponential fit is shown (solid lines).

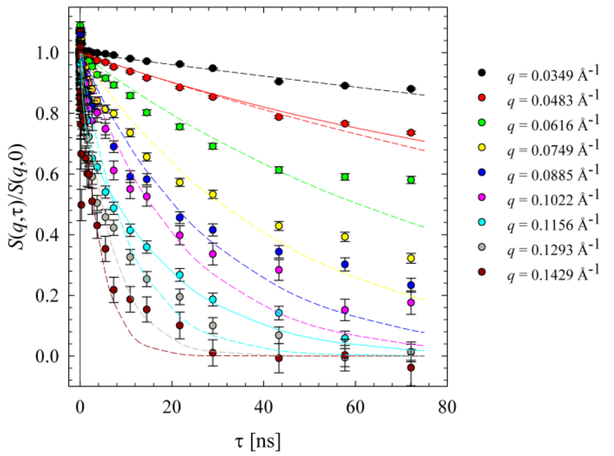

Figure 1: Intermediate scattering function $S(q,t)/S(q,0)$ of the sample D_2O/NaCl – CO_2 – Zonyl FSO 100/Zonyl FSN 100 (w_B = 0.10, γ_a = 0.08, δ_{FSN} = 0.75, ε = 0.01) at T=20°C and p = 200 bar for different q. The data were analysed using a single (dashed lines) as well as double exponential function (solid line) [3]. The double exponential fit is exemplary shown for q = 0.0483 and 0.1156 Å^{-1}. For this pre-evaluation the self-diffusion coefficient D_0 was estimated from the droplet size obtained from SANS [2].

Single exponential fit:

In a first step the obtained correlation functions were analysed using the single exponential function

$$\frac{S(q,t)}{S(q,0)} = \exp(-\Gamma_{\text{eff}}\, t)\,,$$

where Γ_{eff} is the effective relaxation rate. The effective diffusion coefficient D_{eff}, which contains the diffusion motions as well as peanut-like deformations of the droplets, was calculated from $D_{\text{eff}} = \Gamma_{\text{eff}}/q^2$ [4-6]. In Figure 2 the obtained effective diffusion coefficients D_{eff} are plotted versus q^2 for p = 200 bar (left) and p = 300 bar (right).

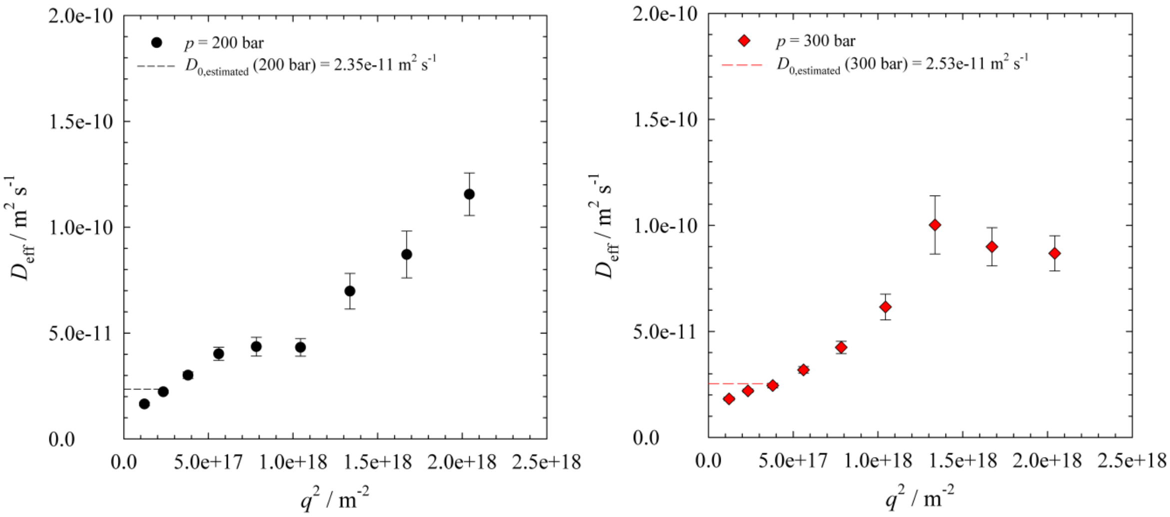

Figure 2: The effective diffusion coefficient D_{eff} obtained from the analysis of the NSE data of the microemulsion D_2O/NaCl (1 wt%) – CO_2 - Zonyl FSO 100/Zonyl FSN 100 (w_B = 0.10, γ_a = 0.08, δ_{FSN} = 0.75, ε = 0.01, T = 20 °C) via a single exponential fit as a function of q^2. The NSE measurements were performed at p = 200 bar (left) and p = 300 bar (right). The dashed lines represent the diffusion coefficient D_0 estimated from the Stokes-Einstein equation.

The diffusion coefficient D_0 (shown as dashed line at low q-values) of the microemulsion droplets can be estimated using the Stokes-Einstein equation

$$D_0 = \frac{kT}{6\pi\eta R_h}$$

with the hydrodynamic radius R_h = 74 Å and 69 Å, respectively estimated by the sum of the mean droplet radius R_0 determined via SANS [2] and an additional hydrodynamic shell of approximately 10 Å. η is the viscosity of D_2O at p = 200 bar and p = 300 bar, respectively.
At low q-values the effective diffusion coefficient D_{eff} is mainly driven by the diffusion of the microemulsion droplets and therefore approaches the diffusion coefficient D_0 [3, 4]. For higher q-values the effective diffusion coefficient D_{eff} increases due to peanut-like deformations of the droplets. The observed increase of D_{eff} with increasing q is also described in literature [3-7]

Double exponential fit:
In order to extract the bending rigidity of the amphiphilic film, the correlation functions were also analysed using the double exponential function

$$\frac{S(q,t)}{S(q,0)} = a\exp(-D_0 q^2 t) + (1-a)\exp(-\Gamma t)$$

with the diffusion coefficient D_0 and two adjustable parameters a and Γ (Figure 1) [7]. This analysis accounts for the diffusion motions and peanut-like deformations (modes with l = 2) of the droplets. The relaxation time

$$\tau_2^{-1} = \Gamma - D_0 q^2$$

is connected to the combination 4κ - $\bar{\kappa}$ of bending elasticity constants via

$$\frac{\tau_2^{-1}\eta R^3 Z(l)}{kT} - \frac{\ln\phi - 1}{4\pi} = 4\kappa - \bar{\kappa}$$

with ϕ being the volume fraction of CO_2 and the factor $Z(l)$ = 1.28 and 1.30, respectively. Neglecting the two highest and lowest q-values

$$4\kappa - \bar{\kappa} = 4.6 \pm 1.0\, kT$$

is obtained. Similar values are found for droplet microemulsions of the type water, n-alkane, non-ionic surfactant [8].
Due to the short beamtime and since this was the first high pressure NSE experiment at the ILL there was no time for a systematically study of the influence of cyclohexane on the membrane properties of a fluorinated amphiphilic film. Furthermore for the analysis of the NSE data (especially the droplet microemulsions) SANS measurements are needed [7].

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