Journal of Colloid and Interface Science 525 (2018) 161–165

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

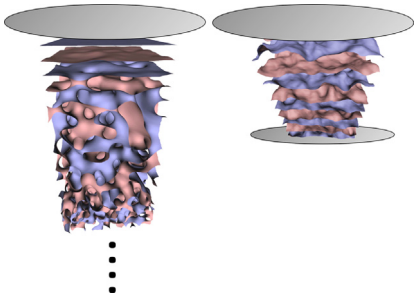
Regular Article

Capillary condensation and gelling of microemulsions with clay additives

Manuchar Gvaramia [a,b], Gaetano Mangiapia [a,c], Peter Falus [d], Michael Ohl [e], Olaf Holderer [a], Henrich Frielinghaus [a,*]

[a] Jülich Centre for Neutron Science at MLZ, Forschungszentrum Jülich GmbH, Lichtenbergstrasse 1, 85747 Garching, Germany
[b] Ilia Vekua Sukhumi Institute of Physics and Technologies, 7 Mindeli Str., 0186 Tbilisi, Georgia
[c] Helmholtz-Zentrum Geesthacht GmbH, German Engineering Materials Science Centre at Heinz Maier-Leibnitz Zentrum, Lichenbergstr. 1, 85748 Garching bei München, Germany
[d] Institut Laue Langevin, 71 Avenue des Martyrs, CS 20156, Cedex 9, 38042 Grenoble, France
[e] Jülich Centre for Neutron Sciences JCNS-1, Forschungszentrum Jülich GmbH, Leo Brandt Straße, 52425 Jülich, Germany

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 March 2018
Revised 6 April 2018
Accepted 6 April 2018
Available online 22 April 2018

Keywords:
Microemulsion
Clay
Capillary condensation
Neutron scattering

ABSTRACT

The capillary condensation in bicontinuous microemulsions takes place when two parallel surfaces are narrowed that result in a completely lamellar microemulsion. We expected that this phase transition is also observable when the amount of hydrophilic surfaces from clay particles is raised, because hydrophilic surfaces induce lamellar ordering locally. Using small angle neutron scattering, the structure of microemulsions was observed as a function of clay content. The critical concentration is indicated by discontinuous structural changes and depends on the platelet diameter and is explained by the free energy of the platelets competing with the fluctuating medium. The gel phase transition is observed in the spectroscopic measurements where the diffusion motion is widely suppressed in the gel phase, but otherwise superimposes with the membrane undulations.

© 2018 Published by Elsevier Inc.

1. Introduction

Microemulsions are thermodynamically stable mixtures of oil and water [1–3] that are mediated by the surfactant. Locally, there are oil and water domains that are observable by scattering experiments [4] that are separated by the surfactant film. The domain sizes are usually a few nanometers and display shapes from spherical droplets over elongated droplets to the bicontinuous sponge

* Corresponding author at: Jülich Centre for Neutron Science at MLZ, Forschungszentrum Jülich GmbH, Lichtenbergstrasse 1, 85747 Garching, Germany.
E-mail address: h.frielinghaus@fz-juelich.de (H. Frielinghaus).

https://doi.org/10.1016/j.jcis.2018.04.032
0021-9797/© 2018 Published by Elsevier Inc.

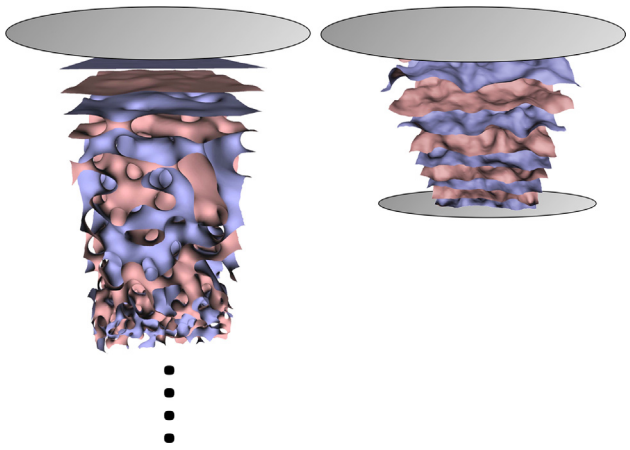


Fig. 1. A sketch for the phase transition of capillary condensation of a microemulsion between clay platelets.

phase. Also liquid crystalline order between the domains can be observed. In the following we restrict ourselves to the bicontinuous microemulsion. The explanation for this choice of the system is a relatively simple handling (equilibrium means reproducibility) and very well documented characterization. For instance, a long history is written on bicontinuous microemulsions with polymeric additives [5–9]. In terms of applications, microemulsions are used as cleaning agents [10] and are discussed as fuels with much less pollutant emissions from the combustion [11,12].

When exposing the microemulsion to hydrophilic surfaces, a lamellar order is locally induced next to the interface [13]. From spectroscopic measurements, we know that the membrane fluctuations in microemulsions are faster in the lamellar state [14]. This is connected to the lubrication effect [15], because the lamellae can slide off easier and the motions are faster. In spectroscopic measurements with hydrophilic clay particles, we could show, that the platelet diameter causes a cutoff of the undulation modes, and larger platelets cause a better order with longer wavelength modes [16]. In rheology experiments this microscopic effect was observed macroscopically [17].

So far, all experiments stayed at relatively low clay concentrations, when the system is still liquid [16,17]. The lamellar fraction in microemulsions with 1% clay is around 25% in volume [16]. From the predictions of a capillary condensation [18,19], we were motivated to study higher clay concentrations (see Fig. 1). An interesting detail of the clay structure in microemulsions is the speculation that the particles arrange on a checkerboard structure where the next layer places particles on holes of the original one [17]. When the layer of lamellar surfactant membrane order keeps its extension, at a particular clay platelet distance the whole system must undergo a phase transition to lamellar only. We tried to observe this phase boundary using small angle neutron scattering (SANS) and neutron spin echo (NSE) spectroscopy. The results are discussed in this order.

2. Materials

The non-ionic surfactant tetra-ethylene glycol mono-decyl ether ($C_{10}E_4$) was purchased from Bachem Distribution Services, Weil am Rhein. The heavy water (D_2O) and perdeuterated n-decane were purchased from Armar Chemicals, Döttingen. All chemicals were used without further purification. The batch microemulsions with film and bulk contrast were mixed with 17 vol% surfactant and 41.5 vol% heavy (normal) water and 41.5 vol % protonated (deuterated) oil, using the densities of 0.974, 1.105 (1.000), 0.840 (0.97) g/cm^3, respectively. All microemulsions were stable at a temperature window of 25 °C (27 °C) (±2K) observed by visual inspection of turbidity.

Clay particles were obtained from Süd Chemie (Rockwood), now belonging to the BYK chemicals group. We received two types of clay: Laponite RD (LRD) that is reported to have a diameter of 25–30 nm, and Montmorillonite (MMT) EXM 757 had a diameter of approx. 500 nm. The Laponite material was used without further cleaning. The Montmorillonite material was dispersed in deionized water by sonication over night, centrifuged, and the liquid portion dried using a rotor vap and a vacuum oven. The particles were dispersed in the microemulsion with given volume percentages using the density of 2.6 g/cm^3. The dispersions were sonicated from 1 to 3 h. The samples were stable in the same temperature range by showing little turbidity – the particles caused light scattering.

3. Experimental

Small angle neutron scattering (SANS) experiments have been performed on KWS-1 [20,21] within the Heinz Maier-Leibnitz Zentrum (MLZ) at the research reactor FRM-2 in Garching/Munich. The neutron velocity selector was set to 5 Å wavelength with a FWHM spread of 10%. The instrument has a length of 20 + 20 m for collimation and detector. The collimation was set to 20 m with an entrance aperture of 3 × 3 cm^2. The detector distance was varied between 20 m, 8 m and 1.5 m to cover the full accessible Q-range. The scattering vector Q was calculated as the function of the scattering angle θ and the wavelength λ according to $Q = 4\pi \sin(\theta/2)/\lambda$. The macroscopic cross section $d\Sigma/d\Omega(Q)$ was calibrated using a secondary plexiglass standard and transmission. Longer measurements (1 h) of plexiglass served for a pixel-wise sensitivity measurement. All measurements were corrected against the empty cell, the empty beam and dark current background. All samples were heated to 25 °C using a Peltier element against water-cooling to obtain the one-phase microemulsion.

Neutron spin echo (NSE) spectroscopy measurements have been performed on J-NSE [22] within the MLZ at the research reactor FRM-II in Garching, at the SNS-NSE at the Spallation Neutron Source in Oak Ridge [23], and at IN-15[24,25] at the Institut Laue Langevin. The neutron velocity selector was set to 8 Å wavelength. Details of the method and calibration are given in Ref. [26]. The result of the measurement is the intermediate scattering function $S(Q,t)$, given by:

$$S_{\mathrm{coh}}\left(\vec{Q},t\right) = \sum_{m,n}\langle exp\left(i\vec{Q}(\vec{r}_m(t) - \vec{r}_n(0))\right)\rangle \quad (1)$$

with $\vec{r}_m$ the position of surfactant molecule m. $S(Q,t)$ is the Fourier transform of the real space van Hove correlation function into reciprocal space. All measurements were calibrated against unwanted background and the instrument resolution.

4. Results

The bulk contrast samples at particle concentrations between 0.5 and 2.5 vol% were characterized using SANS (Fig. 2, Supplementary Material: Fig. S1). We see a clear correlation peak at approx. Q = 0.035 Å^{-1} that results from the oil and water domains that alter on a local scale. An upturn towards lower Q < 0.01 Å^{-1} is observed due to the inhomogeneities that the particles cause. The power law is close to the ideal Porod surface scattering $P \times Q^{-4}$. At high Q > 0.2 Å^{-1} the scattering levels off due to the non-corrected incoherent scattering. It allows for crosschecking the absolute calibration. All scattering curves were fitted by a semi-empirical formula:

Download English Version:

https://daneshyari.com/en/article/6990572

Download Persian Version:

https://daneshyari.com/article/6990572

Daneshyari.com