Characterization of a Bicontinuous Microemulsion Flowing Along a Planar Surface

Henrich FRIELINGHAUS[1]*, Frederik LIPFERT[1,2], Stefan MATTAUCH[1]

[1]*Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science at MLZ, Lichtenberg-strasse 1, D-85747 Garching, Germany*
[2]*Etrality GmbH, Zillenweg 9, D-83115 Neubeuren, Germany*

**E-mail: h.frielinghaus@fz-juelich.de*
(Received July 20, 2018)

We present a study on a bicontinuous microemulsion exposed to a planar hydrophilic surface with a flow field along the interface using neutron reflectometry. The microemulsion displays a lamellar interface ordering. The range of apparent shear rates was ranging from 8 to 600s^{-1}. In this range, no considerable structural change of the lamellar structure was observed. This finding supports previous rheological experiments where the so-called *lubrication* effect was found – an unchanged facilitated flow of the lamellar structure along the surface – for a wide range of shear rates.

KEYWORDS: Complex fluids, Microemulsion, Solid-liquid interface, Neutron Reflectivity

1. Introduction

Microemulsions are thermodynamically stable mixtures of oil and water that are mediated by a surfactant. On the nano-scale, domains of oil and water form with the surfactant film in between. Bicontinuous microemulsions form when nearly equal volumes of oil and water are mixed. The domains have a sponge structure that hosts the other one respectively. A bicontinuous microemulsion displays near surface ordering when being exposed to a planar hydrophilic surface [1]. Then, this higher degree of order is expressed as a lamellar structure with alternating water and oil domains on a similar repeat distance as in the bulk [1]. The dynamics of the lamellar structure is about three times faster than in the bulk [2], which is seen in the context of the so called *lubrication* effect that describes the facilitated flow of the lamellar domains along the solid-liquid interface. These findings so far [1,2] have been observed at macroscopically large planar silicon surfaces. When introducing clay platelets with finite diameters [3], the quality of the lamellar structure increases with the platelet diameter. When increasing the clay concentration, the near surface ordering can prevail [4], and the whole volume is in the lamellar phase. This effect is called *capillary condensation*. Staying at low concentrations of ca. 1%vol, the clay particles lead to decreased macroscopic viscosities with increasing platelet diameter [5,6] in agreement with the lubrication effect. For this observation it was inherently assumed that the lamellar order is not destroyed by the flow-field. The experimental verification is the topic of this manuscript focusing on the flow of a bicontinuous microemulsion along a macroscopic hydrophilic silicon surface.

2. Materials and Methods

N-decane was obtained from Sigma Aldrich. The non-ionic surfactant $C_{10}E_4$ was obtained from Bachem, Weil am Rhein, Germany. Heavy water was obtained from Armar chemicals, Döttingen, Switzerland. All these chemicals were used without further purification. The final microemulsion consisted of 17%vol $C_{10}E_4$, 41.5%vol heavy water, and 41.5%vol n-decane. The microemulsion was kept stable at 25°C ±1K with a safe distance to the 2-phase regions of at least ±2K.

The flow cell for neutron reflectometry and grazing incidence small angle neutron scattering [1,7] hosted a polished silicon slab (150×50×20 mm^2) with a roughness better that 2Å. It was etched before use as described in Refs 1 and 7 to obtain hydrophilicity. The flow along the slab took place on an area of ca. 120×30mm^2; and the gap was 0.5mm. The cell was connected with a Luer Lock® System to a peristaltic pump. An average flow speed of up to 50mm/s could be reached in the cell that translates to a shear rate of 600s^{-1} at the interfaces assuming Hagen-Poiseuille flow. The cell was tempered by a water-thermostat to 25°C, and a limited area around the pump was heated by an electric heat blower. The neutrons impinge on the silicon front face, are reflected from the solid-liquid interface, and leave through the opposite back face.

Neutron Reflectometry was conducted on the instrument MARIA at the MLZ Garching [8,9]. The neutron wavelength was 5Å. The entrance and sample slits were 0.4×148 mm^2 and 0.4×30 mm^2 for the reflectivity data represented here. All data were normalized by a heavy water reference scan such that the total reflectivity plateau was unity. All reflectivities are given as a function of the scattering vector Q.

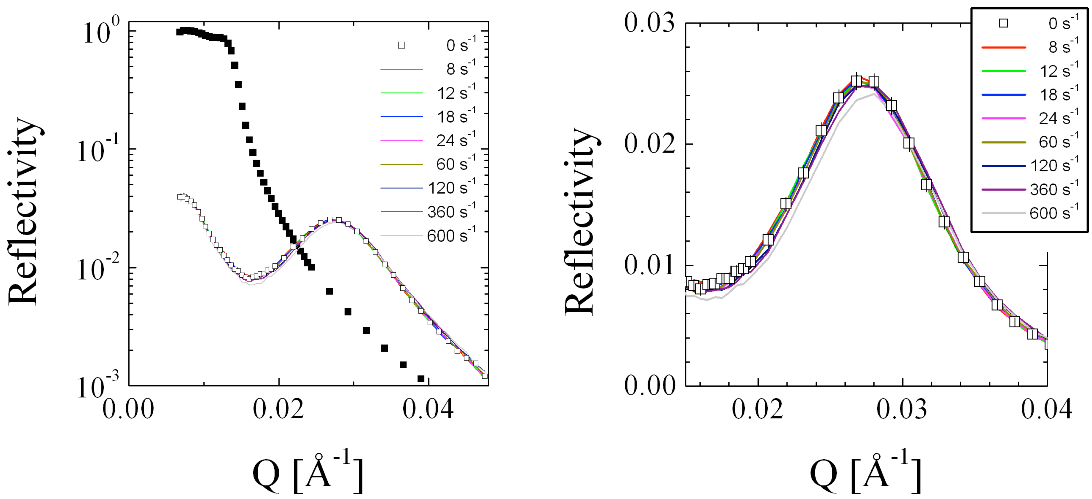

Fig. 1. Reflectivity curves of a microemulsion flowing along a planar surface with symbols according to the legend (open squares, and colored lines with shear rates as indicated). Left: logarithmic scale with pure D_2O scan (solid squares) that served as a reference measurement. Right: linear scale.

3. Results and Discussion

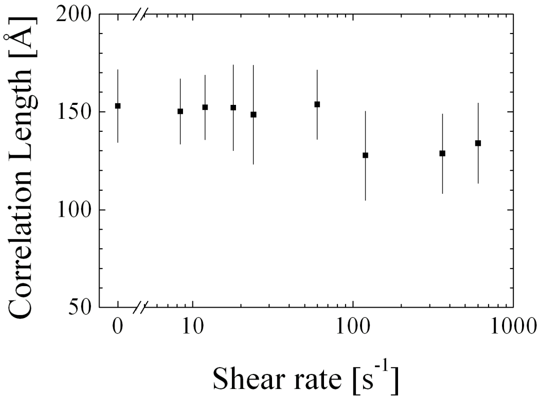

Fig. 2. The correlation length ξ of the lamellar order adjacent to the planar hydrophilic interface as a function of the apparent shear rate.

The reflectivity R of the micro-emulsion adjacent to the hydrophilic silicon slab are displayed in Fig. 1 as a function of the scattering vector Q and the apparent shear rate. All curves have been normalized by a reference measurement of heavy water shown in the left panel. Even in the magnified presentation, very little or nearly negligible changes can be observed. The highest shear rate of $600s^{-1}$ displays the most distinguished curve. Already at this point, we can state that the applied shear had very little effect on the lamellar structure of the near surface order. The bicontinuous microemulsion would not be observable in this instrumental setting because the random non-oriented order of the domains cancels out. For a more quantitative analysis, a simple peak shape was modeled to the data reading:

$$R = \frac{A}{(1+(k^2-Q^2)\xi^2)^2+4Q^2\xi^2} \qquad (1)$$

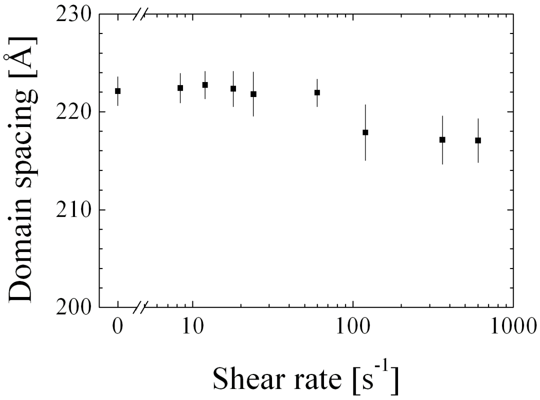

Fig. 3. The domain spacing d of the lamellar order adjacent to the planar interface as a function of the apparent shear rate.

The three parameters refer to: an amplitude A, a preferred wave vector k = $2\pi/d$ with the related domain spacing d, and a correlation length ξ. The simple formula expresses that the correlation decay does not only happen directly at the solid-liquid interface, but also a little deeper in the volume. From previous measurements, we know that the number of perfect (non-perforated) lamellar domains is at least approx. 4 with a total depth of approx. 400Å [1]. From the correlation length ξ (Fig. 2) we can see that this correlation length is much shorter than the number of perfect domains, which means that next neighbor domain correlations are lost much quicker. The correlation length is slightly decaying for shear rates larger than $100s^{-1}$. This decay is nearly within the uncertainty of the statistical errors. For completeness, the measured domain spacing is displayed in Fig. 3. Again, we see very little changes, but due to improved statistics the decay at shear rated above $100s^{-1}$ is clearly significant. From pure rheological measurements [9], we know that beyond shear rates of 2000 to $3000s^{-1}$ the strong field induces larger domain interfaces. This means that then the equilibrium interface with each surfactant molecule having a typical head group area *a* [11] is violated and enlarged by the shear field. For this manuscript we speculate that the onset of enlarged surfactant membrane area is already earlier, maybe at around $100s^{-1}$, where the effect starts gradually. Larger surfactant membrane area agrees with smaller domain spacing and the motion obviously reduces the correlation of neighboring domains a little. However, besides this gradual weak effect, the lamellar structure is preserved. This finding is important for the *lubrication* effect at moderate shear rates, say a few $100s^{-1}$, where the lubricating structure is conserved without significant changes. This inherent assumption was an unspoken prerequisite of References 5 and 6.

3. Conclusion

We have observed a rather robust lamellar near surface order that is nearly not affected by apparent shear rates of $600s^{-1}$ [12]. This finding is a prerequisite for the observation of the so-called *lubrication* effect at similarly high shear rates. In this sense we have proved one unspoken assumption of References 5 and 6.

References

[1] M. Kerscher, P. Busch, S. Mattauch, H. Frielinghaus, D. Richter, M. Belushkin, G. Gompper, Phys. Rev. E 2011, 83, 030401

[2] H. Frielinghaus, M. Kerscher, O. Holderer, M. Monkenbusch, D. Richter, Phys. Rev. E 2012, 85, 041408

[3] F. Lipfert, O. Holderer, H. Frielinghaus, M.-S. Appavou, C. Do, M. Ohl, D. Richter, Nanoscale 2015, 7, 2578-2586

[4] M. Gvaramia, G. Mangiapia, P. Falus, M. Ohl, O. Holderer, H. Frielinghaus, J. Coll. Interf. Sci. 2018, 525, 161-165

[5] M. Gvaramia, G. Mangiapia, V. Pipich, M.-S. Appavou, S. Jaksch, O. Holderer, M. D. Rukhadze, H. Frielinghaus, J. Coll. Interf. Sci. (in preparation)

[6] M. Gvaramia, G. Mangiapia, V. Pipich, M.-S. Appavou, G. Gompper, S. Jaksch, O. Holderer, M.D. Rukhadze, H. Frielinghaus arXiv:1709.05198 (2018)

[7] S. Jaksch, F. Lipfert, A. Koutsioubas, S. Mattauch, O. Holderer, O. Ivanova, H. Frielinghaus, S. Hertrich, S.F. Fischer, B. Nickel, Phys. Rev. E 2015, 91, 022716

[8] S. Mattauch, A. Koutsioubas, S. Pütter, J. large-scale res. facil., http://dx.doi.org/10.17815/jlsrf-1-29

[9] S. Mattauch, A. Koutsioubas, U. Rücker, D. Korolkov, V. Fracassi, J. Daemen, R. Schmitz, K. Bussmann, F. Suxdorf, M. Wagener, P. Kämmerling, H. Kleines, L. Fleischhauer-Fuß, M. Bednareck, V. Ossoviy, A. Nebel, P. Stronciwilk, S. Staringer, M. Gödel, A. Richter, H. Kusche, T. Kohnke, A. Ioffe, E. Babcock, Z. Salhi, T. Bruckel, J. Appl. Cryst. 2018, 51, 646-654

[10] Internal communication.

[11] T. Sottmann, R. Strey, S.-H. Chen, J. Chem. Phys. 1997, 106, 6483-6491

[12] F. Lipfert, M. Kerscher. S. Mattauch, H. Frielinghaus, J. Coll. Interf. Sci. 2019, 534, 31-36