The effect of amphiphilic polymers with a continuous amphiphilicity profile on the membrane properties in a bicontinuous microemulsions studied by neutron scattering

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Abstract. Microemulsion systems consisting of oil, water and surfactant have been studied with neutron scattering techniques. The amount of surfactant needed to form a microemulsion can be dramatically reduced by the addition of small amounts of amphiphilic block copolymers (boosting effect). Here, we studied the influence of block copolymers with gradually changing amphiphilicity from hydrophilic to hydrophobic. Small angle neutron scattering (SANS), neutron spin echo spectroscopy (NSE) and phase diagram measurements in combination give access to the elastic properties of the membrane. The underlying NSE experiments for this interpretation rely on smallest changes of the relaxation curves (of ca. 1% steps) for still small changes of the bending rigidity (of ca. 10% steps). This high reliability of the experiments conducted at the SNS-NSE displays the accuracy of the instrument itself and the latest developments of the evaluation software, which were necessary to interpret such tiny changes of the bending rigidity reliably.

1. Introduction

The combination of neutron spin echo spectroscopy (NSE) with phase diagram measurements and small angle neutron scattering (SANS) is a very powerful combination for the determination of the elastic properties of microemulsions and the determination of the bending rigidity, $\kappa$, and the saddle splay modulus, $\tilde{\kappa}$ [1]. The efficiency of microemulsions (i.e. thermodynamically stable water-oil-surfactant mixtures) can be strongly increased (the so called “boosting effect”) by the addition of amphiphilic diblock copolymers with a hydrophobic and a hydrophilic block. The diblock copolymers are incorporated into the membrane and make it stiffer by increasing the bending rigidity [2,3]. This “boosting effect” of the microemulsion efficiency could be used to reduce the amount of surfactant needed in applications. At high surfactant concentrations, lamellar phases are formed instead of isotropic bicontinuous phases. Recently, a new type of copolymers has been developed with a gradual
change of polarity, i.e. instead of one hydrophilic and one hydrophobic part (similar to the surfactant structure but with a much higher molecular weight), a smooth transition from the hydrophobic to the hydrophilic side has been realized [4]. This new class of “tapered” polymers also behaves in a similar way as the diblock copolymers in the sense that a significantly smaller amount of surfactant can be used to emulsify a given amount of water and oil. But contrary to the diblock copolymers, the tapered polymers suppress at high surfactant concentrations the formation of a lamellar phase instead of favoring it. Also at high surfactant concentrations, an isotropic phase is therefore preserved, which might be of interest for some applications. The elastic properties have been analyzed by a combination of SANS, NSE and phase diagram measurements [5]. Here we show how the strong requirements in measurement precision for the NSE experiments have been satisfied at the SNS-NSE spectrometer at the SNS (Oak Ridge) [6] and how this helps to deduce the elastic properties of the microemulsion together with SANS and phase diagram measurements.

2. Experimental results

The synthesis of the tapered polymers has been described in detail elsewhere [4]. The tapered polymers were made from polybutylene (BO) and polyethylene (EO) blocks, where the copolymer P(BO/EO)22 had a molecular weight of 22 kg/mol. Microemulsions were mixed from water and decane (bulk contrast for SANS: D2O/h-decane, film contrast for NSE: D2O/d-decane) with a water/decane ratio of 1, and with the nonionic surfactant tetraethyleneglycol-mono-n-decylether (C10E4).

![Fig. 1: Sketch of a surfactant membrane layer with tapered diblock copolymer decoration. The gradual change of amphiphilicity allows to slide the anchoring point along the contour of the polymer chain.](image)

The structure of microemulsions has been investigated with SANS experiments and phase diagram measurements (Fig. 2). The typical correlation peak at ~0.02 Å⁻¹ shows the repeating distance of the structure. The width of the peak corresponds inversely to the correlation length ξ according to the well known Teubner-Strey formula \[ I(q) \sim 1/(q^4 - 2(q_0^2 - \xi^2)q^2 + (q_0^2 + \xi^2)^2) \] [7]. The asymptotic behavior shows the typical Porod dependence (although the Teubner-Strey formula would give the same behavior, it is only valid around the peak position). A series of SANS experiments allowed to determine the variation of ξ for varying d from ξ=132 Å (δ=0) to 314 Å (δ=0.3) [5]. Together with the structural length scale, the renormalized bending rigidity \( \kappa_R \) can be determined [3] and the sensitivity parameter \( \Xi \) (the change of bending rigidity with surface coverage of the membrane by diblock polymers) can be determined [5]. The saddle splay modulus comes from the position of the so called fish tail point in phase diagrams (minimum amount of surfactant needed to emulsify a given amount of
oil and water, see [5]). The intermediate scattering function measured by NSE spectroscopy (Fig. 3) allows a direct determination of $\kappa$, and also the determination of the sensitivity parameter $\Xi$.

$$I(q) \propto \exp(-\frac{1}{\xi^2})$$

Fig. 2: Left: SANS scattering curves for bicontinuous microemulsions with no additives and with 20% tapered polymer contents in the membrane [5]. Right: Phase diagrams of the same samples: the pure microemulsion (top) and the one with added polymers (bottom), showing the different phase regions (1: one phase bicontinuous, $L_\alpha$: lamellar phase, 2: oil- or water excess phase). It shows the boosting effect by the shift of the one phase region to lower surfactant concentrations $\gamma$ (i.e. to the left) and the beginning of lamellar phase suppression.

3. Discussion

Combining SANS, NSE and phase diagram measurements gives access to the elastic properties of the membrane. Phase diagram measurements showed that the lamellar phase is suppressed to a large extend in favor of a bicontinuous phase [5]. Here, we focus on the high precision of the NSE experiments needed to detect tiny differences in the resulting relaxation rate. Varying the fraction of tapered copolymers in the membrane, $\delta$, leads to a small but systematic variation of the relaxation rate, as depicted in Fig. 3. The intermediate scattering function has been fitted with a stretched exponential function according to the Zilman-Granek theory [8], $S(q,\tau) = \exp(-\frac{1}{\tau})$. This theory applies only for local membrane patch fluctuations, i.e. it is valid at high $q$ ($q>4q_0$ with $q_0$ from the Teubner-Strey fits, roughly the correlation peak position). There, the stretching exponent takes the value $\beta=2/3$ (Top right of Fig. 3). At lower $q$ closer to the correlation peak (e.g. the top left plot of Fig. 3) the structural influences change the stretching exponent (here to 0.84). The corresponding relaxation rates (for large $q$) as a function of $\delta$ are shown in Fig. 4. The bending rigidity $\kappa$ can be extracted from the relaxation rate either by numerically evaluating the height correlation function of Zilman and Granek instead of the simplified version of the stretched exponential function [9], or by converting the reduced relaxation rate ($\Gamma$ corrected for the average solvent viscosity $\eta$ and the third power of the inverse length scale, $q^3$) taking into account the correlation length $\xi$ from SANS. The dependence of $\kappa$ on both, $\xi$ and $\Gamma$, is the reason that rather small changes of $\Gamma$ can result in significant changes of $\kappa$. A
graphical procedure for this evaluation procedure is shown in Ref. [10]. The bending rigidity $\kappa$ increases in the present case from $\approx 0.8 \ k_BT$ for $\delta=0$ in agreement to the results reported in Refs [9,10] to $1.8 \ k_BT$ for the highest $\delta$.

The determination of the sensitivity parameter $\Xi$ lead to the interesting result, that NSE showed that the influence of the tapered copolymers on the bending rigidity is very similar to the case of the simple diblock copolymers (i.e. with a very well defined anchoring point) studied in Ref. [9]. In both cases, the bending rigidity increased by $\approx 50\%$. On the other hand, SANS showed a significantly reduced value of $\Xi$ i.e. a much smaller influence on the bending rigidity in the case of tapered polymers. A detailed evaluation can be found in Ref. [5]. In both cases, the added polymers are very similar in structure and size. The typical end-to-end distance of a block of PEO or PEP with a molecular weight of 10 kg/mol is around 10 nm. The domain size $d (\approx -2\pi/q)$ is around 20 nm in the studied microemulsions. The difference between NSE and SANS results can be rationalized by the different time scales of the measurements. In the case of NSE, the dynamics is probed on the nanosecond time scale. There, the anchoring points of the tapered copolymers stay at the same position and the diblock copolymers act in a very similar way as the non-tapered equivalents as a “booster” for the microemulsion. SANS on the other hand probes the static structure, i.e. an average over very long time scales. There the tapered copolymers can slide through the membrane, the anchoring point moves to one side of the copolymer chain or to the other. On the different time scales, the copolymers have therefore different signatures on the membrane conformation with an apparent stronger membrane fluctuation due to the possibly different block sizes of the copolymer on both sides. This is also the reason for the suppression of the lamellar phase of the microemulsion.

![Graphs](image)

**Fig. 3:** $S(q,t)$ from NSE experiments for a) $q=0.06$ (top left) and b) $q=0.17$ (top right) as well as a zoom of b) (bottom left, delta increases from top to bottom of the curves) at intermediate Fourier times. Tiny concentration variations of the tapered polymer lead to small but nonetheless systematic variations in the relaxation rate.
Fig. 4: Relaxation rate $\Gamma$ as a function of tapered polymer concentration $\delta$. The rate is given as the dimensionless quantity $\Gamma = (\Gamma_0 / q^3) (\eta / k_B T)$ corrected for the $q$-dependence and viscosity (see [10]).

4. Conclusion

Small changes in the elastic constants have significant influence on macroscopic properties of complex fluids such as microemulsions. High precision NSE experiments are needed to provide the relaxation rate with the required accuracy. The stable operation and magnetic shielding of the SNS-NSE instrument provides a magnetically very stable environment for such measurements. As an example, the reason of the suppression for lamellar phases by tapered copolymers has been studied. Probing the bending rigidity $\kappa$ on different time scales, i.e. the nanosecond time scale with NSE and the seconds time scale with the static SANS experiments, allowed to observe the effect of a slowly sliding anchoring point of the tapered copolymer, where NSE probes the situation where the copolymer is at the same place in the relaxation time scale of $S(q, \tau)$, while the static structure of SANS probes different local chain configurations where the anchoring point slides across the surfactant membrane. This sliding behavior of the tapered polymers is the reason for the suppression of the lamellar phase up to high surfactant concentrations. A microscopically small effect results therefore in a macroscopically useful change of phase behavior. Many scientific questions concerning thermal fluctuations deal with small effects as in our case the small change in surfactant concentration, or as an other example domain motions in proteins, which are observed as a change in the diffusion constant [11]. The present experiments show that NSE is capable of dealing with such small effects.

5. References
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