

Kerr Effect Measurements on a Poly(oxyethylene) Containing Water-in-Oil Microemulsion

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Kerr effect measurements allow the determination of the surfactant monolayer rigidity of microemulsion droplets. For a AOT–water–isooctane microemulsion containing water-soluble poly(oxyethylene) in the interior of the water droplets, we find an increase of the monolayer rigidity up to about $1kT$. This rigidification is caused by attractive interactions between the polymer and the surfactant which lead to a polymer adsorption at the oil/water interface.

Introduction

Water-soluble polymers like poly(oxyethylene) can be dissolved in water-in-oil (w/o) microemulsions consisting of nanometer-sized water droplets in a continuous oil phase. Due to a selective solubility (the oil phase is often a nonsolvent for poly(oxyethylene)), the polymer is confined to the water core of the nanodroplets.^{1–10} Interactions of the polymer with this restricted spatial environment can deeply influence the structure and phase behavior of the underlying microemulsion. For example, polymer molecules larger than the droplets may induce phase separation^{8,10} or droplet aggregation, probably by formation of a “necklace” of droplets strung along the polymer chain.^{1,2,7,10,11} These steric interactions can be suppressed using polymers with an end-to-end distance smaller than the diameter of the water core of the droplets. In this case only interactions between the polymer and the surfactant stabilizing the droplets at the oil/water interface occur. For example, the attractive interactions between poly(oxyethylene) and anionic surfactants may lead to polymer adsorption at the interface,¹² thus eventually influencing the spontaneous curvature and/or rigidity of the surfactant monolayer. Since spontaneous curvature effects should be the result of interactions between segments of the polymer chain and the head group of the surfactant at the interface, the observed influence of the polymer weight on the phase behavior of an AOT/water/isooctane microemulsion containing poly(oxyethylene) has been interpreted as being mainly the result of an increase of the interfacial rigidity.¹⁰

A powerful technique to measure directly this rigidity, i.e., the elastic bending constant κ , of the surfactant monolayer in w/o microemulsions is Kerr effect measurements on diluted microemulsion droplets.^{13–15} In an electric field the spherical nanodroplets deform into spheroids. The eccentricity of the droplets can be found by minimizing the energy of deformation, which is the sum of an electrostatic contribution and surface free energy.^{13,14} For not too large electrical fields the eccentricity is linear in the magnitude of the field. Nonspherical droplets are aligned parallel to the direction of the electric field, and therefore, the system becomes birefringent and the associated Kerr constant can be directly determined. In the infinite dilution limit of the Kerr constant divided by the volume fraction of the droplets, one obtains the single droplet Kerr constant K_0 , which is inversely proportional to the bending elastic modulus κ of the monolayer.

In this paper we report about Kerr effect measurements on a AOT/water/isooctane microemulsion containing poly(oxyeth-

ylene). Adsorption of the polymer at the interface is expected to rigidify the surfactant monolayer without disturbing the structure of the microemulsion (as long as the end-to-end distance of the polymer chains is smaller than the droplet diameter).

Experimental Section

Materials. Microemulsions were prepared by mixing appropriate weight fractions of the surfactant (s), water (w), and oil (o). The surfactant AOT (sodium bis(2-ethylhexyl) sulfosuccinate) and isooctane were obtained from Fluka. The water was bidistilled. The weight fraction $r_w = w/s$ which determines the size of the droplets was kept constant at $r_w = 2.5$. With a surfactant head group area of 0.57 nm^2 the diameter of the water core of the nanodroplets can be calculated to be about 20 nm. Taking into account the thickness of the AOT monolayer around the water core of about 1.5 nm,¹⁴ this value is in good agreement with light scattering data ($24 \pm 2 \text{ nm}$, see below). Assuming ideal mixing behavior, density measurements allow determination of the volume fraction of the droplets ϕ_{nd} from the corresponding weight fractions. The present microemulsions could be diluted down to $\phi_{nd} \approx 0.01$ without phase separation.

Poly(oxyethylenes) with molecular weights of 1000–11 000 g mol^{-1} were obtained from Fluka. They were further purified by repeated precipitation from methanol and diethyl ether and finally freeze-dried to remove water traces. The molecular weights of the polymers were determined by light scattering and gel permeation chromatography. The polydispersity M_w/M_n of the polymers was in the range $M_w/M_n = 1.1–1.3$.

Assuming Gaussian statistics for the polymer coil and excluded-volume interactions, the end-to-end distance of poly(oxyethylene) with molecular weight $\leq 11\,000 \text{ g mol}^{-1}$ is calculated to be $\leq 16 \text{ nm}$,¹⁶ which is clearly smaller than the diameter of the water core of the droplets. The mass concentration of the polymer in the water phase was 12 g L^{-1} at the highest concentration in our experiments, corresponding to an average number of poly(oxyethylene) chains per droplet ranging from 40 (for $M_w = 11\,000 \text{ g mol}^{-1}$) to about 400 (for $M_w = 1000 \text{ g mol}^{-1}$). The overlap concentration c^* of a polymer chain in solution can be estimated from $c^* \approx M/N_A R_G^3$ with N_A the Avogadro number and R_G the radius of gyration.¹⁷ For our poly(oxyethylenes) we obtain $c^* \geq 65 \text{ g L}^{-1}$; i.e., the solutions were always in the dilute regime.

Measurements. Birefringence of the samples was measured at $T = 298 \text{ K}$ using a conventional Kerr effect apparatus with static electric fields of $10^5–10^6 \text{ V m}^{-1}$ and a probing laser beam

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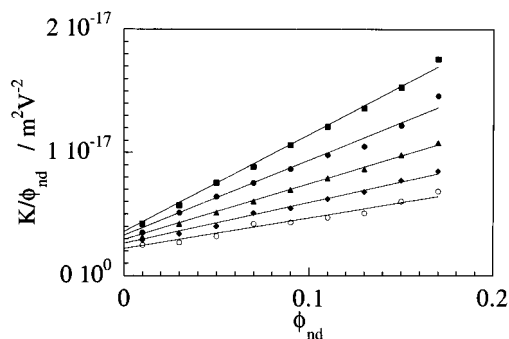


Figure 1. Kerr constant K divided by the respective droplet volume ϕ_{nd} as a function of droplet volume fraction ϕ_{nd} for a water-in-oil microemulsion containing various concentrations c_p of poly(oxyethylene) ($M_w = 11\,000\text{ g mol}^{-1}$) in the water droplets for c_p (■) 0, (●) 5×10^{-4} , (▲) 10^{-3} , (◆) 4×10^{-3} , and (○) $8 \times 10^{-3}\text{ g L}^{-1}$.

of 633 nm.¹³ The measured Kerr constant divided by the volume fraction of the droplets was extrapolated to infinite dilution to obtain the single droplet Kerr constant K_0 (see below). The procedure to evaluate the surfactant monolayer rigidity κ is described in detail in ref 13.

The radius r of the droplets was determined by dynamic light scattering using an ALV-5000/E correlator, second cumulant analysis, and extrapolation of the data to infinite dilution. In agreement with the observations of refs 4 and 18, the radius was found, independent of the polymer content, to be $r = 12 \pm 1\text{ nm}$. The refractive index increment $dn/d\phi_{nd}$ used to calculate the optical polarizability contribution was determined to $-dn/d\phi_{nd} = 0.056$ (also independent of the polymer content within experimental accuracy) using a Brice Phoenix differential refractometer.

Since measurements were performed for diluted polymer solutions ($c_p \leq 12\text{ g L}^{-1}$), the polydispersity of the droplets was assumed to be approximately 10%,¹⁹ independent of the polymer concentration. The calculated value of κ , however, depends only very little on the polydispersity.¹³

Results and Discussion

In Kerr effect experiments on microemulsions three contributions to the measured electric birefringence and therefore the Kerr constant can be observed. The first contribution is due to the continuous oil phase. This contribution can be neglected in our case because of the small Kerr constant of isooctane ($3.7 \times 10^{-22}\text{ m}^2\text{ V}^{-2}$).²⁰ The second contribution is due to the droplet deformation (i.e., depending on the surfactant monolayer rigidity) and hence linear in the droplet volume fraction ϕ_{nd} . However, not all of the droplets are isolated. A temperature- and volume fraction-dependent part forms aggregates. Droplet pairs give rise for an excess polarizability, and consequently aggregates lead to an additional contribution to the overall Kerr constant.^{21,22} This contribution scales with ϕ_{nd}^2 for sufficiently small droplet volume fractions. To evaluate the single droplet Kerr constant K_0 , which is here of interest, the measured Kerr constants are divided by their respective droplet volume fractions ϕ_{nd} and plotted against ϕ_{nd} (see Figure 1). Extrapolation to zero droplet volume fraction gives K_0 associated with droplet deformation, and the slope reflects the contribution K_a of the aggregates. This is shown in Figure 1 for a microemulsion containing varying concentrations of poly(oxyethylene) with a molecular weight of $M_w = 11\,000\text{ g mol}^{-1}$. With increasing polymer concentration the extrapolated value K_0 as well as the slope of the straight lines (i.e., K_a) decreases.

The polymer concentrations in the droplets were always very low ($\leq 12\text{ g L}^{-1}$) so that the influence of the dissolved polymer

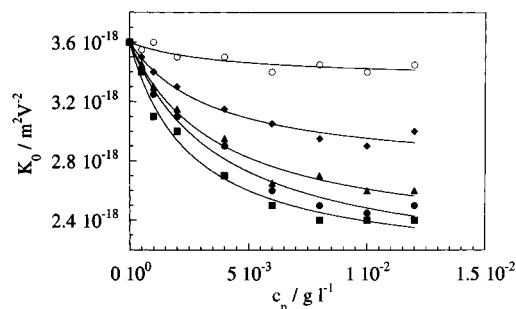


Figure 2. Single droplet Kerr constant K_0 as a function of polymer concentration c_p in the water droplets for various molecular weights of poly(oxyethylene). $M_w =$ (○) 1000, (◆) 3000, (▲) 6000, (●) 8000, and (■) $11\,000\text{ g mol}^{-1}$.

on the polarizability of the water cores of the droplets is negligible. Consequently, the change in K_a must be the result of a decreasing attractive interdroplet interaction due to the polymer in the droplets. This agrees with previously reported observations on similar systems.^{1,9}

The variation of K_0 with increasing poly(oxyethylene) concentration in the droplets is shown in Figure 2. The different curves refer to systems containing poly(oxyethylene) of different molecular weight. It can be easily seen that K_0 depends not only on the concentration of the polymer but also on the molecular weight. The Kerr constant K_0 associated with the droplet deformation is given for larger droplet sizes by

$$K_0 = Cr^3 \langle |u_{2m}|^2 \rangle \quad (1)$$

with r the radius of the droplets, $\langle |u_{2m}|^2 \rangle$ the mean square of the ellipsoidal fluctuation amplitude which is inversely proportional to the surfactant monolayer rigidity κ , and C a constant which can be calculated from the refractive indices and dielectric constants of the nanodroplets and the solvent.^{13,14} As already mentioned, due to the low concentration of the poly(oxyethylene), variations of C can be neglected. Consequently, the decrease of K_0 with increasing polymer concentration must be the result of either a decrease of the droplet radius or an increase of the elastic bending constant κ : a decrease in droplet dimensions, however, could be caused (i) by a higher density of the polymer solution in the droplets compared to a pure water droplet core or (ii) by a larger head group area of the surfactant at the interface due to interactions with the poly(oxyethylene).

In the low polymer concentration regime investigated the density of the water phase can be regarded as being constant (the density variation being below 1‰). A variation of the spontaneous curvature (or the head group area of the surfactants) must be the result of an interaction between short segments of the polymer chain (i.e., several monomeric units) and the surfactant molecules at the interface. Polymer/surfactant interactions influencing the spontaneous curvature should, therefore, depend only on the concentration and not on the molecular weight of the polymer. In Figure 2, however, clearly a molecular weight dependence is displayed. Furthermore, as already mentioned (see Experimental Section) light scattering investigations find within experimental accuracy the droplet radius of the nanodroplets to be constant, independent of the polymer content (see also refs 4 and 18).

Consequently, the observed decrease of the single droplet Kerr constant must be the result of a polymer-induced rigidification of the surfactant monolayer.¹² An increase of the surfactant monolayer's rigidity upon variation of molecular weight or concentration of poly(oxyethylene) is also in agreement with the decreasing rate constant of material exchange between

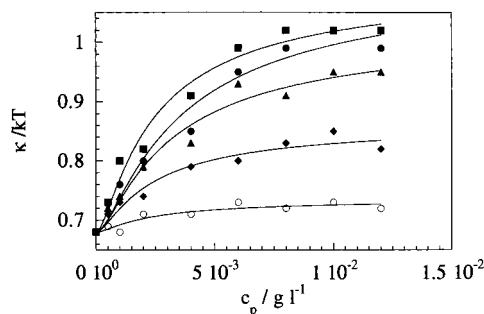


Figure 3. Rigidity of surfactant monolayer κ/kT as a function of poly(oxyethylene) concentration c_p in the droplets for various molecular weights. $M_w = (\circ) 1000, (\blacklozenge) 3000, (\blacktriangle) 6000, (\bullet) 8000$, and $(\blacksquare) 11\,000 \text{ g mol}^{-1}$.

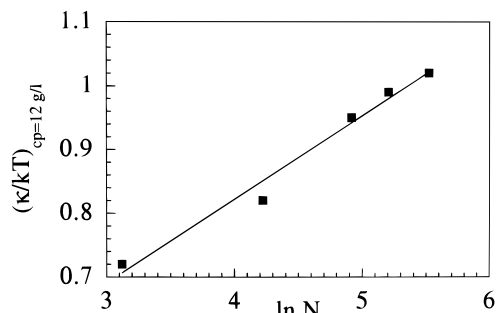


Figure 4. Rigidity of the surfactant monolayer κ/kT at $c_p = 12 \text{ g L}^{-1}$ as a function of the logarithmic degree of polymerization N of poly(oxyethylene).

colliding droplets observed by time-resolved fluorescence quenching on similar systems.^{5,9} Following the procedure of ref 13, the monolayer rigidity as a function of poly(oxyethylene) concentration can be calculated. The results are shown in Figure 3 for several molecular weights of the polymer. In good agreement with previous theoretical and experimental findings,^{13–15,23–32} the bending constant is found to be $\kappa = (0.68 \pm 0.1)kT$ for the pure polymer free microemulsion. With increasing polymer concentrations κ increases up to about $1kT$. This increase must be the consequence of the attractive interactions between poly(oxyethylene) and the anionic surfactant AOT, which lead to a polymer adsorption at the interface. A scaling analysis of the rigidity κ due to polymer adsorption at a surfactant interface¹² leads to

$$\Delta\kappa \propto \text{const} + \text{const}' \ln N + \text{const}'' \ln c_p \quad (2)$$

i.e., the variation of κ depends logarithmically on both the degree of polymerization N and the concentration c_p of the adsorbed polymer. As shown in Figure 3 a logarithmic fit is able to describe the concentration dependence for fixed N reasonably well. Figure 4 shows for a fixed polymer concentration $c_p = 12 \text{ g L}^{-1}$ a plot of κ as a function of $\ln N$. The predicted linear dependence holds fairly well, thus confirming the rigidification of the interface to be caused by polymer adsorption.

Conclusion

Kerr effect measurements are a powerful tool to determine the rigidity of the surfactant monolayer covering the nanodrop-

lets of a water-in-oil microemulsion. In this paper we applied this method for the first time on systems containing a water-soluble polymer confined to the interior of the water droplets. Attractive interactions between the polymer and the surfactant at the oil/water interface lead to a polymer induced rigidification of the surfactant monolayer; i.e., the polymer/surfactant interactions can be used as a sensitive method to influence the elasticity of the surfactant monolayer in microemulsions.

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