Experimental report

Proposal:	9-12-5	571			Council: 4/2019		
Title:	Interactions of negatively chargedO/W Microemulsion Droplets with Polyelectrolytes						
Research area: Soft condensed matter							
This proposal is a new proposal							
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Samples:	decane						
	TDMAO C14H29NO(CH3)2						
	1-hexanol						
	JR400 (C25H48O14NCl)n						
Poly-(diallyldimethylammonium chloride) (PDADMAC)							
quarternized Chitosan							
	SDS C12H2	25NaO4S					
Instrument			Requested days	Allocated days	From	То	
D11			2	1	17/01/2020	18/01/2020	

Abstract:

D33

Admixing polyelectrolytes to oppositely charged colloids allows to control structure and rheology of the system. Many applications use microemulsions as carriers for drug molecules, pollutants, reactants etc that otherwise couldn't be dispersed in the solvent. It is therefore of great importance to investigate the behavior of 'loaded carriers' as it can be different to that of normal (empty) micelles. Oil-in-water microemulsion droplets already contain a substantial amount of hydrophobic loading and can be studied in detail by SANS measurements, because of the good contrast conditions and having an appropriate size range. While previous studies focused on positively charged microemulsion droplets, we now want to investigate the interactions of negatively charged droplets with positively charged polyelectrolytes as this combination is much more relevant in biological systems. The important parameters to be addressed will be the charge density on the droplets and the nature of the polyelectrolyte, with a focus on biopolymers. The experiments shall give interesting insights into the complexation mechanism, as it is important for controlled uptake, delivery and release of the carriers.

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Interaction of hydrophobically modified thermo-responsive polymers with bio-compatible microemulsions

Experimental report for experiment 9-12-571 at D11 (Jan. 17–18, 2020) Berlin, March 31, 2020

Experimental setup and samples We studied the behaviour of oil in water ($^{O}/w$) microemulsion droplets (ME) in interaction with hydrophobically modified thermo-responsive (HMTR) polymers. The ME droplets were composed of isopropyl palmitate (IPP) as oil, poly(ethylene oxide) (20) sorbitan monolaurate (Tween20) as surfactant and 2-ethylhexyl-glycerin (EHG) as cosurfactant. HMTR polymers are composed of a C₁₂ end-cap, about 200 units of *N*-dimethylacrylamide (DMA) and about 20 or 40 units of a thermo-responsive monomer with a lower critical solution temperature (LCST). The focus was set to the investigation of the temperature dependency for varying HMTR polymer concentration. It includes six HMTR and the reference polymer as well as three polymer concentrations between 0.5 and 2.0 %_{wt}.

Small-angle neutron scattering (SANS) measurements were performed at the instrument D11. We used a neutron wavelength of 6.0 Å and three configurations with detector positions of 1.4, 8.0 and 39 m and collimations of 4, 8 and 40.5 m, respectively. The explored q space was in the range of 0.002–0.4 Å⁻¹. All samples were measured in round 1 mm Hellma QS quarz cuvettes and a round aperture of 15 mm was used.

The samples were prepared from stock solutions by mixing the corresponding amounts. The final ME concentration was prepared as 50 mM, 50 mM and 20 mM of Tween20, EHG and IPP, respectively. The polymer concentrations were set to 0.5, 1.0 and 2.0 $\%_{wt}$. All samples were prepared in filtered D₂O.

Experimental data The reference ME and two HMTR polymer and the reference polymer are shown in the following Fig. 1–4. The selected polymers were MH005 (reference, DMA_{213}) and the two HMTR polymers with the PNIPAM block MH007 ($DMA_{213}NIPAM_{11}$) and MH015 ($DMA_{213}NIPAM_{34}$). The ME scattering data show a structure factor for all three measured concentration. With increasing temperature the structure factor decreases due to the decreasing hydration of ethylene oxide units in the head group of Tween20. The same decrease of the structure factor is also seen for the samples with polymer added. The focus of our work lies in the differences in the structure factor between bare ME and ME with added polymer. These small changes can be enhanced by calculating an effective structure factor.



Figure 1: Scattering data are displayed of the used ME for three different concentrations and temperatures. The concentrations are stated as "Cx-y-z" where x, y and z correspond to the concentration in mM of Tween20, EHG and IPP, respectively.



Figure 2: Scattering data of the HMTR polymer MH005 (DMA₂₁₃) with ME are shown with subtracted background. Left side: Variation of the polymer concentration is plotted for 0.5, 1.0 and 2.0 $\%_{wt}$ stated as C050, C100, C200, respectively. The ME concentration was held constant at about C50-50-20 (see Fig. 1). Right side: Variation of the ME concentration is plotted for three concentration. The polymer concentration was held constant at of 1.0 $\%_{wt}$.



Figure 3: Scattering data of the HMTR polymer MH007 (DMA₂₁₃NIPAM₁₁) with ME are shown with subtracted background. Left side: Variation of the polymer concentration is plotted for 0.5, 1.0 and $2.0 \%_{wt}$ stated as C050, C100, C200, respectively. The ME concentration was held constant at about C50-50-20 (see Fig. 1). Right side: Variation of the ME concentration is plotted for three concentration. The polymer concentration was held constant at of $1.0 \%_{wt}$.



Figure 4: Scattering data of the HMTR polymer MH015 (DMA₂₁₃NIPAM₃₄) with ME are shown with subtracted background. Left side: Variation of the polymer concentration is plotted for 0.5, 1.0 and $2.0 \%_{wt}$ stated as C050, C100, C200, respectively. The ME concentration was held constant at about C50-50-20 (see Fig. 1). Right side: Variation of the ME concentration is plotted for three concentration. The polymer concentration was held constant at of $1.0 \%_{wt}$.