Experimental report

02/03/2019

Proposal: **9-12-539**

Council: 4/2018

Title: Understanding the Origins of Enhanced Viscosities in Oppositely Charged Polyelectrolyte/Surfactant Mixtures

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Sodium Octyl Sulphate (deuterated)
Sodium Octyl Sulphate (Hydrogenated)
Sodium Tetradecyl Sulphate
Sodium Tetradecyl Sulphate (deuterated)
JR 400 (cationically modified cellulose)

Instrument	Requested days	Allocated days	From	To
D11	2	0		
D33	2	1	20/09/2018	21/09/2018
D22	2	0		
IN15	5	4	12/09/2018	16/09/2018

Abstract:

Mixtures of oppositely charged surfactant and polyelectrolyte show rich aggregation behaviour that varies over a large size range. Some of these systems allow to control the rheological properties of water-based systems over a broad range of viscosities and relaxation times by the addition of rather small amounts of material. Accordingly they have many applications e.g. in cosmetics, detergency, and drug delivery. In the semi-dilute regime a strong increase in viscosity is observed as surfactant is added to the cationic, cellulose based polyelectrolyte JR 400 as long as the charge ratio Z (polyelectrolyte charges/ surfactant charges) between polyelectrolyte and surfactant is larger than 1, and the alkyl chain of the surfactant is sufficiently long. Here, we want to elucidate the structural differences between a system in which the viscosity is increased and a system where it is not affected by the addition of surfactant to better understand the underlying mechanisms.

Experimental Report for: Understanding the Origins of Enhanced Viscosities in Oppositely Charged Polyelectrolyte/Surfactant Mixtures (Experiment No. 9-12-539)

Complexes of oppositely charged surfactant and PE exhibit rich aggregation behaviour. Furthermore they allow to modify the rheological properties of the corresponding water-based systems largely already at relatively moderate concentrations. Accordingly they have many applications e.g. in cosmetics, detergency, and drug delivery[1]. Typically in the semi-dilute regime a strong increase in viscosity is observed as surfactant is added to the PE as long as an excess of polyelectrolyte charges is present. It is known, that the increase in viscosity is accompanied by the formation of mixed PE/surfactant aggregates, interconnecting several PE chains. In the case of the system JR 400/SDS the aggregates have been shown to be rodlike[2, 3]. Here, we varied the length of the surfactant alkyl chain and measured samples with SOS (sodium octyl sulphate) and STS (sodium tetradecylsulphate) in both hydrogenated and deuterated form to study the influence of the surfactant chain length with both SANS and NSE after viscosity measurements had shown that an increase in viscosity with STS is observed, while SOS has almost no influence.

SANS data with STS show similar rodlike aggregates (Q^{-1} slope) as had been observed for SDS before (see fig. 1, top), while with SOS very little changes relative to the pure polyelectrolyte JR 400 can be observed ((see fig. 1, bottom)). Using deuterated STS, it can be seen that the Q^{-1} slope extents over a longer Q range compared to the pure PE ((see fig. 1, top right)), meaning that the PE chains in the aggregates are stretched. Having observed little changes with hydrogenated surfactant, unsurprisingly only small changes can be observed using deuterated SOS ((see fig. 1, bottom right)).

NSE measurements with hydrogenated STS yield apparent diffusion coefficients (D_{app}) in agreement with the diffusion of rodlike aggregates with a length of a few ten *nm*. Using deuterated surfactant, significantly higher D_{app} (see fig. 2, left). Whether this is only because of the higher relative intensity weight of free PE chains or if the PE chains in the aggregates are free to move will be revealed by a more detailed analysis, later. In agreement with the SANS data, the D_{app} of samples with both dSOS and hSOS are left more or less unchanged compared to the pure PE (see fig. 2), indicating that there are just individual surfactant molecules adsorbed to the PE chain, which do not significantly influence its dynamics.

These findings clearly indicate that the *nm* sized rodlike aggregates which we see in STS and SDS are crucial for an enhanced viscosity in oppositely charged PE surfactant complexes and no change in viscosity is observed if no aggregates are formed.

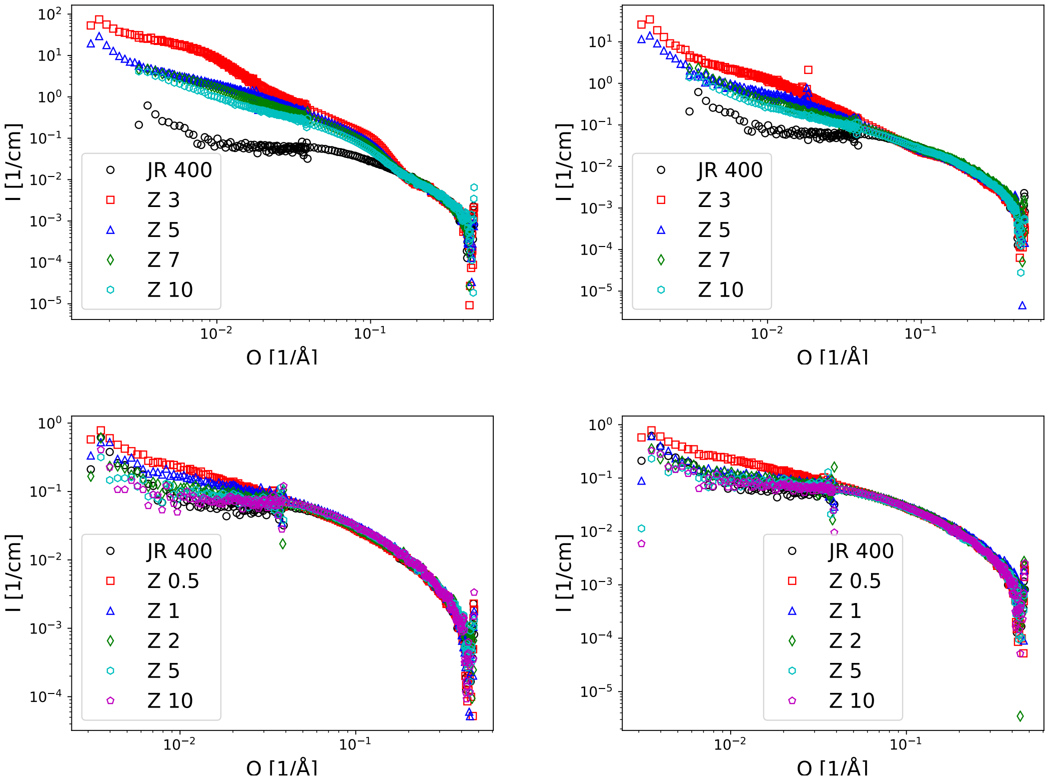

Figure 1: SANS curves of 1 wt% JR 400 with STS (top left), dSTS (top right), SOS (bottom left), dSOS (bottom right). Rodlike surfactant aggregates are formed with STS but not with SOS.

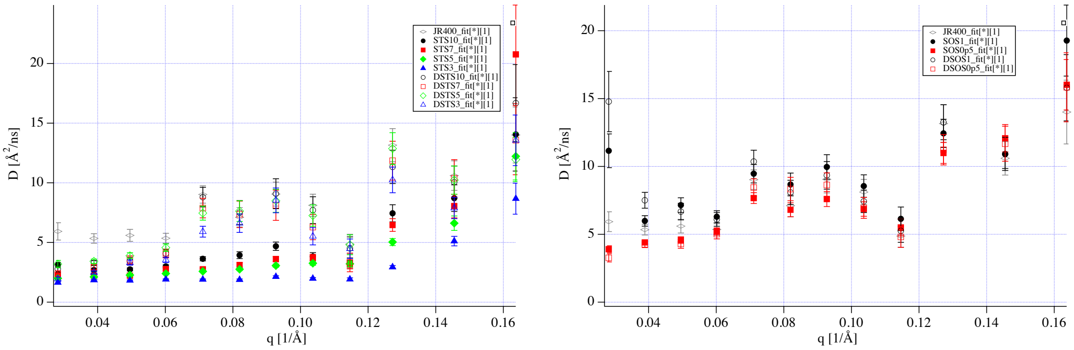

Figure 2: Left: Apparent diffusion coefficient of 1 wt% JR 400/STS; right: Apparent diffusion coefficient of 1 wt% JR 400/SOS, full symbols: hydrogenated surfactant, open symbols: deuterated surfactant. The aggregates formed with STS reduce the apparent diffusion coefficient, while only very small changes are observed with SOS.

References

[1] L. Chiappisi, I. Hoffmann, and M. Gradzielski. Complexes of oppositely charged polyelectrolytes and surfactants - recent developments in the field of biologically derived polyelectrolytes. *Soft Matter*, 9:3896–3909, 2013.

[2] I. Hoffmann, P. Heunemann, S. Prévost, R. Schweins, N. J. Wagner, and M. Gradzielski. Self-aggregation of mixtures of oppositely charged polyelectrolytes and surfactants studied by rheology, dynamic light scattering and small-angle neutron scattering. *Langmuir*, 27:4386–4396, 2011.

[3] I. Hoffmann, B. Farago, R. Schweins, P. Falus, M. Sharp, and M. Gradzielski. Structure and dynamics of polyelectrolytes in viscous polyelectrolyte-surfactant complexes at the mesoscale. *Europhys. Lett.*, 104:28001–, 2013.

[4] R. Michel, T. Plostica, L. Abezgauz, D. Danino, and M. Gradzielski. Control of the stability and structure of liposomes by means of nanoparticles. *Soft Matter*, 9:4167–4177, 2013.