Experimental Report

13/01/2014

Proposal:	**9-12-327**	**Council:**	10/2012

Title: Mesoscopic dynamics of the polyelectrolyte in oppositely charged polyelectrolyte/surfactant systems studied by contrast variation NSE

This proposal is resubmission of: 9-12-311

Researh Area: Soft condensed matter

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Samples:
d-SDS, C12D25SO4 Na
h-SDS, C12H25SO4 Na
JR400, approx: C15.7H48.2O11.1N0.23 Cl0.23
D2O
pDADMAC, C8H16NCl

Instrument	Req. Days	All. Days	From	To
IN15 Standard	5	5	29/04/2013	02/05/2013

Abstract:

Oppositely charged polyelectrolyte/surfactant systems show complex behaviour with respect to their structural and dynamical features. Especially the dynamic properties, which are related to their interesting rheological features, are still only rather poorly understood. A key role here plays the polyelectrolyte but its individual mesoscopic dynamics is difficult to study, except by the unique option of employing NSE and the concept of contrast variation. By using d-SDS or h-SDS and protiated JR 400 and PDADMAC as polycation we will be able to see individually the dynamics of the whole complex and of the polycation alone. A test measurement with d-SDS and JR 400 suggests that the polyelectrolyte is free to move within the aggregates but is hindered in its motion on times scales long enough for it to explore the limits of the aggregate. With this experiment we intend to further investigate this behaviour and explore its dependence on polyelectrolye charge density. It is to be expected that this NSE experiment can shed light on the mesoscopic dynamics of such systems that can not be obtained from any other experimental method.

Experimental Report for: Mesoscopic dynamics of the polyelectrolyte (PE) in oppositely charged polyelectrolyte/surfactant systems studied by contrast variation NSE (Experiment No. 9-12-327)

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]. If an excess of surfactant is present, the viscosity is strongly reduced.

In this experiment, we were investigating the dynamics of samples with an excess of surfactant charges. Macroscopically, it is observed that the viscosity drops by up to 4 orders of magnitude compared to samples with an excess of PE charges. SANS measurements have shown the presence of spherical micelles. In addition they have shown, that the PE maintains the more elongated shape it has, when adding smaller amounts of surfactants. Therefore, it is not clear from the SANS measurements, if the rodlike aggregates are still present and the observed spherical aggregates are simply free spherical micelles or if the spherical surfactant aggregates are actually attached to the PE. In other more dilute systems, the presence of a peak at high Q can show that the surfactant forms a necklace of pearls along the PE chain, but in these rather concentrated samples the position of the structure peak should occur at a very similar Q, anyway. Therefore, we have performed NSE measurements with both hydrogenated and deuterated SDS (h-SDS and d-SDS). This allowed us to highlight the scattering from either the surfactant (h-SDS) or the PE (d-SDS). The measurements showed that the obtained diffusion coefficient is essentially the same in both cases and higher than the diffusion coefficient that has been observed previously for the viscous samples (see fig. 1, left). Two conclusions can be drawn from these findings. I) The spherical micellar aggregates observed in SANS are attached to the PE chains. II) The rodlike aggregates are most likely to be destroyed. These findings support the previously suggested mechanism for the reduction of viscosity upon addition of an excess of surfactant[2]: With the increase of the surfactant concentration and an increase of the surfactant/PE ratio in the aggregates, the probability for aggregates involving different PE chains is reduced and therefore the mixed aggregates are less likely to interconnect different chains.

Phospholipid vesicles (liposomes) are another class of systems which are of potential interest for targeted drug delivery, as they can host both hydrophobic (in the bilayer) and hydrophilic compounds (in their aqueous

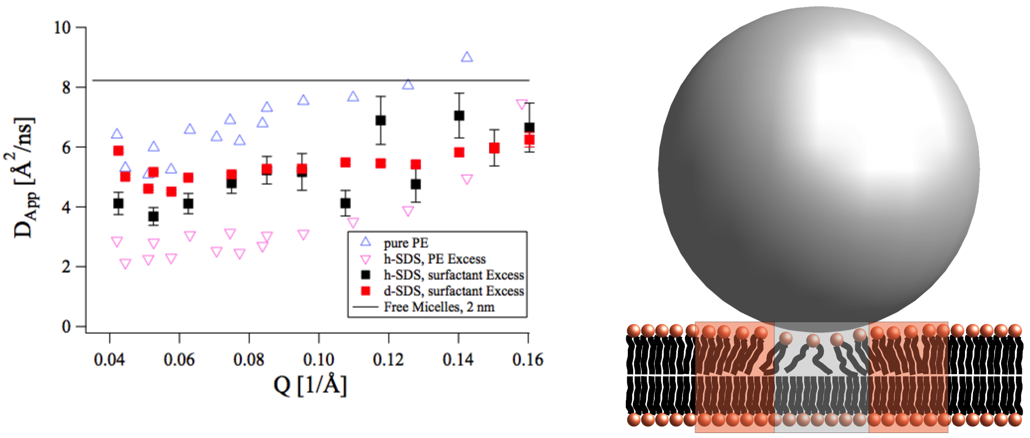

Figure 1: Left: Apparent diffusion coefficient of 1 wt% JR 400/SDS mixtures with a tenfold surfactant excess with hydrogenated (red) and deuterated (black) SDS, the values are roughly the same. Right: Sketch of a NP adsorbed on a phospholipid bilayer. Directly at its adsorption site, undulation movements of the membrane are suppressed (grey region), in the adjacent regions, the membrane is softened as its structure is perturbed (orange region).

interior). It has been shown previously, that the addition of silica nanoparticles (NPs) can affect the stability of such vesicles[4]. In addition they can serve as simple model systems for cells and the study of the interactions between NPs and liposomes may shed some light on questions concerning the toxicity of NPs.

Therefore we investigated samples liposomes with and without added NPs with the aid of NSE. The data could be explained in the framework of the Zilman-Granek theory and it was found, that the addition of NPs causes a slight softening of the membrane by about 10%. Intuitively it might be assumed, that the membrane becomes stiffer, as undulation movements should be suppressed at the adsorption site of the NP. However our data suggests, that the NPs are a perturbation to the structure of the bilayer and therefore cause a softening (see fig. 1, right). These 2 opposing effects might also explain, why the overall effect is rather weak.

References

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[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.