Experimental report

20/04/2020

Proposal:	**9-12-490**	**Council:**	10/2016

Title: Biofriendly Multilamellar Vesicles(MLVs) Controlled by Admixing Modified Chitosan

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: $C_{12}H_{25}(EO)_5CH_2COONa$

Instrument	Requested days	Allocated days	From	To
D11	3	2	16/06/2018	18/06/2018

Abstract:

By the addition of chitosan one can control the number of shells in multilamellar vesicles (MLVs) of alkylethoxycarboxylates, which are mild surfactants. However, due to the solubility of chitosan this is only possible at lower pH. In the planned experiments this pH range therefore is to be extended by the use of quaternized chitosan, which is soluble at any pH. By a systematic variation of pH, mixing ratio, degree of quaternization and type of vesicle forming surfactant, we want to gain a comprehensive picture of the MLVs formed in these systems. This can be achieved in a unique fashion by SANS and then allows to have predictive power over the behaviour of such systems. This is highly important as via the number of shells and the thickness of the single bilayers one should be able to control in a systematic fashion the permeability of the MLVs, which is a key property for their use as delivery systems. As such they are highly interesting as they have strongly pH dependent properties and thereby can be triggered by pH on demand, once their structures are known, which is the key aim of this proposal.

Biofriendly Multilamellar Vesicles(MLVs) Controlled by Admixing Modified Chitosan

Experiment Report for experiment 9-12-490 at D11 (June 16-18, 2018)
Berlin, April 20, 2020

The main purpose of this study was to extend the applicable pH-range of chitosan-alkylethoxycarboxylate surfactants multilamellar vesicles (MLVs) from low pH to the full pH range by replacing chitosan (CS) with N,N,N-tri-methyl quaternized chitosan (tmCS). Such systems are expected to have high potential for applications in biorelated fields, e.g. cosmetic and pharmaceutical formulations or in detergency; especially they are expected to posses marked pH-dependent behavior.

We wanted to have a comprehensive view of the MKVs formed of such systems by variation of pH, mixing ratio, degree of quaternization (DQ) and type of vesicle forming surfactant. We expected from this SANS beamtime to elucidate how the structure of the MLVs is controlled by the surfactant/polyelectrolyte mixture and what is the detailed effect of pH. Here we defined the charge mixing ratio $Z = [-]_{\mathrm{Surfactant}} / [+]_{\mathrm{xCS}}$.

Data analysis

As first step, we compared the complex structures of C12E4.5CH2COOH/Na (RLM45, MW: 444 Da) surfactant with CS and tmCS respectively at low pH. SANS measurement successfully proved that both had formed same structure MLVs with layer-layer distance of about 7 nm at pH 4.0, as shown in Fig 1.

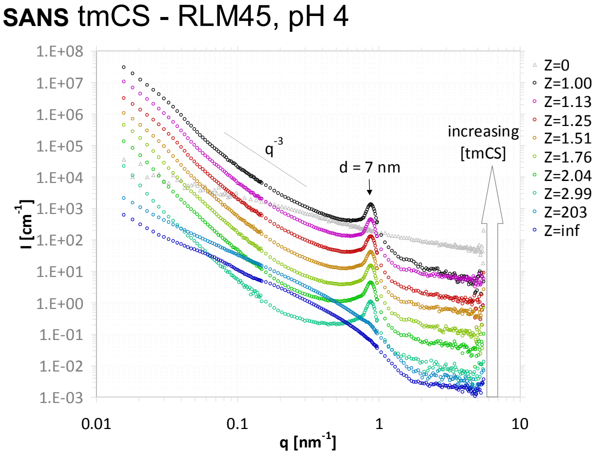
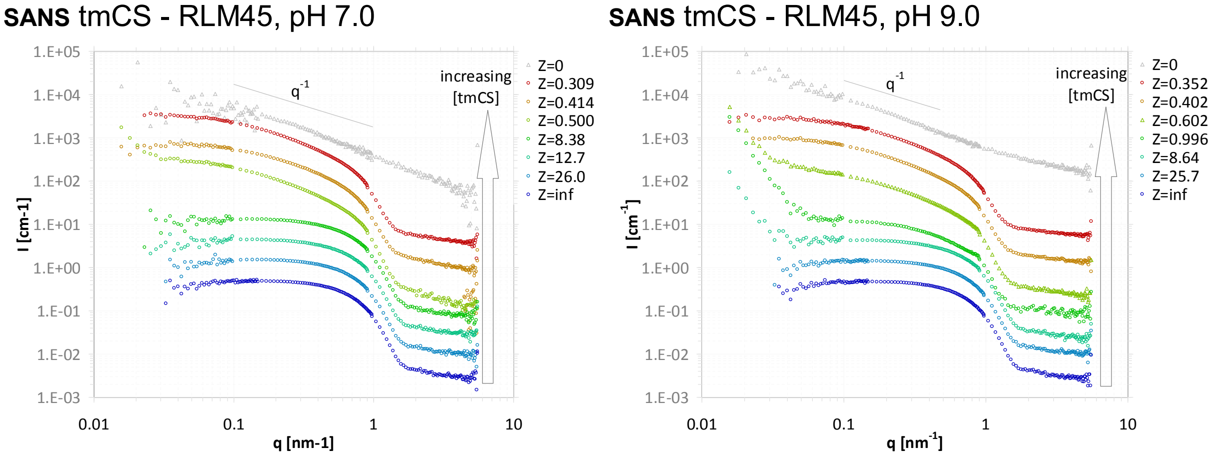


Fig. 1: *SANS curves of mixture of 0.2 mol/l RLM45 and variable mixing ratio to CS/tmCS at pH 4.0, defined as* $Z=[-]_{\mathrm{Surfactant}}/[+]_{xCS}$ *at pH 4.0.*

Subsequently we raised the pH and investigated the complex structure at high pH of 7.0 and 9.0. The result is shown in Fig. 2.

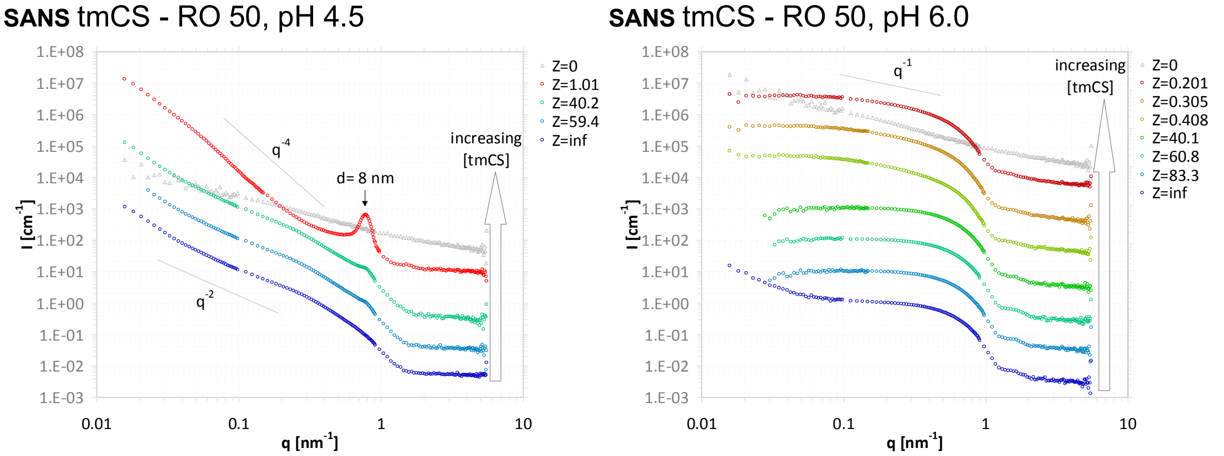

SANS tmCS - RLM45, pH 7.0

SANS tmCS - RLM45, pH 9.0

Fig. 2: *SANS curves of mixture of 0.2 mol/l RLM45 and variable mixing ratio to tmCS at pH 7.0 and 9.0*

At higher pH, the carboxyl groups become negatively charged and the surfactant forms were changing from MLV to micelles, which were orientated by the positive polymer chain to form 1-D structures. The size and MW of the complex structures were reduced. By pH 9 it was observed at very low q some big aggregates, which should be further analyzed.

In the next step, we changed the HLB of the surfactant by replacing the RLM45 with CH3(CH2)15/17:1(OCH2CH2)5OCH2COOH (RO 50, MW: 711 Da), which had about 33% longer alkyl chain. The result is shown in Fig. 3.

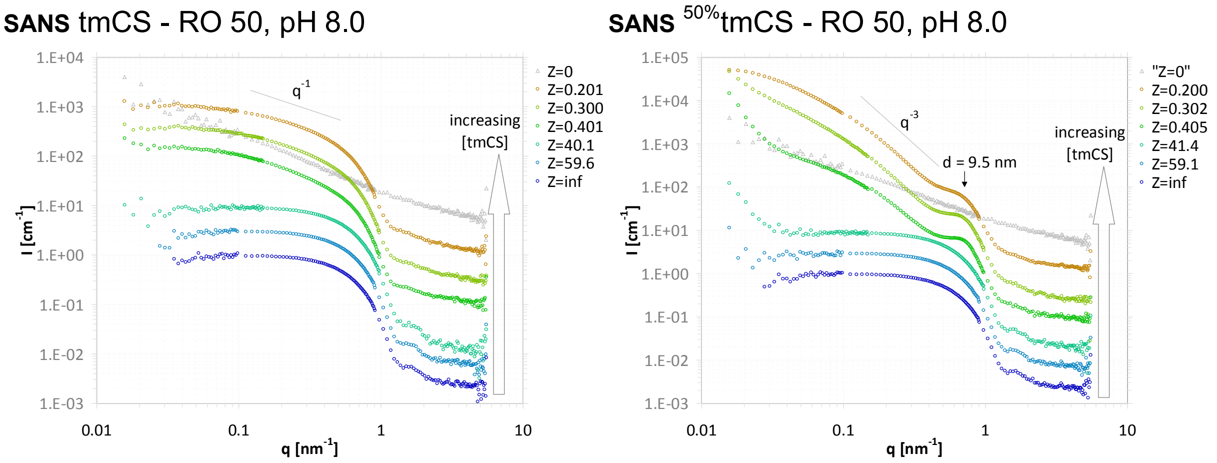

SANS tmCS - RO 50, pH 4.5

SANS tmCS - RO 50, pH 6.0

Fig. 3: *SANS curves of mixture of 0.2 mol/l RO50 and variable mixing ratio to tmCS at pH 4.5 and 6.0*

A tendency of structure change from lamella/vesicle to micelle was observed. The MW of the structure was larger than that of RLM 45 series, due to the increased hydrophobic interaction. The layer to layer distance was about 8 nm, which was bigger than for the lower hydrophobic component.

We also check the influence of the quaternization degree (DQ) of tmCS. The trend is shown in Fig. 4.


SANS tmCS - RO 50, pH 8.0

SANS $^{50\%}$tmCS - RO 50, pH 8.0

Fig. 4: *SANS curves of mixture of 0.2 mol/l RO50 and variable mixing ratio to tmCS of different DQ at pH 8.0*

By reducing DQ, much bigger aggregates were observed at smaller z. The higher q-range showed that increased hydrophobicity resulted in additional intermolecular structuring.

Conclusion

As conclusion, with this SANS beamtime we successfully investigated the complex structure of our surfactant-chitosan system, and evaluated different factors to fine-tune these structures. The results are coincided with our expectation in the proposal. With further analysis we should be able to gain deep-in detailed information. Based on that a guideline for designing such complex systems with tunable structures can be achieved in the future in an efficient way.

Acknowledgement

We would like to thank ILL (D11) for this beam time and all the participants for the fruitful discussions.