EUROPEAN SYNCHROTRON RADIATION FACILITY

ESRF User Office

BP 220, F-38043 GRENOBLE CEDEX, France

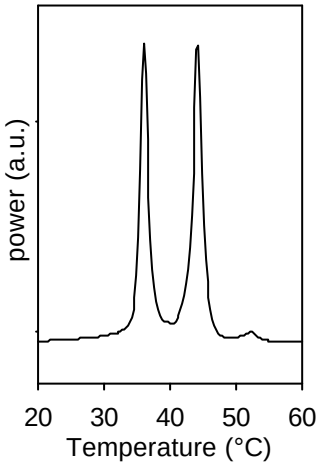
Delivery address: 6 rue Jules Horowitz, 38043 GRENOBLE, France

Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: useroff@esrf.fr; web: http://www.esrf.fr

Application for beam time at ESRF – Experimental Method

Aims of the experiment and scientific background

Vesicles are composed of closed bilayer shells of natural of synthetic lipids. Because of their similar structure they are used in research on cell membrane processes.[1] Besides they were successfully applied as gene or drug delivery agents.[2] Needless to say that it is important to understand their physical properties. In spite of the great number of studies, the gel to liquid-crystalline phase transition of lipids is not completely understood. In the figure the differential scanning calorimetry (DSC) thermogram of a 5 mM dioctadecyldimethylammonium bromide (DODAB) in water is shown. The behaviour was observed before[3] and is surprisingly complicated for a system containing only one surfactant. It is the aim of the proposed experiments to characterize these transitions. The melting of the alkyl-chains may occur in steps or there may be a structural reorganization involved.



After sonicating the DODAB dispersion, a similar behaviour was observed. However, a DSC scan of a 5 mM dioctadecyldimethylammonium chloride (DODAC) dispersion showed only one peak (results not shown), indicating a counterion dependence of the melting process.

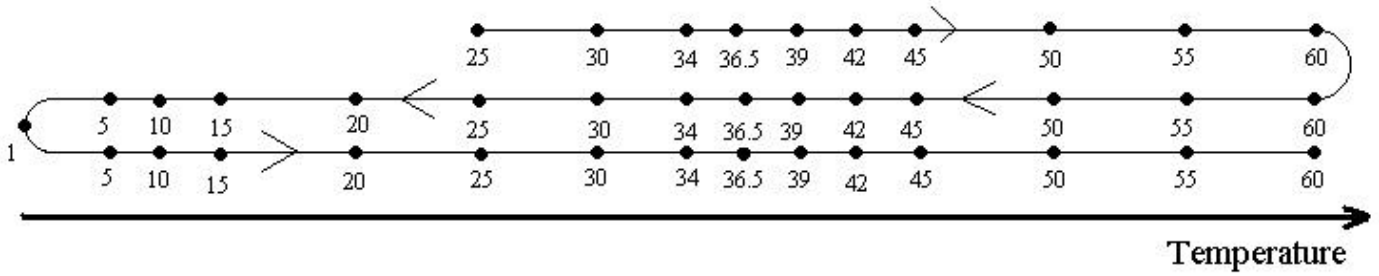
Experimental method

For this project, one needs to combine first, WAXS to probe the local organization of the alkyl-chains and second, SAXS to investigate structural reorganisation on the nanometer length-scale. SAXS is useful in particular to find structure changes mainly of the unilamellar sonicated vesicles which are about 50 nm in size.[4] The bilayer thickness can be derived from the SAXS spectrum in order to detect phenomena like interdigitation or tilting of the alkyl chains.

This specific behaviour described above was only observed at relatively low concentrations which makes the use of synchrotron radiation necessary. The surfactant fraction will be as low as 0.3 %(v/v).

Samples are prepared by hydration of DODAB at 60°C under continuous stirring. We will prepare the samples at ESRF. We will bring all the necessary equipment.

First we will cool the freshly prepared 5 mM sample to 25 °C. Then we will record both SAXS and WAXS spectra according to the following scheme. The black dots represent measurements. Two different fresh samples are subjected each to one of the 2 scans. The scanrate can be 0.5 °C/min, corresponding to 1 measurement every 10 minutes, in the cooling part and 1 °C/min, corresponding to 1 measurement every 5 minutes, in the heating part.



We propose to investigate 5 mM DODAB dispersions, both sonicated and unsonicated and a 5 mM DODAC dispersion according to the scheme above. Thus on each of the three dispersions there will be 39 measurements performed.

Results expected

There are 2 possible hypothesis in our opinion.

The DSC-peak at 36 °C could be the first step in the melting of the alkyl chain. In this case there will be no structural reorganisation, and thus no change in the SAXS spectrum. The WAXS-spectrum on the other hand is severely affected by the state of the alkyl chains.

The DSC peak at 36 °C could be a structural reorganisation of the DODAB vesicles. In this case the state of the alkyl chains and thus also the WAXS spectrum will be unaffected. SAXS is in this case the ideal tool to identify the changes.

References

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3. Blandamer, M.J.; Briggs, B.; Cullis, P.M.; Green, J.A.; Waters, M.; Soldi, G.; Engberts, J.B.F.N.; Hoekstra, D. (1992). Differential scanning microcalorimetric study of vesicles in aqueous solutions formed by dimethyldioctadecylammonium bromide. Journal of the Chemical Society - Faraday Transactions, 88(23), 3431-3434.

4. Cocquyt, J.; Olsson, U.; Olofsson, G.; Van der Meeren, P. (2004). Temperature quenched DODAB dispersions: fluid and solid state coexistence and complex formation with oppositely charged surfactant. Langmuir, 20(10), 3906-3912.