Experimental report

09/02/2016

Proposal: 9-12-402 **Council:** 10/2014

Title: Using SANS to understand the behaviour of surfactants at oil/sugar interfaces in chocolate

Research area: Physics

This proposal is a new proposal

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Samples: sucrose
DPPE/DPPC
PGPR
triglcerides

Instrument	Requested days	Allocated days	From	To
D33	2	2	25/04/2015	27/04/2015

Abstract:

The high dynamic range diffractometer will be used to measure the SANS from mixtures of oil and sucrose as a model for molten chocolate. The oil and sucrose will be contrast matched such that the SANS is dominated by the scattering from the lipid surfactant components found in chocolate (DPPC/DPPE) and the polymeric surfactant PGPR. The ultimate goal is to link the interfacial structure to the rheological properties, which is relevant to processing and mouth feel.

SANS studies of Model chocolate - Report

Experimental details: SANS studies were carried out on a 65% (w/w) sucrose suspension in sucrose-matched oil with surfactants, model chocolate, on the D33 instrument at ILL, Grenoble. For the oil phase triolein was doped with 30.5% tributyrin. Choosing a deuterated tributyrin enabled the oil phase to be contrast matched to the sucrose phase, eliminating the scattering from the sucrose/oil interface. Tributyrin was chosen as it is found in fat and the deuterated version is easily synthesised. The sucrose used was supplied by Mars UK with mean particle size of 8 μm. The samples, with a toal weight of 900 mg, were produced by mixing the required amounts of ingredients (65% sucrose, 34.2%-35% d-oil and 0-0.8%surfactants) and then subjecting them to high shear using an IKA disperser for ∼2 mins till a smooth paste was obtained. Single and binary mixtures of the surfactants were studied, shown in the table below.

	Lecithin	PGPR	DPPC	DPPE
Lecithin	(0.2), (0.6), (0.8)	(0.2, 0.6), (0.4, 0.4)		
PGPR		(0.2), (0.5), (0.8)		
DPPC		(0.2, 0.3), (0.35, 0.15)	(0.15), (0.3), (0.5)	
DPPE		(0.2, 0.3), (0.35, 0.15)	(0.25, 0.25)	(0.15),(0.3),(0.5)

The concentrations in the table below are weight percentages of surfactants in the total weight of the sample. The concentrations of binary mixtures have the PGPR composition first followed by the concentration of the lipid.

Rheological observations of the samples: The sucrose in d-oil sample without any surfactant is very grainy like a dried paste, it does not flow. Addition of any of the above surfactant dissolved the grains to form a homogenous paste. PGPR makes the suspension flow easier and addition of combination of PGPR with lecithin or DPPC makes it extremely runny, as they reduce the both the viscosity and yield stress. Lecithin and DPPC reduce the viscosity of the suspension and so does DPPE however not to the same observable extent.

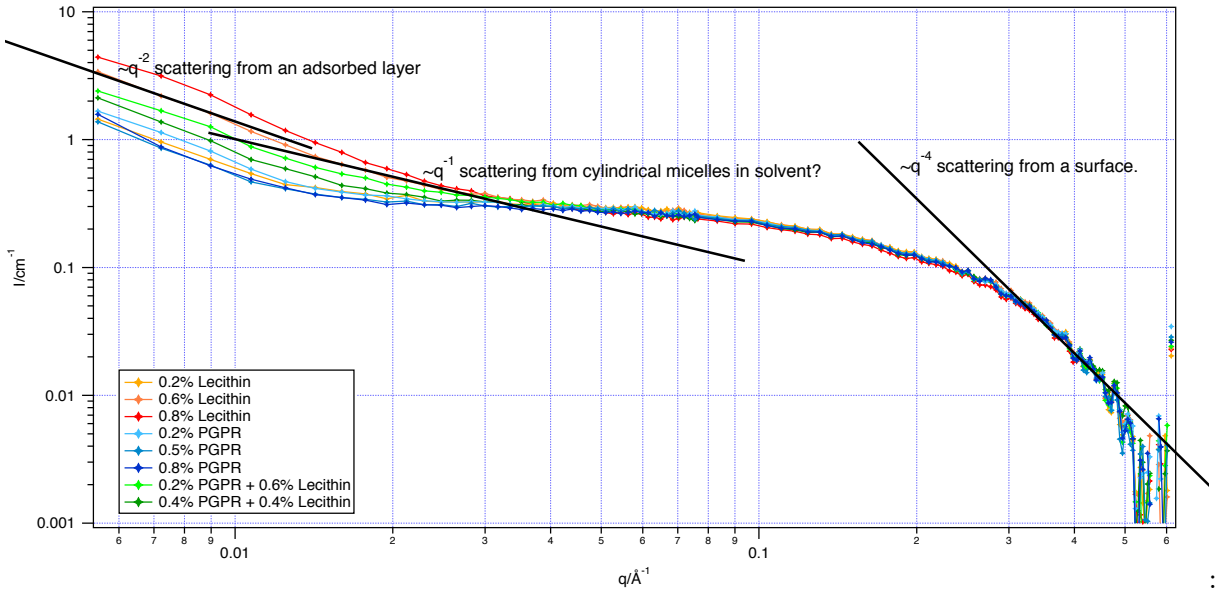

Figure 1: SANS data for 65% w/w sucrose/oil suspensions with 0.2, 0.6, 0.8% Lecithin, 0.2, 0.5, 0.8% PGPR and 0.2% PGPR+ 0.8% Lecithin, 0.4% PGPR+0.4% Lecithin.

Qualitative analysis of the data: For analysis of the data, we subtracted the high q, 0.56 Å^{-1}< q < 0.6 Å^{-1}, background scattering for each sample as shown in figure 1. For scattering from sucrose/oil suspensions with Lecithin, DPPC and DPPE, apart from the lowest

concentrations, we observe three regions: a q^{-4} region associated with the sucrose/oil interface which can be used to get the surface area of the interface; a q^{-2} region associated with an extended 2-D interfacial layer that could be the layer of adsorbed surfactant which can be used to get knowledge about the structure adopted by the surfactant at the interface; and a q^{-1} region which could be due to cylindrical micelles in the system, caused by the presence of water or other components, or might be the transition of the q^{-2} to a flat region. For suspensions with PGPR and the lowest concentration of Lecithin, DPPC and DPPE the q^{-4} and q^{-2} regions are observed. However the q^{-1} region is not observed, which suggests that no cylindrical worm-like micelles are present in these suspensions. Also, it was observed that increasing the concentration of Lecithin, DPPC and DPPE increased low 'q' scattering, whereas when the concentration of PGPR was increased a decrease in low q scattering was observed, possibly because PGPR is soluble in the oil phase.

Quantitative analysis of the data: For quantitative analysis of the data, I adopted a Kratky Porod type model as used by King *et al.*[1]. Subtractiing the 0.2% lecithin model chocolate data from the 0.6% and 0.8% lecithin model chocolate and doing similar analysis for DPPC and DPPE based model chocolate, we get linear fits for q^2*I vs q^2 at low 'q' validating Kratky Porod type analysis.

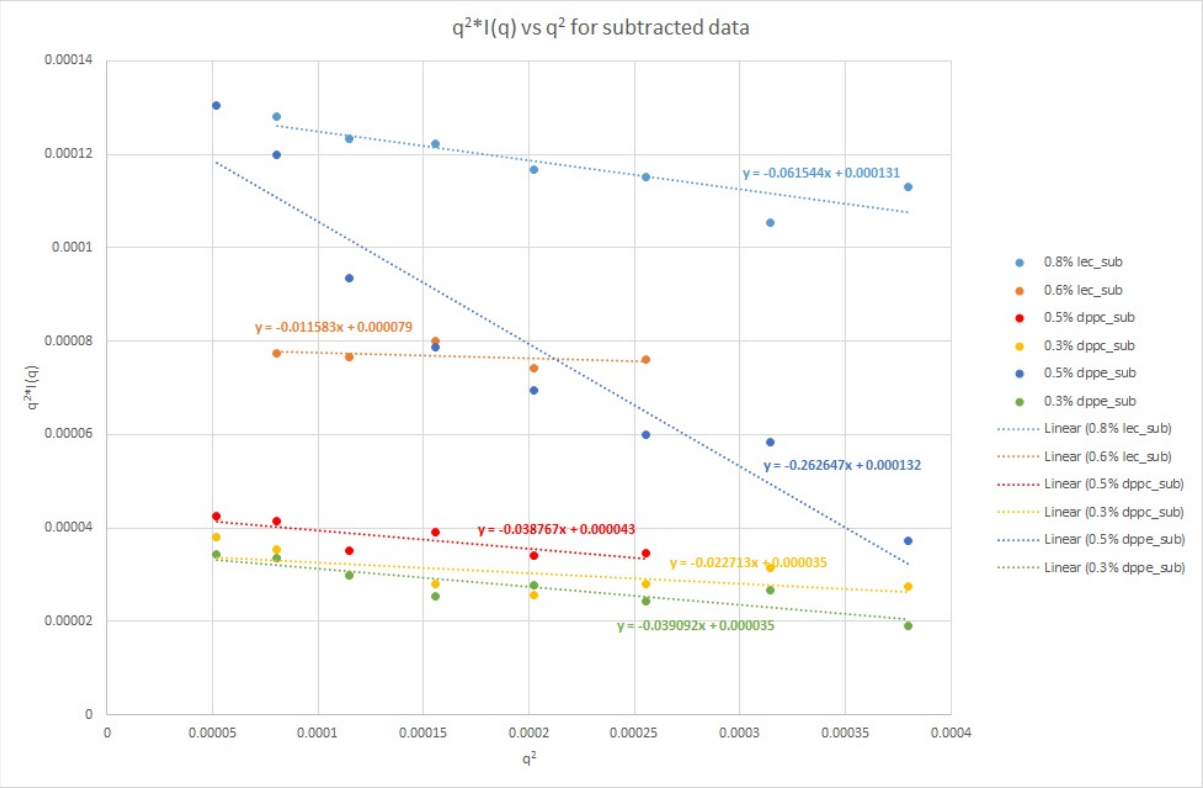

Figure 2: Linear fits, at low q, for q^2*I vs q^2 to the subtracted model chocolate data with 0.6%, 0.8% Lecithin, 0.3%, 0.5% DPPC & 0.3%, 0.5% DPPE

These fits give absorbed layer thickness of 75 Åfor lecithin model chocolate, 88 Åfor DPPC model chocolate and 120 Åfor DPPE model chocolate. These adsorbed amount thickness suggest mutilayer adsorption of phospholipids on the sucrose surface for model chocolate: 3 layers for DPPC and lecithin and 5 layers for DPPE. An odd number makes sense with the head group attached to the sucrose and the tail in the oil. It must, however, be noted that there is a large error in these fits because of the few number of data points at low q, q< 0.02 $Å^{-1}$.

[1]S. King, C. Washington, D. Attwood, C. Booth, S. Mai, Y. W. Yang, and T. Cosgrove. Polymer bristles: a SANS study. Journal of Applied Crystallography, 33:664-668, 2000.