Experimental report

18/11/2015

Proposal: **9-11-1721** **Council:** 10/2014

Title: Structural studies of thermal responsive nanogels at the oil-water interface

Research area: Chemistry

This proposal is a new proposal

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Local contacts: Richard CAMPBELL

Samples: N-propylacrylamide
N-isopropylacrylamide (H & D)

Instrument	Requested days	Allocated days	From	To
FIGARO	4	4	23/04/2015	27/04/2015

Abstract:

Nanogels because of their tunable chemical and three-dimensional physical structure as well as their stimuli-responsive properties have emerged as one of the most significant trends in nanomedicine, skin care products, cell encapsulation and many other applications. Our goal is to resolve structure of the nanogels at the buried oil-water interface. This will contribute to our current understanding of their many important physic-chemical processes such as the transport properties through cell membranes and stabilisation of emulsions used for drug delivery.

Structural studies of thermal responsive nanogels at the oil-water interface

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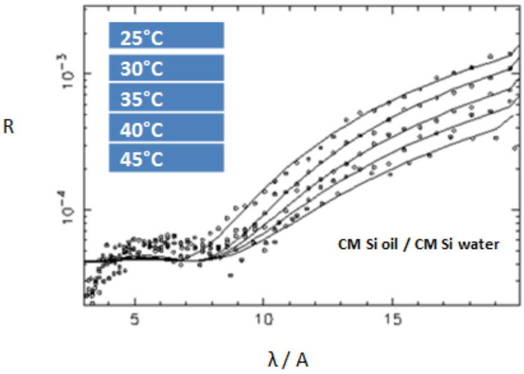
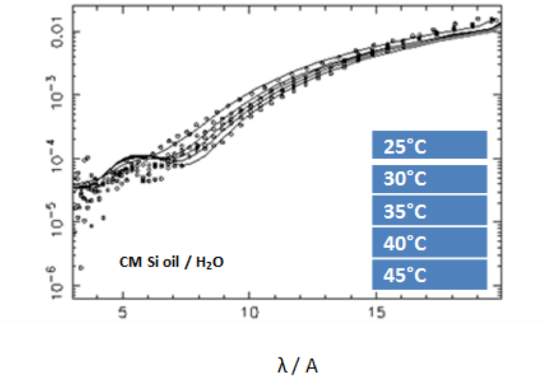
"Smart" nanogels have been shown to possess the capability to stabilise the oil-water interface resulting in macroscale emulsion structures (Pickering emulsions). However, there is still a challenge in forming nanoscale emulsion droplet using nanoparticles. Thermo-responsive nanogels can stabilise emulsion with the unique advantage of being able to form and break down the emulsion as a result of application of external stimuli relying on the 'shape memory effect'.

In the class of stimuli-responsive nanogels, the most studied are the temperature-responsive systems such as poly(*N*-isopropylacrylamide) (PNIPAM) nanogels. They have the unique characteristics of being able to alter their size, volume occupied and hydrophobic character as a result of changes in the temperature of the solution. Upon dissolution in water, polymer backbone forms favourable hydrogen bonds with hydrophilic amide groups resulting in negative entropy of mixing. The enthalpy effect balances this change in entropy and the nanogels remain in solution. However as the temperature of the solution is increased above Lower Critical Solution Temperature (LCST) the entropy terms start to dominate over the exothermic enthalpy change with the overall free energy of the system becoming positive, hence an increase in surface activity ultimately would lead to phase separation.

In this experiment we have used our previously developed technique for examining the partly deuterated and fully protonated forms of nanogels at the hexadecane/water interface, with contrast matched silicon oil and water, and the protonated ones with D_2O (forming the aqueous sub-phase) and contrast matched silicon oil.

The data for an oil layer of 2.1 micro are shown below. The simultaneous fits to the data are shown by the solid line. The corresponding scattering length density profiles for oil CM Si/CM Si Water are also shown below. The preliminary fits to the data indicate that nanogels conformation changes as function of temperature. The nanoparticles conformations changes to an elongated form as temperature increases, as the majority of the hydrophobic moieties being solvated (i.e. pulled) to the oil-side of the interface. The full analysis of the data would contribute further to our understanding of applications of these nanoparticles as emulsion stabilisers.


25°C
30°C
35°C
40°C
45°C
R
10^{-3}
10^{-4}
CM Si oil / CM Si water
5
10
15
λ / A


0.01
10^{-3}
10^{-4}
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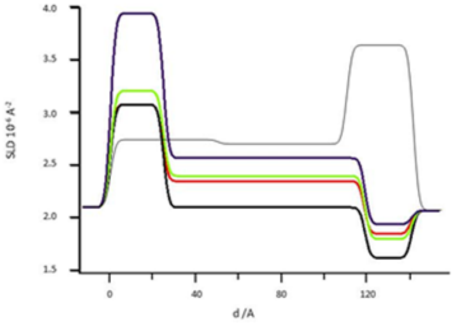
25°C
30°C
35°C
40°C
45°C
CM Si oil / H_2O
5
10
15
λ / A


4.0
3.5
3.0
2.5
2.0
1.5
SLD 10^{-6} A^{-2}
0
40
80
120
d /A