# Experimental report

10/07/2018

**Proposal:** 9-11-1839 **Council:** 4/2017

**Title:** Adsorption versus aggregation; Particles and surface of matching material

**Research area:** Chemistry

**This proposal is a continuation of 9-11-1786**


**Main proposer:** Ali ZARBAKHSH

**Experimental team:** Pengfei LIU
Ali ZARBAKHSH

**Local contacts:** Armando MAESTRO


**Samples:** NIPAM nanogels with different % of crosslinking (10-30% of MBA)

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| FIGARO | 3 | 2 | 04/06/2018 | 06/06/2018 |


**Abstract:**

The balance between particle-surface and particle-particle interactions is entropically driven. We would like to investigate wherever a multiplayer layer adsorption on a hydrophobic surface for thermal responsive NIPAM nanogels is preferred as concentration increases as has been observed at the air-water interface.

## 1 PRINCIPAL INVESTIGATOR

Name and institution of the Principal Investigator

Dr A Zarbakhsh
Department of Chemistry
Queen Mary University of London
UNITED KINGDOM

## 2 EXPERIMENT DETAILS

Experiment: 9-11-1839

Title: Interfacial behaviour of L-proline based dual thermal responsive and pH switchable nanogels at the sapphire/water interface

Instrument: FIGARO

| Dates scheduled: 4th June 2018 to 5th June 2018 | No. Days allocated: 2 |
|---|---|

Date of experimental report: 09/07/2018

## 3 EXPERIMENT OBJECTIVES

Recently, we reported an L-proline based thermal responsive and pH switchable nanogel as drug delivery vehicle. N-acryloyl-L-Proline (A-Pro-OH) and N-n-propylacrylamide (NPAM) based dual pH-temperature responsive nanogels (short as NPAMP) showed highest drug release performance at lowest pH (5.2) and higher temperature (43ºC, close to VPTT of the nanogels). The results make this type of nanogels very useful in applications in cancer therapy and the treatment of inflammatory conditions, where the lower pH of the tumour cell, together with higher localised heat, would favour drug release and minimise side effects

In the first session of our back-to-back experiments at ILL, we have successfully used neutron reflectivity (NR) to study the structural conformations of these charged NPAMP nanogels, cross-linked with 5% and 10% methylene-bis-acrylamide (MBA), at the air-water interface. Preliminary results from neutron reflectivity demonstrated that a well-ordered layer-by-layer and compact packing structure at the air-water interface around the isoelectric point of these charged nanogels.

In this experiment the main aim was to gain more comprehensive information on the main factors influencing the surface behaviour of these thermal responsive and pH switchable nanogels at hydrophobic solid-water interface as a function of pH and temperature. Sapphire single crystal whose scattering length density (sapphire $5.72\times10^{-6}$ Å$^{-2}$) is close to that of $D_2O$ provides a better contrast for these nanogels. For this reason, sapphire substrates offer substantial promise for neutron reflectometry investigations of low-density structures and in addition, the fact the surface of sapphire is naturally hydrophobic means no surface modification is needed.

## 4 EXPERIMENT REPORT

We have investigated adsorption process of NPAMP based nanogels crosslinked with 5% and 10%MBA at the sapphire/water interface at 0.1 mg/ml as a function of temperature (27 and 40ºC) as well as a function of pH ( 4.0, 6.0, 7.4 and 9.2). The sub-phase is contrast matched to sapphire water. Detailed data analysis is still ongoing

Exemplary NR profiles of NPAMP nanogels with 5% crosslinker are presented as a function of pH at 27ºC (Fig 1a)

and 40ºC (Fig 1b), respectively. The preliminary data analysis suggests the thickest layer formation near the isoelectric point of the sapphire substrate. At pH=9.2, the sapphire is negatively charged, the repulsive interactions between sapphire the nanogels is unfavourable for the adsorption of nanogels onto the interface. This explains the decreasing adsorbed amount of these charged nanogels at the pH=9.2. We should have expected that the adsorbed amount would be maximised at lower pH value. However, we found even less nanogels at the sapphire-water interface compare with that of pH=9.2 regardless of their attractive interactions. This is unusual and cannot be demonstrated solely by the electrostatic force. Proper complete analysis of these NR data is essential for the verification of this interesting observation.

Another different interfacial behaviour of these charged nanogels is that their interfacial conformations do not change too much when temperature increases close to the VPTT. In the case of these nanogels dissolved in the deionised water at the air/water interface, a much thicker layer formation was found at 40ºC compare with that at room temperature. This indicates ions in the bulk may play a significant role in the thermal responsiveness of charged nanogels.

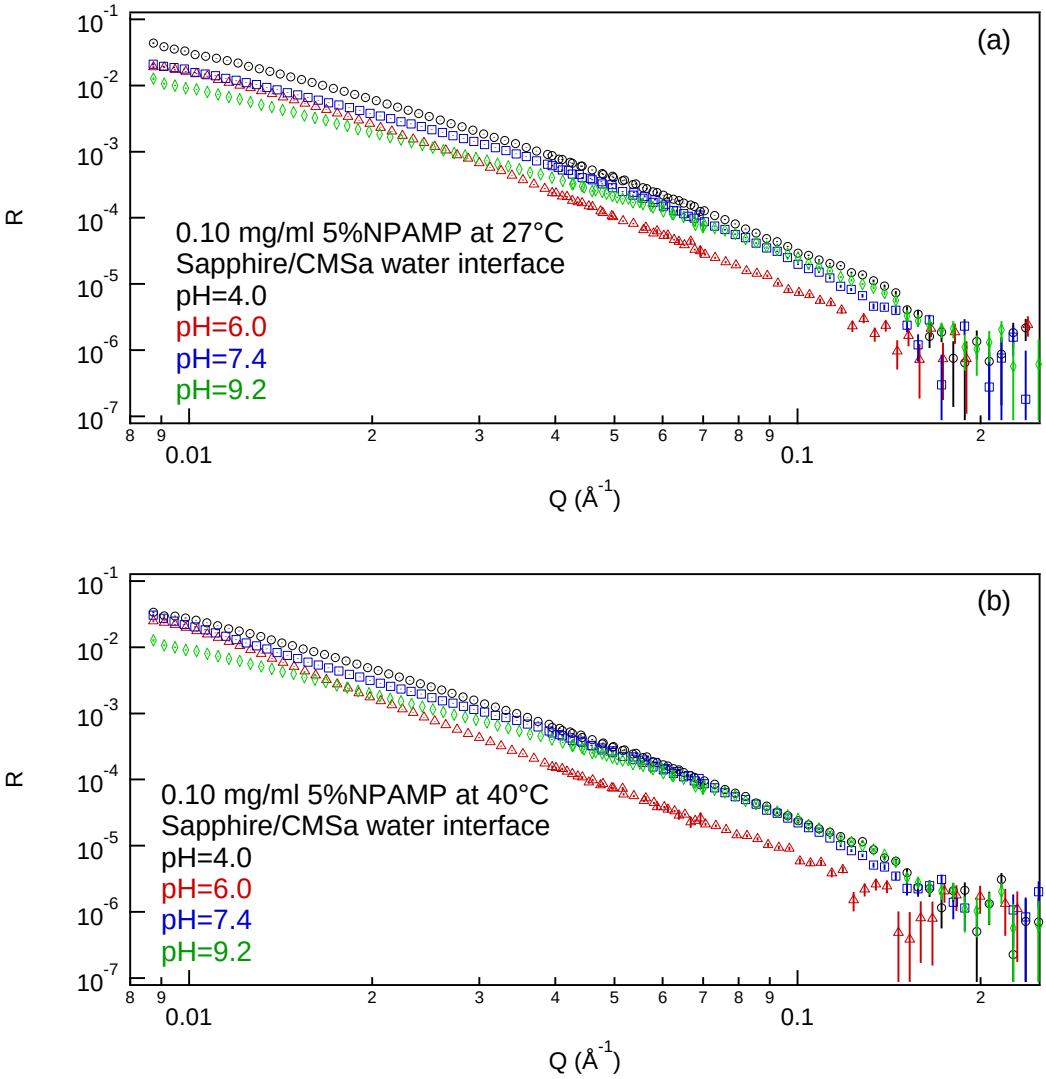


Fig. 1. NR profiles for 92.5%NPAM, 2.5%A-Pro-OH and 5%MBA nanogels at the sapphire-water interface as a function of pH at 27 ºC (a) and 40 ºC (b)

| **5 LIKELY OUTCOMEs FROM EXPERIMENT**<br>*Please indicate what the experiment is likely to lead to by putting an 'x' next to one or more of the possible outcomes below.* | |
|---|---|
| *Likely outcome* | |
| Journal publication | *x* |
| Data for thesis | *x* |
| Follow-up experiment at ILL | **-** |
| Follow-up experiment at another facility | *x* |
| Other | *x* |
| No outcome anticipated | **-** |

| **6 SUGGESTIONS FOR IMPROVEMENTS TO YOUR EXPERIMENT, EQUIPMENT OR THE FACILITY** |
|---|

NA