Experimental Report

20/10/2013

Proposal:	**9-12-334**	**Council:**	10/2012
Title:	Ion-mediated surfactant adsorptionon cellulose films		

This proposal is resubmission of: 9-12-315

Researh Area: Chemistry

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Samples: cellulose (($(C_6H_{10}O_5)_n$)), SDS ($C_{12}H_{25}OSO_3Na$), NaCl, D_2O, dSDS ($C_{12}D_{25}OSO_3Na$)
cellulose (($(C_6H_{10}O_5)_n$)), octaethylene glycol dodecyl ether ($C_{12}H_{25}(OC_2H_5)_8OH$ or $C_{12}D_{25}(OC_2H_5)_8OH$), $CaCl_2$

Instrument	Req. Days	All. Days	From	To
D17	3	3	04/05/2013	07/05/2013

Abstract:

In recent work with Unilever we have been investigating the structure of gels formed by partially oxidised cellulose nanofibrils for use in sustainable personal care products. These nanofibrils form strong gels with anionic surfactants, but nonionic surfactants gel the nanofibrils only in the presence of salts. Nonionic surfactants have been shown in neutron reflectivity studies to adsorb on cellulose surfaces but no studies of anionic surfactants have been reported in the literature. Here we propose to compare the adsorption of anionic and nonionic surfactants on films prepared from oxidised cellulose nanofibrils in the presence and absence of monovalent and divalent cations as a model system to understand interactions between surfactants, cations and the cellulose surfaces. This will help us to determine the role of micelle binding to the cellulose in the formation of gels in this system. This is a resubmission of a previous unsuccessful proposal, where the panel requested more pre-characterisation of the oxidised cellulose films. AFM and X-ray reflectivity results on our films have now been added to the proposal to demonstrate the suitability of our films for these experiments.

Currently a large proportion of surfactant used in aqueous formulations for personal care is added for viscosity modification rather than the primary purpose of cleaning. Surfactants often have undesirable environmental consequences when released during/after use, so in this project we aim to replace a large amount of surfactant in such materials with partially C6 oxidised cellulose nanofibrils which are biodegradable, cheaper than natural plant-oil-based surfactants and which can be prepared with minimal chemical modification from waste such as wood pulp. Similar fibrils have until now, largely been used in polymer nanocomposites[1] ie as fillers in bulk polymer materials. Little exists in the literature on the behaviour of suspensions of oxidised cellulose fibrils and their interactions with surfactants. Most work has concentrated on functionalised soluble cellulose species such as hydroxymethylcellulose or carboxymethylcellulose, which act as discrete dissolved polymer molecules rather than nanoparticles.

In collaboration with Unilever we are investigating partially oxidised cellulose (oxcel) nanofibrils 3-4 nm wide, and several microns long, produced by oxidation of cotton fibres or wood pulp using TEMPO,[2, 3] as thickeners in aqueous formulations.[4, 5] We have studied the structure of gels formed by oxcel for use in sustainable personal care products. We found that gels form at pH 7 upon addition of monovalent salts, but stronger gels form when anionic surfactants are added to the cellulose suspension (in the absence of salt).[6] Non-ionic surfactants, however, only gel the cellulose suspensions when some salt is added, although less salt is needed to achieve gelation in the presence of the non-ionic surfactants than when salt alone is used.

Three suggestions have been made as to why surfactants assist gelation of cellulose: 1. The micelles cause a depletion flocculation interaction, causing the nanofibres to be pushed closer together and so to interact causing gelation (although then non-ionic and anionic micelles should have similar effects whereas only anionic surfactants form gel with nanofibrils alone). 2. Micelles adsorb to the cellulose surfaces forming crosslinks between the nanofibres (unlikely for an anionic surfactant to adsorb directly onto a negatively charged cellulose surface) or 3. The cations from the anionic surfactants adsorb onto the cellulose neutralising the charge and either allowing the nanofibres to touch (and so form a gel) or allow the surfactant micelles to adsorb through a mediating counterion. We have recently studied the structure of these cellulose and cellulose/surfactant suspensions using SAXS and SANS. These experiments suggest that the apparent micelle concentration (reflected in the structure factor) and shape does not significantly change in the presence of oxcel.[7]

Nonionic surfactants have been shown in neutron reflectivity studies to adsorb on cellulose surfaces[8] while more recently, sodium dodecylsulphate (SDS) has been reported to adsorb and swell surfaces made from soluble cellulose, especially in the presence of salt.[9] Here we wanted to compare the structure of our thicker, more substantial oxidised cellulose nanofibril films in solutions with SDS in the presence and absence of NaCl as a model system to understand interactions between surfactants, salt and the cellulose surfaces found in our gels. This will help us to determine the role of micelle binding to the cellulose in the formation of gels in this system.

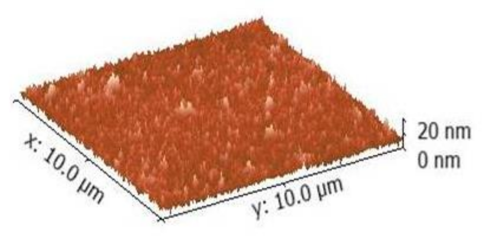

Figure 1: AFM image of partially oxidised cellulose film, roughness 1.3nm

In this experiment, we coated clean silicon blocks with an aminosilane layer, which was protonated by dipping in dilute HCl solution. This was followed by deposition of the oxcel fibrils by dip-coating to form a smooth film (Figure 1). The reflectivity patterns from these oxidised cellulose films were measured on D17 for films dry in air, in D_2O, and then at several contrasts after washing the surface with solutions of SDS (6mM) in the absence and then presence of NaCl (0.2M). Deuterated and hydrogenated SDS were both used to allow different contrasts to highlight the position of SDS in the films. Figure 2 shows the neutron reflectivity of the film pre and post SDS wash, using h-SDS. Clearly the film becomes thicker in the presence of the SDS. However, this series of patterns suggests that SDS has only weak interactions with the oxcel film at this concentration since no SDS remains on or in the film after washing. This would suggest that gelation could be due to the depletion mechanism or counterion adsorption but is unlikely to be due to direct micelle binding onto or between the oxcel nanofibrils. Unfortunately we did not manage to make equivalent measurements on the films in the presence of nonionic surfactant due to limited measurement time. Further analysis of data by fitting of the reflectivity profiles for the h-SDS and d-SDS samples will help us understand the position of SDS in the oxcel films.

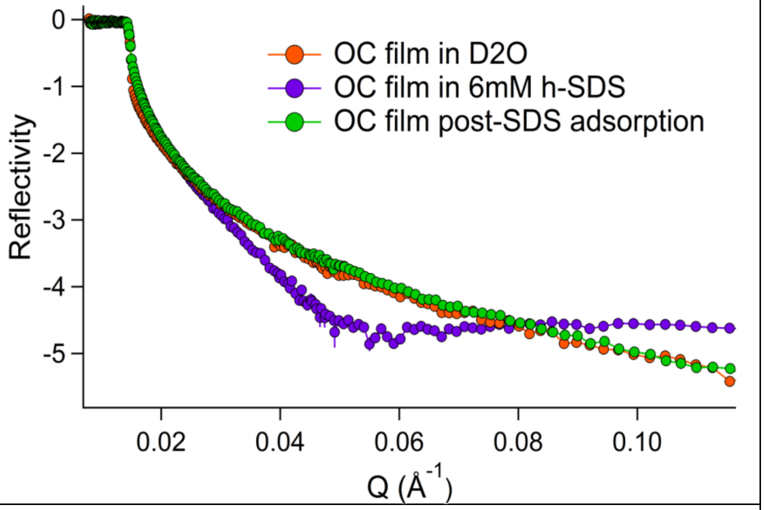

Figure 2: Neutron reflectivity data for an oxcell film before and after SDS adsorption followed by washing with D_2O

References:

1. Samir, M.; Alloin, F.; Dufresne, A., *Biomacromol.* **2005,** *6* (2), 612-626.

2. Saito, T.; Kimura, S.; Nishiyama, Y.; Isogai, A., *Biomacromol.* **2007,** *8* (8), 2485-2491.

3. Saito, T.; Nishiyama, Y.; Putaux, J. L.; Vignon, M.; Isogai, A., *Biomacromol.* **2006,** *7* (6), 1687-1691.

4. Bercea, M.; Navard, P., *Macromolecules* **2000,** *33* (16), 6011-6016.

5. Lasseuguette, E.; Roux, D.; Nishiyama, Y., *Cellulose* **2008,** *15* (3), 425-433.

6. Crawford, R. J.; Edler, K. J.; Lindhoud, S.; Scott, J. L.; Unali, G., *Green Chem.* **2012,** *14* (2), 300-303.

7. Lindhoud, S.; Wasbrough, M. J.; Scott, J. L.; Edler, K. J., **2013**, in preparation.

8. Tucker, I.; Petkov, J.; Penfold, J.; Thomas, R. K., *Langmuir* **2010,** *26* (11), 8036-8048.

9. Tucker, I. M.; Petkov, J. T.; Penfold, J.; Thomas, R. K., *Langmuir* **2012,** *28* (27), 10223-10229.