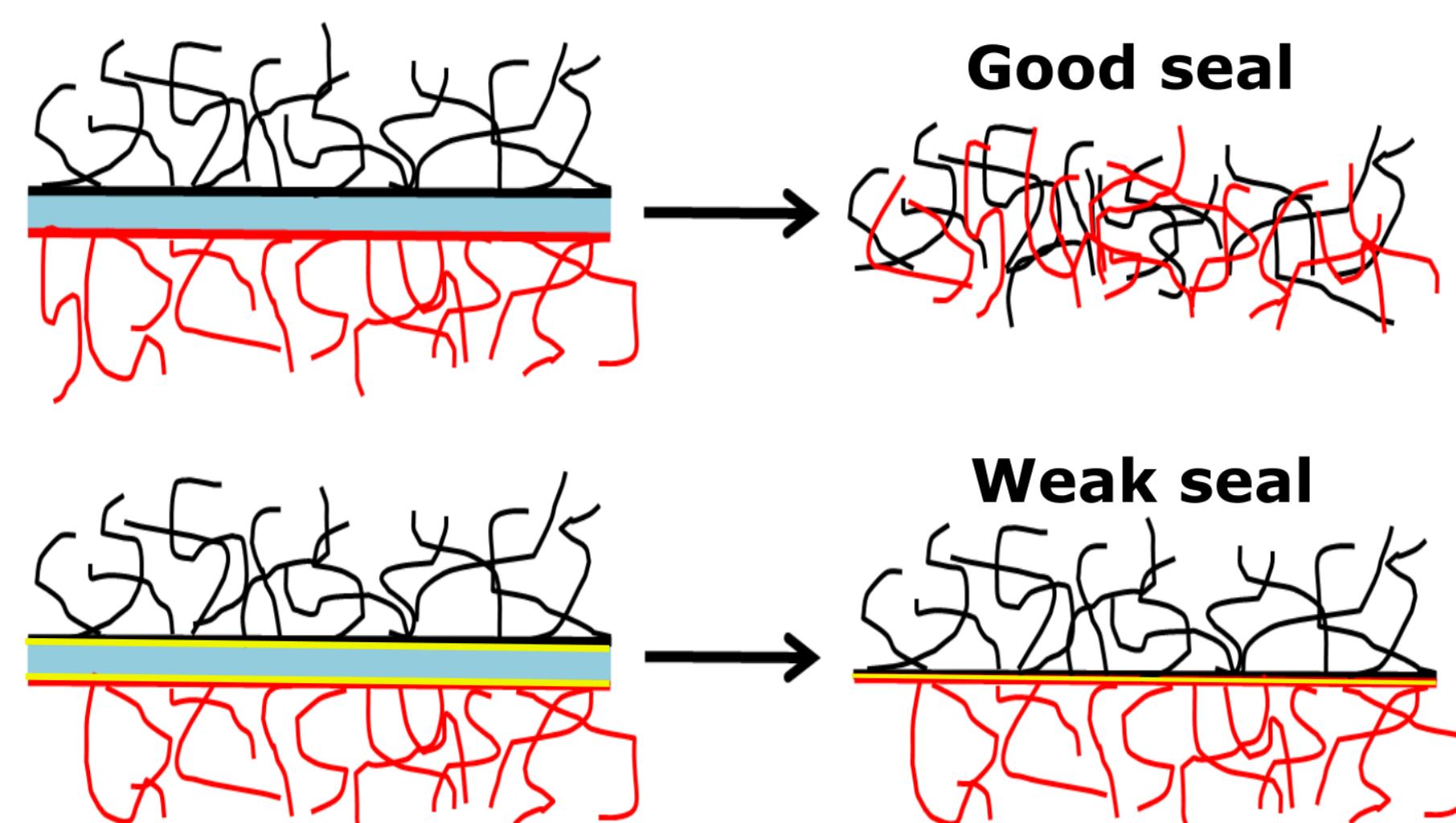


Small Molecule Migration in Thin PVA Films

Rebecca Fong (rebecca.j.fong@durham.ac.uk), Dr Richard Thompson

Background

The migration of small molecules in multi-component soft matter systems is of huge commercial importance. It is particularly relevant in the migration and segregation of components in poly(vinyl alcohol) (PVA) films used for liquitabs.¹



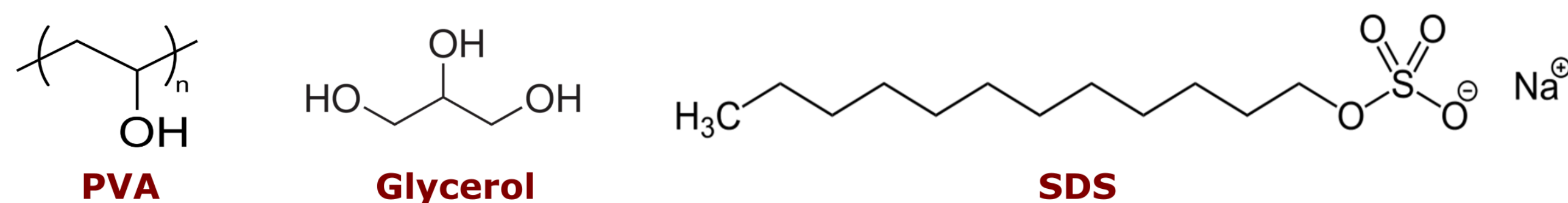
PVA is a semicrystalline polymer used to encapsulate liquid detergents. Seals are formed by wetting the films and pressing them together, allowing the polymer chains to interdiffuse.

Small molecules are susceptible to migrate to the surface which can affect the sealing ability of the films.

Film Components

Commercial films require plasticisers to give them the desirable mechanical properties. Here glycerol is used as a model plasticiser.

The ionic surfactant sodium dodecyl sulfate (SDS) is used as a model film additive.



Approaches

The ultimate aim is to be able to predict the influences of crystallinity, polarity and compatibility on the extent and rate of migration in polymer films. A number of approaches can be taken including:

Depth Profiling

Neutron reflectivity (NR) can be used to depth profile the surfactant in the films. NR is capable of resolving the surface surfactant nanostructure and allows measurement under atmospheric conditions.

Self Assembly

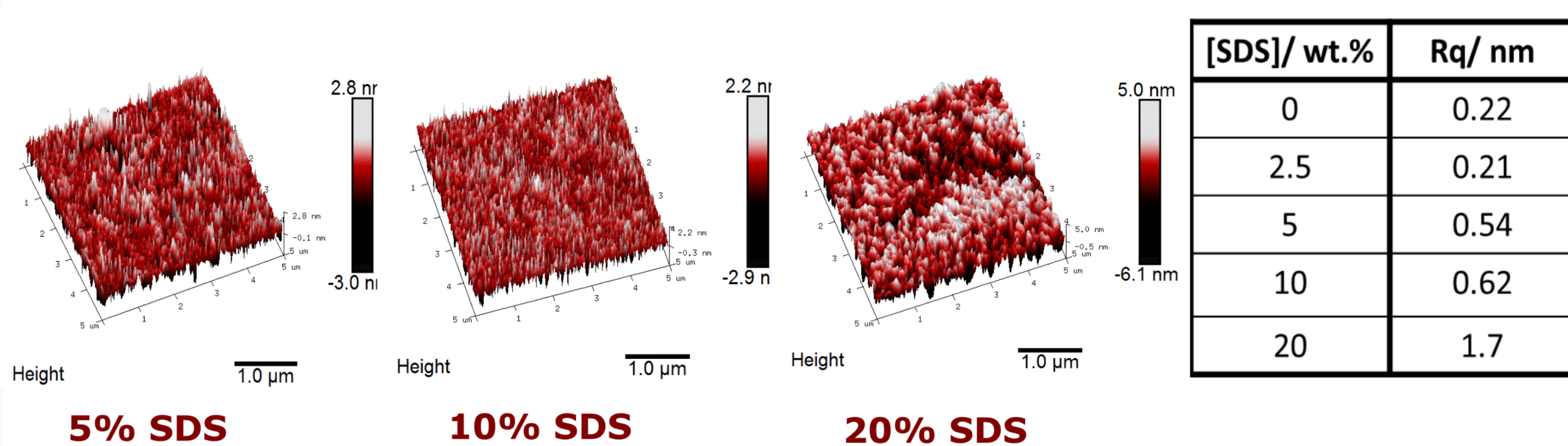
Small angle neutron scattering (SANS) can help to understand the nanoscale self-organisation of surfactants in the PVA matrix.

Film Surface Characterisation

Atomic force microscopy (AFM) was used to characterise the surface of the spin cast films of different surfactant loading. AFM was also used to identify if any evolution of the surface occurs with ageing.

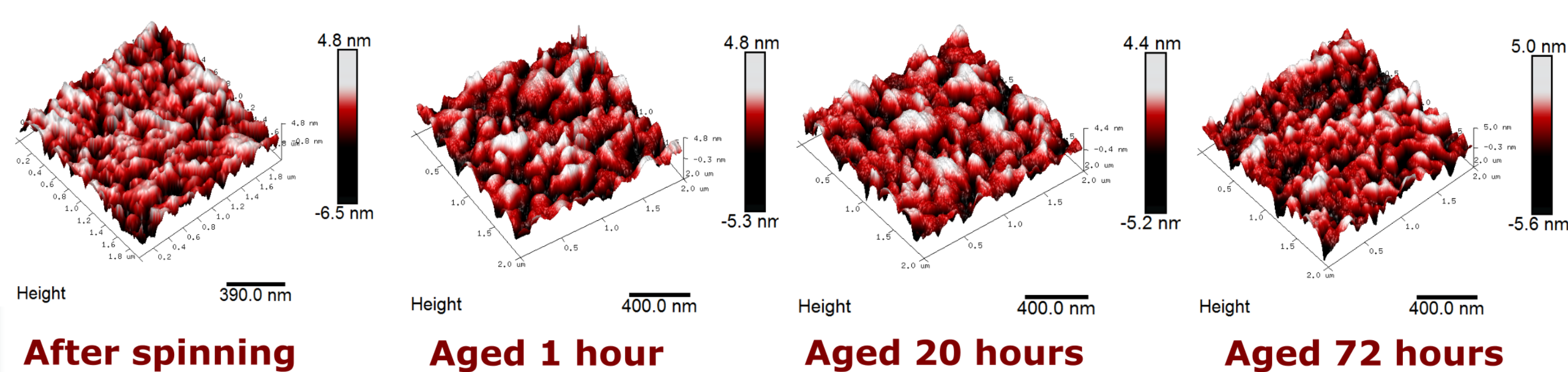
Effect of SDS Concentration on the Film Surface

AFM images of spin-cast PVA films show that the presence of SDS causes an increase in the surface roughness of non-plasticised films.



Effect of Film Ageing on Surface Structure of Binary Films

NR revealed the presence of SDS in the bulk, which does not initially segregate to the surface. It is important to know whether this is capable of migrating over time.

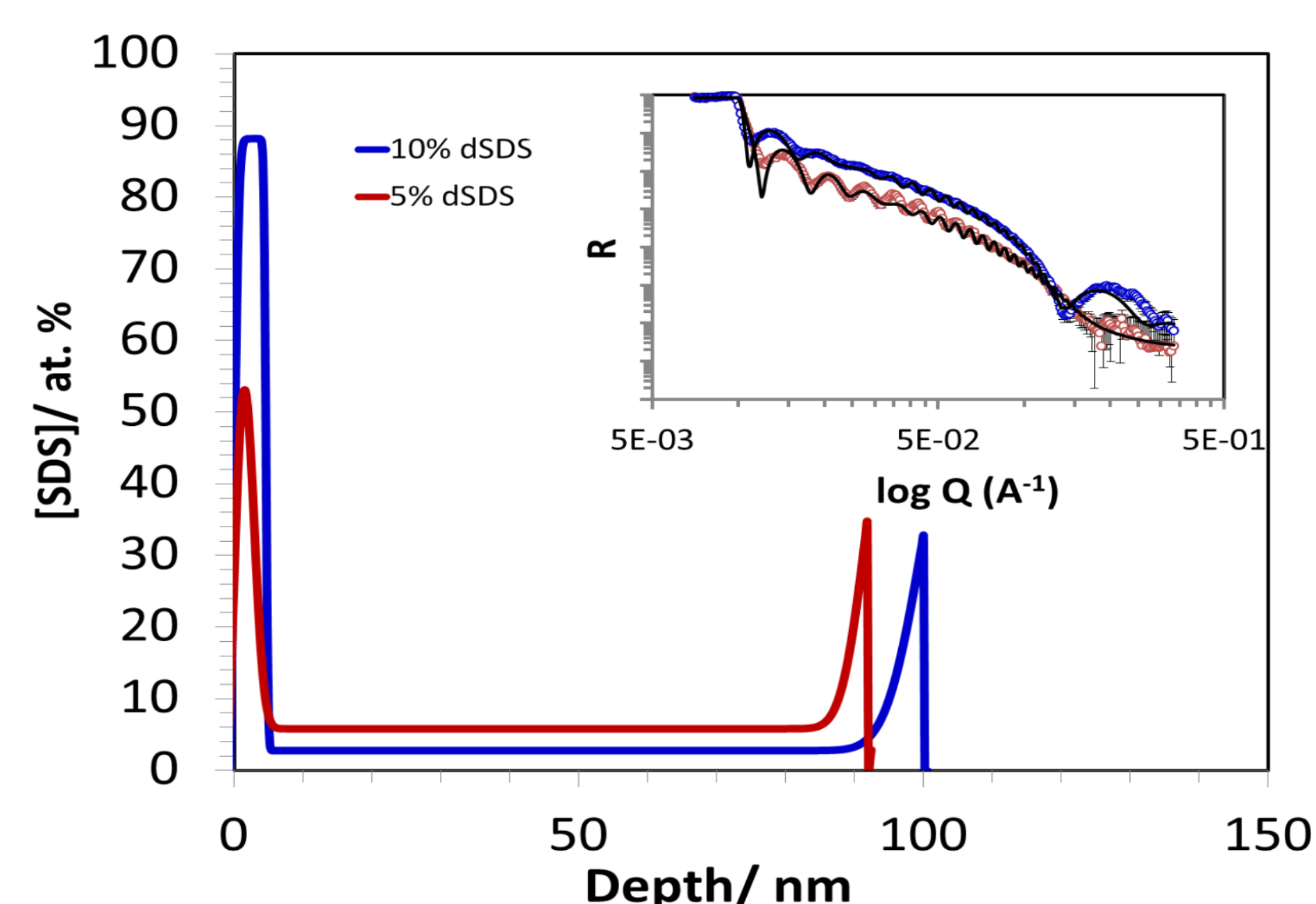


AFM showed no development the strucutre of the surface or significant increase in film roughness. This could mean that, as a solid, SDS is trapped out of equilibrium.

Surfactant Depth Profiling

NR was used to obtain depth profiles of deuterated SDS in spin coated PVA films.

Non-plasticised film

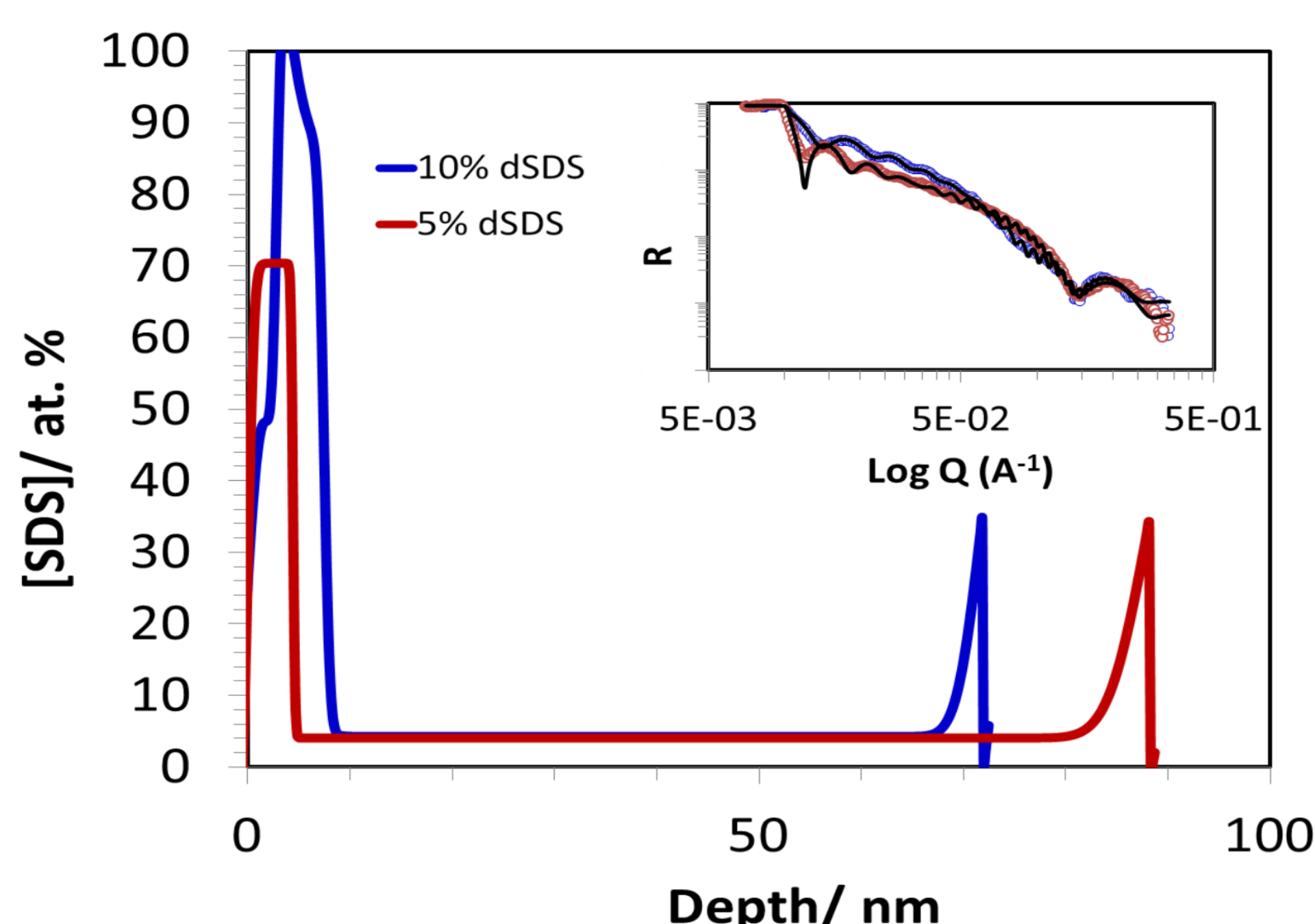


At both 5% and 10% surfactant loading, binary films exhibit a surface excess.

SDS spontaneously migrates to the surface of the spin cast film. This could be driven by the surface energy differences between the components.

Plasticised film

NR was used to see the effect of plasticiser incorporation on the surfactant depth profile. A loading of 20% glycerol was used.



Addition of glycerol causes the surface excess to increase.

This could be caused by changes in the surfactant nanostructure brought about by interaction with the plasticiser.

Future NR experiments

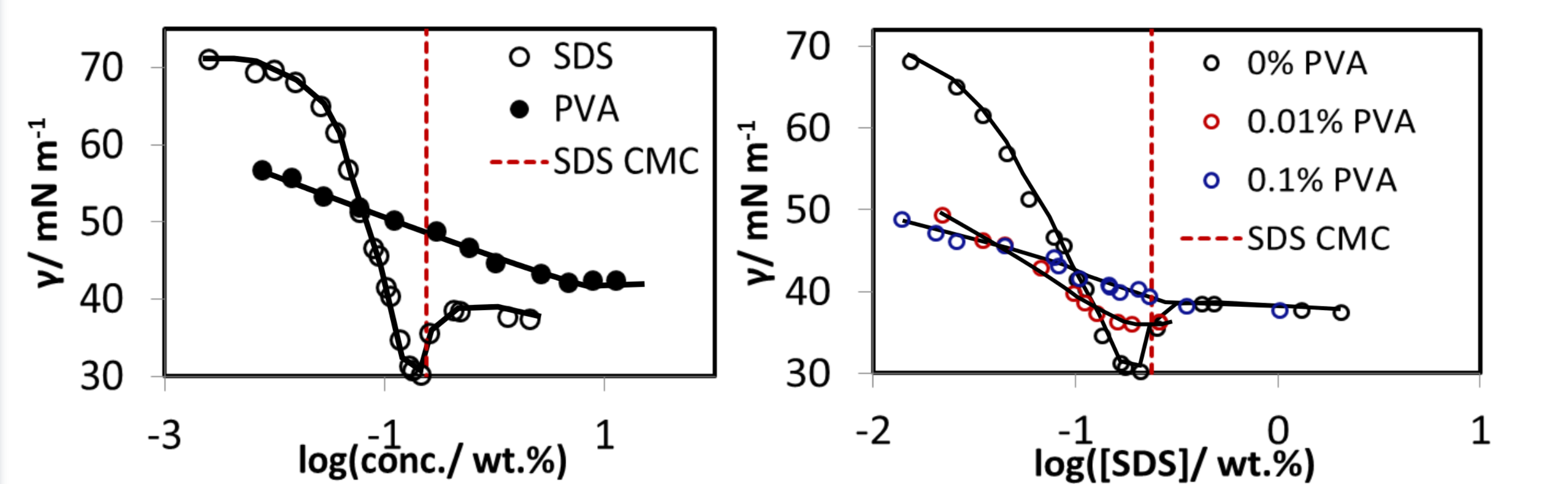
Further NR experiments will explore the effect of film thickness on the surfactant distribution and nanostructure, bridging the gap between the model and commercial films and aiming to answer:

1. if the plasticiser enhances the surface excess for kinetic or thermodynamic reasons?
2. if the extent or nanostructure of the surface excess evolves over time?

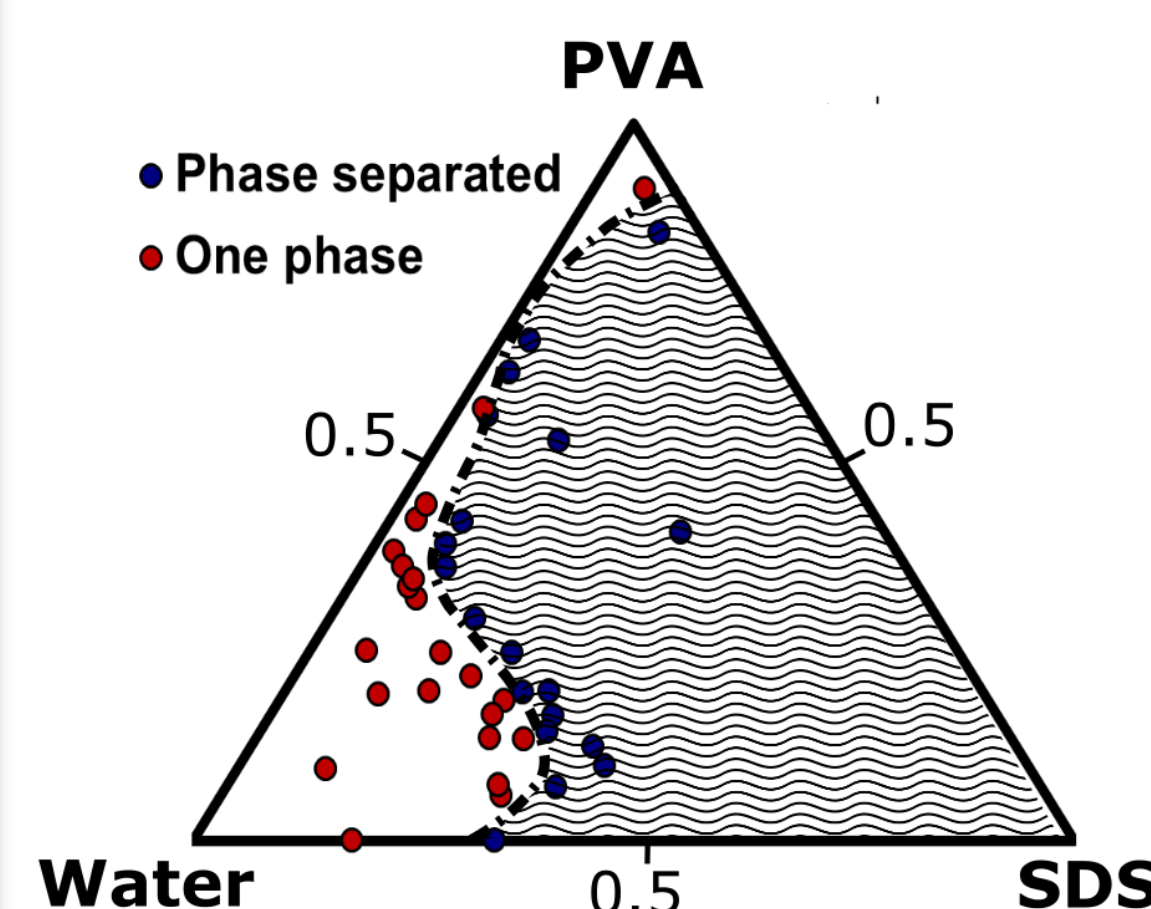
Interaction between film components

The interaction between film compmponents was investigated in order to rationalise the segregation behaviour of SDS.

Surface energy differences are a possible driving force for migration. Although the surface tension (γ) of pure PVA (40 mN m^{-1})² is lower than pure SDS (50 mN m^{-1})³, suggesting no driving force for SDS segregation, it is useful to compare the surface activity of the components in solution



Aqueous surface tension behaviour of PVA Aqueous surface tension behaviour of PVA/SDS



Surface tension experiments showed that at higher concentrations SDS is more surface active in solution. This is therefore a likely driving force for migration. In PVA/SDS solutions [SDS] has only a small effect on γ .

A phase diagram was determined, showing the incompatibility of SDS and PVA in the absence of water. This is also a likely driving force for segregation.

References

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