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Molecular Migration in Poly(vinyl alcohol) Mixtures

Katarzyna Majerczak, Dr Zhenyu Jason Zhang, Prof. Peter Fryer

School of Chemical Engineering, University of Birmingham

Molecular Migration in Complex Formulations

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Durham University

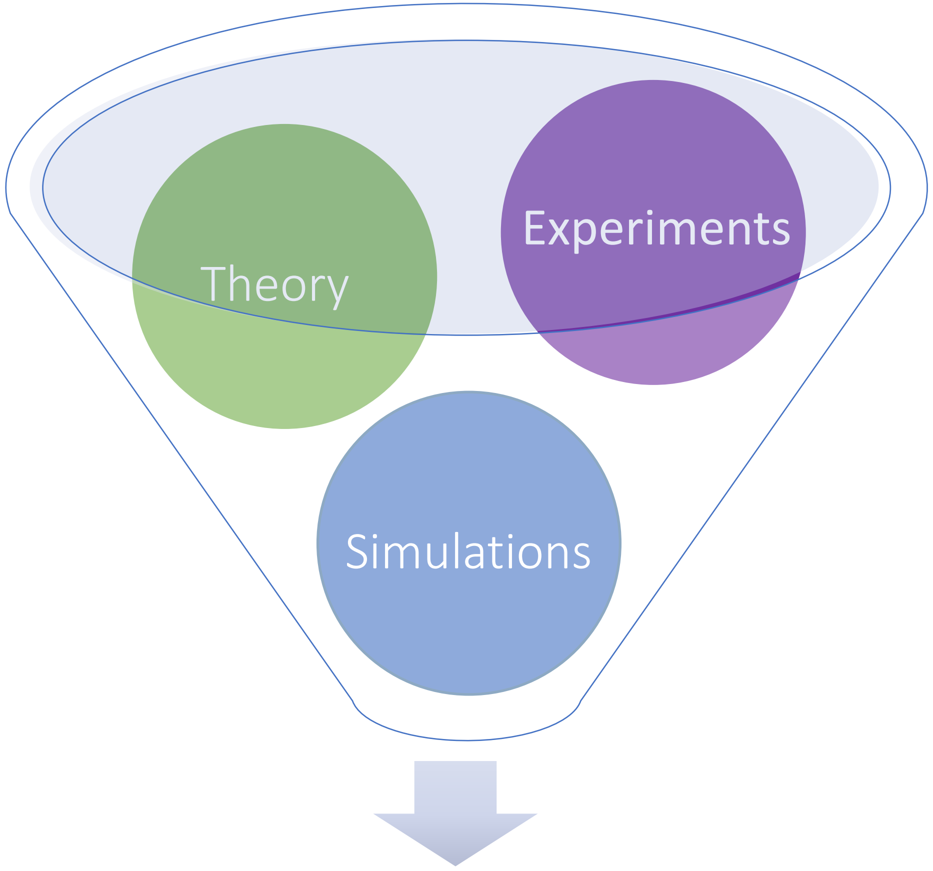
The University Of Sheffield.

- Understand how small additive molecules migrate through complex matrix.
- Build modelling toolbox.
- Pave the way to optimise formulations.

P&G

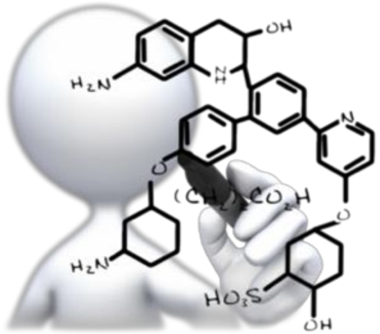
Mondelēz International

AkzoNobel



Molecular migration

Aim and objectives

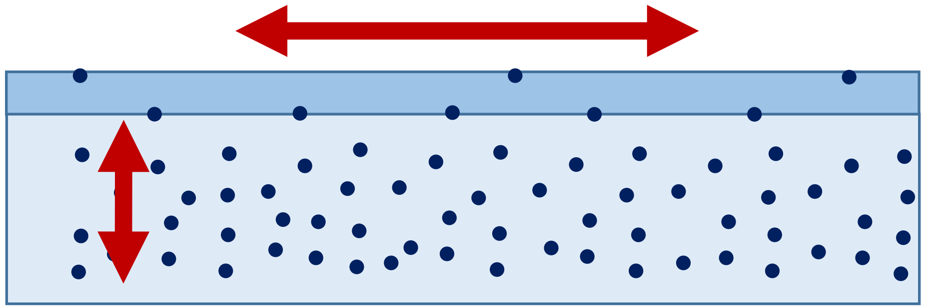


Development of the methodology to probe molecular migration based on advanced fluorescence techniques.

Quantitative evaluation of the effect of environmental conditions on molecular migration in complex mixtures.

Identification of the factors controlling lateral migration.

Understanding the kinetics of molecular migration both in two and three dimensional context.



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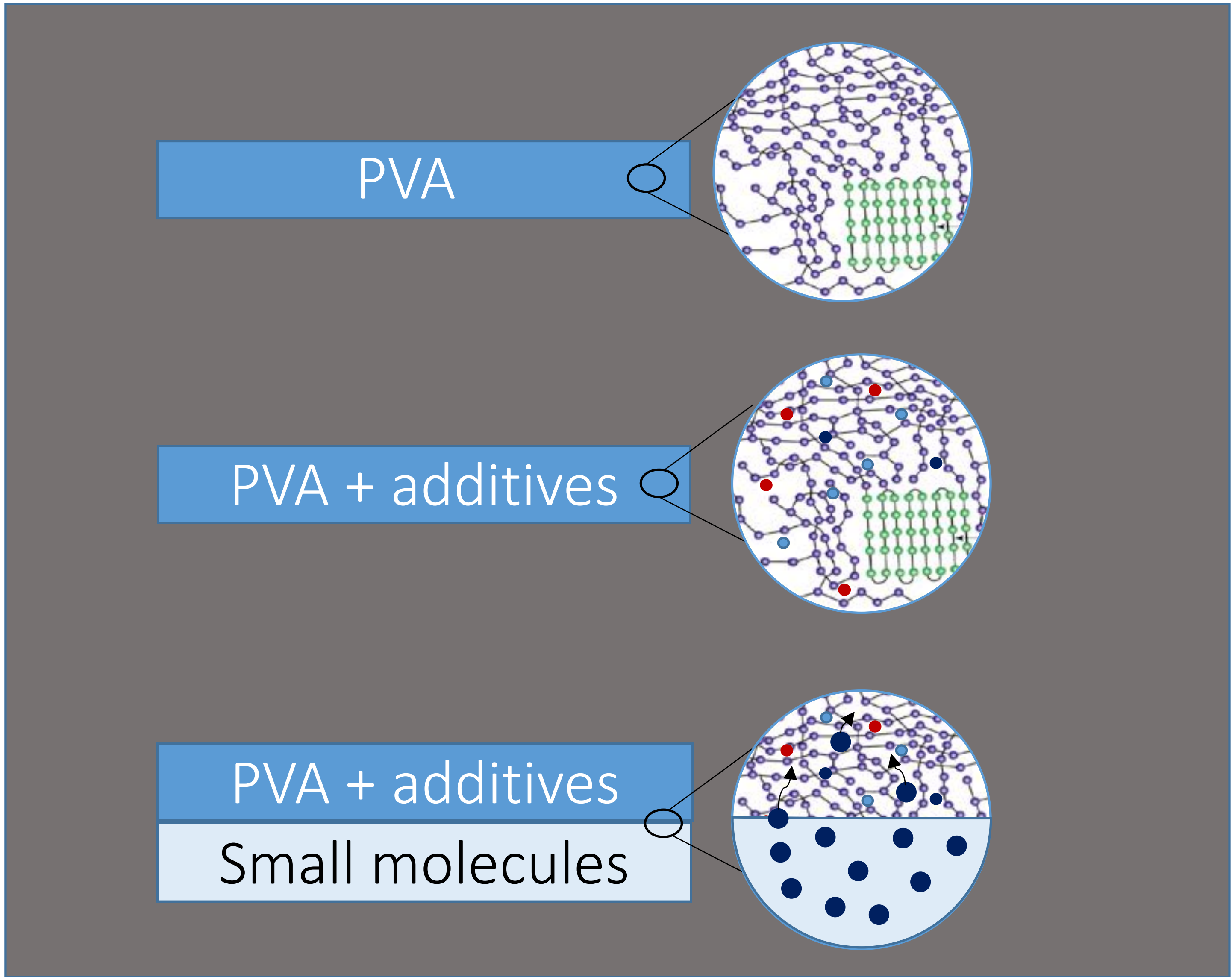
Industrial applications of PVA films



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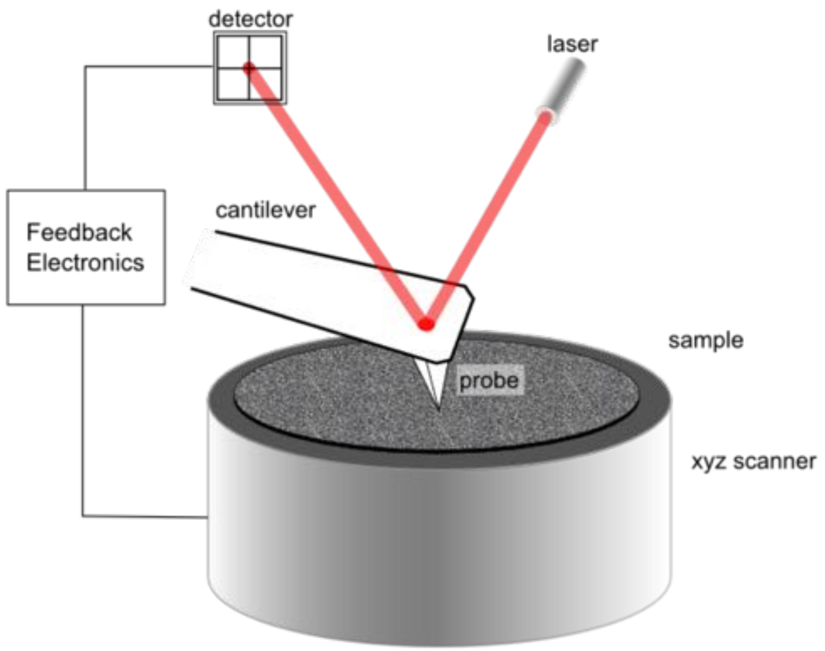
Atomic force microscopy



Works in ambient environment and liquid media, allowing us to investigate the influence of environmental factors.

Provides three dimensional topographic information as well as tip-surface interactions.

Operates both in contact and intermittent contact mode, providing information about topography, mechanical properties, impurities and phases.

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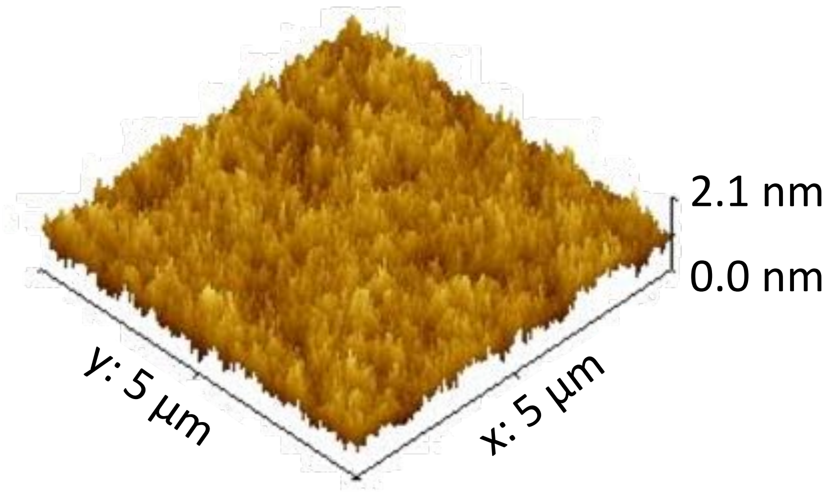
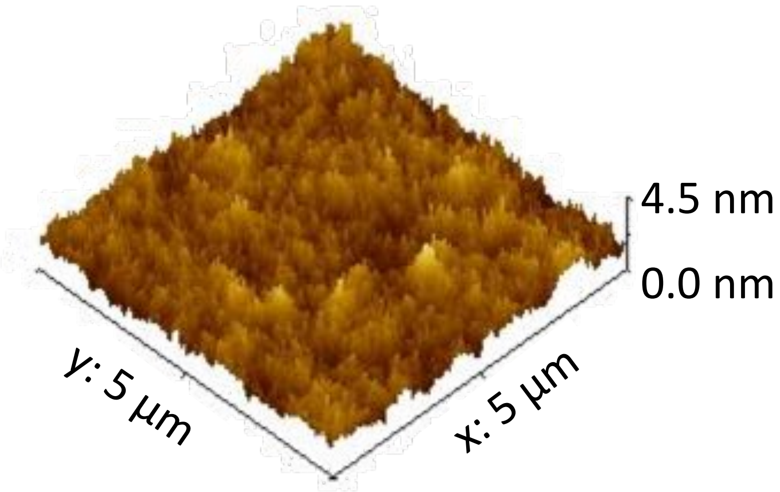
Influence of surfactant on film morphology

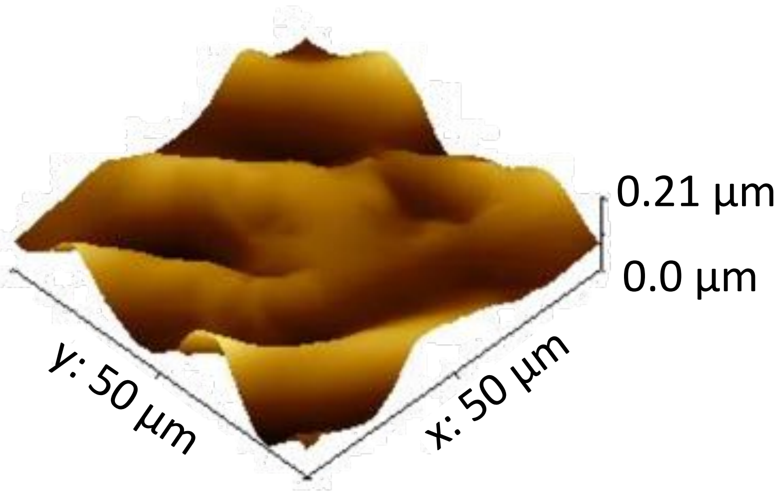
PVA



PVA+glycerol



PVA+glycerol+10 wt% SDS



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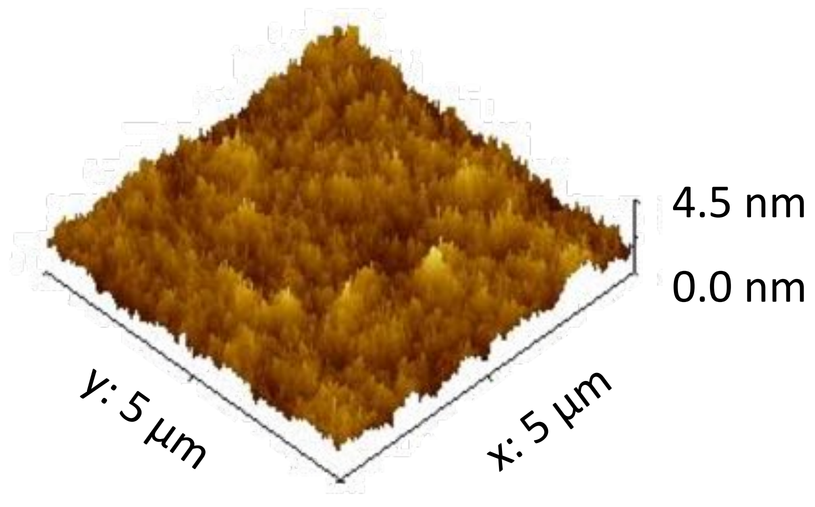
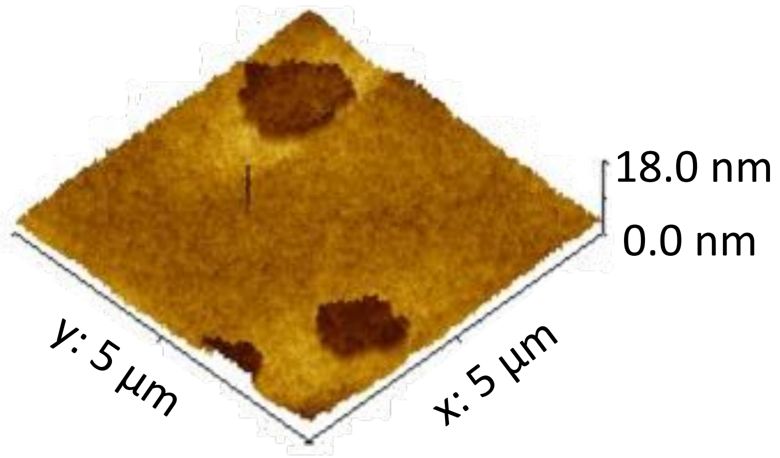
- Addition of plasticiser does not influence morphology of the films.
- High concentration of the surfactant in the film results in drastically increased roughness of the film.

Influence of surfactant on film morphology

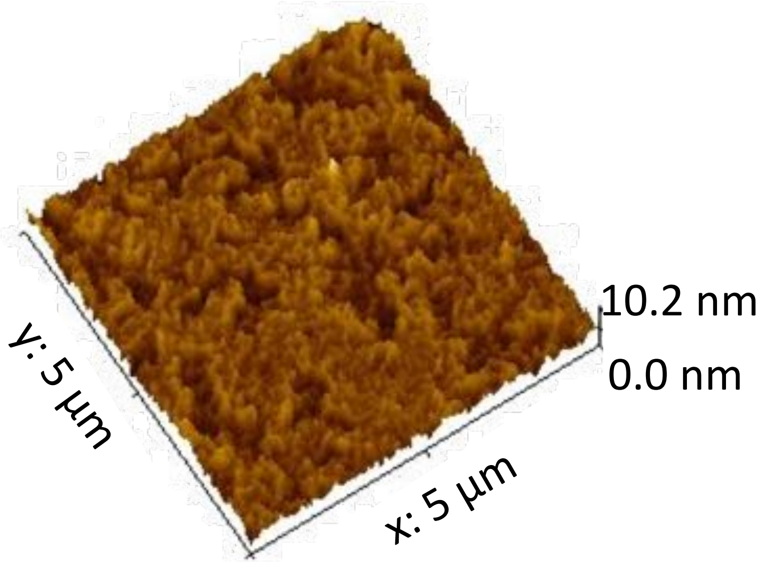
PVA+glycerol



PVA+glycerol+1 wt% SDS



PVA+glycerol+3 wt% SDS



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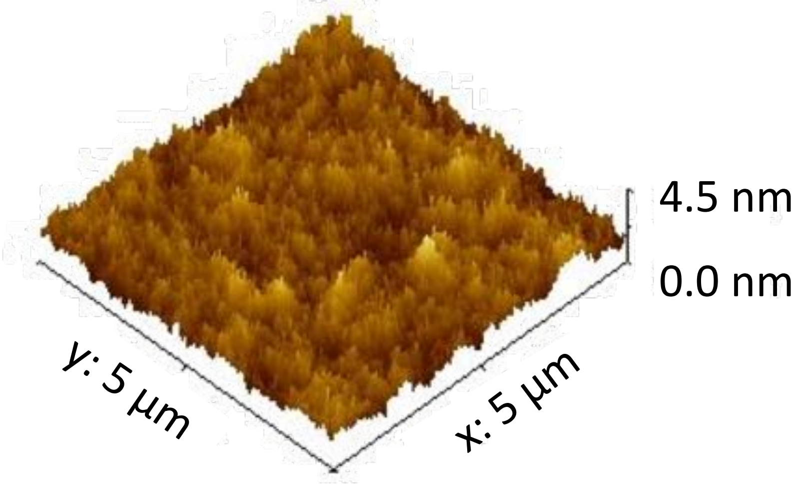
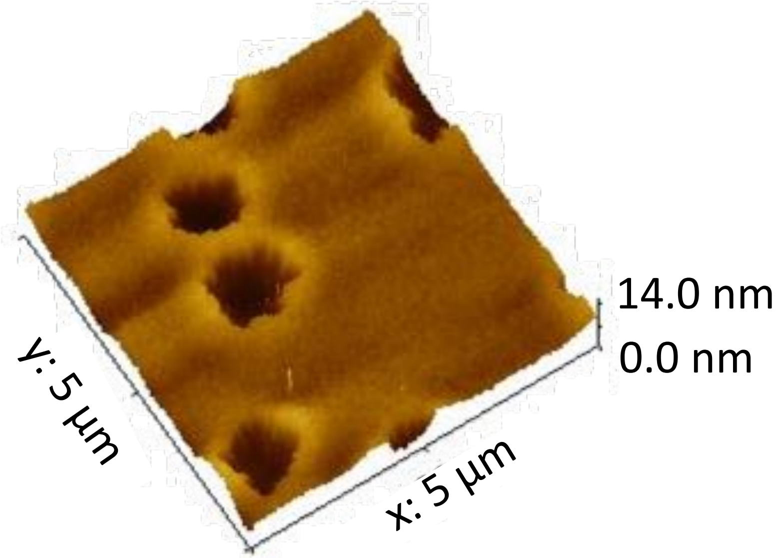
- Even small addition of SDS changes morphology of the film.
- Amount of surfactant that has bloomed on the surface for 1 wt% SDS film changes with time.

Influence of surfactant chemistry on film morphology

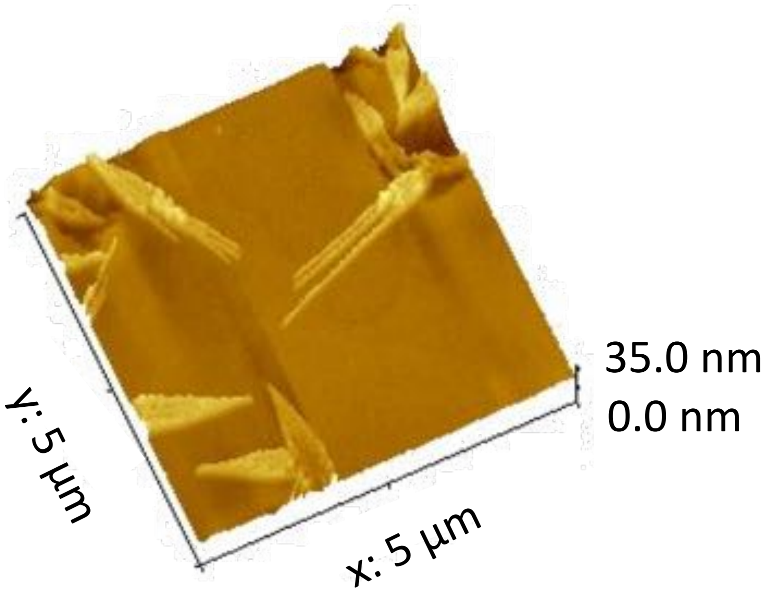
PVA + glycerol



PVA+glycerol+3 wt% CTAB



PVA+glycerol+5 wt% CTAB



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- Longer time and higher concentration are required for morphology change to take place for films with CTAB addition.
- No changes within this concentration range were observed for non-anionic surfactant.

Proof of concept

- Chemistry of surfactants
- Concentration of surfactants
- Time
- Humidity

→ Migration kinetics

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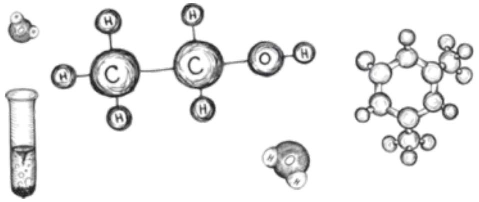
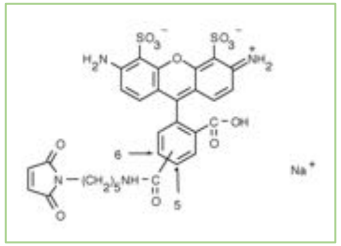
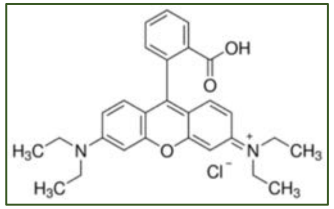


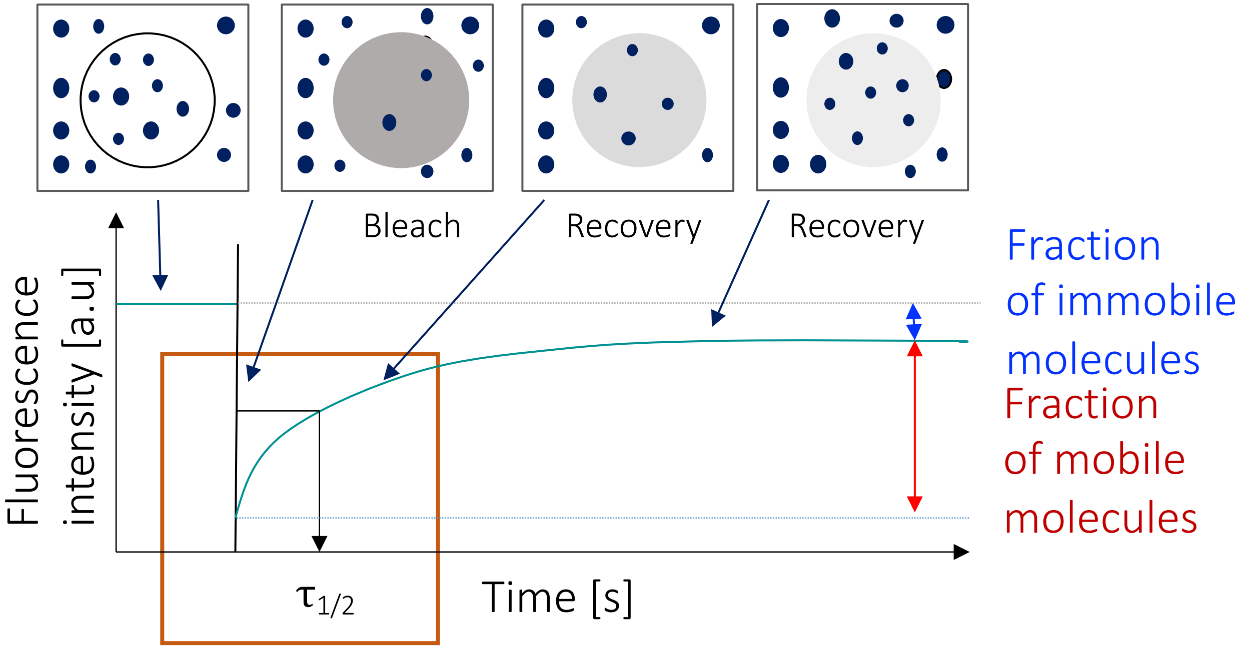
Fluorescence Recovery After Photobleaching (FRAP)



Alexa Fluor 488 C5 - Maleimide



Rhodamine B

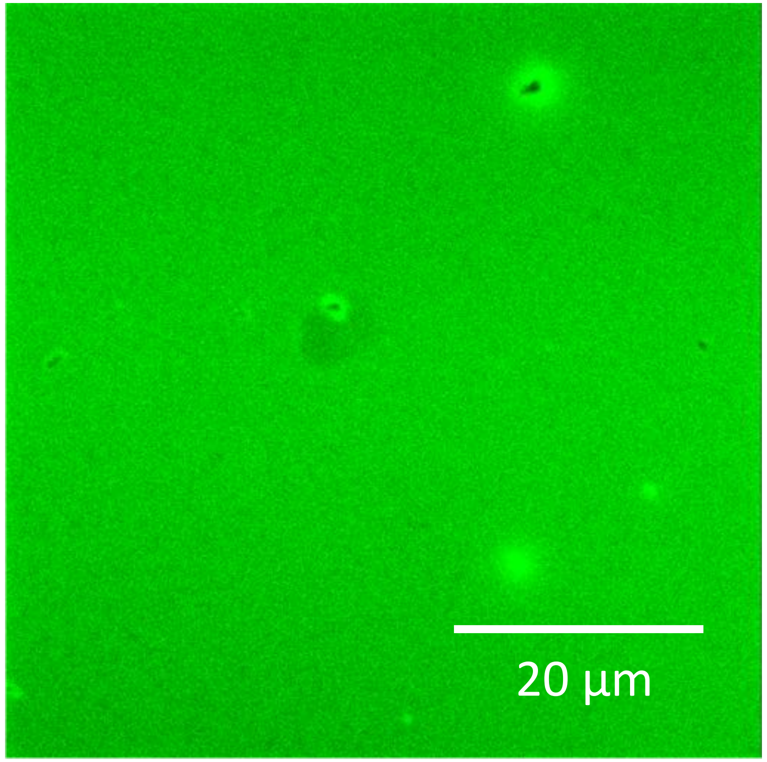


$$D = \frac{r_i^2 + r_{ab}^2}{8\tau_{1/2}}$$

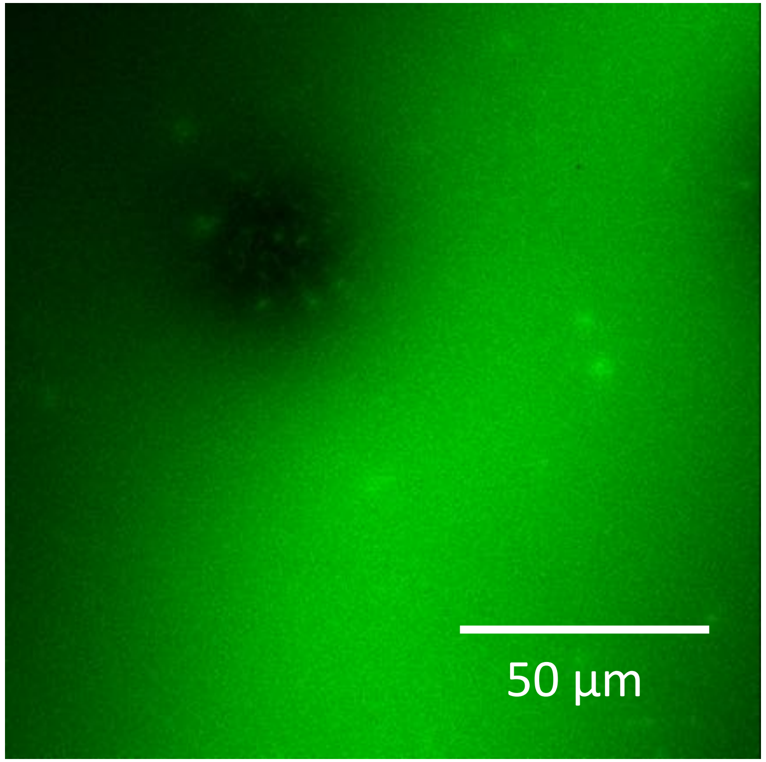
Assumptions:

1. Post-bleach profile described as Gaussian function.
2. Diffusion during photobleaching.

Surface morphology of films with fluorophores



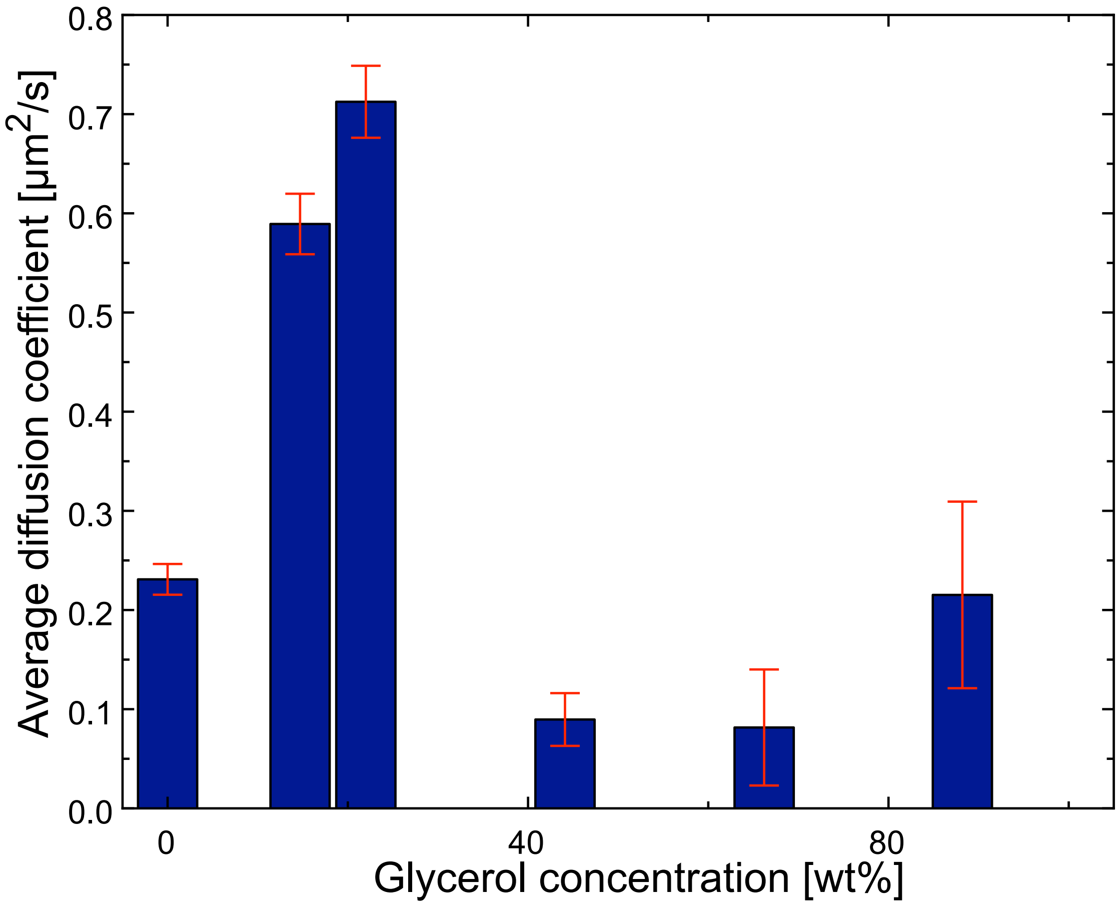
PVA + glycerol + Rhodamine B

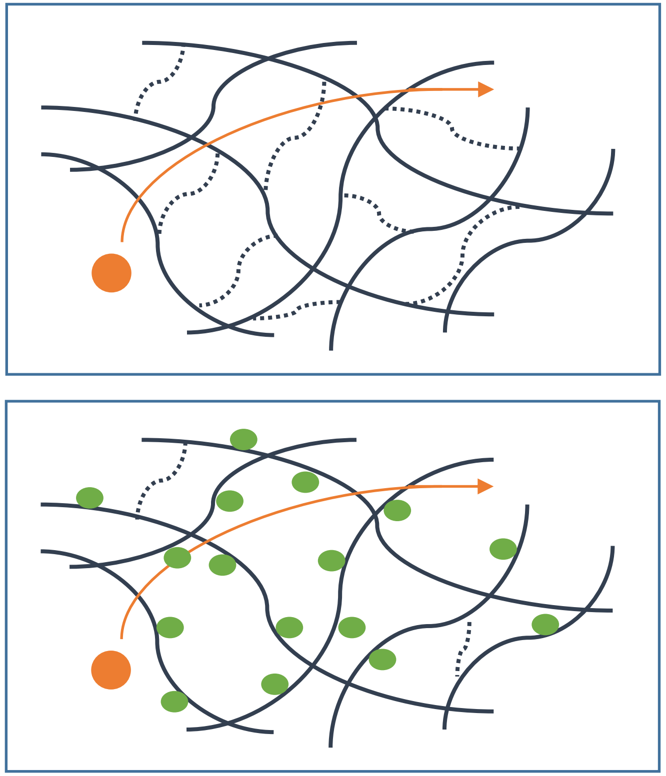


PVA + glycerol + Alexa Fluor 488 Maleimide

- The size of the regions of lower fluorescence intensity varies.
- Regions of increased fluorescence intensity visible on every sample.

Effect of glycerol on mobility of fluorophore

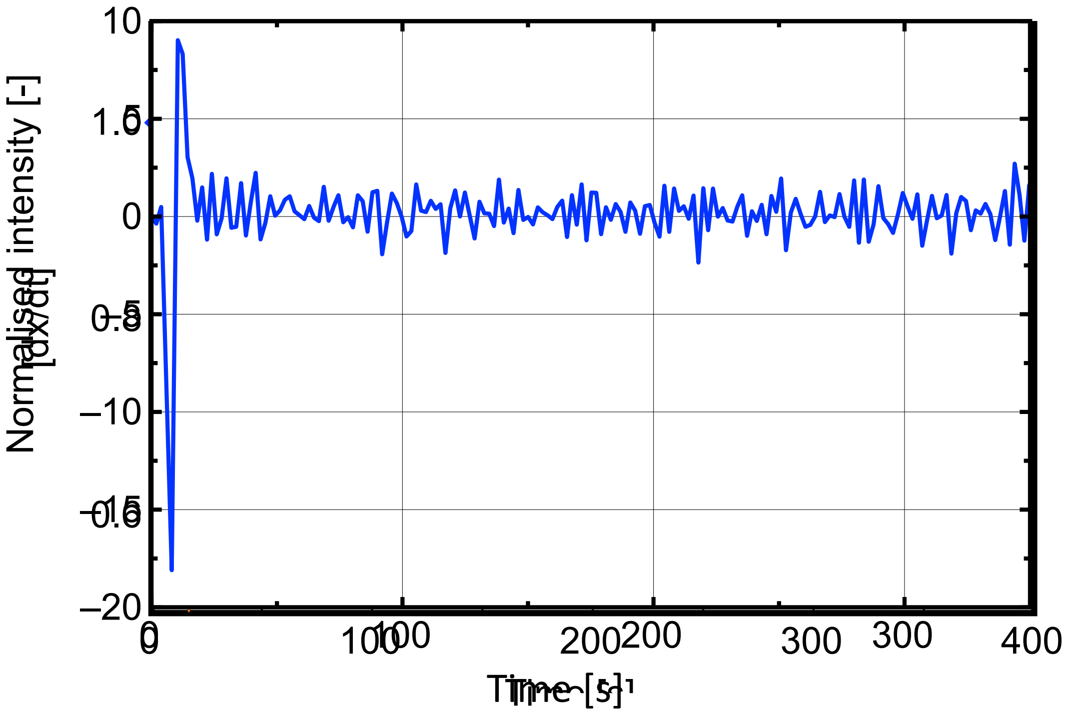




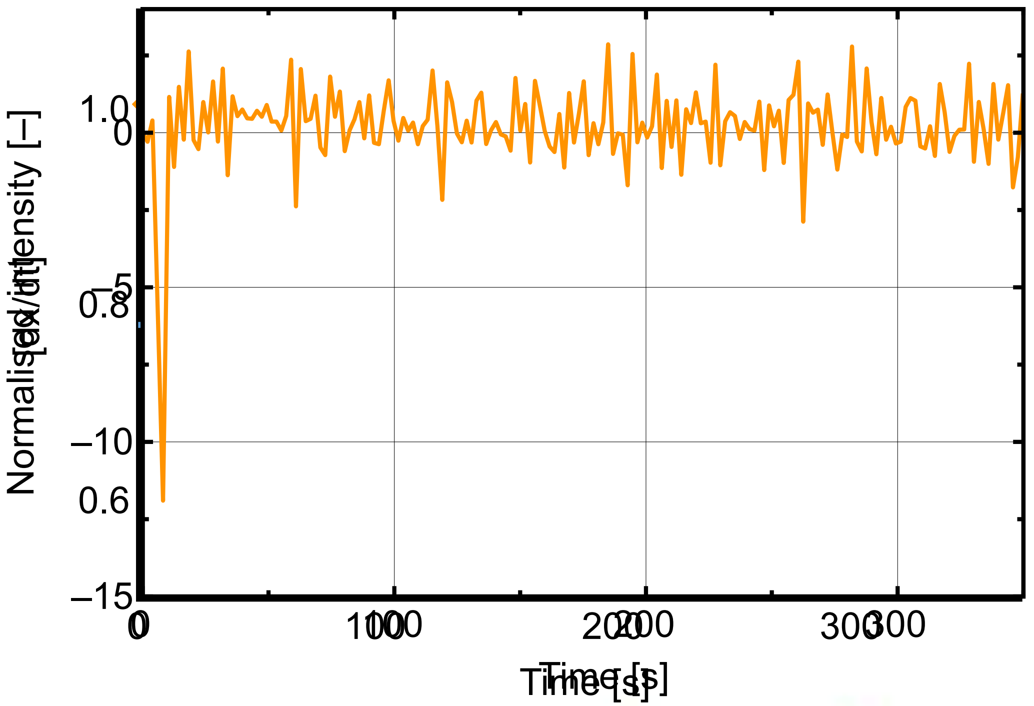
The diffusion coefficient initially increases to be decreased for the sample with PVA:glycerol mass ratio equal to 1:1.
After reaching this level, diffusion coefficient of the tracer is lower compared to system without plasticiser.

Diffusion characteristics vs glycerol fraction

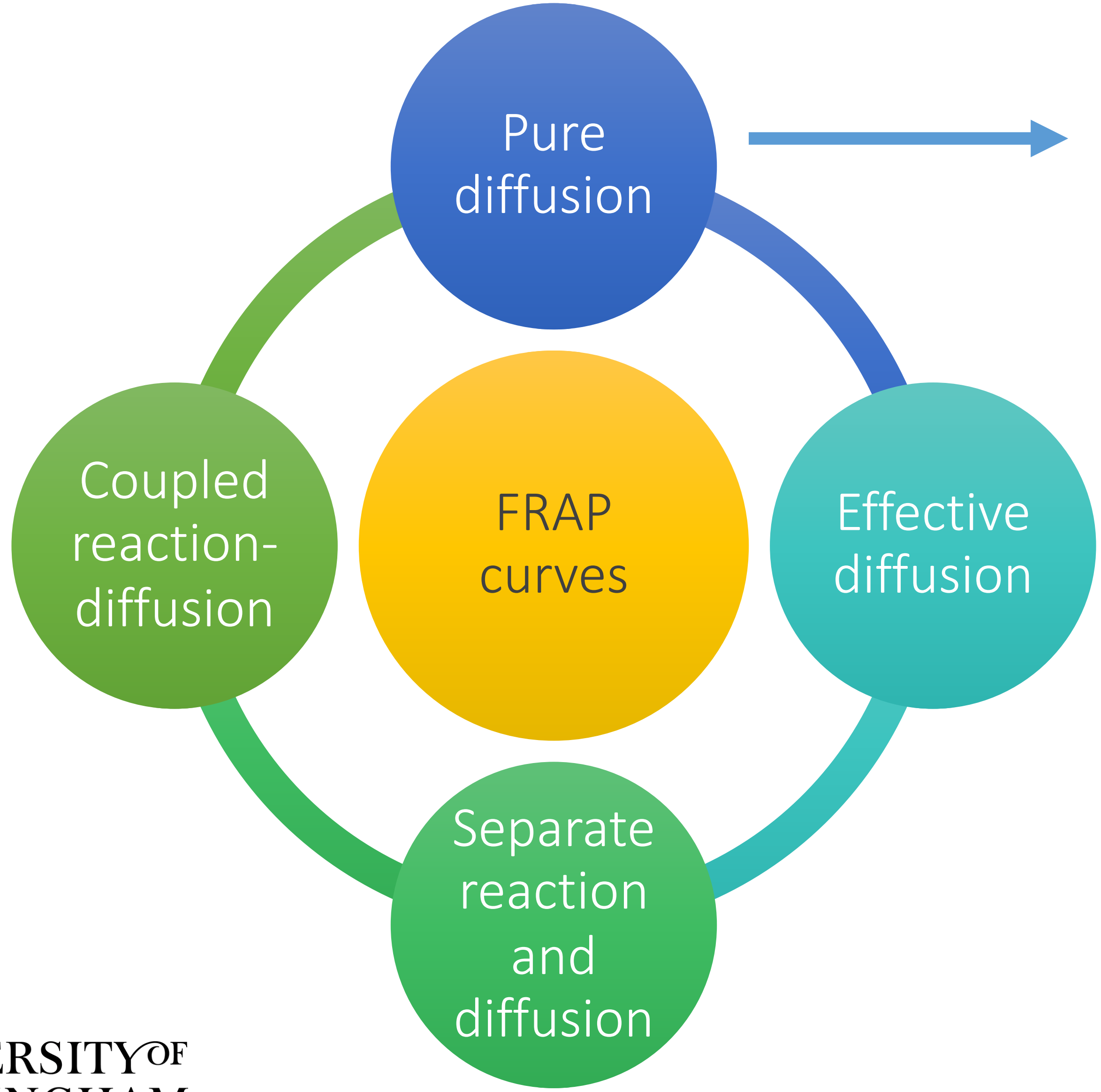
15 wt% glycerol



44 wt% glycerol



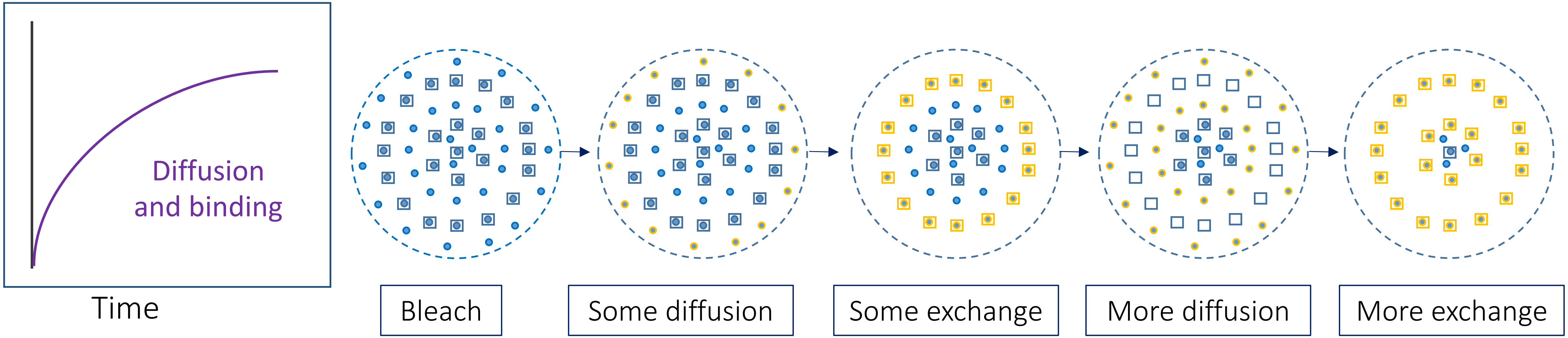
Possible migration mechanisms

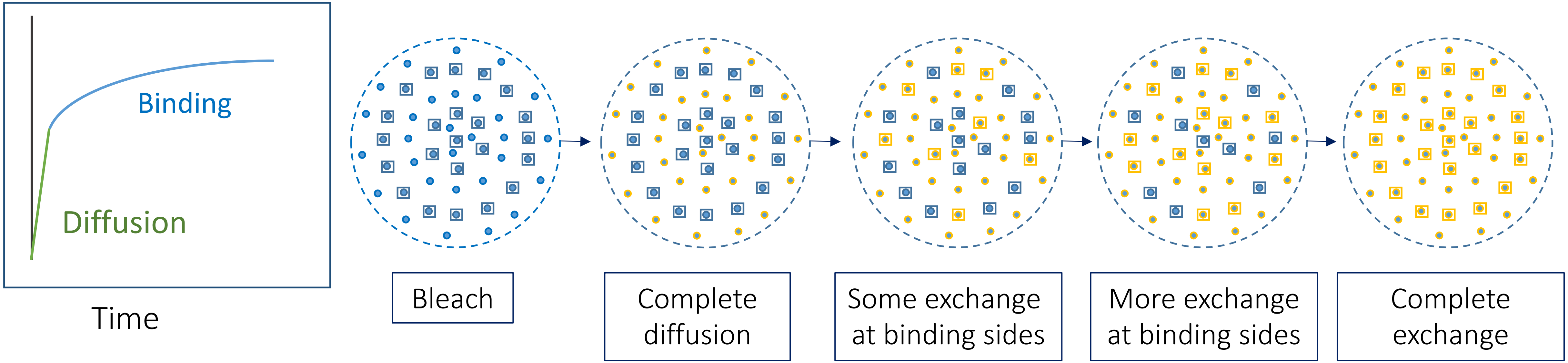


Diffusion-uncoupled mechanism

Diffusion-coupled mechanism

Diffusion kinetics





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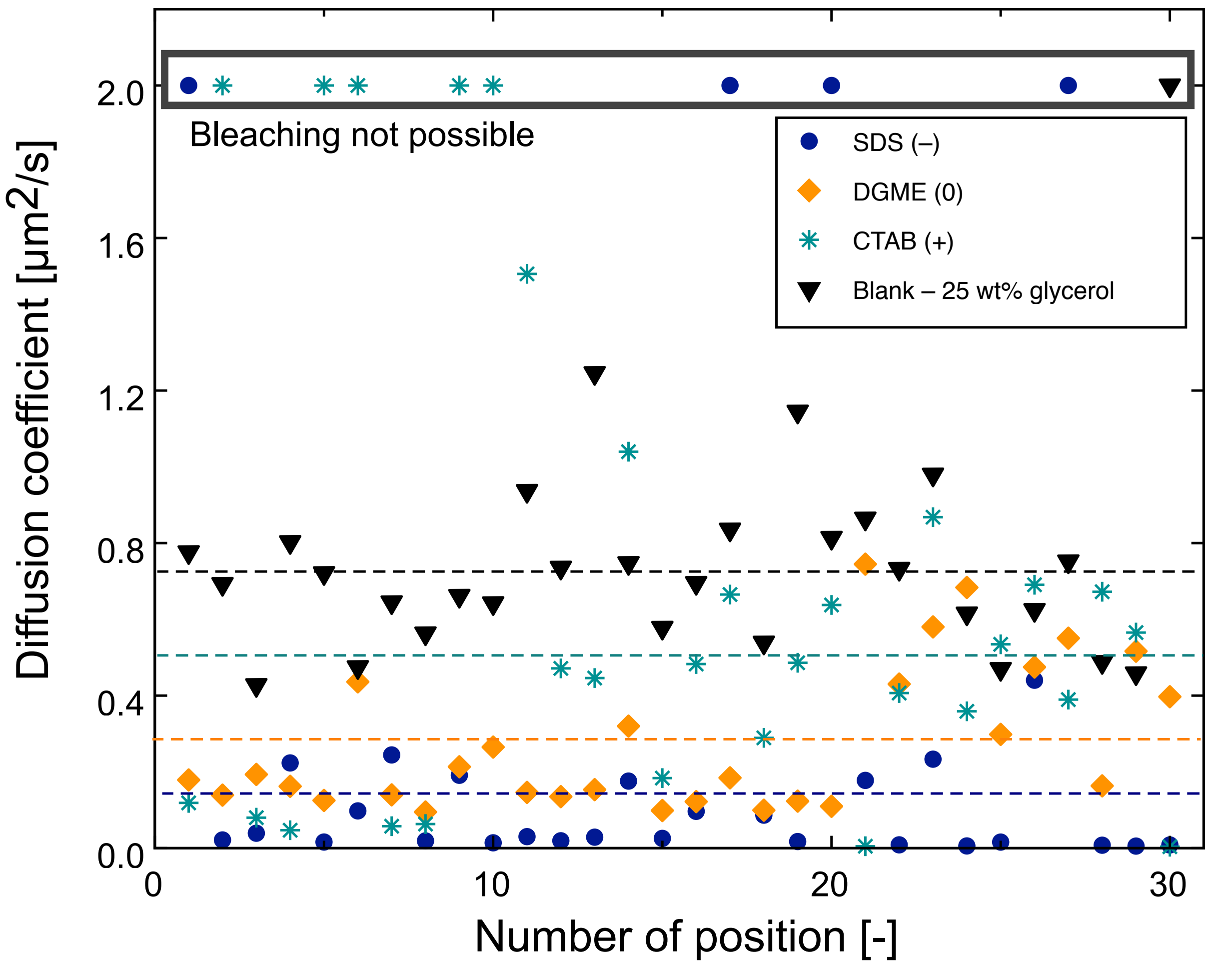
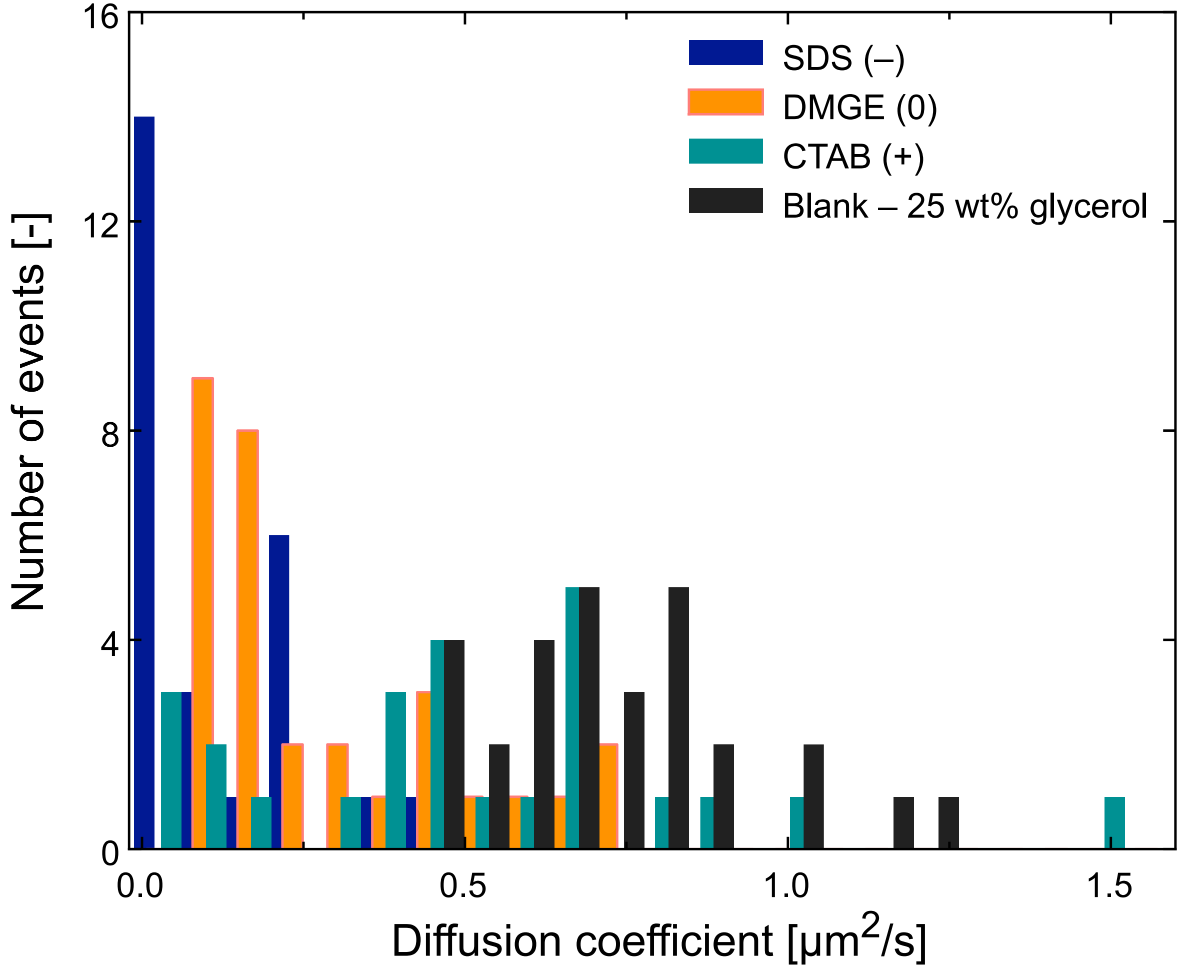
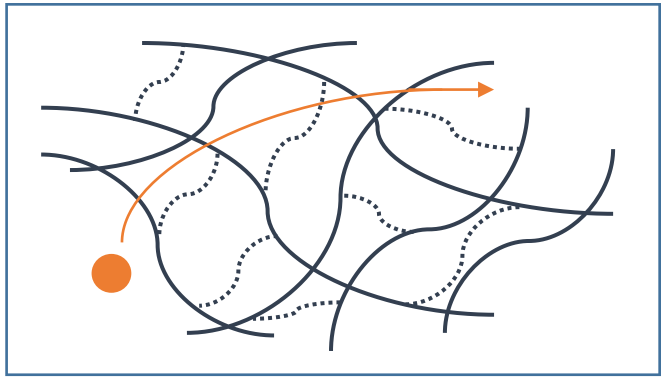
Influence of surfactant on diffusivity of the tracer



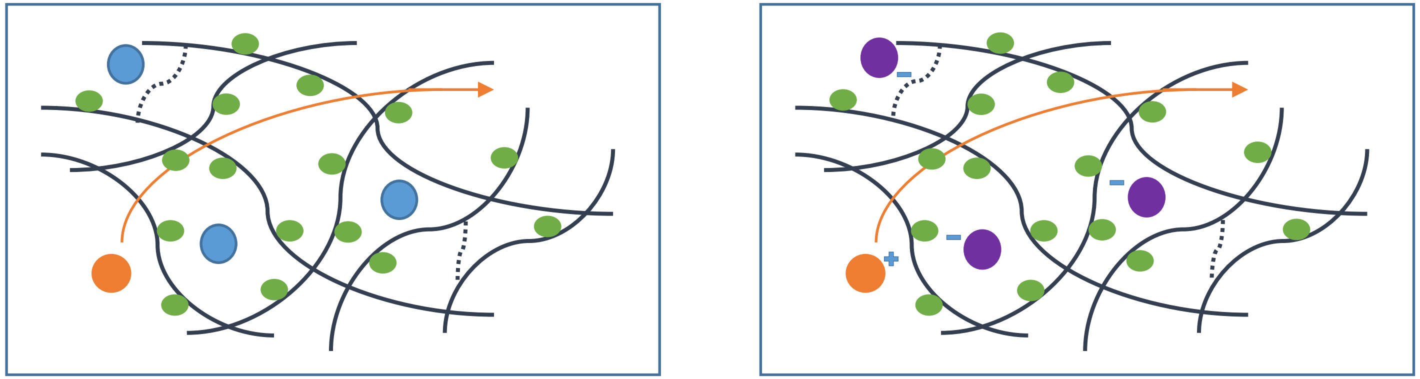


Diffusion in PVA film - hypothesis

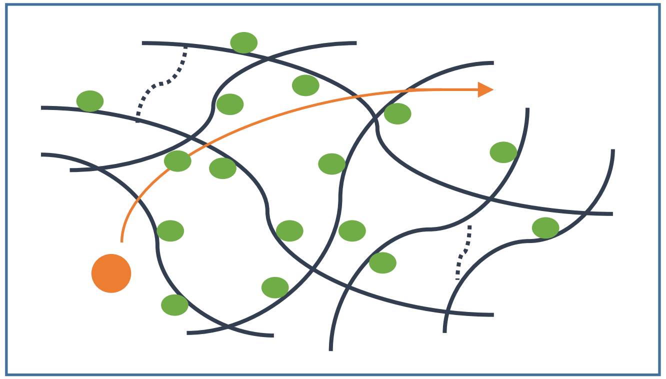
PVA



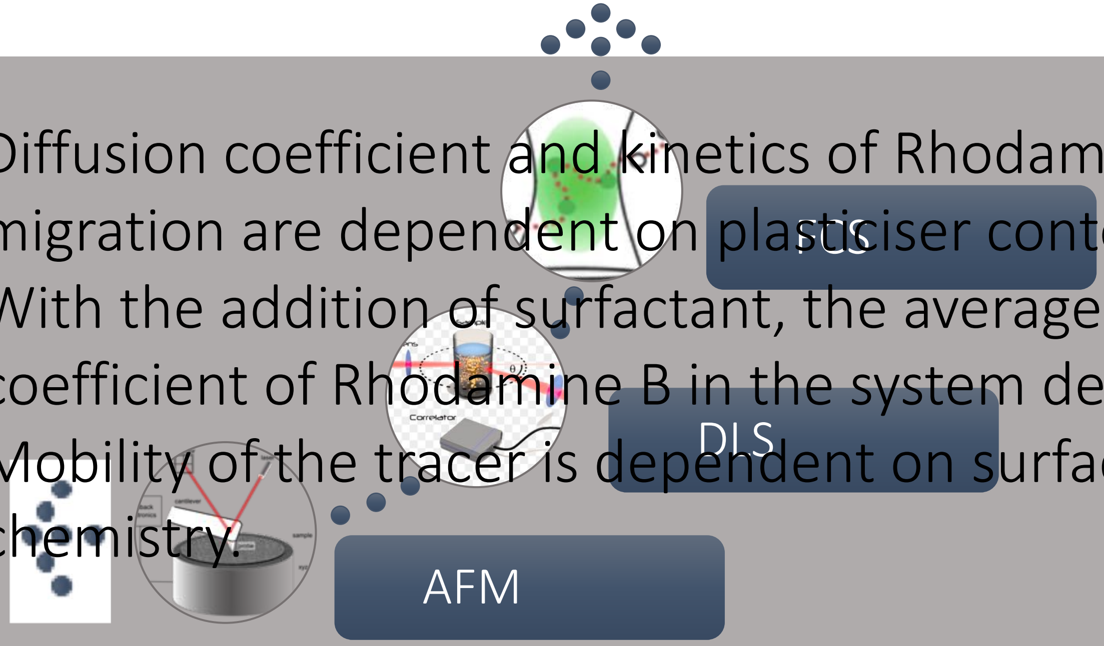
PVA + glycerol + surfactant



PVA + glycerol



- Diffusion coefficient and kinetics of Rhodamine B migration are dependent on plasticiser content.
- With the addition of surfactant, the average diffusion coefficient of Rhodamine B in the system decreases.
- Mobility of the tracer is dependent on surfactant chemistry.



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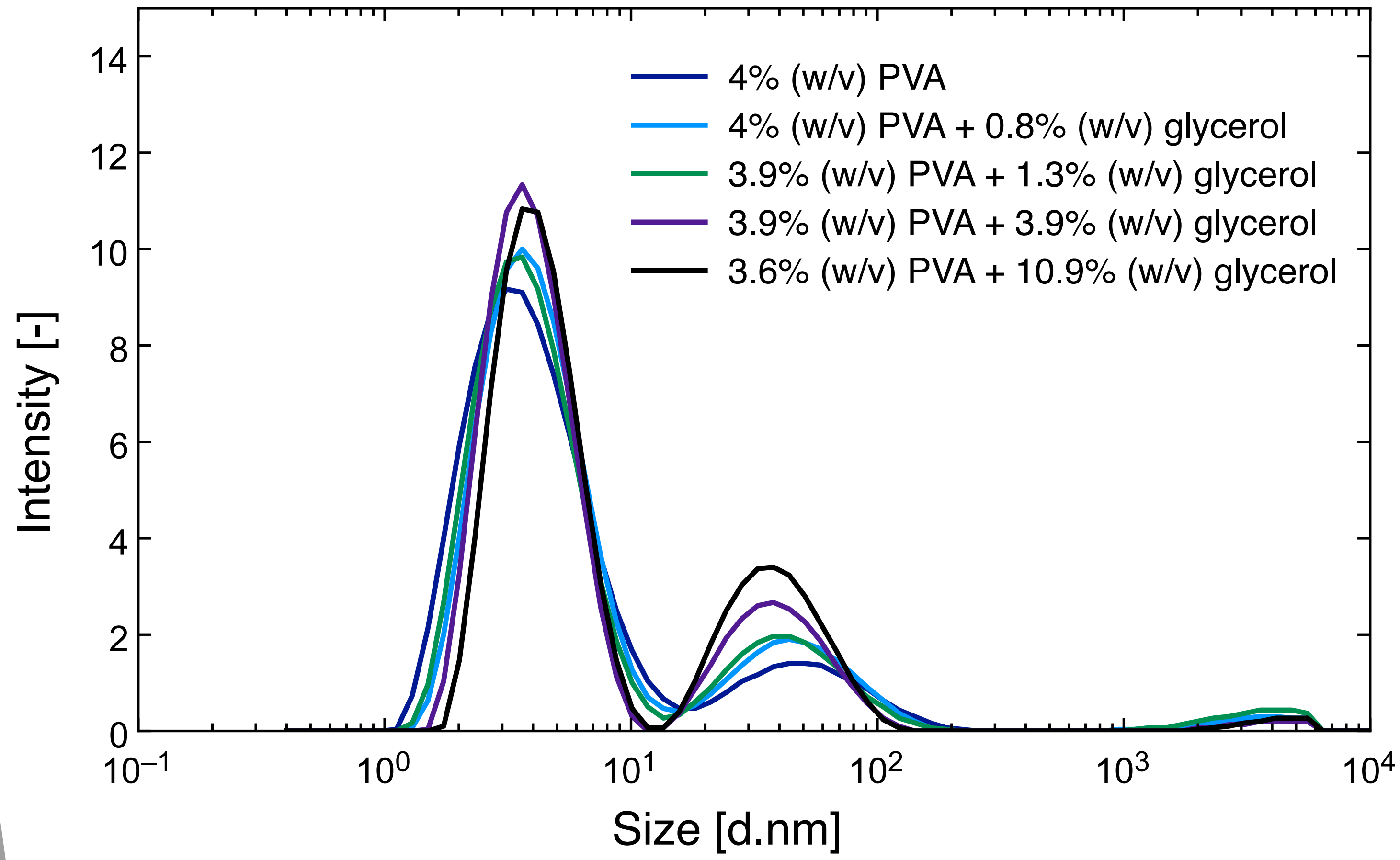
Effect of glycerol on molecular size



- Average particle size does not change significantly after addition of pure glycerol.
- Intensity for DLS data changes, what suggests increasing number of particles of the same size.

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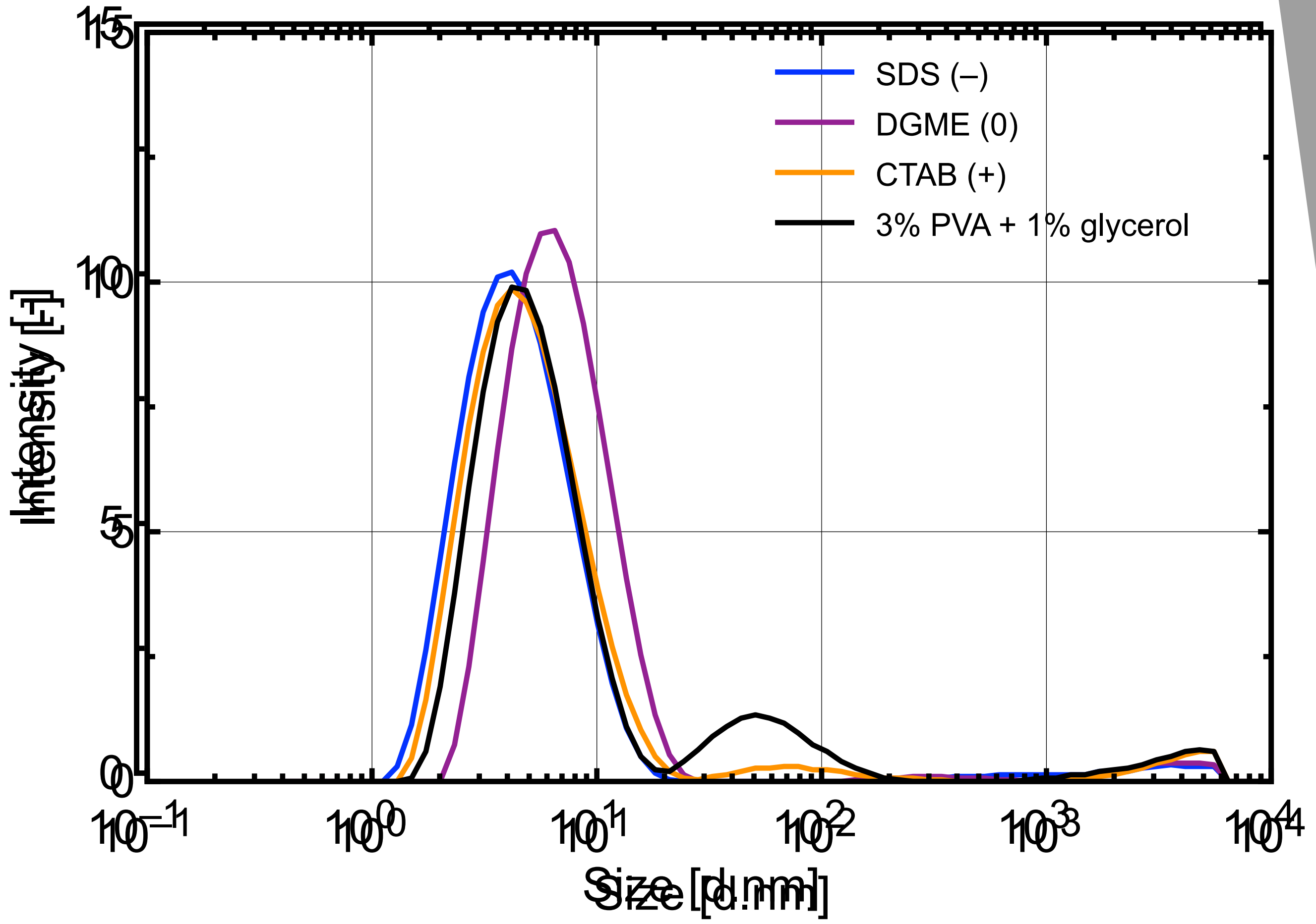
Effect of surfactants on molecular size

- SDS and CTAB: no noticeable impact.
- DGME: causing change.
- Change in the diffusion coefficient is a consequence of spatial effects and interactions between the charged molecules.



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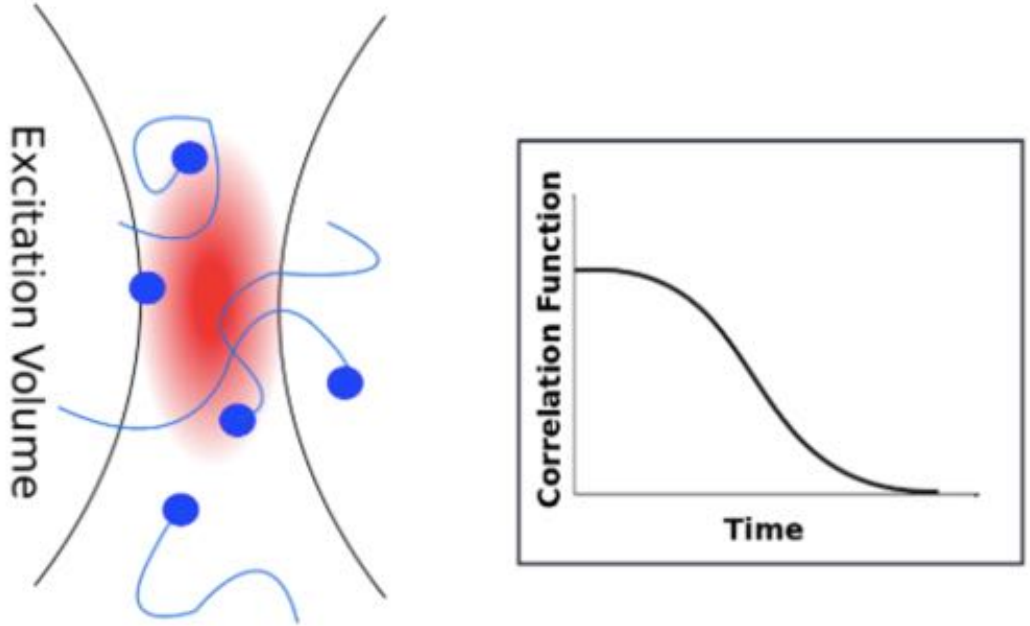
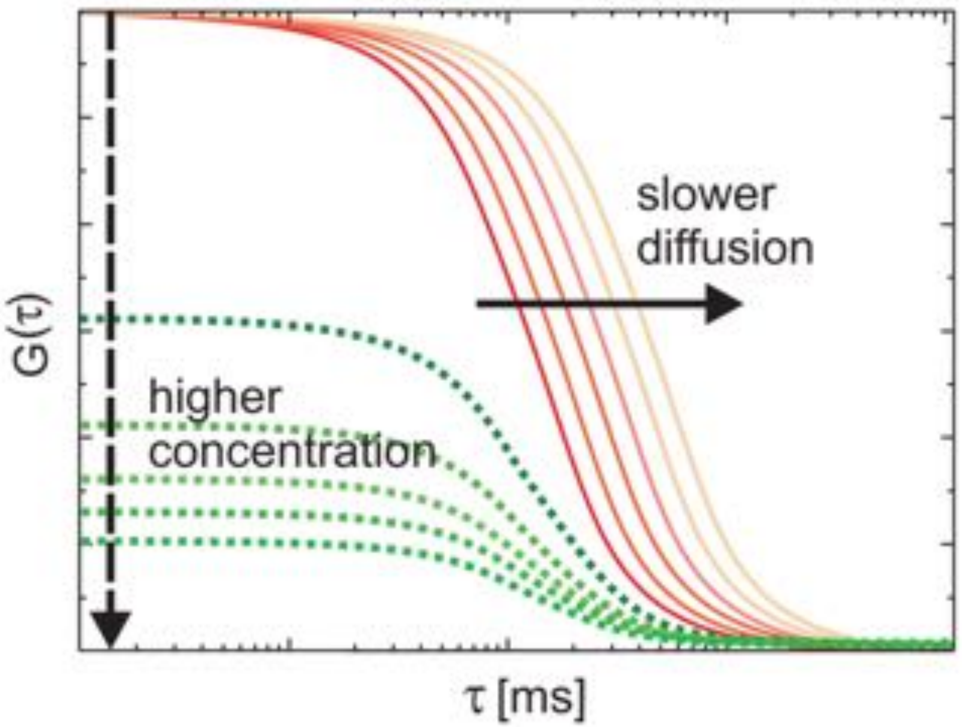
Fluorescence Correlation Spectroscopy (FCS)





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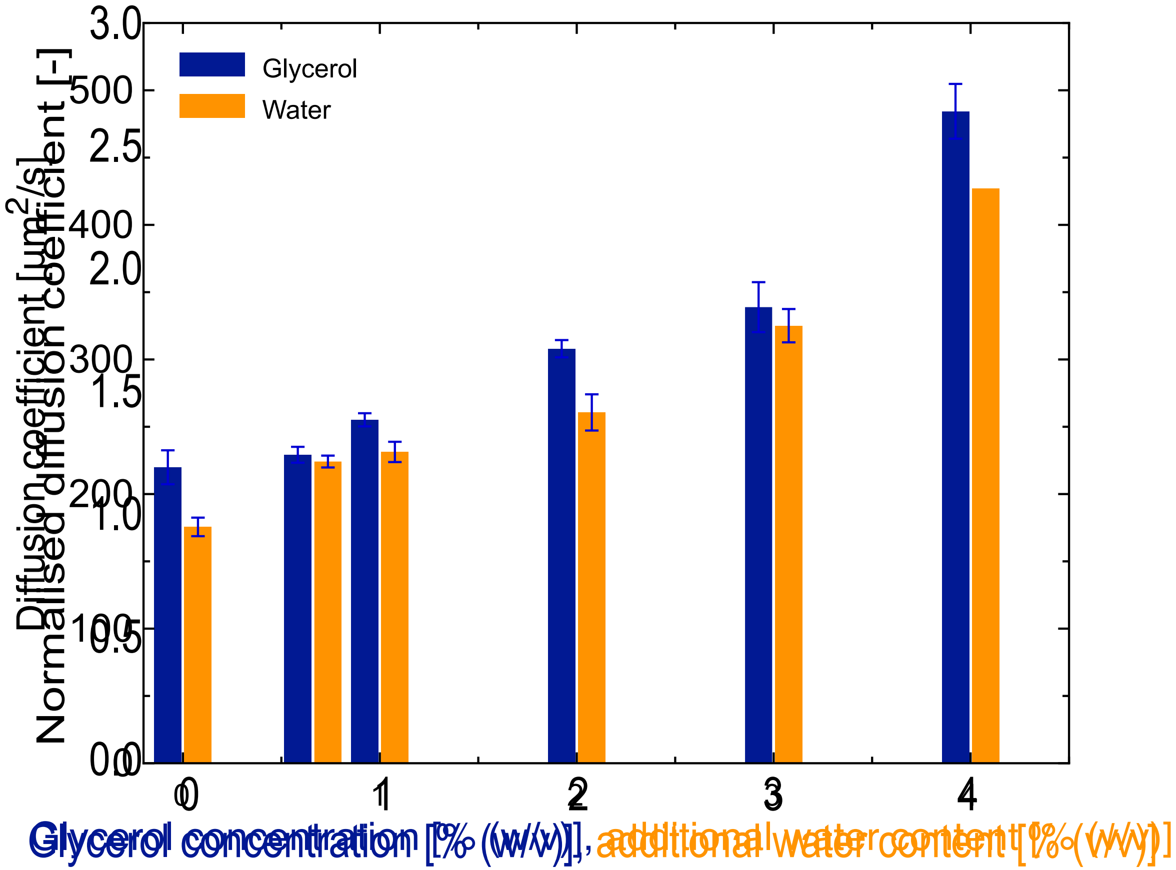
Single molecule tracking – 50 nM concentration – allows to make a conclusion about interactions present in the system.

Diffusion coefficient obtained from fitting autocorrelation function to the appropriate model.

Diffusion coefficients of RhB *vs* PVA concentration



- The measurements were performed on different days (different laser output, different temperature) - correction only for temperature would not give representative results.
- Normalised diffusion coefficient (diffusion coefficient of tracer in given solution/diffusion coefficient of tracer in 4% (w/v) PVA solution) was calculated and compared.

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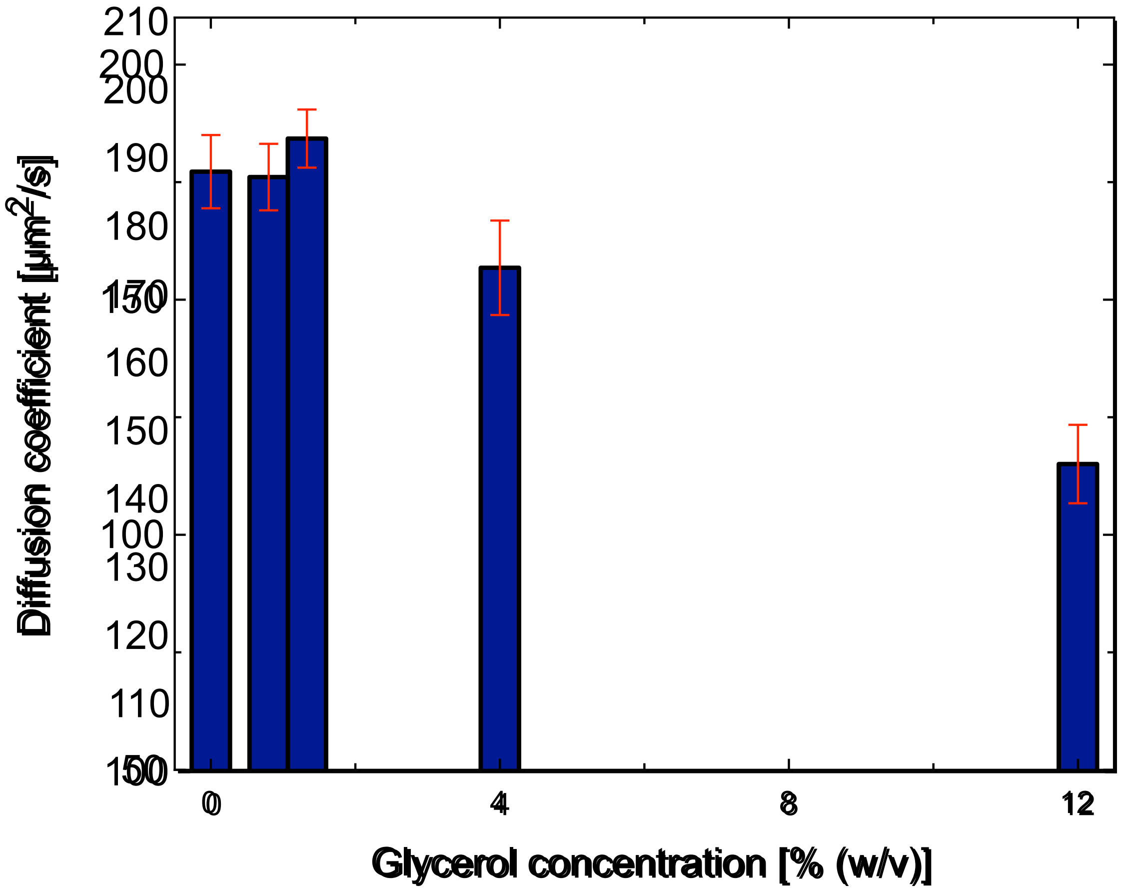
Plasticising effect of glycerol

- The trend is very similar to the one observed for thin films with various glycerol content.
- For small glycerol concentrations, the diffusion coefficient of Rhodamine B oscillates around diffusivity in 4% (w/v) PVA solution and then decreases for higher glycerol concentration.



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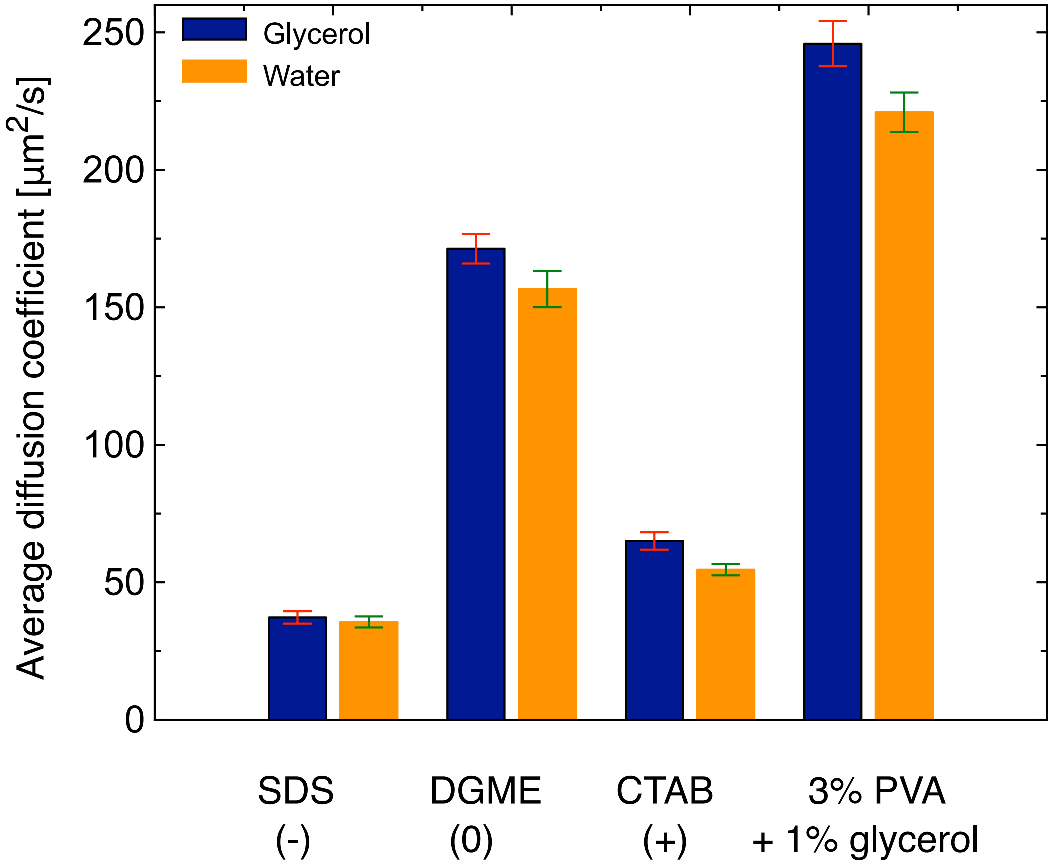
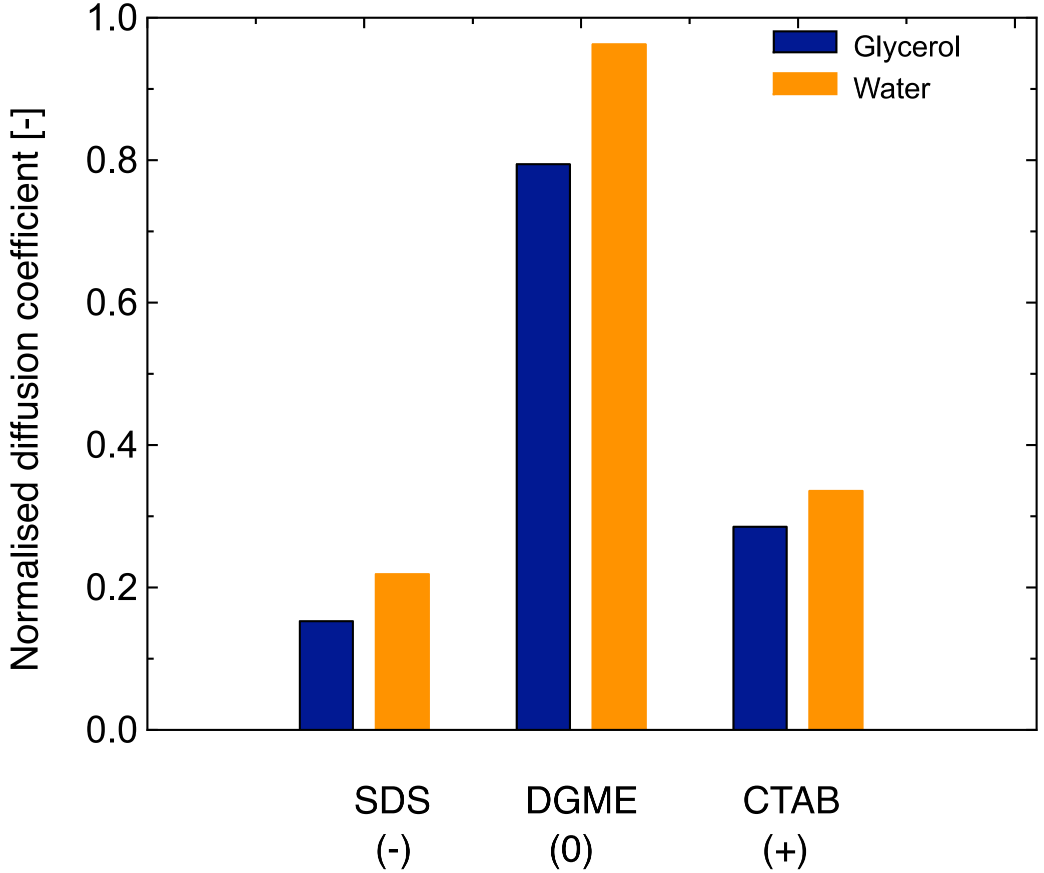
Diffusion of the fluorophore in PVA/surfactant solutions

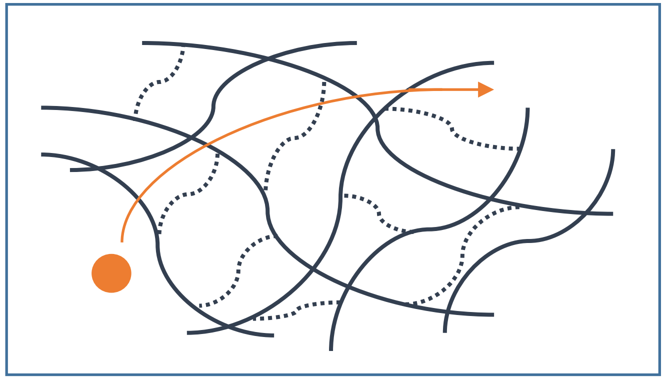




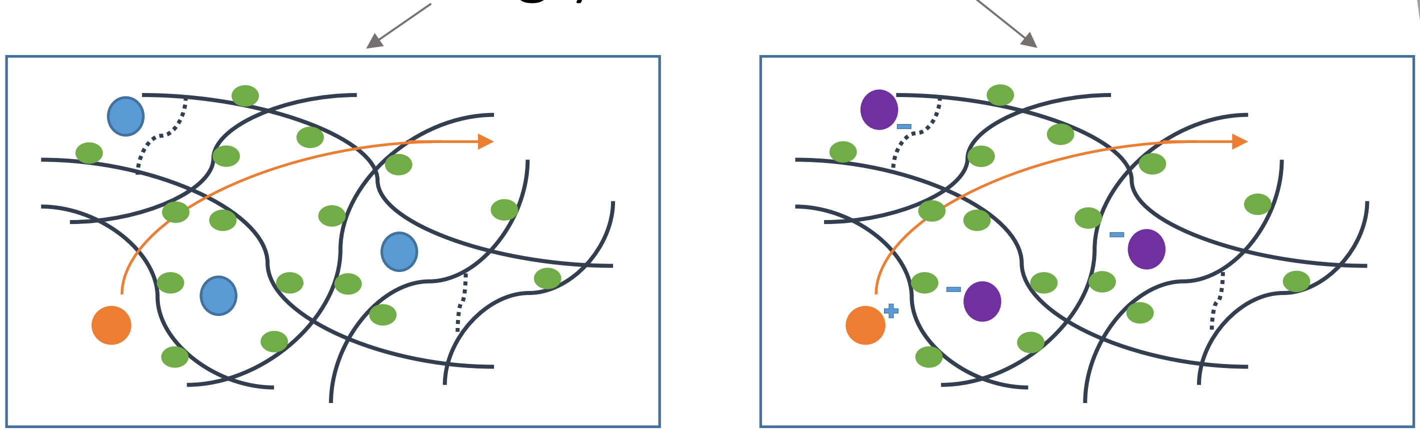
- Dilution with water increases diffusion coefficient more than addition of glycerol solution.
- Rhodamine B – surfactant interactions as well as increasing size and number of molecules are probably responsible for decreasing diffusion coefficient in the systems doped with surfactants.

Conclusions

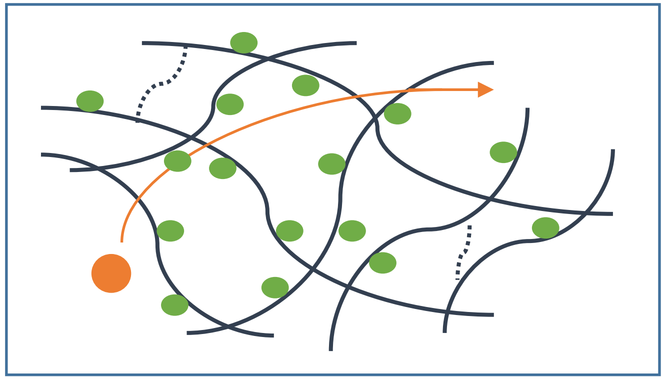
PVA



PVA + glycerol + surfactant



PVA + glycerol



- Migration in investigated system depends on chemistry and concentration of additives, time, and humidity.
- Surfactants present in the system lead to changes in morphology of the films as well as decreasing diffusion coefficient of the tracer.
- Glycerol content influences diffusion coefficient of the tracer and migration kinetics.

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Thank you for your kind attention.

kxm654@student.bham.ac.uk

Plasticisation effect on diffusivity of the tracer

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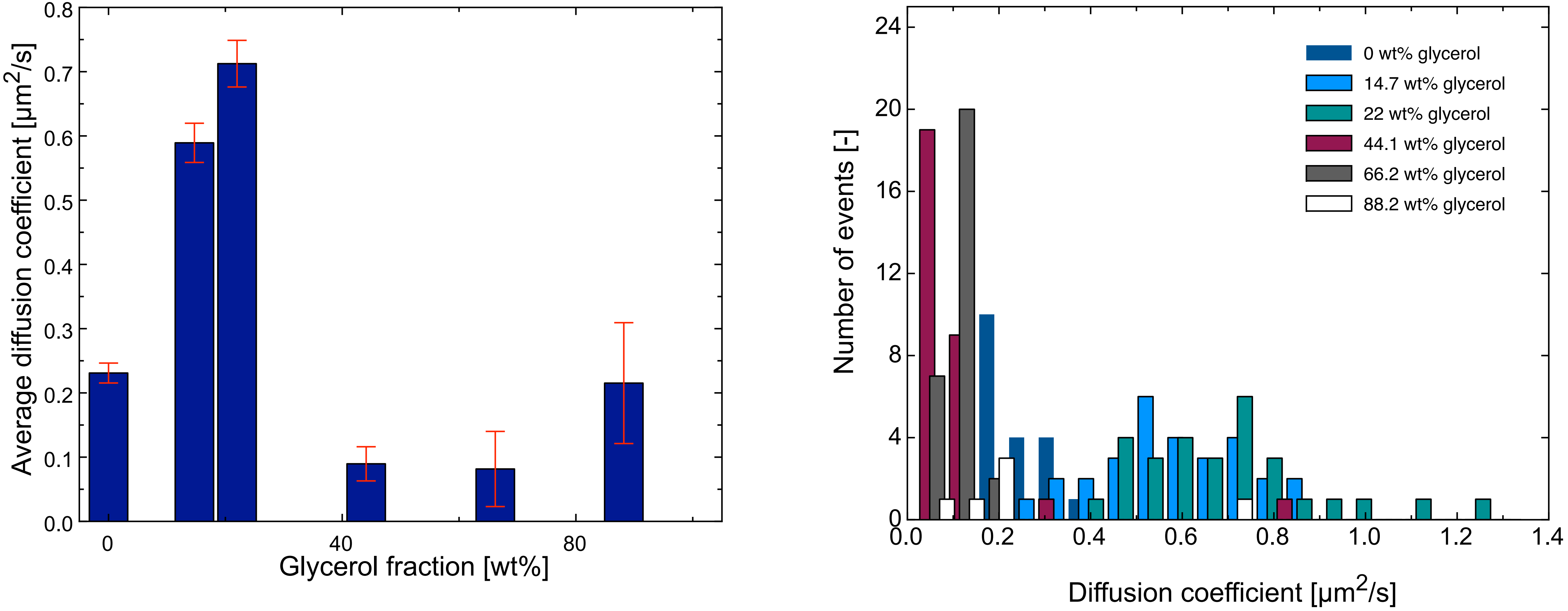

The diffusion coefficient initially increases to be decreased for the sample with PVA:glycerol mass ratio equal to 1:1. After reaching this level, diffusion coefficient is lower than for pure PVA.

DLS – influence of polymer concentration

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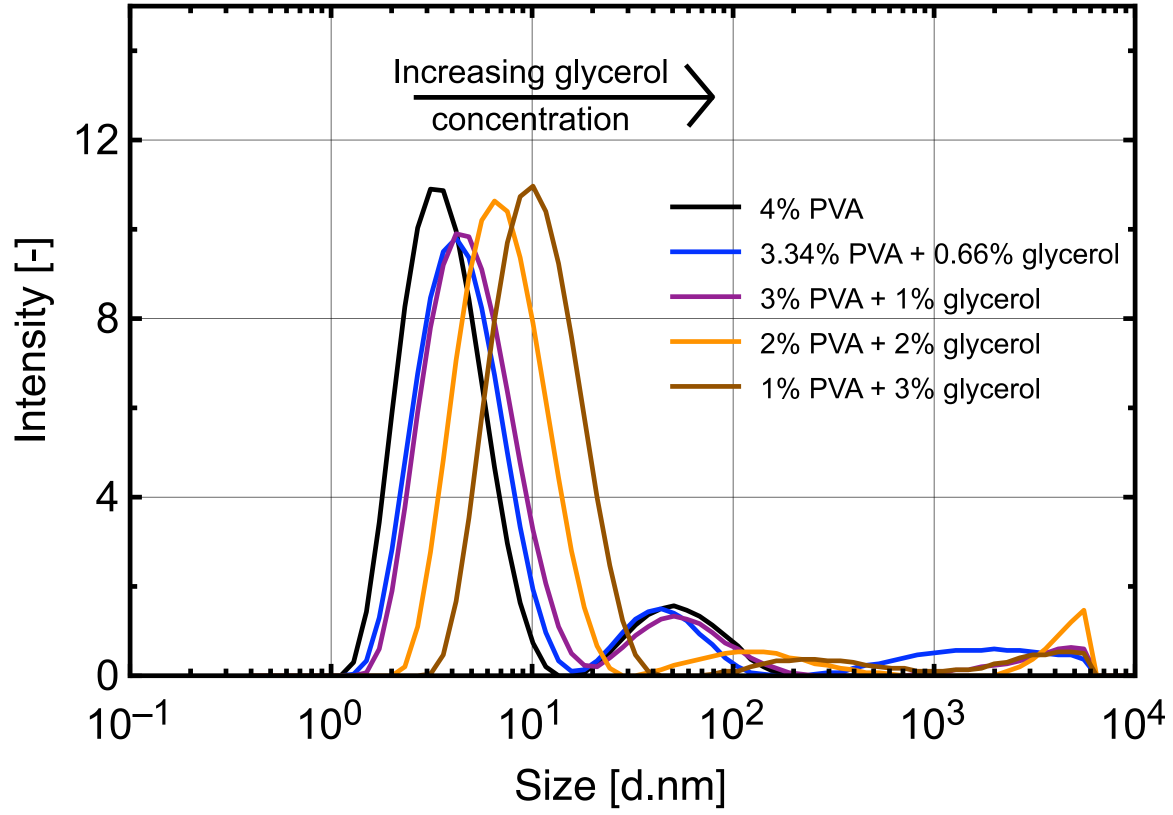

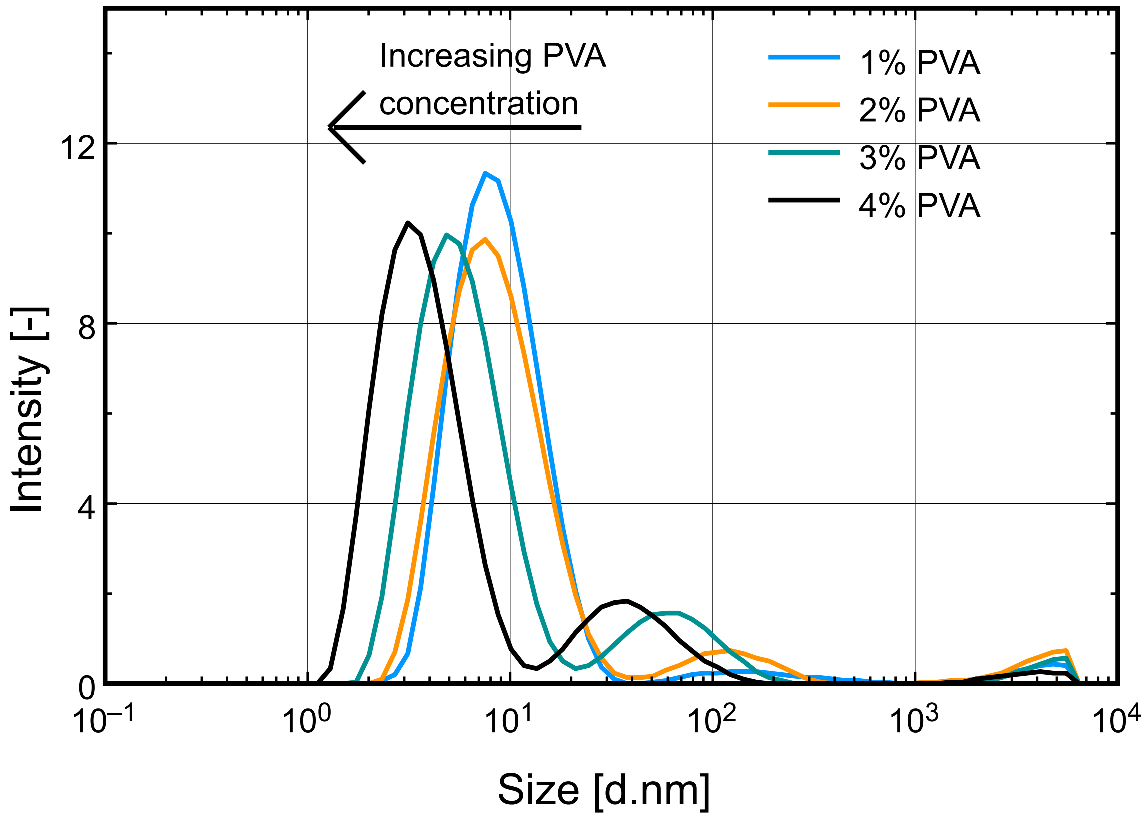

Solvation might be responsible for increase in average size with decreasing PVA concentration.
Trend for PVA solutions of various concentration is very similar to the one observed for addition of 4 wt% glycerol solution.