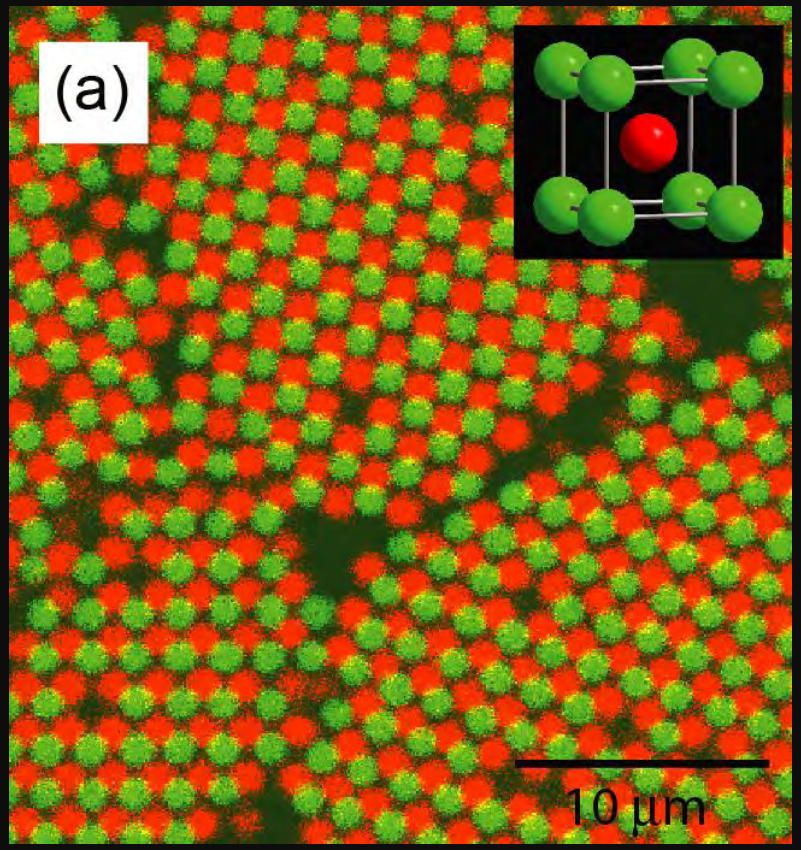
Nano-ions: How do you produce charge in a non-polar world?



Charged: *ordered CsCl superlattice*

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School of Chemistry, University of Bristol, UK.

Why are ions so difficult to generate in non-polar solvents?

Bjerrum length

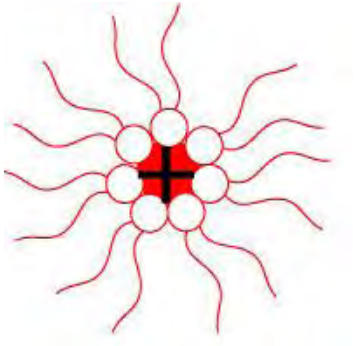
$$\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$$

Separation of unit charges at which:

Coulombic energy = $k_B T$

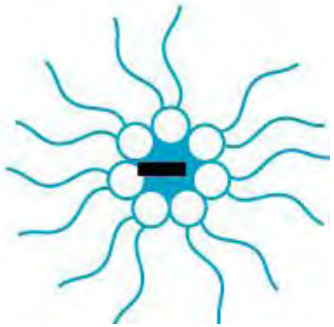
$$\lambda_B = 0.7 \text{ nm} \quad \epsilon_r \sim 80$$

$$\lambda_B = 28 \text{ nm} \quad \epsilon_r \sim 2$$

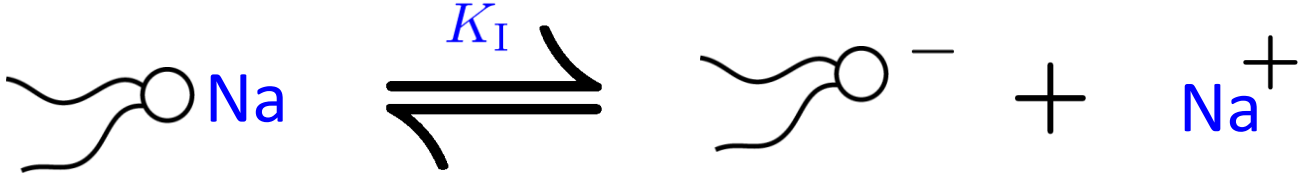


In non-polar solvents ions must be embedded in *larger* structures such as reverse micelles or microemulsion drops

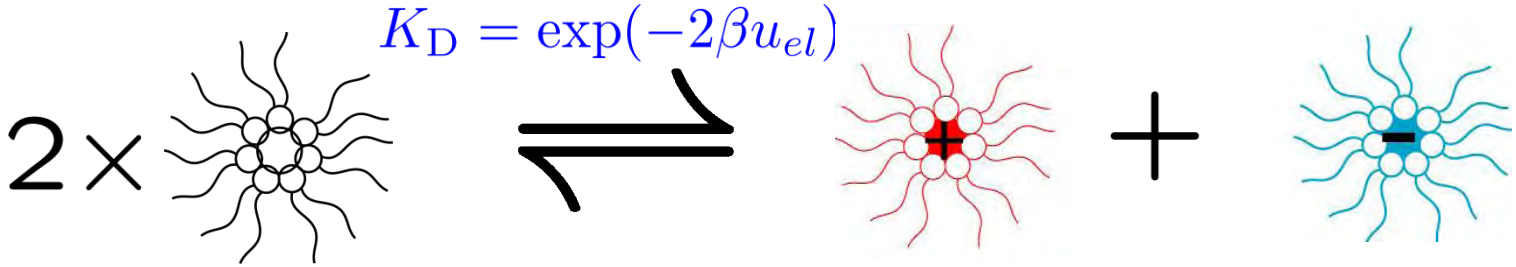
Nano-ions



Formation by ionization *or* thermal disproportionation



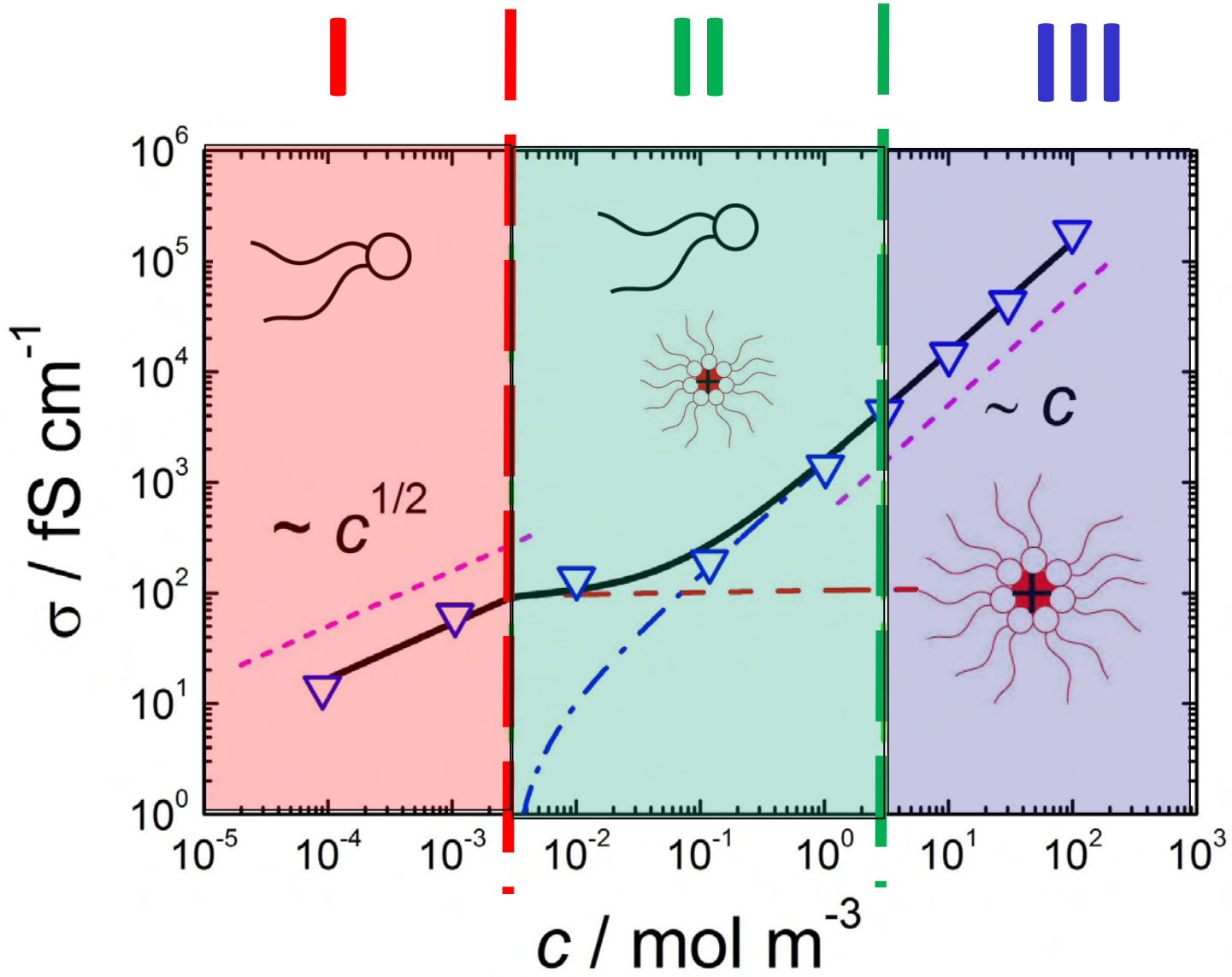
$$K_I = \frac{c_{ion}^2}{c} \rightarrow \boxed{c_{ion} \propto c^{1/2}}$$



Electrostatic energy to charge a micelle of radius *r* $\beta u_{el} = \frac{\lambda_B}{2r}$

$$K_D = \frac{c_{ion}^2}{c^2} \rightarrow \boxed{c_{ion} \propto c}$$

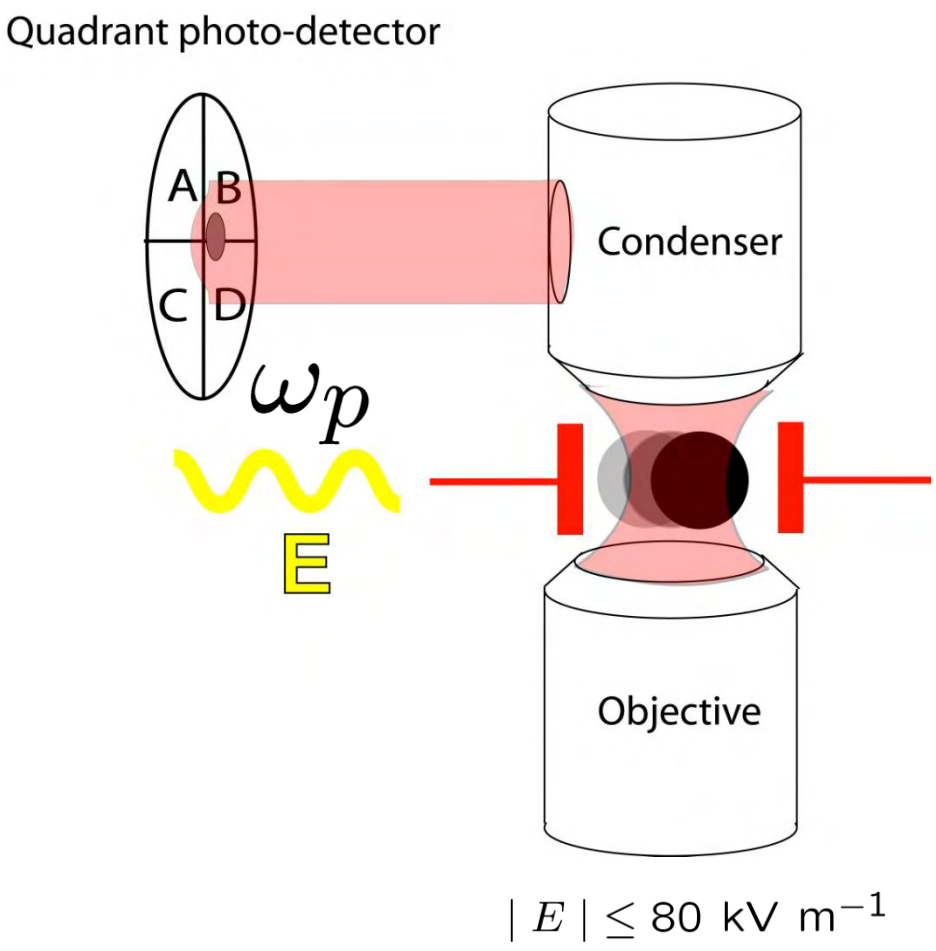
Conductivity of AOT in dodecane

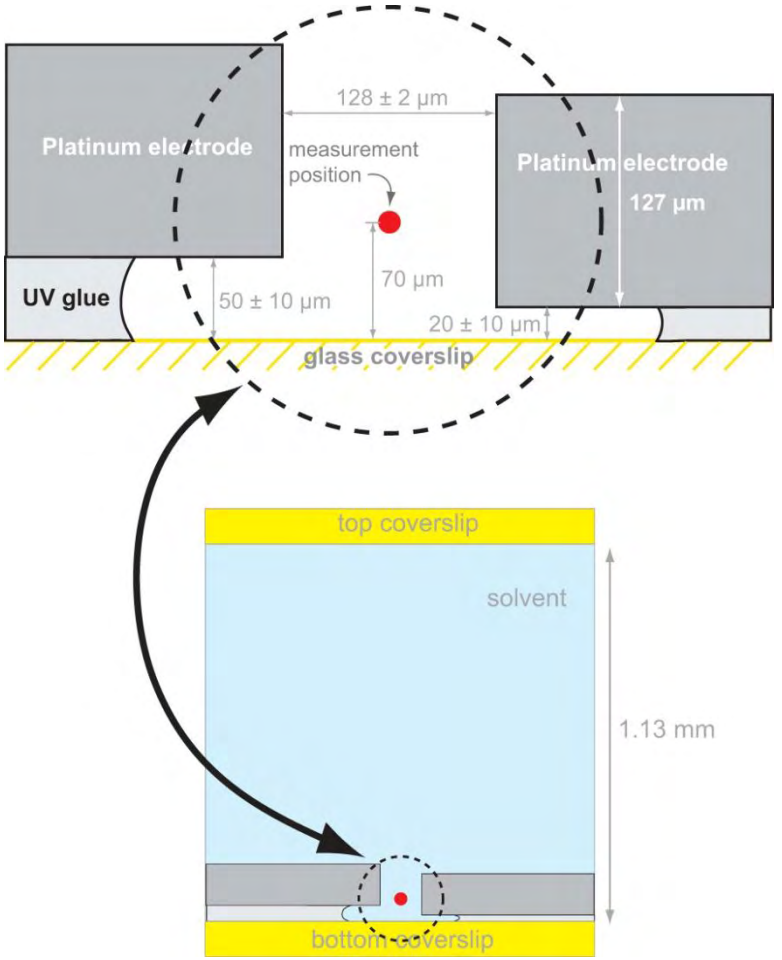


Open questions?

- How do colloids charge in non-polar environments?
- How can we control the level and sign of the charge?

Single particle optical microelectophoresis (SPOM)

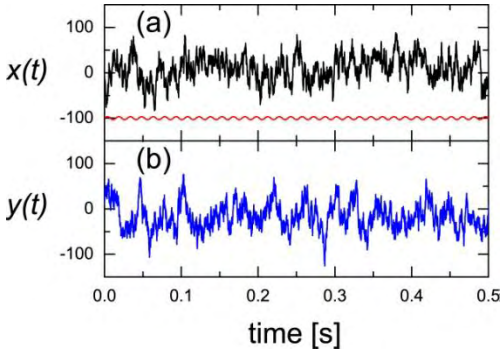


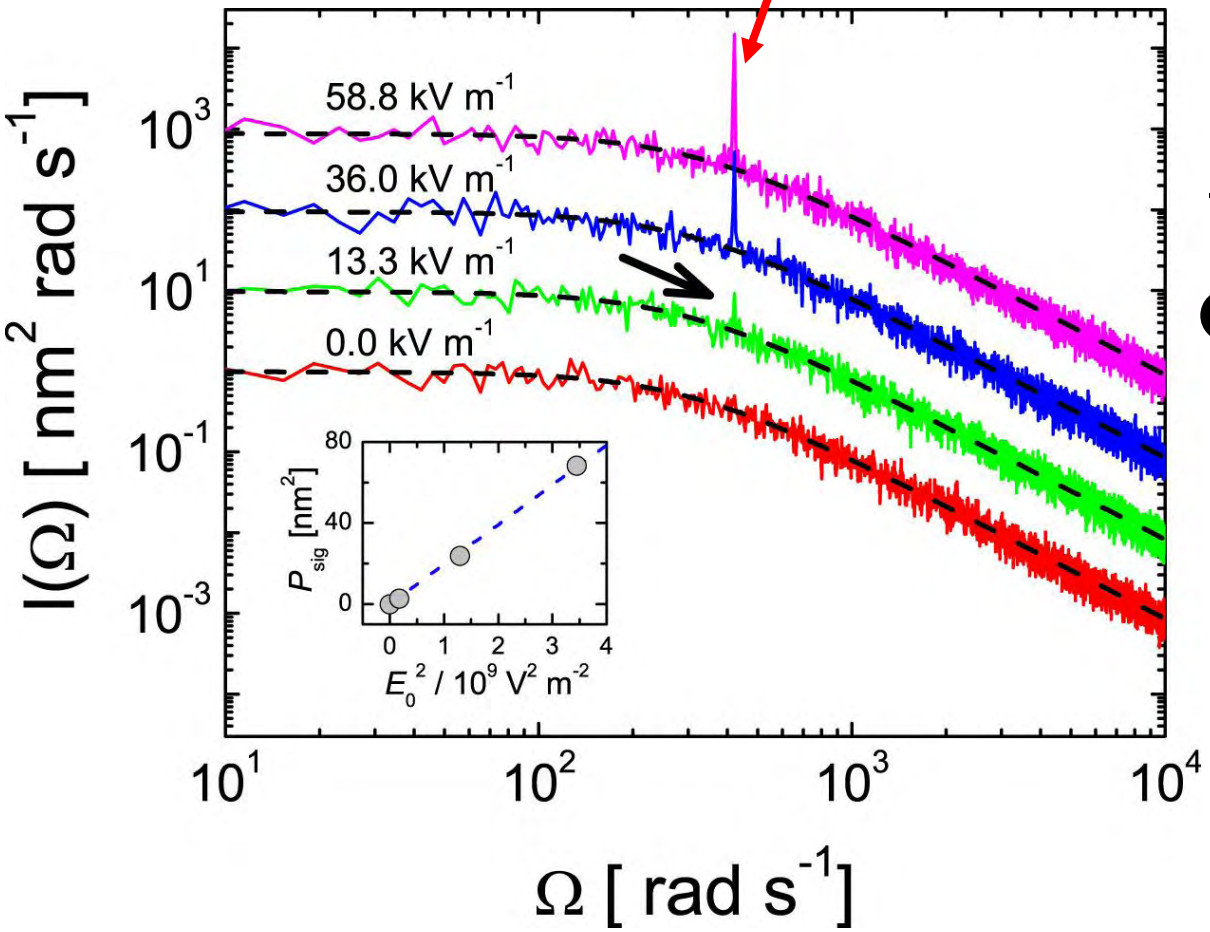


Single particle optical microelectrophoresis

$\propto Z^2$

F.T.





Advantages:

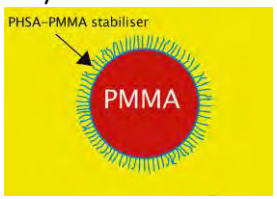
- Highly sensitive:

  Minimum detectable charge ~ 0.25 e

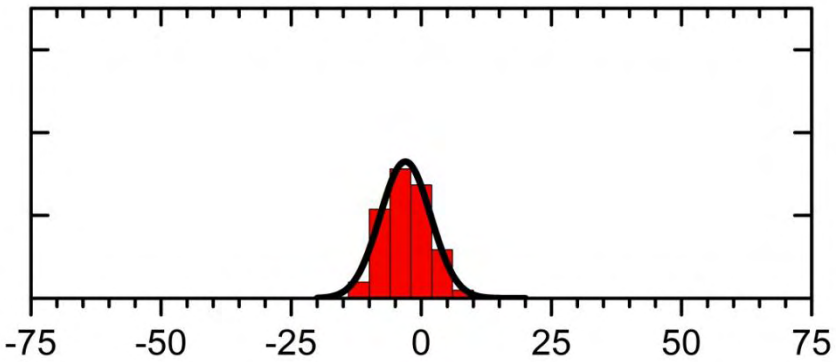
- Measure charge distribution directly, not averages.

Charging-up colloids in non-polar environments

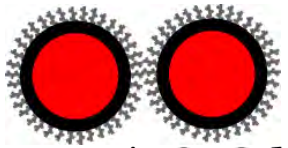
$\langle R \rangle = 610$ nm



Dry dodecane



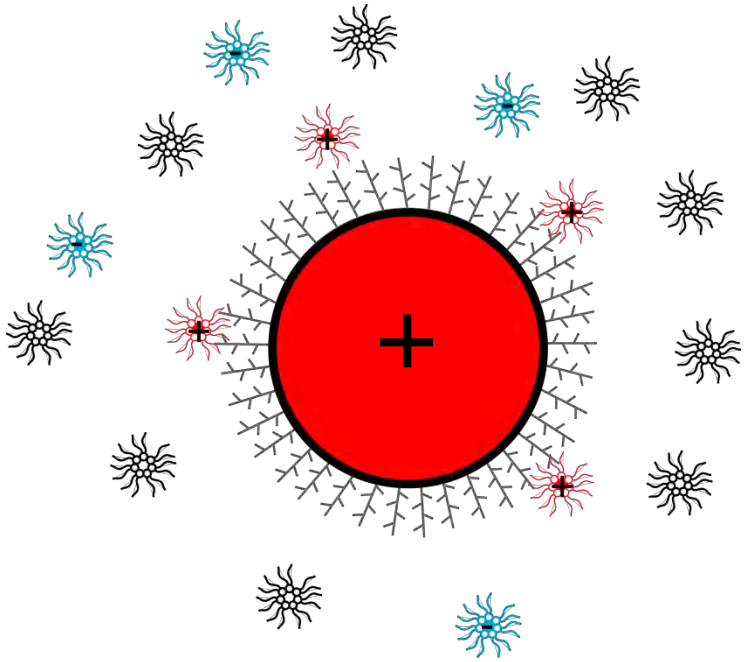
$\langle Z_{\text{eff}} \rangle = -2.9$



$U_c = +0.2 k_B T$

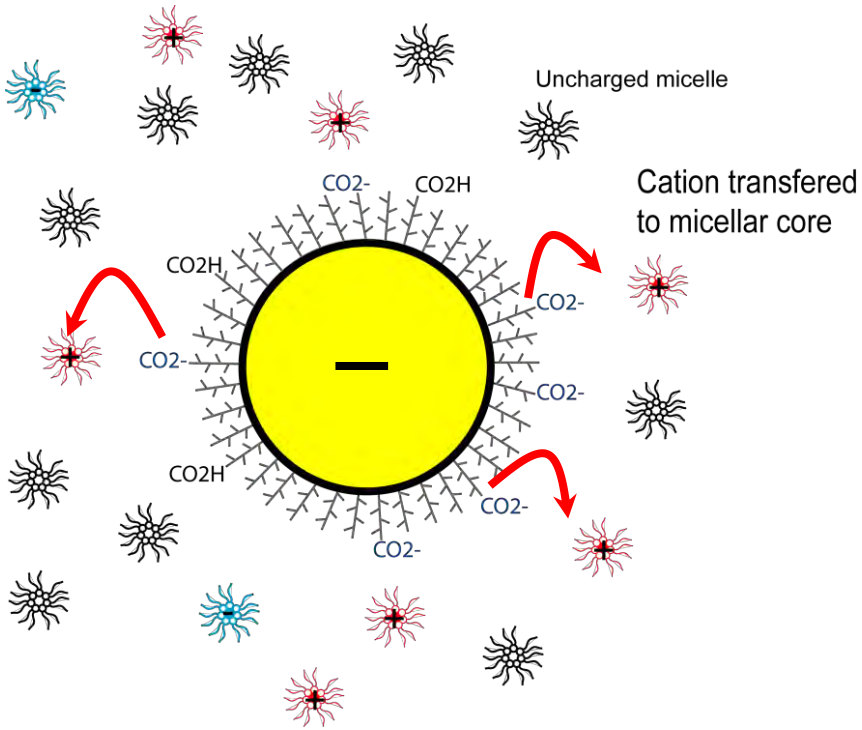
Non-polar charging mechanisms

I. Adsorption of nano-ions / surfactants



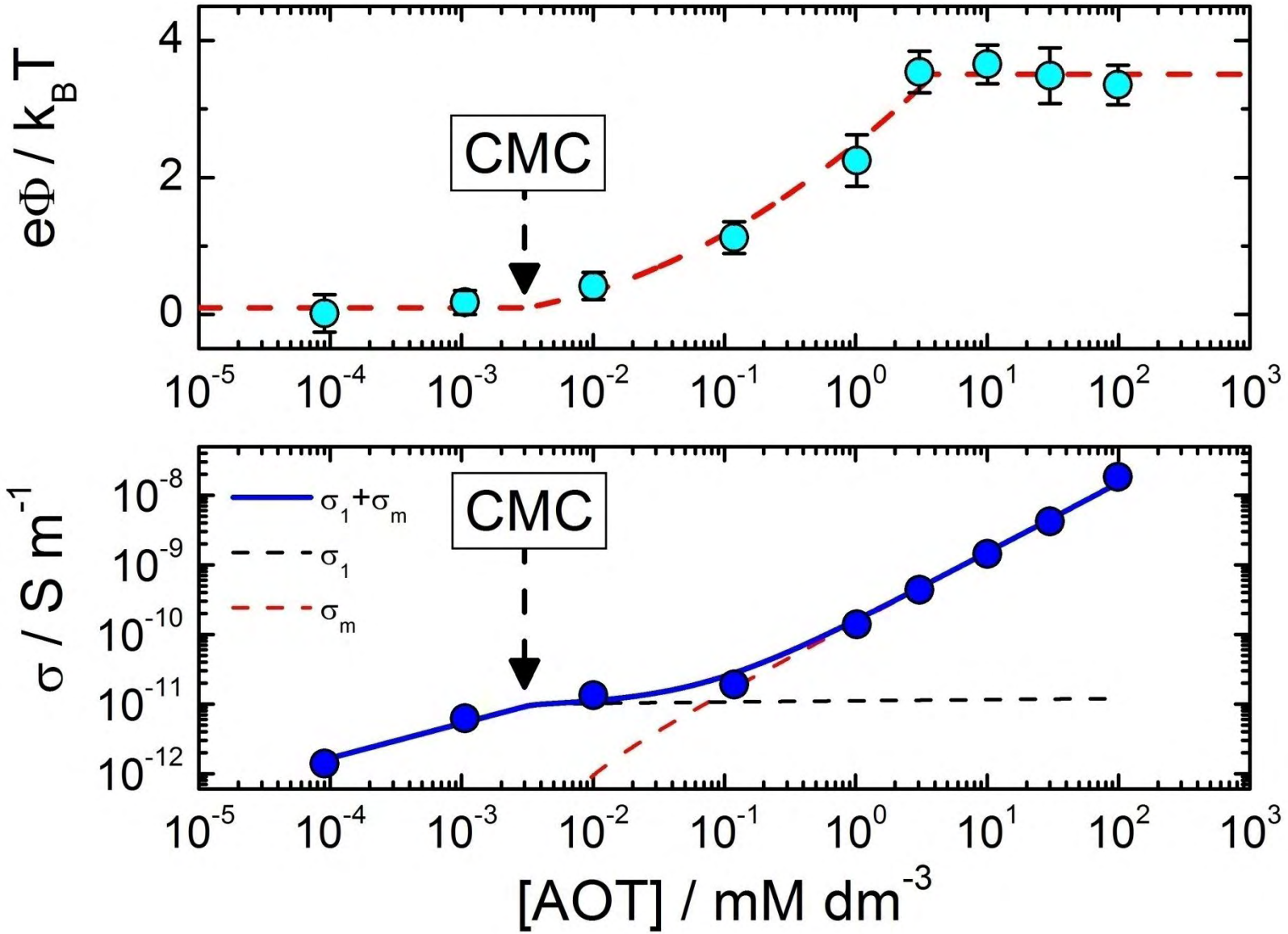
Positive or negative charge depending on adsorption characteristics

2. Ionization of surface groups



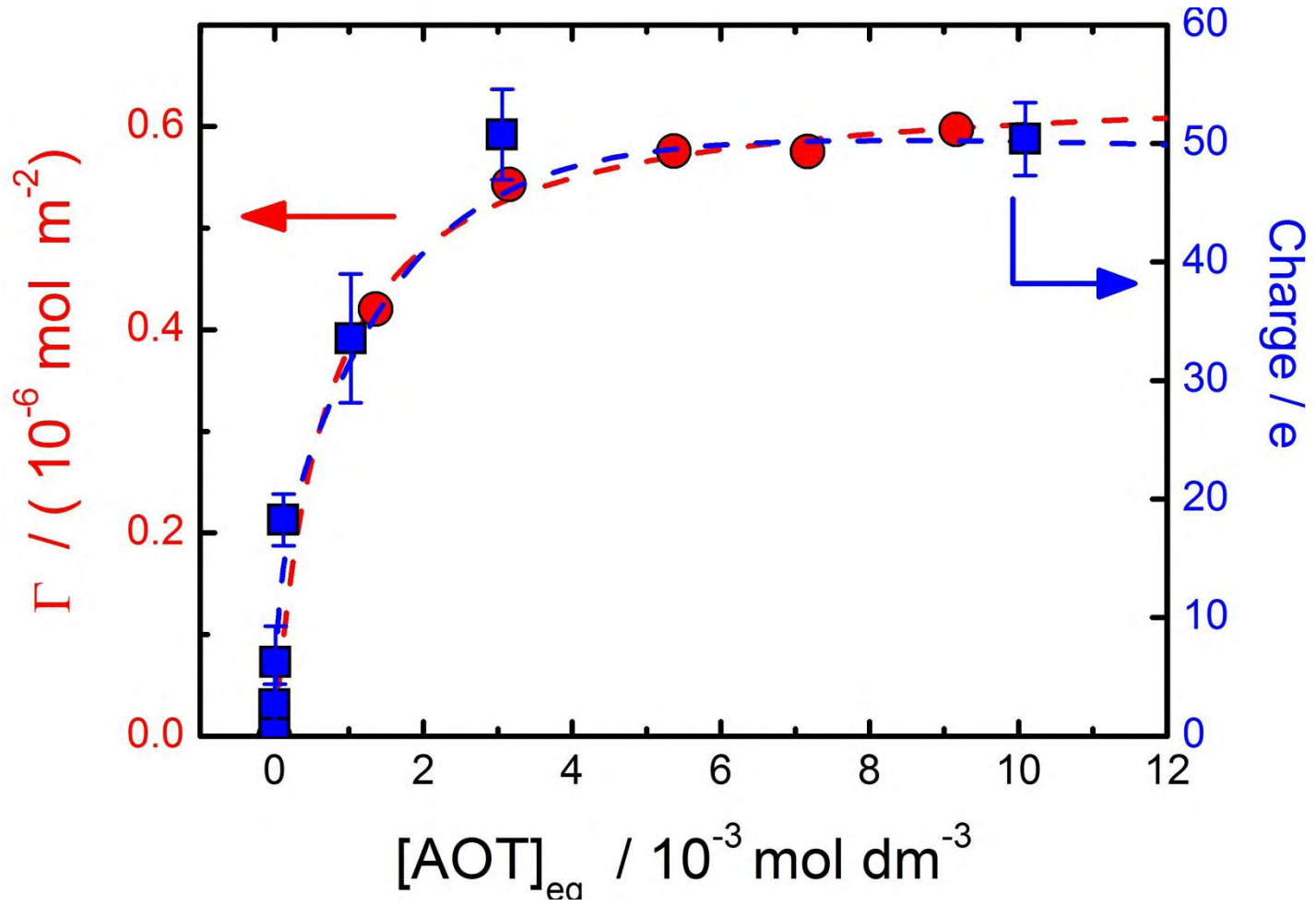
Sign of charge fixed by nature of surface

(a) Particles charge only in presence of reverse micelles



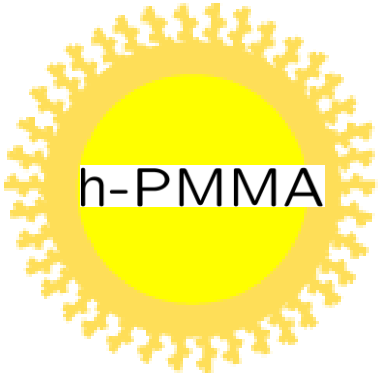
(b) Charge mirrors concentration of adsorbed surfactant

Area per AOT molecule, $a \sim 260$ Å^2



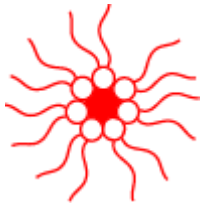
(c) Small-angle neutron scattering measurements

Contrast variation

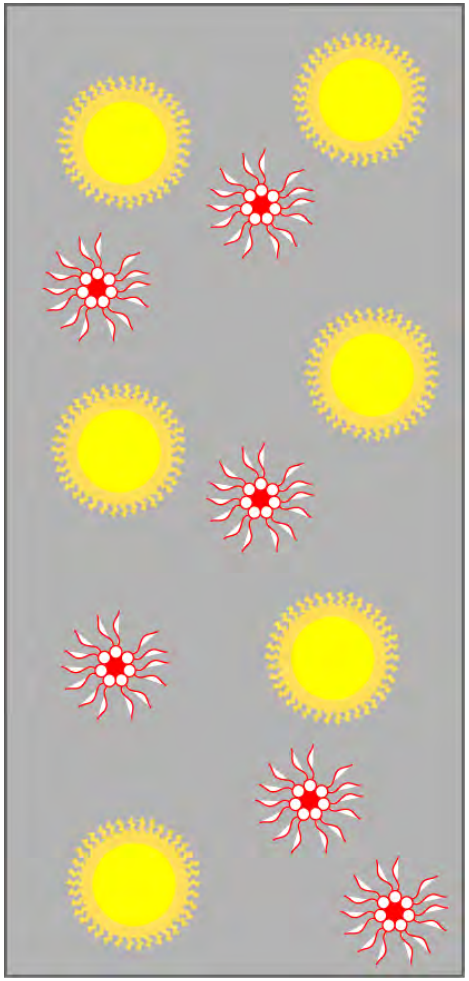


$\langle R \rangle = 45.7$ nm

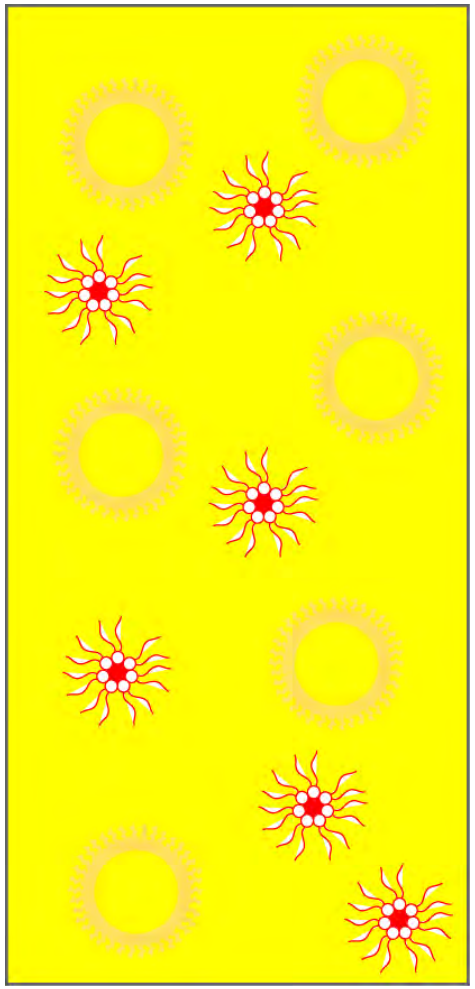
d-AOT



$\langle R \rangle = 1.49$ nm

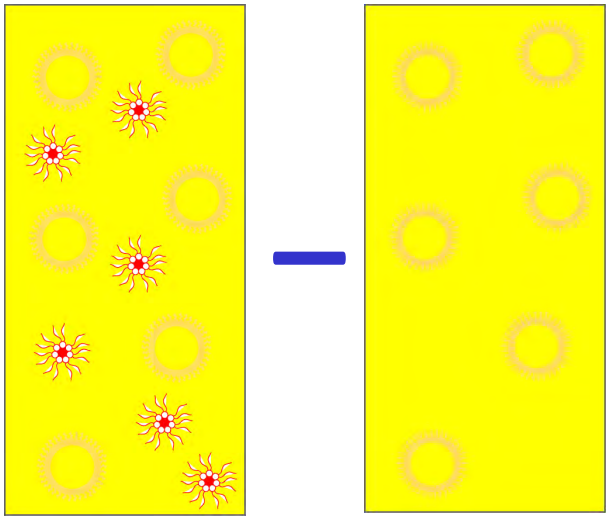


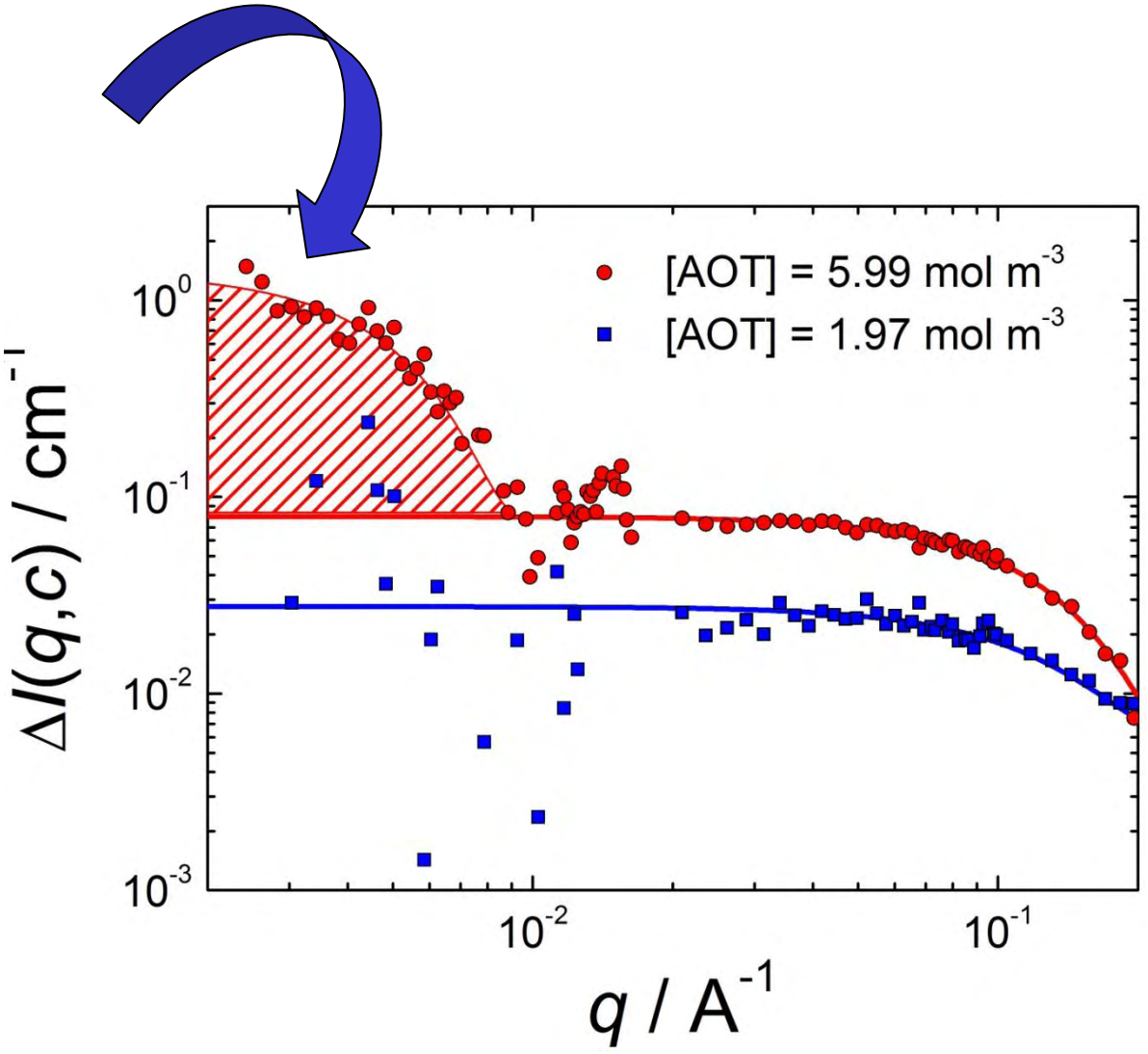
Off-match



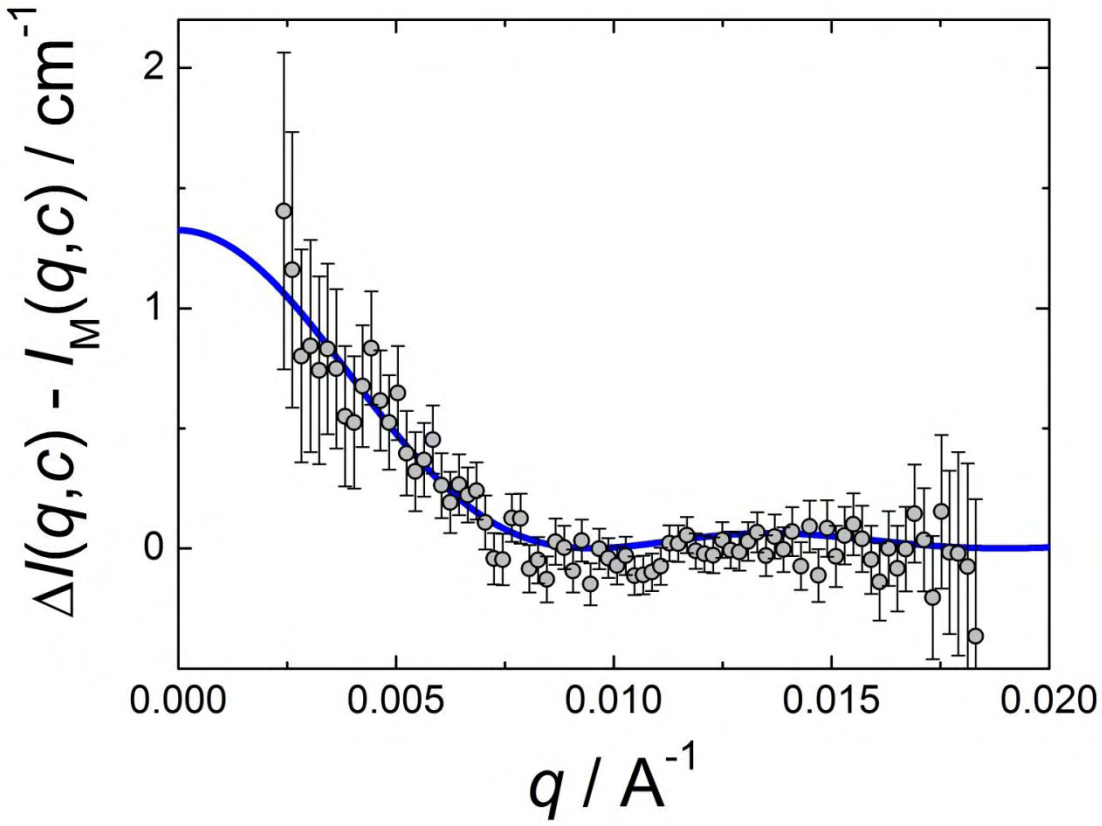
Core-match

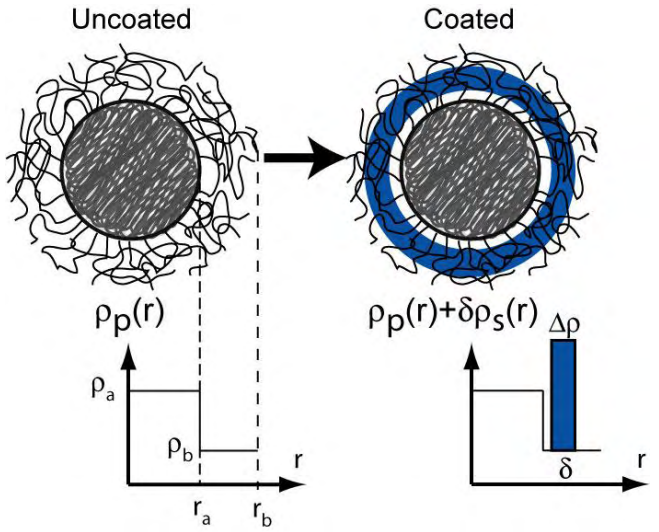
Where is the surfactant?



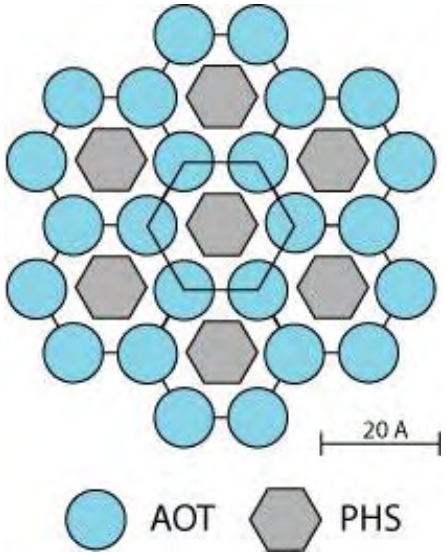


... in the polymer shell surrounding each particle





Is there enough room?



Nano-ions: How do you produce charge in a non-polar world?

- Add inverse micelles!
- Charge is generated by ionization of adsorbed surfactant
- Micelles act as a reservoir for the liberated ions
- Other methods to generate charge?