

# **Role of organic matter, calcium, phosphate, pH, and ionic strength on the stability of nanoparticles**

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## Once in the natural environment...

Nanoparticles **properties would be modified** due to their interaction with natural compounds

 Natural Organic Matter (NOM), Ca, PO<sub>4</sub>, etc.



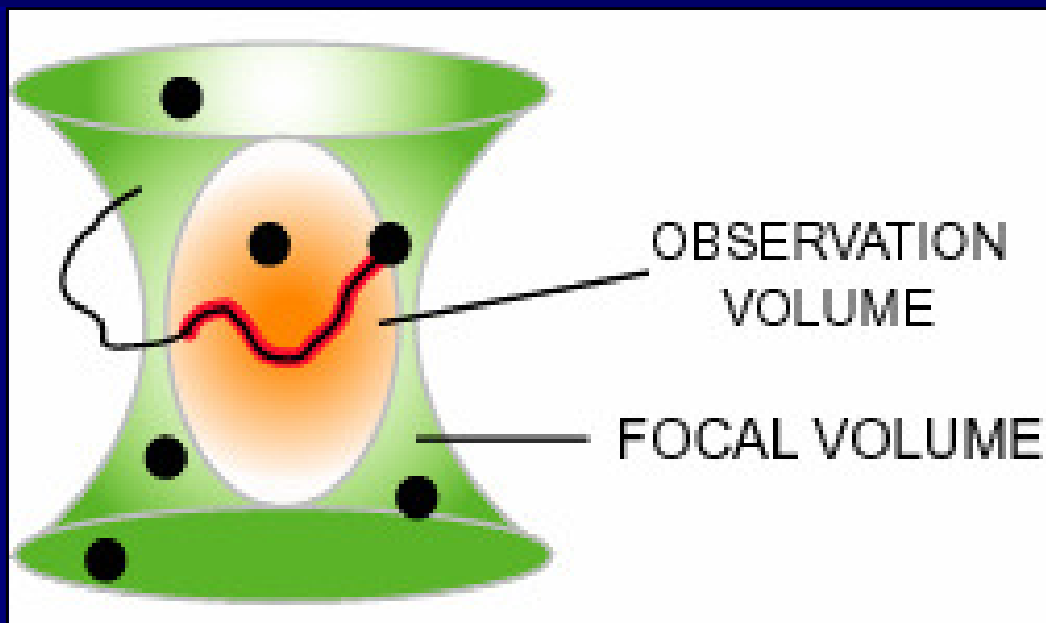
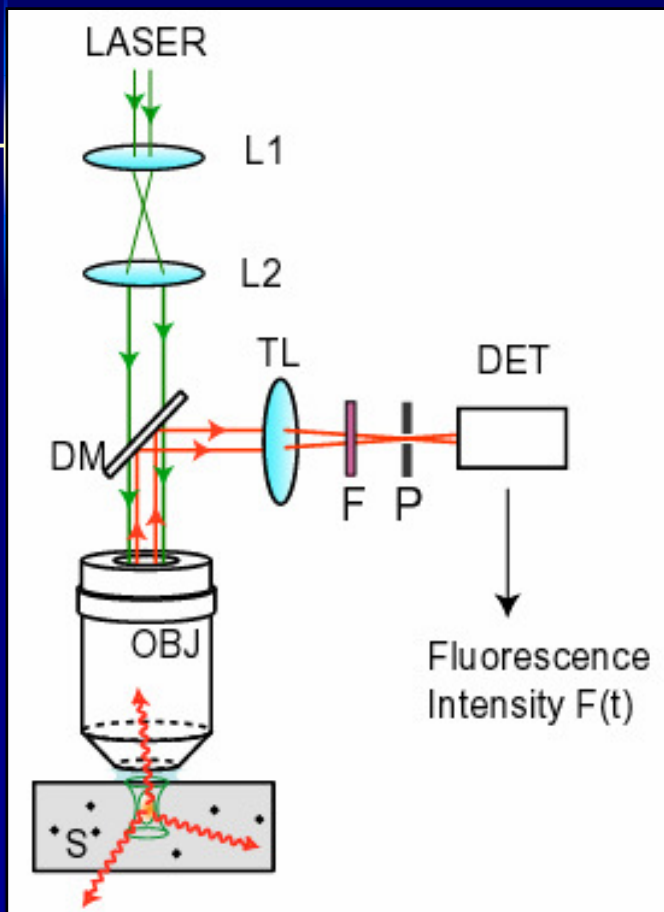
Can substantially modify the **surface properties** of the nanoparticles.

 Electric charge, size, chemical nature of the exposed surface sites.



Significantly influencing their transport, fate and bioavailability.

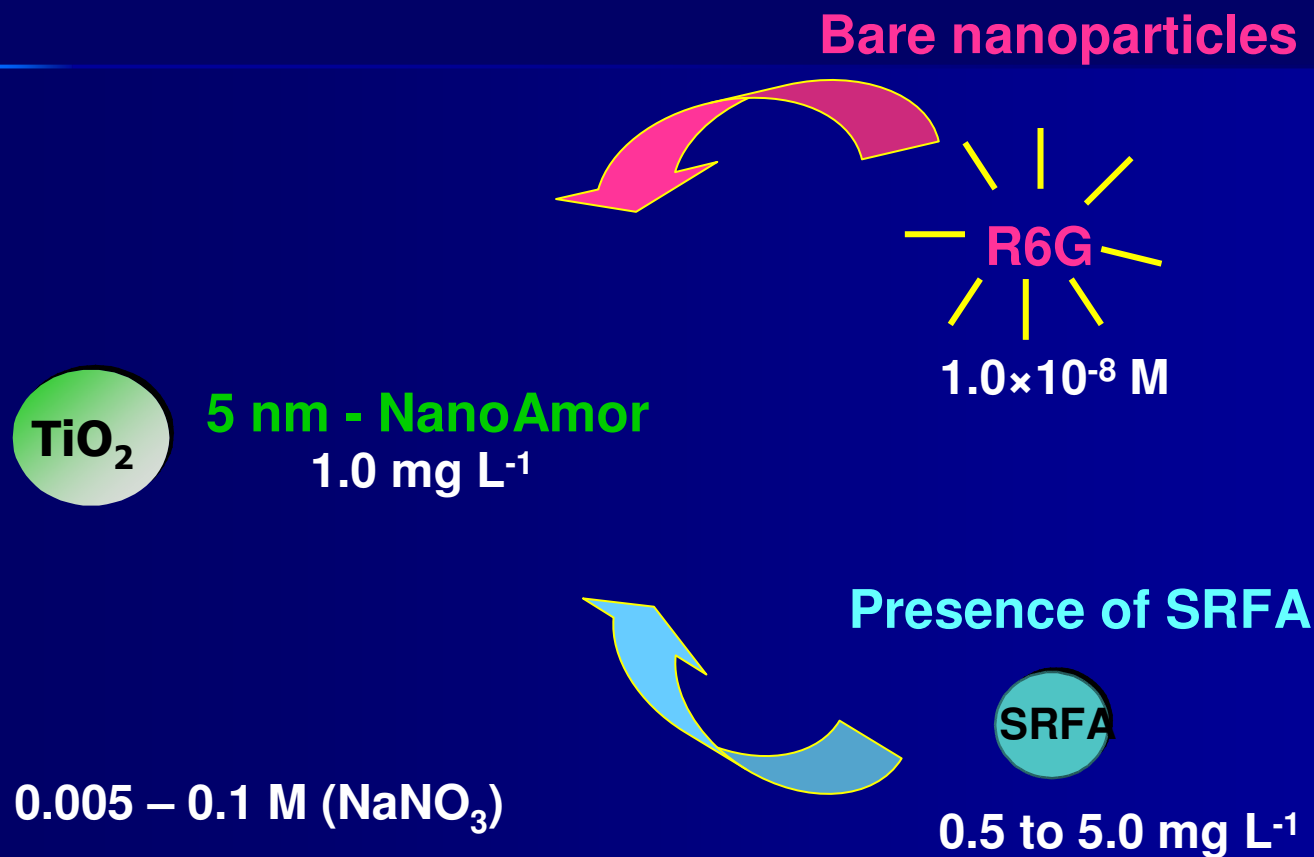
# Fluorescence Correlation Spectroscopy (FCS)



With FCS:

- ✓ extremely low concentrations : 0.1 to 10 mg L<sup>-1</sup>.
- ✓ ideally size between 1 to 200 nm.

## Conditions studied



$I_T = 0.005 - 0.1 \text{ M (NaNO}_3)$

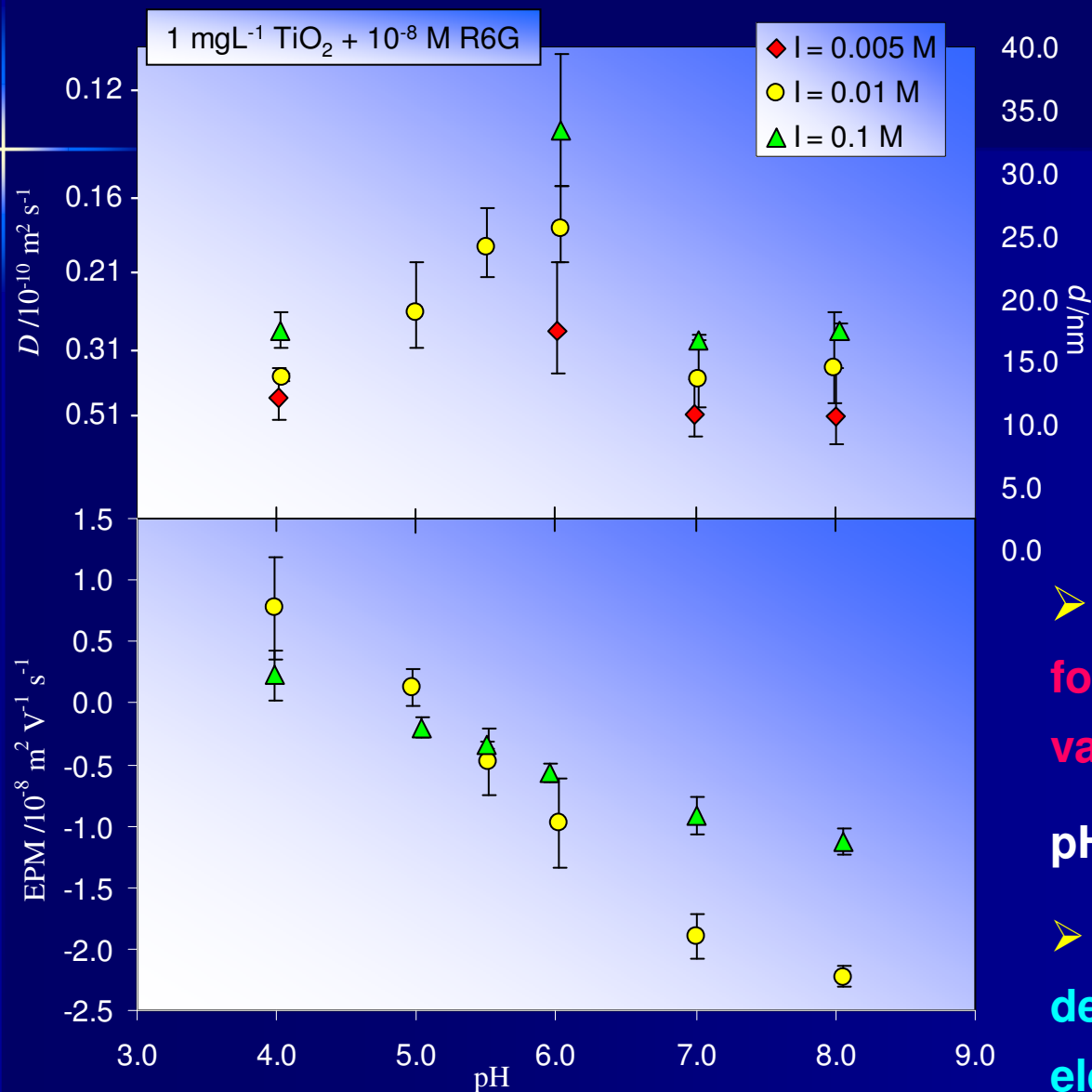
$\text{pH} = 4.0 - 8.0$

$C(\text{Ca}^{2+}) = 10^{-4} - 3.3 \times 10^{-3} \text{ M}$

$C(\text{PO}_4^{3-}) = 10^{-6} - 10^{-3} \text{ M}$

**Equilibration time: 24 h**

# Bare TiO<sub>2</sub> in function of pH and I

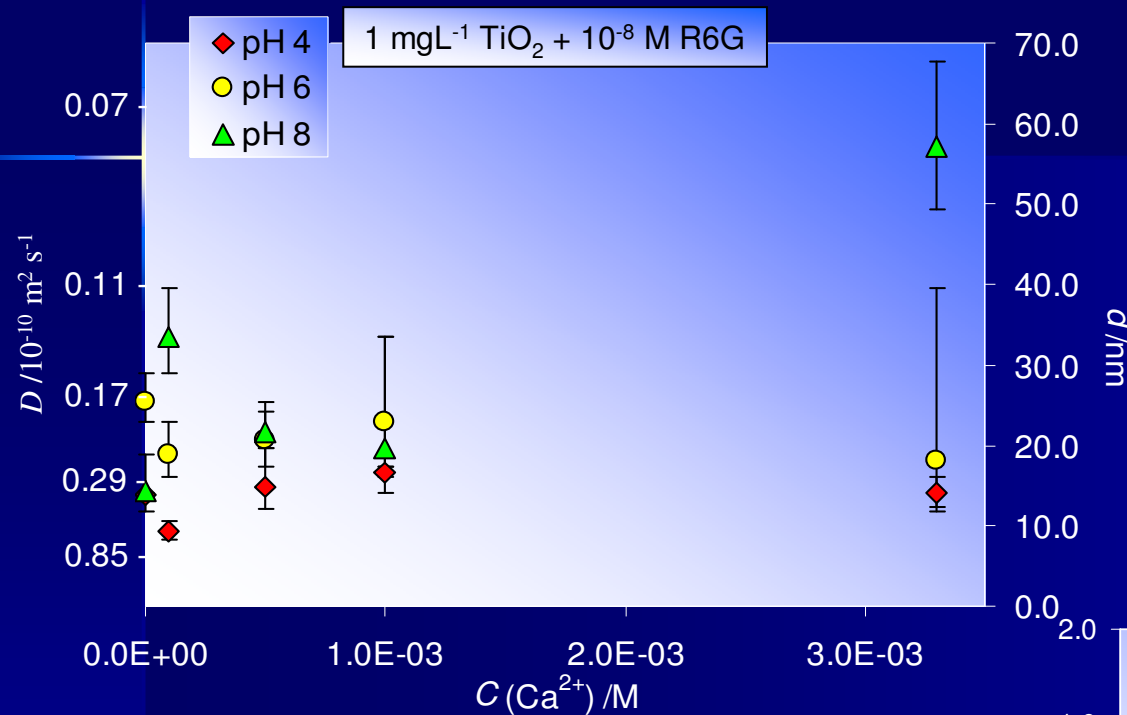


➤ Larger particle sizes for intermediate pH values

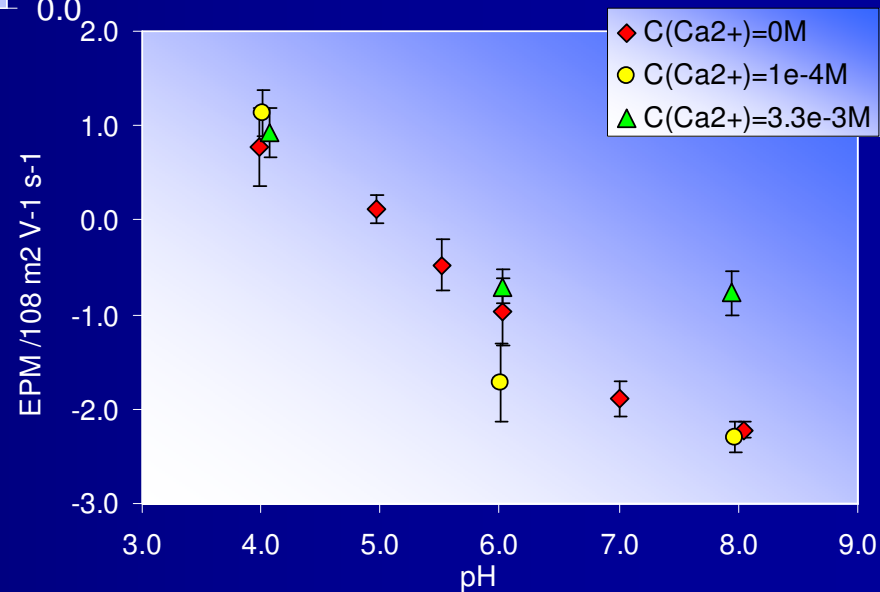
pH<sub>pzc</sub> ≈ 4.5 – 5.2

➤ Stability of the system decrease with the electrolyte addition

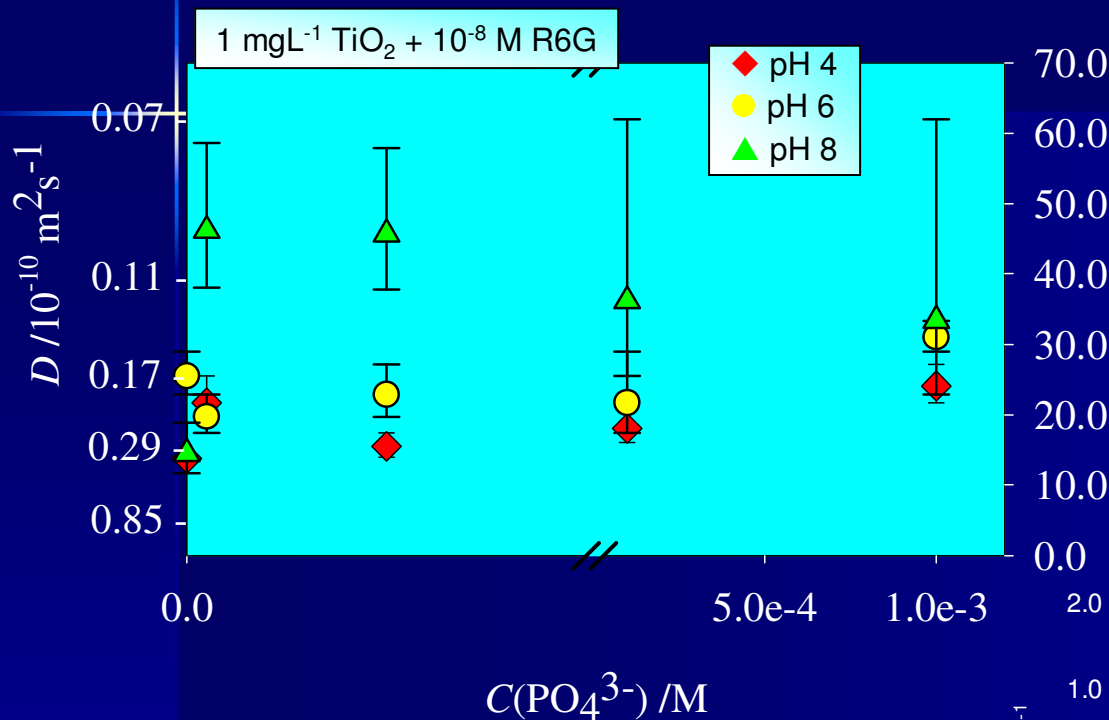
# Bare TiO<sub>2</sub> in function of pH and Ca



➤ Particle size increased in presence of Ca – greater effect at pH > pH<sub>zpc</sub>

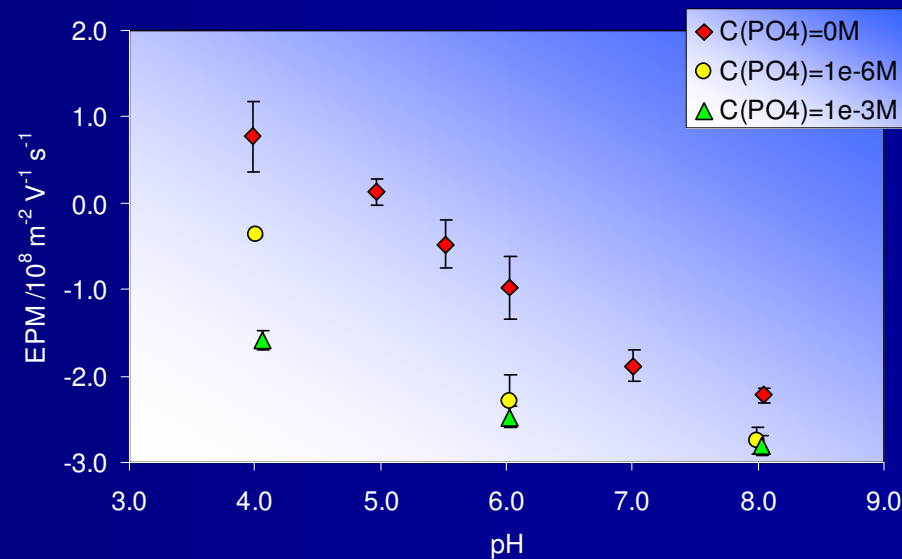


# Bare TiO<sub>2</sub> in function of pH and PO<sub>4</sub>

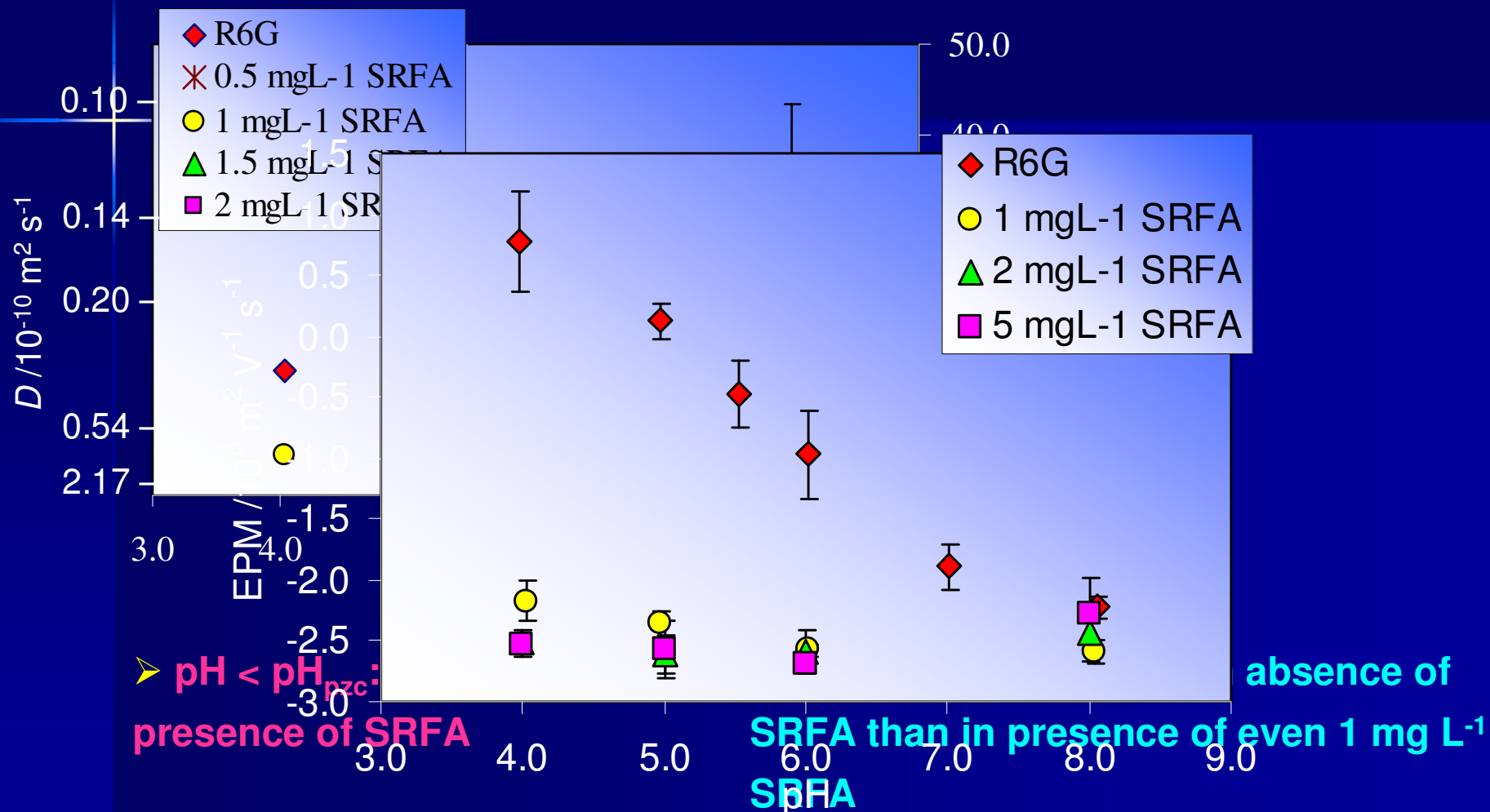


➤ Presence of PO<sub>4</sub> leads to more negative EPM values

➤ At pH 4 and 6 *d* is almost the same in absence and presence of PO<sub>4</sub>.



# Presence of SRFA in function of pH



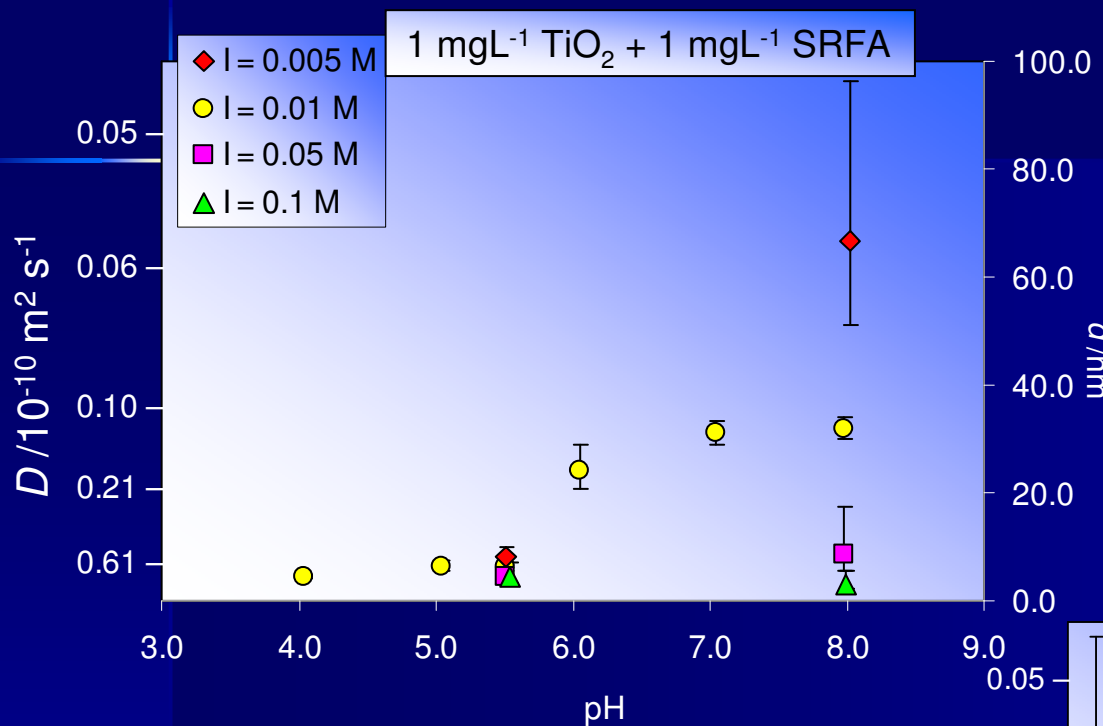
➤  $\text{pH} < \text{pH}_{\text{pzc}}$ :  
presence of SRFA

absence of SRFA

Higher concentrations of SRFA were necessary to complete disaggregation



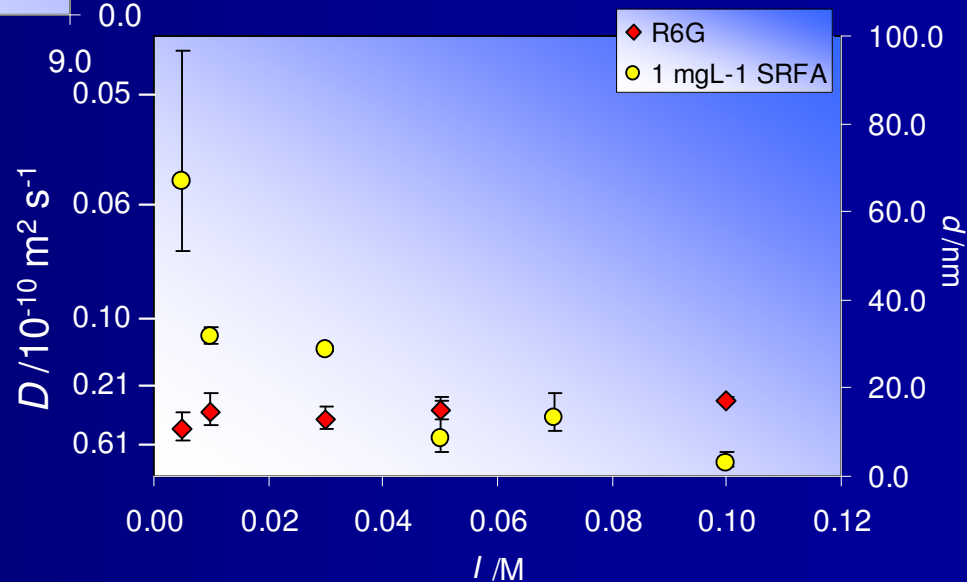
# Presence of SRFA in function of $I$



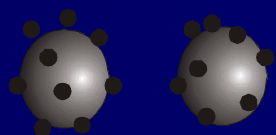
➤ pH < pH<sub>zpc</sub>: changes in  $I$  had little effect

➤ pH > pH<sub>zpc</sub>: significant  $I$  effect that was opposite to that observed in absence of SRFA

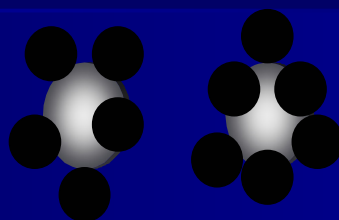
➤ Increasing  $I$  in presence of SRFA resulted in decreased aggregation at pH 8.



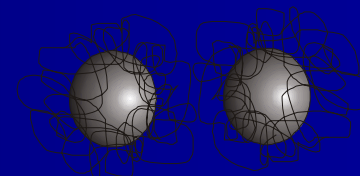
## Role of Natural Organic Matter



Charge modification



Steric stabilisation



Bridging flocculation

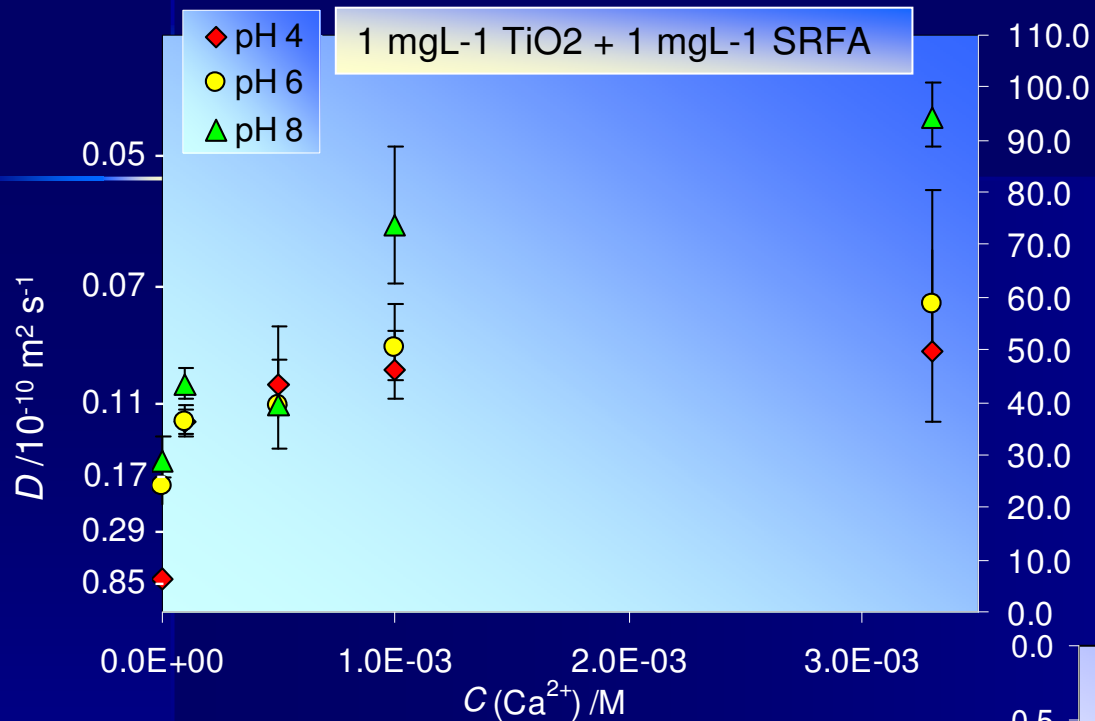


- ✓ Decrease of the Aggregation with the Increase of SRFA
- ✓ Decrease of the Aggregation with the Increase of  $I$  in presence of SRFA

TiO<sub>2</sub> have a nominal size between 3 to 5 nm

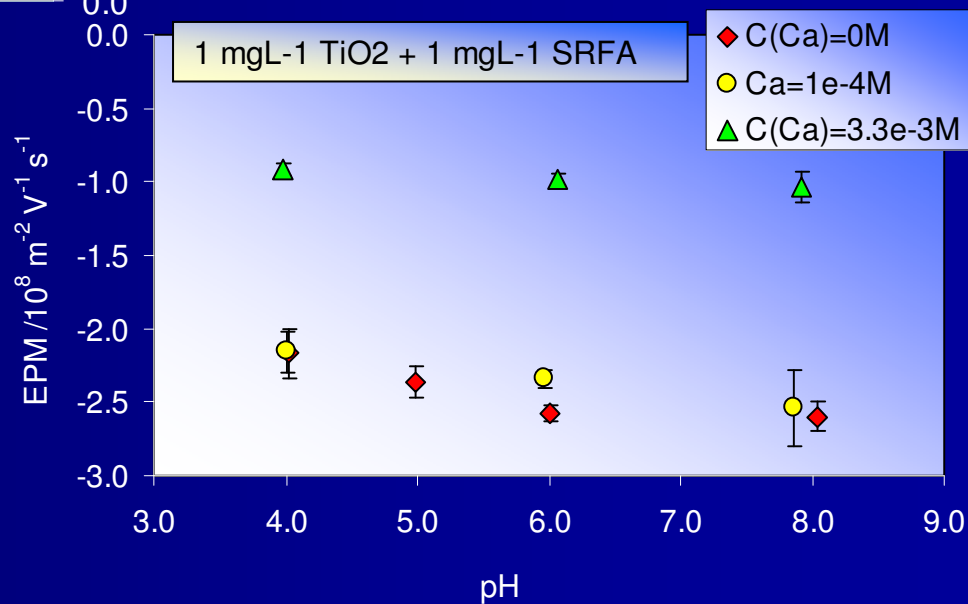
SRFA have a size between 1.3 to 1.6 nm

# Presence of SRFA in function of Ca



➤ *d* increased with increasing Ca concentrations consistent with EPM values

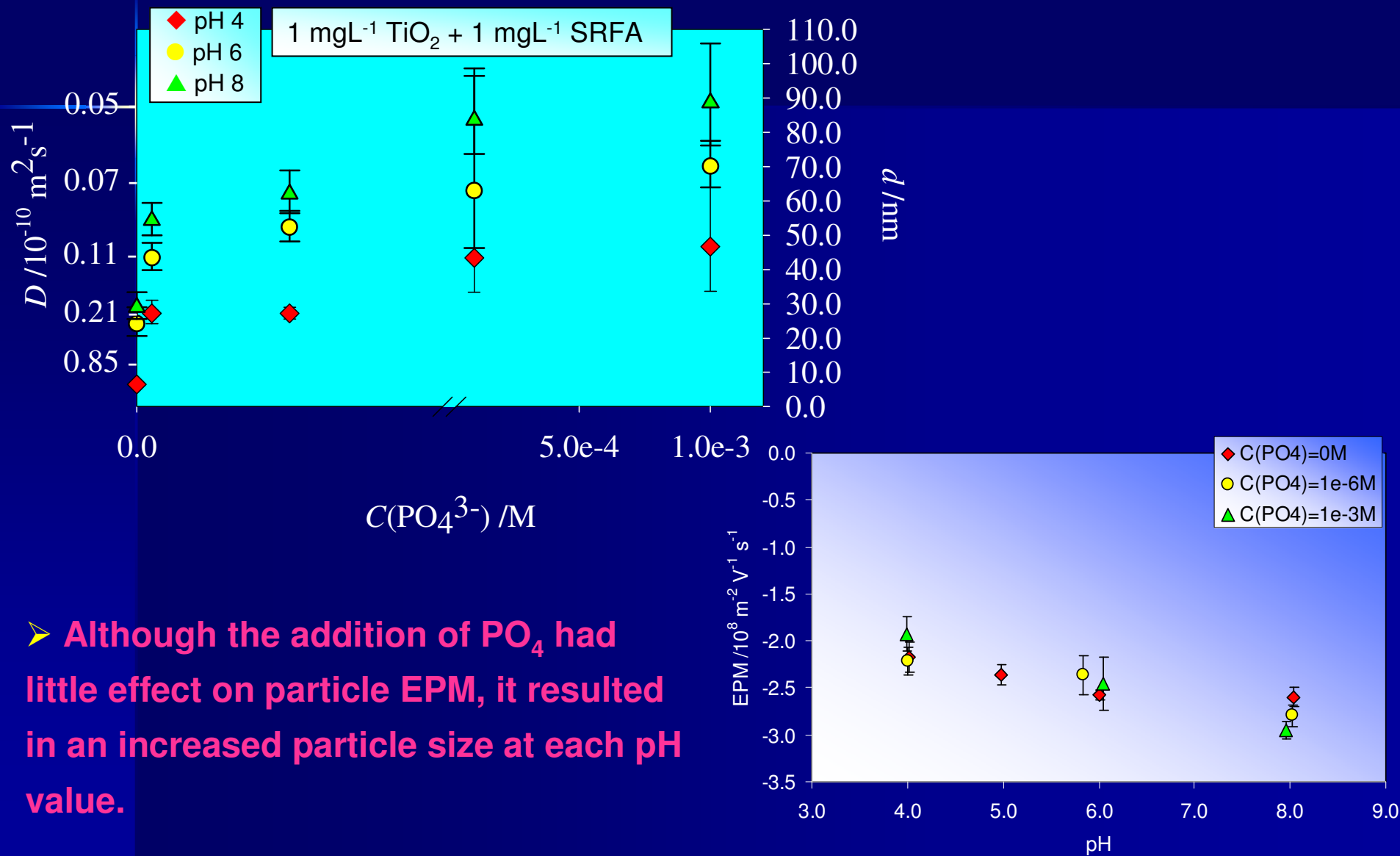
➤ at high [Ca] *d* were larger in presence of SRFA than is its absence, in spite of the similarity of EPM



## Presence of SRFA in function of Ca

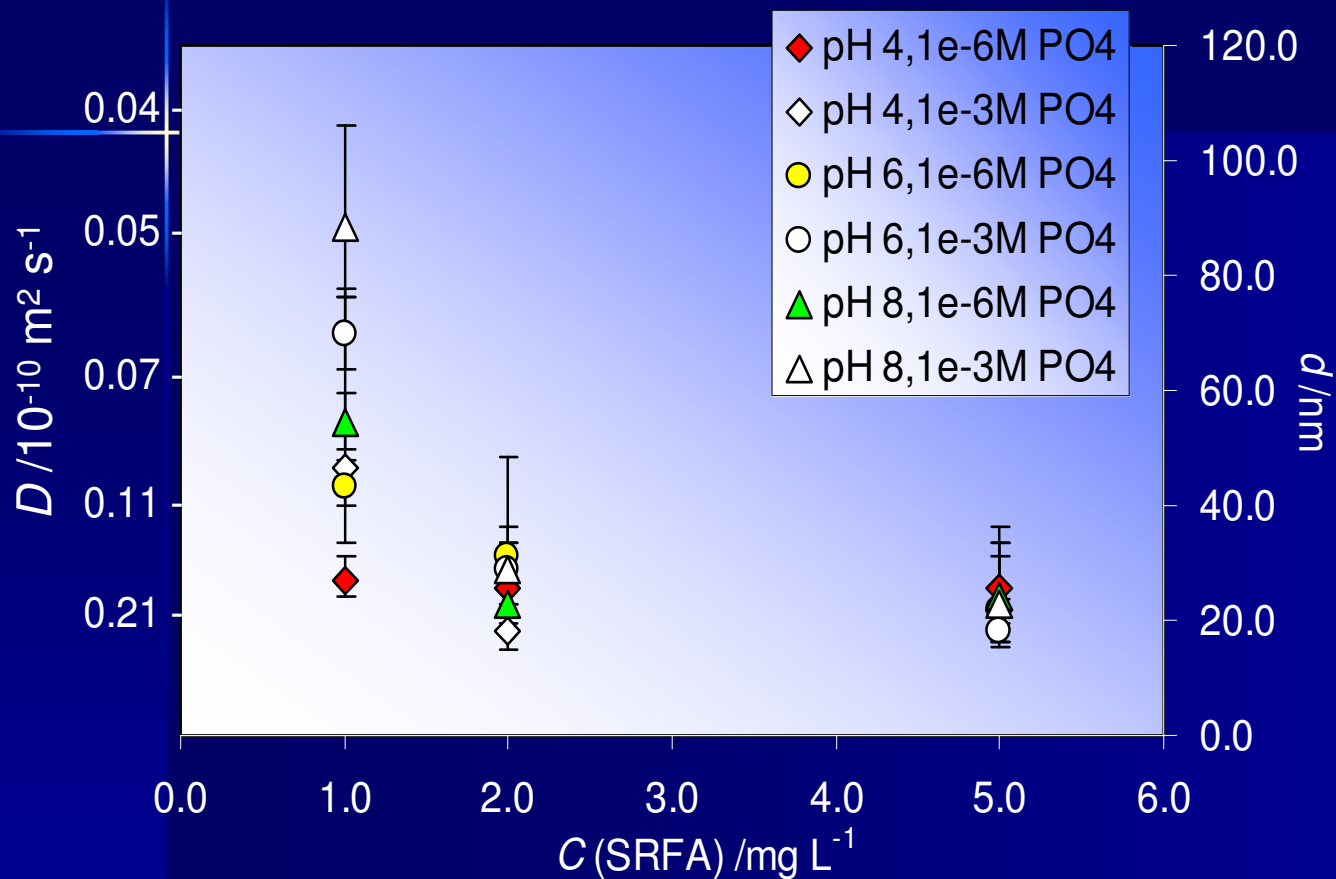
pH	C(Ca <sup>2+</sup> )/M	C(SRFA)/mgL <sup>-1</sup>	d/nm
4	1e-4	1.0	36.2
		2.0	62.0
		5.0	54.2
	3.3e-3	1.0	49.9
		2.0	72.3
		5.0	36.2
6	1e-4	1.0	36.2
		2.0	59.4
		5.0	33.4
	3.3e-3	1.0	58.6
		2.0	83.4
		5.0	27.1
8	1e-4	1.0	43.4
		2.0	43.4
		5.0	31.0
	3.3e-3	1.0	94.3
		2.0	36.2
		5.0	39.4

# Presence of SRFA in function of $\text{PO}_4$



➤ Although the addition of  $\text{PO}_4$  had little effect on particle EPM, it resulted in an increased particle size at each pH value.

## Presence of SRFA in function of $\text{PO}_4$



➤ Even 5 mg L<sup>-1</sup> SRFA was not enough to completely disaggregate the TiO<sub>2</sub> NPs in presence of PO<sub>4</sub><sup>-</sup>.

## Conclusions

- FA generally had a tendency to stabilise the  $\text{TiO}_2$  suspension, but both  $\text{PO}_4$  and Ca resulted in its destabilisation.
  - Particle charge alone is not enough to explain the destabilisation and stabilisation of the  $\text{TiO}_2$  samples.
  - Aggregation and thus mobility and bioavailability of  $\text{TiO}_2$  NPs will be greatly affected by the presence of FA,  $\text{PO}_4$  and Ca and indeed mixtures of the three.
- ✓ In the natural environment or in toxicity experiments in lab, mobility and bioavailability of  $\text{TiO}_2$  will greatly depend upon the precise experimental mixtures being studied.**

## Acknowledgments

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