Polyelektrolyt-modifizierte Mikroemulsionen als Templatphase für die Nanopartikelbildung

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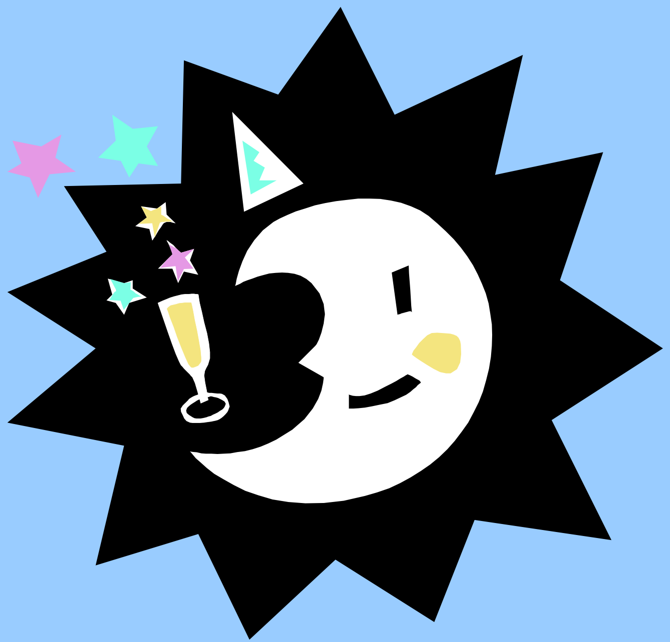
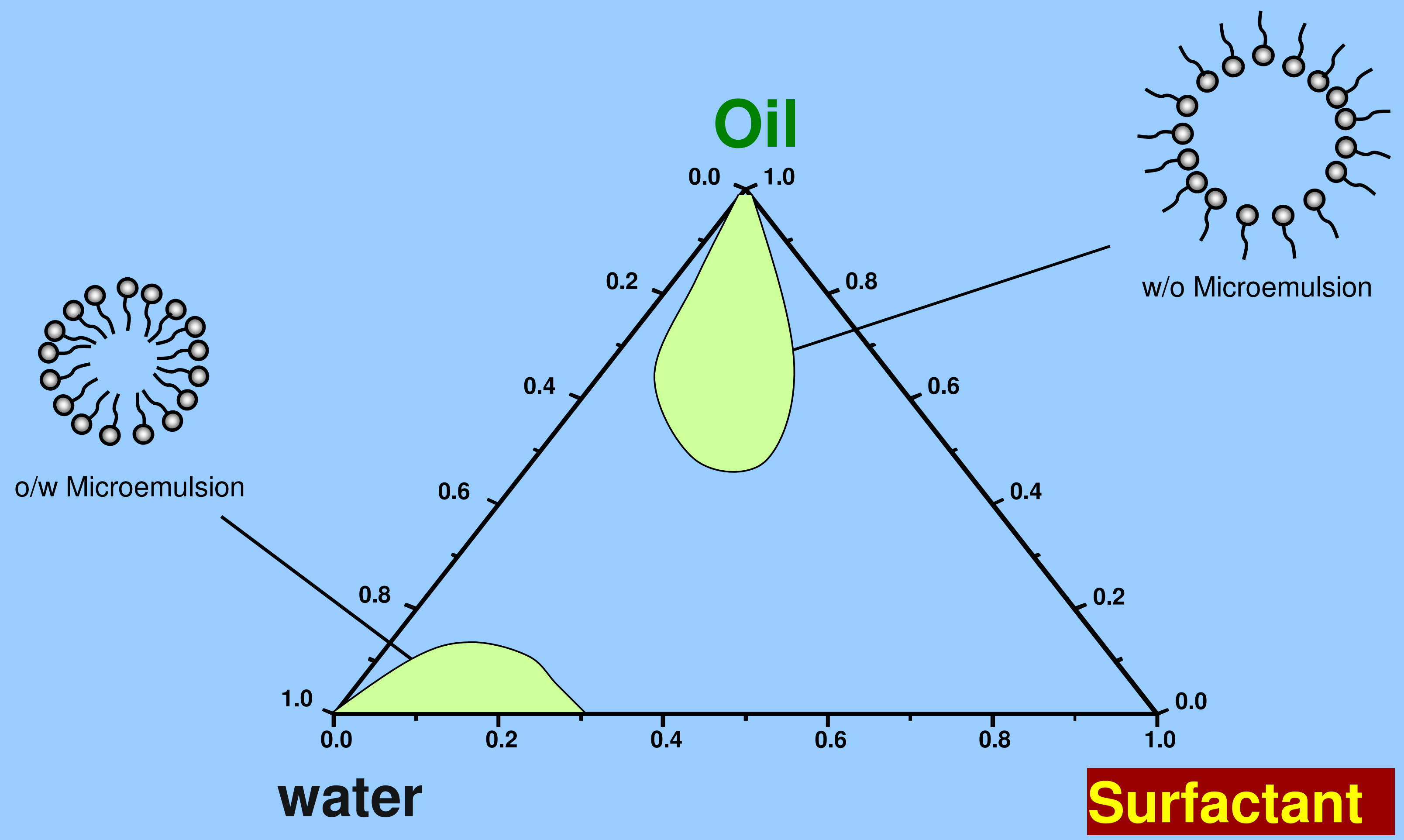
Self-assembled template phases:



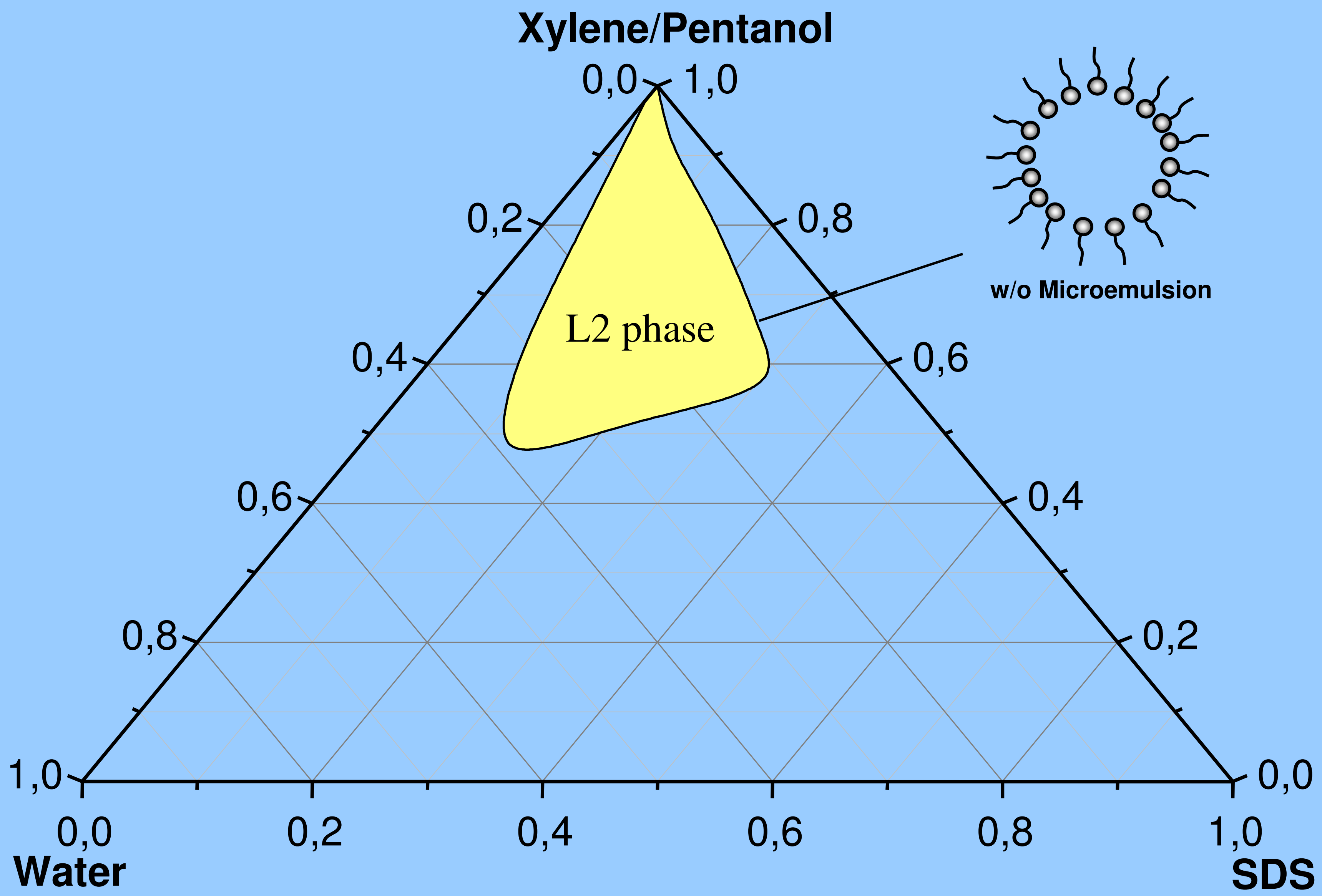
- **Microemulsions**

Microemulsions

- Isotropic, optically clear
- Thermodynamically stable
- Newtonian-flow behaviour
- Low surface tension
- Reversible temperature behaviour
- Droplet size between 2 and 20 nm

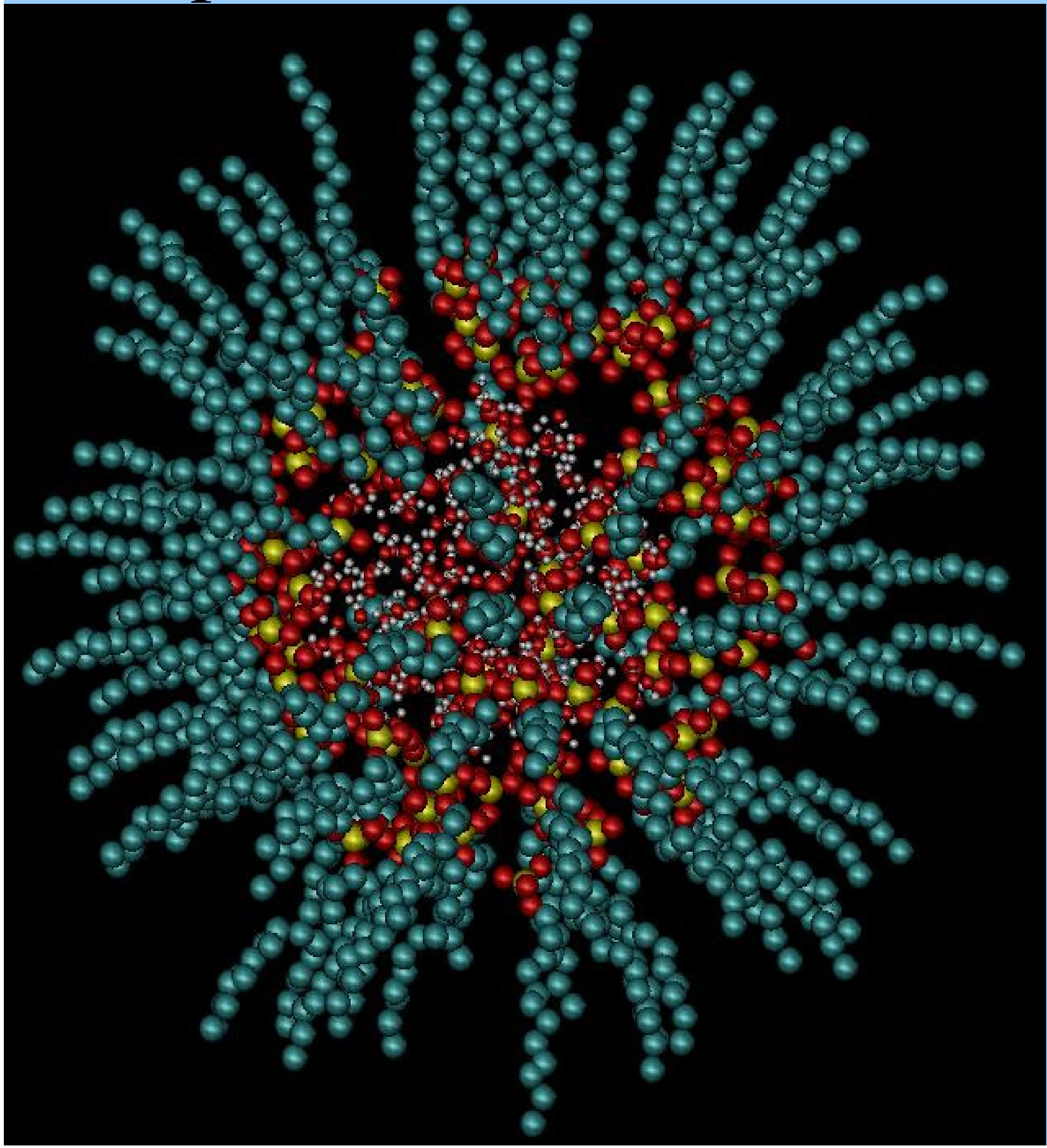


Oil
water
Surfactant
o/w Microemulsion
w/o Microemulsion
0.0
0.2
0.4
0.6
0.8
1.0

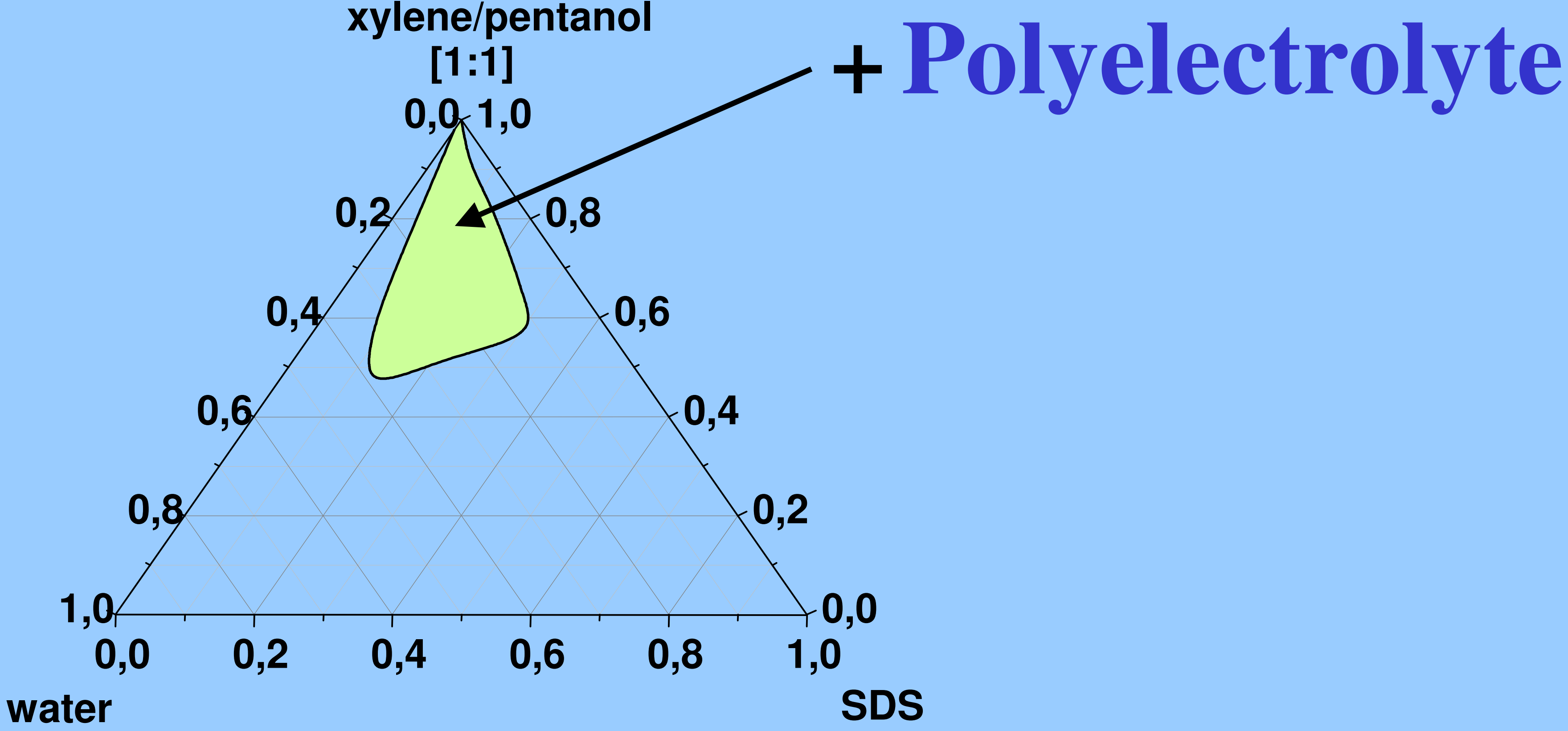


Xylene/Pentanol
0,0
1,0
0,2
0,8
0,4
0,6
0,6
0,4
0,8
0,2
1,0
0,0
0,0
0,2
0,4
0,6
0,8
1,0
Water
SDS
L2 phase
w/o Microemulsion

Snapshot of an inverse microemulsion droplet

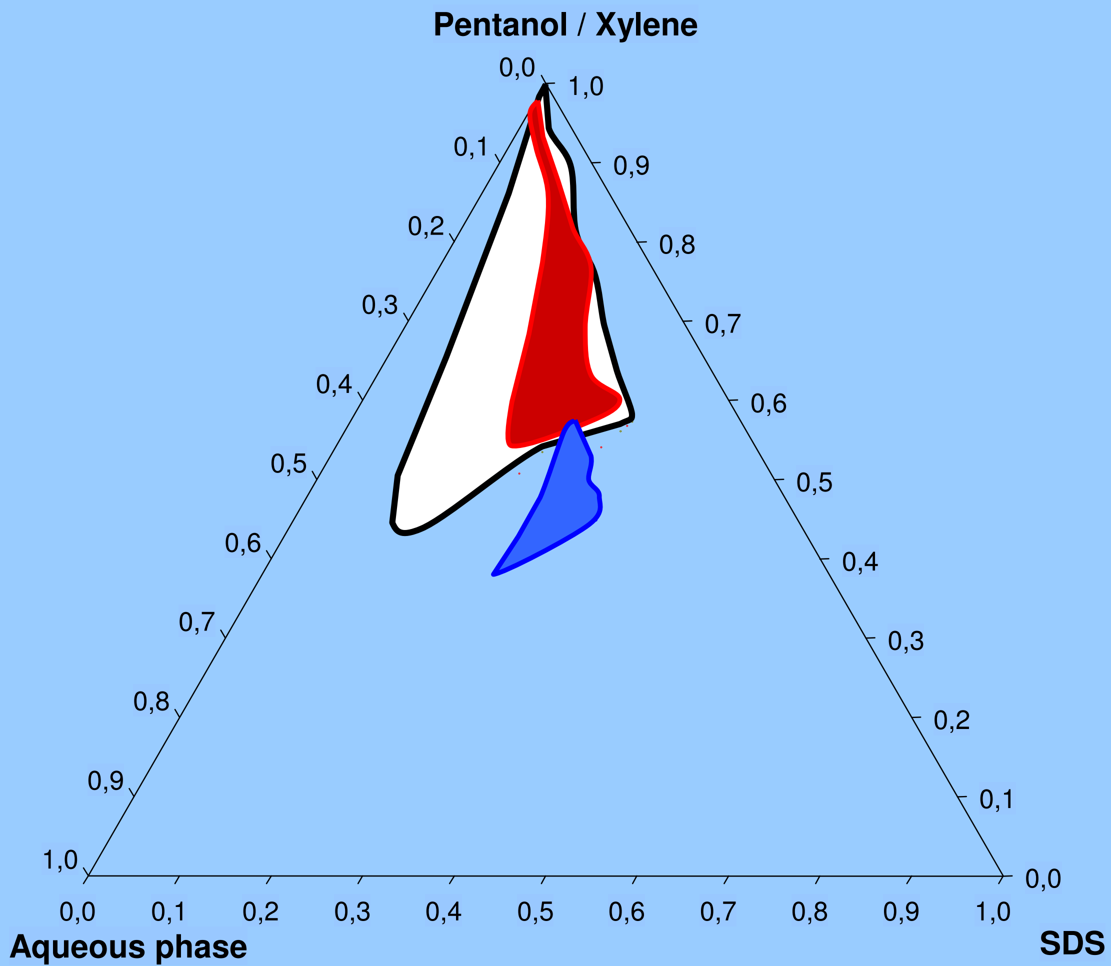


A.Poghosyan,L.Arsenyan,
H.Gharbekyan,
S.Falkenhagen,
J.Koetz, A.Shahinyan:
J. Colloid & Interface Science 358 (2011) 175-181

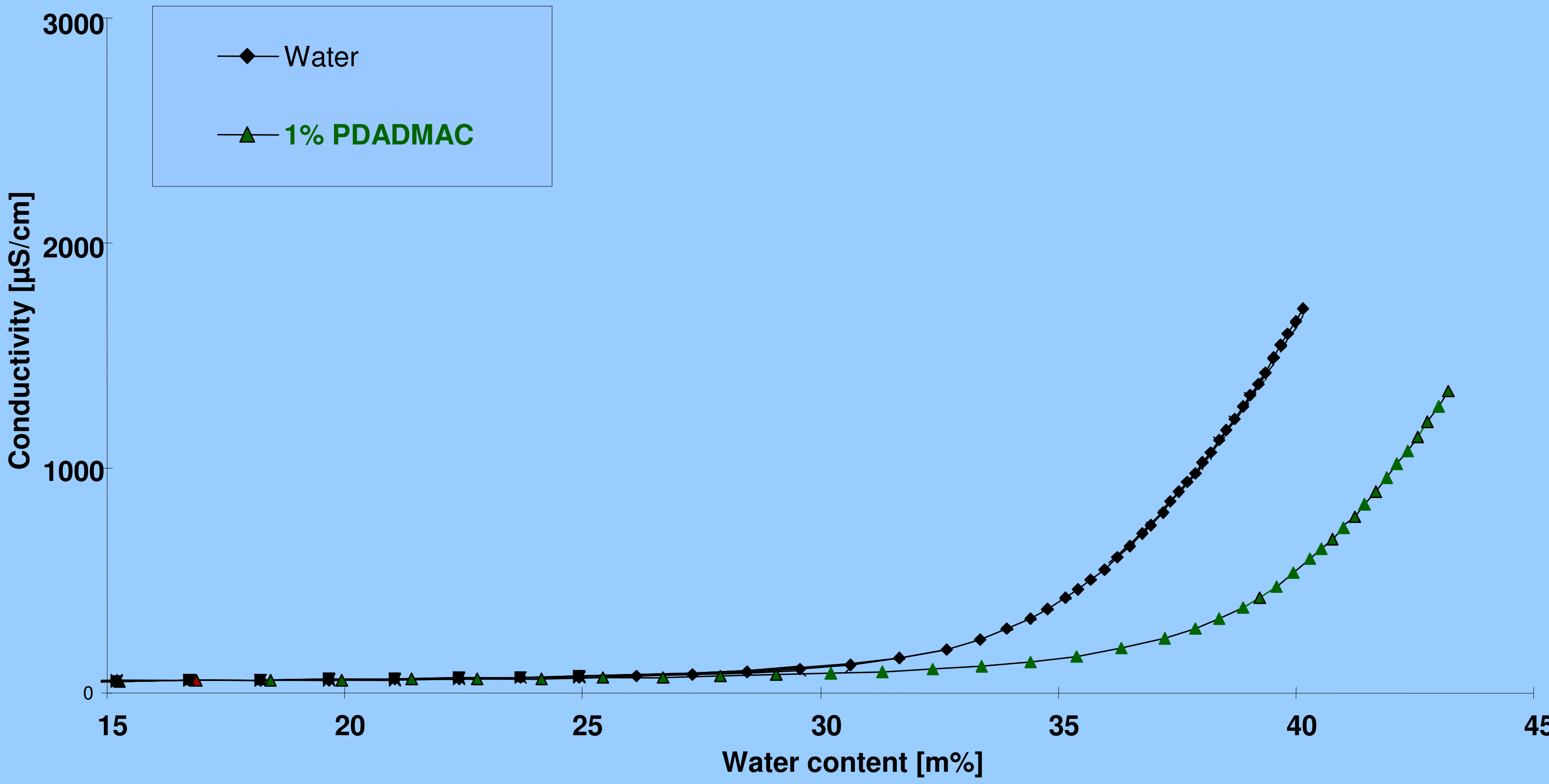


xylene/pentanol
[1:1]
+ Polyelectrolyte
0,0
1,0
0,2
0,8
0,4
0,6
0,6
0,4
0,8
0,2
1,0
0,0
0,0
0,2
0,4
0,6
0,8
1,0
water
SDS

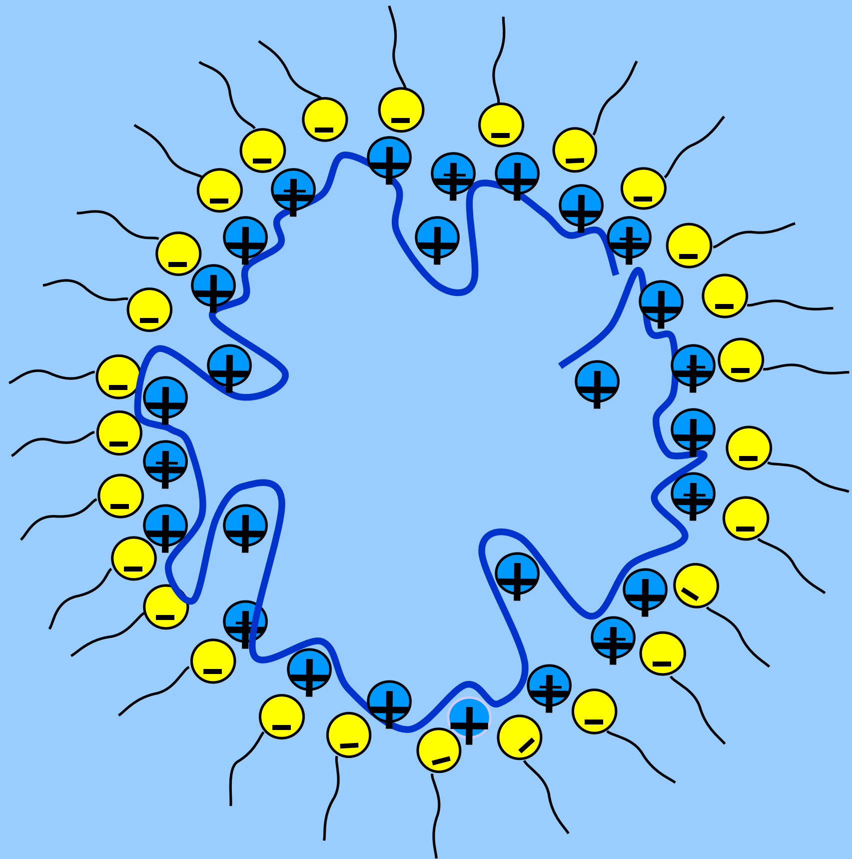
Partial phase diagram of water / SDS / pentanol / xylene system in dependence on the PDADMAC-concentration (— 1 weight% ; —10 weight% , — 30 weight%)



T. Beitz, J.Koetz, S.E. Friberg; Progress in Colloid & Polymer Sci. (1998) 111, 100-106.



PDADMAC-modified microemulsions



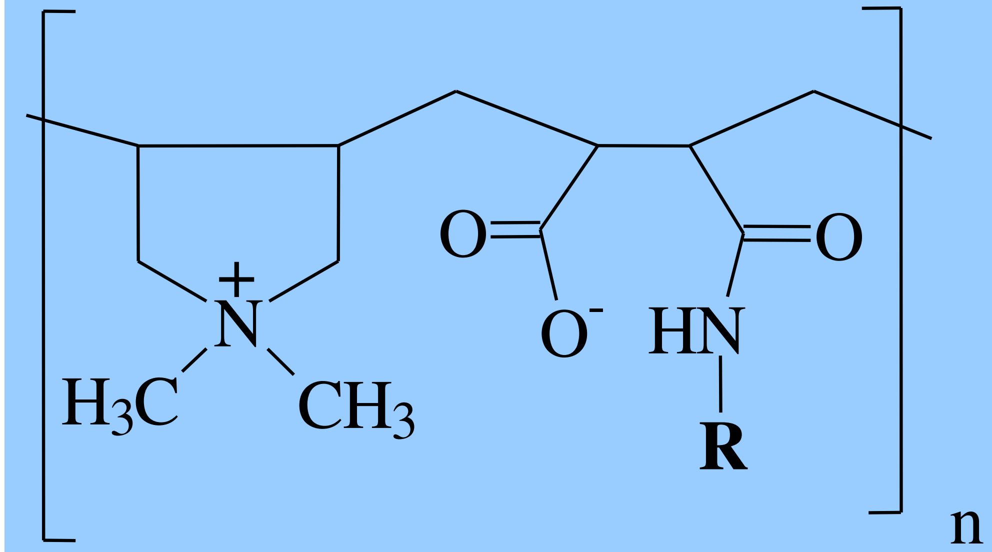
→ **Oppositely charged PDADMAC can be incorporated !!**

→ **PDADMAC increase the stability of the surfactant film !!**

SDS-based system modified by adding:

- Poly(dimethyldiallylammonium chloride) (PDADMAC)
- **Polyampholytes (Mw ~ 22,000 g/mol)**

Poly-(N,N-diallyl-N,N-dimethylammonium-alt-maleamic carboxylate)



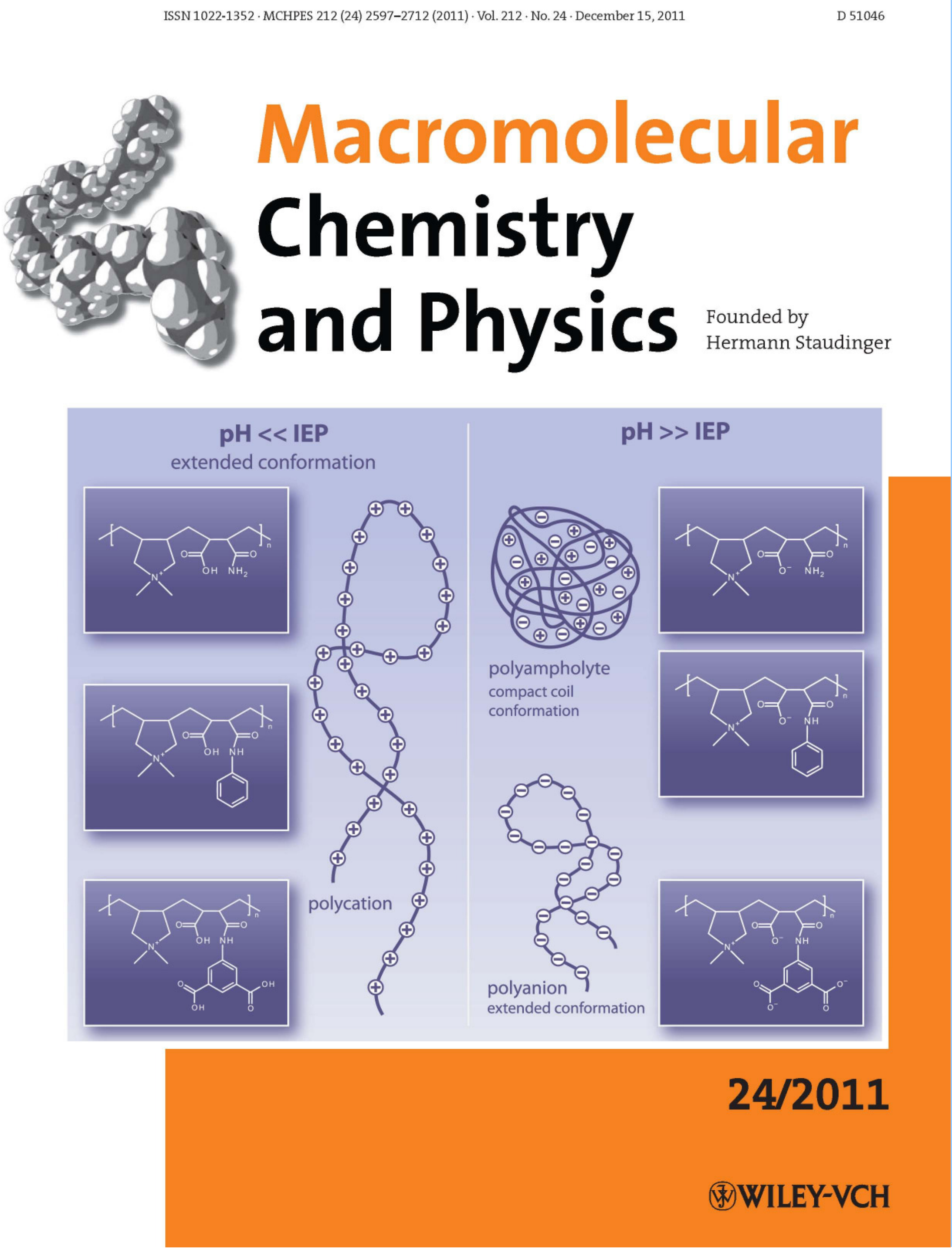
PalR

PalH R= hydrogen

PalPh R= phenyl

PalPhBisCarb

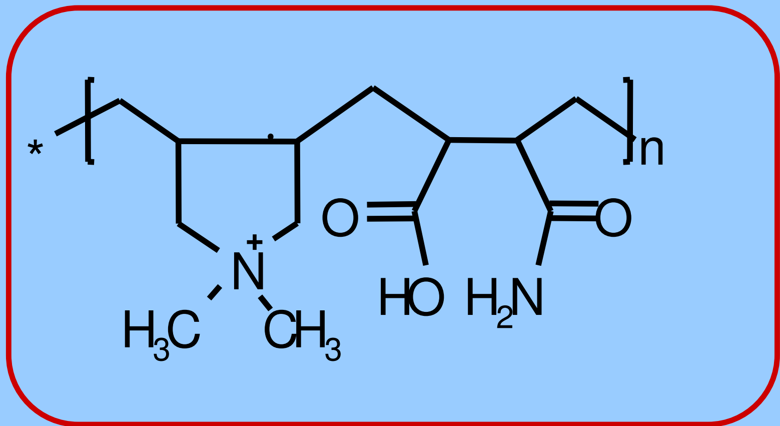
R= phenylbiscarb



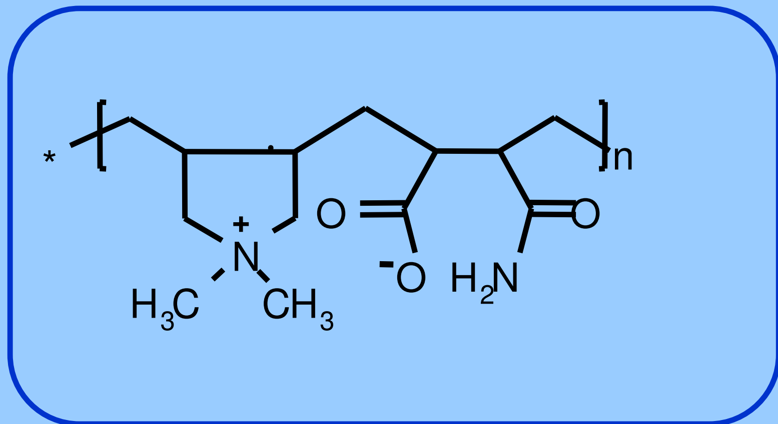
M. Fechner, J. Koetz;
Macromol. Chem. Phys.
(2011) 212, 2691-2699

Poly-(N,N-diallyl-N,N-dimethylammonium-alt-maleamic carboxylate) PalH

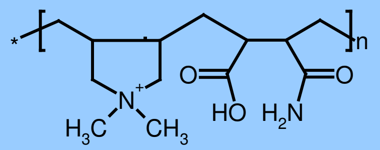
pH 4



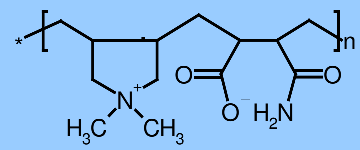
pH 9



$pK_a^0 = 6.6$

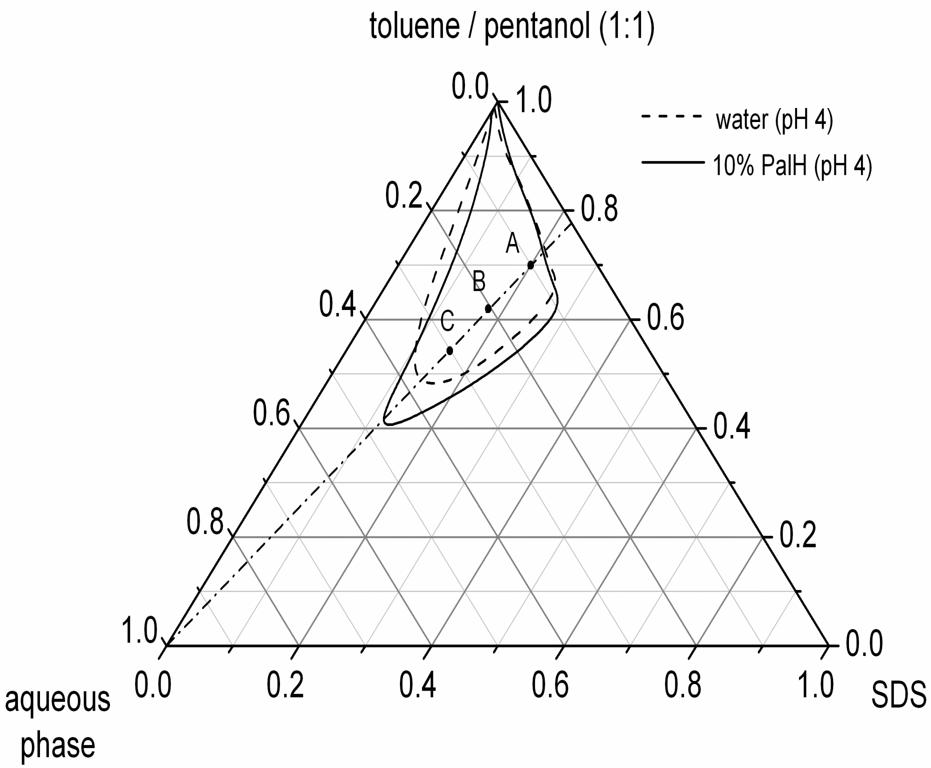


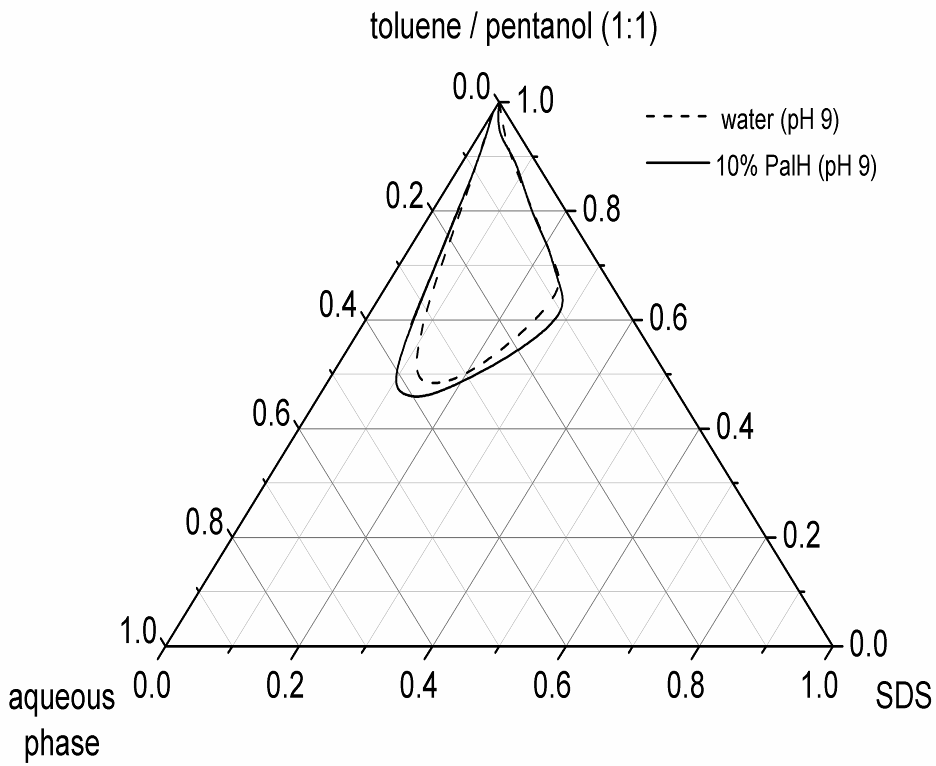
pH 4



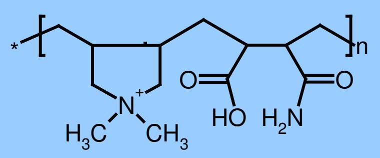
pH 9

Partial Phase diagrams

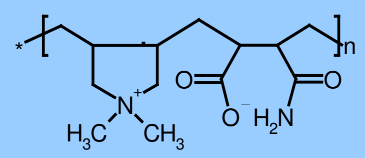




M. Fechner, M. Kramer, E. Kleinpeter, J. Koetz; Colloid Polymer Sci 287 (2009), 1145-1153.

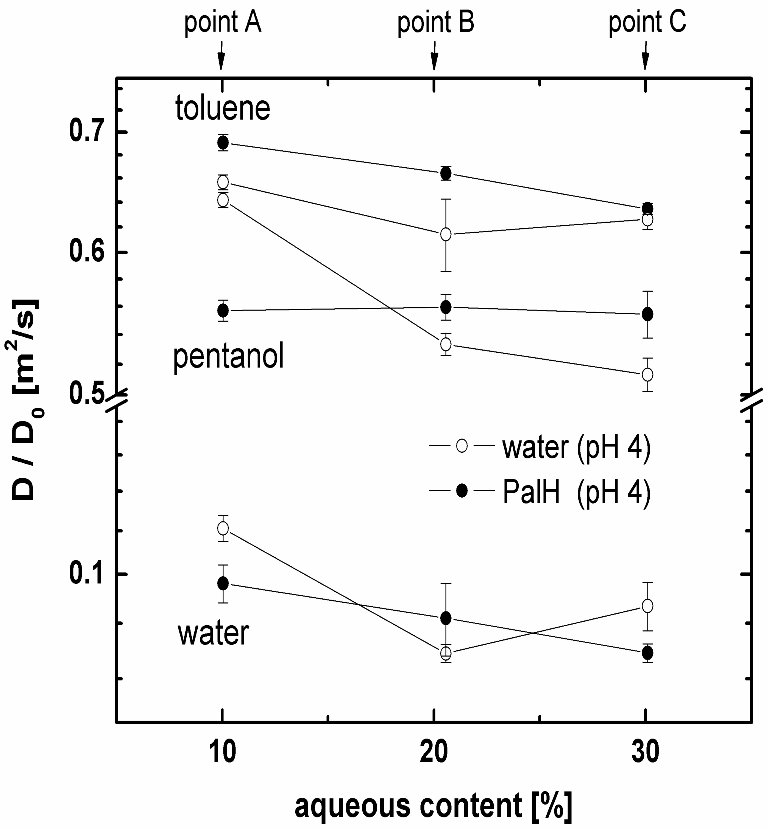


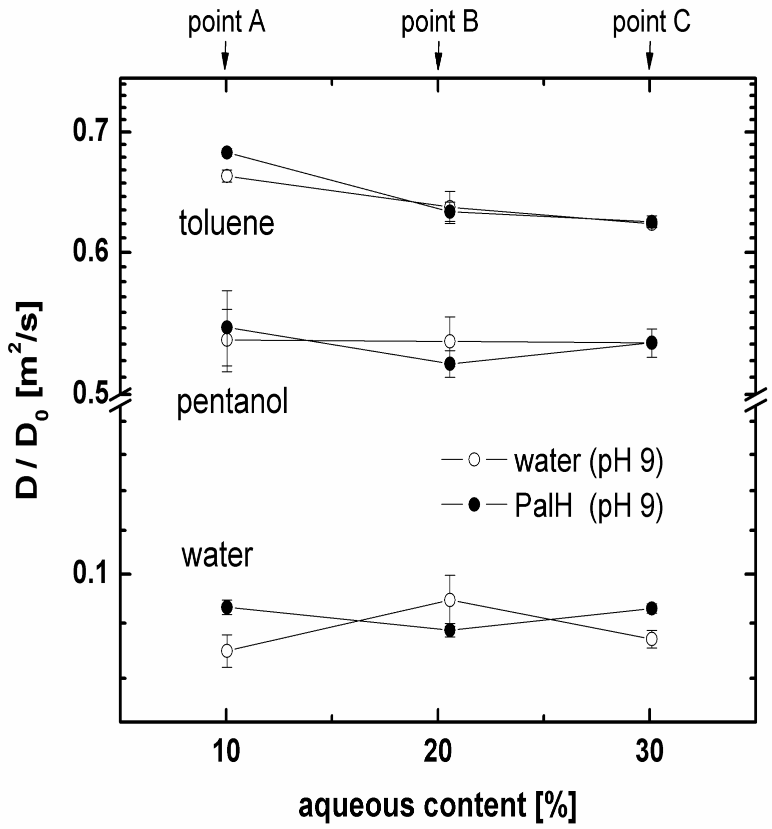
pH 4



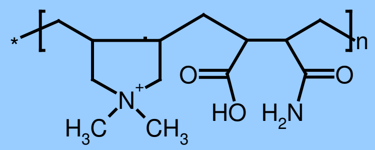
pH 9

Reduced diffusion coefficients determined by NMR

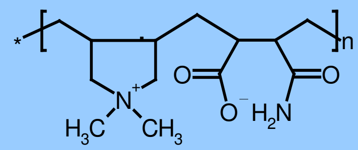




M. Fechner, M. Kramer, E. Kleinpeter, J. Koetz; Colloid Polymer Sci 287 (2009), 1145-1153.

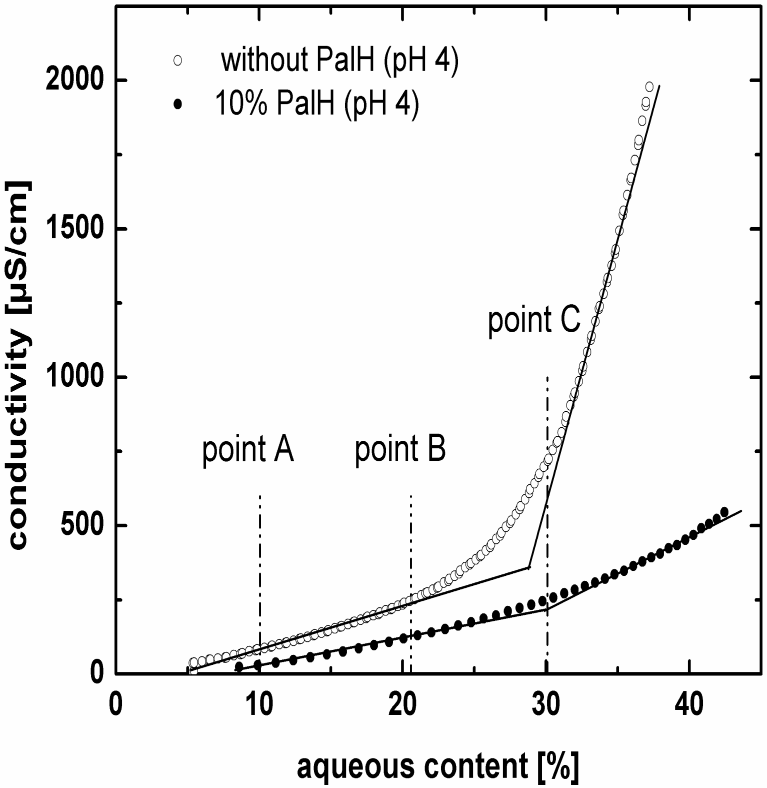


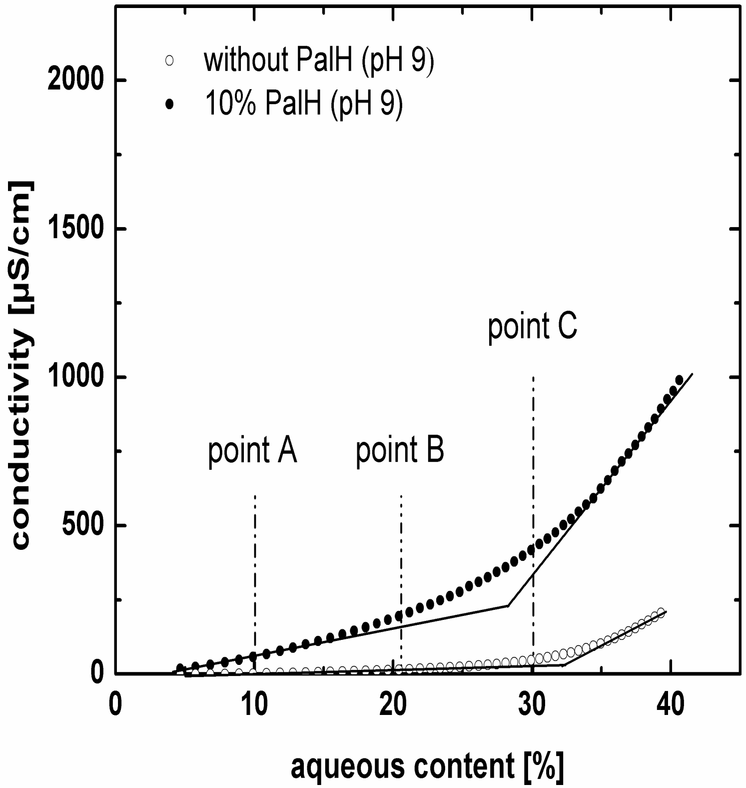
pH 4



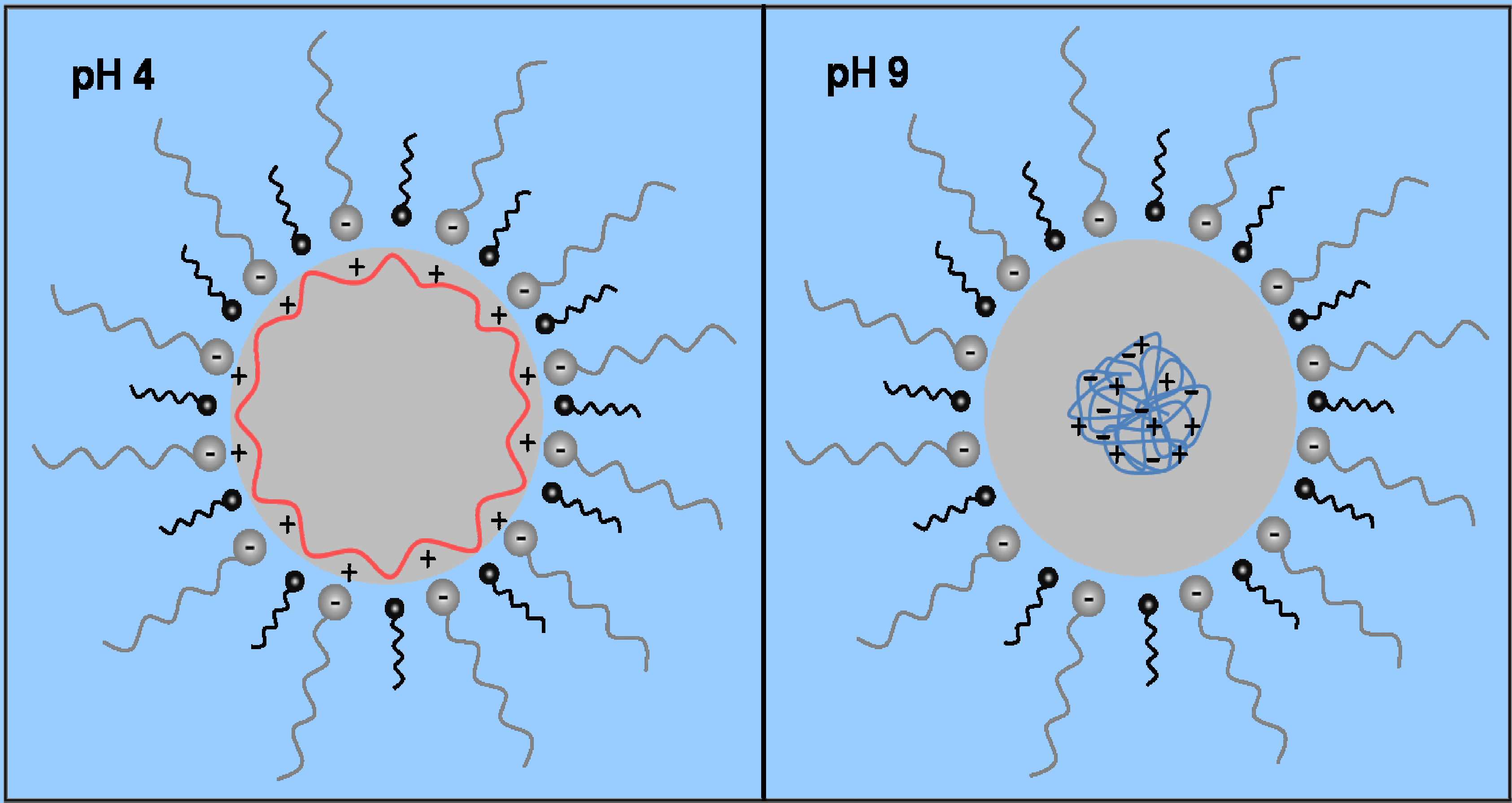
pH 9

Conductometric titrations





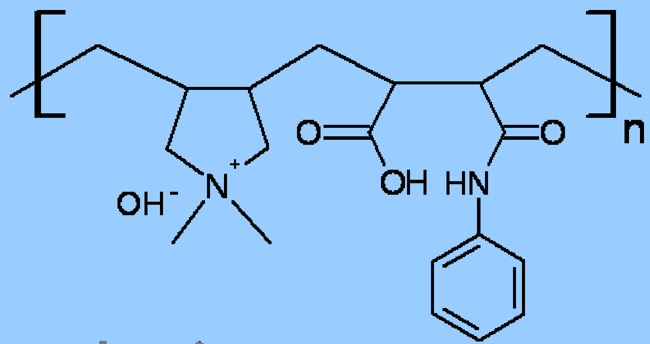
M. Fechner, M. Kramer, E. Kleinpeter, J. Koetz; Colloid Polymer Sci 287 (2009), 1145-1153.



M. Fechner, M. Kramer, E. Kleinpeter, J. Koetz; Colloid Polymer Sci 287 (2009), 1145-1153.

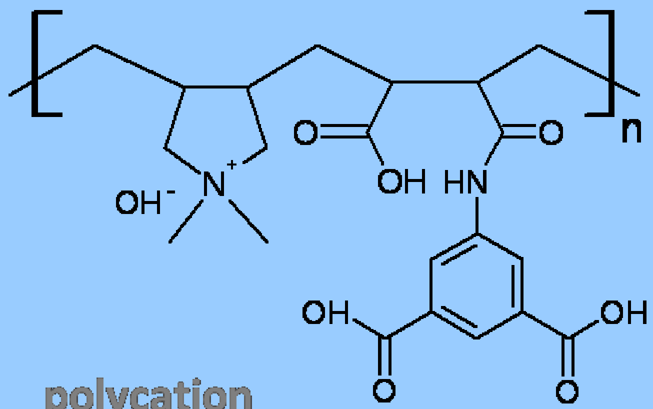
pH << IEP

PalPh



polycation

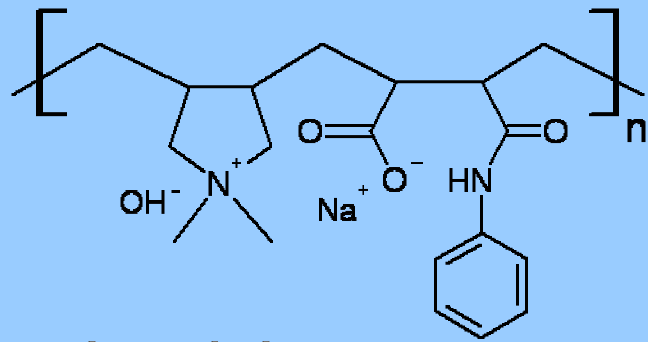
PalPhBisCarb



polycation

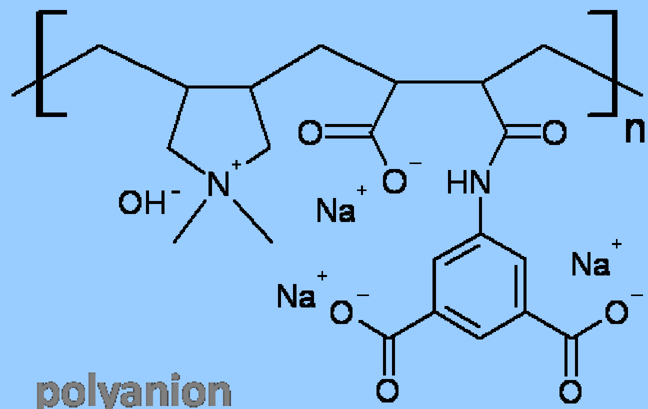
pH >> IEP

PalPh



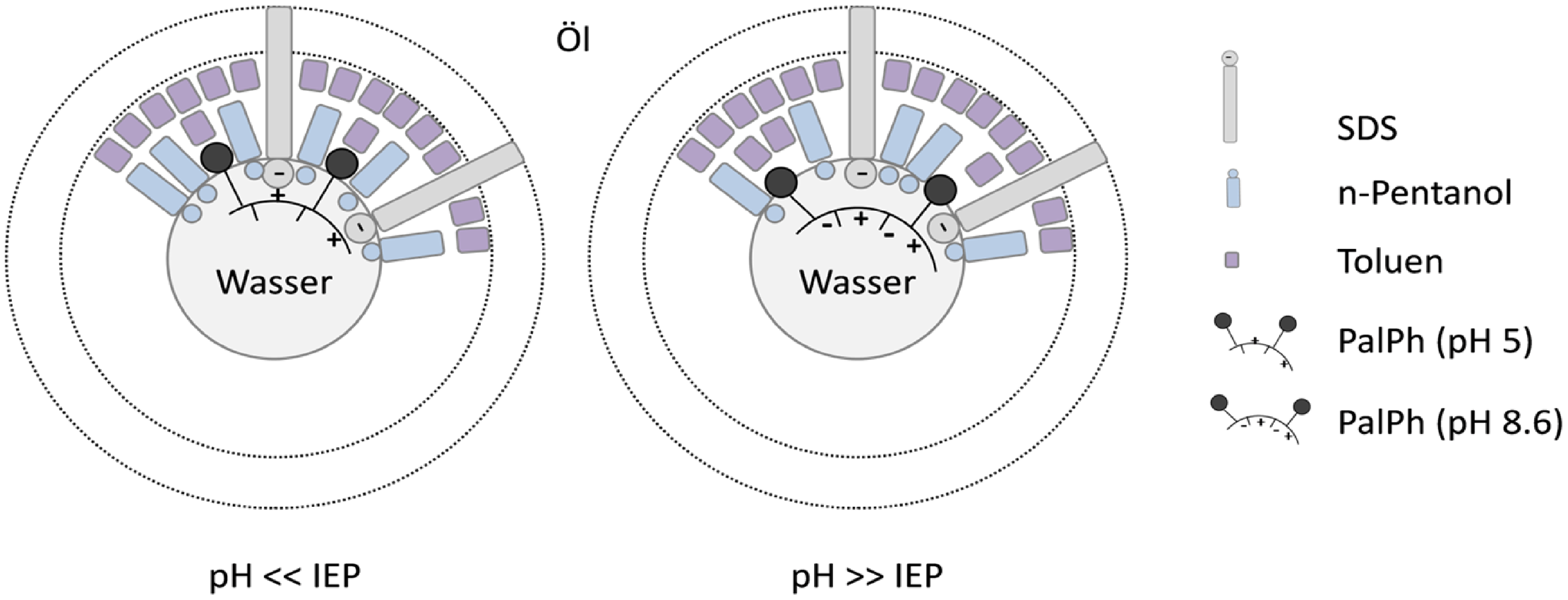
polyampholyte

PalPhBisCarb



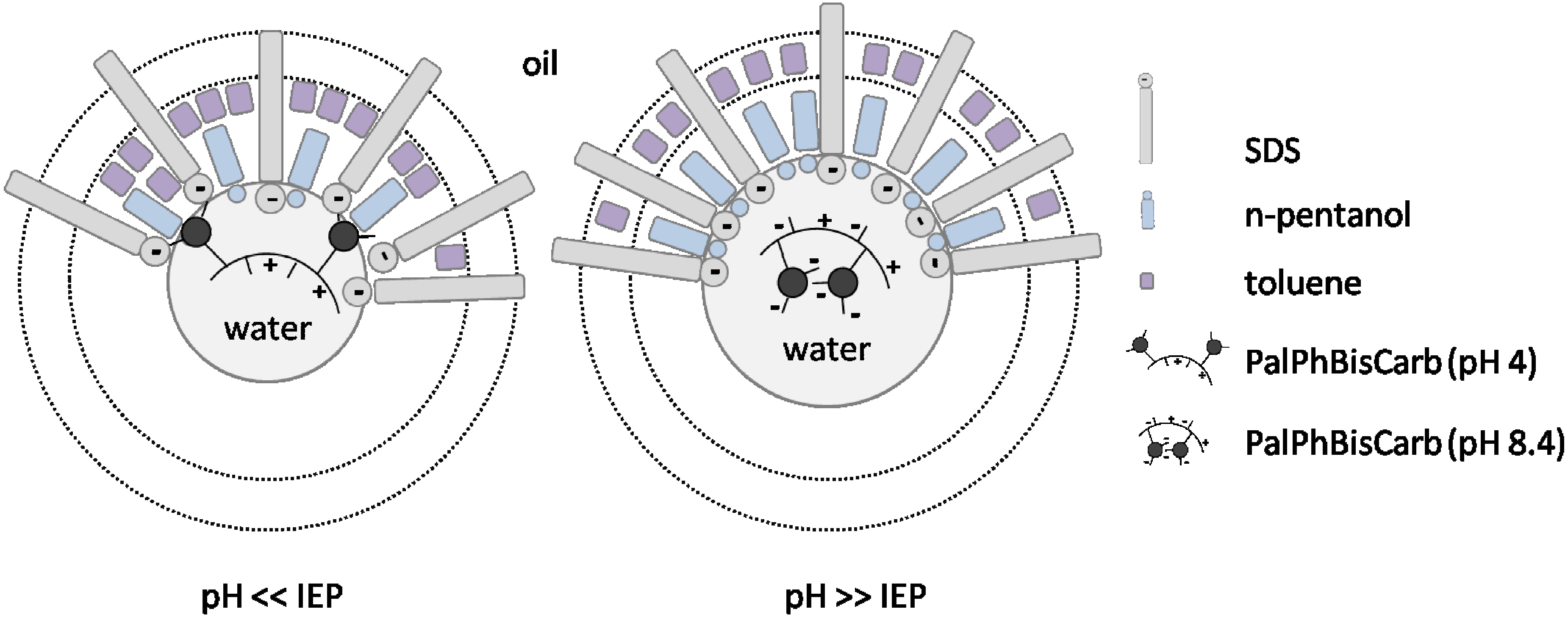
polyanion

PalPh



M. Fechner, J. Koetz; Langmuir 27 (2011) 5316-5323

PalBisCarb



M. Fechner, J. Koetz; Langmuir 27 (2011) 5316-5323

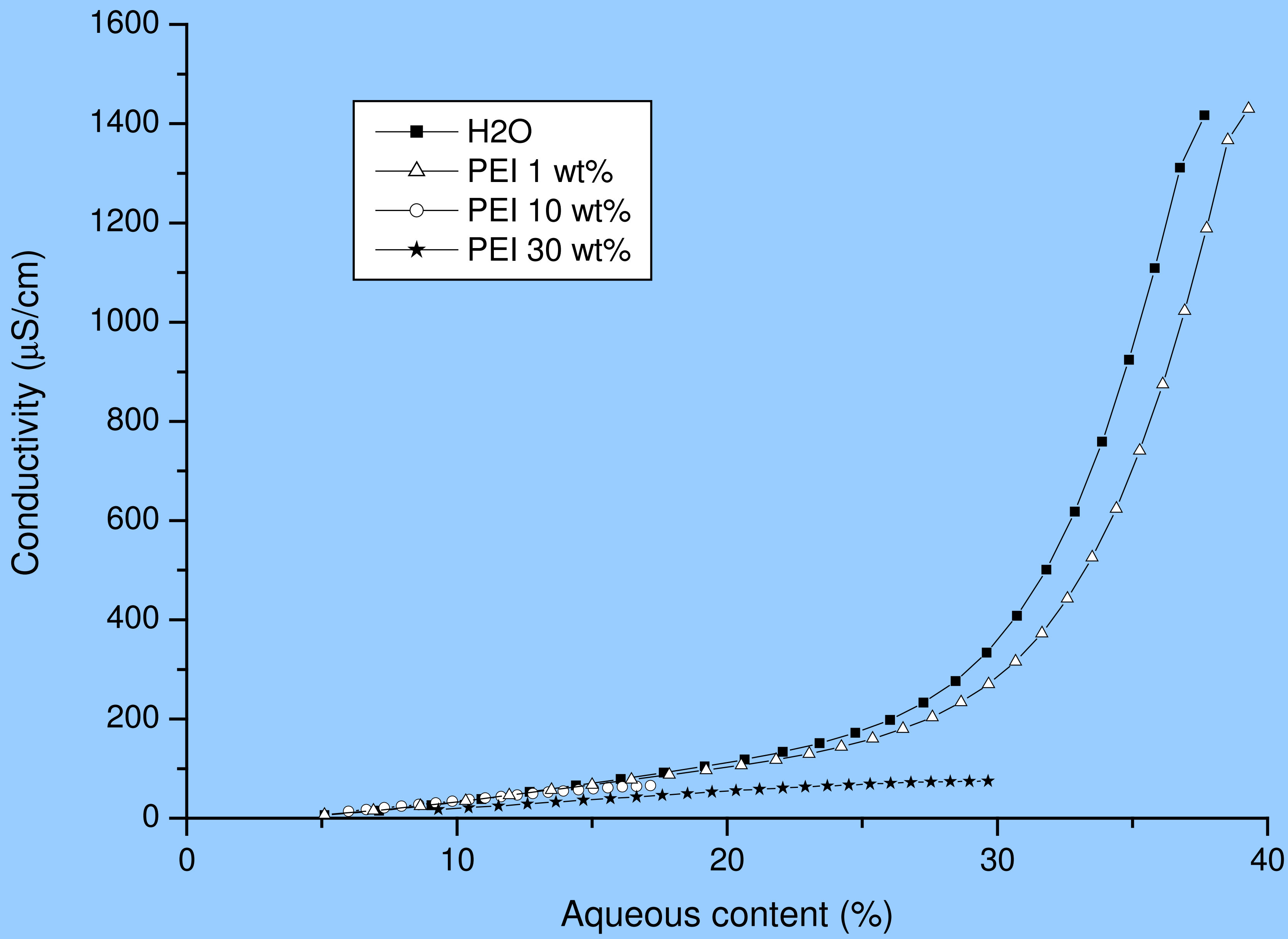
By varying the pH value of the polyampholyte:

→ **the location of the polyampholyte inside the droplets can be tuned**

→ **the droplet-droplet interactions can be changed**

SDS-based system modified by adding:

- Poly(dimethyldiallylammonium chloride) (PDADMAC)
- Polyampholytes (Mw ~ 22,000 g/mol)
- **Poly(ethyleneimine) (PEI; Mw = 25000 - 600000 g/mol)**



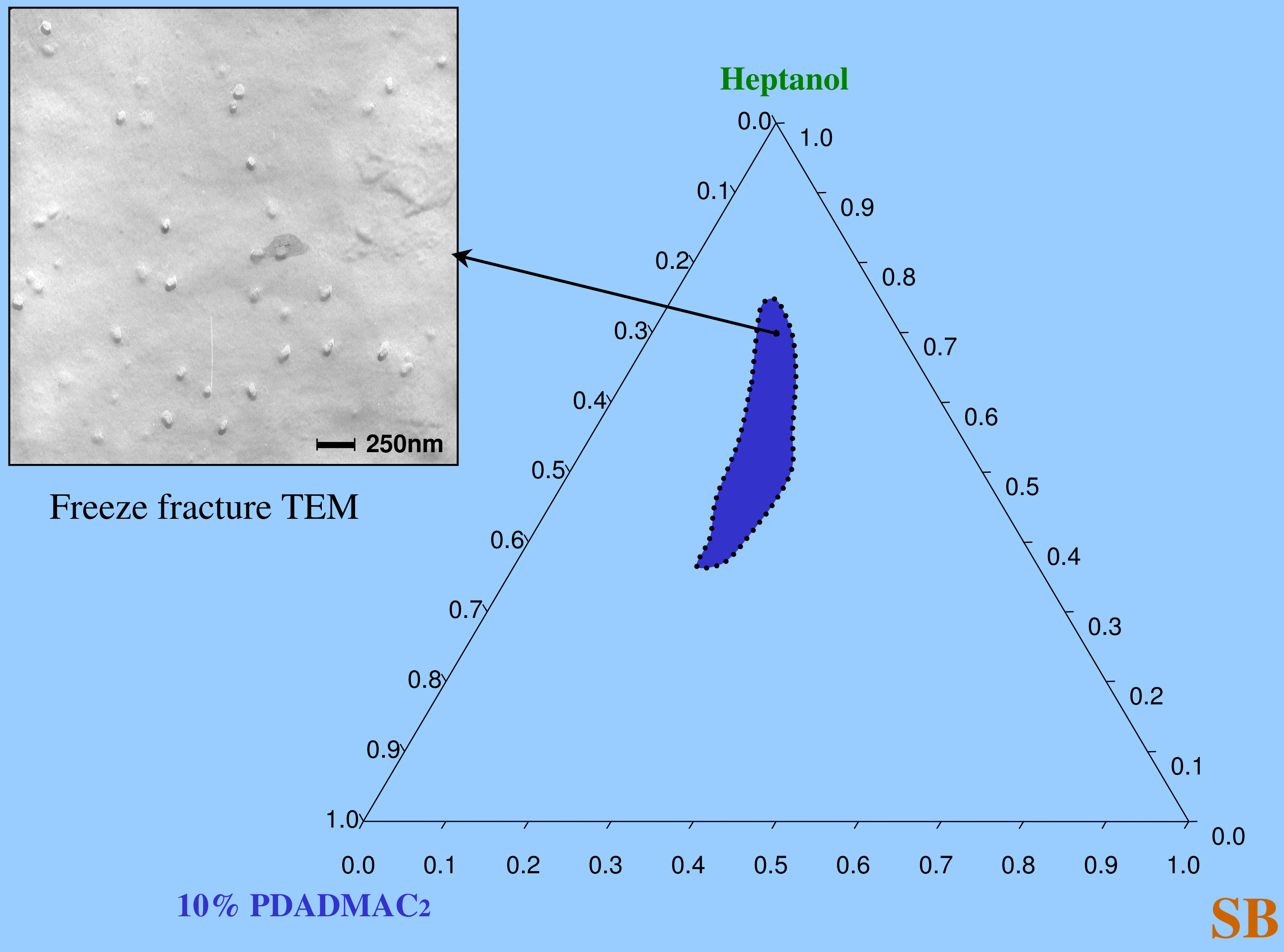
C. Note, S. Kosmella, J. Koetz J. of Colloid and Interface Sci. 302 (2006) 662-668

PEL-modified microemulsions

- Water / Alcohol / **SB**

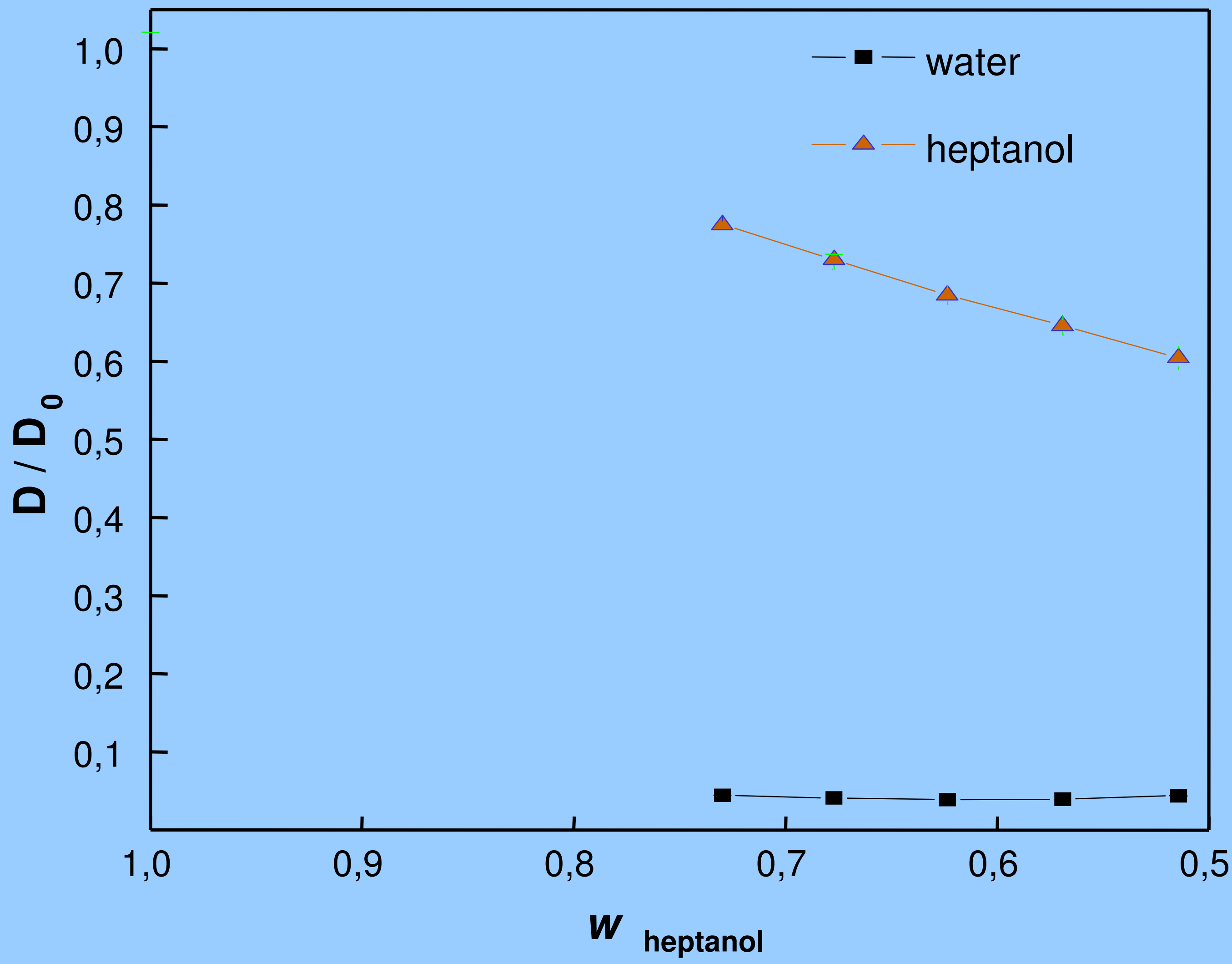
  L2 - phase

  + PDADMAC

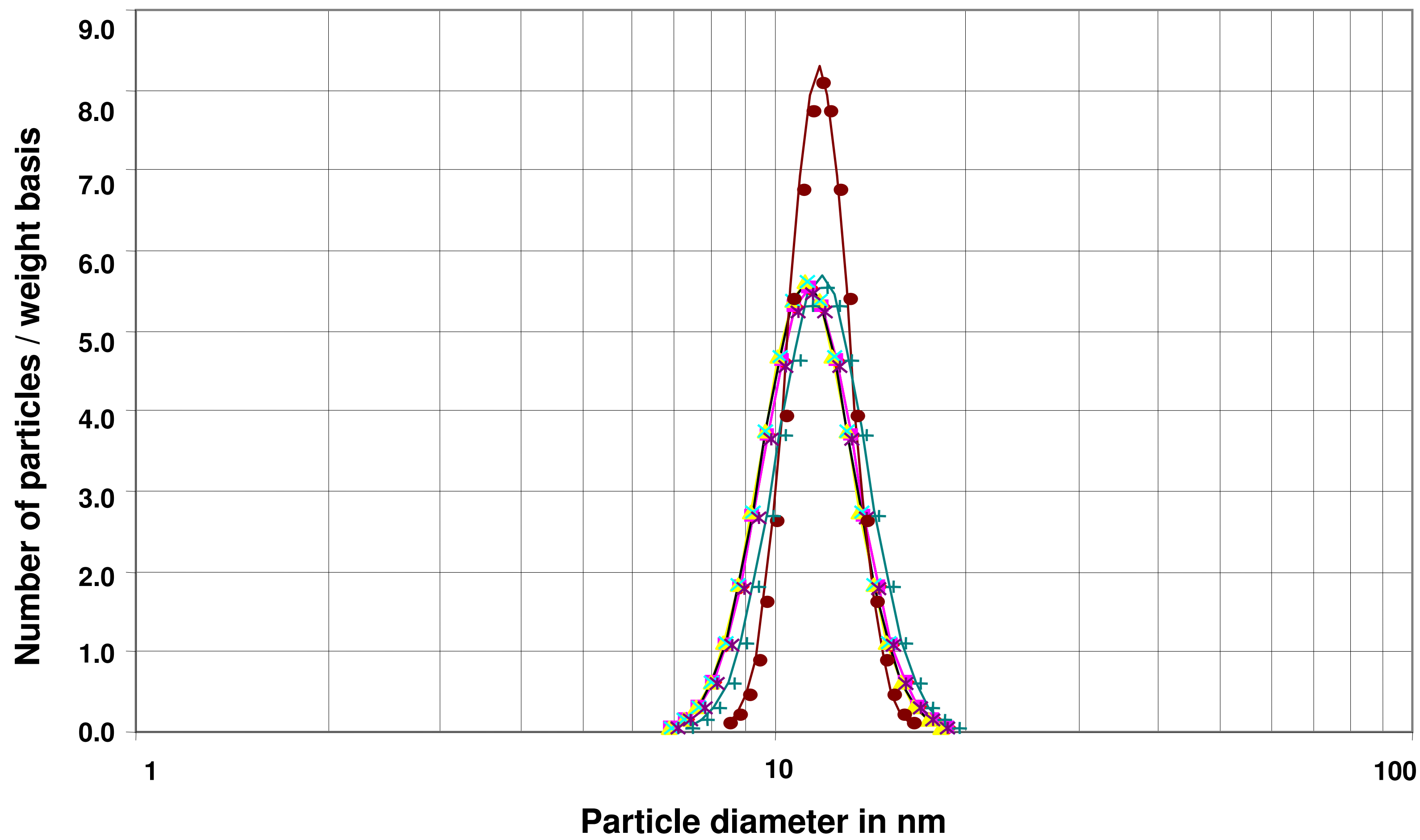


250nm
Freeze fracture TEM
Heptanol
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
10% PDADMAC2
SB

Reduced diffusion coefficients D/D_0 of a polymer-modified microemulsion (10% PDADMAC/SB/heptanol)



Particle size distribution determined by ultrasound relaxation at point P1



J. Baier, J. Koetz, S. Kosmella, B. Tiersch, H. Rehage; ***J. of Physical Chemistry B*** *111 (2007) 8612-8618*

PEL-modified microemulsions

- Water / Alcohol / **SB**

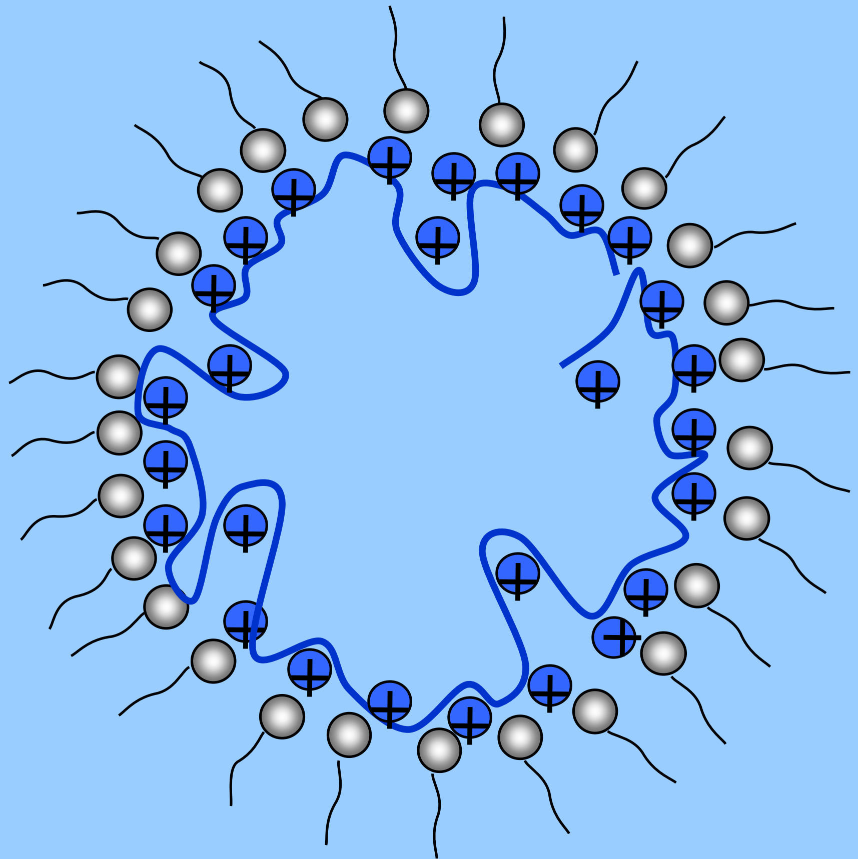
  L2 - phase

+ PDADMAC

+ PEI

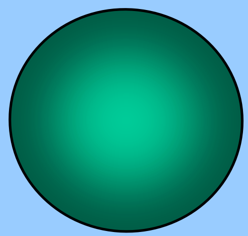
Polyelectrolytes

- **Can be incorporated into w/o microemulsions !**
- **Can „boosting“ the L2 phase !**
- **Can influence the droplet-droplet interactions !**
- **Can tune the surfactant film stability !**

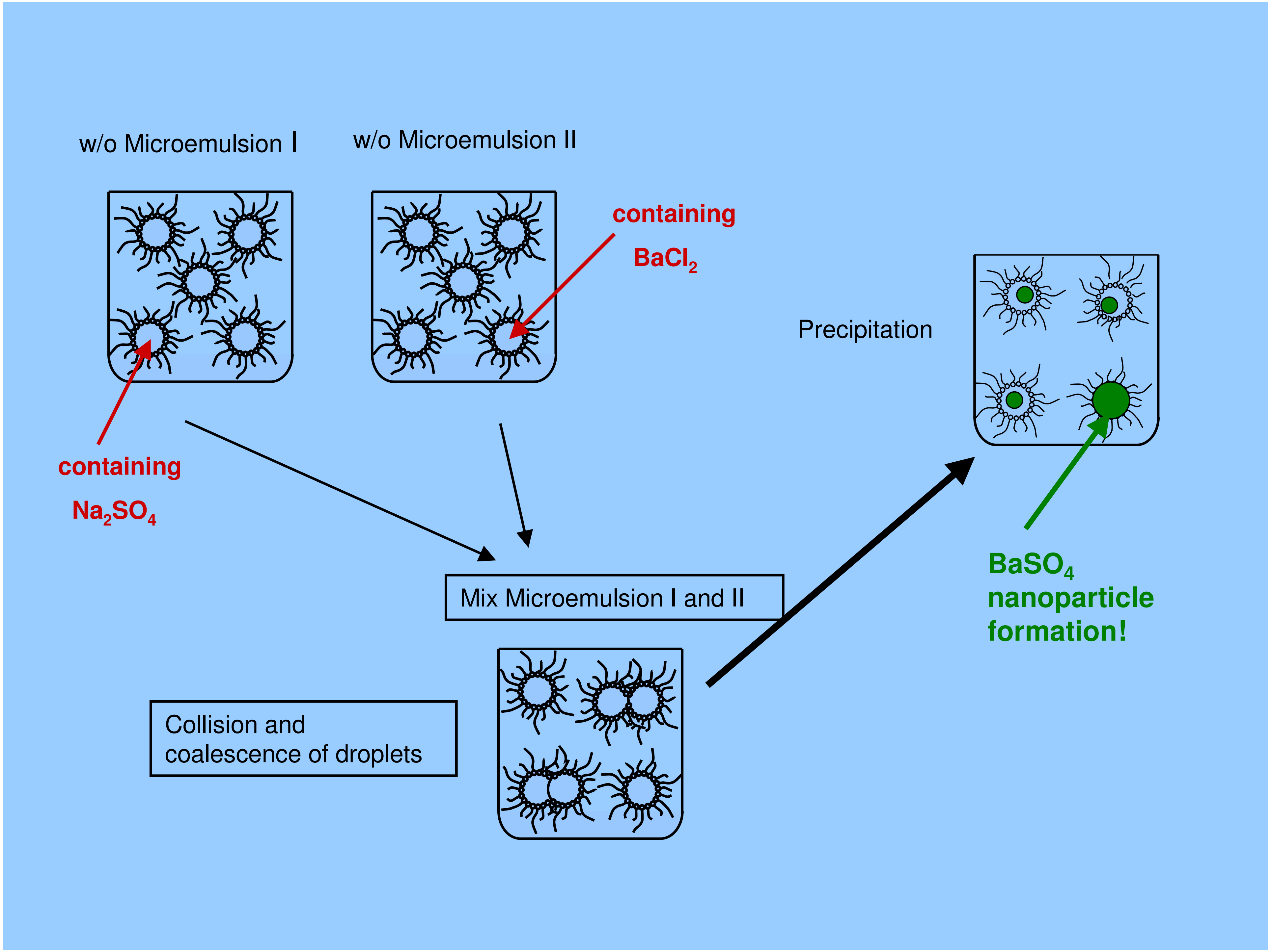


PEL-modified microemulsions as templates for the nanoparticle formation

Nanoparticle formation in reverse PEL-modified microemulsions



- ***BaSO4***
- ***ZnS***
- **CdS**
- ***Magnetite***
- ***Hydroxylapatite***
- ***Gold***



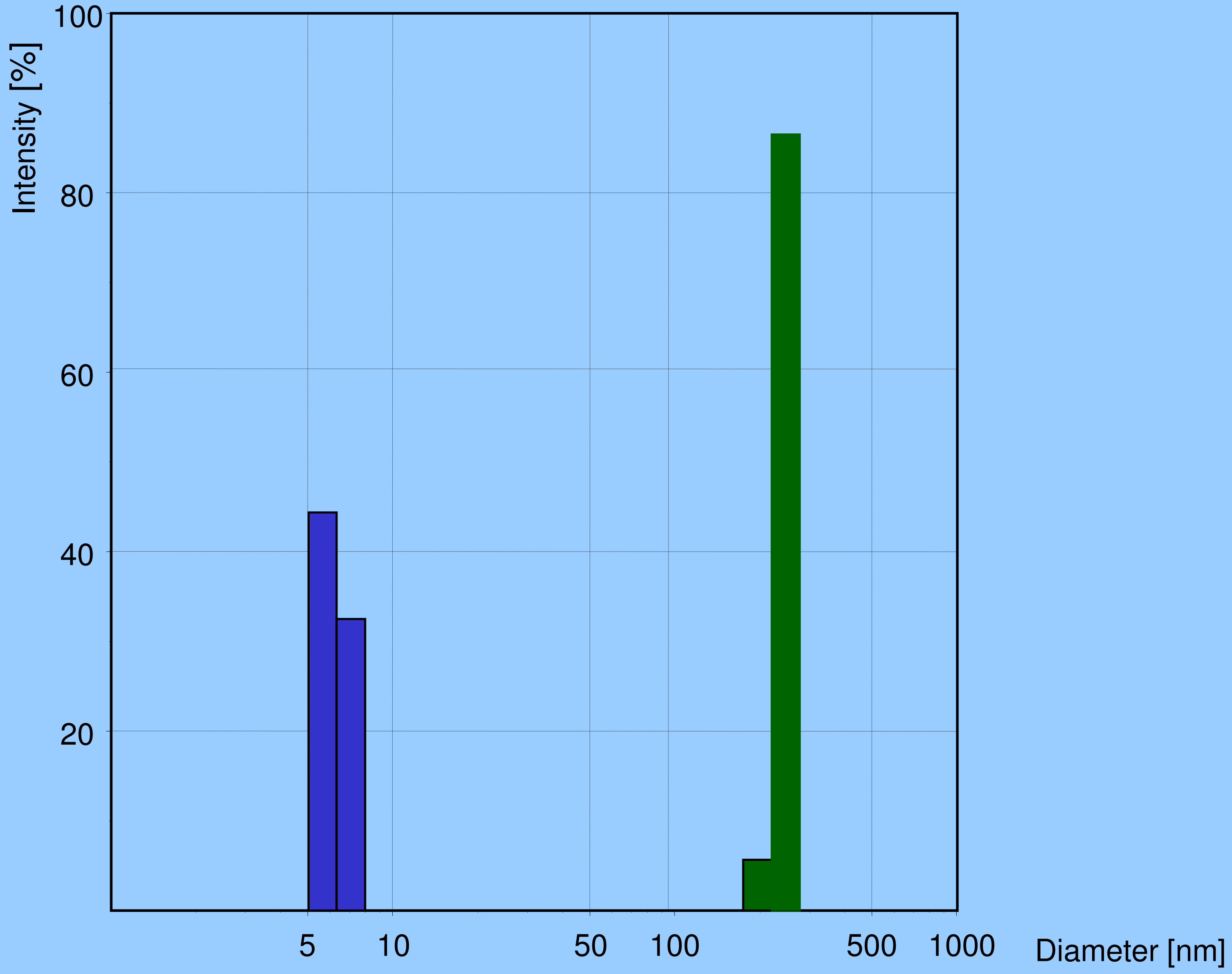
w/o Microemulsion I
w/o Microemulsion II
containing
BaCl$_2$
containing
Na$_2$SO$_4$
Precipitation
Mix Microemulsion I and II
BaSO$_4$
nanoparticle
formation!
Collision and
coalescence of droplets

Polymer-modified Nanoparticles

Nanoparticle formation in polymer-modified w/o microemulsions

Solvent evaporation

Redispersion of the polymer-stabilizied nanoparticles

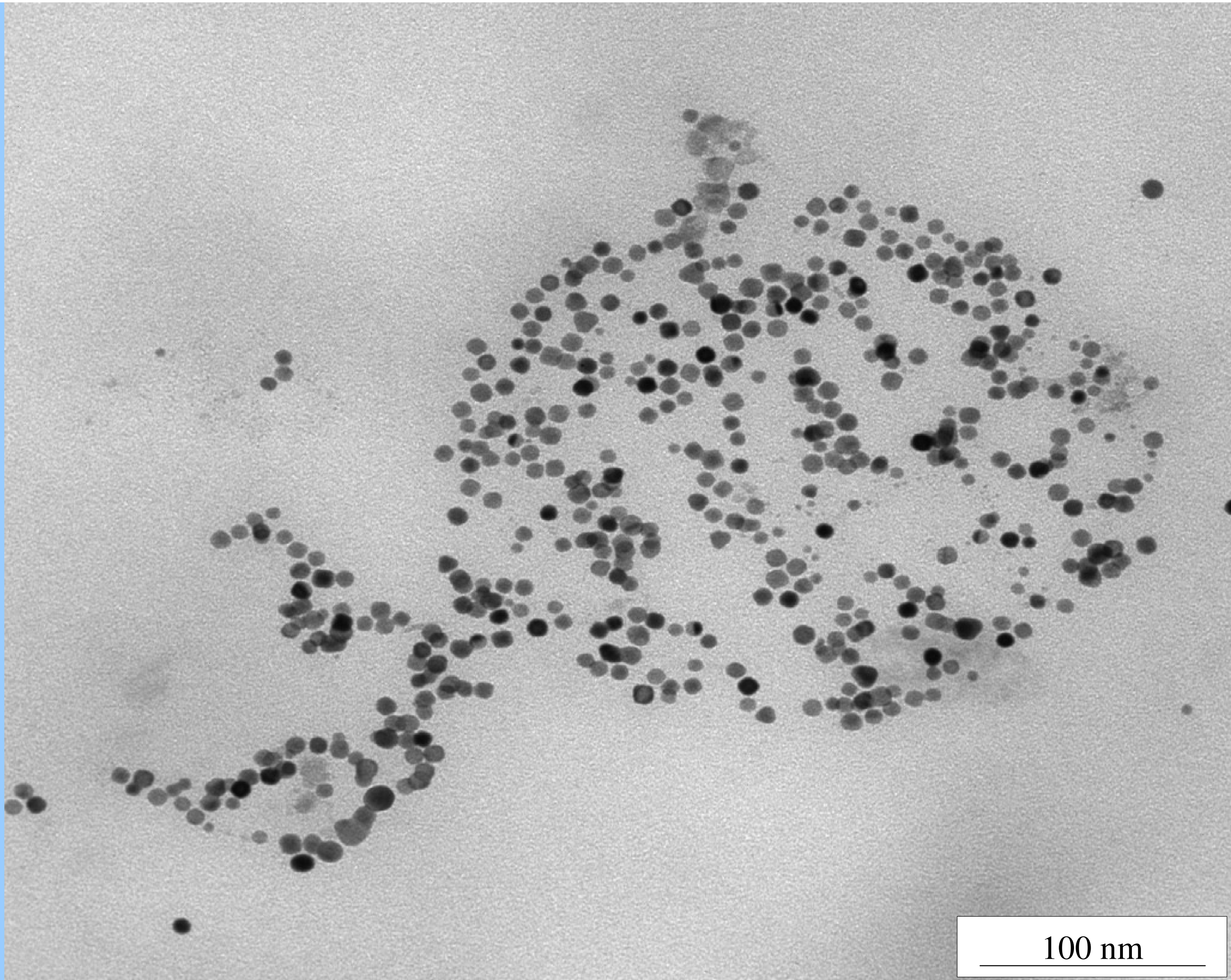


The average $BaSO_4$-particle size of the main fracture (detected by dynamic light scattering) in sample A **in presence of PDADMAC (blue)** and **in absence of PDADMAC (green)**

Particle size and zeta potential of redispersed $BaSO_4$–particles determined by dynamic light scattering

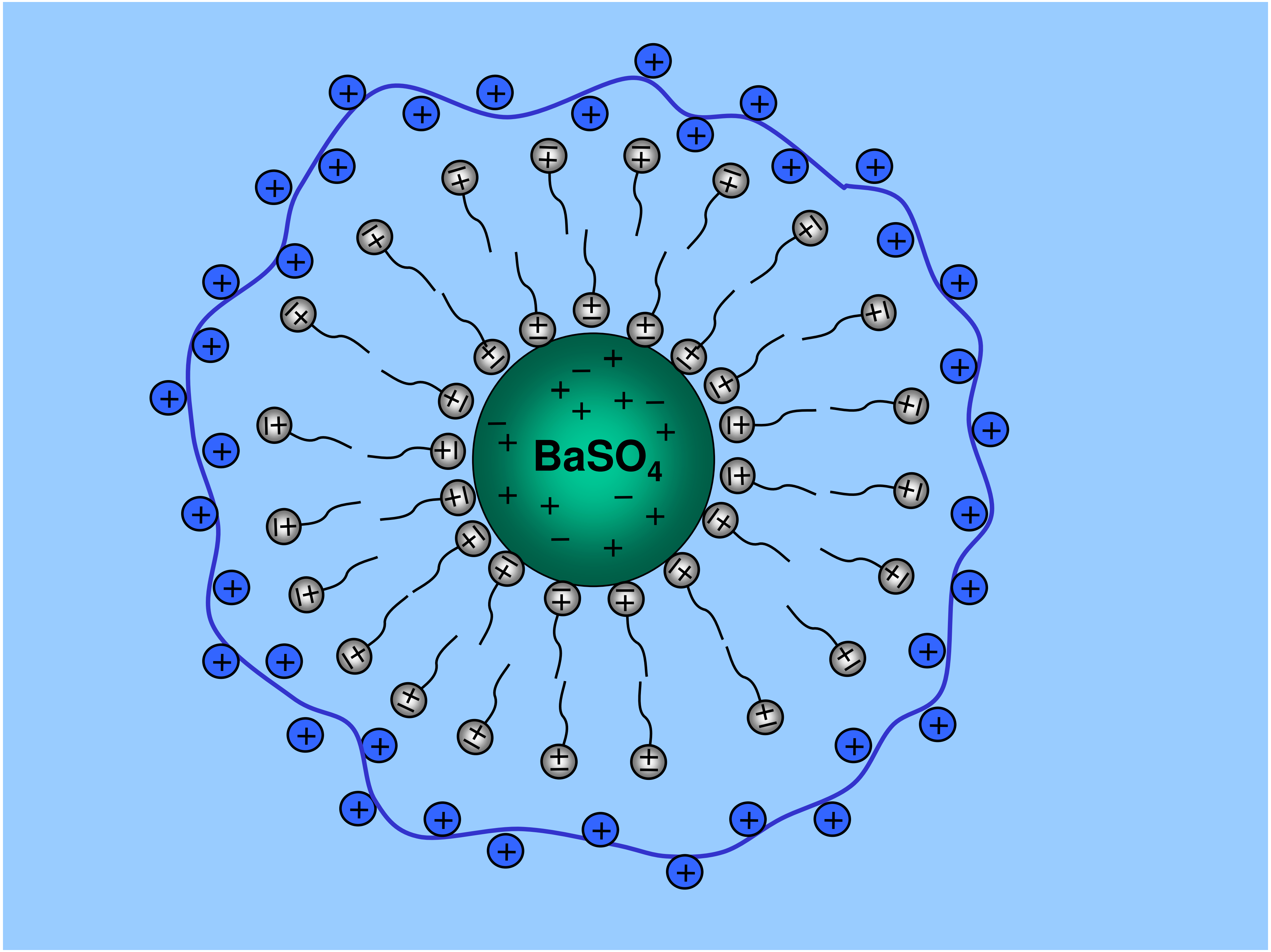
sample	particle size [nm] (dynamic light scattering*)	particle size [nm] (ultracentifugation)	zeta potential [mV]
A (without polymer)	312.8 ± 39.6		+8.3 ± 2.9
A	6.9 ± 2.2	4.4 ± 0.3	+27.1 ± 1.6
B	6.6 ± 4.7	5.1 ± 0.5	+24.0 ± 0.8
C	6.1 ± 1.1	6.5 ± 0.2	+24.0 ± 6.6
D	6.3 ± 1.9		+27.4 ± 4.4
E	6.0 ± 0.5		+33.6 ± 3.4

*average size of the main fraction automatic peak analysis by intensity



Redispersed $BaSO_4$ nanoparticles: 7.5 ± 1.4 nm

in presence of PDADMAC

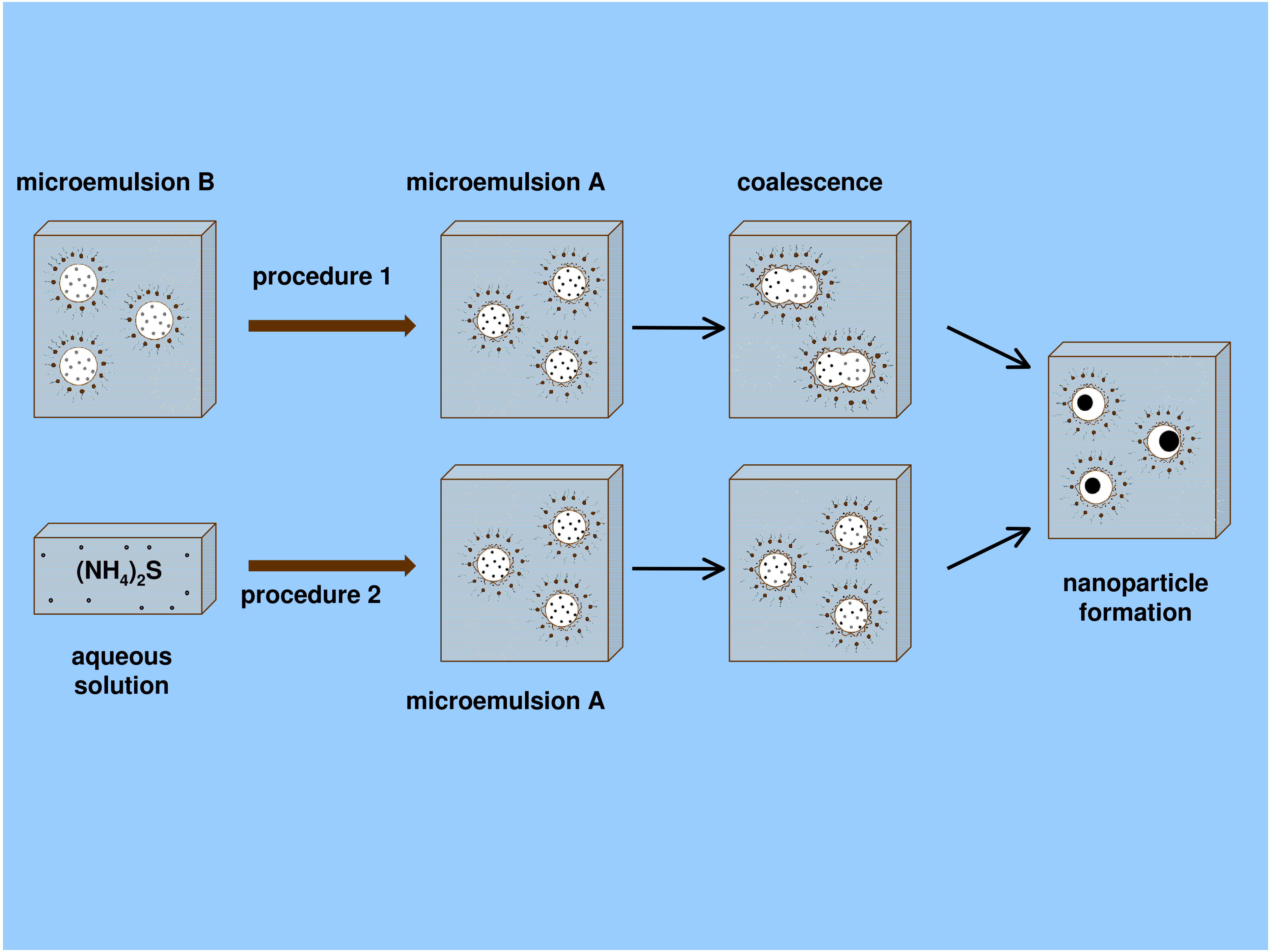


$BaSO_4$

Part 1: $BaSO_4$

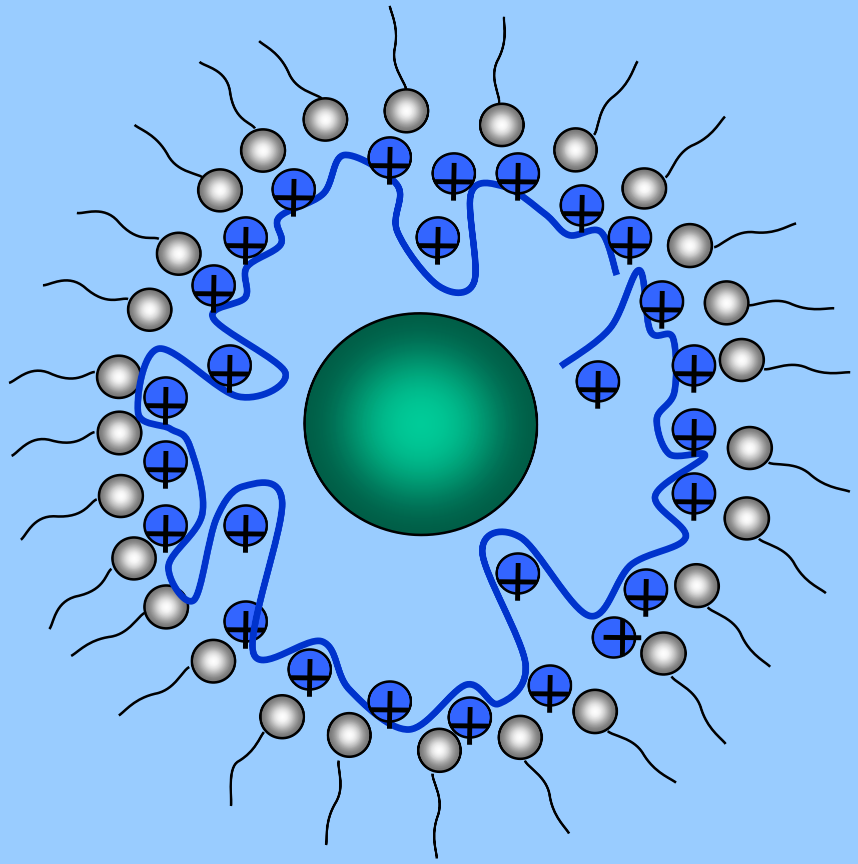
- **Polyelectrolyte–stabilized $BaSO_4$ – nanoparticles with particle diameter of 5-7 nm can be redispersed in presence of low molecular weight PDADMAC !!**

J. Koetz, J. Bahnemann, G. Lucas, B. Tiersch, S. Kosmella:
Colloids and Surfaces A: Physicochem. Eng. Aspects 250 (2004) 423-430



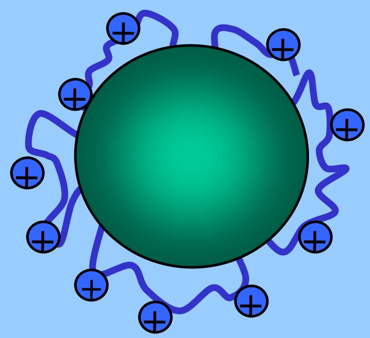
microemulsion B
procedure 1
microemulsion A
coalescence
$(NH_4)_2S$
aqueous solution
procedure 2
microemulsion A
nanoparticle formation

CONCLUSIONS:
Polyelectrolyte-modified microemulsions as nanoreactors



→ **PEL control the particle growing process !!**

CONCLUSIONS:
Polyelectrolyte-modified microemulsions as nanoreactors



→**PEL stabilize the nanoparticles during the redispersion process !!**