Polymer-Surfactant Interaction

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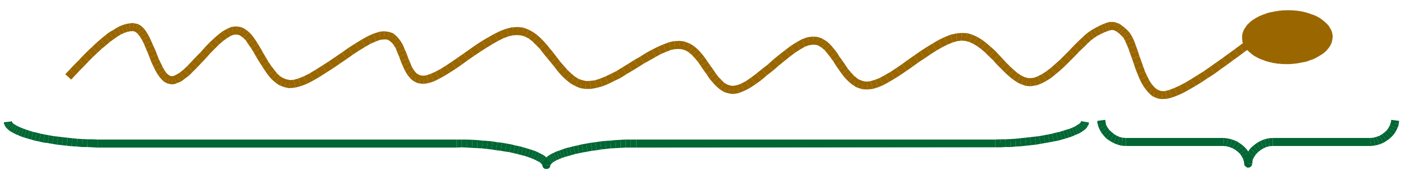
Surfactants

Surfactants (Surface Active Agents) are amphipathic molecules (have a hydrophilic part and a hydrophobic part).



The hydrophobic part is a long hydrocarbon chain that (could be also branched).

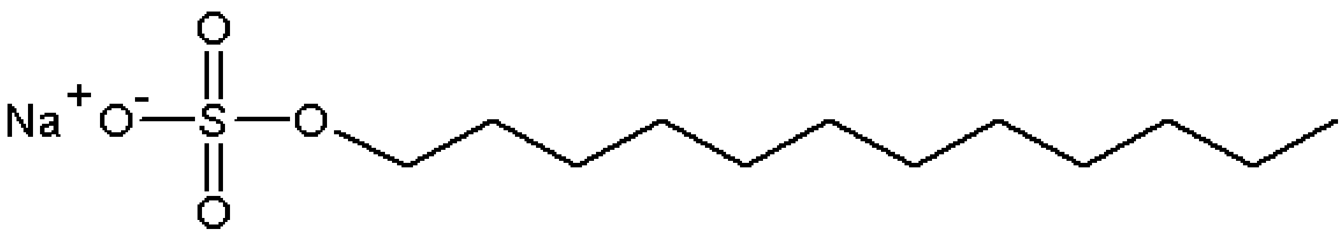
The hydrophilic part could be anionic (SO_3^-), cationic (R_3N^+) or simply a polar group (OH).

Types of Surfactants

- Ionic surfactants
  - Anionic Surfactants

A surfactant with a negatively charged head group such as:

Sodium Dodecyl Sulfonate (SDS)

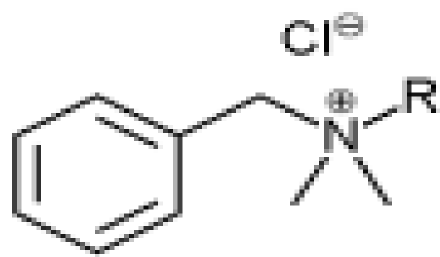


Types of Surfactants (cont.)

- Ionic Surfactants

  - Cationic Surfactants

A surfactant with a cationic group such as: Benalkonium Chloride



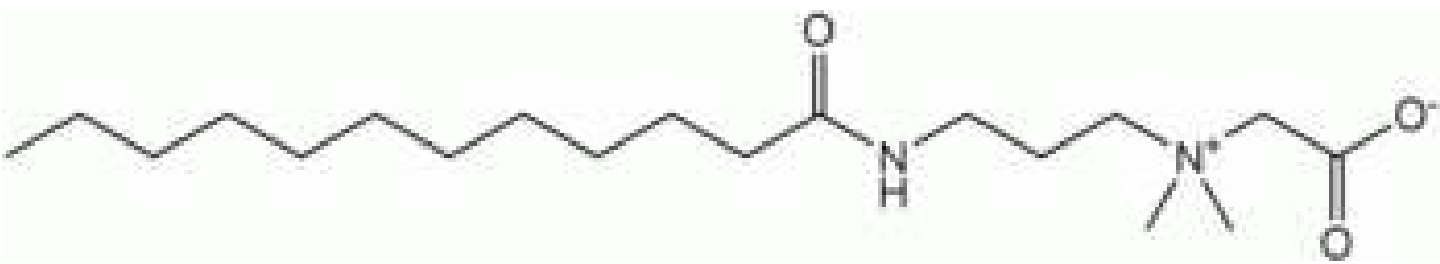
$R = C_8H_{17} - C_{18}H_{37}$

Types of Surfactants (cont.)

- Zwitterionic (Amphoteric) Surfactants

A surfactant with two oppositely charged groups such as:

Cocamidopropyl betain

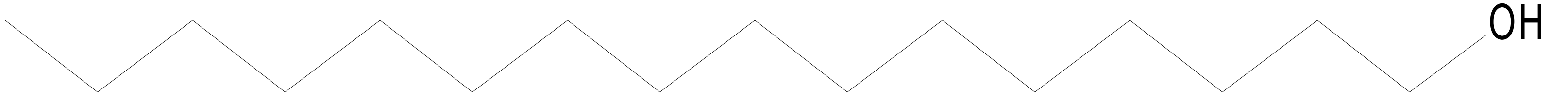


Types of Surfactants (cont.)

- Nonionic Surfactants

A surfactant with no charge group

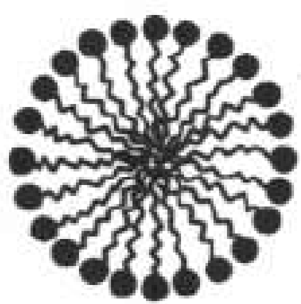
Such as Cetyl alcohol

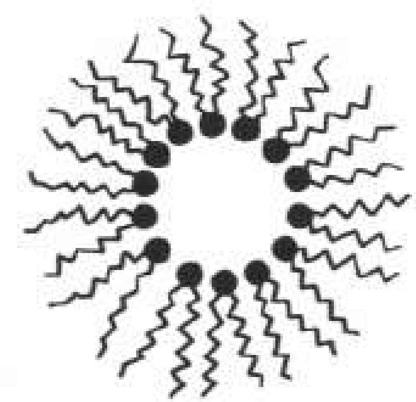


Micellization

- Micelles form when the concentration of the surfactant goes above a certain limit called critical micelle concentration (cmc).
- The micelles formation is driven by entropy (because the entropy penalty of surfactants molecules gather to form a micelle is less than the entropy penalty of water molecules (or solvent) gathering together via hydrogen bonding to isolate the hydrophobic part in a cage like structures).

In a polar medium

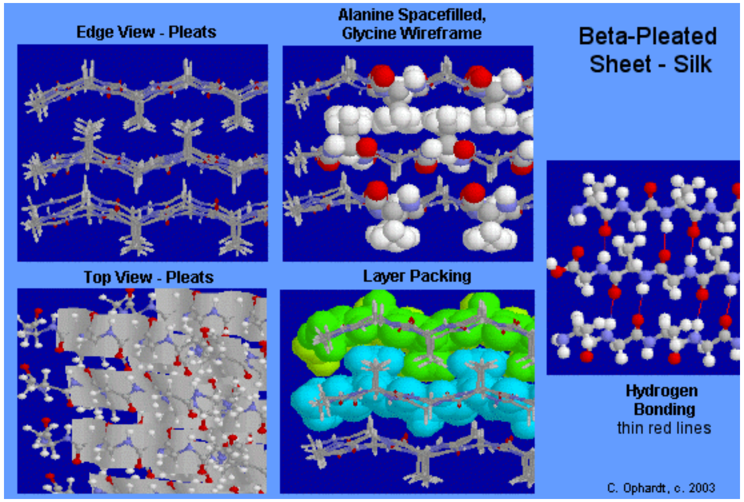




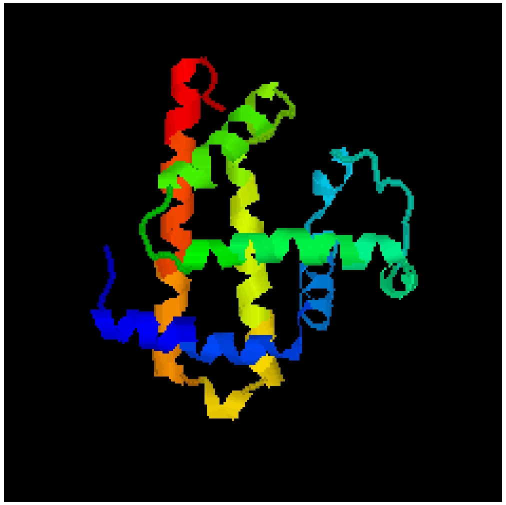
In a non-polar medium

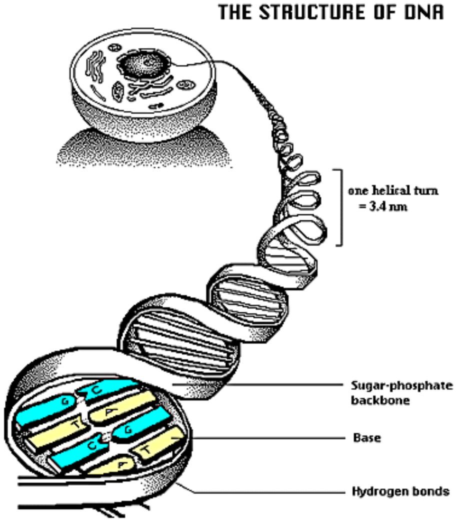
Polymers

- Polymers are long chain giant molecules assembled from smaller units (monomers).
- There are natural polymers such as: silk, proteins, rubber, carbohydrates, DNA….etc.
- Synthetic polymers such as: polyurethane, polystyrene, polyvinyl chloride…..etc.



Myoglobin





Polymers Classification

- Homopolymers

(Polypropylene)

A-A-A-A-A-A-A-A- = $-A_n-$

- Copolymers, could be

- Alternating

A-B-A-B-A-B-A-B-A-B = $-(AB)_n-$

- Random

A-A-B-A-B-A-A-A-B-B-A-…..

- Block copolymer

A-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B………..

Polymers Classification

Polymers are also classified according to method of preparation:

- Addition polymers

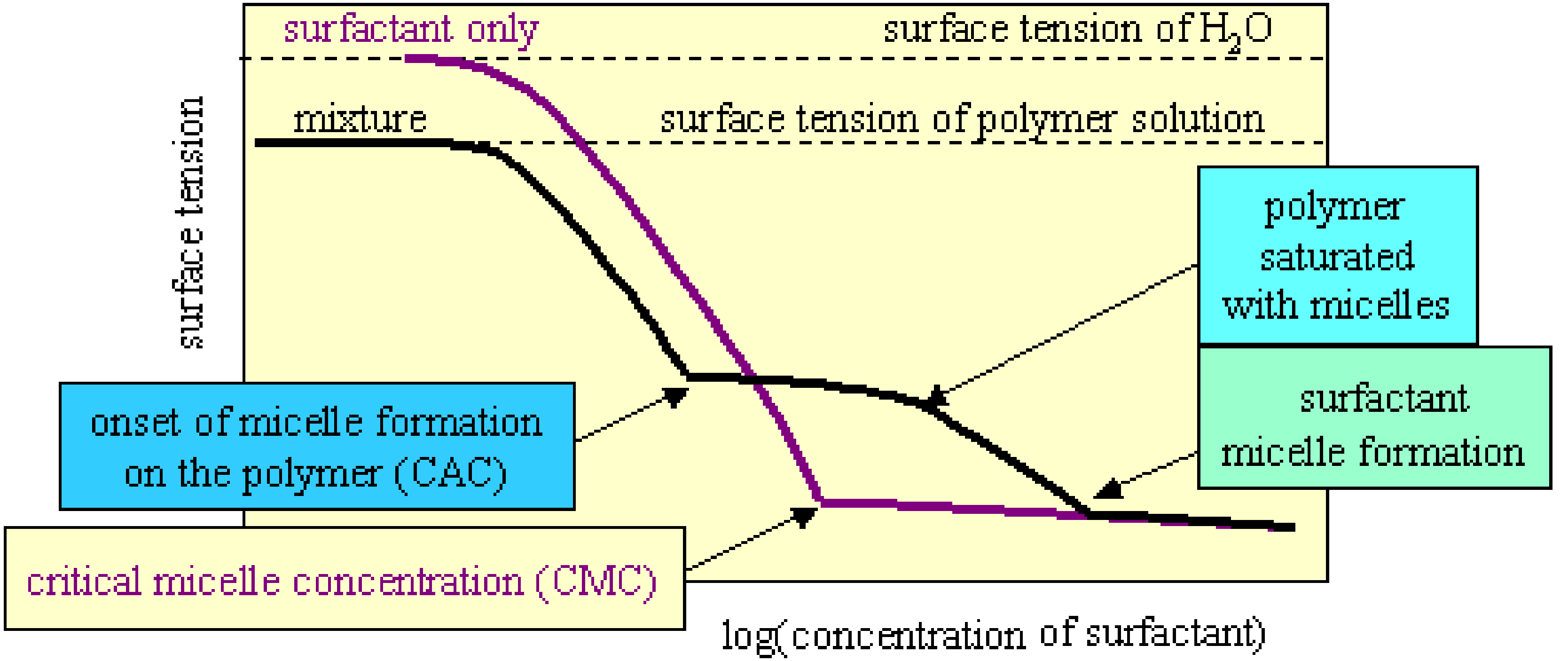
Usually the monomers are unsaturated (Alkenes) ex. Polyethylene

- Condensation polymers

Usually the monomers have functional groups like acids and hydroxyl ex. Polyamides (Nylon)

Effect of Polymer-Surface Interaction

Polymers induce aggregation

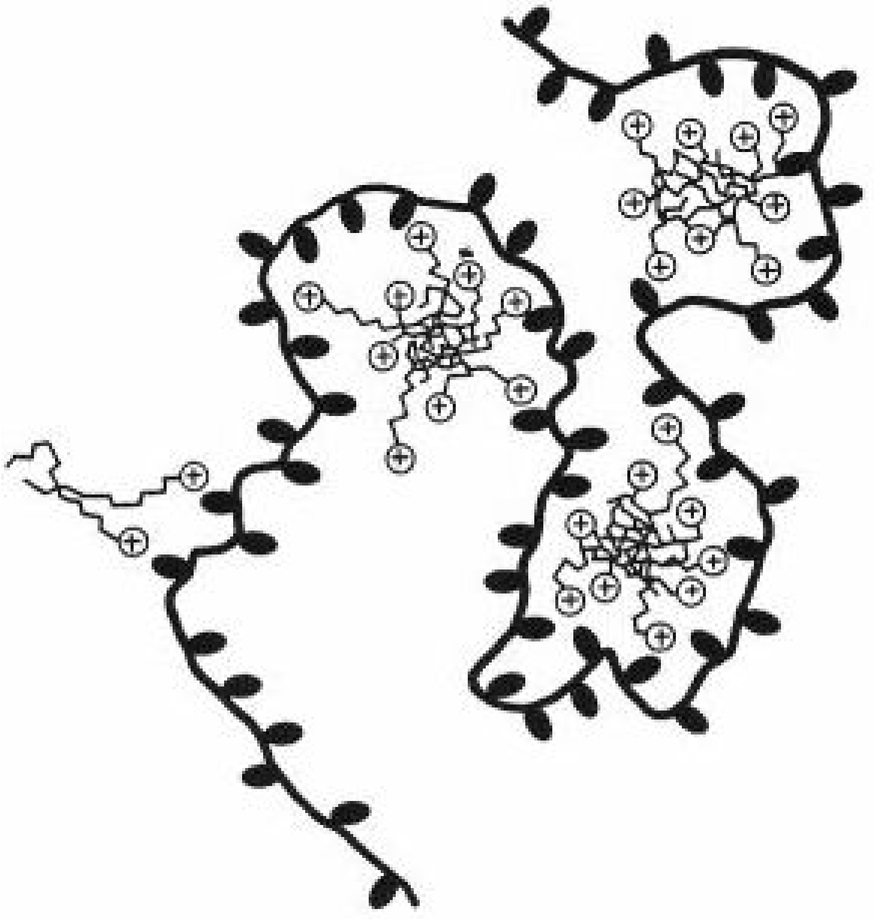


Polymer-Surfactant Interaction

Types of interactions:

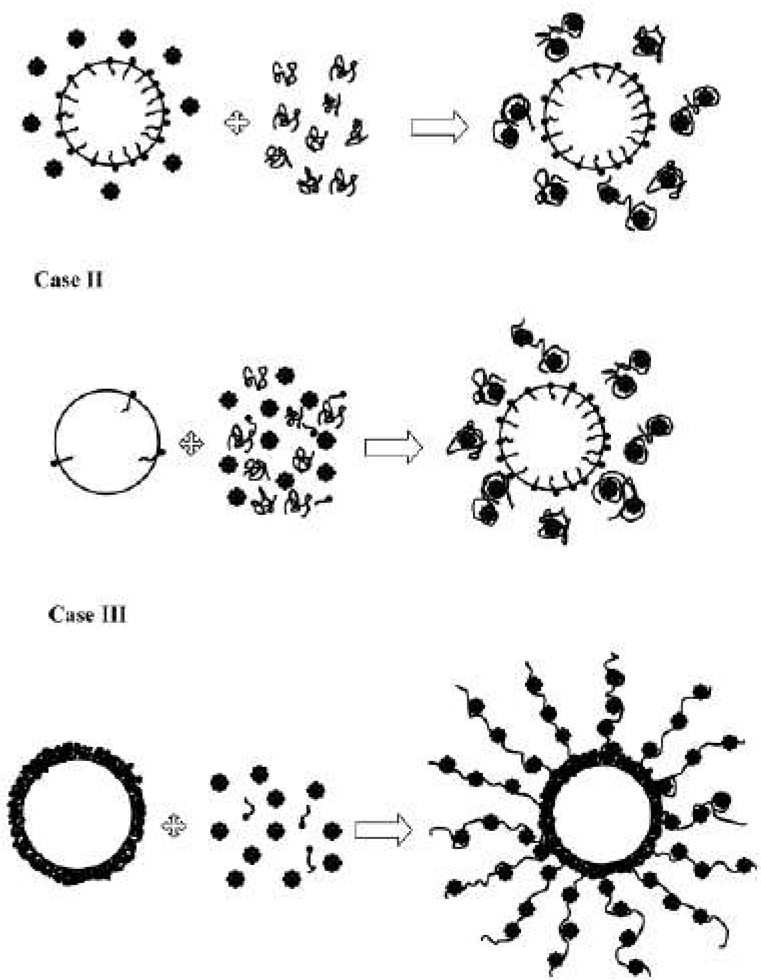
- Electrostatic Interactions (if the polymer and the surfactant are oppositely charged).

- Hydrophobic Interactions (between the hydrophobic parts of both the polymer and surfactant).



- The presence of polymeric chains induces the formation of micelles.
- The presence of similarities between the surfactant and the polymer attract the surfactant molecules to certain positions in the polymer.

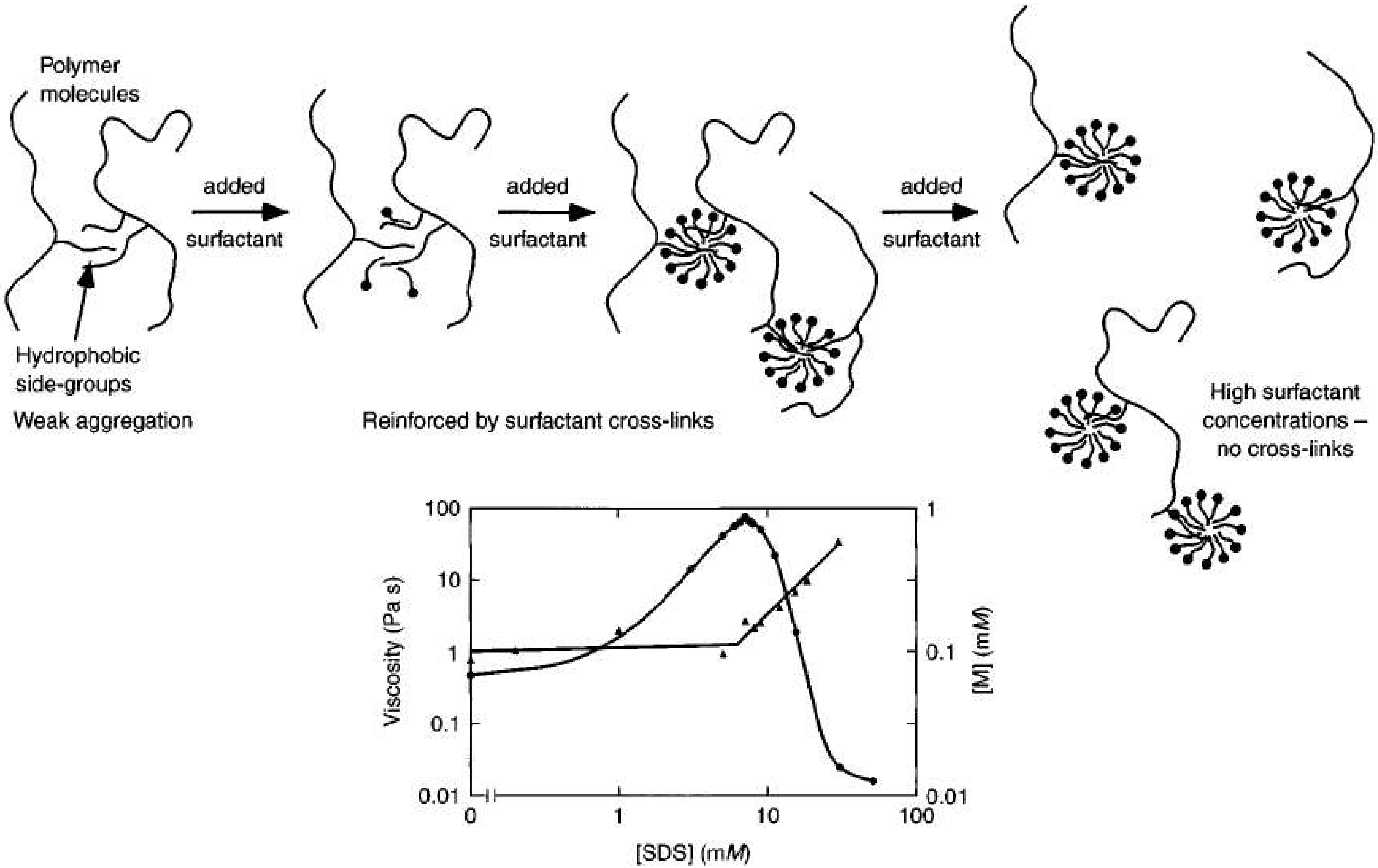
Abuin, E. B. and Scaiano, J. C. *Journal of American Chemical Society* **1984**, 106, 6274.)



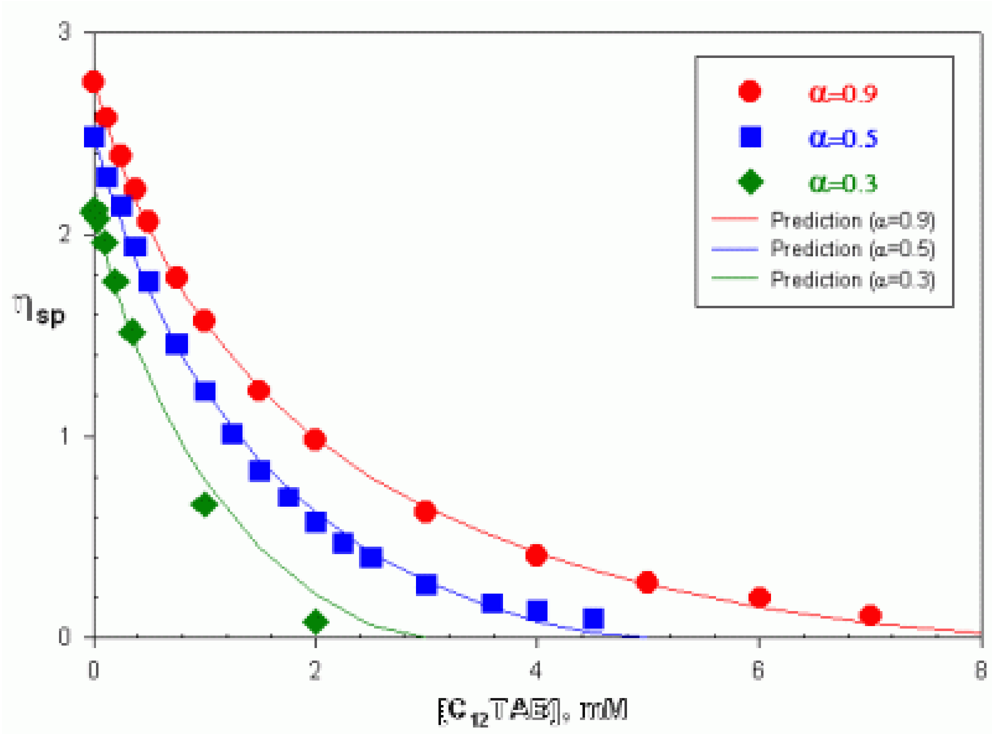
Ref. 13

Polymer-Surfactant Interaction (cont.)

- The main attraction forces are still hydrophobic interactions.
- The same mechanism and entropy balance hold for micellization in presence of polymer
- Usually the same aggregate size and aggregation number.
- The presence of oppositely charged species do enhance interaction



Polymer
molecules
added
surfactant
added
surfactant
added
surfactant
Hydrophobic
side-groups
Weak aggregation
Reinforced by surfactant cross-links
High surfactant
concentrations –
no cross-links
100
10
1
0.1
0.01
Viscosity (Pa s)
1
0.1
0.01
[M] (mM)
0
1
10
100
[SDS] (mM)



The specific viscosity of 0.01M PAA with different degrees of neutralization, a, as a function of added C_{12}TAB compared between experimental data (filled symbols) and the predictions (solid lines).

Applications of Polymer-Surfactant Mixtures

Polymers are added to surfactants to:

- Control the phase behavior (e.g. to solubilize water insoluble polymers).
- Control the interfacial properties (e.g. to stabilize suspensions which depends on a complex interplay between different pair interactions. Addition of a polymer can either remove a surfactant from a surface or enhance its adsorption to a surface).

Applications of Polymer-Surfactant Mixtures

- To achieve a suitable rheology (thickening and gelation effect).
- The polymer induced micellization lead to a lower surfactant free molecules concentration and activity (e.g. in skin formulations, free surfactant molecules cause skin irritation).

Table 1
cmc of the investigated surfactants in water and values of the cac in the presence of PEO or PVP

Surfactant	Polymer	T (°C)	cmc or cac (mM)	cac/cmc	C_2 (mM)
SDS		25	8.0[a]		
SDS	0.1 wt% PEO	25	4.4[a]	0.55	
SDS	0.1 wt% PVP	25	2.1[a]	0.26	
CsDS		30	6.2		
CsDS	0.1 wt% PEO	30	4.2	0.68	9.6
CsDS	0.1 wt% PVP	30	4.1	0.66	8.4
TMADS		25	5.4[b]		
TMADS	0.1 wt% PEO	25	4.6	0.85	8.0
TMADS	1 wt% PEO	25	4.7	0.87	
TMADS	0.1 wt% PVP	25	4.6	0.85	8.6
TEADS		25	3.7[b]		
TEADS	0.1 wt% PEO	25	3.7	1.0	
TEADS		40	3.8[b]		
TEADS	0.1 wt% PEO	40	3.8	1.0	
TPADS		25	2.2[b]		
TPADS	1 wt% PEO	25	2.2	1.0	
TPADS	0.1 wt% PVP	25	2.25	1.01	
TBADS		25	1.15[b]		
TBADS	0.1 wt% PEO	25	1.15	1.0	
TBADS	1 wt% PEO	25	1.15	1.0	

Mohamed Benrraou, Baeney Bales and Raoul Zana, J. Coll. Inter. Sci., (2003), 267, 519-523.

Techniques Used to Study Polymer-Surfactant Interactions

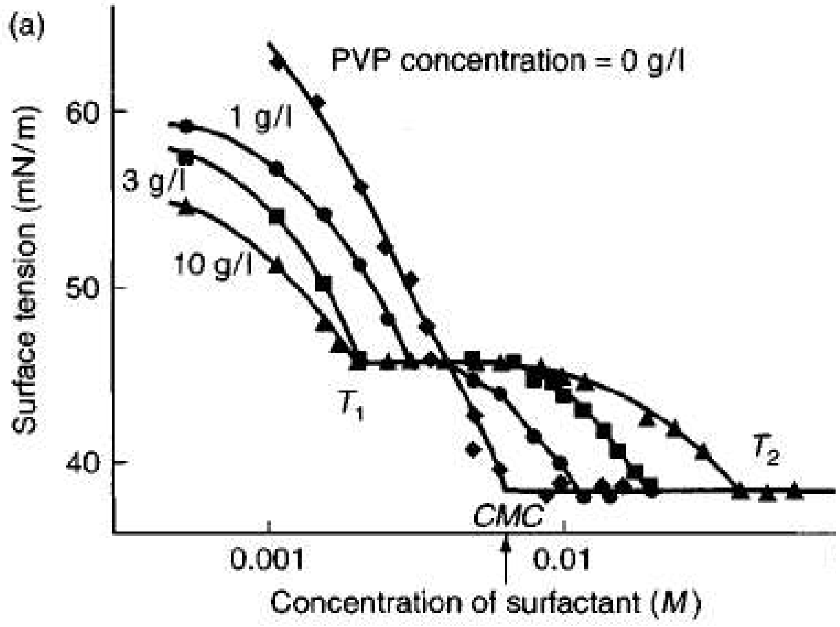
There are several techniques to study polymer-surfactant interactions such as:

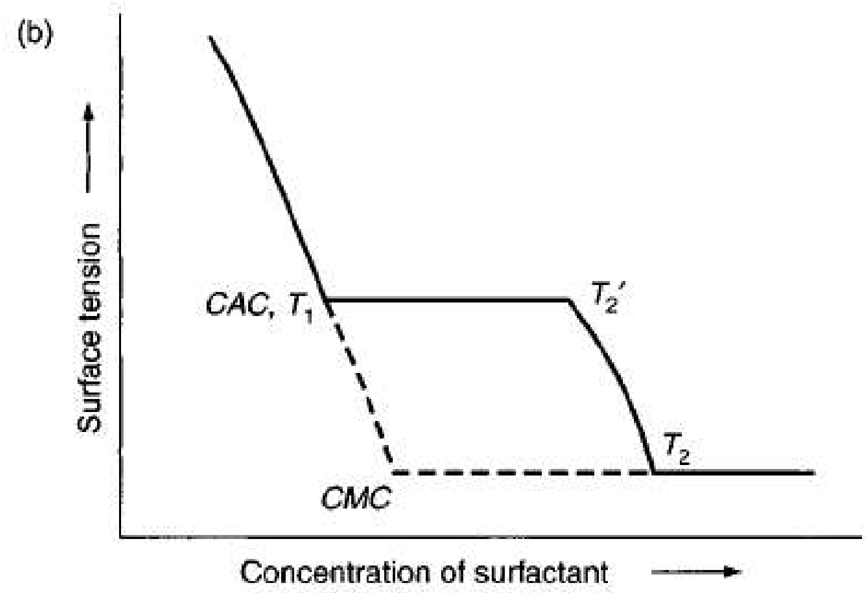
- Calorimetric Measurements
- Nuclear Magnetic Resonance (NMR)
- Flourescence
- Conductivity
- Gel Permeation Chromatography (GPC)
- Viscosity Measurements
- FT Infrared Spectroscopy (FTIR)
- Surface Tension Measurements
- Light Scattering Techniques
- Electromotive Force (emf)

Surface Tension Studies

- Surface tension measurements are widely used for studying micellization and surfactant-polymer interaction.
- Adding surfactants reduces surface tension.
- Even in presence of polymers, the surface tension reduction still occur.
- The effect of the polymer depends on the surfactant concentration

Surface Tension Studies

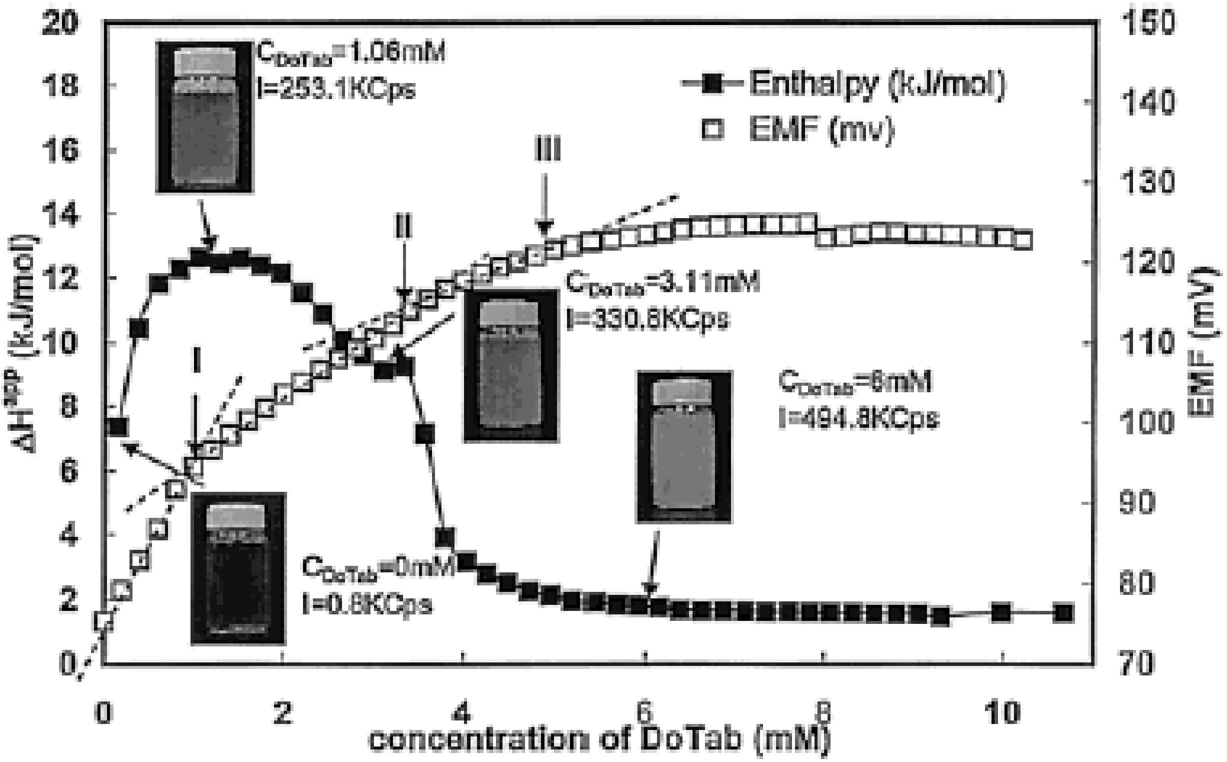




PVP=poly(vinyl pyrrolidone

Surfactant= SDS

Isothermal Titration Calorimetry and EMF



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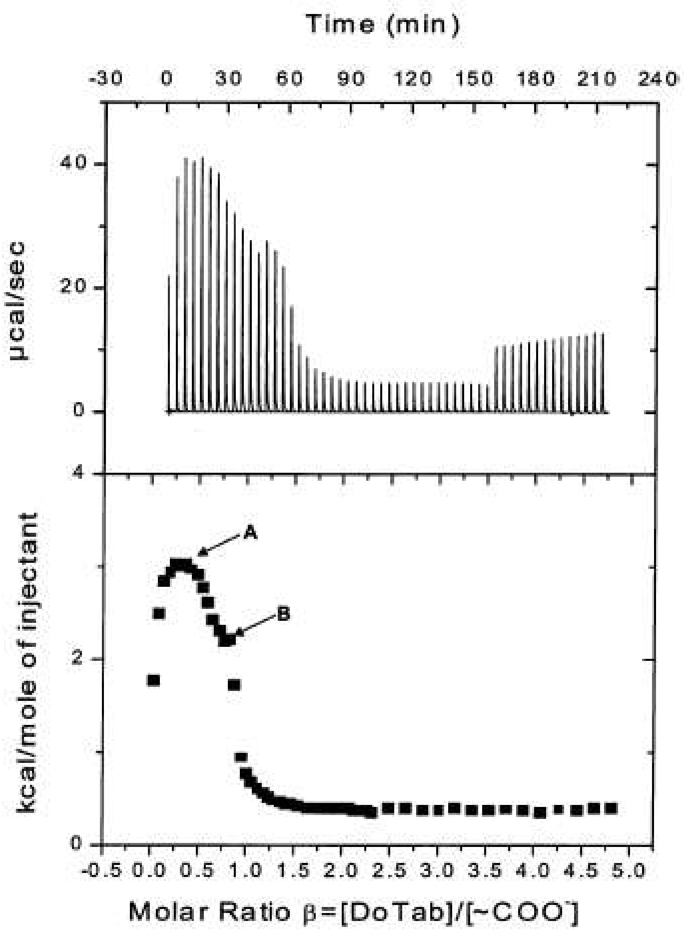
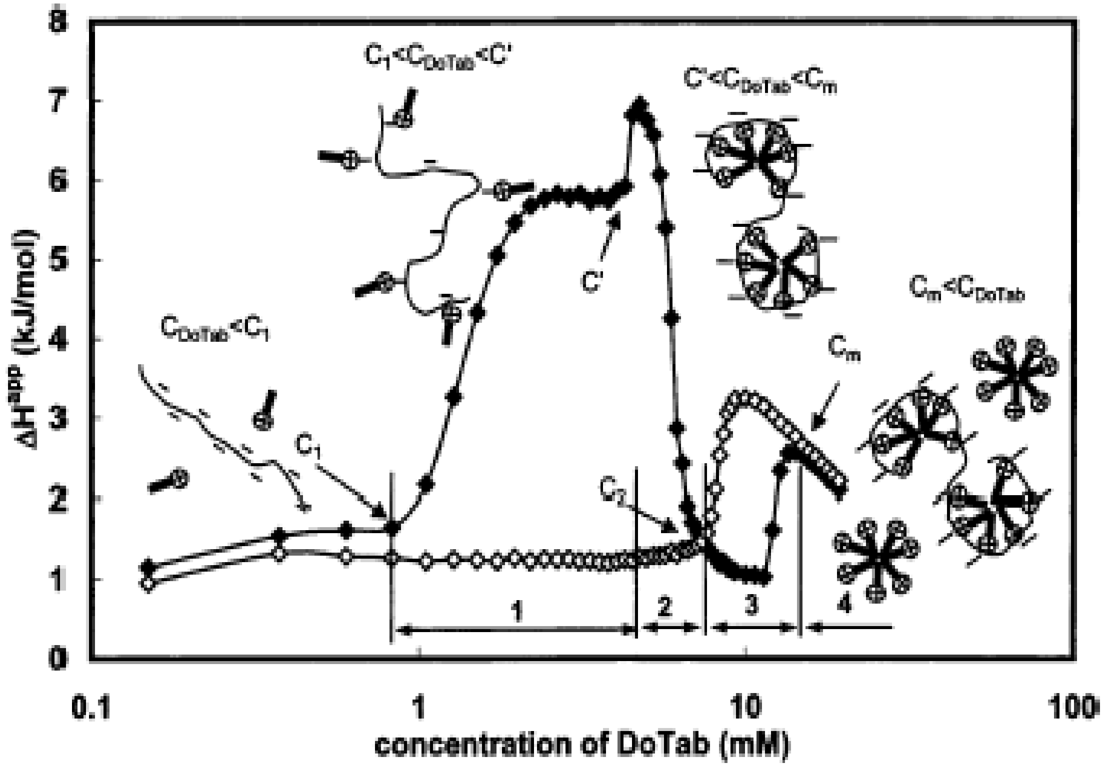
Calorimetric Techniques





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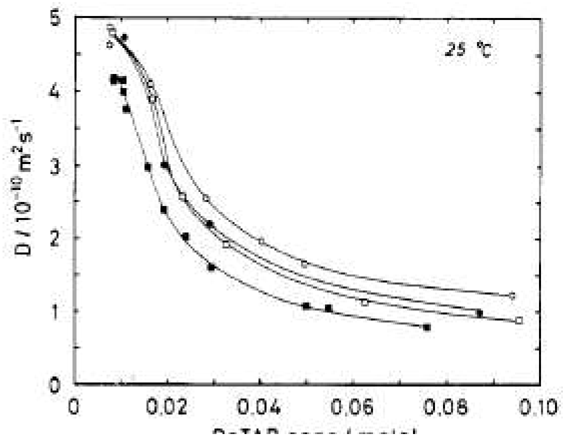
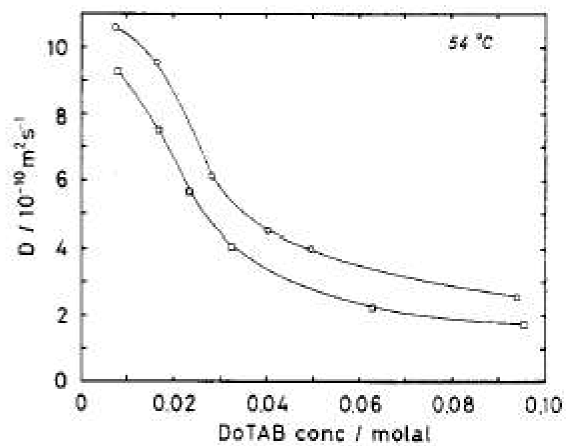
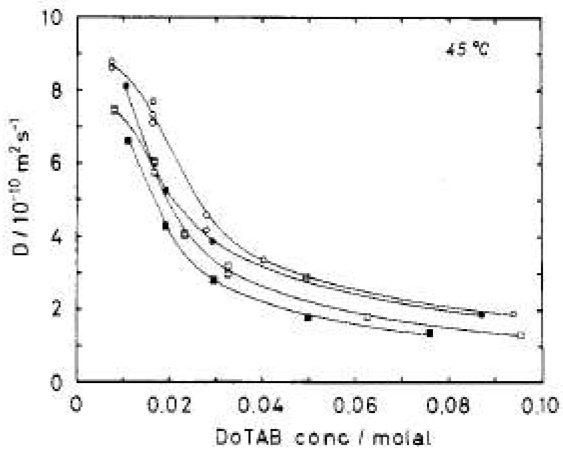
Nuclear Magnetic Resonance

Diffusion Measurements

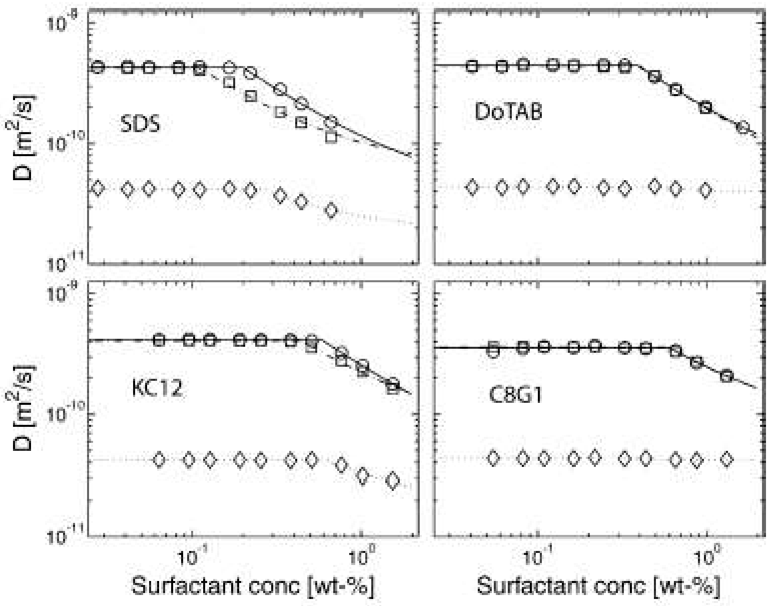


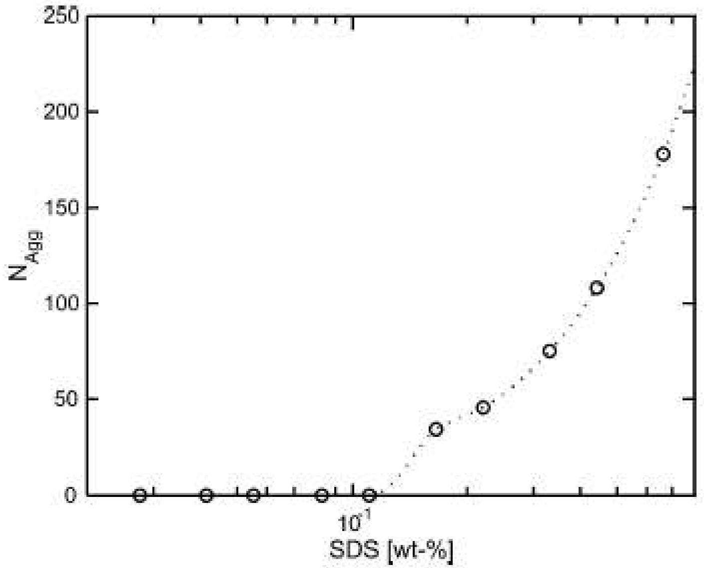




Ref. 6

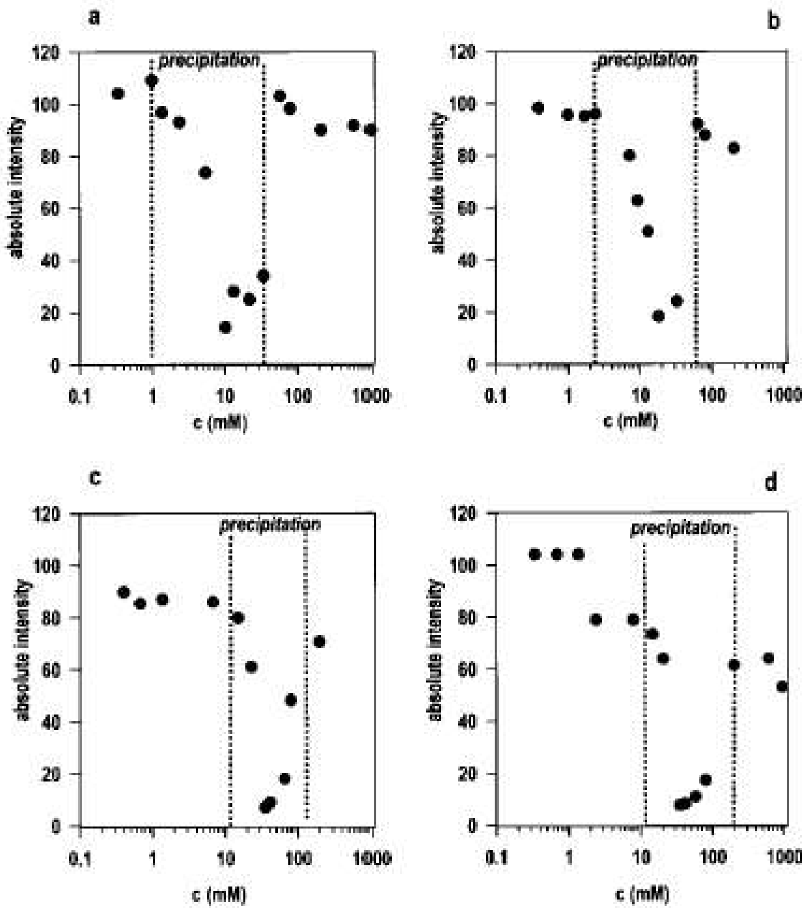
Nuclear Magnetic Resonance Diffusion Measurements





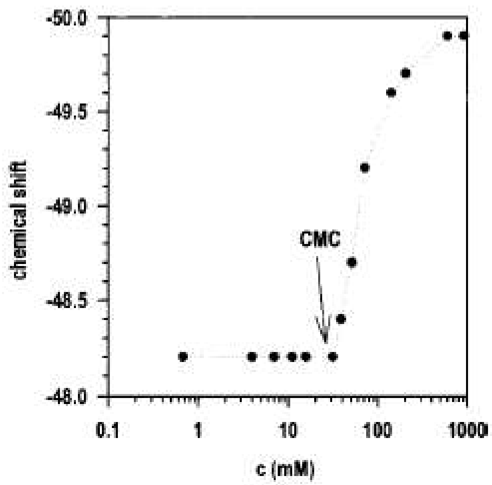
Ref. 9

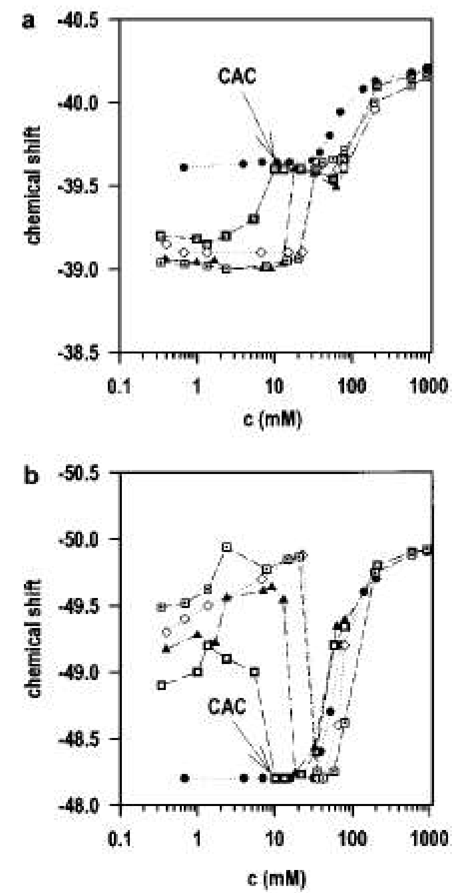
Nuclear Magnetic Resonance
^{1}H-NMR



Nuclear Magnetic Resonance

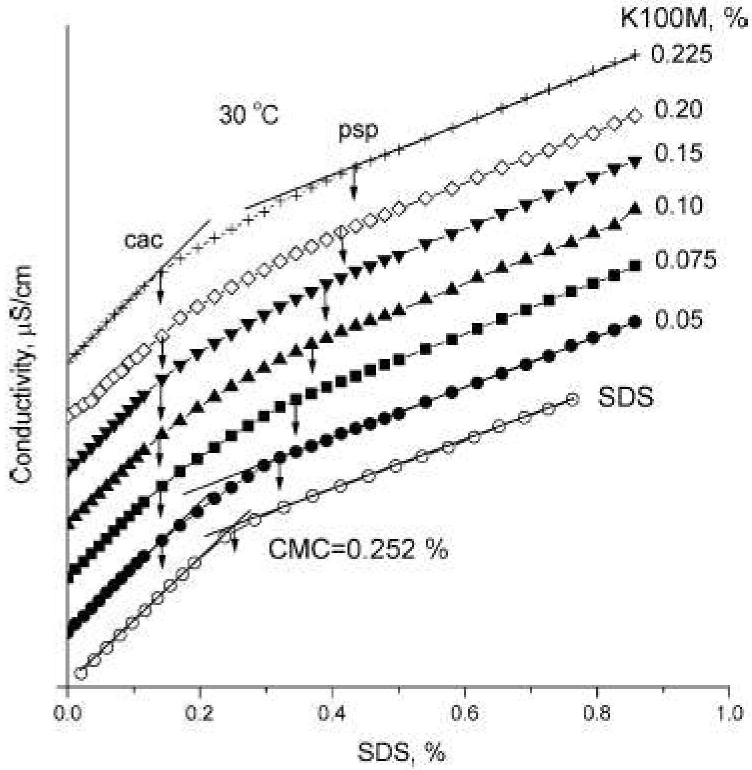
^{19}F-NMR





Ref. 10

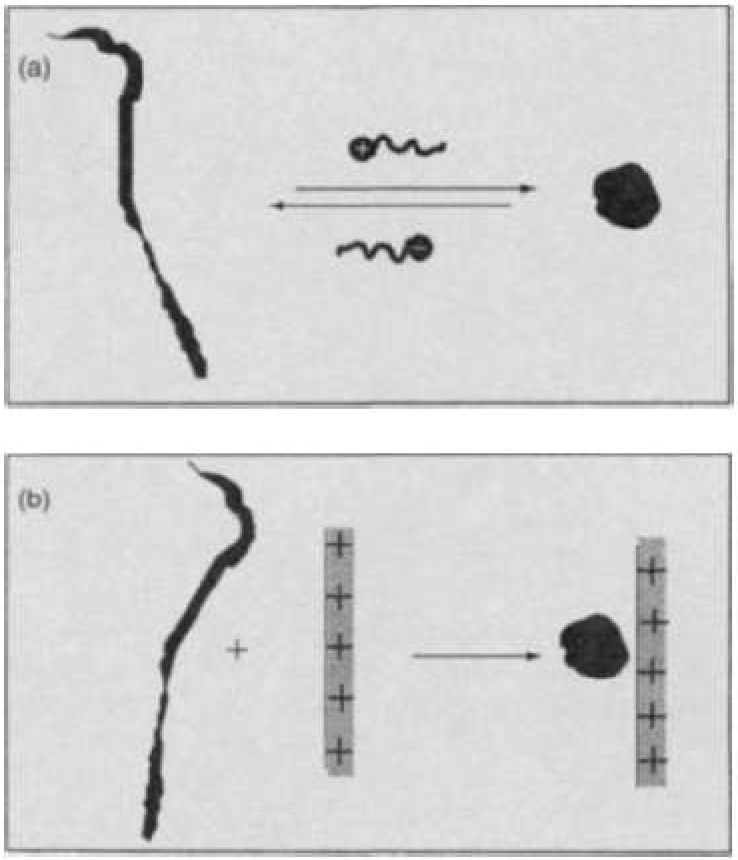
Conductivity Measurements



The effect of adding increasing amounts of surfactant to different concentrations of the polymer (HPMC) on the conductivity in water

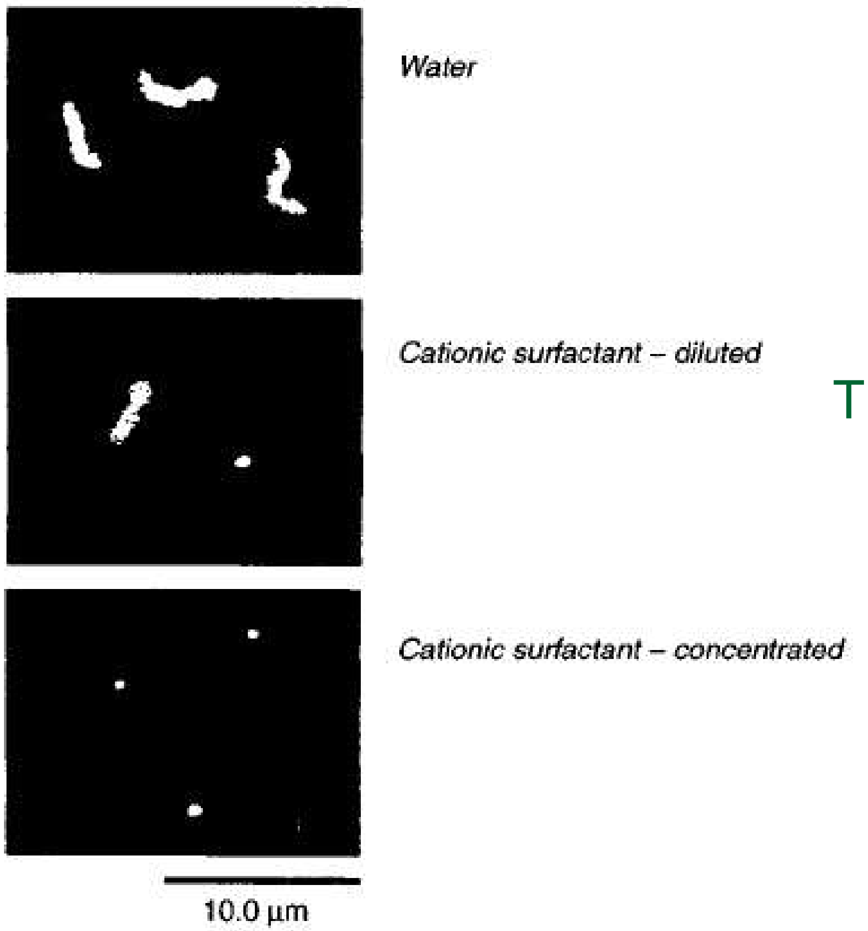
Ref. 11

Case Study #1



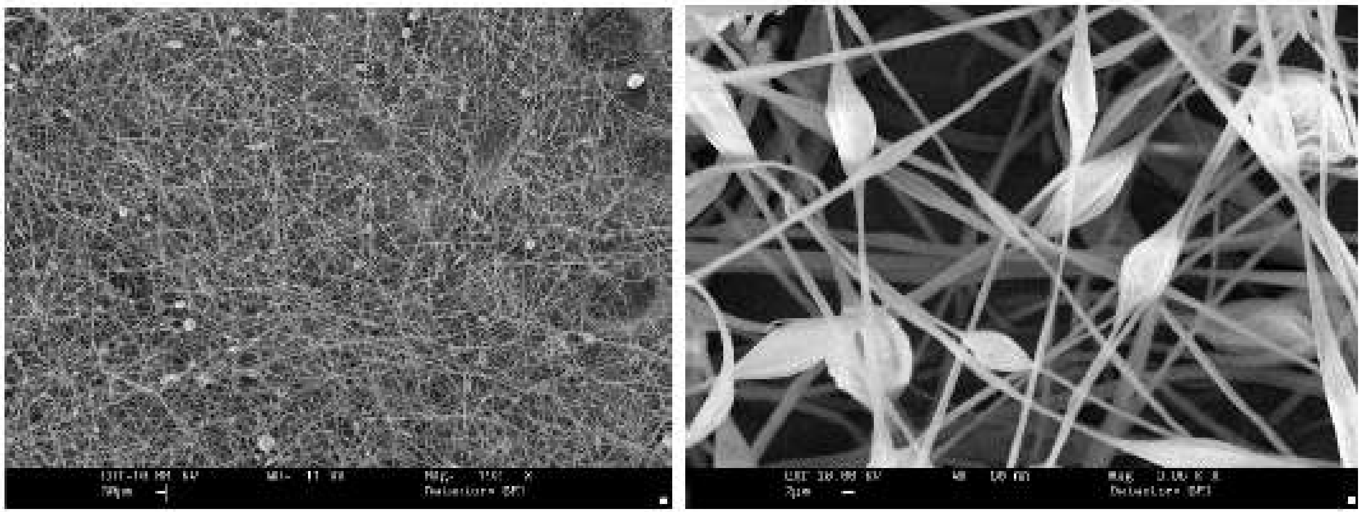
The compaction of DNA due to addition of a cationic surfactant is a reversible process that can be reversed upon the addition of anionic surfactant

Ref. 14



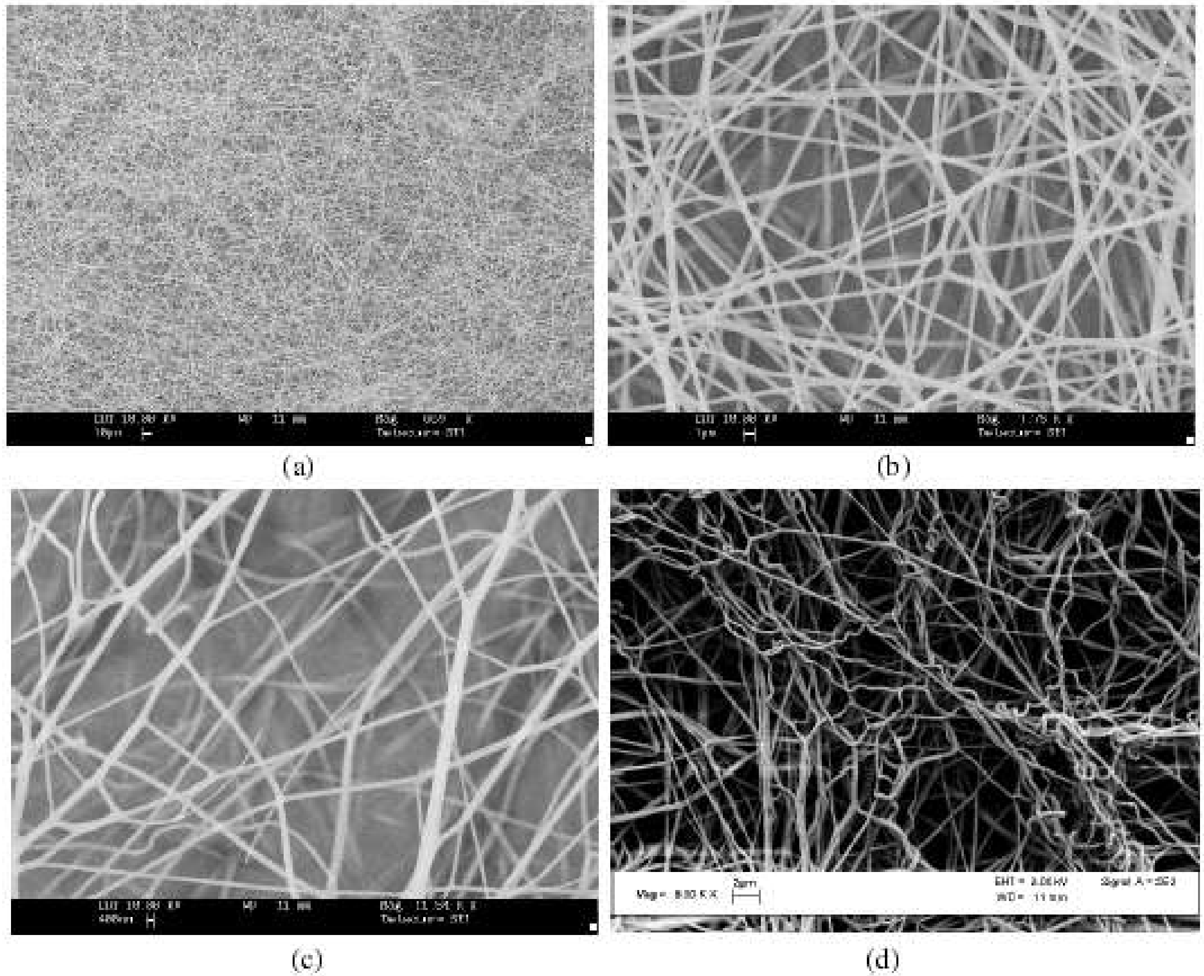
The compaction of DNA due to addition of a cationic surfactant visualized by fluorescence microscopy

Case Study # 2

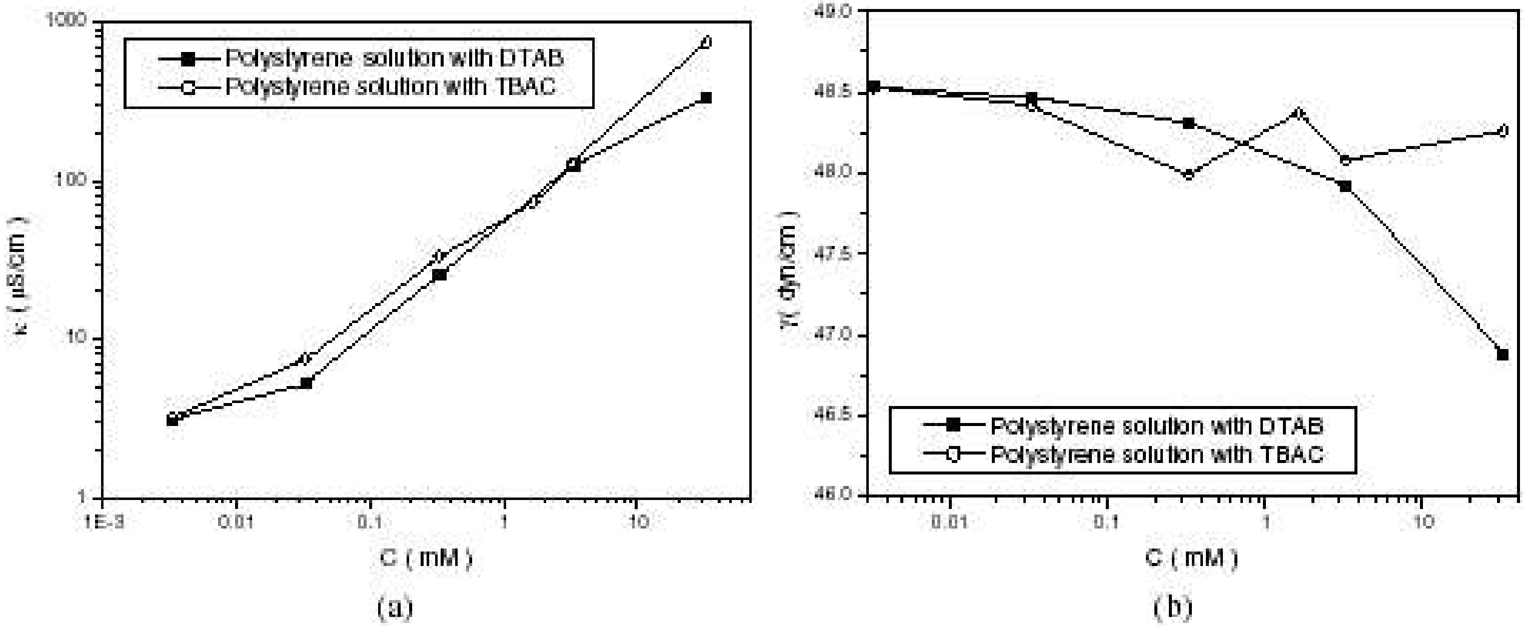


Nanofibers of polystyrene when electrospun from 10% polystyrene solution in a 1:1 (w/v) DMF/THF

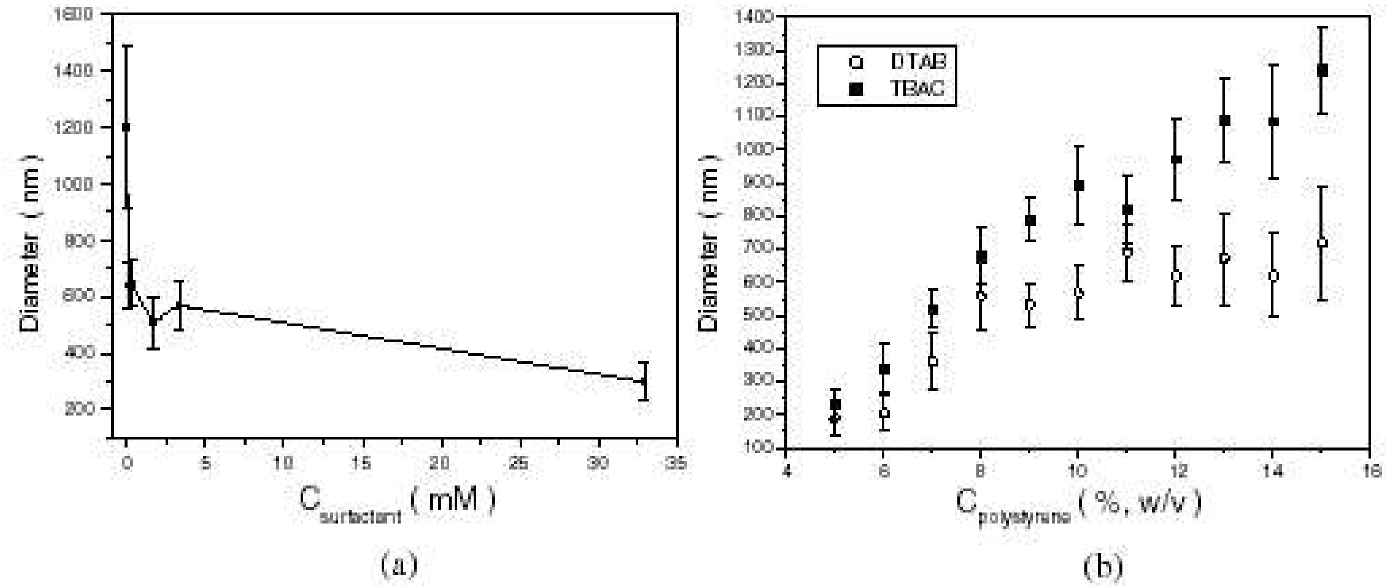
Ref. 12



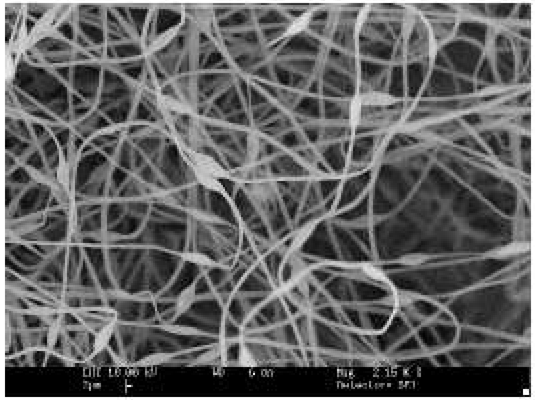
Nanofibers of polystyrenes electrospun in presence of 0.1mM TBAC (a and b), 10mM TBAC (c) and 10mM DTAB



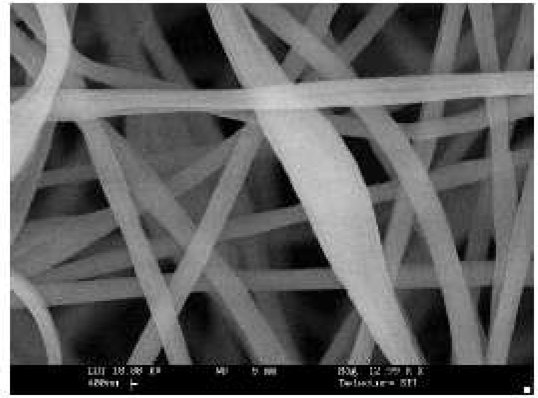
Conductivity (a) and surface tension (b) measurements of polystyrene solutions with and without surfactant.



Average fiber diameter measurements with (a) constant amount of polymer and increasing amounts of surfactant (b) different amounts of polystyrene while keeping polymer/surfactant ratio constant.

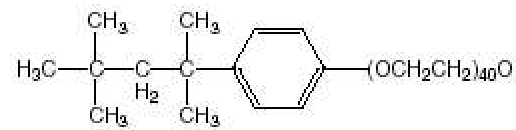


(a)



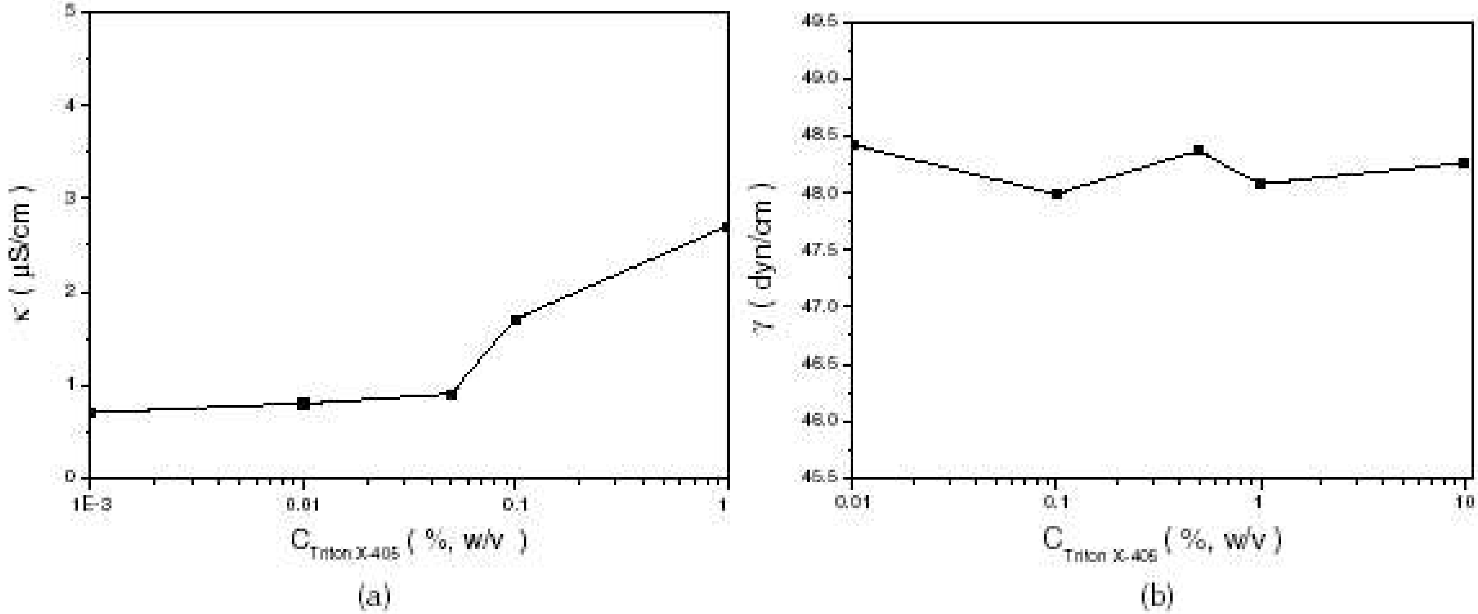
(b)

(c)



Triton x-405

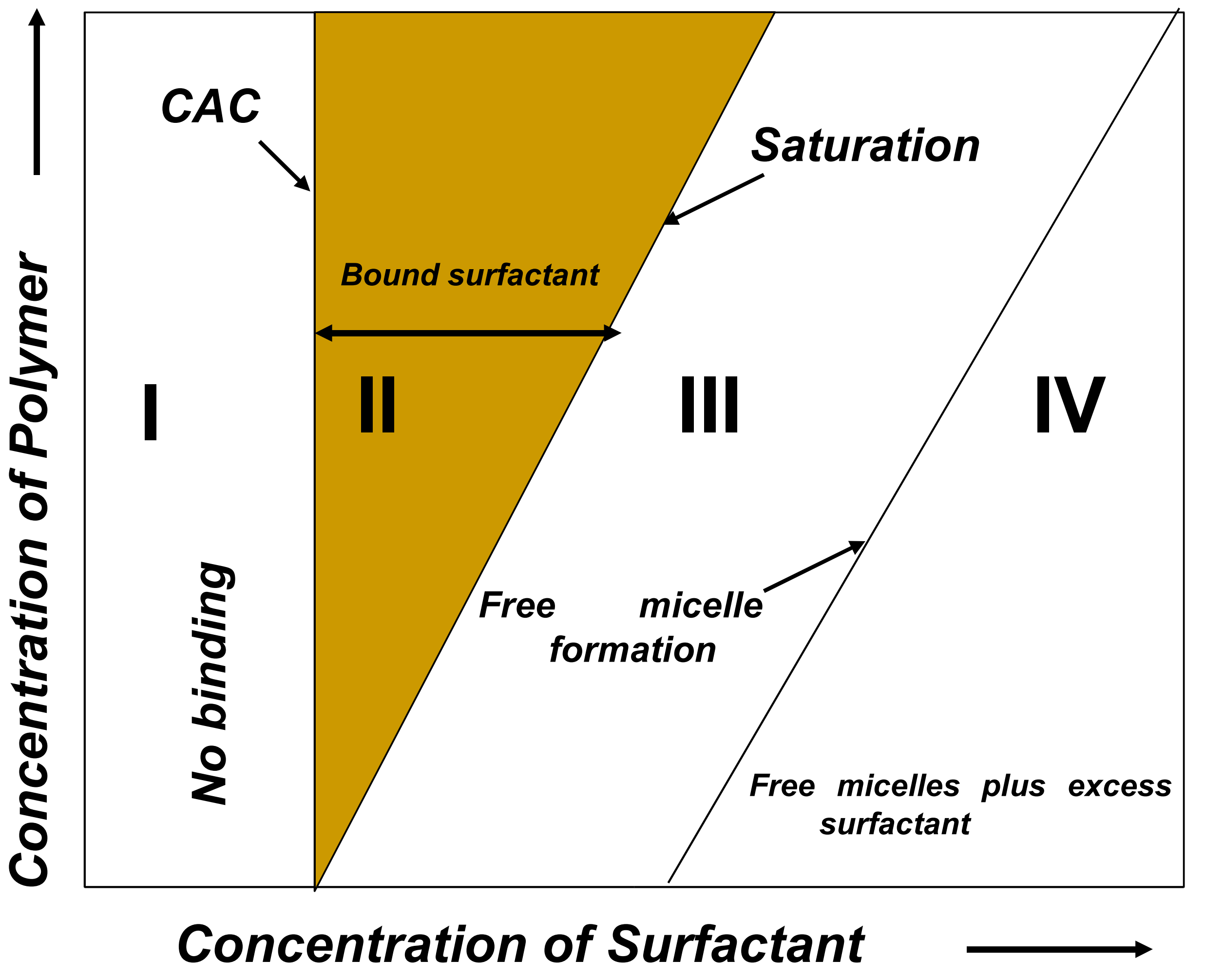
Nanofibers of polystyrenes electrospun in presence of 0.01% (a), 0.1% (b) and 1% (c) of Triton X-405



Conductivity (a) and surface tension (b) measurements of polystyrene solutions with and without Triton X-405.

Conclusions

- As a general trend, the presence of polymers reduces the cmc concentration for the surfactant especially if the polymer has an opposite charge compared to the surfactant.
- The combination of surfactant and polymers improve the desired properties of the product (surfactants are usually added to control the dispersions, flocculation and wetting properties of suspensions while polymers are main added to meet rheological requirements).
- The surfactant-polymer interaction can range from very strong interaction to no interaction at all.
- Usually the same methods used to study micellization, dispersions and surfactant behavior are utilized successfully for surfactant-polymer interaction studies.


CAC
Saturation
Bound surfactant
I
II
III
IV
No binding
Free micelle formation
Free micelles plus excess surfactant
Concentration of Polymer
Concentration of Surfactant

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Thank You…..

QUESTIONS ?