Polymer-Surfactant Interaction

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Contents

- Introduction
  - Surfactants
  - Polymers
- Polymer-Surfactant Interaction and its Effects
- Importance of these Interactions
- Methods Used to study Polymer-Surfactant Interaction
- Conclusions
- References
Surfactants (Surface Active Agents) are amphipathic molecules (have a hydrophilic part and a hydrophobic part).

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

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

\[ \text{OH} \]
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).
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.
Polymers Classification

- **Homopolymers**
  (Polypropylene)
- **Copolymers, could be**
  - Alternating
  \[ A-B-A-B-A-B-A-B-A-B \quad = \quad -(AB)_n- \]
  - Random
  - Block copolymer
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

- surfactant only
- mixture
- surface tension of H₂O
- surface tension of polymer solution

- onset of micelle formation on the polymer (CAC)
- critical micelle concentration (CMC)
- log(concentration of surfactant)
- polymer saturated with micelles
- surfactant micelle formation
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.

Ref. 13
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
The specific viscosity of 0.01M PAA with different degrees of neutralization, $\alpha$, 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>
<thead>
<tr>
<th>Surfactant</th>
<th>Polymer</th>
<th>T (°C)</th>
<th>cmc or cac (mM)</th>
<th>cac/cmc</th>
<th>C_2 (mM)</th>
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<td>SDS</td>
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<td>25</td>
<td>8.0^a</td>
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<td>25</td>
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Techniques Used to Study Polymer-Surfactant Interactions

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

- Calorimetric Measurements
- Nuclear Magnetic Resonance (NMR)
- Fluorescence
- 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

Ref.4
Calorimetric Techniques

Ref.4
Nuclear Magnetic Resonance Diffusion Measurements

Ref. 6
Nuclear Magnetic Resonance Diffusion Measurements
Nuclear Magnetic Resonance
$^1$H-NMR
Nuclear Magnetic Resonance

$^{19}\text{F-NMR}$

Ref. 10
Conductivity Measurements

The effect of adding increasing amounts of surfactant to different concentrations of the polymer (HPMC) on the conductivity in water.
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.
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.
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.
Polymer-Surfactant Interaction

Concentration of Polymer

Concentration of Surfactant

I

II

III

IV

No binding

Bound surfactant

Free micelle formation

Free micelles plus excess surfactant

CAC

Saturation
References


References (cont.)


References (cont.)


 Thank You.....

QUESTIONS ?