

**SURFACTANT/POLYMER INTERACTIONS WITH SOLIDS: applications in flocculation/dispersion, flotation, coatings, nanocomposites and biomaterials**

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**Outline**

- \* Importance of conformation/orientation of surfactants, polymers and their mixtures**
- \* Techniques used to monitor adsorption/conformation and flocculation/dispersion**
- \* Conformation of surfactant adsorbed layer**
- \* Role of structures in surfactant adsorption**
- \* Polymer adsorption/conformation**
- \* Flocculation with dispersants at low dosage and double flocculants**
- \* Hydrophobically modified polymers**
- \* Deposition under difficult conditions**
- \* Nanocomposites and biomaterials**

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## **Extended Abstract**

### **Introduction**

Polymers, surfactants and their mixtures are widely used in many important industrial processes such as dispersion/flocculation, selective flocculation, flotation, rheological control, deposition/coating, detergency, oil recovery and materials processing in general. In these processes, interfacial behavior of particulates is determined by the adsorption of polymers/surfactants and, equally importantly, by the nature of micro- and nano-structures of the adsorbed layers. Monitoring and controlling of the adsorption, particularly conformation, orientation and association of adsorbed species, can improve the efficiency of these processes and enable design of new processing schemes and reagents.

Our efforts to explore and control the adsorbed layer depend on a multi-pronged approach involving the use of fluorescence, ESR, NMR, CT Scan, SPR, QCM and AFM techniques, along with conventional techniques to measure flocculation, surface potential and hydrophobicity. Results obtained using these techniques will be discussed along with possible new applications.

### **Surfactant Adsorption**

Adsorption can be considered as selective partitioning of the reagents into the interfacial region, resulting from the more energetically favorable interactions between the adsorbate and the solid than those between the former and the species in the bulk solution. Interactions leading to adsorption include chemical bonding, electrostatic interaction, desolvation of the surfactant polar group and the mineral surface species, hydrogen bonding, van de Waals interactions, etc. By changing the nature of solid surface, solution conditions or structure of the surfactants/polymers,

adsorption as well as conformation of the adsorbed layer can be controlled. Manipulation of the adsorbed layers for desired performance will be discussed in this talk.

In surfactant systems, in addition to solid-surfactant interactions, surfactant has the tendency to form two dimensional aggregates called solloids (surface colloids) or hemi-micelles due to the association of surfactant hydrophobic chains. This self association not only increases the adsorption, but also changes the conformation of the adsorption layer and consequently the interfacial processes involved.

The adsorbed layer can be affected by the structural modification of the surfactants such as chain length variation, branching, aryl, alkyl and ethoxyl additions. Even the position of the functional groups on the aromatic ring of a xylene sulfonate was found to measurably affect their adsorption. Changes in the nature of the functional group also affect the adsorption; for example, sugar-based nonionic surfactants show unexpected selective adsorption behavior, opposite to that shown by nonionic ethoxylated surfactants. These surfactants are particularly attractive since they are environmentally benign. Another way to change adsorption/conformation is by adding a second surfactant. The synergistic or competitive effects between two surfactants can drastically affect the adsorption process. Since mixtures of surfactants are widely used commercially, the behavior of mixtures on the adsorption/conformation have practical implications.

### Polymer Adsorption

Polymers are also used in mineral and material processing and their conformation can be manipulated by changing solutions conditions such as pH, addition of a second polymer or surfactant, by polymer hydrophobization or even by the order of addition. Such manipulation can lead to flocculation or dispersion even at the SAME adsorption density. Even the so called low

molecular weight dispersants can act as good flocculants under appropriate dosage conditions

Hydrophobic modification of polymers have the powerful ability to impart controllable surface activity to polymers. Such combination of polymers and surfactants may yield useful properties not exhibited by either individual component. For example, these polymers can be used to obtain flocculation or dispersion in aqueous or non-aqueous systems of hydrophobic or hydrophilic solids!

There are many approaches to control the polymer conformation. For example, pH shift of a suspension can change coiling of the adsorbed polymer to yield better flocculation or dispersion.

#### Deposition and Nanocomposite

It was recently observed that deposition of particles can be achieved even under unfavorable conditions by incorporating appropriate tethers (hairs) on the particles. We propose such deposition to be due to reformation of the hairs on the particle with the complimentary groups reaching out to tether and the antagonistic ones retracting. AFM experiments show that the zwitterionic particles of net negative charge to exhibit attraction as they are brought close to a negative glass surface while anionic particles of the same negative potential experience only repulsion

Control of the adsorption and conformation of polymers and their mixtures have important future applications in many processes. Thus a layer-by-layer deposition process has been developed to prepare core-shell nanocomposite particles using controlled polymer adsorption. Ceramics constituted by such nanosize granules show enhanced properties in various applications. Submicron size alumina particles chosen as starting core particles are first dispersed in this process by pH control and then modified by adsorption of anionic polyacrylic acid to facilitate subsequent deposition of nanoparticles on them. A key step in the processing involved removal of excess

polymer in the supernatant after the adsorption by controlled washing so that the added nanoparticles do not self flocculate among themselves. Coating of nanosize particles was indicated by the charge reversal of the micronsize composite particles. The isoelectric point of the composite particle was found to be close to that of nanosize particles under both low and high coverage conditions. Scanning electron microscopic observation of coated particles showed full monolayer coverage of nanoparticles on core particles confirming the efficiency of the coating scheme discussed here. The compacts prepared using this technique exhibited improved flexibility and green density. This work revealed the feasibility of coating nanoparticles onto micronsize core particles using controlled polymer bridging for preparation of multilayer nanocomposite powders.

Other applications will be illustrated with examples from the biomaterials area.

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### NSF Industry/University Cooperative Research Center for Advanced Studies in Novel Surfactants

#### Research Areas:

- Surfactants and Polymers for Colloidal Processes (Dispersion/Flocculation).
- Environmentally Benign Surfactants.
- Surface Active Agents' Interaction with Microbes and Biosurfaces.
- Characterization of Novel Surface Active Reagents and Adsorbed Layers: Advanced Spectroscopy for micro- and nano-adsorbed layers.
- Surfactant and Polymer Aided Electrodeposition, Corrosion Control, Crystallization and Polymerization.

#### Faculty:

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#### Sponsors:

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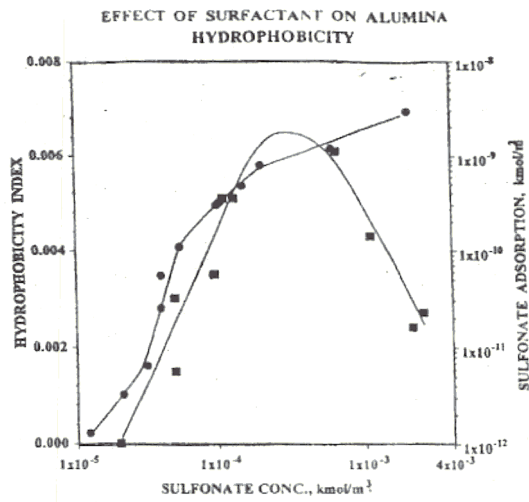


#### CENTER OBJECTIVES

- Elucidate mechanisms of interfacial effects as a function of STRUCTURE of surfactants and polymers for various solids and media. → Structure-property relationships.
- Modify surface active agents with functional groups to enhance and control behavior.
- Design more efficient agents for optimum performance.
- Devise processing schemes for desired product properties.
- Investigate and develop environmentally benign surfactants.
- Better commercial products and processes.

## **Introduction**

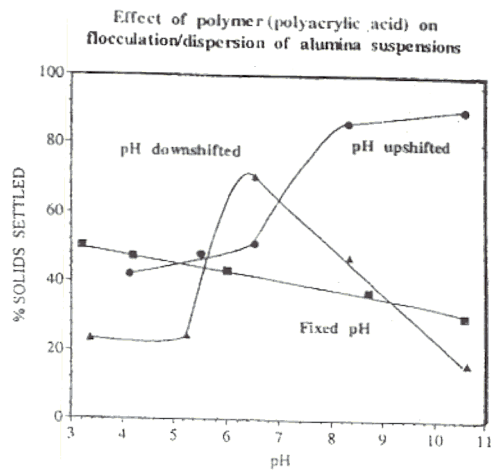
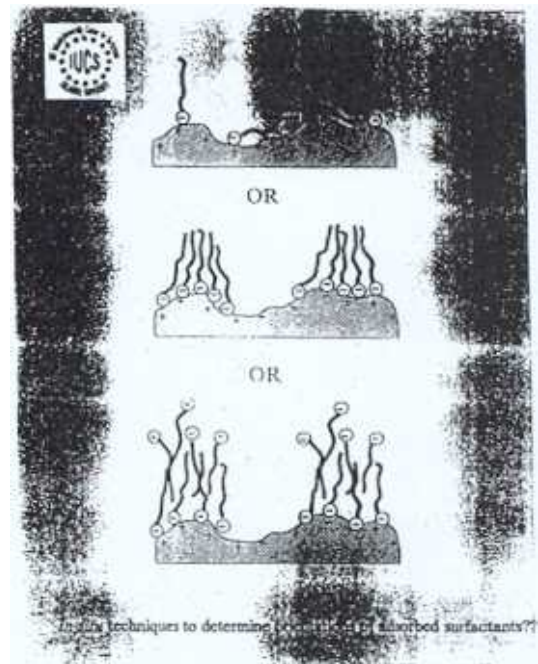
# **The importance of configuration of adsorbed species**



Particles become hydrophobic with sulfonate addition, but hydrophobicity **DECREASES** at higher concentrations.

Surfactant adsorption increases over the entire range, so why did the hydrophobicity decrease.

Orientation of the adsorbed molecules ???



Complete adsorption of polymer added (20 ppm).

Suspensions are either flocculated or dispersed for similar adsorption densities.

Role of polymer conformation at the solid-liquid interface??

**Which polymer conformation is better for aggregation, dispersion, adhesion and deposition?**

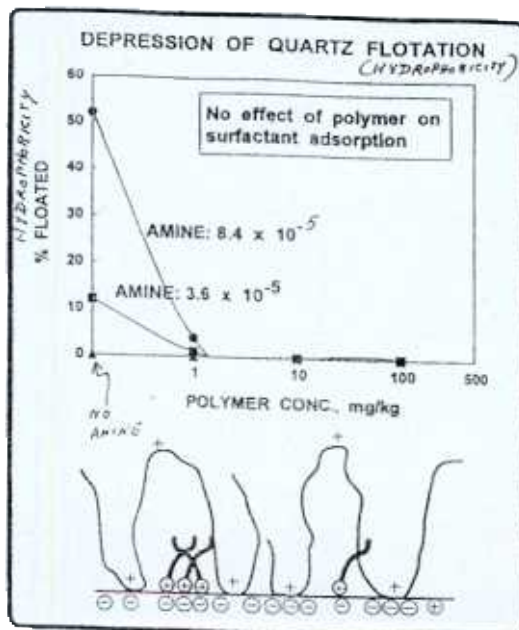


The performance of a polymer depends not only upon its adsorption density but also on its conformation and orientation at the interface.

**Problem:**

**Lack of *in-situ* techniques to determine**

- the conformation and orientation at solid/liquid interface.
- changes in them
- dynamics involved



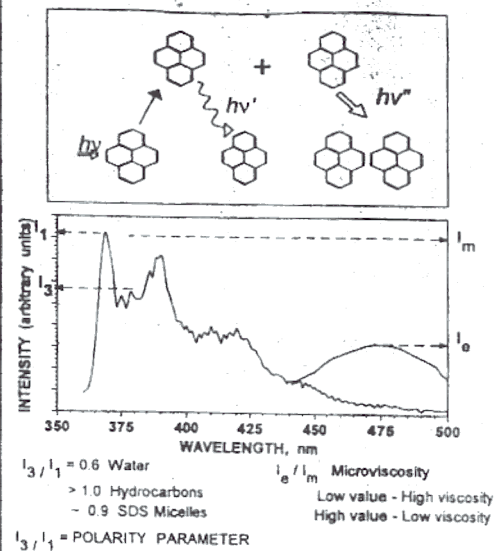


# Techniques

## IN-SITU VERSUS EX-SITU TECHNIQUES

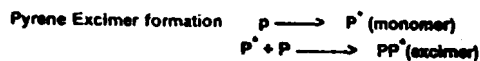
EX-SITU	ESCA, AUGER, etc. (High vacuum; irreversible processes)
IN-SITU	
<u>BULK METHODS</u>	Adsorption density Zeta potential Hydrophobicity Wettability, etc. <b>FLOCCULATION CAT SCAN</b>
<u>SPECTROSCOPIC METHODS</u>	OPTICAL UV/VIS IR RAMAN LUMINESCENCE  MAGNETIC NMR ESR

## PYRENE FLUORESCENCE



## Method

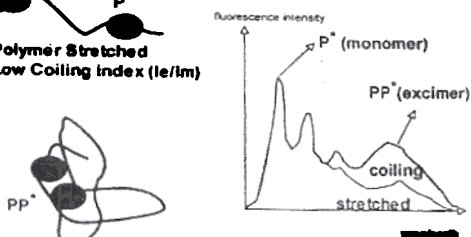
### Probing conformational behavior of polymers using pyrene labeled Polymers



**Polymer Stretched**  
Low Coiling Index ( $I_3/I_1$ )



**Polymer Coiled**  
High Coiling Index ( $I_3/I_1$ )



Flocculation/dispersion Turro

### Electron Spin Resonance (ESR) micro-viscosity & micro-polarity

Typical spectrum of nitroxide in solution



Typical spectrum of nitroxides in a restricted environment, e.g. solid/liquid interface



### FLOCCULATION TESTS:

1. **Supernatant clarity**, in % transmittance, was measured by dipping a Brinkman probe just below the liquid surface.
2. **Settling volume** was read on the graduated cylinder after 12 hours.
2. **Settling rate** was measured by CAT scan. It was taken as the initial slope of the upper interface, determined by CAT scan, as a function of time.
4. **Percent solid settled** was determined either by CAT scan or by suction technique. Using the CAT scan technique, the percent solid settled was calculated by dividing the area below the lower interface by the total area from the plot of solid-concentration profiles measured by CAT scan. Using the suction technique, the percent solid settled was estimated from measurement of the solid content in the lower-half portion after the upper-half suspension was removed by suction.

*Zeta Potential  
Configuration & orientation of Polymers  
Surfactants using fluorescence, ESR,  
TRRRAMAN, NMR, ...*

CAT scan is capable of characterizing sedimentation experiments

CAT scan can be used to characterize the internal structure of a macro-floc without destroying it.



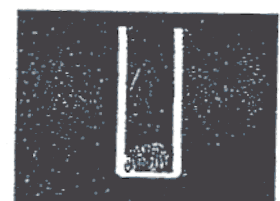
Suspension of sodium kaolinite in water



Single macro-floc produced by adding polycrylamide to a suspension of sodium kaolinite/sodium montmorillonite mixture.



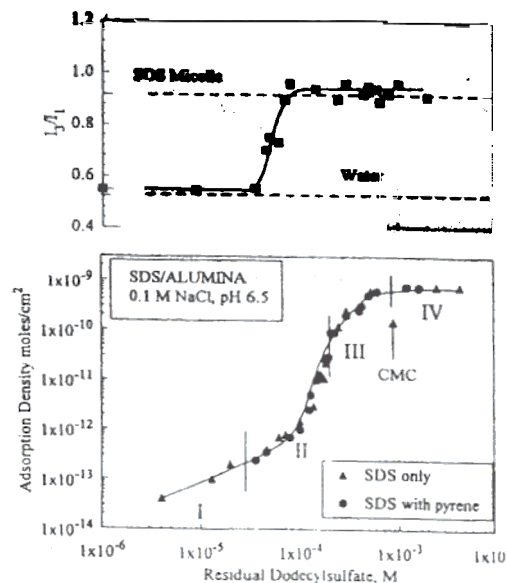
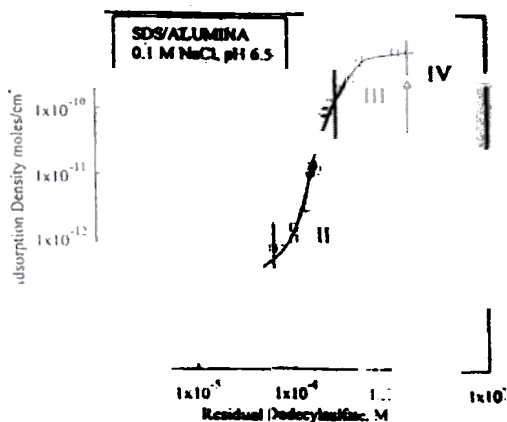
CAT scan image of the kaolinite suspension shown above



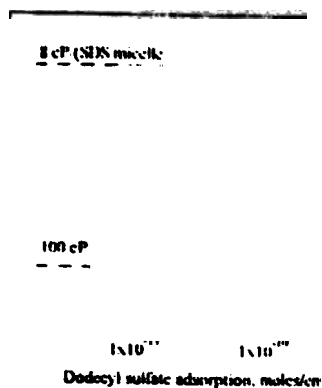
CAT scan of a macro-floc similar to that shown above

# Surfactant Adsorption

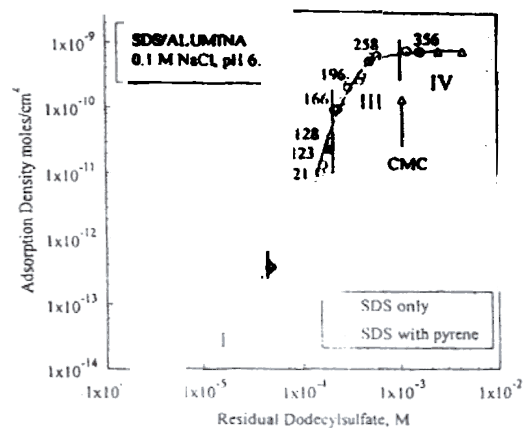
# ADSORPTION OF DODECYSULFATE ON ALUMINA



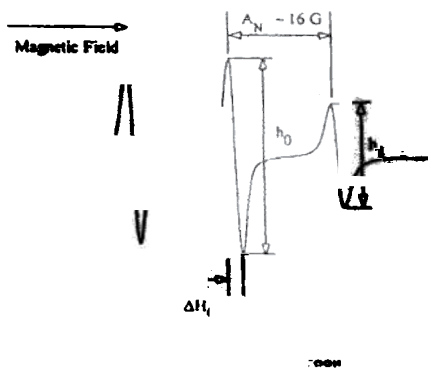
Excimer to monomer ratio ( $I_e/I_m$ ) of dinaphthyl propane (DNP) in SDS-alumina slurries as a function of SDS adsorption density (0.1 M NaCl, pH 6.5)



Surfactant aggregation numbers determined at various adsorption densities



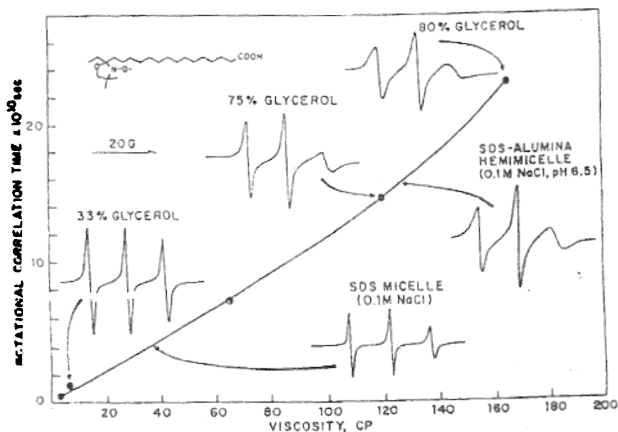
Typical ESR Spectrum of DOXYL Stearic Acid



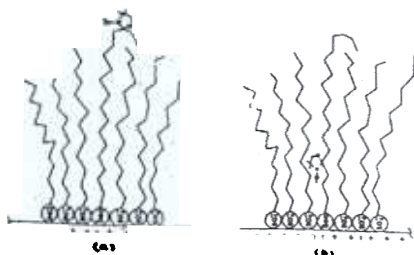
$A_N$ : Environment Polarity  
~ 16 G in Water, ~ 14 G in Hydrocarbon

Rotational Correlation Time: Local Viscosity

6.5 x 10<sup>-10</sup> s



13. Comparison of ESR spectra of 18-doxyl stearic acid in SDS soltoids, micellas and ethanol-glycerol mixtures



15. Schematic representation of surfactant structure showing flexibility of chain segments as reported by nitroxide of doxyl stearic acid in 16<sup>th</sup> position (a) and 5<sup>th</sup> position (b).

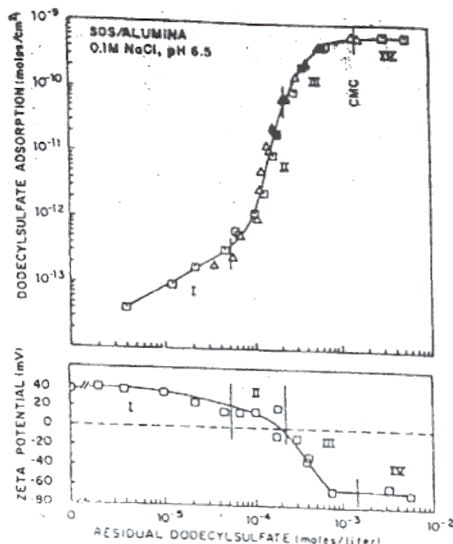
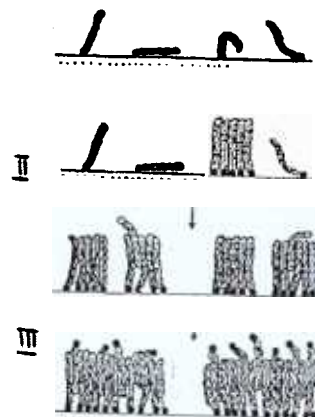
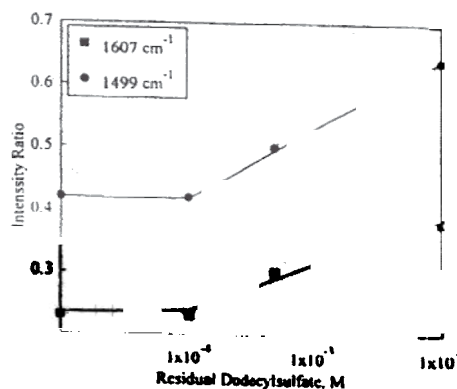


FIG. 1. Adsorption and zeta potential behavior of dodecylsulfate alumina system showing various adsorption regimes (Ref. 23).

Intensity of Raman lines (normalized with respect to 1286  $\text{cm}^{-1}$  line) as a function of SDS adsorption density



**ROLE OF STRUCTURE?**

Typical anionic surfactant - ALKYL SULFONATE

1. Chain length variation:  $\text{---S}$

2. Branching:  $\text{---S}$

3. Aryl addition:  $\text{---S}$

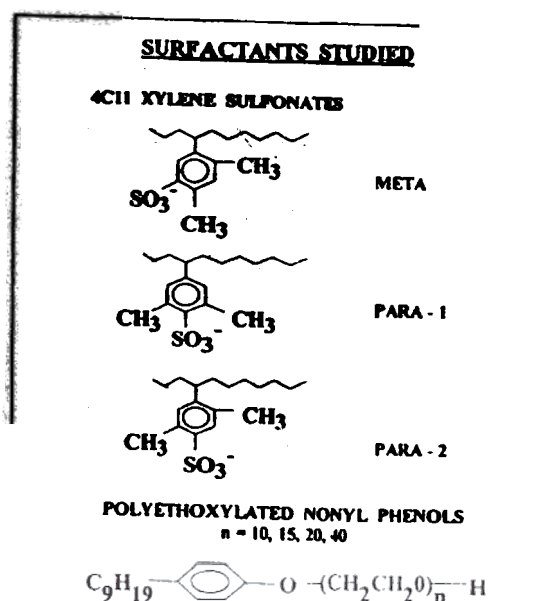
4. Alkyl addition:  $\text{---S}$

5. Ethoxyl addition:  $\text{---S}$

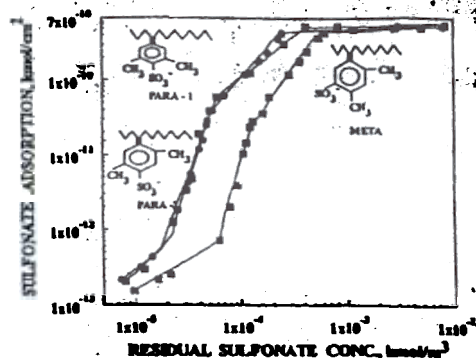
All these variations in structure affect solution and interfacial properties significantly.

Another structural variation is the position of the functional group on the aromatic ring. No systematic work in this area using pure surfactants.

CHELATING GROUPS, SUGAR BASED, NON-IONICS

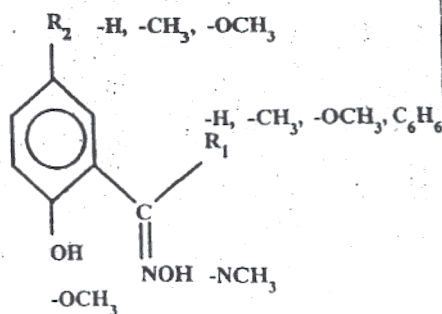


# ADSORPTION OF XYLENE SULFONATES ON ALUMINA Effect of change in position of functional groups



1. Adsorption of META is lower than that of PARA-I.
2. Lower hydrophobicity of the alkyl chain of META - this was confirmed using HPLC.
3. Steric hindrance to packing into hemi-micelles (micelles) due to asymmetry & reduced shielding of sulfonate (anionic sulfonate closer to alkyl chain in META).
4. Higher electronic charge of sulfonate on PARA than on META because of proximity to electron donating methyl groups.
5. Adsorption of the two PARAXYLENE sulfonates is similar.
6. Position of the methyl groups not as important as that of sulfonate groups.

## Salicylaldehyde Structurally related derivatives



## INTRODUCTION

### Features of sugar-based surfactants:

- Made from fatty alcohols and sugar, both are naturally occurring renewable material.
- Lower surface & interfacial tensions effectively.
- Have great tolerance for electrolytes.
- Offer good detergency properties and are mild to skin.
- Easily biodegradable.

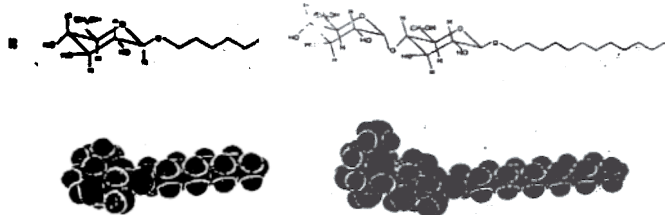
### Potential applications:

- Dispersion, Emulsion.
- Mineral processing.
- Detergents and cosmetic products.

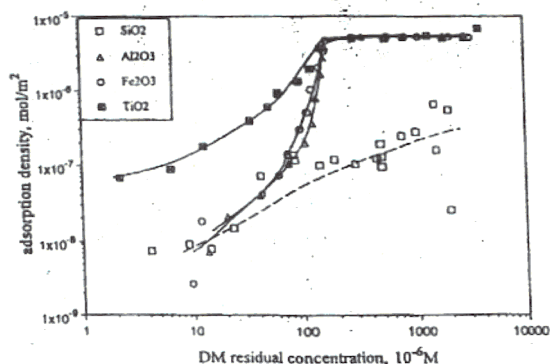
## Chemical Structures and Molecular Models of Typical Sugar-based Surfactants (I)

n-octyl-β-D-glucoside

n-dodecyl-β-D-maltoside



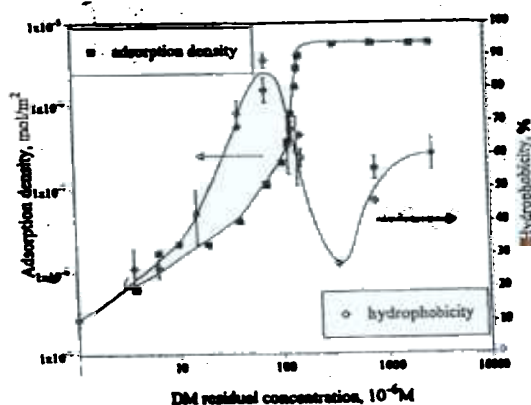
## Adsorption Isotherm of n-Dodecyl-β-D-Maltoside on Various Solids



n-dodecyl-β-D-maltoside can adsorb on basic solids alumina, titania and hematite, but it does not adsorb on acidic solids such as silica. Another nonionic surfactant polyethylene oxide surfactant was reported to show strong adsorption on silica, but not on alumina. The unique adsorption behavior of n-dodecyl-β-D-maltoside may find application in separation processes.

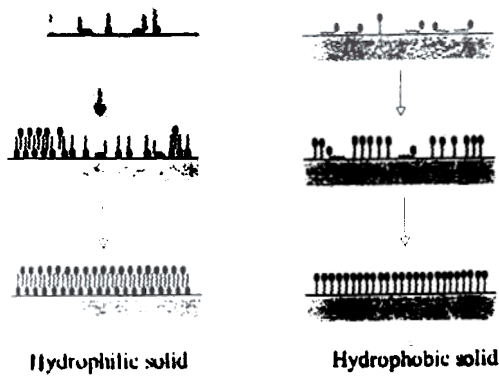
At the maximum adsorption density, the surface area per molecule adsorbed on the alumina surface is more than that required to form a theoretical monolayer and is close to that required for a double layer.

## Hydrophobicity of Alumina Particles After n-Dodecyl-β-D-Maltoside Adsorption



The change of hydrophobicity suggest changes in surfactant orientation at different adsorption stage.

# **Proposed Conformation Model for the Adsorption of n-Dodecyl- $\beta$ -D-Maltoside on Hydrophilic and Hydrophobic Surfaces in Aqueous Media**



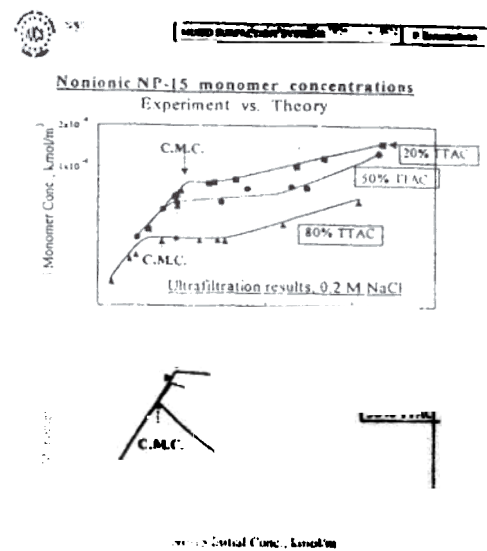
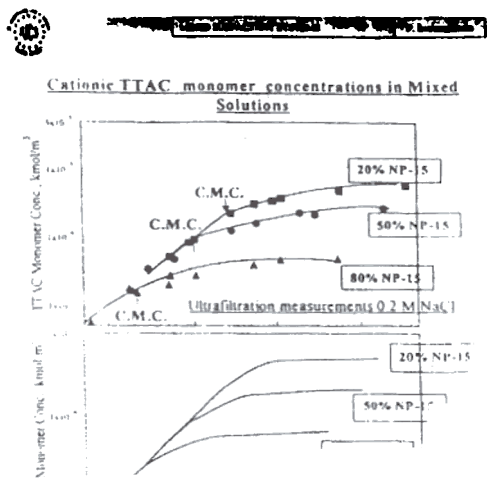
## **Why Surfactant Mixtures ?**

### **Importance of mixed surfactant system:**

Surfactants used commercially are invariably mixtures because of the economics as well as beneficial effects of mixtures over individual surfactants.

New techniques such as ultrafiltration are available for directly measuring monomer concentrations in mixed surfactant systems:

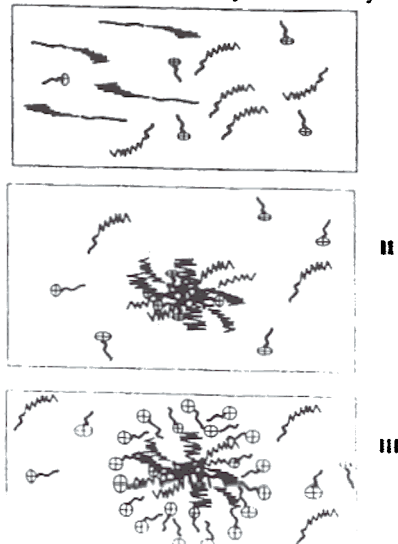
Current models for mixed Surfactant systems are not suitable to predict the behavior of surfactant mixtures



Unlike for cationic TTAC, measured and predicted nonionic monomer concentrations differ significantly. In high concentration range, NP-15 monomer concentrations continuously increases. Regular solution theory not suitable for this system!

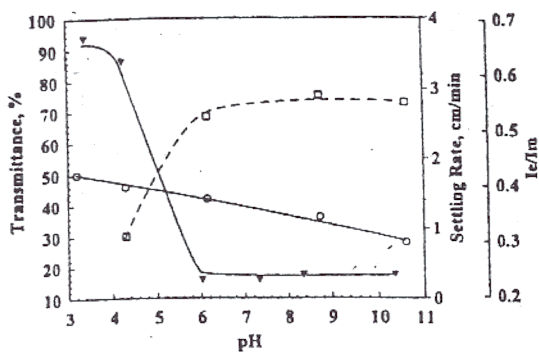
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## **Schematic model for binary surfactant system**

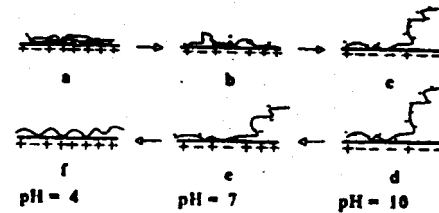
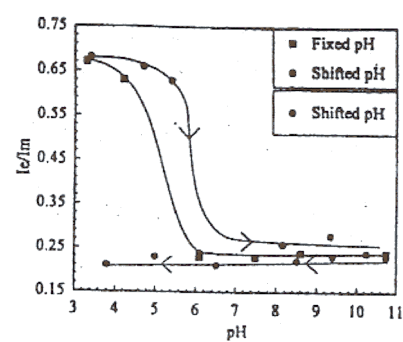


**Polymer Adsorption**  
**flocculation/dispersion**

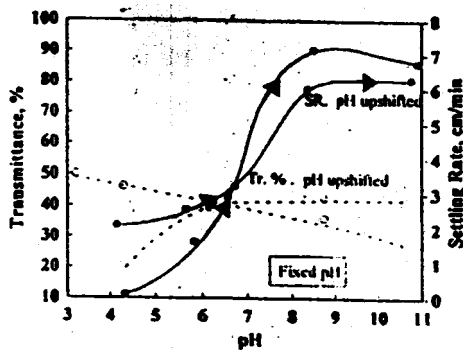




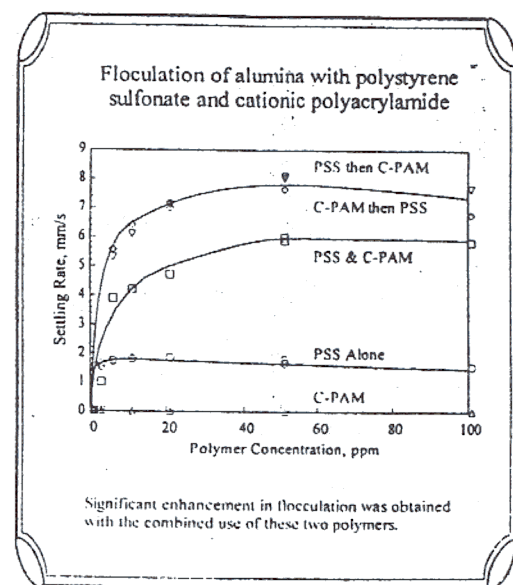
- The polymer stretches out with increase in pH because of the electrostatic repulsion caused by the ionization of carboxylic groups of the polymer.
- The flocculation is better at low pH in terms of clarity of supernatant, suggesting good capture of fine particles by the oppositely charged polymer.
- At high pH, the flocculation is better in terms of settling rate, indicating the stretched polymer provides better bridging effect. (CAT scan image proved that bigger flocs were formed)



Effect of pH on PAA conformation and flocculation responses of alumina suspension with PAA



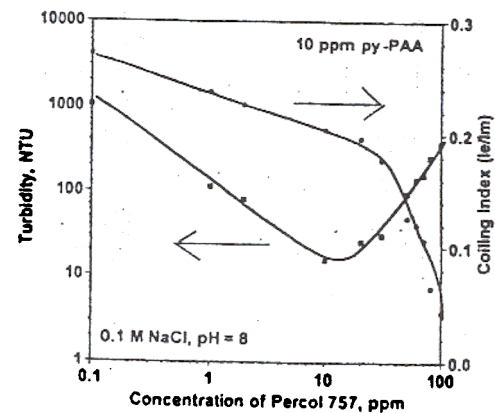
- Flocculation of alumina suspension is significantly enhanced in both terms of supernatant clarity and settling rate.



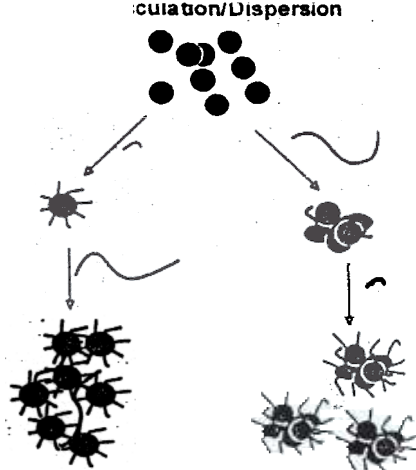
Significant enhancement in flocculation was obtained with the combined use of these two polymers.

### Current Work (supplementary study on polymer conformation)

#### PAA conformational change and flocculation response as a function of Percol concentration

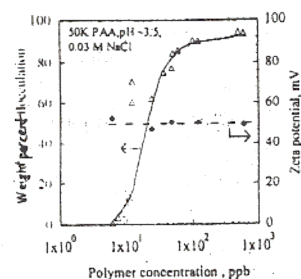


The pre-adsorbed anchor polymer gets stretched with increasing the second larger polymer. Maximum flocculation at intermediate stretching!!



Dual Polymer Flocculation

Dispersion of Micro-flocs

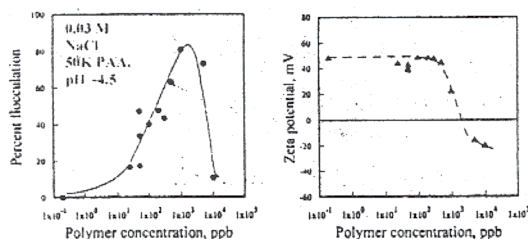


- \* Flocculation of alumina with ultra-low dosage of low molecular weight polymer
- \* Note no change in zeta potential
- \* Mechanism: Charge patch neutralization assisted by bridging

\*\*\* DYNAMICS OF REAGENTS \*\*\*



### Effect of polymer dosage on alumina flocculation at pH ~ 4.5

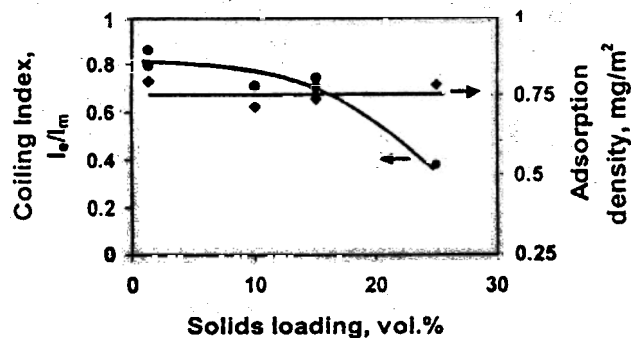


- \* At high concentrations, same polymer causes flocculation
- above 2000 ppb dosage, there is a fall in flocculation
- intra-segmental interaction maximum at pKa
- less segments available for bridging.

- \* Flocculation takes place even at negative zeta potential

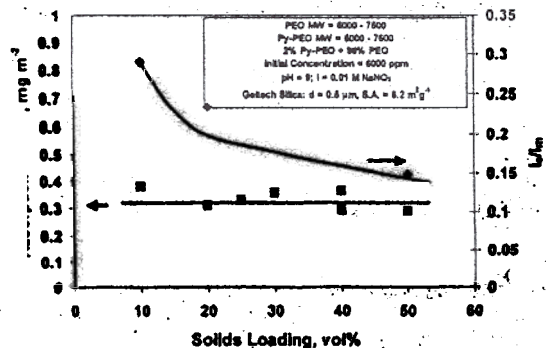
### Effect of Solids Loading on Conformation of PAA Adsorbed on AKP-50 Alumina

(Inl. pH=4, PAA MW=90k, py-PAA MW=76k, py-PAA:PAA=3:97, Temp.=25°C, 0.03 M NaNO<sub>3</sub>)



- \* PAA molecules become more extended as solids loading increases.

### Effects of Solids Loading on Conformation of PEO Adsorbed on Geltech Silica



- \* PEO also becomes stretched with increasing solids loading.
- \* Both findings suggest that polymers adopt a more space-saving conformation due to increased particle crowding.

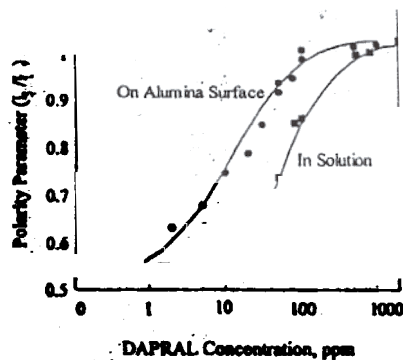
### Aggregation of Hydrophobically Modified and Comb - Like Polymers

C. Maltesh, Qun Xu, K. Sivadasan and P. Somasundaran

Langmuir Center for Colloids and Interfaces  
Columbia University, New York.

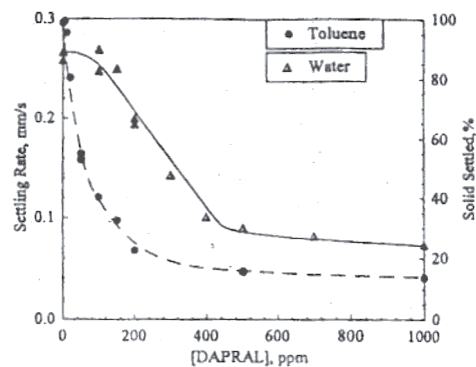
- \* Effect of Hydrophobic Modification of Water-Soluble Polymers on their Solution Behavior
- \* Aggregation behavior of Comb-like Polymers
- \* Interactions of the Modified Polymers with Surfactants and Inorganics





The polarity parameter increases as increase in DAPRAL concentration suggesting polymer molecules associate due to hydrophobic interaction.

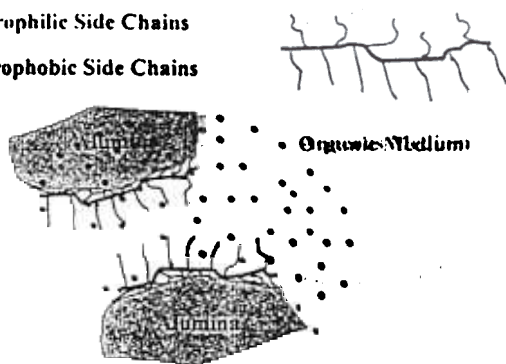
The polymer association starts at a much lower concentration on the alumina surface than in the solution.



Hydrophobically modified polymer, DAPRAL, stabilizes both aqueous and nonaqueous alumina suspensions

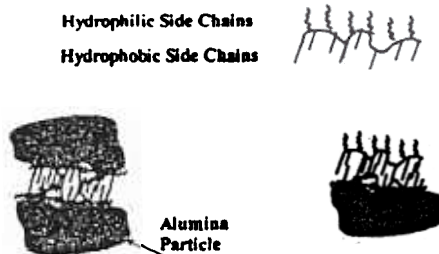
Hydrophilic Side Chains

Hydrophobic Side Chains



Hydrophilic Side Chains

Hydrophobic Side Chains

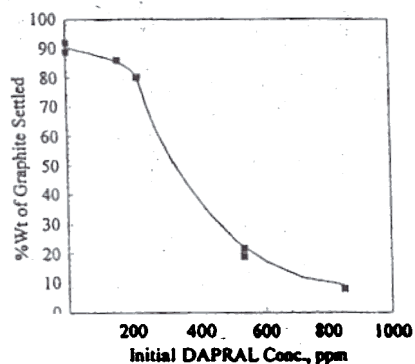


Low DAPRAL Concentration  
Hydrophobic Flocculation &  
Electrostatic Stabilization

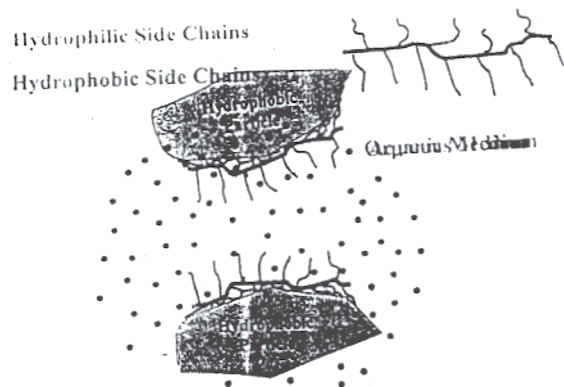
High DAPRAL Concentration  
Electrostatic and Steric  
Stabilization

Influence of DAPRAL on the Stability of Alumina Suspension

EFFECT OF DAPRAL GE202 ON THE  
DISPERSION OF GRAPHITE POWDER IN  
AQUEOUS SYSTEM



DAPRAL Causes Dispersion of Graphite, Like the Anionic/Nonionic Surfactant Mixture



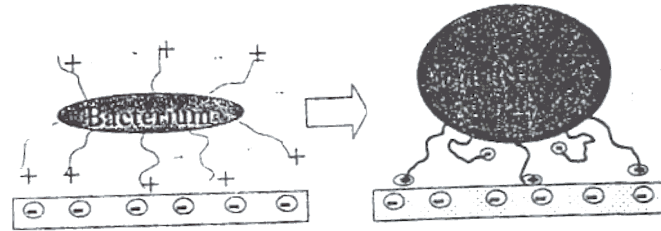
## **Deposition, Nanocomposites, etc**

## A Novel Scheme for Particle Deposition/Detachment under Unfavorable Conditions; Role of Reconformation of Tethers

A. Campbell, J. Adler\*, S. Shrotri, K. P. Ananth and P. Somasundaran

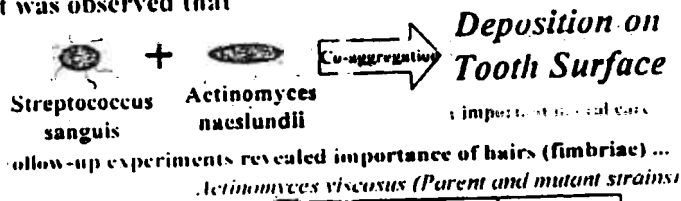
NSF Industry/University Cooperative Center in Novel Surfactants  
Langmuir Center for Colloids and Interfaces, Columbia University  
\*ERC in Particle Science and Technology, UF

Use strategies learned from nature to develop particles capable of facilitating/preventing deposition as desired.



## Motivation

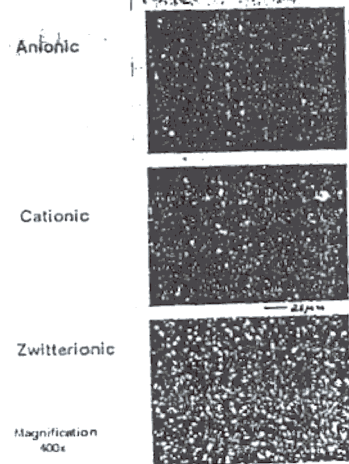
It was observed that



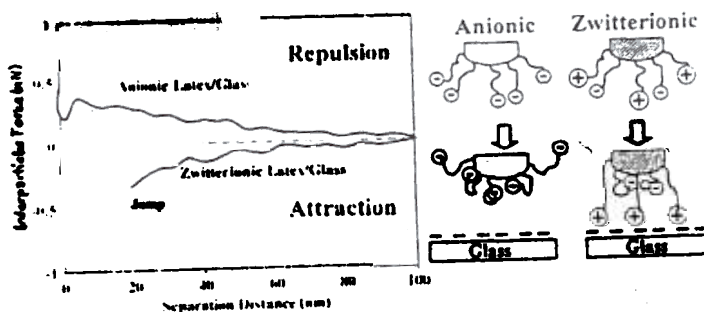
<i>S. sanguis</i>				
Hydroxyapatite				

☺ = aggregation/deposition    ☹ = no interaction

DEPOSITION FROM 250 mM (7%) SDS USING CATIONIC IPBOM POLYMER

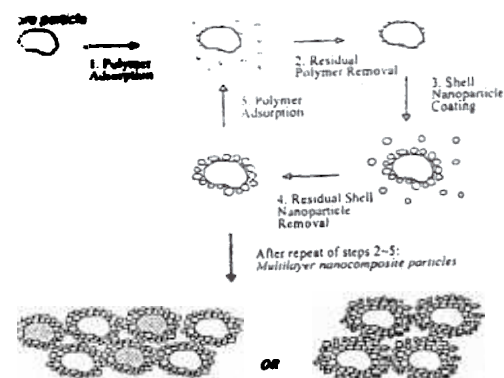


## AFM Measurements of Particle-Surface Interaction



• Note that anionic latex particles (of the same net negative zeta potential) experience only repulsion, whereas the zwitterionic latex particles experience an attraction.

## Preparation Procedure for Multilayer Nanocomposite Particles







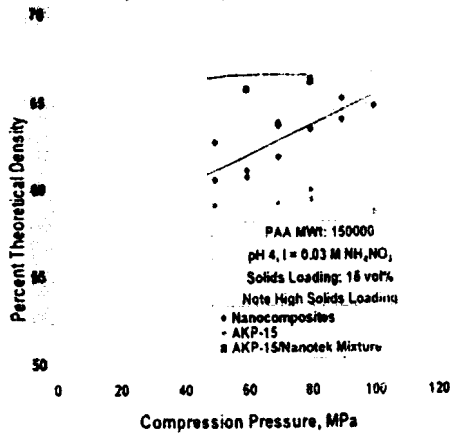
Nanotek alumina coated AKP-15 composite particles  
- with polymers



Mixture of Nanotek alumina and AKP-15 particles  
- no polymer

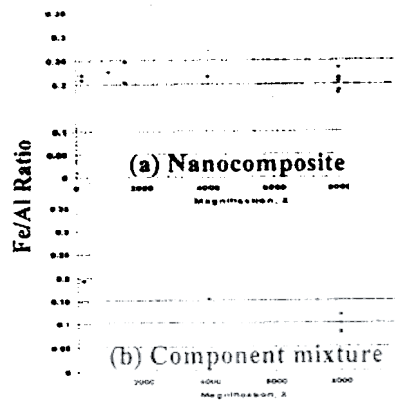
- After the coating process, composite particles with grainy surface feature were observed.
- Mixture of core and shell particles show no sign of interactions between them.

#### Effect of Compression Pressure on Green Density of Composite Compacts



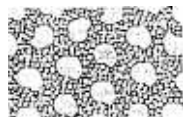
- In contrast to components (individual or mixed), nanocomposites yield a linear relationship of green density with compression pressure. This suggests flexibility of the nanocomposite structures.

#### Homogeneity of AKP-15/Nanotek Hematite (a) Nanocomposites and (b) Mixtures. Monitored using EDS Measurements



- The nanocomposite disks result in better component distribution.

#### Potential Applications of the controlled polymer adsorption process



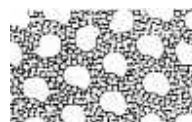
Bulk nanocomposites



Nanocomposite coating



Nanocomposite film



Foamy nanoceramics

