



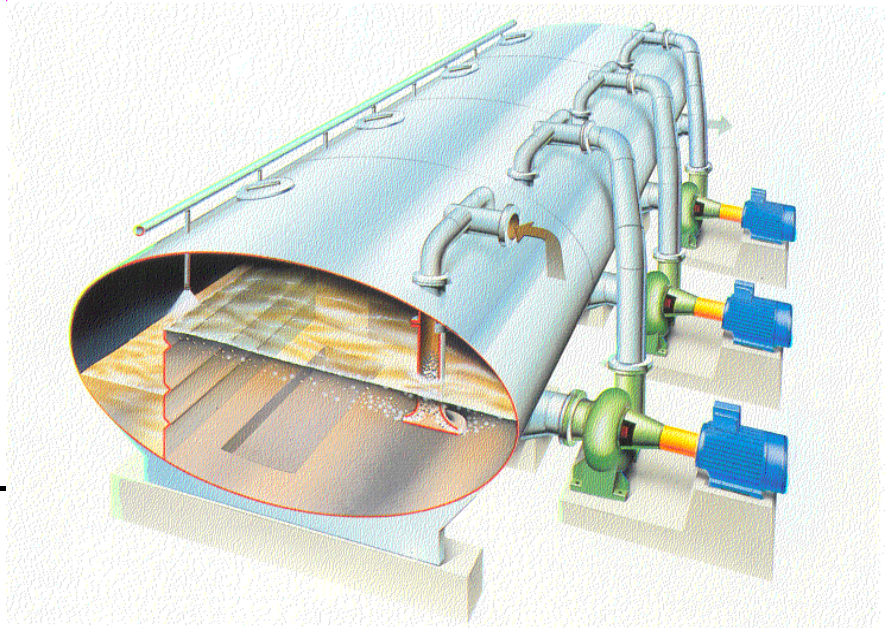
Natural Surfactants for Flotation Deinking in Paper Recycling

**R. A. Venditti, O. J. Rojas, H. Morris, J. Tucker,
K. Spence, C. Austin and L. G. Castillo**

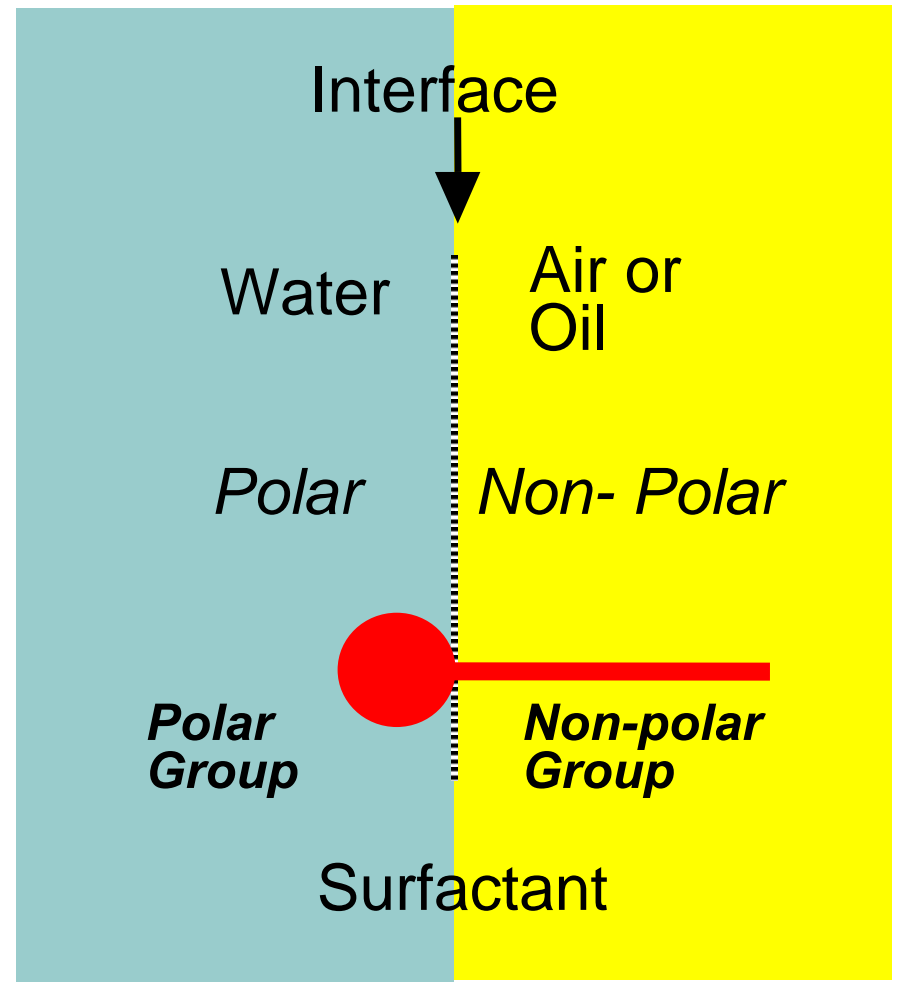
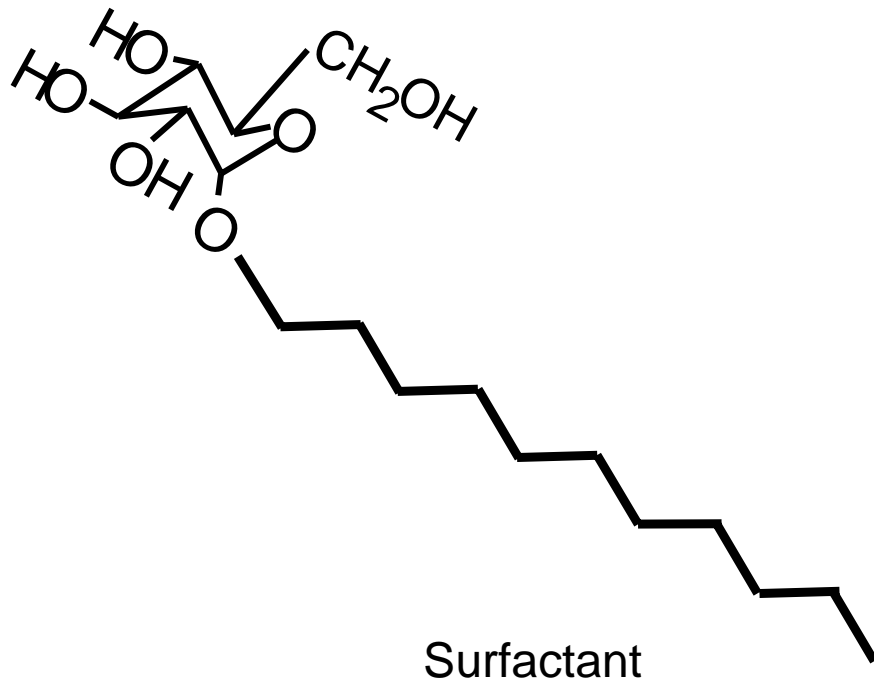
Forest Biomaterials Science and Engineering, North
Carolina State University, Raleigh USA

Introduction

- The flotation process necessitates stable foams to allow the separation of ink from fiber
- Foaming agents may be added to stock at 0.02 to 0.2 % of solids
- Currently, many of the foaming agents are petroleum-based and may not be environmentally friendly
- Are there more green alternatives that may lessen dependence on petroleum feedstocks?
- How to evaluate?

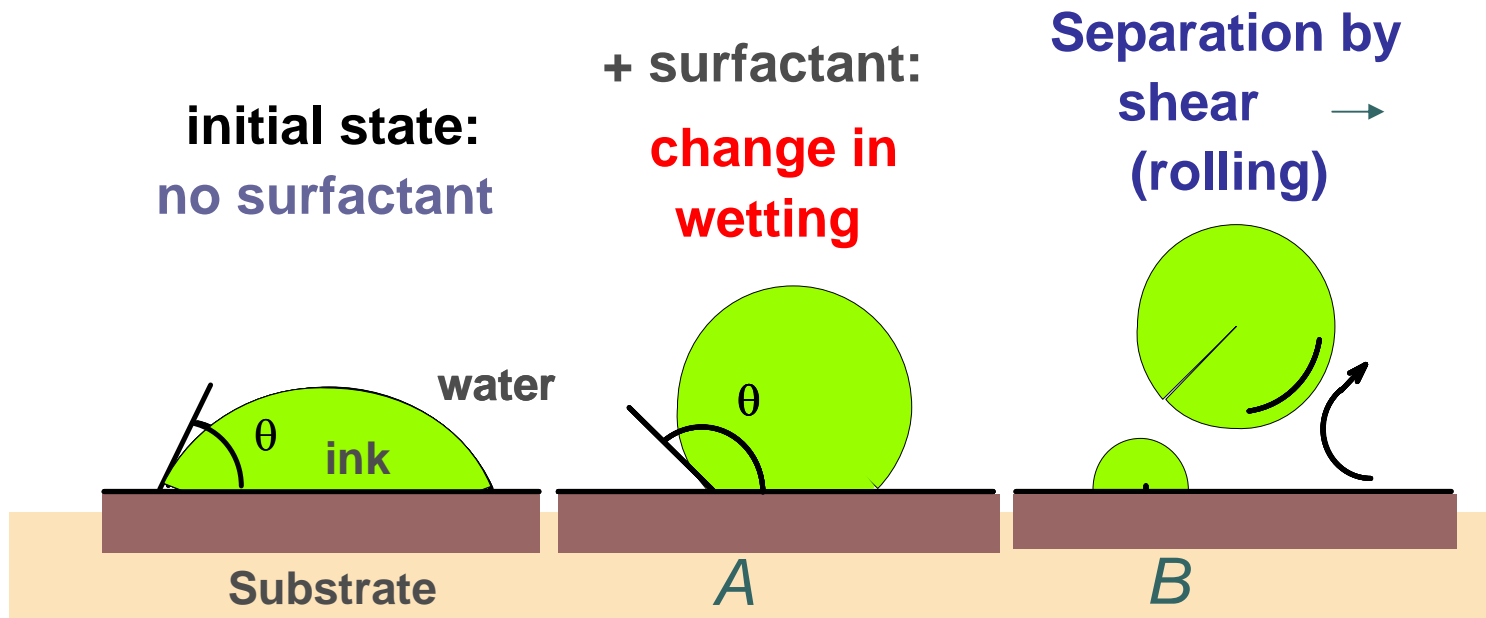


Surfactant at Interfaces:
Modification of the surface energy



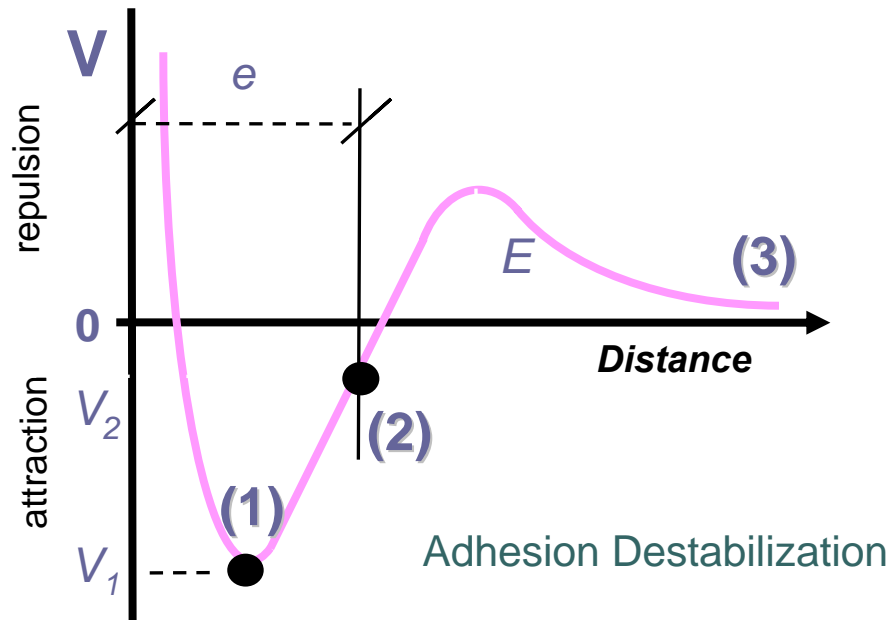
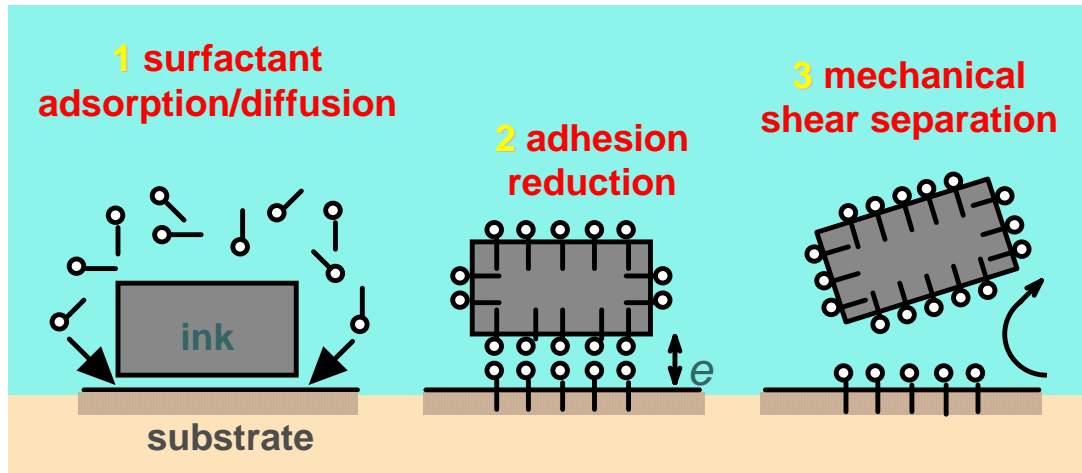


Detergency



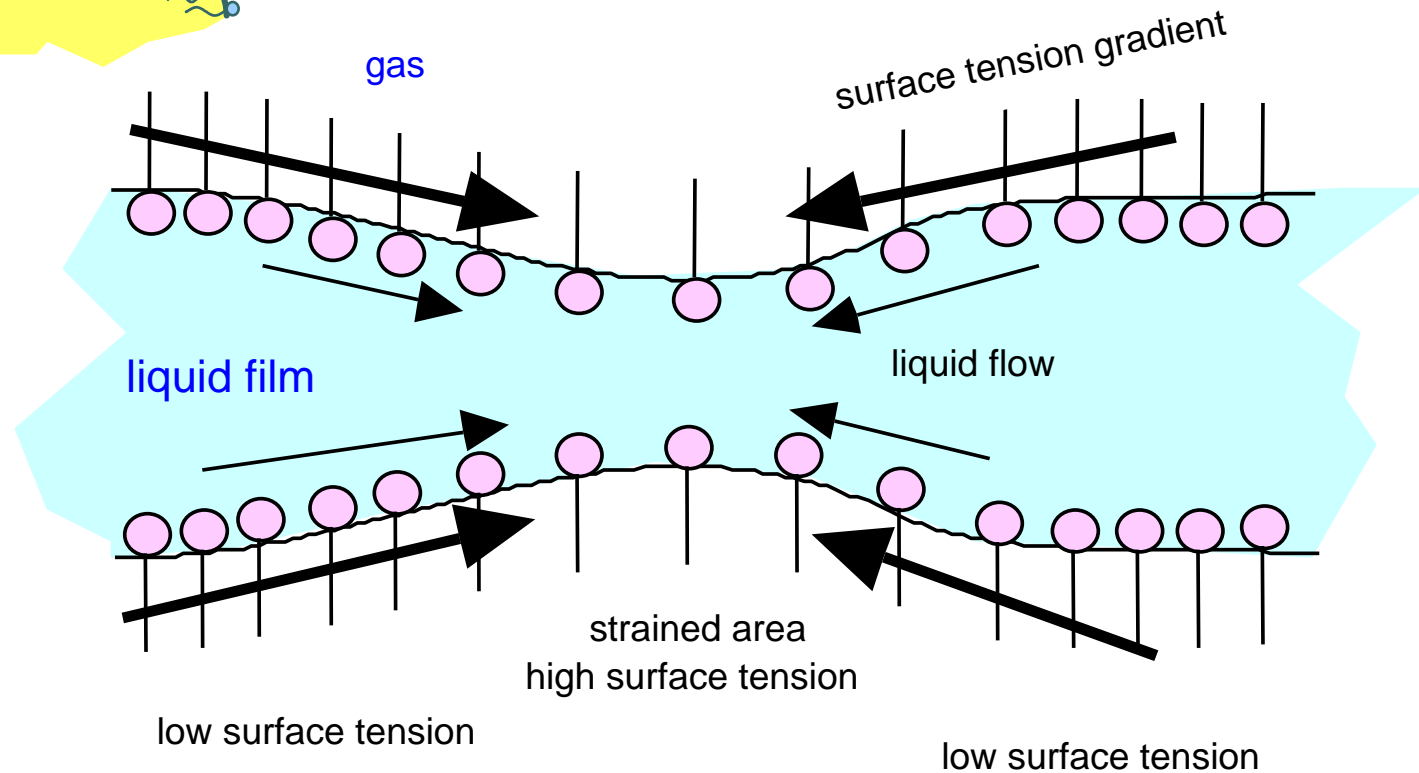
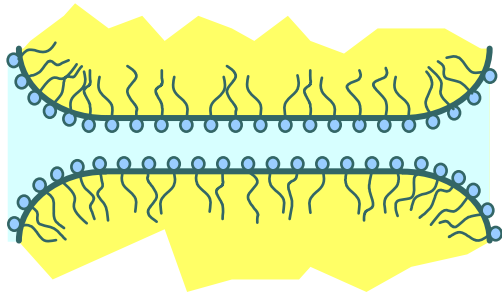


Detergency



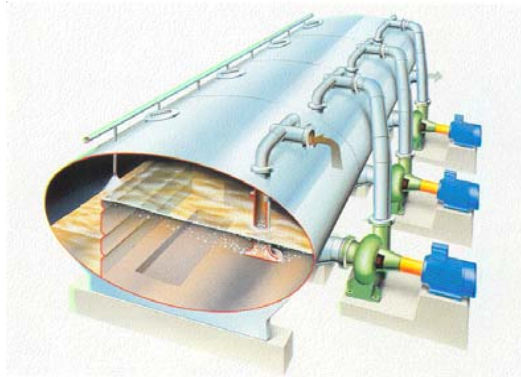
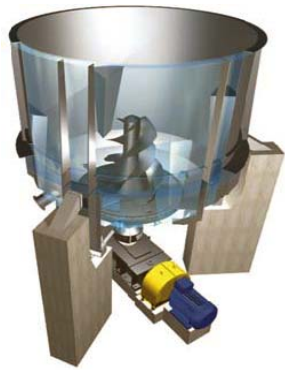
- (1) adhered particle
- (2) particle separation
- (3) particle removal

Surfactant at Air-Water Interface: Foam Stability



Introduction

- The flotation process is a complex process requiring multiple steps to occur:
 - Release of the ink from fiber
 - Attachment of ink to air bubble
 - Air bubble to be incorporated into stable foam
 - Foam to be separated from the liquid phase
- A surfactant can impact all of these steps.....its effect on flotation can be difficult to interpret



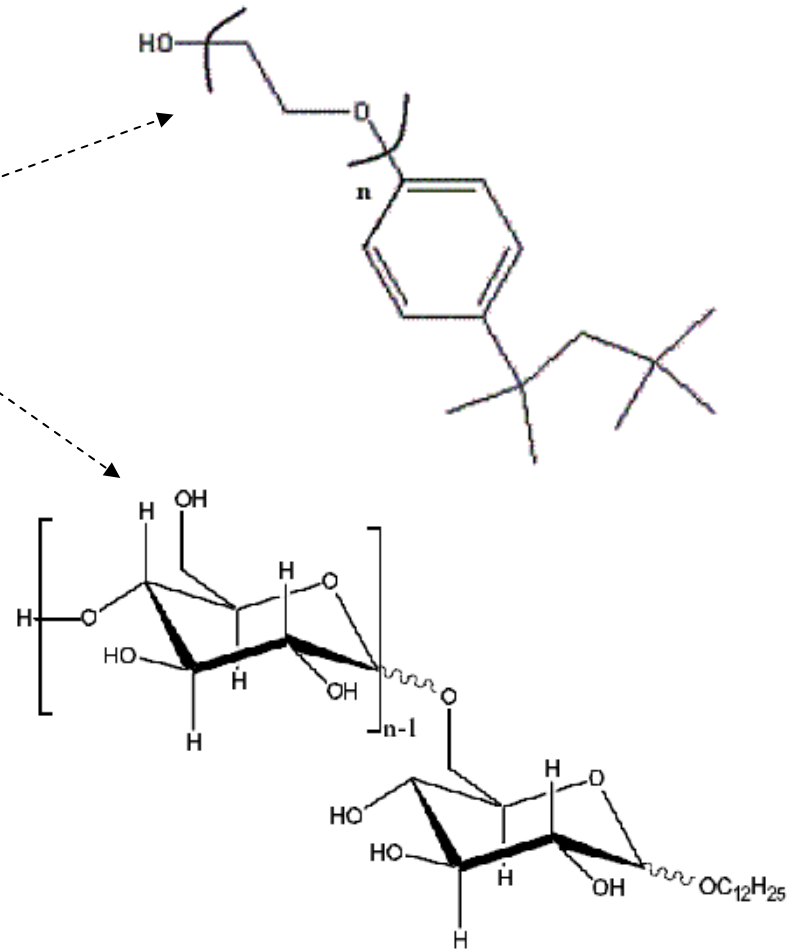


Outline

- Introduction
- Materials
- Results and Discussion
 - Detergency
 - Adsorption
 - Foamability
 - Flotation Deinking
- Conclusions
- Questions

Surfactants Studied

- Alkyl phenol ethoxylate (APE)
- Alkyl (C10-C16) mono and oligomeric D- glucopyranose
- Protein-based surfactant from soybean
- Commercially formulated surfactant blend



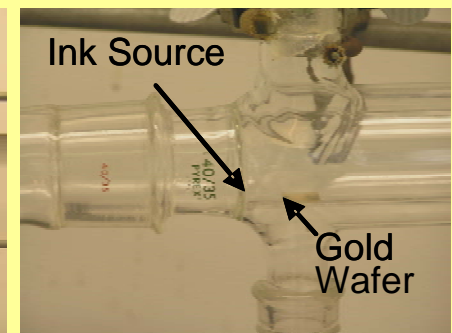
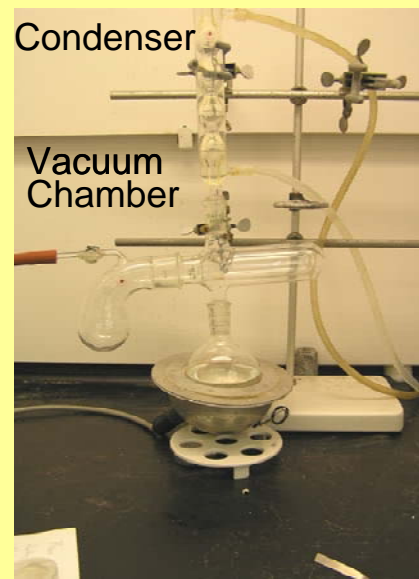


Recovered Paper Material

- Recycled Xeroxcopy Paper of 92 brightness and 30% recycled content
- Copied with text on both sides of the paper with a xerographic toner
- Pulped at 3% consistency in Tappi Disintegrator

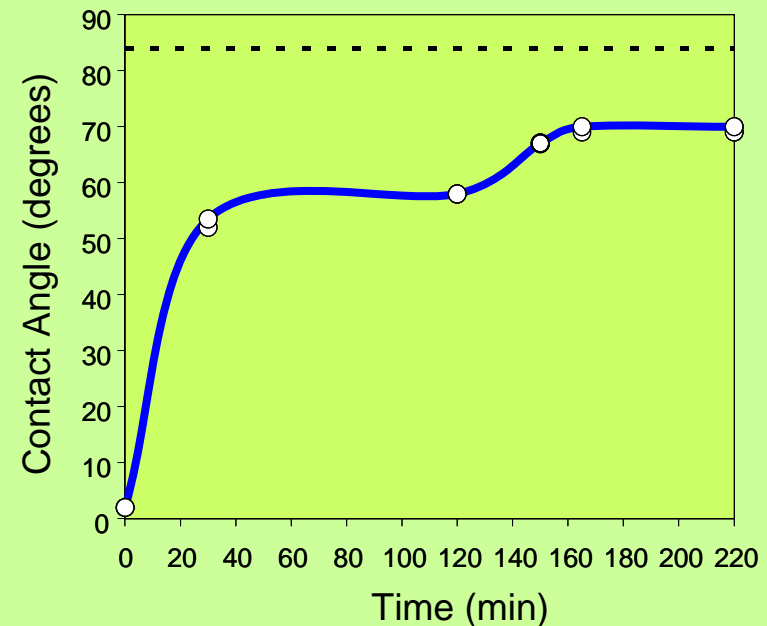
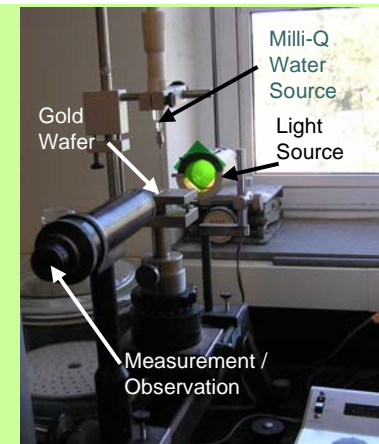
Detergency Analysis

- Preparation of films via sublimation of tripalmitin, a fatty acid model of an ink
- Exposed ink surface to surfactant solution with shear in beaker
- Measured contact angle of water drop on surface of treated film



Detergency Analysis

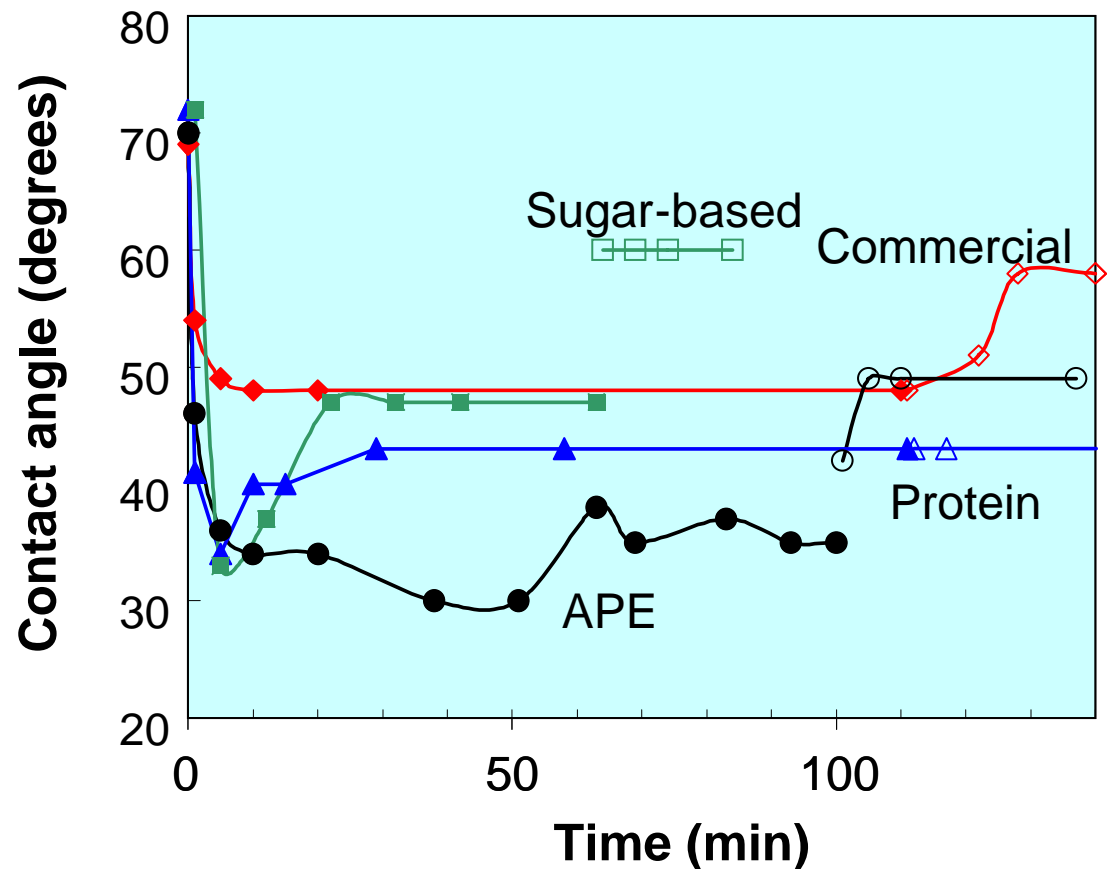
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Detergency Analysis:

- Changes in contact angle after treatment of “printed” surfaces with surfactants, before (solid symbol) and after rinsing with water (washing, open symbols)
- Surfactants make inks more hydrophilic
- Different response to rinsing: different surface affinity





Detergency Analysis (Contact Angles):

- Changes in contact angle after treatment of “printed” surfaces with surfactants, before (solid symbol) and after rinsing with water (washing, open symbols)
- Surfactants make inks more hydrophilic
- Different response to rinsing: different surface affinity

Surfactant	% Change on Treatment	% Change on Rinsing
Commercial	30	15
APE	50	30
Protein-Based	40	42
Sugar Based	35	17

$$\% \text{ Change Treat} = 100\% * [CA(\text{no treat}) - CA(\text{treat})]/CA(\text{no treat})$$

$$\% \text{ Change Rinse} = 100\% * [CA(\text{no treat}) - CA(\text{treat/rinse})]/CA(\text{no treat})$$

● ● ● Quartz Crystal Microbalance

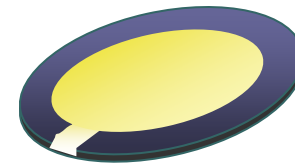
- Piezoelectric quartz crystal, sandwiched between a pair of electrodes
- Measures the resonance frequency and dissipation due to adsorption on surface
- .9 ng/cm² sensitivity in water



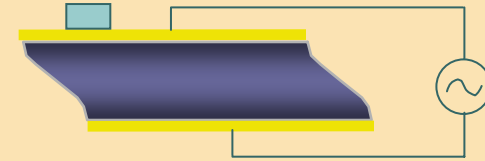
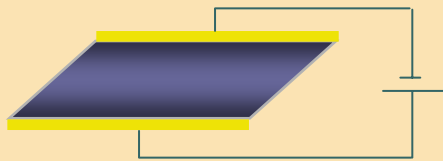
$$\Delta m = \frac{-\rho_q t_q \Delta f}{f_0 n} = \frac{-\rho_q v_q \Delta f}{2 f_0^2 n} = -\frac{C \Delta f}{n}$$

Q-Sense E4 unit

QCM-D ping principle

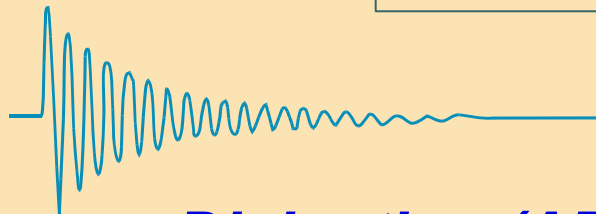
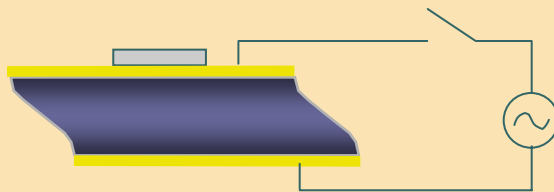


Qcmddemo.exe

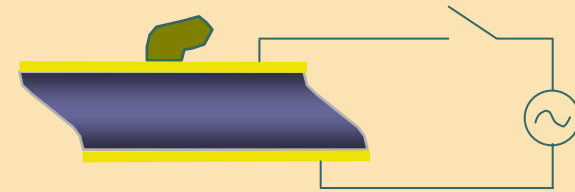


Frequency change (Δf): related to the mass of the attached film

“rigid” film

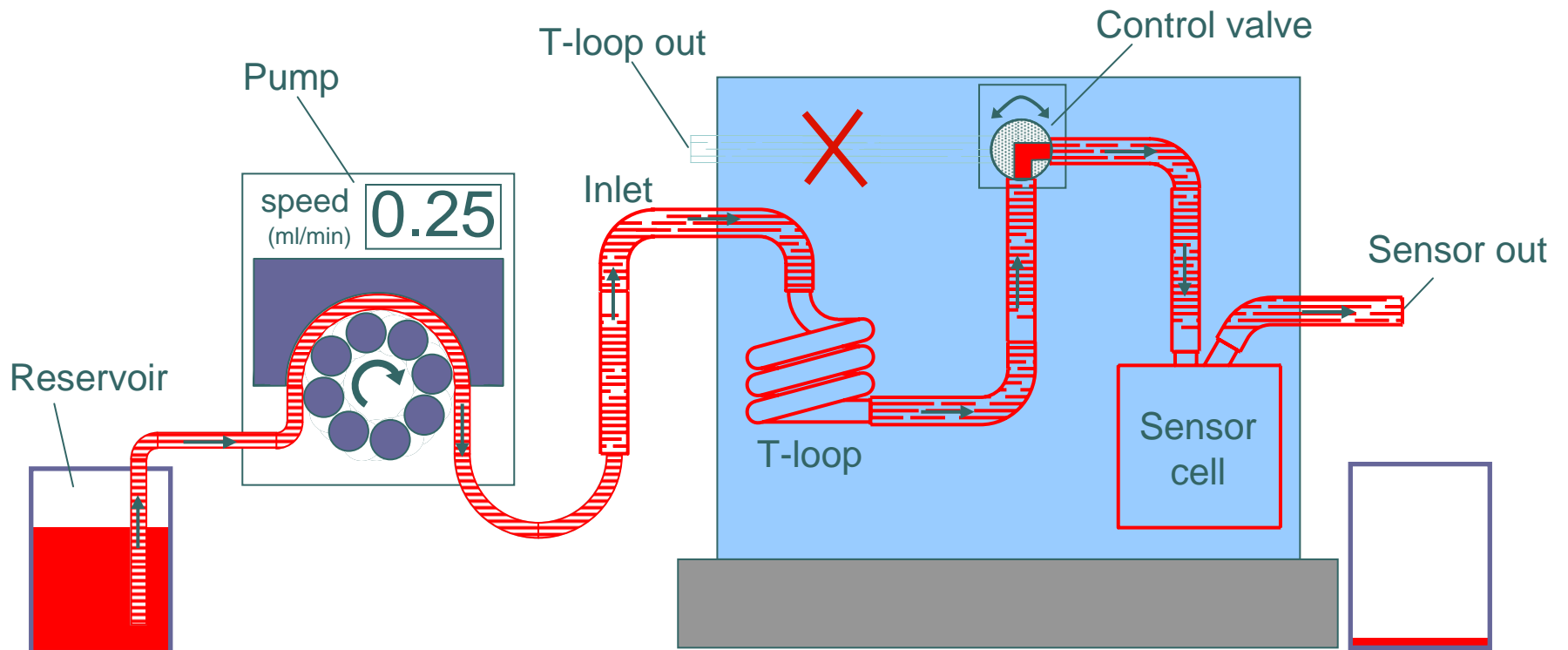


“soft” film

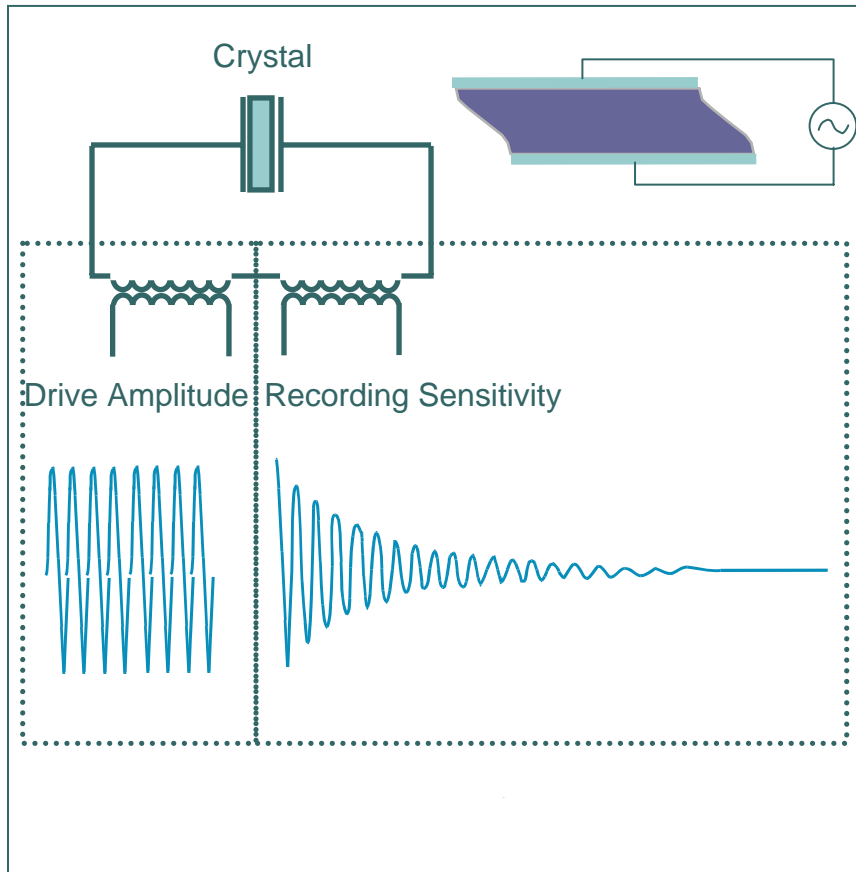


Disipation (ΔD): related to the viscoelasticity

Flow with T-loop – Liquid Transport



QCM: Measurement principle



Mathematical representation of the decay curve

$$A(t) = A_0 \cdot \exp(-t/\tau) \cdot \sin(2\pi f t + \phi)$$

$$D = 1 / \pi f \tau$$

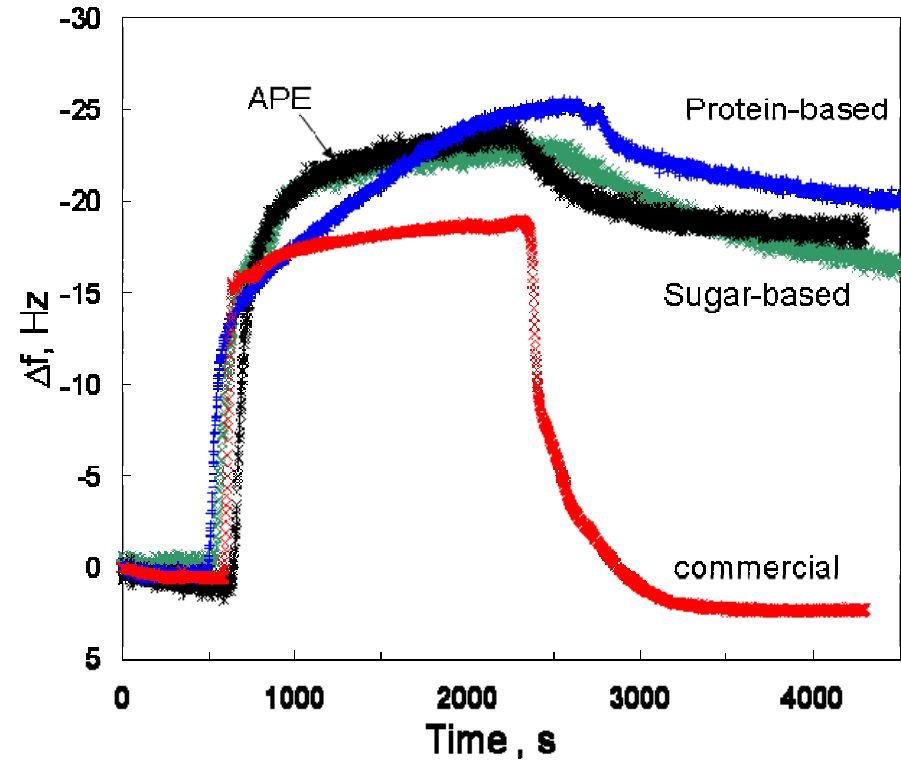
Fitting routine; Levenberg-Marquandt's (Numerical Recipes)

- Decay recording – electronics unit
- Decay fitting - PC



QCM Results

- Surfactant solution injected around 500 s
- Rinsing with water at about 2500 s
- Commercial surfactant had lowest affinity to model ink film
- Protein had highest affinity
- Kinetics revealed



Type	Amount adsorbed (ng)	Surfactant released (ng)
Commercial	10.1	11.3
Synthetic	12.8	3.0
Protein-based	13.6	3.1
Sugar-based	12.4	3.7

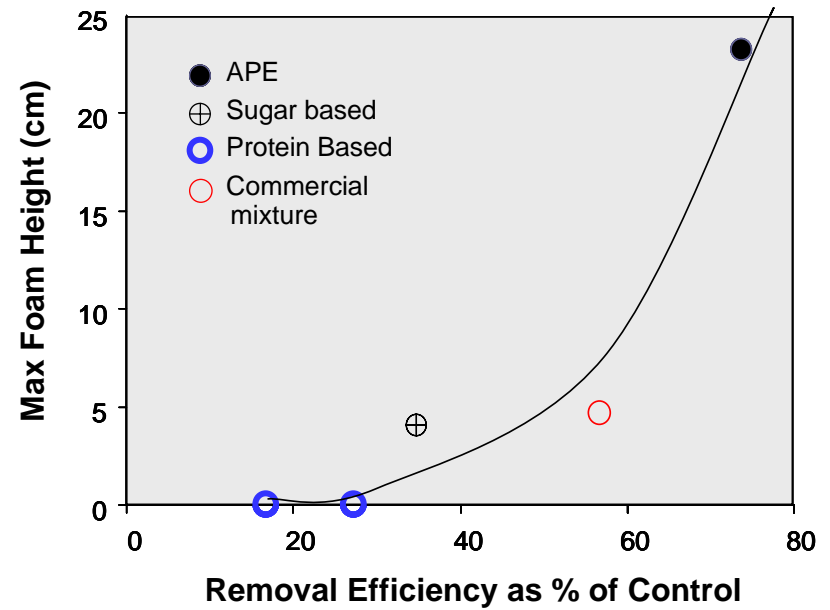
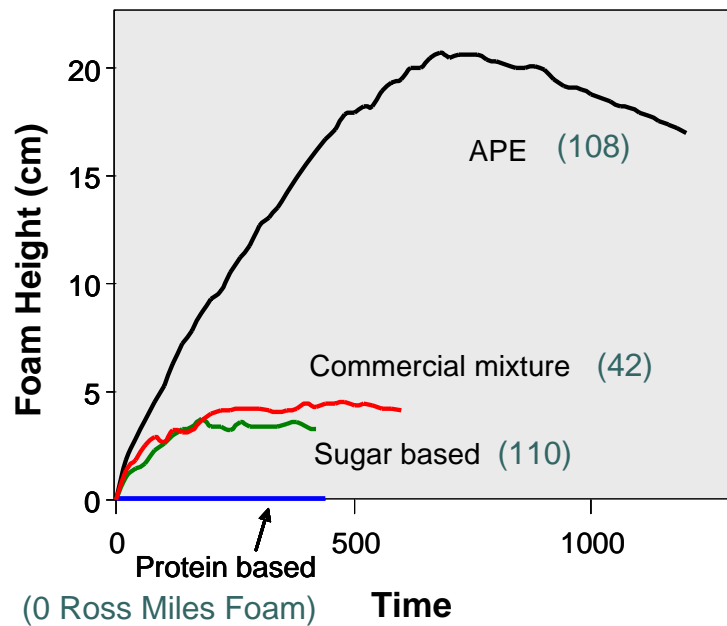
● ● ● | Dynamic Foamability

- 400 ml of 0.025 g/L surfactant solution
- Air flow of 185 ml/min through air dispersing stone
- Foam height recorded vs time





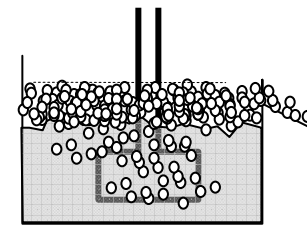
Dynamic Foamability



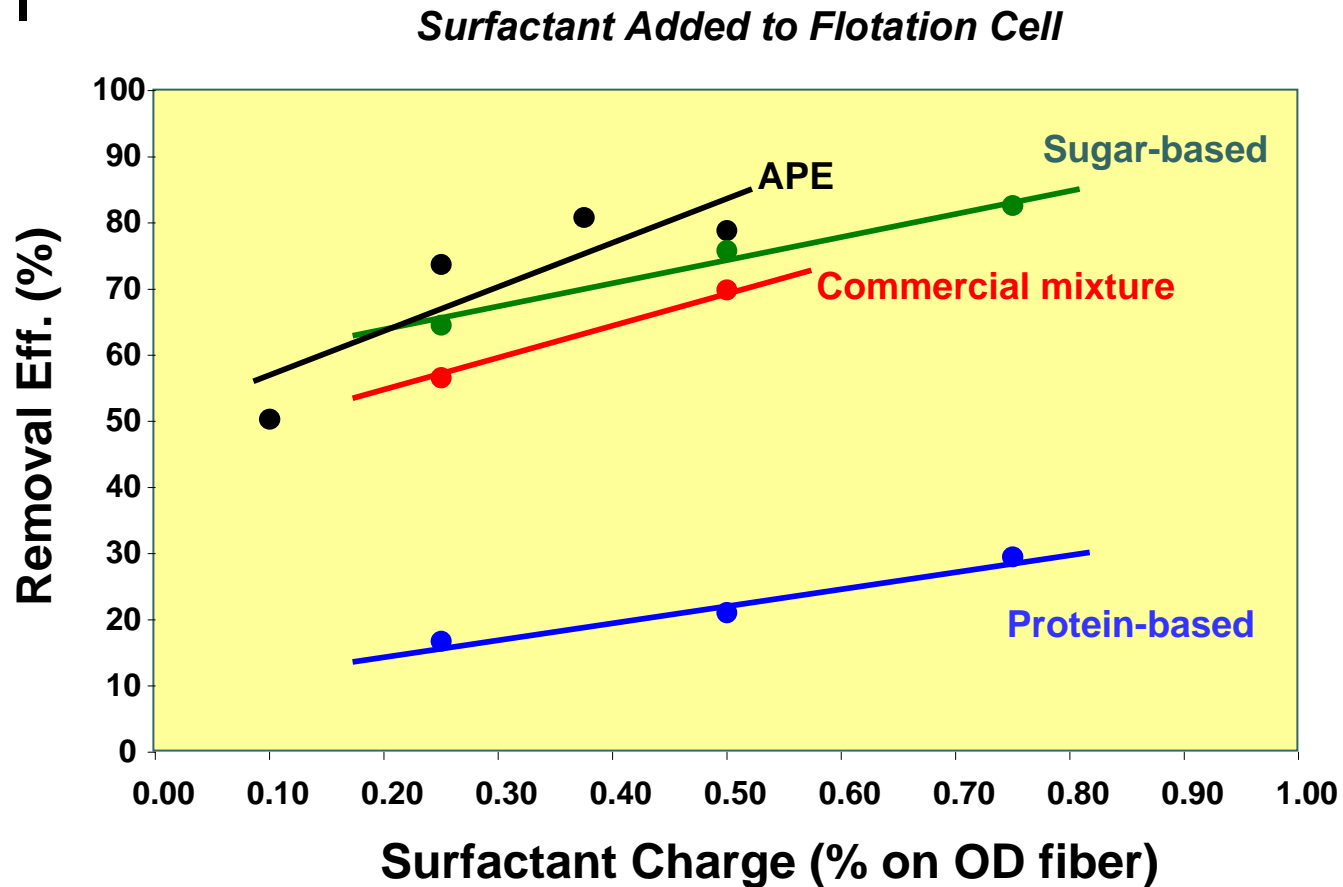
Flotation Deinking Experiments

- Pulping 3% K, 10 min, 50 C, Tappi Disintegrator
- Flotation Wemco Lab Cell, 1% K, RT, stopped when foam production ceased, ranged from 60-210 s
- Image Analysis, Scanner system, 0.007 mm² smallest particle size considered

$$RE\% = \frac{(PPM_{Control} - PPM_{Sample})}{PPM_{Control}} * 100$$



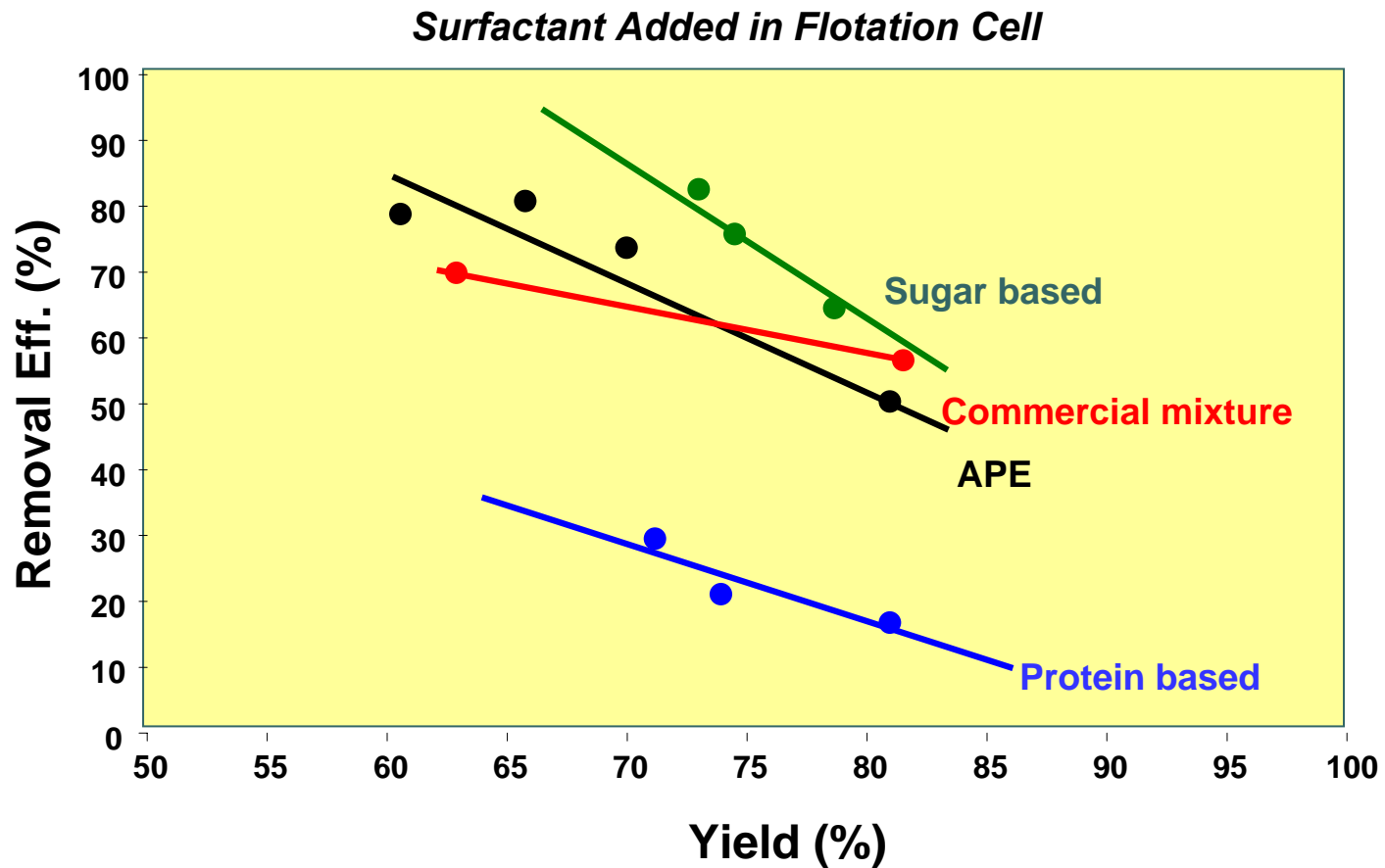
Flotation Results: Efficiency vs surfactant charge



- At a given surfactant charge, the removal efficiency correlates with the foamability → does not reflect selectivity of separation

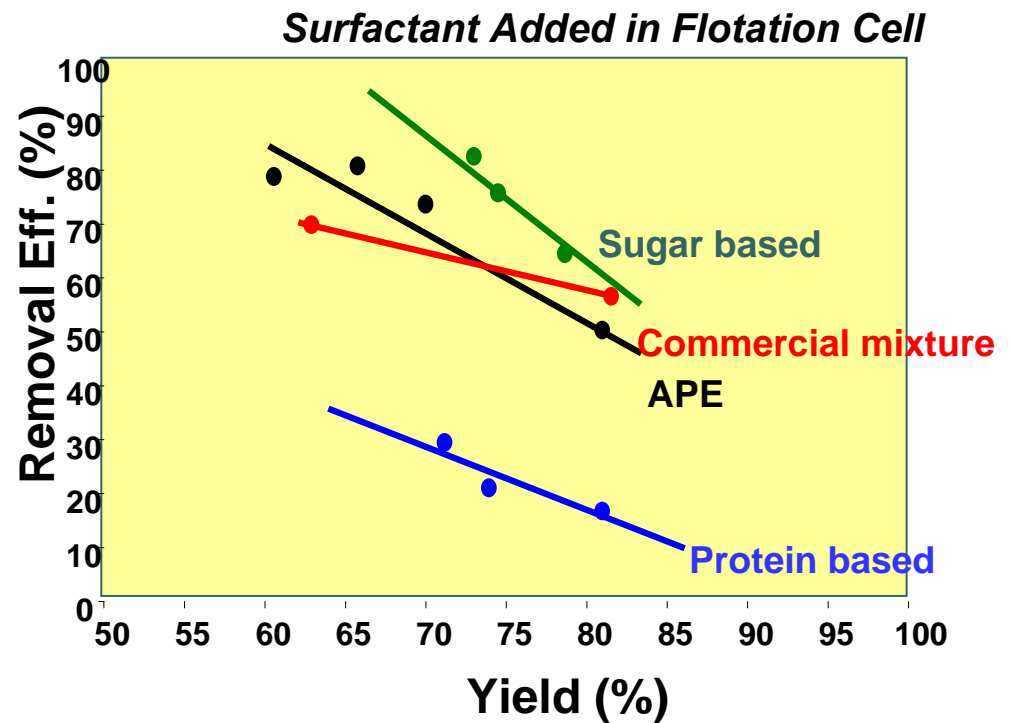


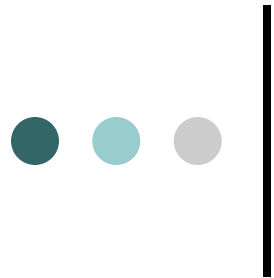
Flotation Results: Selectivity



Flotation Results: Selectivity

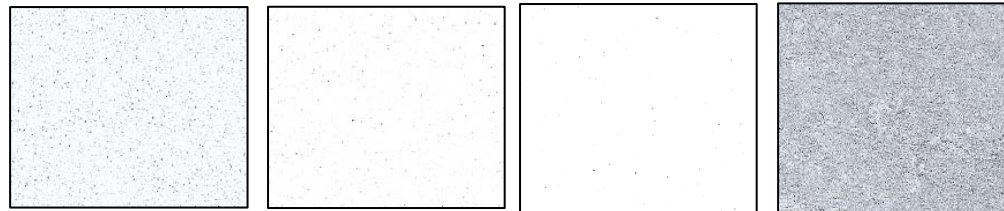
- Protein-based surfactant has significantly lower selectivity:
 - highest adsorption onto model ink (QCM)
 - largest decrease in contact angle on model ink
 - Higher MW, charged material
- Indication that the protein-based surfactant sterically stabilizes toner in water
 - Cationic starch interference of toner agglomeration (*Berg and coworkers, 1994; Venditti and coworkers 1999*)
 - Acrylate adhesive anti-deposition on polyester by cationic starch (*Venditti and coworkers, 1999*)





Conclusions

- Methods to distinguish differences in adsorption, desorption and detergency between different surfactants have been demonstrated
- Foamability has a strong correlation with removal efficiency, independent of yield considerations
- Selectivity is related to adsorption, surface modification of toner (contact angle) and steric stabilization of ink particles
- The surfactant with the sugar moieties had similar flotation removal efficiencies than did synthetic (APE) surfactants





Acknowledgements

- NCSU Undergraduate Research Program and
- EPA People Prosperity and the Planet (P3).
- Support by University of Guadalajara for visiting research experience of Luis Castillo at NCSU is gratefully acknowledged.

- We would also like to acknowledge the assistance of Dr. Xavier Turon with the QCM experiments.

