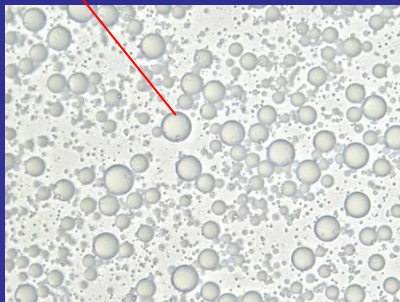
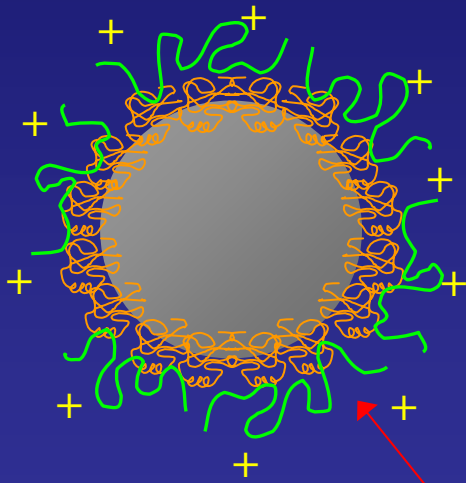


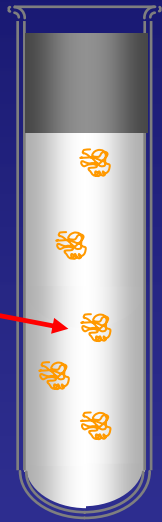
Utilization of Interfacial Engineering to Improve Food Emulsion Properties



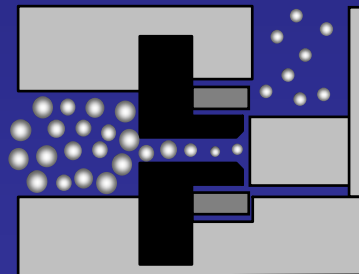
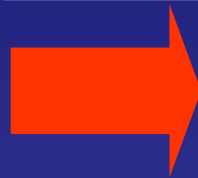
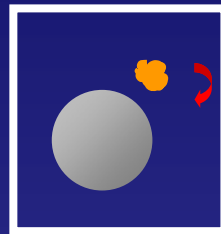
David Julian McClements
Department of Food Science
University of Massachusetts

Traditional (Single-Step) Method of Emulsion Formation

Separate Oil
and Water Phases

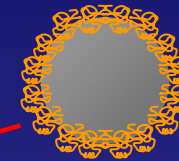
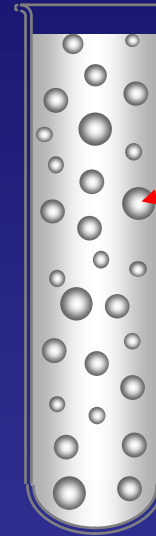


Formation

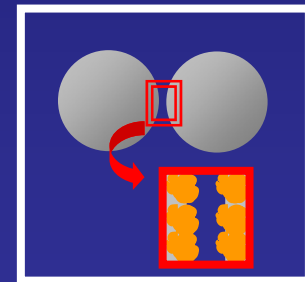


Homogenization


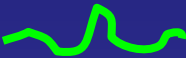
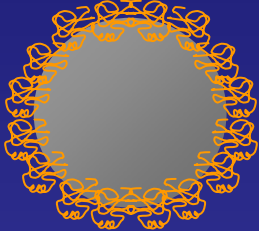
Emulsion



Stabilization



Limitations of Single-Step Method

- Some emulsifiers are efficient at forming **small droplets** during homogenization, but not at providing good stability. 
- Some emulsifiers provide good **stability**, but are inefficient at forming small droplets during homogenization. 
- Existing emulsifiers provide limited scope for developing **encapsulation & delivery** systems. 

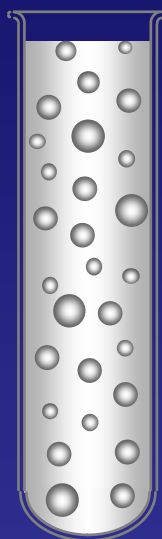
Hypothesis: Can we develop a new emulsifier strategy that combines the fast adsorption of small molecules and the good stability of large polymers to create emulsions with improved performance and functionality?

Multi-Step Emulsion Formation

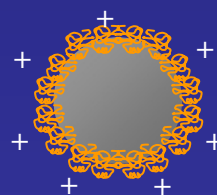
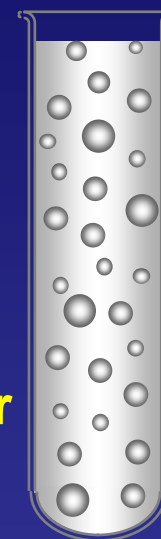
Separate Oil and Water Phases



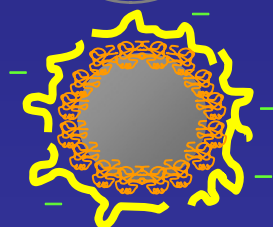
Primary Emulsion



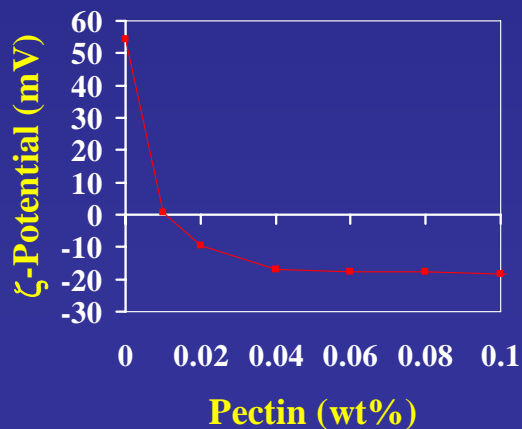
Secondary Emulsion



Single-Layer



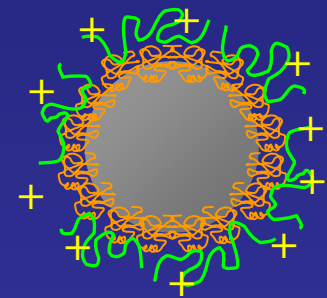
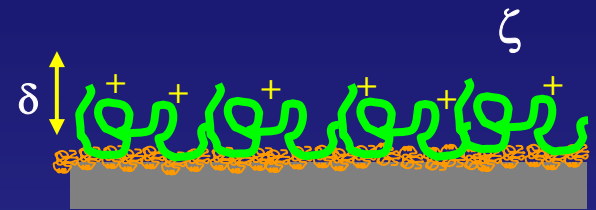
Two Layers



LbL

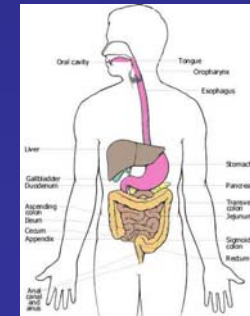
Control of Interfacial Characteristics

- **Control of Interfacial Properties**
 - **Charge Sign and Density**
 - **Thickness**
 - **Packing & Permeability**
 - **Rheology**
 - **Responsiveness**
- **Control of Emulsion Properties**
 - **Stability, Rheology, Release**



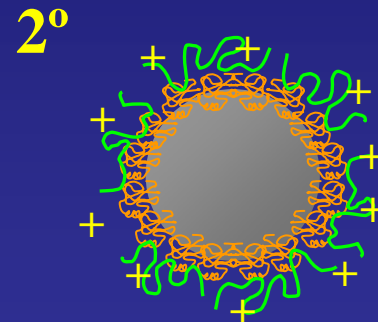
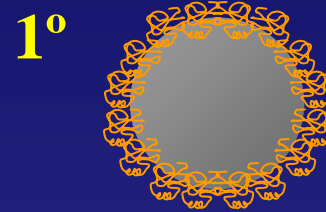
Potential Advantages of Multilayer Emulsions

- **Improvement in Stability of Emulsions to Environmental Stresses**
 - pH, Ionic Strength
 - Heating, Chilling, Freezing
 - Dehydration
- **Encapsulation and Delivery of Functional Components**
 - Protection of Labile Ingredients
 - Controlled or Triggered Release



Potential Disadvantages of Multilayer Emulsions

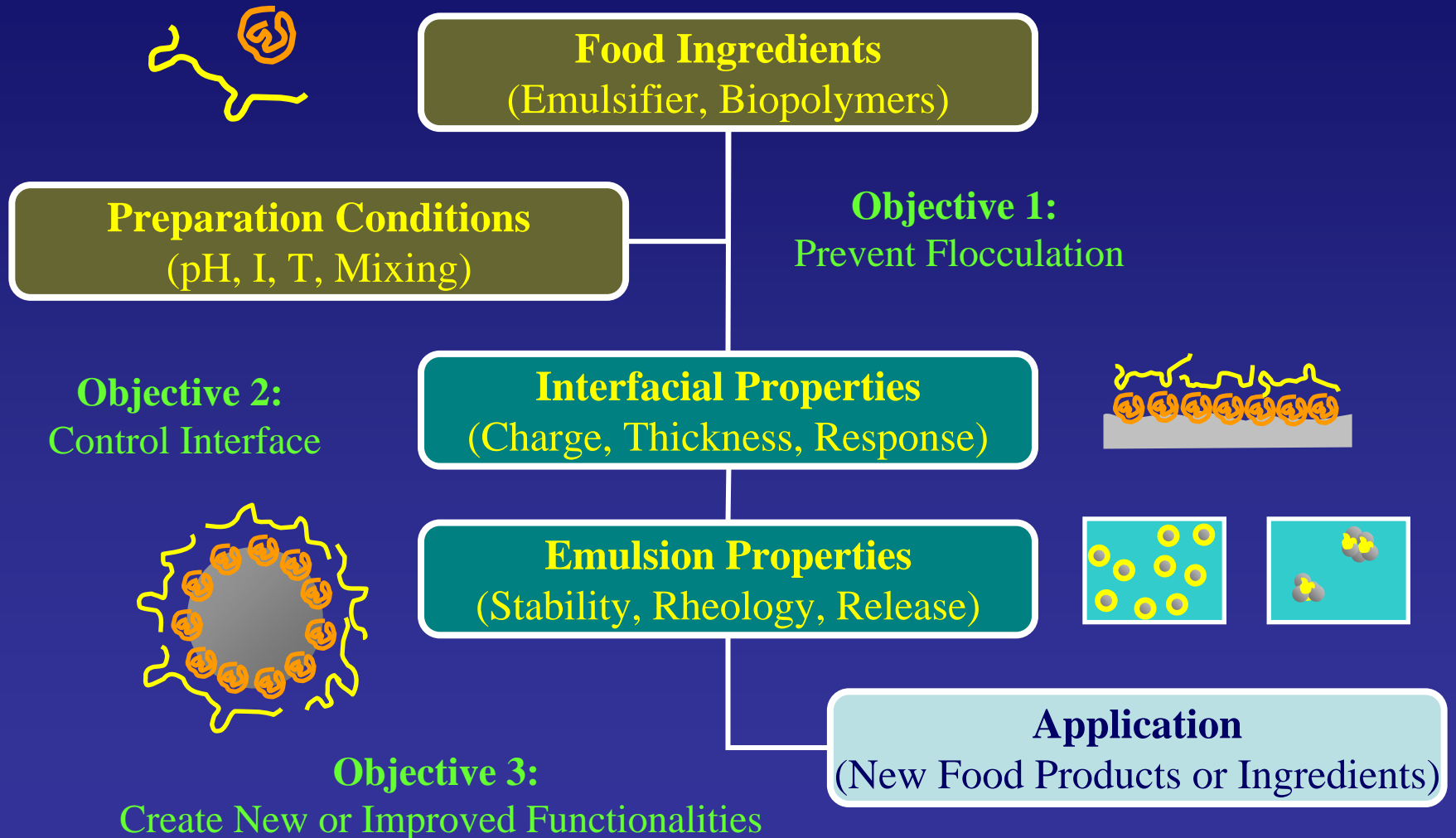
- **More Difficult to Prepare**
 - Prone to flocculation
- **More Expensive to Prepare**
 - Additional ingredients required
 - Additional processing required



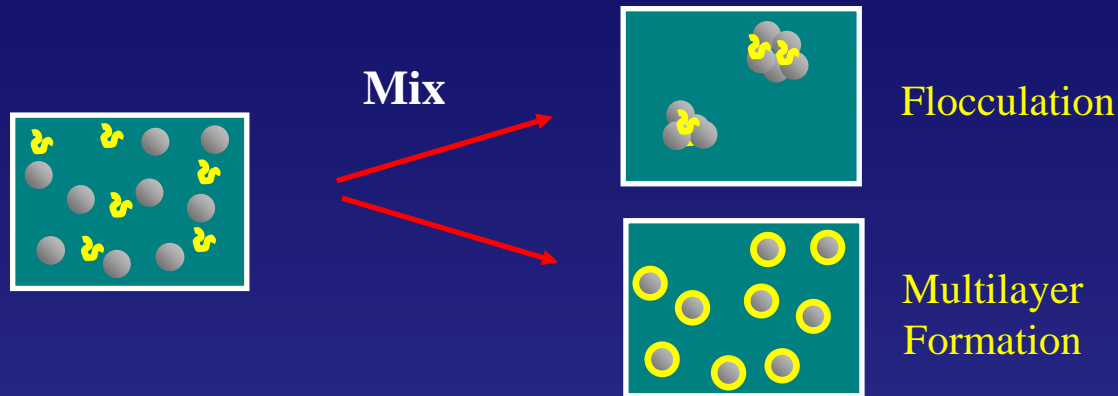
Problem: Research is needed to establish optimum preparation conditions (ingredients and processes) for preparation of multilayer emulsions with specific performance and functionality.

Overall Project Objectives

Optimization & Application of Multilayer Technology



Understanding Formation of Multilayer Emulsions: Theoretical Model



C_{SAT} = **Characteristic Saturation Concentration**

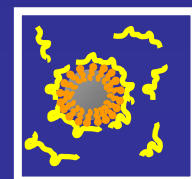
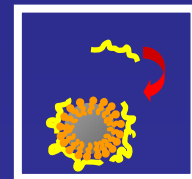
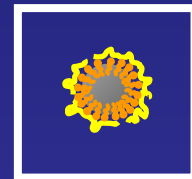
- The minimum amount of polymer required to completely cover all of the droplet surfaces.

C_{ADS} = **Characteristic Adsorption Concentration**

- The minimum polymer concentration required to ensure adsorption occurs faster than collisions.

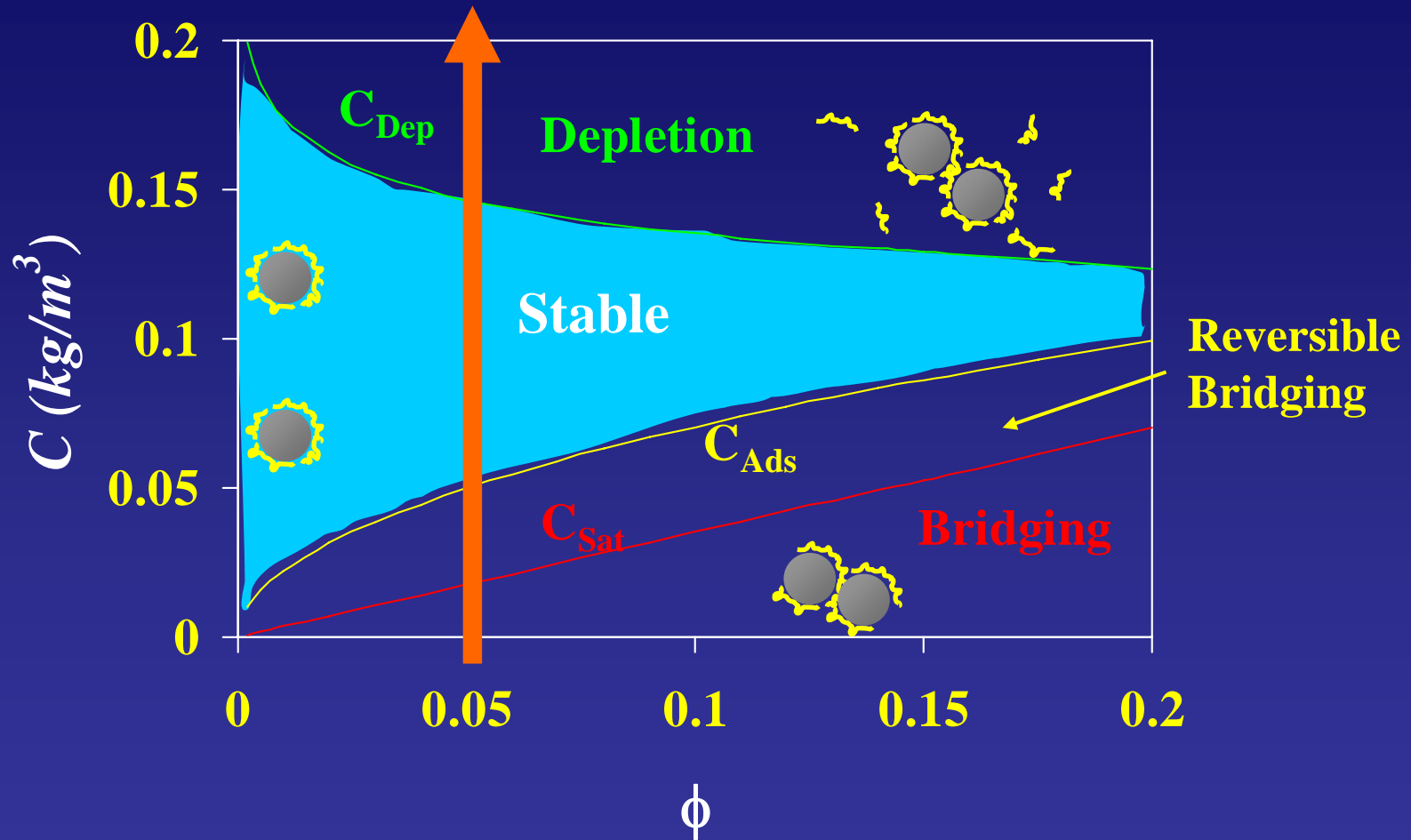
C_{DEP} = **Characteristic Depletion Concentration**

- The polymer concentration where depletion flocculation is first observed.



Theoretical Stability Map

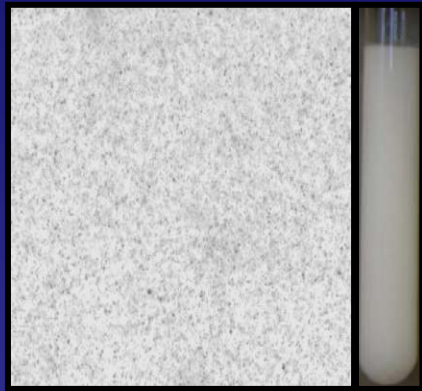
Effect of Droplet & Polymer Concentration



For stable system: $C_{Ads} < C < C_{Dep}$

Multilayer Emulsion Formation: Bridging & Depletion (pH 3.5)

Pectin Concentration



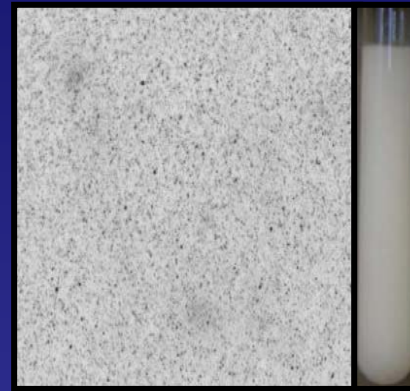
0%



0.01 wt%

Bridging
Flocculation

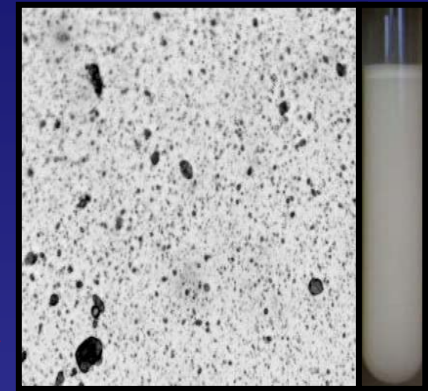
c_{Sat}



0.04 wt%

Multilayer
Droplets

c_{Dep}

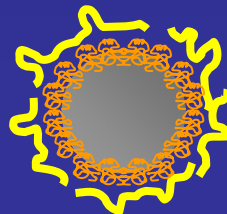


0.5 wt%

Depletion
Flocculation

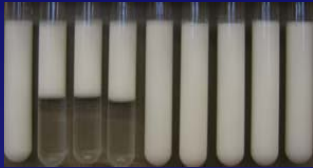
Coating Properties:

- Surface load (Γ)
- Thickness (δ)
- Permeability
- Responsiveness

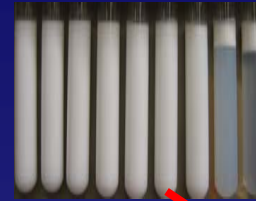


Droplet Concentration: 1 wt%

Multilayer Emulsion Formation: Establishment of “Creaming Stability” Map



pH 3.5



pH 7.0

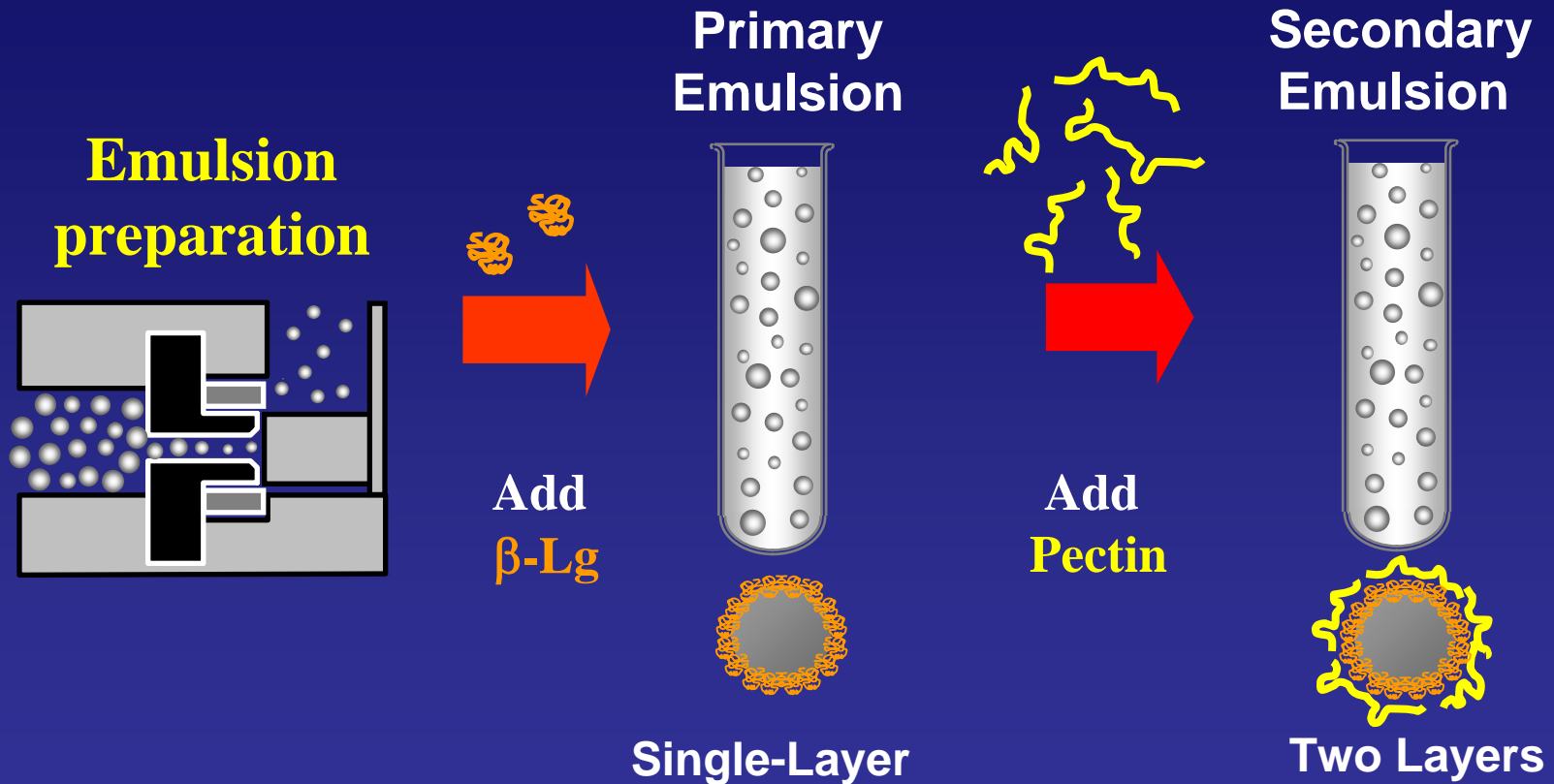
pH < pI		Droplet Concentration (wt %)					
		0.5	1	3	5	8	10
Pectin (wt %)	0	S	S	S	S	S	S
	0.01	S	C	C	C	S	S
	0.02	S	S	C	C	S	S
	0.04	S	S	C	C	C	S
	0.06	S	S	S	C	C	C
	0.08	S	S	S	C	C	C
	0.10	S	S	S	C	C	C
	0.30	S	S	S	S	S	S
	0.50	C	C	S	S	S	S

pH > pI		Droplet Concentration (wt %)					
		0.5	1	3	5	8	10
Pectin (wt %)	0	S	S	S	S	S	S
	0.01	S	S	S	S	S	S
	0.02	S	S	S	S	S	S
	0.04	S	S	S	S	S	S
	0.06	S	S	S	S	S	S
	0.08	S	S	S	S	S	S
	0.10	C	C	C	C	C	C
	0.30	C	C	C	C	C	C
	0.50	C	C	C	C	C	C

Bridging

Depletion

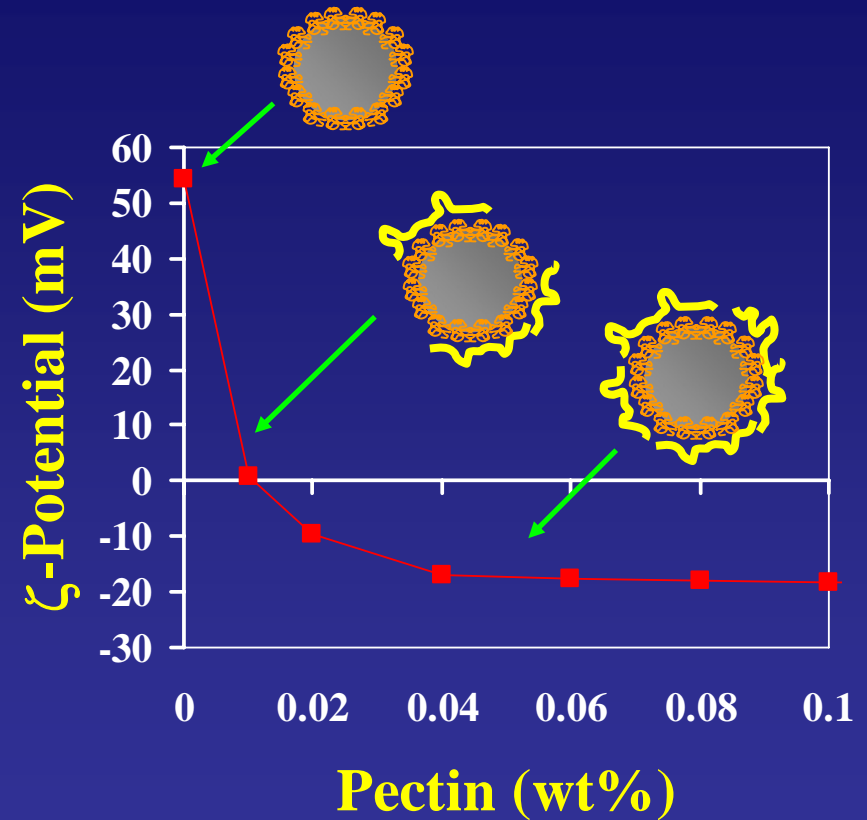
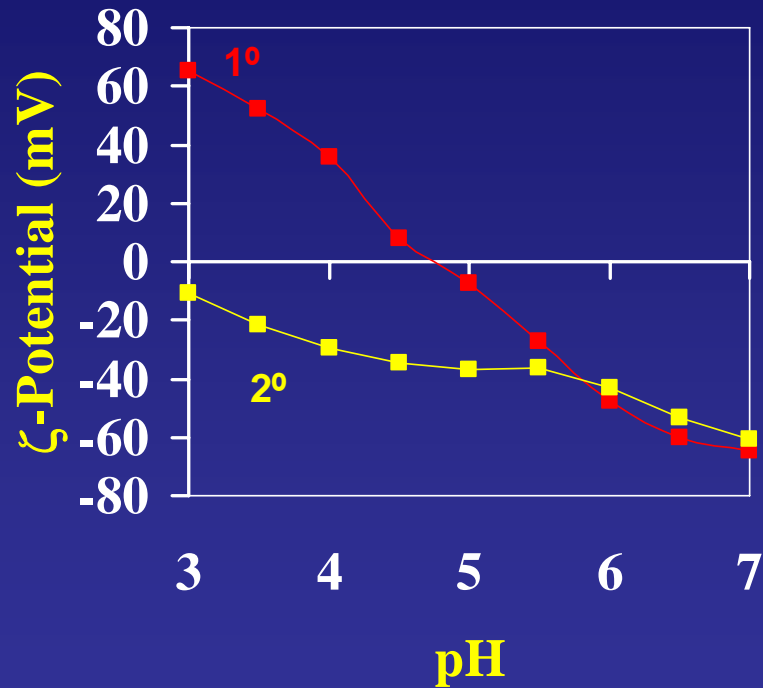
Understanding Formation of Multilayer Emulsions: Experiments



Measure:

- Adsorption (ζ -potential); Microstructure (Microscopy); Stability (Laser Diffraction, Creaming); Rheology (Shear rheometry)

Multilayer Emulsion Formation: Establishment of Adsorption Range



ζ -Potential Measurements Show Where Adsorption Occurs

Interfacial Characteristics:

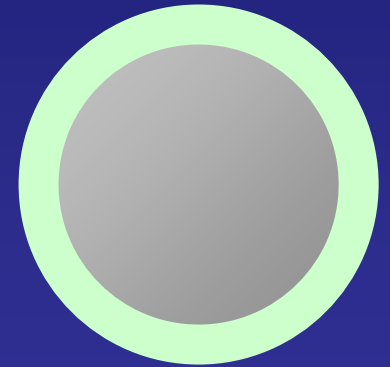
Determination of Interfacial Properties



ζ -Potential
Dynamic Light Scattering

Interfacial Properties:

- Polymer Concentration
- Thickness
- Packing
- Charge



Protein-Pectin Multilayers: $\Gamma_{\text{Sat}} = 1.6 \text{ mg m}^{-2}$; $\delta = 45 \text{ nm}$; $\phi = 2\%$

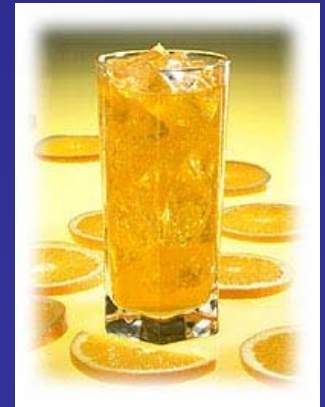
Application of Technology: Improving Emulsion Stability

Motivation

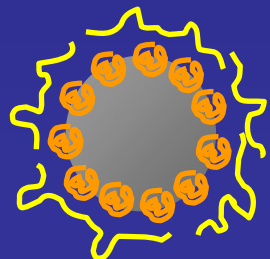
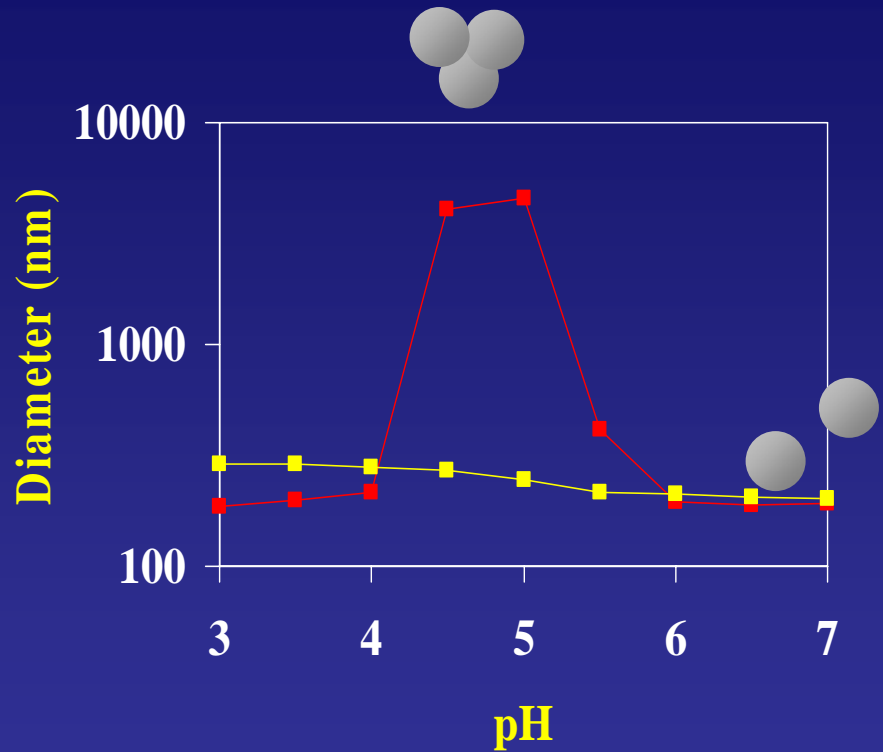
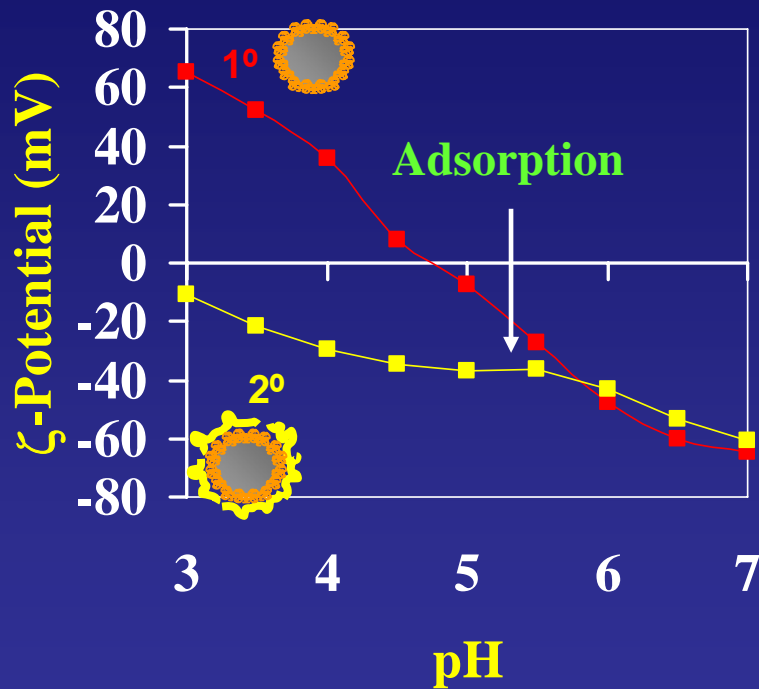
- Multilayer technology could be used to improve the stability of many food emulsions to environmental stresses

Environmental Stresses

- pH, Ionic Strength
- Thermal processing, Chilling, Freezing
- Dehydration



Multilayer Emulsion Properties: Extension of pH Range



1° β-Lg
2° Pectin



Primary

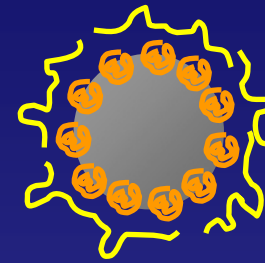
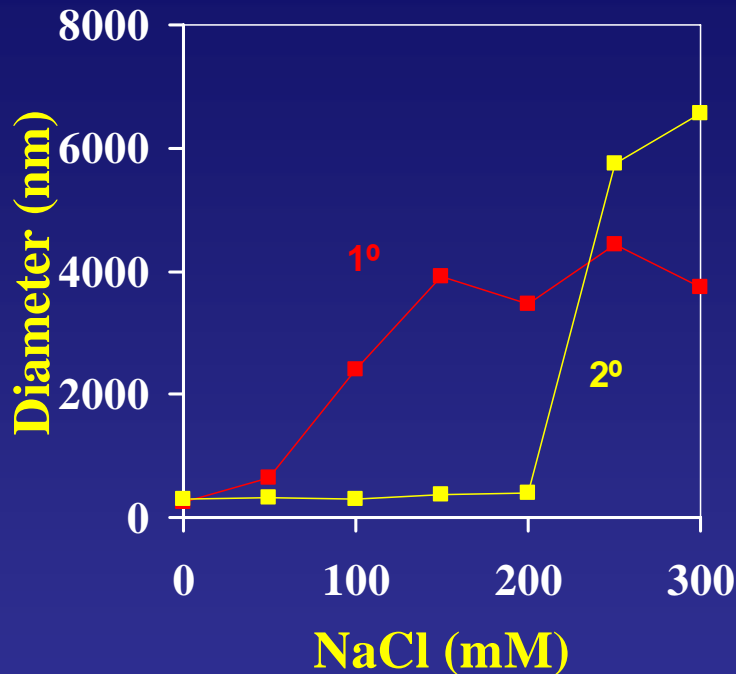
3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0



Secondary

3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0

Multilayer Emulsion Properties: Extension of NaCl Stability Range



1° β -Lg
2° Pectin

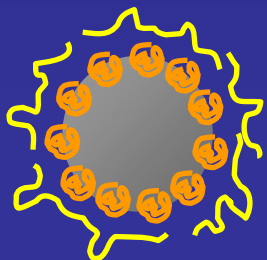
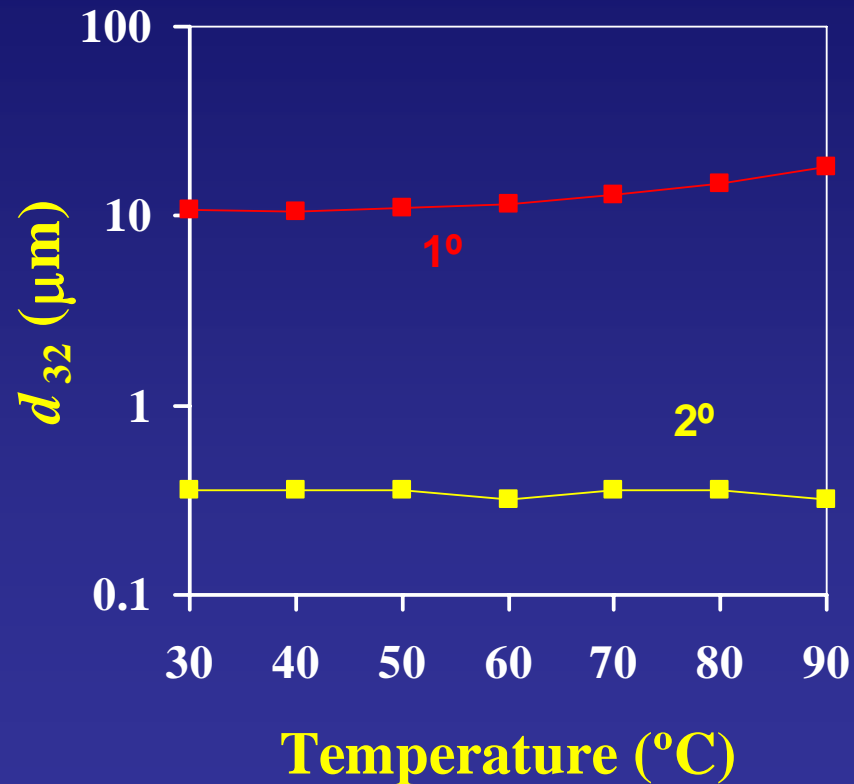
Origin of Stability:

- Reduction in VDW
- Increase in ES
- Increase in Steric



pH 3.5

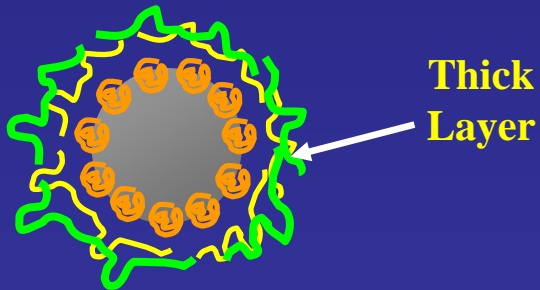
Multilayer Emulsion Properties: Improvement of Thermal Stability



1° β -Lg
2° Pectin

pH 4

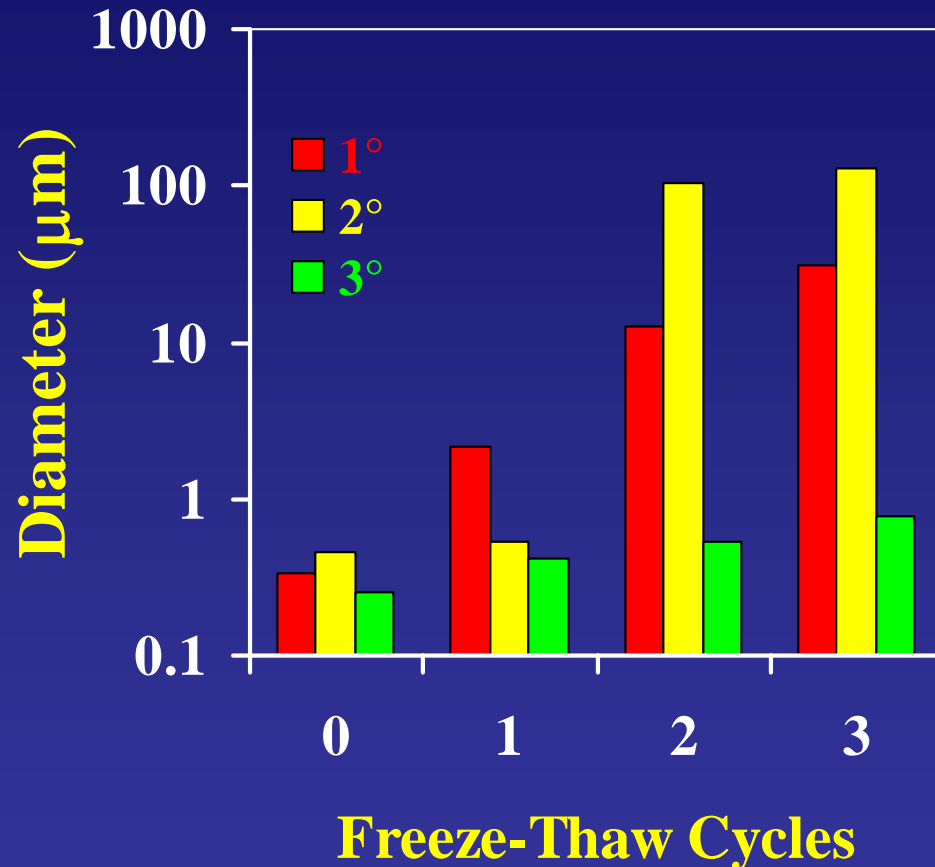
Multilayer Emulsion Properties: Improvement of Freeze-Thaw Stability



1° β -Lg

2° Carrageenan

3° Gelatin



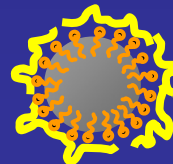
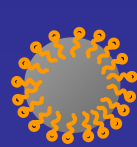
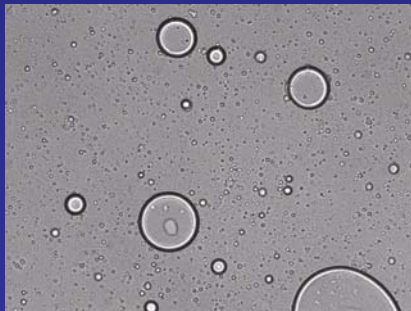
0% Sucrose

Multilayer Emulsion Properties: Improvement of Dehydration Stability

Primary



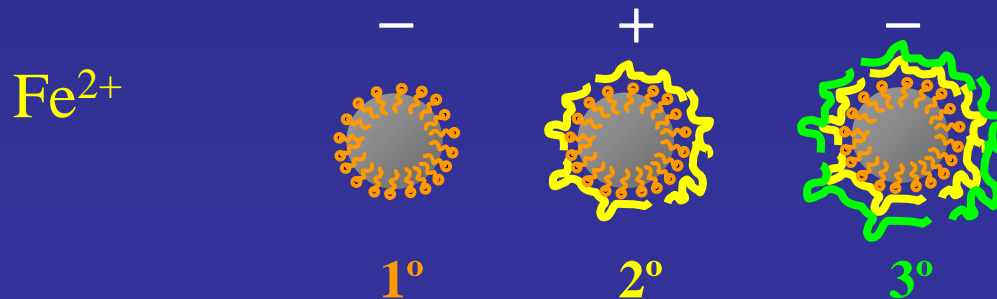
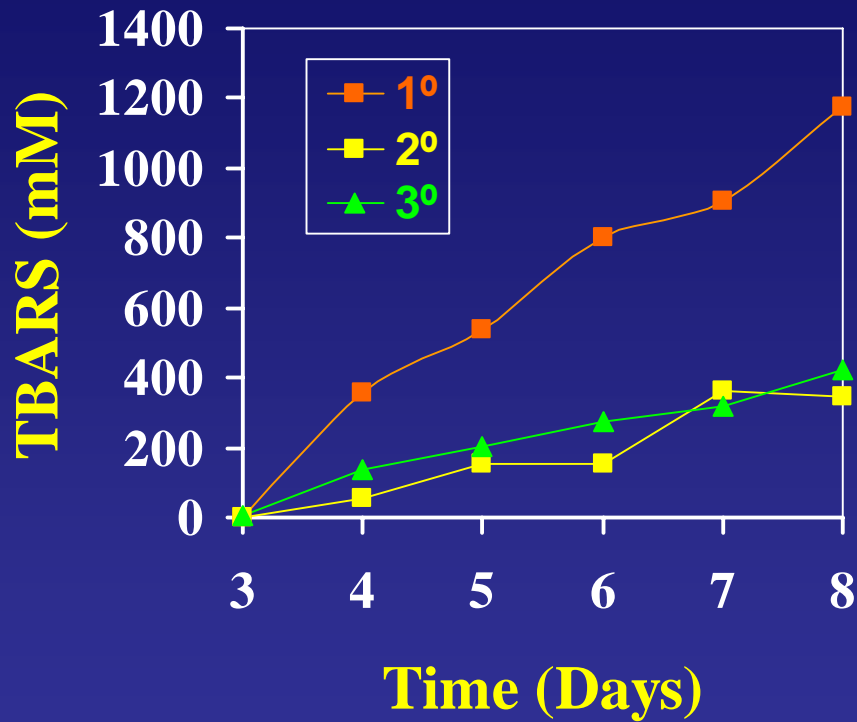
Secondary



1°

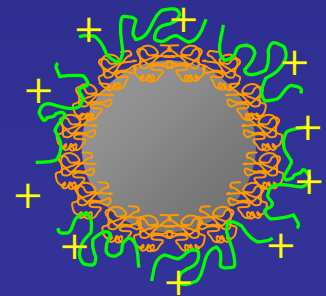
2°

Multilayer Emulsion Properties: Improvement of Oxidative Stability



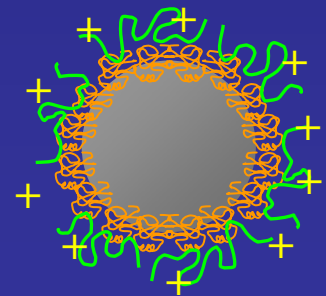
Current Status of Multilayer Emulsions

- Emulsions containing lipid droplets coated by nano-laminated layers can be prepared by a simple **cost effective** method using **food ingredients**
- These emulsions have **improved stability** to environmental stresses, such as heating, freezing, drying, pH extremes, and high mineral contents
- Future studies are needed to determine their suitability for use in **real foods** (encapsulation, controlled release, triggered release)



Future Work

- Investigate use of mixed biopolymers to form the outer interfacial layers (so can control charge and thickness).
- Investigate methods of cross-linking adsorbed layers so that they retain functionality over wider range of conditions.
- Investigate digestibility of multilayer emulsions.
- Investigate applications to real food systems, *e.g.*, beverage emulsions.



Publications

- 1. Djordjevic D, Cercaci L, Alamed J, Decker EA, McClements DJ. Chemical and physical stability of citral and limonene in sodium dodecyl sulfate-chitosan and gum arabic-stabilized oil-in-water emulsions. *JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY* 55 (9): 3585-3591 MAY 2 2007
- 2. Shaw LA, McClements DJ, Decker EA. Spray-dried multilayered emulsions as a delivery method for omega-3 fatty acids into food systems. *JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY* 55 (8): 3112-3119 APR 18 2007
- 3. Hong YH, McClements DJ. Modulation of pH sensitivity of surface charge and aggregation stability of protein-coated lipid droplets by chitosan addition. *FOOD BIOPHYSICS* 2 (1): 46-55 MAR 2007
- 4. Gu YS, Decker EA, McClements DJ. Application of multi-component biopolymer layers to improve the freeze-thaw stability of oil-in-water emulsions: beta-lactoglobulin-iota-carrageenan-gelatin. *JOURNAL OF FOOD ENGINEERING* 80 (4): 1246-1254 JUN 2007
- 5. Guzey D, McClements DJ. Formation, stability and properties of multilayer emulsions for application in the food industry. *ADVANCES IN COLLOID AND INTERFACE SCIENCE* 128: 227-248 DEC 21 2006
- 6. Gu YS, Decker EA, McClements DJ. Formation of colloidosomes by adsorption of small charged oil droplets onto the surface of large oppositely charged oil droplets. *FOOD HYDROCOLLOIDS* 21 (4): 516-526 JUN 2007
- 7. Guzey D, McClements DJ. Impact of electrostatic interactions on formation and stability of emulsions containing oil droplets coated by beta-lactoglobulin-pectin complexes. *JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY* 55 (2): 475-485 JAN 24 2007
- 8. Mun S, Decker EA, Park Y, McClements DJ. Influence of interfacial composition on in vitro digestibility of emulsified lipids: Potential mechanism for chitosan's ability to inhibit fat digestion. *FOOD BIOPHYSICS* 1 (1): 21-29 MAR 2006
- 9. Guzey D, McClements DJ. Influence of environmental stresses on O/W emulsions stabilized by beta-lactoglobulin-pectin and beta-lactoglobulin-pectin-chitosan membranes produced by the electrostatic layer-by-layer deposition technique. *FOOD BIOPHYSICS* 1 (1): 30-40 MAR 2006
- 10. Pongsawatmanit R, Harnsilawat T, McClements DJ. Influence of alginate, pH and ultrasound treatment on palm oil-in-water emulsions stabilized by beta-lactoglobulin. *COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS* 287 (1-3): 59-67 SEP 15 2006
- 11. Mun S, Decker EA, McClements DJ. Effect of molecular weight and degree of deacetylation of chitosan on the formation of oil-in-water emulsions stabilized by surfactant-chitosan membranes. *JOURNAL OF COLLOID AND INTERFACE SCIENCE* 296 (2): 581-590 APR 15 2006
- 12. Klinkesorn U, Sophanodora P, Chinachoti P, Decker EA, McClements DJ. Characterization of spray-dried tuna oil emulsified in two-layered interfacial membranes prepared using electrostatic layer-by-layer deposition. *FOOD RESEARCH INTERNATIONAL* 39 (4): 449-457 2006
- 13. Surh J, Decker EA, McClements DJ. Influence of pH and pectin type on properties and stability of sodium-caseinate stabilized oil-in-water emulsions. *FOOD HYDROCOLLOIDS* 20 (5): 607-618 JUL 2006
- 14. Mun SH, McClements DJ. Influence of interfacial characteristics on Ostwald ripening in hydrocarbon oil-in-water emulsions. *LANGMUIR* 22 (4): 1551-1554 FEB 14 2006
- 15. Klinkesorn U, Sophanodora P, Chinachoti P, Decker EA, McClements DJ. Stability of spray-dried tuna oil emulsions encapsulated with two-layered interfacial membranes. *JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY* 53 (21): 8365-8371 OCT 19 2005
- 16. Mun S, Decker EA, McClements DJ. Influence of droplet characteristics on the formation of oil-in-water emulsions stabilized by surfactant-chitosan layers. *LANGMUIR* 21 (14): 6228-6234 JUL 5 2005
- 17. Klinkesorn U, Sophanodora P, Chinachoti P, Decker EA, McClements DJ. Encapsulation of emulsified tuna oil in two-layered interfacial membranes prepared using electrostatic layer-by-layer deposition. *FOOD HYDROCOLLOIDS* 19 (6): 1044-1053 NOV 2005
- 18. Gu YS, Decker EA, McClements DJ. Production and characterization of oil-in-water emulsions containing droplets stabilized by multilayer membranes consisting of beta-lactoglobulin, iota-carrageenan and gelatin. *LANGMUIR* 21 (13): 5752-5760 JUN 21 2005
- 19. Klinkesorn U, Sophanodora P, Chinachoti P, Decker EA, McClements DJ. Increasing the oxidative stability of liquid and dried tuna oil-in-water emulsions with electrostatic layer-by-layer deposition technology. *JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY* 53 (11): 4561-4566 JUN 1 2005
- 20. Surh J, Gu YS, Decker EA, McClements DJ. Influence of environmental stresses on stability of OM emulsions containing cationic droplets stabilized by SDS-fish gelatin membranes. *JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY* 53 (10): 4236-4244 MAY 18 2005
- 21. Aoki T, Decker EA, McClements DJ. Influence of environmental stresses on stability of O/W emulsions containing droplets stabilized by multilayered membranes produced by a layer-by-layer electrostatic deposition technique. *FOOD HYDROCOLLOIDS* 19 (2): 209-220 MAR 2005
- 22. Cho YH, McClements DJ. In situ electroacoustic monitoring of polyelectrolyte adsorption onto protein-coated oil droplets. *LANGMUIR* 23 (7): 3932-3936 MAR 27 2007
- 23. Gu YS, Decker EA, McClements DJ. Irreversible thermal denaturation of beta-lactoglobulin retards adsorption of carrageenan onto beta-lactoglobulin-coated droplets. *LANGMUIR* 22 (18): 7480-7486 AUG 29 2006
- 24. McClements DJ. Theoretical analysis of factors affecting the formation and stability of multilayered colloidal dispersions. *LANGMUIR* 21 (21): 9777-9785 OCT 11 2005.