



**innospec**

Touching Everyday Lives

## **Structured Liquid Surfactants Systems for Personal Cleansing Applications**

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Cologne

June 2015

# Presentation Overview

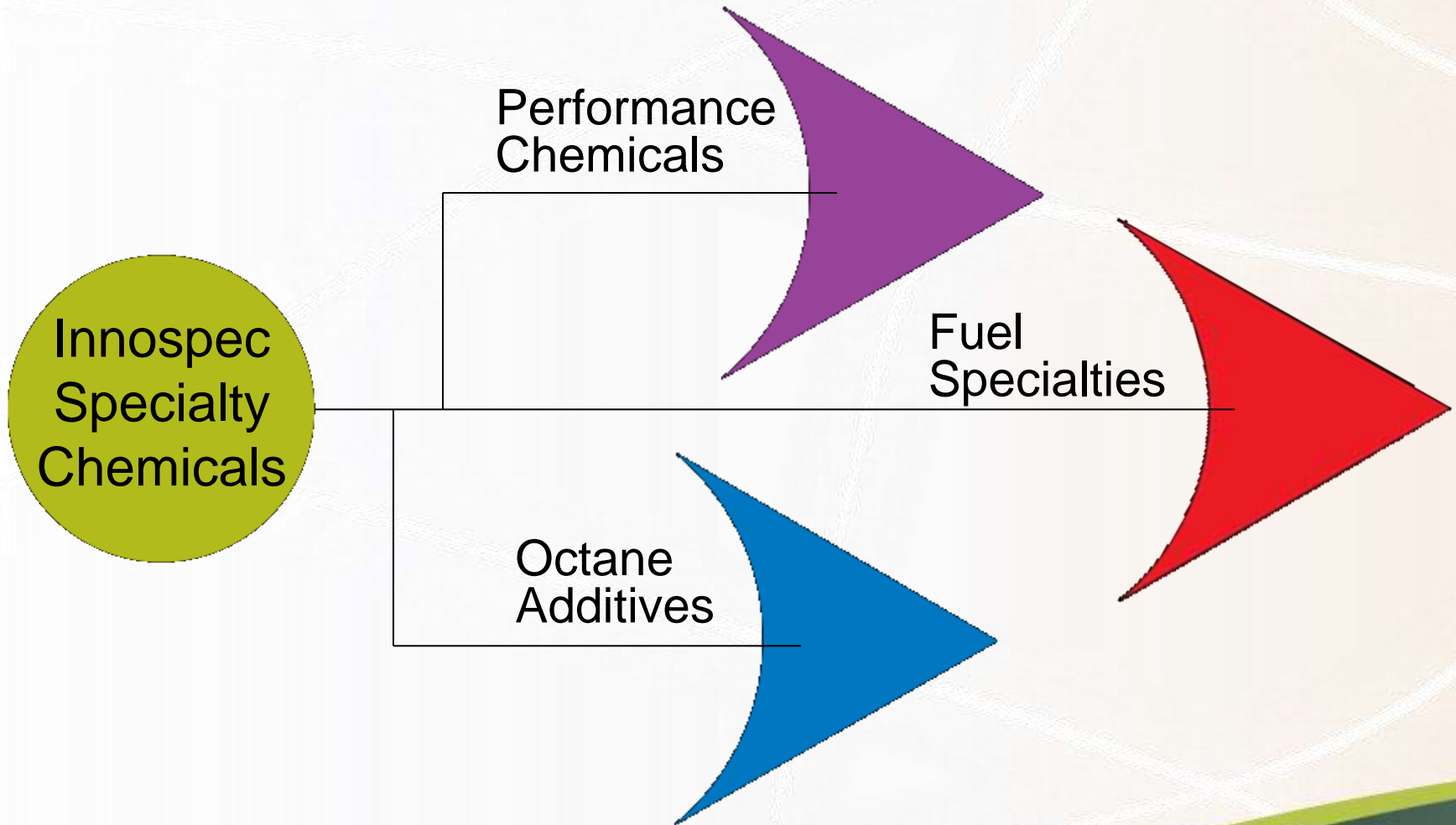
- Introduction to Innospec
- Structured Liquid Systems (SLS)
- Advantages of using SLS in Personal Care
- Current Market Technology and Products
- How to produce a SLS
- Determination and Characterisation
- Example Formulation

# Innospec – At a Glance

- ▶ Focused on Specialty Chemicals
- ▶ 1000 employees
- ▶ 23 countries
- ▶ NASDAQ listed
- ▶ UK HQ in Ellesmere Port
- ▶ Turnover 960\$m in 2014



Innospec consists of three market sectors



# Performance Chemicals' markets

- ▶ Personal Care
- ▶ HI & I
- ▶ Plastics and Polymers
- ▶ Fragrances



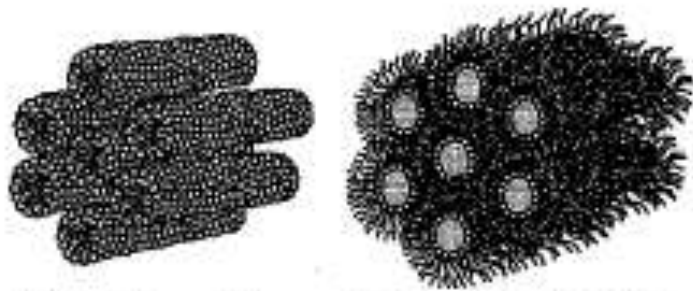
# Introduction to structured liquid systems

- ▶ Systems where the surfactants are in liquid crystalline phases, particularly of interest lamellar phase
- ▶ Typically formed at high surfactant concentrations
- ▶ They are used in a variety of applications
  - Personal care
  - Liquid laundry detergents
  - Pharmaceutical



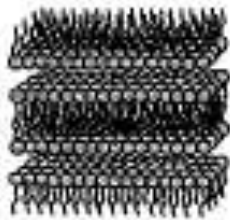
Schematic of Lamellar Phase

# Surfactant Phases – packing diagram



Hexagonal phase (H<sub>1</sub>)

Inverse hexagonal phase (H<sub>2</sub>)



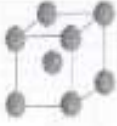








Lamellar phase (L<sub>α</sub>)



Cubic phase (I<sub>1</sub>)



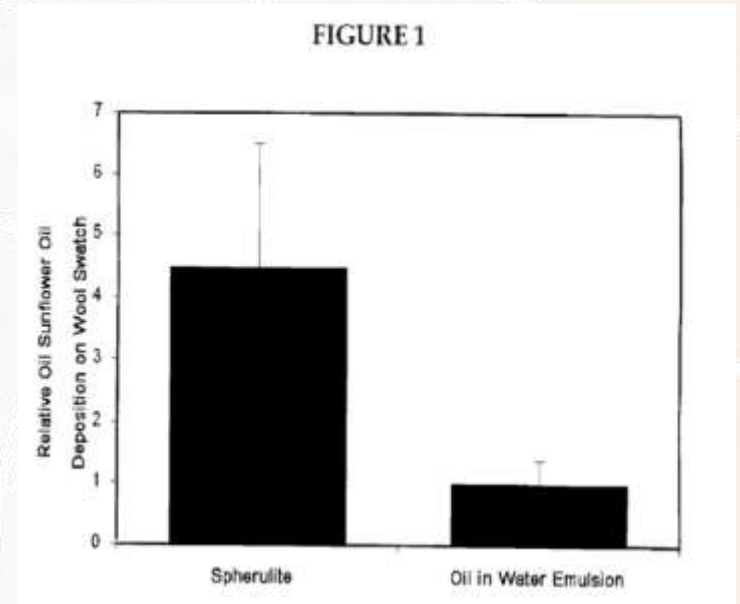
Bicontinuous cubic phase (V<sub>1</sub>)

Micelle Shape	Liquid Crystal	Packing Constraints	LC and Surfactant		Notation
Spherical	Cubic	$a \leq \frac{3v}{l_t}$			I <sub>1</sub>
Rod	Hexagonal	$a \leq \frac{2v}{l_t}$			H <sub>1</sub>
-	Cubic	-		-	V <sub>1</sub>
Disc	Lamellar	$a \leq \frac{v}{l_t}$			L <sub>α</sub>
Curved Continuous Bilayer	Cubic	-			V <sub>2</sub>

Where  $a$  is the head group cross sectional surface area,  $v$  is the volume of the hydrophobic group and  $l_t$  the all trans length of the alkyl chain.

# Advantages of SLS Formulations

- ▶ Allows the suspension of particles (e.g beads)
- ▶ Allows high levels of oil to be incorporated
- ▶ Improved deposition of oils and fragrances on to hair and skin compared to micellar systems<sup>1,2,3</sup>
- ▶ Stable under high temperature conditions
- ▶ Incorporation of usually incompatible materials e.g. UV filters
- ▶ Easy pumping and delivery from packaging



1. D. Bendejaque, *Cosmetics and toiletries*, Vol 125, No: 11, p22-29
2. C. Mabile, *Cosmetics and toiletries*, Vol 128, No :1, p34-41
3. US2007155638A1 (Figure 1)



# Incorporated Oil levels in SLS Systems

Cosmetic Oil	Formulation typical values %
Dimethicone	1-5
Dimethiconol	1-5
Rapeseed Oil	5-50
Sunflower Oil	5-50
C12-C15 Alkylbenzoate	5-15
Dipropylene glycol dibenzoate	5-15
Argan Oil	1-5
Avocado Oil	1-5
Coconut Oil	5-50
Olive Oil	5-50

# Key Personal Care Applications

## ▶ Shower gels

- Enhanced (24 hour) moisturization (high oil levels with foaming)
- Visual effects are desired e.g. layers
- Incompatible ingredients can be an issue

## ▶ Skin cleanser

- Suspend objects for either visual or performance (beads)
- Incompatible ingredients can be an issue

## ▶ Shampoos

- Improved deposition of conditioners on the hair
- Good foaming properties
- Incompatible ingredients can be an issue
- Visual effects are desired

# Example products on the market



Aqua, **Sodium Lauryl Methyl Isethionate**, **Sodium Lauroamphoacetate**, **Cocamide MIPA**, Oryza Sativa (Rice) Bran oil, Glycerin, Dimethicone, Xanthan Gum, Cellulose Gum, Guar Hydroxypropyltrimonium Chloride, Citric Acid, Butyrospermum Parkii Butter Extract (Shea Butter), Carica Papaya Seed Oil, Parfum (Fragrance), Citrus Sinensis Peel Oil Expressed, Laureth-8, Succinoglycan, Methylchloroisothiazolinone, Methylisothiazolinone, Sodium Benzoate



Aqua, Glycerin, Helianthus Annuus Seed Oil, Hydrogenated Soybean Oil, **Cocamidopropyl Betaine**, Sodium Hydroxypropyl Starch Phosphate, **Sodium Laureth Sulfate**, **Sodium Cocoyl Glycinate**, **Lauric Acid**, Parfum, **Sodium Lauroyl Isethionate**, **Sodium chloride**, Stearic Acid, Guar Hydroxypropyltrimonium Chloride, Citric acid, Sodium Palmitate, BHT, Sodium Isethionate, Sodium Stearate, Tetrasodium EDTA, Sodium Palm Kernelate, Zinc Oxide, Tetrasodium Etidronate, Alumina, DMDM Hydantoin, Sodium benzoate, Benzyl alcohol, Butylphenyl Methylpropional, Citronellol, Hexyl Cinnamal, Limonene, Linalool, CI 77891



Water, Petrolatum, Mineral Oil, **Sodium Trideceth Sulfate**, **Sodium Lauryl Sulfate**, **Sodium Lauroamphoacetate**, **Sodium Chloride**, **Trideceth-3**, Fragrance, Prunus Amygdalus Dulcis (Sweet Almond) Oil, Citric Acid, Guar Hydroxypropyltrimonium Chloride, Acrylonitrile/Methacrylonitrile/ Methyl Methacrylate Copolymer, Isopentane, Xanthan Gum, Sodium Benzoate, PEG-90M, Disodium EDTA, Methylchloroisothiazolinone, Methylisothiazolinone, Sodium Hydroxide, Red 7



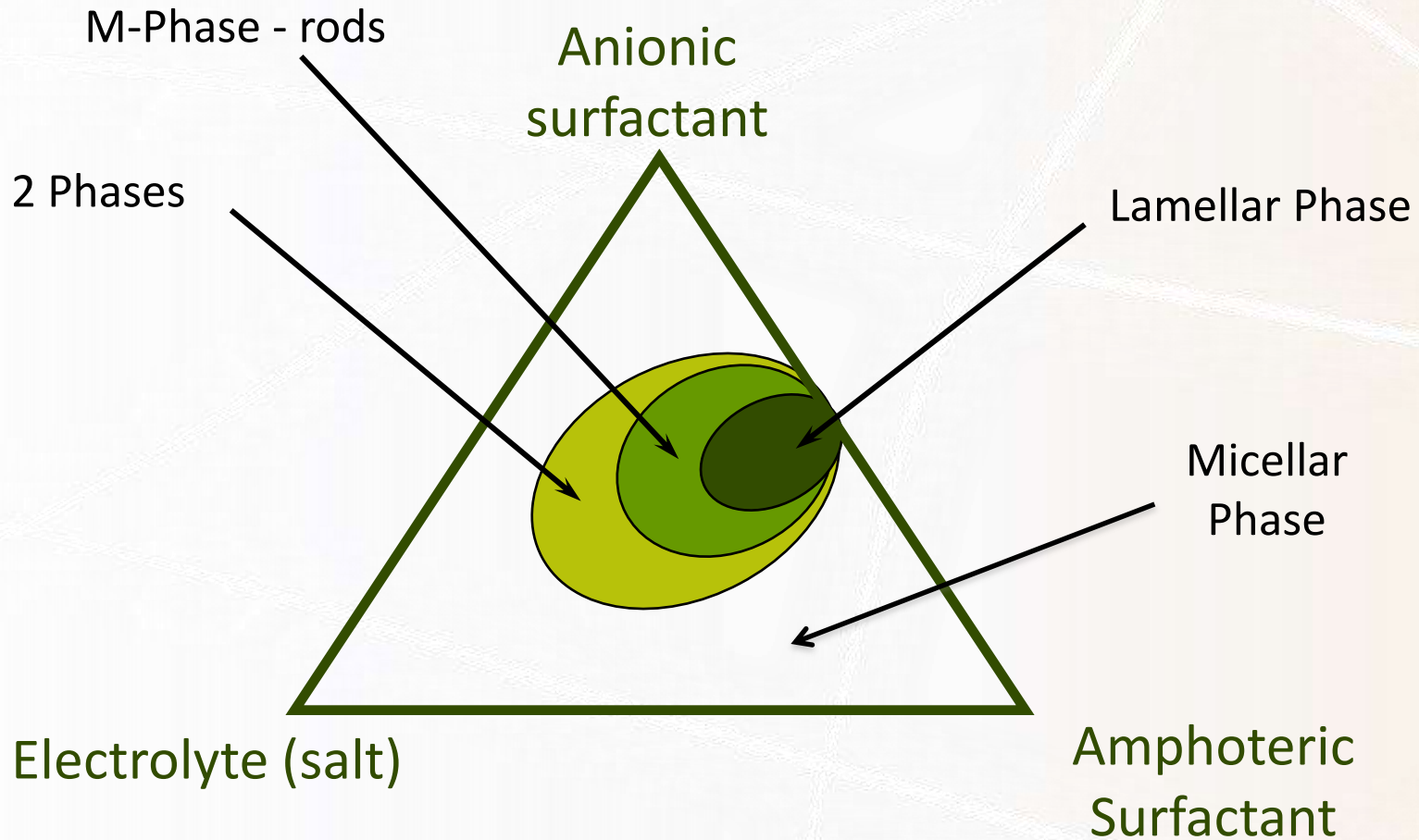
Aqua (Water), Helianthus annuus (Sunflower) seed oil, **Sodium trideceth sulphate**, Butyrospermum parkii (Shea butter), Glycerin, **Sodium chloride**, **Sodium lauroamphoacetate**, **Cocamide MEA**, Parfum (Fragrance), Tocopheryl acetate, Guar gum, Guar hydroxypropyltrimonium chloride, Citric acid, Benzyl salicylate, Linalool, Benzyl benzoate, Hexyl cinnamal, Limonene, Disodium EDTA, Magnesium nitrate, Methylisothiazolinone, Methylchloroisothiazolinone, Magnesium chloride

# Formulating Structured Surfactant Systems

- ▶ Determine the phase properties/diagram of surfactant system.
- ▶ Surfactant system needs to be in lamellar phase
- ▶ Lamellar phase when sheared can deform to form multi lamellar vesicles/ spherulites
- ▶ Some surfactant systems which can form spherulites:-
  - Sodium tetradecyl sulfate/Sodium lauroamphoacetate/cocamide MEA
  - Sodium lauroyl methyl isethionate/sodium lauroamphoacetate/ cocamide MEA
  - Sodium bis (2-ethylhexylsulfosuccinate) /SDS/Salt
  - Poly(oxyethylene alcohol)/water
  - Didecylpyrrolidium bromide



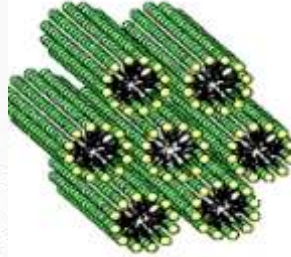
# Typical Phase Diagram



# Surfactant Phase Transition In SLS Formulations



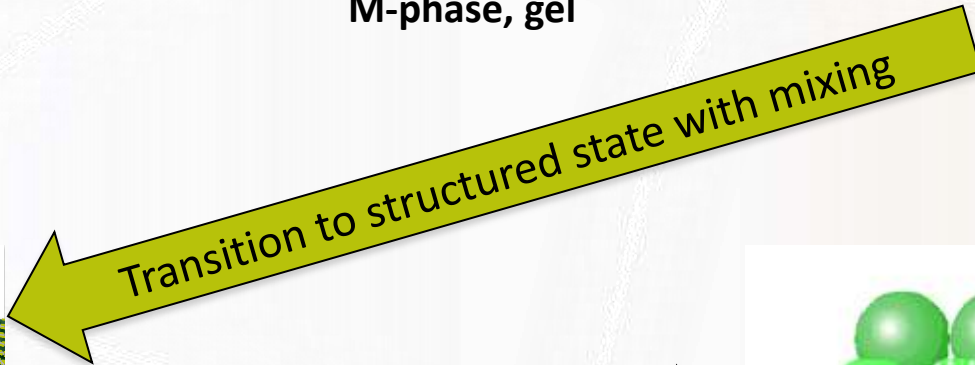
Micellar state



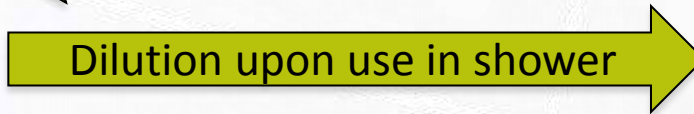
M-phase, gel



Sheer thinning  
Lamellar state



Spherulite  
Structured system

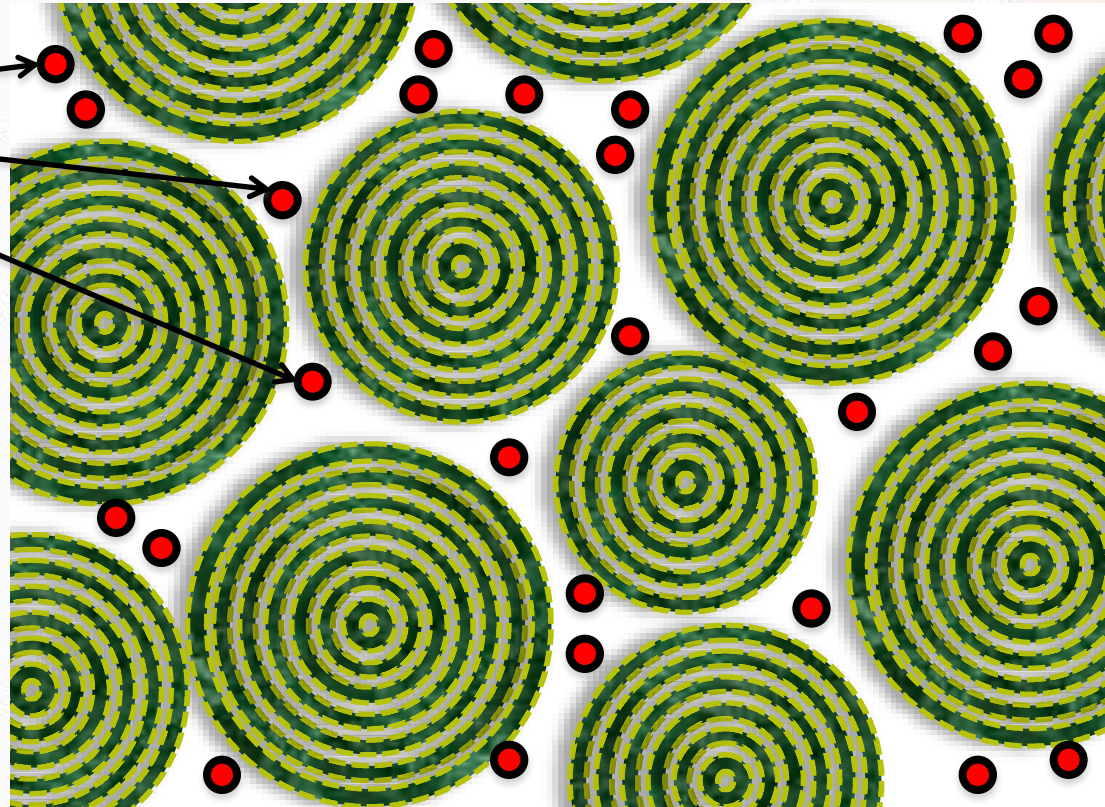


Micellar state

- Foaming
- Cleansing
- Deposition

# Structured surfactant formulation

Insoluble Or  
Incompatible  
Materials





# How do I know I have a SLS?

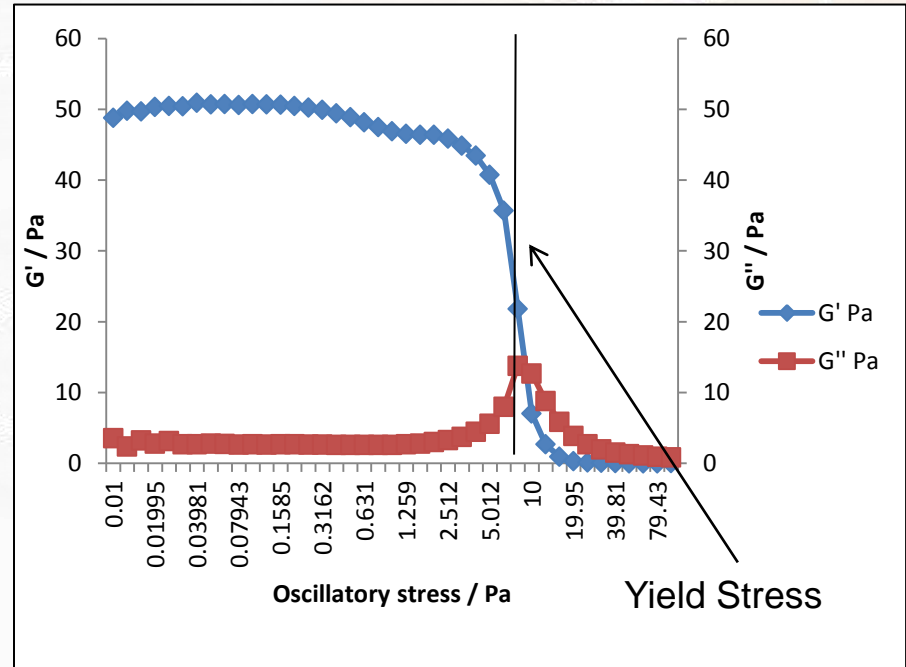
- ▶ Rheology
  - High zero shear viscosity/yield point - shear thinning
- ▶ Polarised Light Microscopy
  - Lamellar phases are birefringent and give characteristic patterns when viewed using polarised light.
- ▶ SAXS
  - Lamellar phases can be determined by characteristic d line spacing and broad peak at 4.5Å.
- ▶ Electron Microscopy
  - Images show round spheres of spherulites in cryo SEM or layers in cryo TEM

# Rheology

Rheology of lamellar phase and spherulites can be studied using rheology

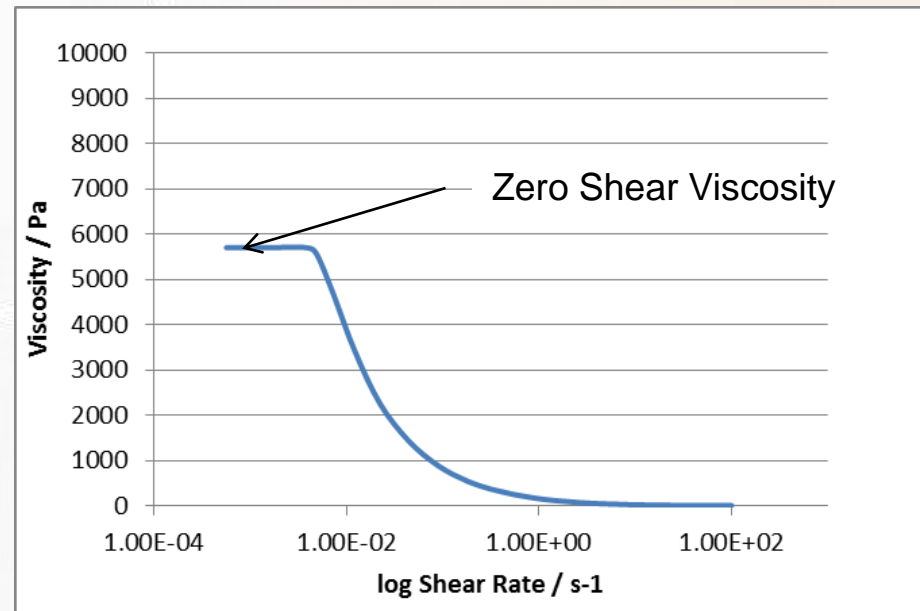
## Oscillatory methods

- ▶ linear visco-elastic region
  - Poking a Jelly



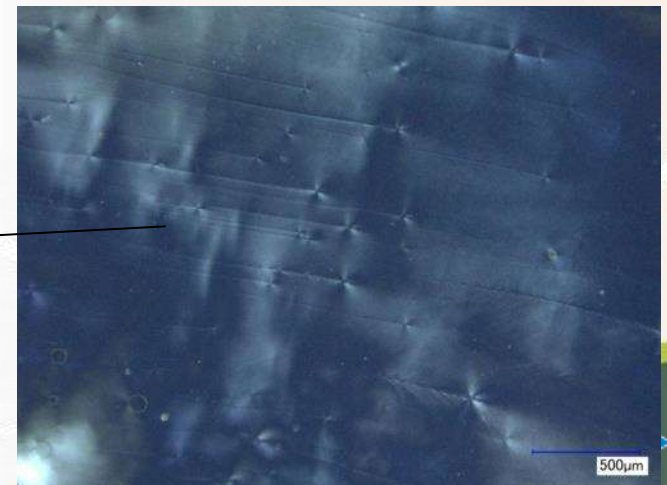
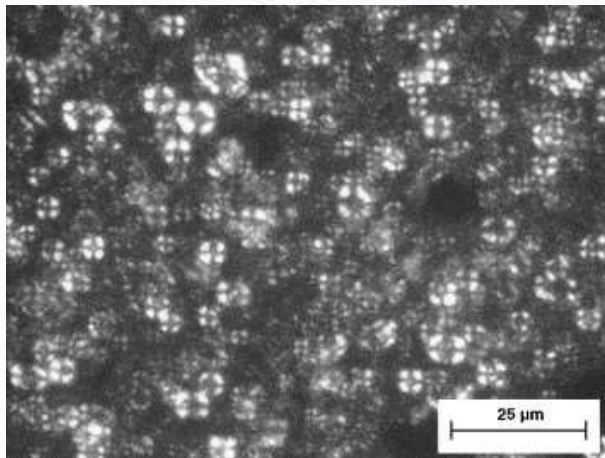
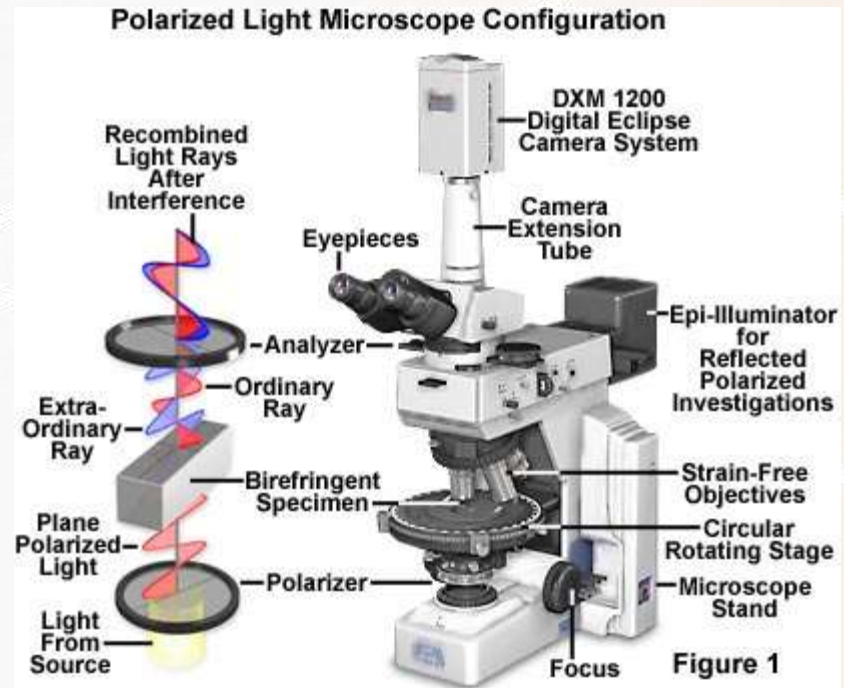
## Flow methods

- ▶ Equilibrium shear rate ramp
- ▶ Linear region at low shear rate (Zero Shear viscosity)



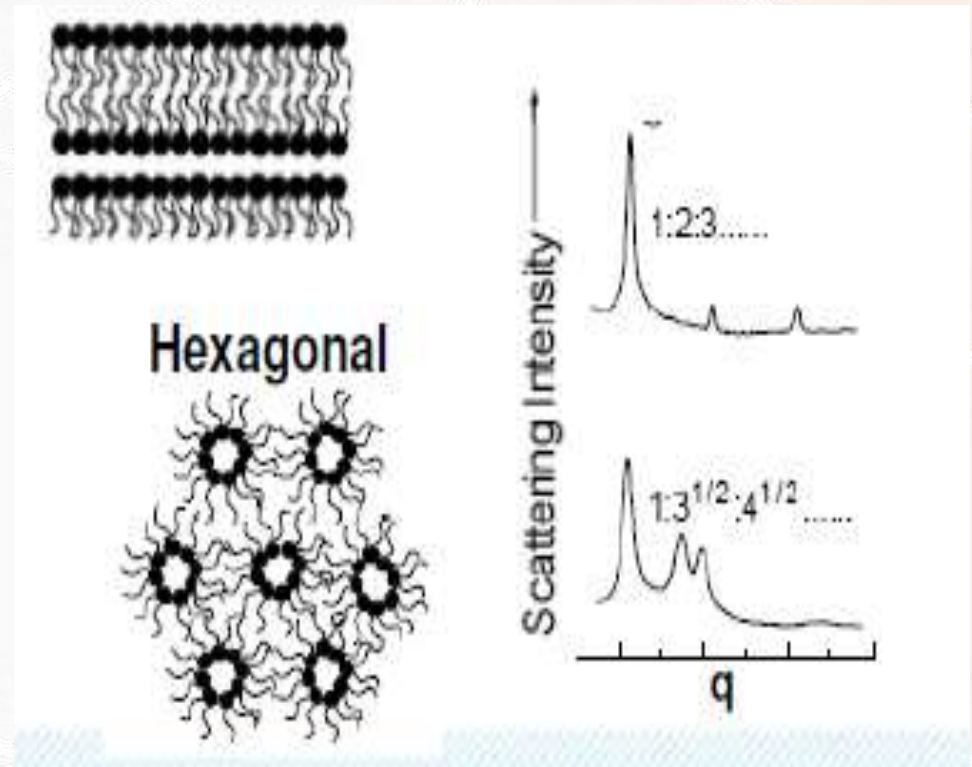
# Polarised Light Microscopy

- ▶ Lamellar phase surfactant systems are birefringent materials
- ▶ Refractive index dependant on polarisation of light
- ▶ Defects in lamellar phase cause characteristic Maltese cross patterns



# SAXS Analysis

- ▶ Definitive characterisation technique
- ▶ Determination of d spacing distance between layers
- ▶ Expensive and limited research institutions where it can be done



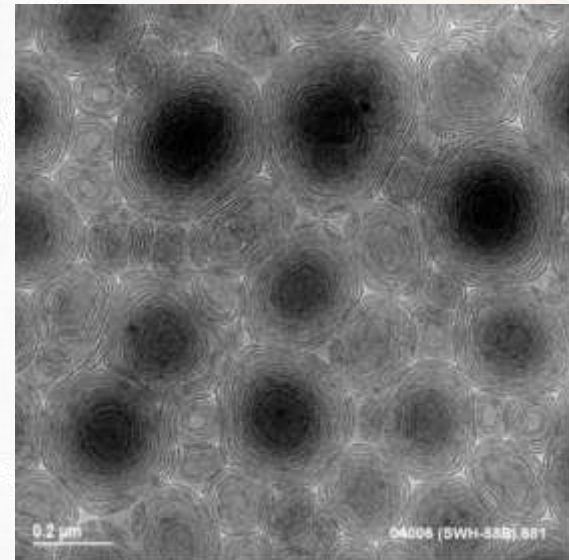
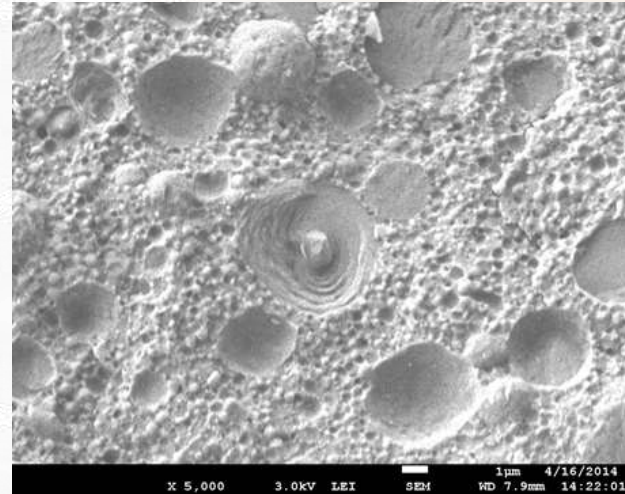
# Electron Microscopy

Electron Microscopy one of the most definitive characterisation techniques

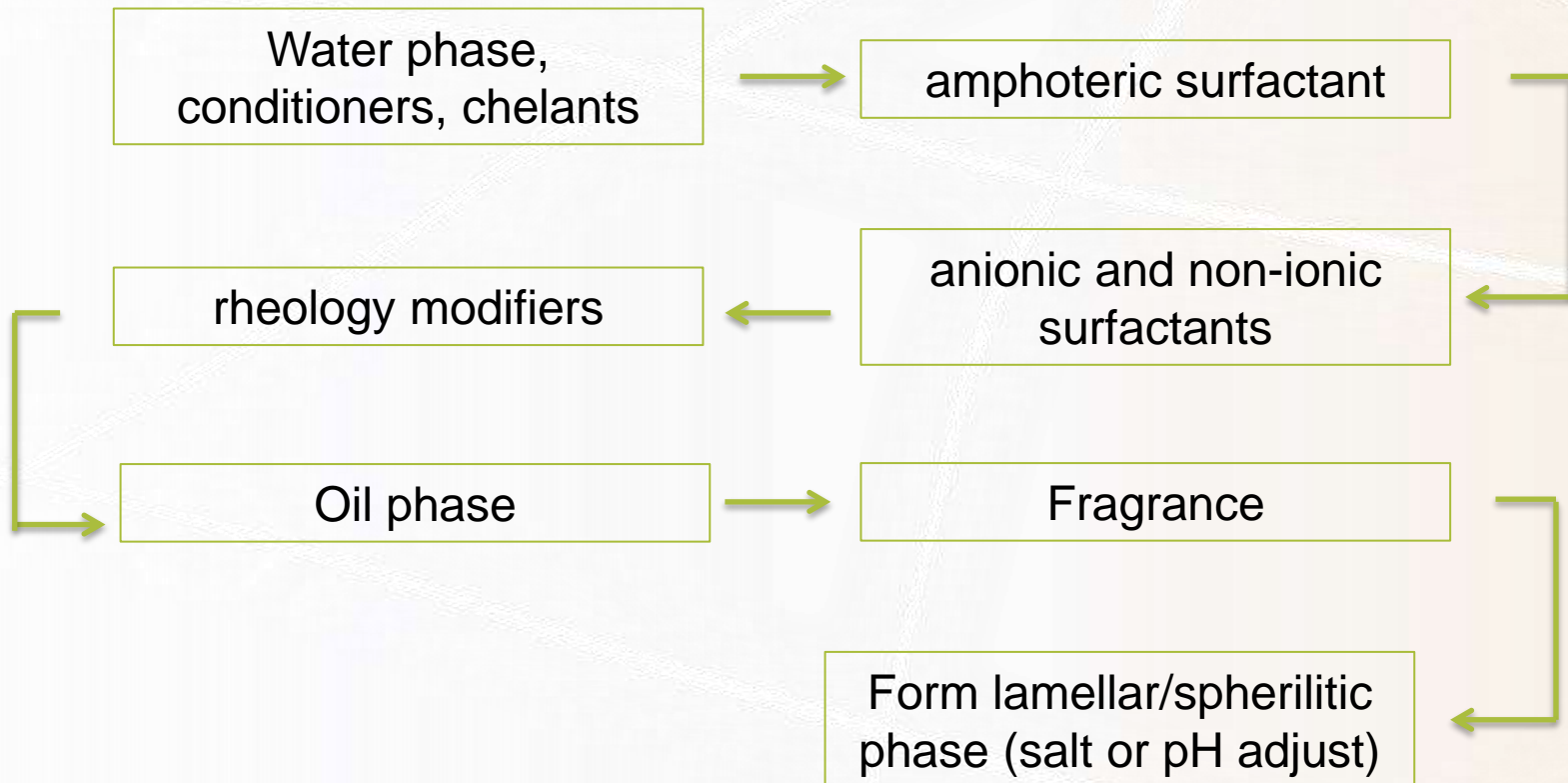
Cryo SEM with high resolution see spherical structures

Cryo TEM high resolution see layers in 2D structure

Expensive and equipment availability  
Outsourced either in academia or test institutes



# Classical Formulation Procedure



# Structured Liquid System Concentrates

- ▶ Ease of formulation (lamellar phase already formed)
- ▶ SLS surfactant concentrates developed:-
  - Based on sulfates
    - Sodium trideceth sulfate, Sodium lauroamphoacetate, cocamide MEA
  - Based on sulfate-free technology (Innospec technology)
    - Sodium lauroyl methyl isethionate, Sodium lauroamphoacetates, Cocamide MEA

# Benefits of Sodium Lauroyl Methyl Isethionate vs Sodium Trideceth sulfate in personal care

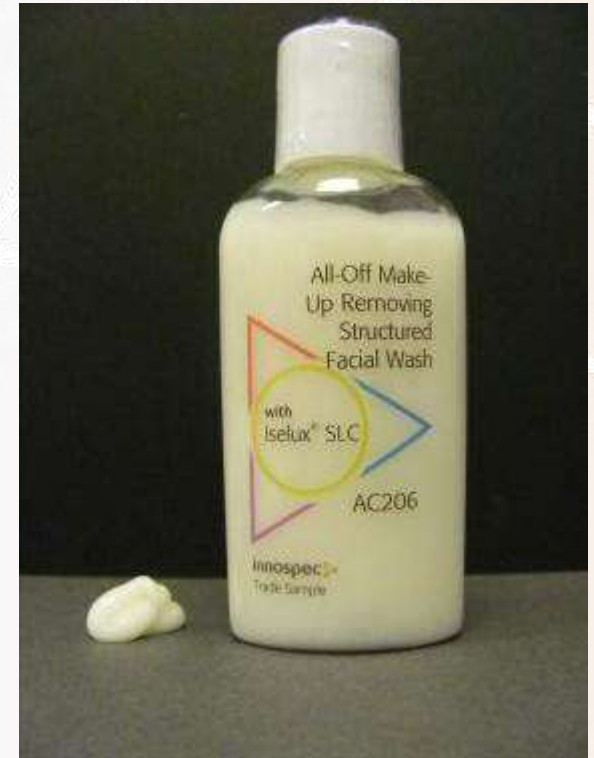
<b>Property</b>	<b>Sodium Lauroyl Methyl Isethionate*</b>	<b>Sodium Trideceth Sulphate</b>
Sulfate Free	Yes	No
1,4 Dioxane Free	Yes	No
Ethylene Oxide Free	Yes	No
Biodegradability	Readily	Inherently
Hydrophobe Origin	Natural	PetroChemical
Foam Type	Tight/Small	Larger/ More Open
Mildness	Mild As Is	Mildness Must Be "Created"

\* Sodium Lauroyl Methyl Isethionate is available from Innospec under the tradename Iselux®



# Innospec Formulation – Make up Remover

INCI Ingredient	% w/w Active
A) Aqua	q.s to 100
Sodium Chloride	4.00
Citric Acid	Trace
B) Guar Hydroxypropyltiamonium Chloride	0.20
C) <b>Disodium Cocoamphoacetate</b>	2.85
<b>Sodium Methyl Cocoyl Taurate</b>	2.3
D) Cyamopsis Tetragonoloba Guar Gum	0.5
Glycerine	1.00
E) <b>Sodium Lauroyl Methyl Isethionate</b>	9.6
<b>Cocamide MEA</b>	3.50
<b>Cocamidopropyl Betaine</b>	3.0
F) <b>Rapeseed Oil</b>	10.00
C12-C15 Alkyl Benzoate	2.00
G) Preservative, dye, fragrance	q.S
H) Citric Acid (50% w/w soln)	q.s to pH 5.0-6.0



# Summary

Structured Liquid Systems in personal care can give:-

- High oil incorporation
- Good foaming properties
- Enhanced deposition of actives, oils and fragrance
- Can be formed with using a range of surfactants
- Improved temperature stability
- Surfactant concentrates can be used to simplify manufacture



**Thank you for your attention**

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