Anionic / Cationic Silicone

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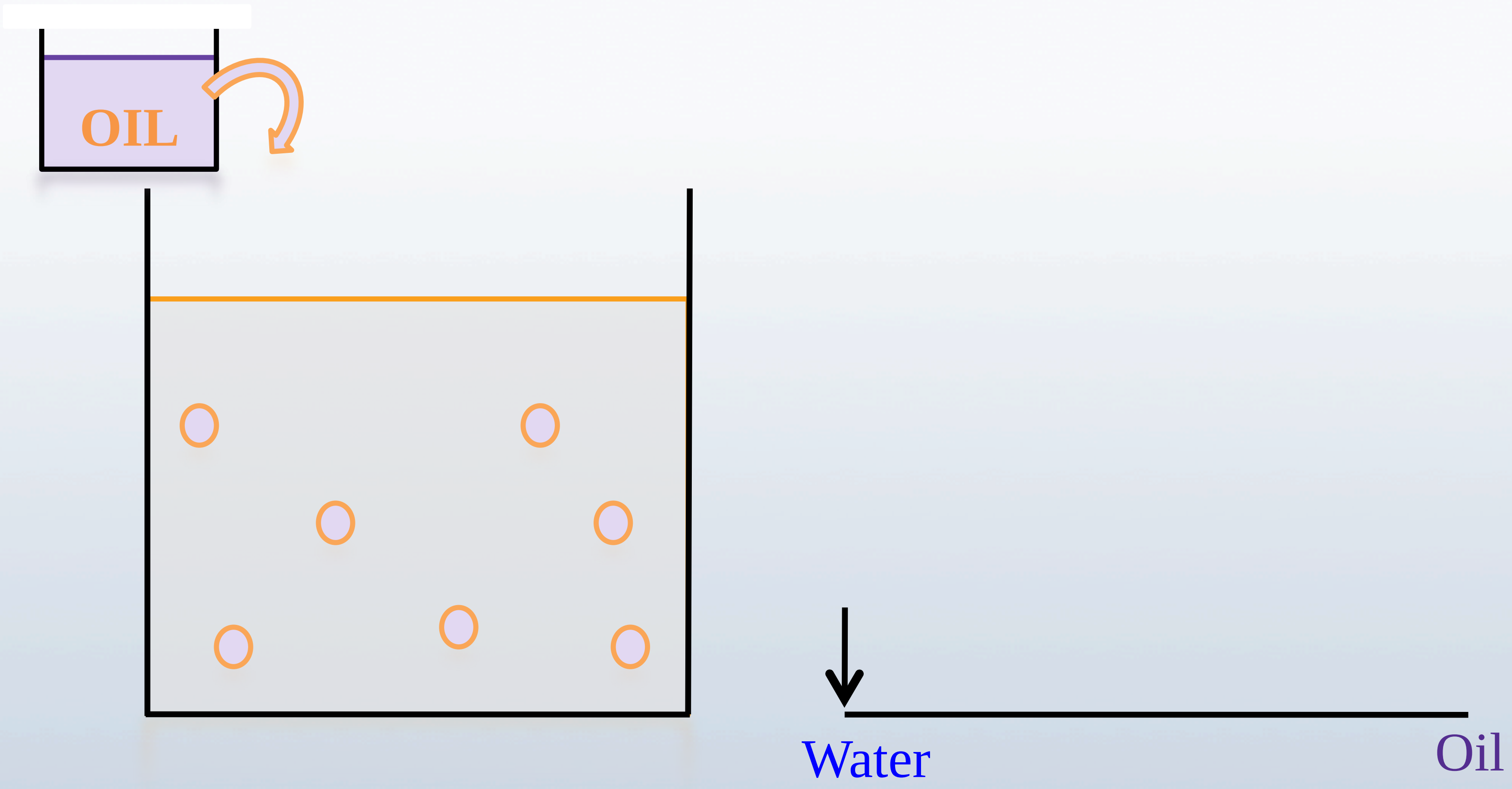
Emulsion to Lamellar Structures

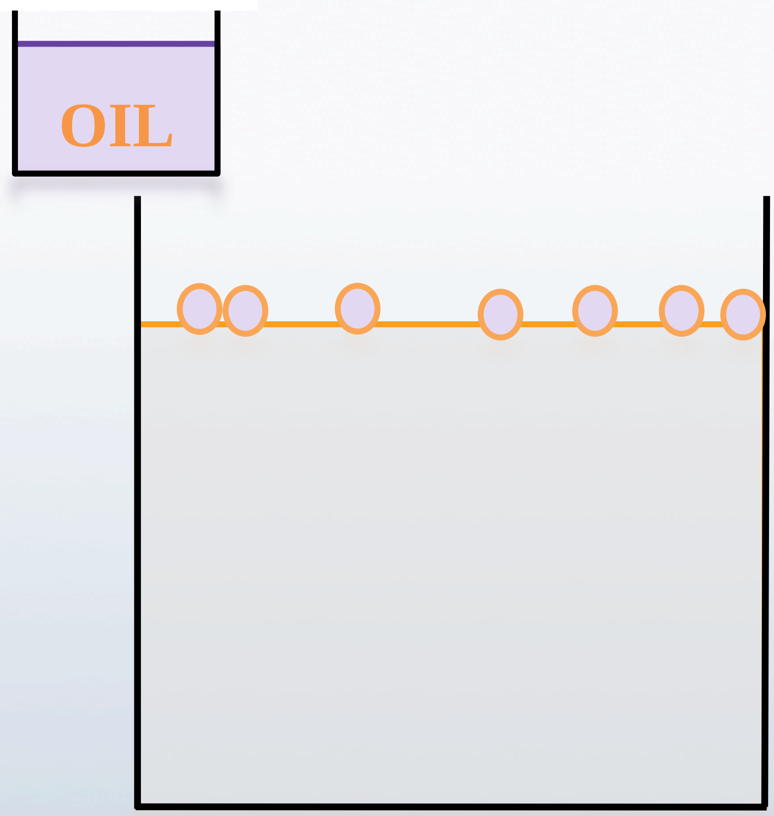
- Surfactant gels are formed by the association of hydrated or solvated surfactant molecules.[1]
- The aggregation of surfactants in a lamellar array can be facilitated if there is a High enough surfactant concentration[1]
- Lamellar aggregates are also formed from delicate mixtures of anionic and cationic surfactants in water[2] or mixtures of ionic surfactants and long-chain alcohols in water.[3]

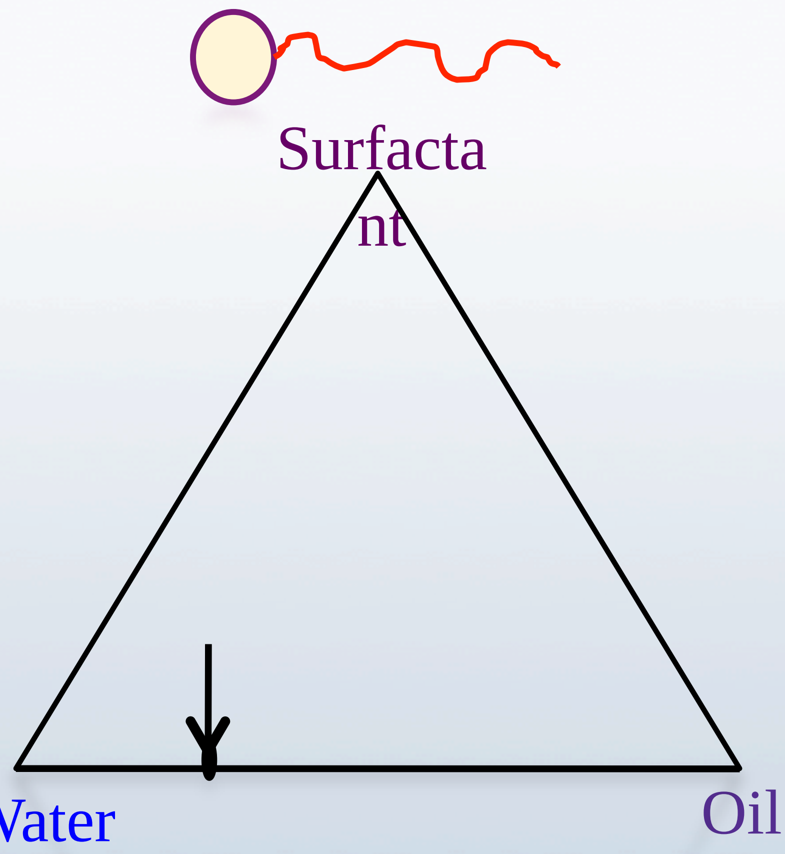
1. http://www.dermotopics.de/english/issue_2_02_e/daniels_novelgels_2_02_e.htm
2. Sein, A.; Engberts, J. *Langmuir* **1995**, *11*, 455 – 465
3. Kaler, E. W.; Herrington, K. L., Murthy, A.K., Zasadzinski, J. A. N. *J. Phys. Chem.* **1992**, *96*, 6698.
4. Strey, R.; Jahn, W.; Porte, G. *Langmuir* **1990**, *6*, 1635

Emulsion to Lamellar Structures



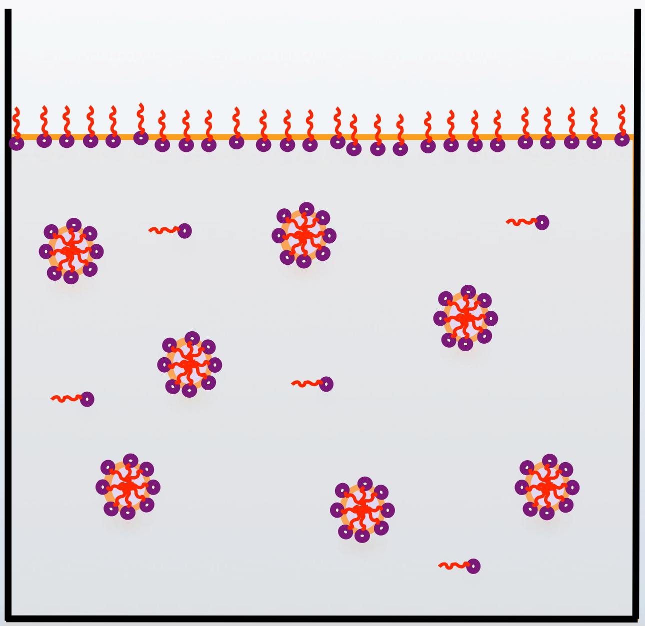
Emulsion to Lamellar Structures

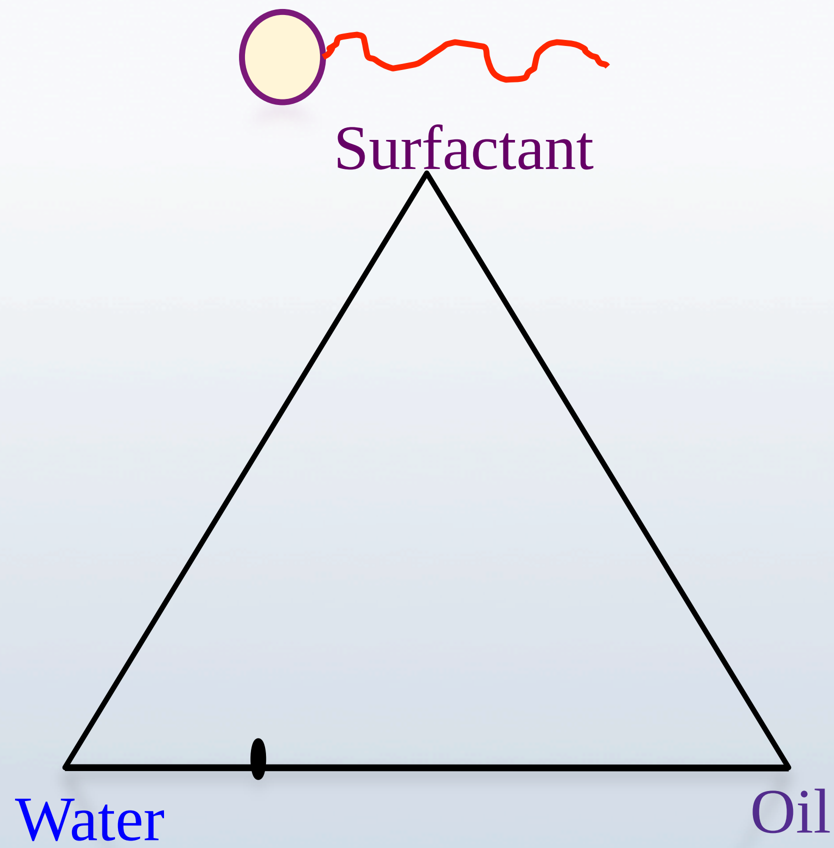




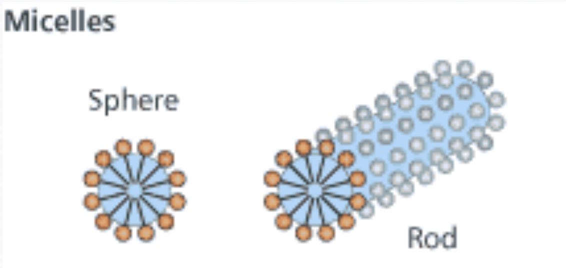
Add Surfactant to stabilize the oil droplets in the water.

Emulsion to Lamellar Structures





Add Surfactant to stabilize the oil droplets in the water.



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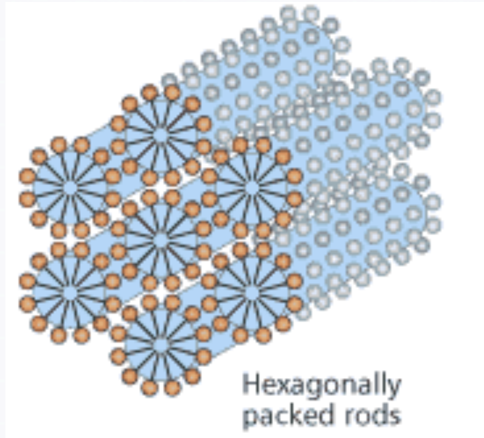
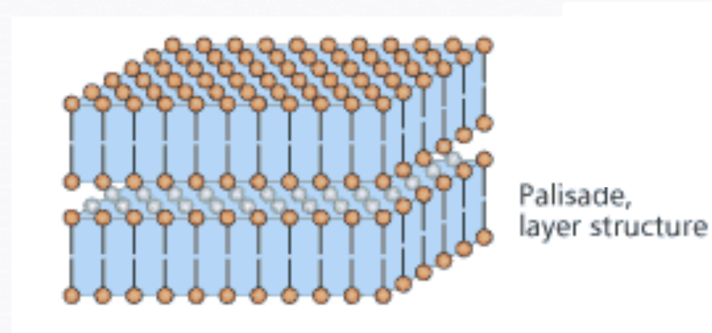
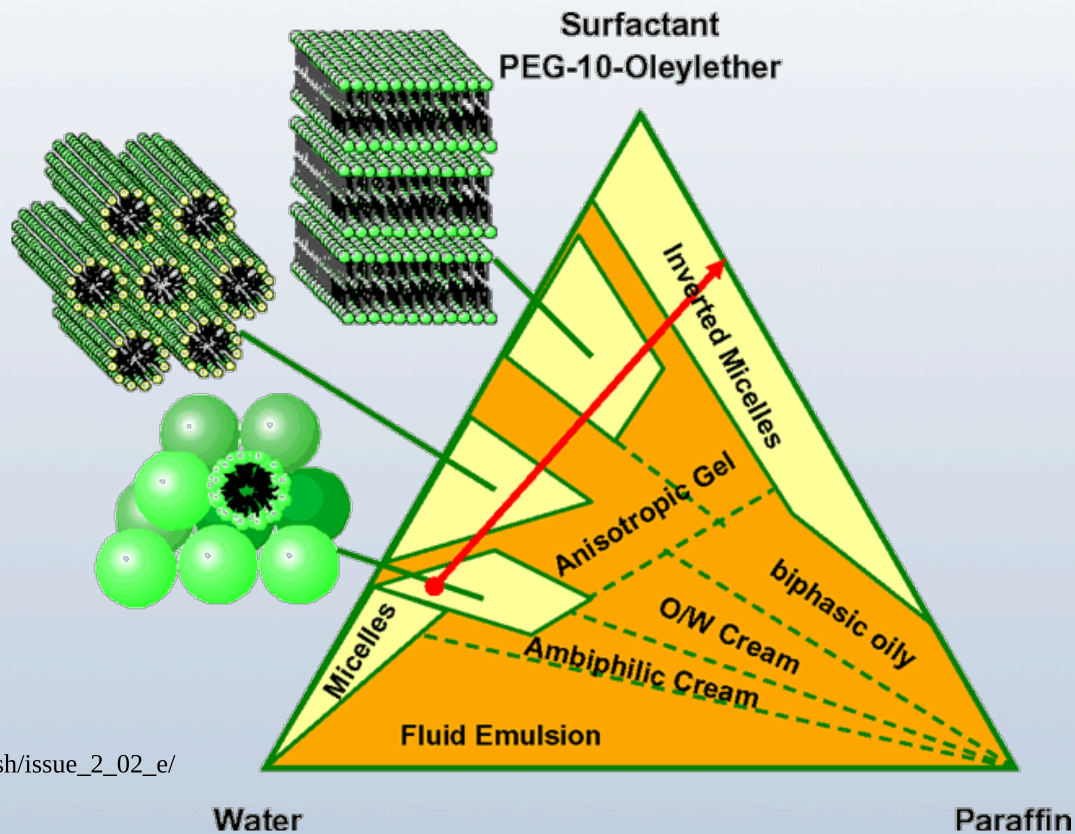




Increasing concentration



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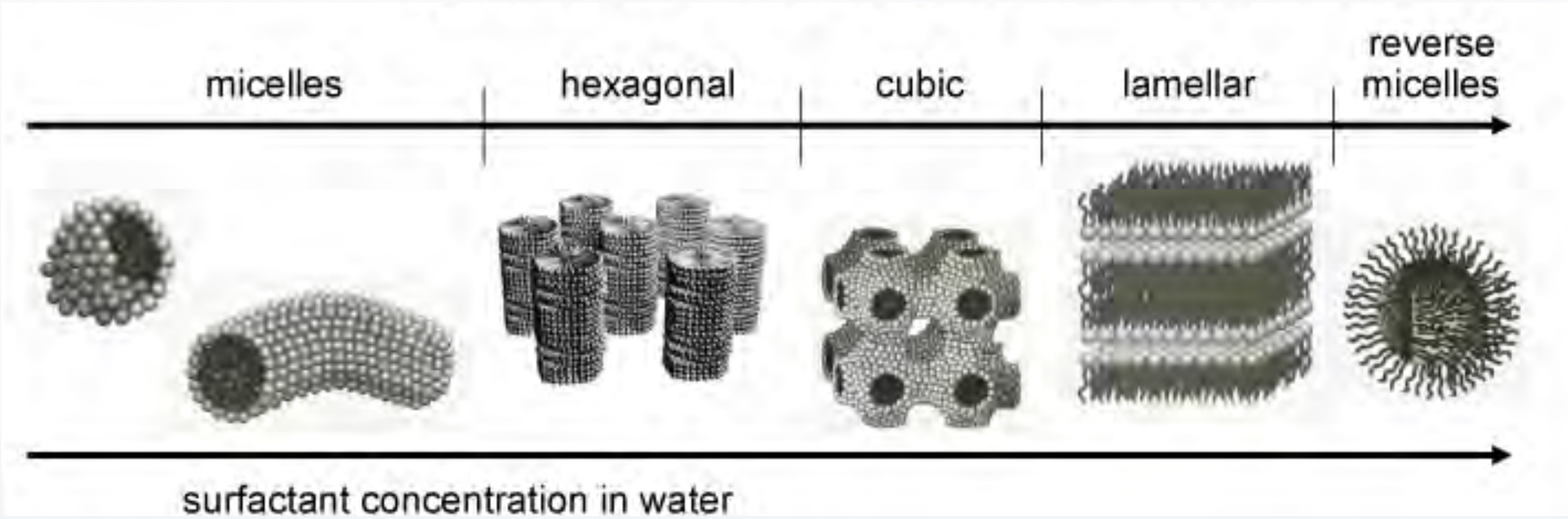
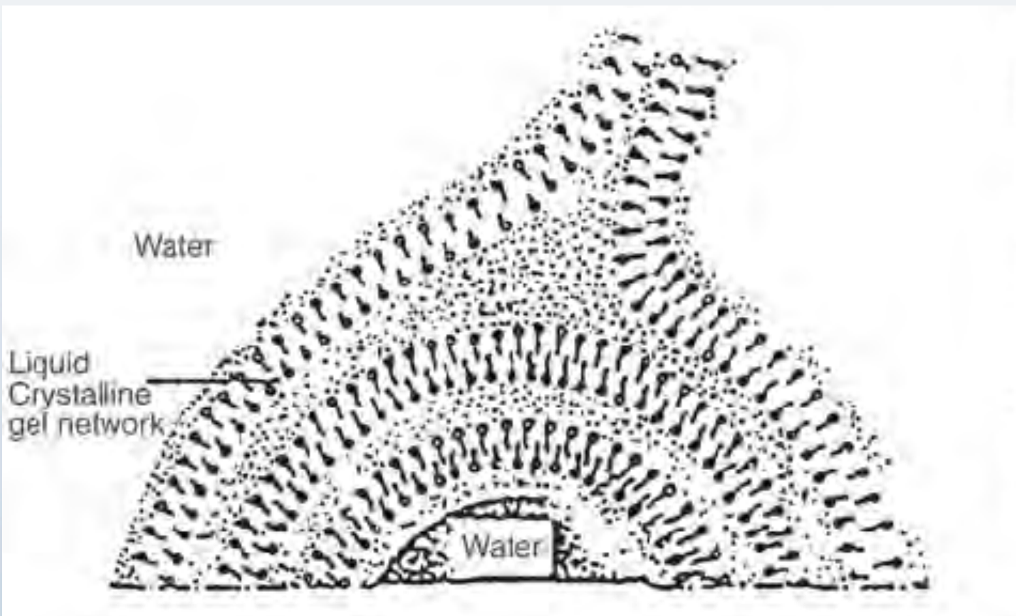
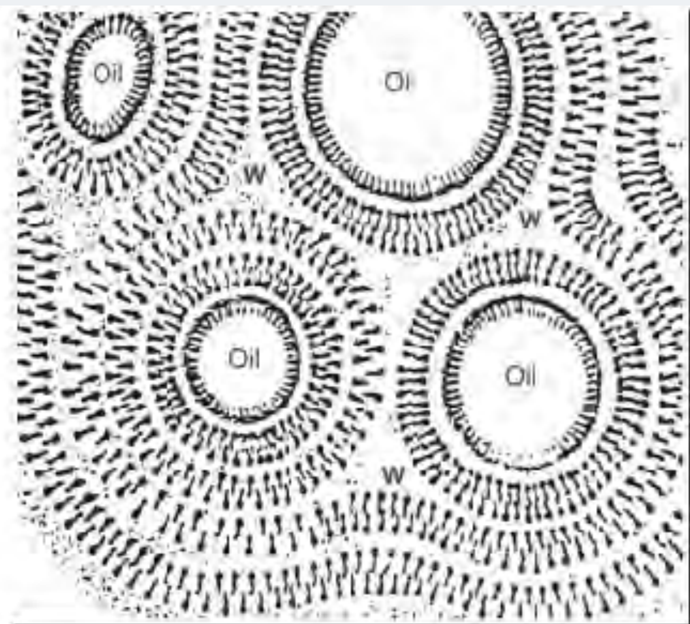
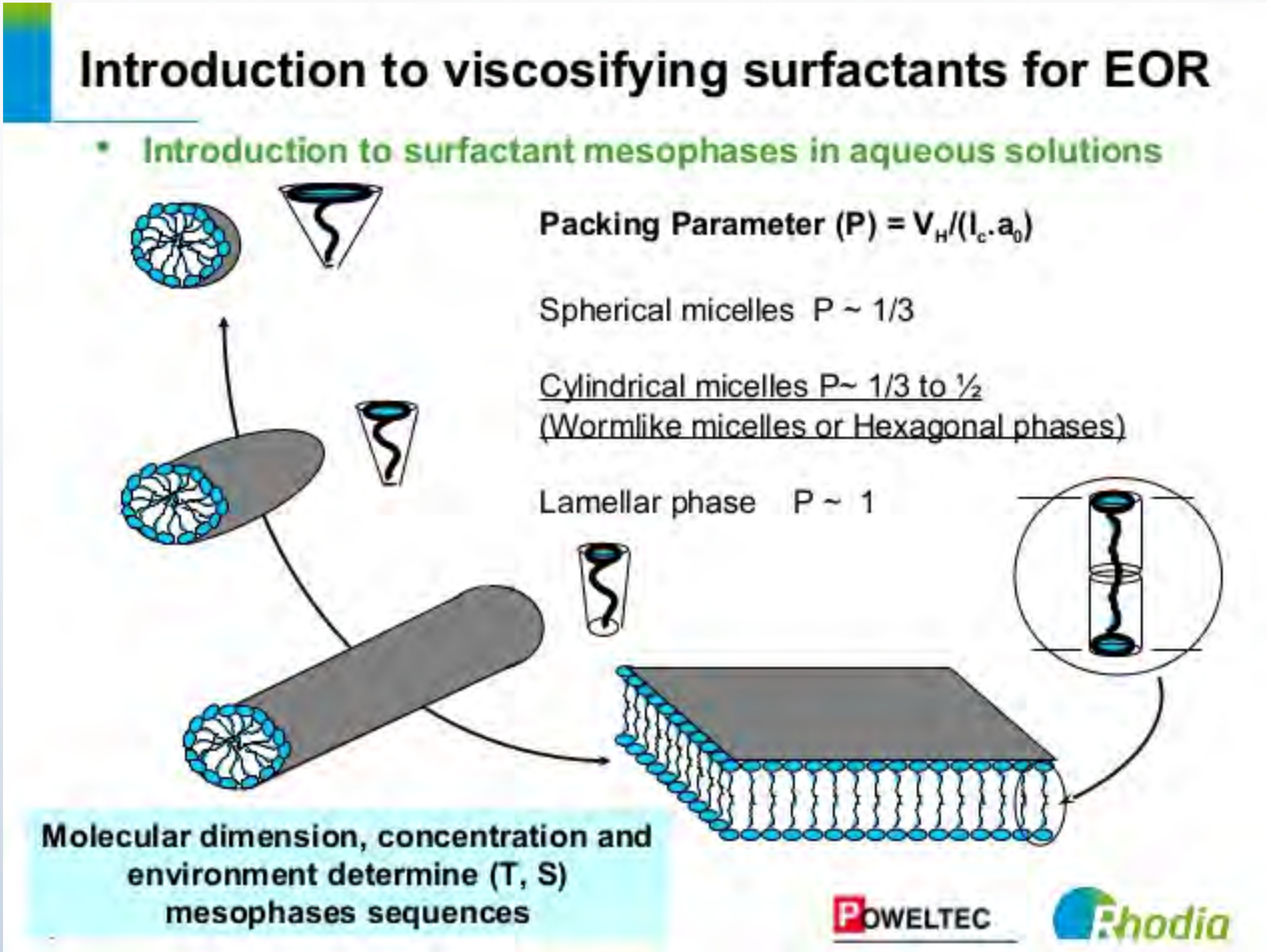


http://cohengroup.lassp.cornell.edu/content/droplet-breakup-structured-fluids





http://www.intechopen.com/books/latest-research-into-quality-control/cosmetics-quality-control



http://www.slideshare.net/
kumar_vic/viscosifying

New Approach

- Anionic and Cationic surfactants when properly chosen can be compatible in emulsion systems.
- These systems can be tailored to make Lamellar emulsions.

- The proper choice of anionic and cationic materials can result in soluble complexes that provide outstanding conditioning, build viscosity in formulation, have low irritation and provide outstanding foam*.

* *Surfactants Strategic Personal Car Ingredients* Allured Publishing 2005 p. 122-1229

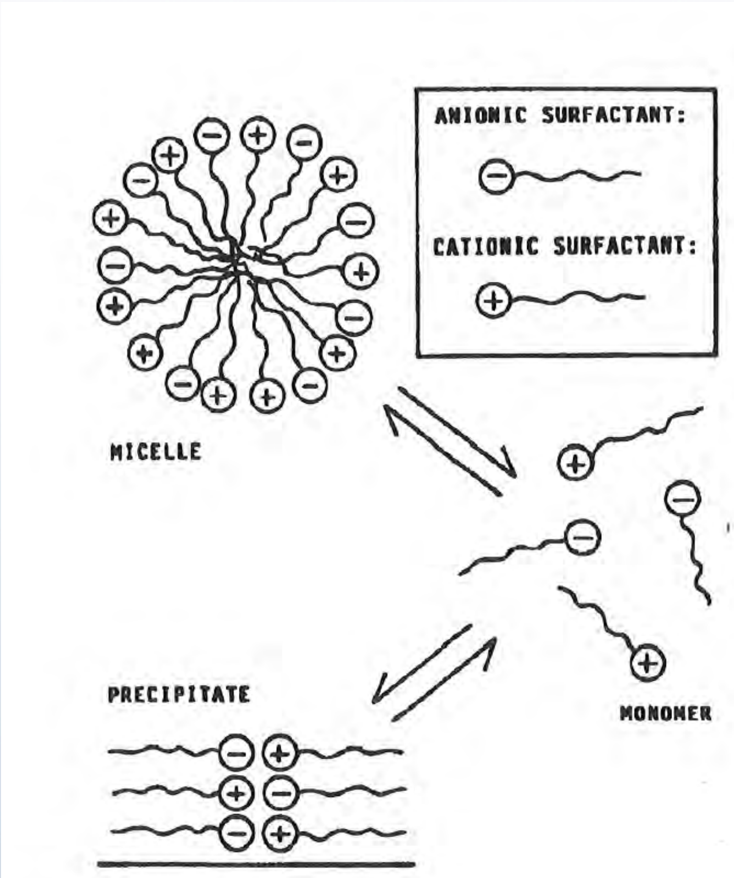
Hard and Soft Anionics and Cationics

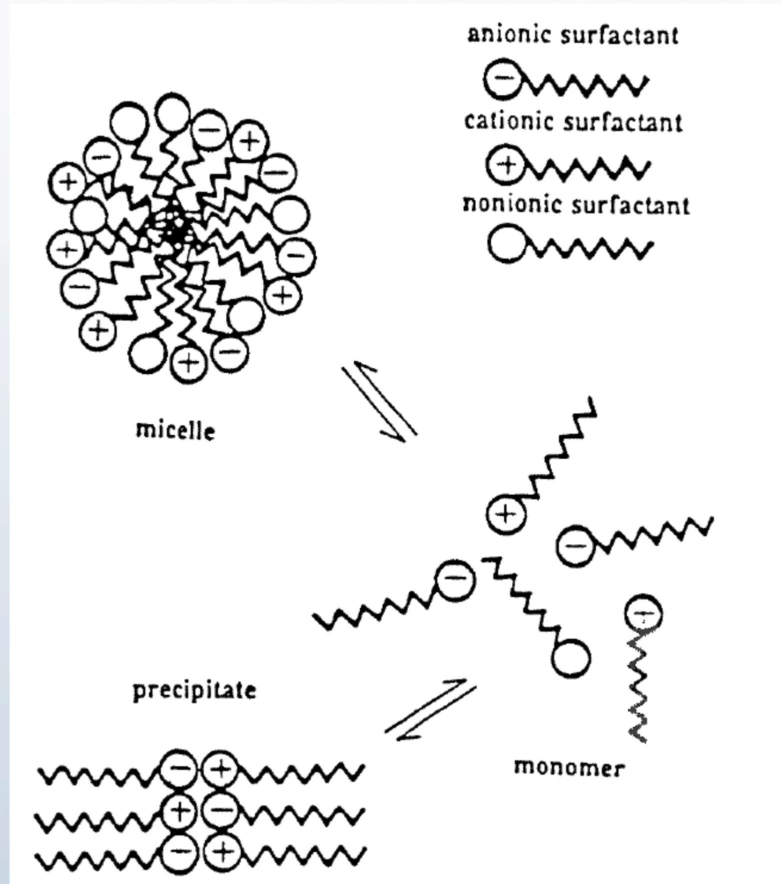
- In 1981 Lucassen-Reyenders et al observed that anionic and cationic materials may be combined, forming aggregates that lower surface tension.

- The concept is that the large aggregates break up more hydrogen bonding than do the counter ions and that energetically these go to the surface first.

Journal of Colloid and Interface Science Vol. 81 No. 1 May 1988

Interactions





J Surfact Deterg (2008) 11:1–11

Interactions

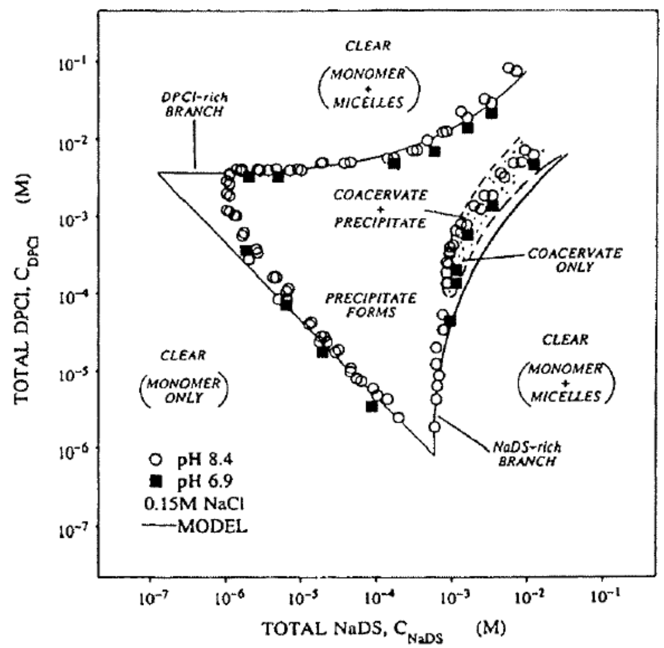


Fig. 3 Effect of the pH on the precipitation phase boundary. Reprinted from [13], with permission from Elsevier

J Surfact Deterg (2008) 11:1–11

Hard and Soft Anionics and Cationics

- In 2005 this observation was extended to other surfactant properties like foam, viscosity building, detergency and the like.
- The description, borrowing from Pearson, was introduced in 2005, showing that there are certain anionic and cationic materials that can be combined to improve the properties of shampoo systems, including anionic and cationic products.

Anionic / Cationic Complex Cosmetics and Toiletries Vol 120 No. 11 Nov 2005

Interaction Chemistry

- In 2006 the concept of using interactions between the surfactants was expanded to amphoterics.
- Some amphoteric materials interact with anionic surfactants to provide benefit to formulations.

- Amphoteric / Anionic Interactions Cosmetics and Toiletries Vol 121 No. 3 March 2006
- Review on anionic/ Cationic Surfactant mixtures Kume et al J. Surfact Deterg (2008) 11:1-11

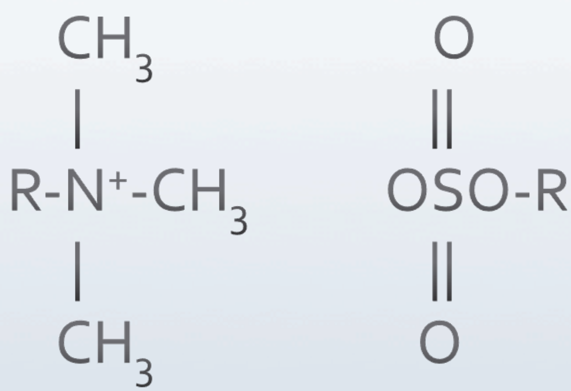
- This approach allows for simple formulation of conditioning shampoos.

- One should re-evaluate other ingredients.

Consider an aqueous solution of:

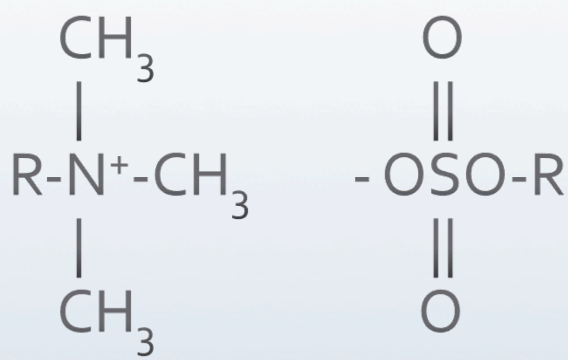
$$
\begin{array}{l}
CH_3 \\
| \\
R\text{-}N^{+}\text{-}CH_3\ \ Cl^{-} \\
| \\
CH_3
\end{array}
\quad \text{and} \quad
\begin{array}{l}
\qquad\quad O \\
\qquad\quad \| \\
Na^{+}\ {}^{-}OSO\text{-}R \\
\qquad\quad \| \\
\qquad\quad O
\end{array}
$$

In solution there is a mixture of:



Na^+ Cl^-

The least soluble of which is:



The anionic/cationic complex

Conditioners

- One aspect of conditioning is wet comb, which is the ability to effortlessly comb the hair in a wet state.

- Another aspect of conditioning relates to providing the hair with a treatment that the consumer perceives as soft and conditioned many hours after the hair has been treated.

Conditioners

- Materials which function in wet comb are not necessarily the same as those that function as dry comb agents.
- The agents that best alter the feel of hair after drying are polymers and most commonly high molecular weight insoluble silicones.

Observation

- Some quats are very insoluble when added to anionic surfactant, others have improved compatibility.

Goal

- Begin to understanding the interaction between specific quats and specific anionic systems allowing for clear high viscosity systems with minimal effect upon other attributes like foam.

- The nature of the anionic / cationic interaction is key to predicting functionality, or lack of functionality of conditioners

Name	R^1	R^2	R^3	Description
AMB	Alkyl (C12)	CH_3	Benzyl	Coco dimethyl benzyl ammonium chloride
AME	Alkyl (C12)	CH_2CH_2OH	CH_3	Coco di-2 hydroxyethyl methyl ammonium chloride
AMG	Alkyl (C12)	CH_3	Glyceryl	Coco dimethyl glyceryl ammonium chloride
AMM	Alkyl (C12)	CH_3	CH_3	Coco tri-methyl ammonium chloride
AEB	Alkyl (C12)	CH_2CH_2OH	Benzyl	Coco di-2 hydroxyethyl benzyl ammonium chloride
AEG	Alkyl (C12)	CH_2CH_2OH	Glyceryl	Coco di-2 hydroxyethyl glyceryl ammonium chloride
CaMB	Castor Amido	CH_3	Benzyl	Ricinoleylamidopropyl dimethyl benzyl ammonium chloride
CaMG	Castor Amido	CH_3	Glyceryl	Ricinoleylamidopropyl dimethyl glyceryl ammonium chloride
DMB	Dimer Amido	CH_3	Benzyl	Dilinoleylamidopropyl dimethyl benzyl ammonium chloride
DMG	Dimer Amido	CH_3	Glyceryl	Dilinoleylamidopropyl dimethyl glyceryl ammonium chloride
DMM	Dimer Amido	CH_3	CH_3	Dilinoleylamidopropyl trimethyl ammonium chloride
MMB	Cocamido	CH_3	Benzyl	Cocamidopropyl dimethyl benzyl ammonium chloride
MMG	Cocamido	CH_3	Glyceryl	Cocamidopropyl dimethyl glyceryl ammonium chloride
MMM	Cocamido	CH_3	CH_3	Cocamidopropyl trimethyl ammonium chloride

Anionic Compatibility

Anionic Compatibility Procedure

- Prepare a 10% active solution of SLS or SLES-2
- Prepare a 10% active solution of Quat to be tested.

Anionic Compatibility Procedure (cont'd)

- Titrate 10% solution of quat into 100 grams of 10% solution of anionic.

- End point is cloudiness or precipitate.

Titration Data (SLS)

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AMB	9.75	4,400	opaque
AME	6.28	<10	Did not form a gel
AMG	30.49	<10	Did not form a gel
AMM	17.63	<10	Did not form a gel
AEB	14.58	<10	Did not form a gel
AEG	29.53	<10	Did not form a gel
CaMB	25.72	1,000	Formed a gel
CaMG	44.47	1,000	Formed a gel
DMB	18.33	<10	Did not form a gel
DMG	40.25	12,000	Formed a gel
DMM	23.85	6,000	Formed a gel
MMB	15.28	14,000	Formed a gel
MMG	31.02	13,000	Formed a gel
MMM	21.25	13,400	Formed a gel

Titration Data (SLS)
Hard Quats – No Gel in Sodium Lauryl Sulfate

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AMB	9.75	<10	Did not form a gel
AME	6.28	<10	Did not form a gel
AEB	14.58	<10	Did not form a gel
AMM	17.63	<10	Did not form a gel
DMB	18.33	<10	Did not form a gel
AEG	29.53	<10	Did not form a gel
AMG	30.49	<10	Did not form a gel

Gel Formers in SLS

Soft Quats

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
MMB	15.28	14,000	Formed a gel
MMM	21.25	13,400	Formed a gel
DMM	23.85	6,000	Formed a gel
CaMB	25.72	1,000	Formed a gel
MMG	31.02	19,200	Formed a gel
DMG	40.25	12,000	Formed a gel

Titration Data (SLES 2)

Quat Sample	Amount of quat solution added to achieve haze point in SLES (g)	Viscosity (cps)	Notes
AMB	18.67	<10	Did not form a gel
AME	4.47	<10	Formed a gel
AMG	25.04	1,000	Formed a gel
AMM	17.44	<10	Did not form a gel
AEB	18.35	<10	Did not form a gel
AEG	38.72	1,000	Formed a gel
CaMB	24.31	1,000	Formed a gel
CaMG	46.23	1,000	Formed a gel
DMB	11.09	<10	Did not form a gel
DMG	28.37	6,800	Formed a gel
DMM	20.00	6,200	Formed a gel
MMB	25.00	<10	Formed a gel.
MMG	26.68	40,000	Formed a gel
MMM	20.23	50,000	Formed a gel

Titration Data (SLES 2)
Hard Quats
No Gel in Sodium Laureth-2-Sulfate

Quat Sample	Amount of quat solution added to achieve haze point in SLES (g)	Viscosity (cps)	Notes
AMB	18.67	<10	Did not form a gel
AMM	17.44	<10	Did not form a gel
AEB	18.35	<10	Did not form a gel
DMB	11.09	<10	Did not form a gel

Gel in Sodium Laureth-2-Sulfate

Quat Sample	Amount of quat solution added to achieve haze point in SLES (g)	Viscosity (cps)	Notes
AME	4.47	7,000	Formed a gel
DMM	20.00	6,200	Formed a gel
MMM	20.23	50,000	Formed a gel
CaMB	24.31	1,000	Formed a gel
AMG	25.04	1,000	Formed a gel
MMB	25.00	9,800	Formed a gel
MMG	26.68	40,000	Formed a gel
DMG	28.37	6,800	Formed a gel
AEG	38.72	1,000	Formed a gel
CaMG	46.23	1,000	Formed a gel

Results

- All quat compounds reached a cloud point when titrated into anionic. However the amount necessary to reach the haze point was different and the nature of the end point was different.

Results

- The so-called hard quats have very little tolerance for anionic, forming insoluble precipitates with very little addition.

Results

- Quaternary compounds having intermediate hardness show compatibility with anionic surfactants at near stoichiometric amounts, but do eventually haze.

Results

- Soft quats do not exhibit a haze, but rather show a clear gel of differing viscosity.

Foam

Anionic/Cationic Surfactants (gels)

Shake Foam Testing

Foam Heights of Standards

Control	Foam $Height_{max}$ (mL)	Foam $Height_{inital}$ (mL)	Foam $Height_{final}$ (mL)	Foam Stability (min)
SLS	600	500	350	25.0
SLES-3	450	350	275	180.0

Foam Heights of SLS Titrations

Quat Sample	Foam Height$_{max}$ (mL)	Foam Height$_{inital}$ (mL)	Foam Height$_{final}$ (mL)	Foam Stability (min)
AMB	-	-	-	Does not foam
AME	190	90	140	30.0
AMG	500	400	300	30.0
AMM	600	500	350	15.0
AEB	300	200	200	40.5
AEG	200	100	150	40.0
CaMB	250	150	175	95.0
CaMG	200	100	150	79.0
DMB	400	300	250	14.0
DMG	300	200	200	8.0
DMM	250	150	150	13.0
MMB	400	300	250	29.0
MMG	400	300	250	97.0
MMM	400	300	250	1440.0

Foam Heights of SLES Titrations

Quat Sample	Foam Height$_{max}$ (mL)	Foam Height$_{inital}$ (mL)	Foam Height$_{final}$ (mL)	Foam Stability (min)
AMB	150	50	100	141.0
AME	250	150	175	1440.0
AMG	350	250	225	240.0
AMM	200	100	150	1440.0
AEB	200	100	150	47.0
AEG	300	200	200	1440.0
CaMB	150	50	125	8.50
CaMG	150	50	125	6.0
DMB	150	50	125	5.5
DMG	200	100	150	75.0
DMM	150	50	125	9.0
MMB	200	100	150	1440.0
MMG	250	150	175	146.5
MMM	300	200	200	1440.0

- All quat solutions, with the exception of three, (AEG, AMG, CaMG) exhibited cationic sub stantivity when delivered to hair tresses in a 0.5% aqueous solution.

- Quat DMG, containing a glyceryl group, did exhibit cationic substantivity.

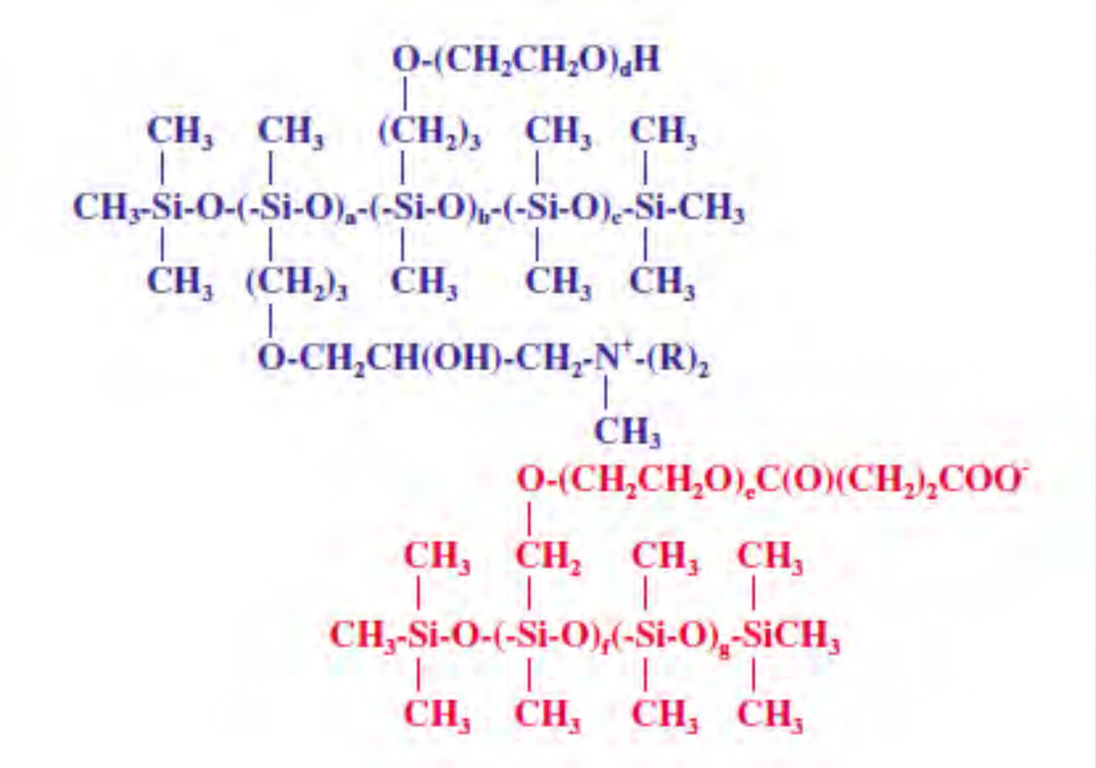
Silicone Complexes

Silicone Complexes

- Anionic and cationic silicone polymers to give complexes that deposit on the hair and skin.

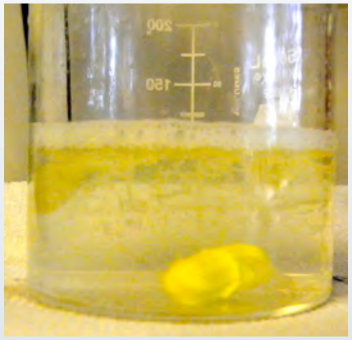
Silicone Complexes

INCI: Silicone Quaternium 20



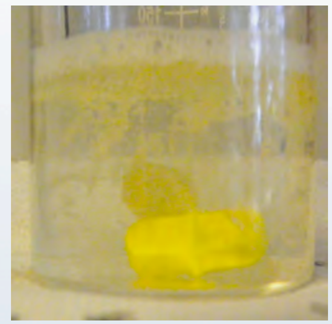
Sodium Lauryl Sulfate 10%

SLS / Silicone complex
50/50



SLS / Silicone Quat
90/ 10

Sodium Lauryl Sulfate 10% Solution



SLES / Silicone complex
50/50

SLES / Silicone Quat
90/ 10

- Used in baby shampoo at 0.5% to make a family product.
- Used in body wash
- Very effective for Asian hair.

Shampoo Formulation

2 in 1 Shampoo (Coacervate) FH183D

Part ID	Description (Supplier)	INCI Name	weight %
A			
	D.I. Water	Aqua	22.000
	Carbopol Aqua SF-1 Polymer (1%)	Acrylates copolymer	2.500
	TEA 99%	Triethanolamine	0.200
	Na2EDTA	Disodium EDTA	0.100
	Sodium Laureth Sulfate	Sodium Laureth-2 Sulfate	27.500
	Cocamidopropyl Betaine	Cocamidopropyl Betaine	6.000
B			
	D.I. Water	Aqua	18.000
	Sodium Laureth Sulfate	Sodium Laureth-2 Sulfate	5.500
	Cocamidopropyl Betaine	Cocamidopropyl Betaine	4.000
	Ninol COMF	Cocamide MEA	1.200
	EGDS	Ethylene Glycol Distearate	3.000
C			
	Silplex J2-S (Siltech LLC)	Silicone Quaternium-20	1.000
	Cosmo*Surf*® CE-100 (SurfaTech)	Octyldodecyl citrate crosspolymer	1.000
	Wheat Protein	Wheat Protein	0.500
	Hemp Seed Oil	Cannabis Sativa (Hemp) Seed Oil	1.000
	Nipaguard DMDMH	DMDM Hydantoin	0.500
D			
	Decyl Glucoside	Decyl Glucoside	3.000
	Amphosol 2C	Disodium Cocoamphodiacetate	3.000
	Citric Acid (40% aq)	Citric Acid	q.s.
	Sodium Chloride (if needed)	Sodium Chloride	q.s.
	Crothix (Croda) (if needed)	PEG-150 Pentaerythrityl Tetrastearate	q.s.
	Fruity Herbal	Fragrance	q.s.
		Total	100.000

Procedure:	**1.** Into a clean and sanitized stainless steel container equipped with propeller mixer, add water in Phase B
	2. Add SLES-2 and Betaine, heat up to 70 to 75 C, slowly add Cocamide MEA and EGDS, mix slowly while minimizing air incorporation. Mix until uniform, then cool down to room temperature.
	3. In another clean and sanitized stainless steel tank equipped with propeller mixer, add water and the rest of ingredients of phase A one by one while minimizing air incorporation. Mix until uniform.
	4. Add phase B slowly into Phase A. Mix until uniform
	5. Premix Silplex J2-S and Cosmosurf CE-100 until uniform, then add into Phase A+B, mix well. Add the rest of ingredients in Phase C one by one into Phase A+B until homogeneous while minimizing air incorporation.
	6. Add ingredients in Phase D one by one. Adjust pH by using citric acid to pH = 5.5 ~ 6.5, and adjust viscosity to 6,000 cps ~ 12, 000 cps by adding q.s. NaCl and Crothix. Add fragrance if necessary.

Viscosity (cps)	12,000
pH	5.70
Appearance	Opaque white cream

FOAM

Method: All products were evaluated with the same procedure. A 1000 mL cylinder with 10 mL increments was used. All samples and distilled water was prepared at 25 °C. 1.00 gram of test material was used and 100 mL distill water was added to dissolve the test material in a 250 mL beaker. After the test material was totally dissolved, the solution was transferred into the cylinder. An outlet of air pump was sited on the bottom of the cylinder to generate the bubbles. Record the foam height within 20 seconds for each test materials, each material was evaluated 3 times and their averages were documented. The scale for Foam Height is 1000 mL is outstanding and 100 mL is very poor. The type of foam was also noted whether it is tight or loose. Bubbles were generated by electronic air pump.

Sample (**Bubble for 20 sec**)	Initial Reading (**Average, mL**)	Two Minute Reading (**average, mL**)	Five Minute Reading (**average, mL**)
FH183D	700	690	670

Foam was tight and uniform.

Wet Comb

All products were evaluated on 10-inch Virgin Brown Hair. Two x 2-gram swatches were used for each material tested, all from the same lot. All swatches were wet with 25 °C water and one gram of test material was used for each swatch. Swatches were washed and then rinsed for at least one minute per swatch. Wet Comb Evaluation was then performed. No blow-drying of hair was done. All swatches air-dried then the Dry Comb Evaluation was performed once hair was completely dry.

Scale used is 1 to 5, 5 being the best. Used for wet and dry combing.

Evaluation / Sample	**Wet Comb**	**Rinse off**	**Clean Feel (Scroop)**	**Shine**	**Residual Feel**	**Average**
Control Water only	1.0	3.0	2.0	2.0	2.0	2.0
FH183D	4.5	4.5	4.5	3.0	3.0	3.9

Dry Comb

Evaluation / Sample	**Dry Comb**	**Dry Feel**	**Clean Feel /Look**	Shine	**Fullness /Manageable**	**Fly-away**	**Residual Feel**	**Static**	**Aver-age**
Control Water only	3.0	3.0	2.0	1.0	1.0	1.0	1.0	2.0	**1.750**
FH183D	4.4	4.5	4.0	4.0	4.4	4.2	3.5	4.0	**4.125**

Salt Tolerance, pH, Viscosity, Ease of Formulation, Effect on Formulation Stability:

Scale used is 1 to 5, 5 being the best, only for salt tolerance, Ease of formulation, effect on formulation stability. Viscosity was tested by using Brookfiled, LVT, #4 spindle, 12 rpm.

Evaluation / Formula	Salt Tolerance	pH	Viscosity, cps	Ease of Formulation	Effect on formulation Stability	Average
FH183D	2.5	5.70	12,000	4.0	4.5	3.67

Conclusions

- The ability to choose specific anionic and cationic materials that interact to build viscosity, provide foam and act to make coacervates offer the formulator unique possibilities.

Conclusions

- Silicone complexes offer advantages in hair care to deliver oils for conditioning, or other oily actives to the hair.

- These systems can be optimized for specific formulations.

- Thank You!
- Questions?