

Surface-active solutes
“Surface-active agents”
“Surfactants”

Lecture 2

Etymology

English	Greek	Latin
oil	lipo-	oleo-
water	hydro-	aqua-
solvent	lyo-	solvo-
both	amphi-	
flow	rheo-	
affinity	-philic	
lack-of-affinity	-phobic	
nature	-pathic	
science	-logy	

English meanings are not literal translations, but interpretations of how the words are understood in this branch of science.

Technical terms (neologisms) are formed by combinations of these words, such as the following adjectives:

- amphipathic** = combining both natures (oil and water understood)
- amphiphilic** = with affinity for both (oil and water understood)
- hydrophilic** = with affinity for water
- lipophilic** = with affinity for oil
- lyophilic** = with affinity for the solvent
- lyophobic** = lack of affinity for the solvent

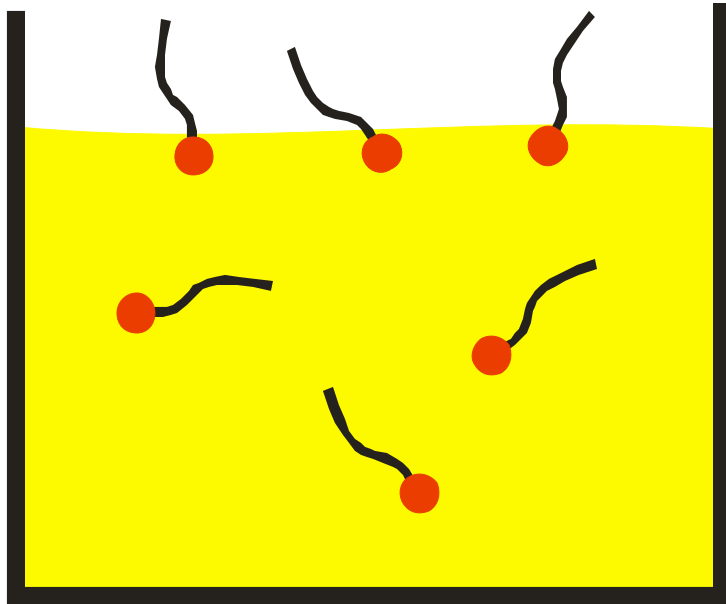
Classification of surfactants

Classified by the hydrophilic group:

- Anionic
 - Carboxylic
 - Sulfuric esters
 - Alkane sulfonic acids
 - Alkyl aromatic sulfonic acids
 - Others: Phosphates, phosphoric acids, ...
- Cationic
 - Amine salts (primary, secondary, and tertiary)
 - Quaternary salts
- Nonionic
 - Ethers
 - Esters
 - Amides
- Amphoteric

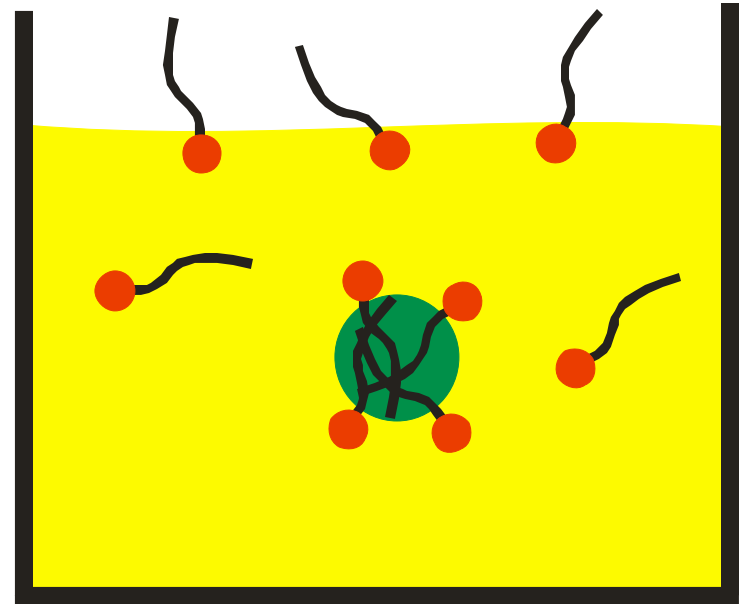
Adsorption lowers the energy

At the air/liquid interface:



Lowers surface tension.

At the solid/liquid interface:



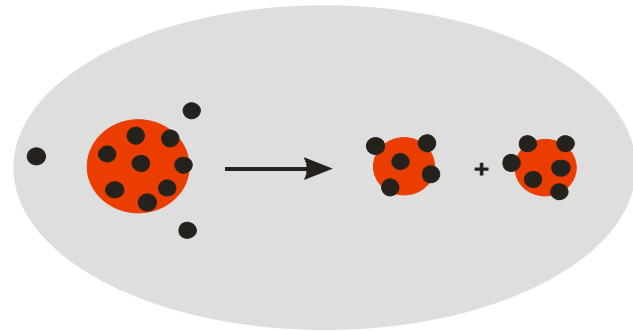
Stabilizes dispersions.

Adsorption of surfactant decreases the work needed for:

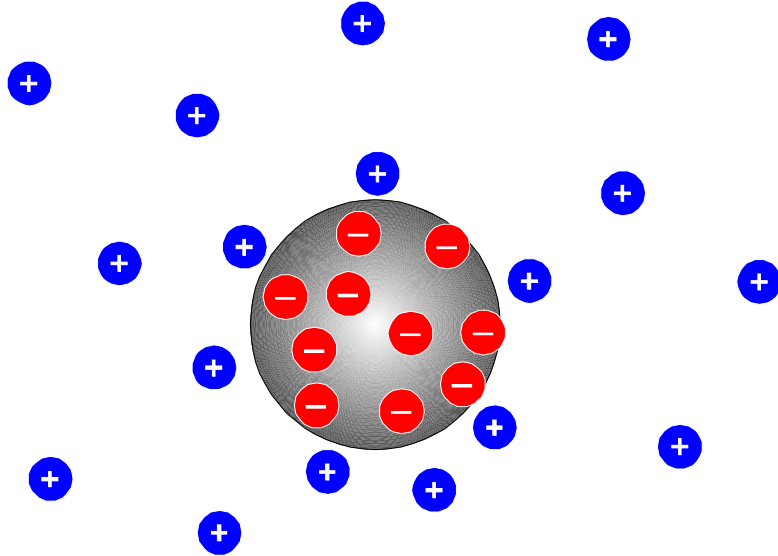
Spreading and wetting.



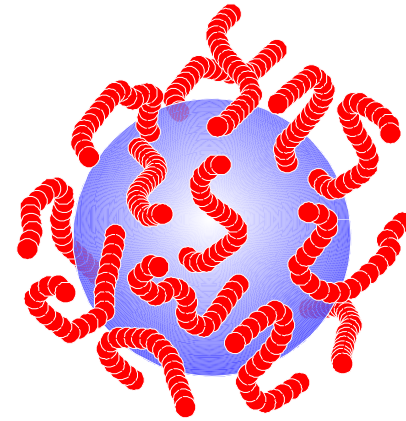
Emulsification and dispersion.



Surfactants on drops or particles

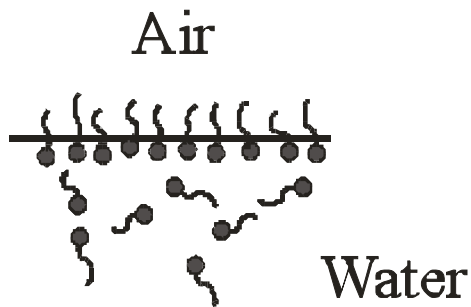


Ionic surfactants
produce charged
surfaces.

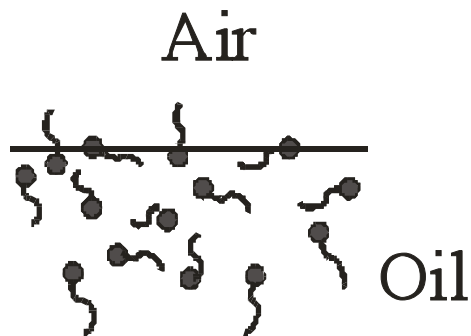


Nonionic surfactants
produce protective
coatings.

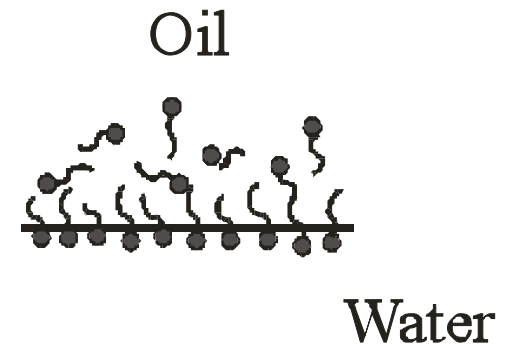
Adsorption at water and organic surfaces



Strong adsorption, substantial lowering of surface tension.



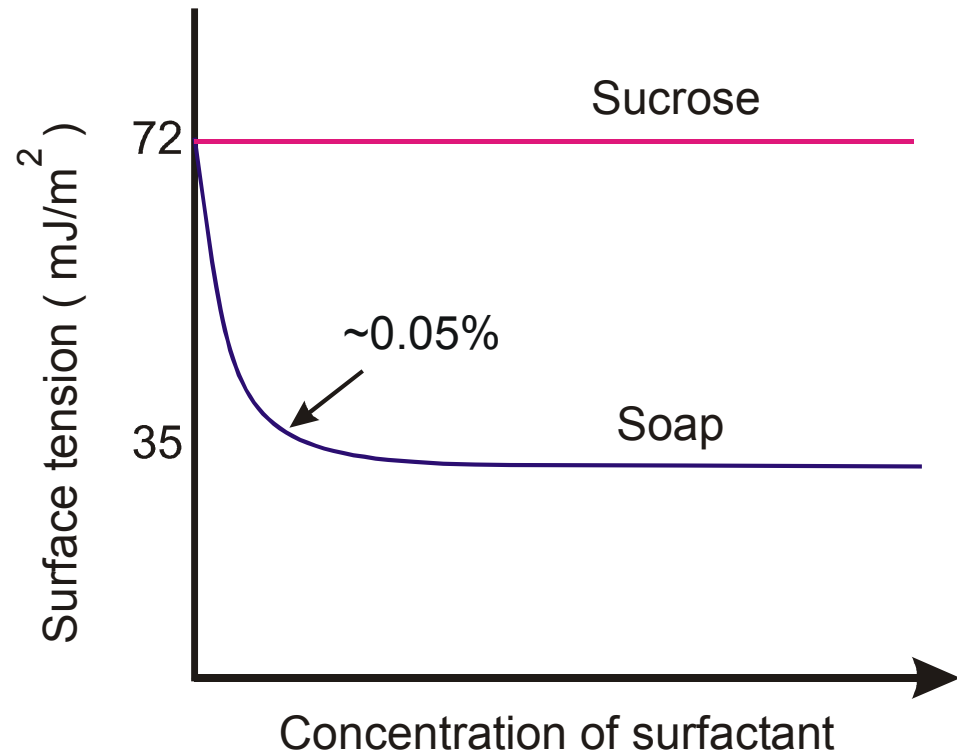
Little adsorption, little lowering of surface tension.



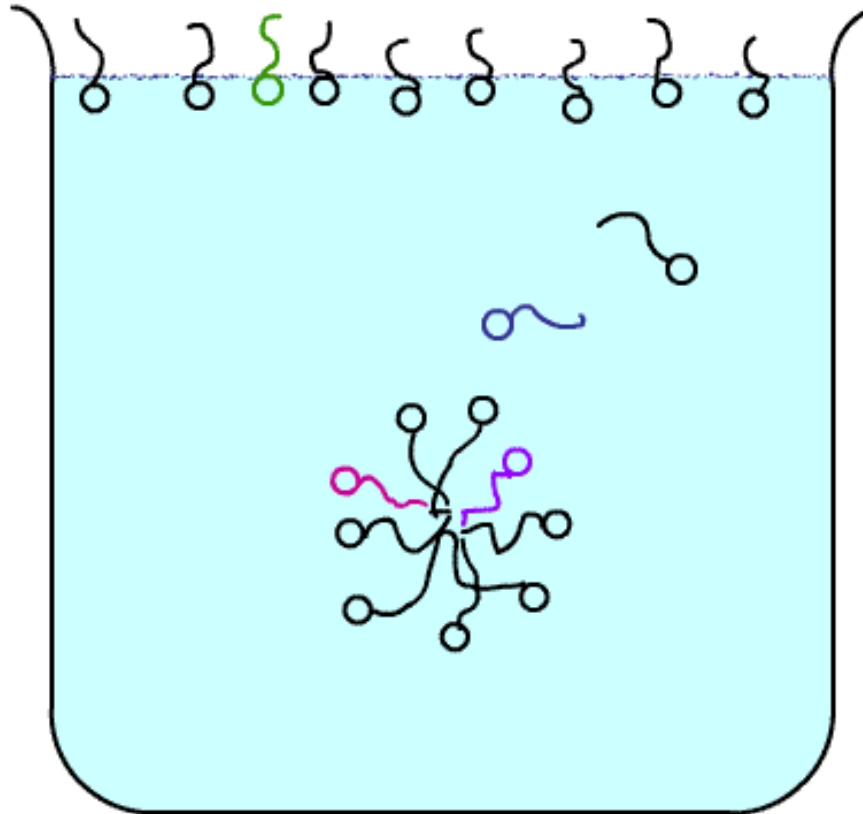
Strong adsorption, substantial lowering of interfacial tension.

Lowering of surface tensions with surfactants

The surface tension drops but reaches a limit:



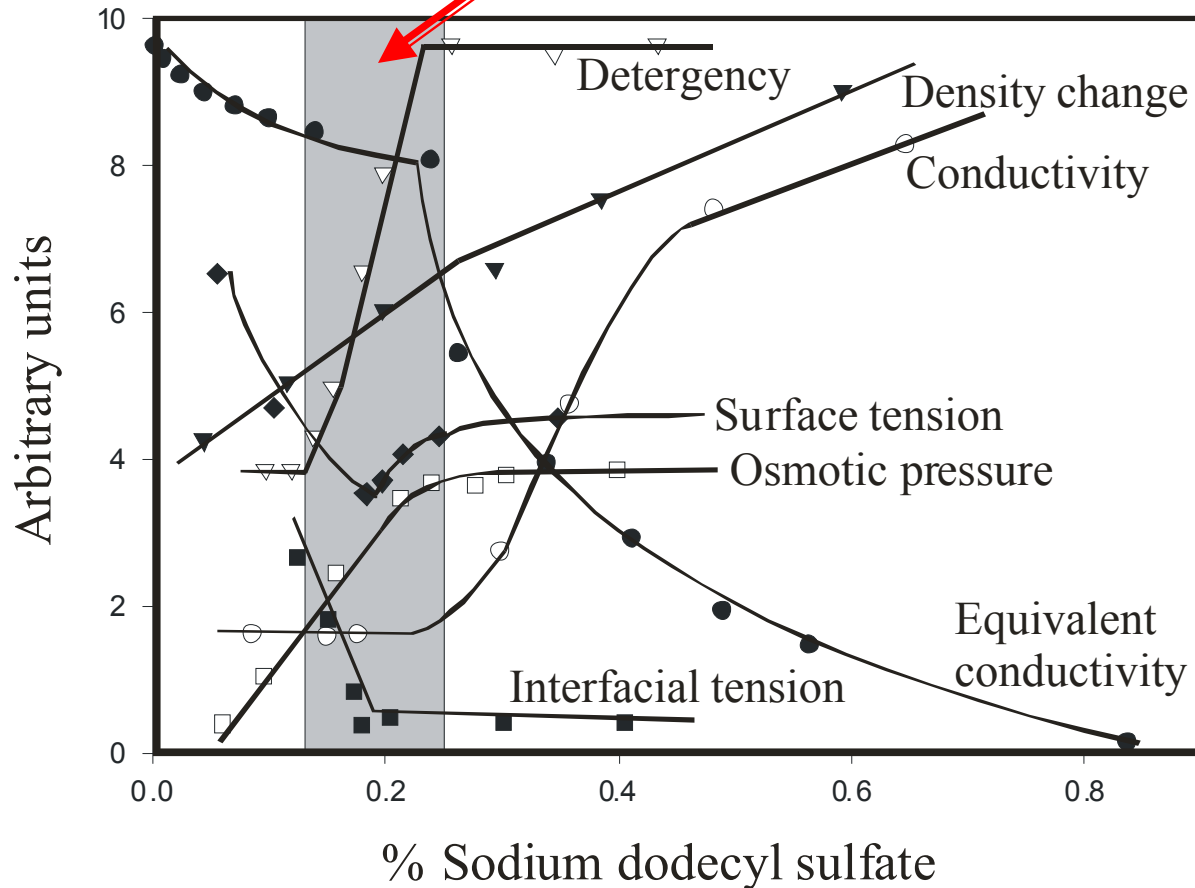
Surfactants can create their own “surface” - Micelles



Adsorption and micellization are competing processes.

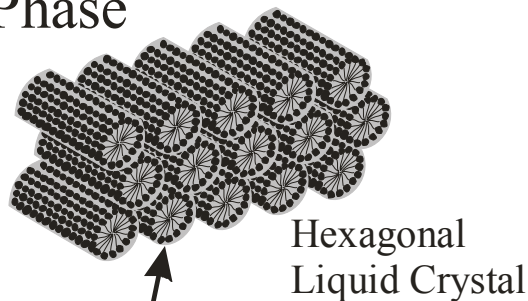
Physical properties of surfactant solutions

The critical micelle concentration.



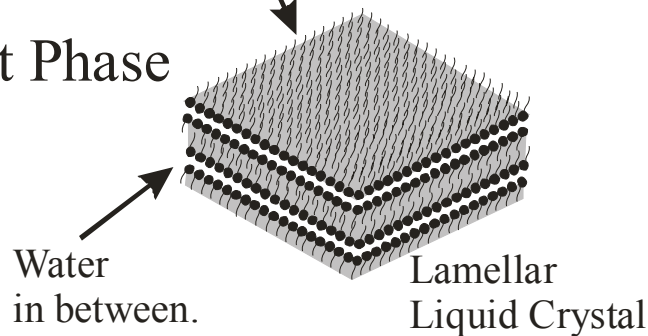
Surfactant “phases”

Middle Phase



Surfactant

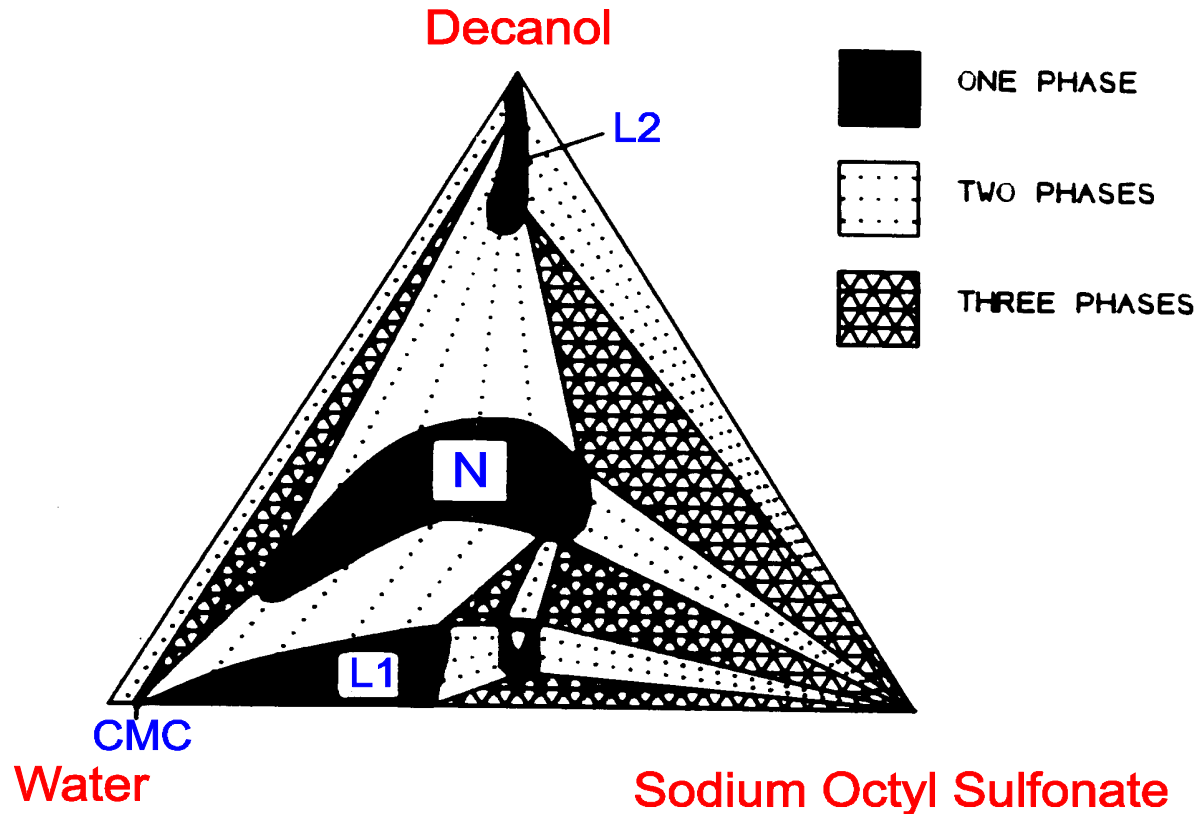
Neat Phase



These terms come from the old soap makers literature.

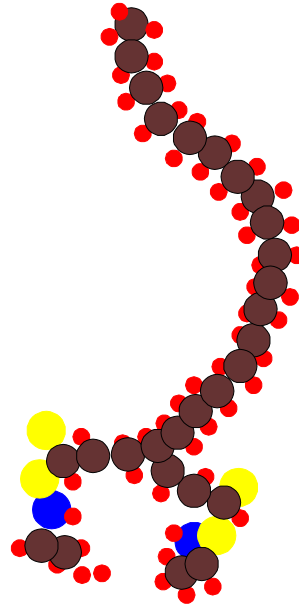
Different liquid crystal phases “look” different.

Phase diagrams can be constructed



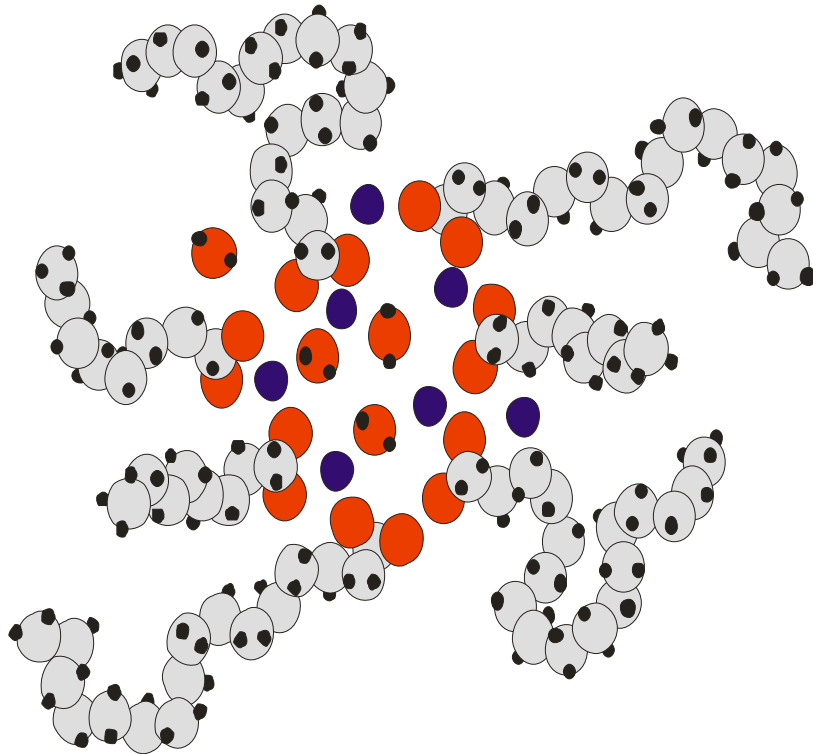
(Consider taking the ACS short course on emulsions for much more information.)

Oil-soluble surfactants



A widely used additive that combines both high molecular weight and basic function is polyisobutylene succinimide, marketed as OLOA 1200 by the Chevron Chemical Co. It provides low-temperature sludge and varnish control in gasoline engines and effective dispersancy in diesel engine, natural gas engine, and marine cylinder lubricants.

Oil “electrolytes” form inverse micelles



The micelle core is highly polar.

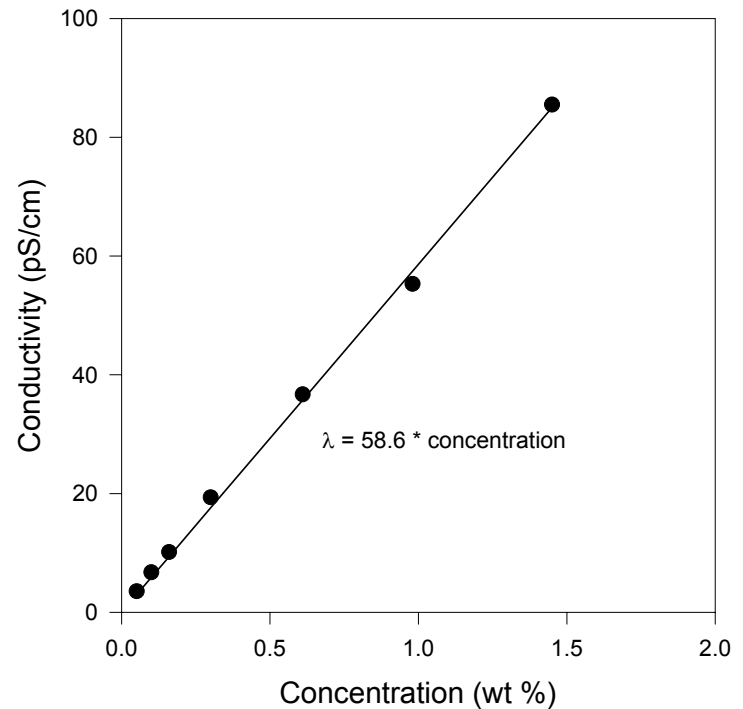
The diameters are 10's of nanometers.

Single polymer molecules may be sufficient.

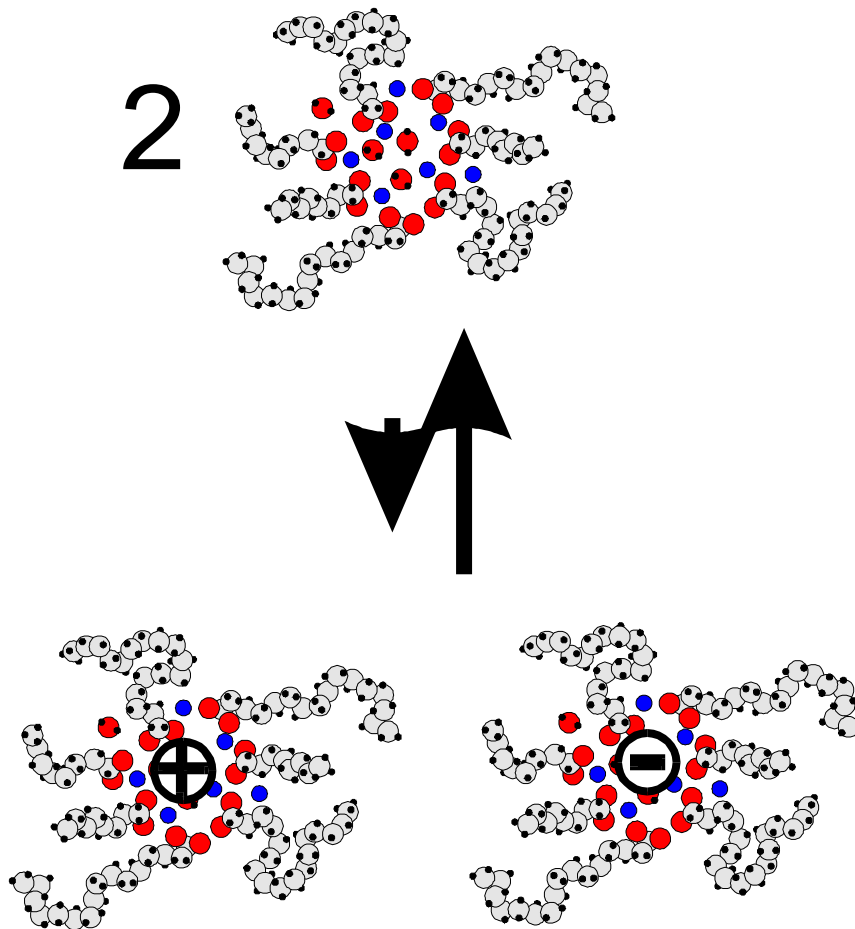
Linear conductivity of nonpolar electrolytes?

The conductivity of weak electrolytes should vary with the square root of concentration.

Conductivity of OLOA 1200
in dodecane (25^o C)



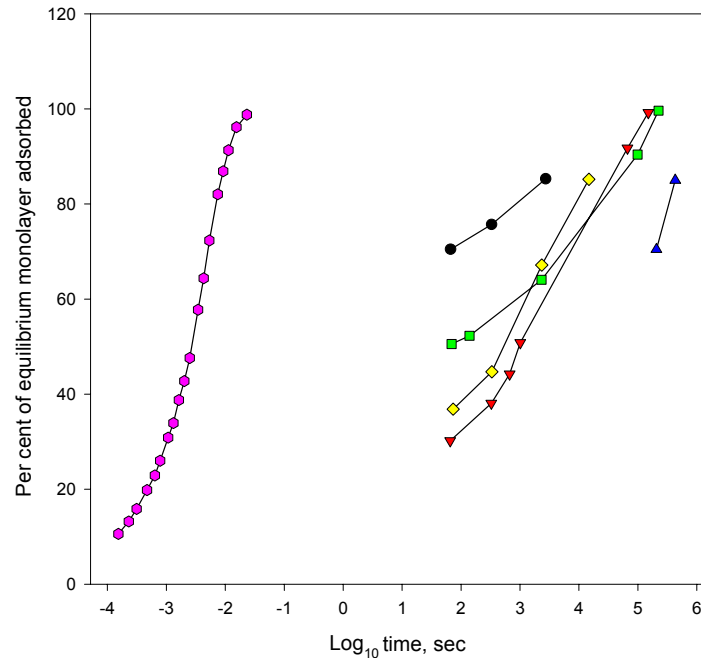
Creation of charged micelles:



Micelles exchange ions with each other and with surfaces.

The equilibrium is a dynamic balance.

Adsorption is a slow process

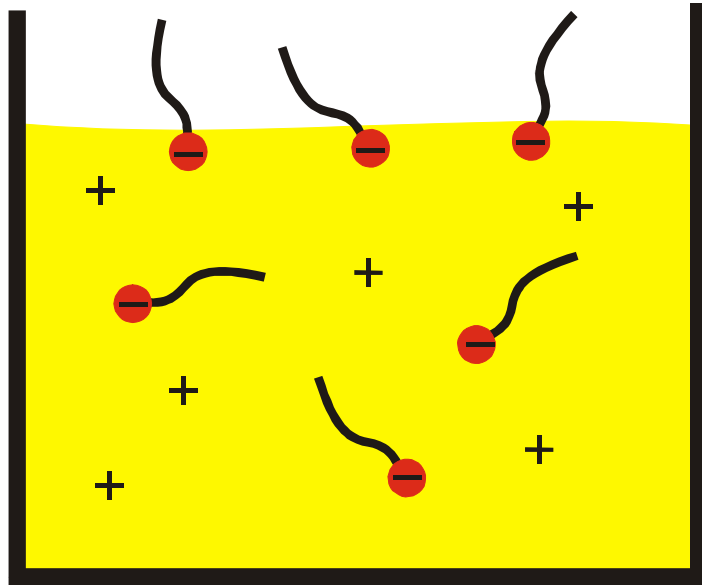


The adsorption of surfactants is much! slower than is estimated by molecular diffusion.

Time is required for molecules to rearrange at the solid/liquid interface.

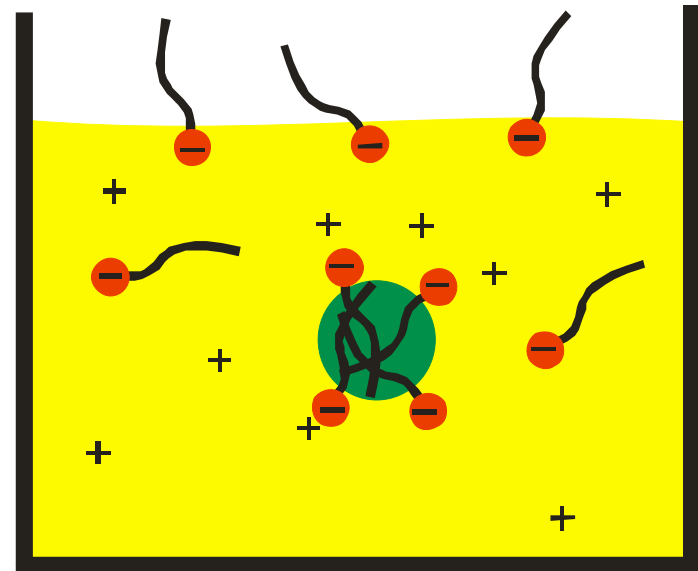
Adsorption of ionic surfactants

At the air/liquid interface:



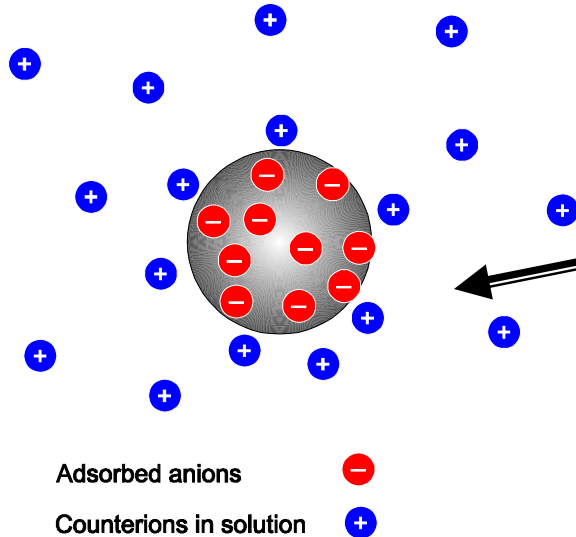
Lowers surface tension.

At the solid/liquid interface:



Charges the particle and stabilizes the dispersion.

Model of a charged particle in suspension

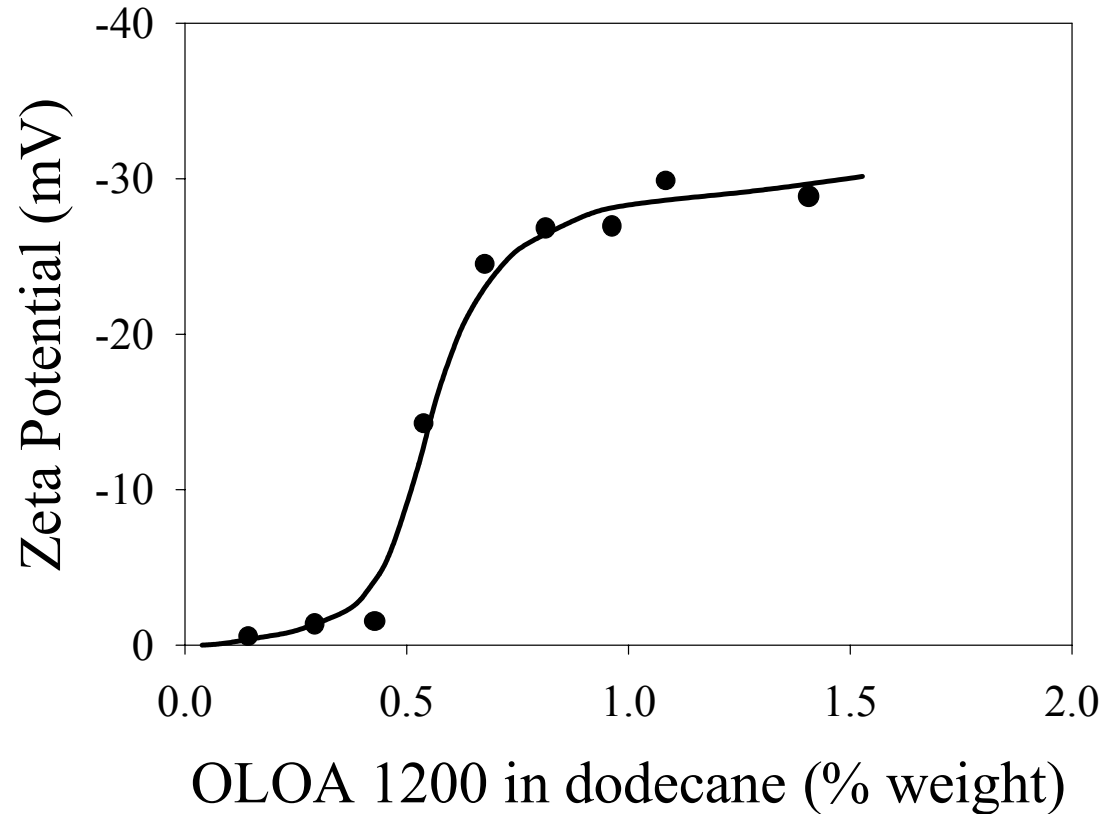


The loosely held countercharges form the “electrical double layer.”

The electric potential between the particle surface and the liquid at infinite distance is called the zeta potential.

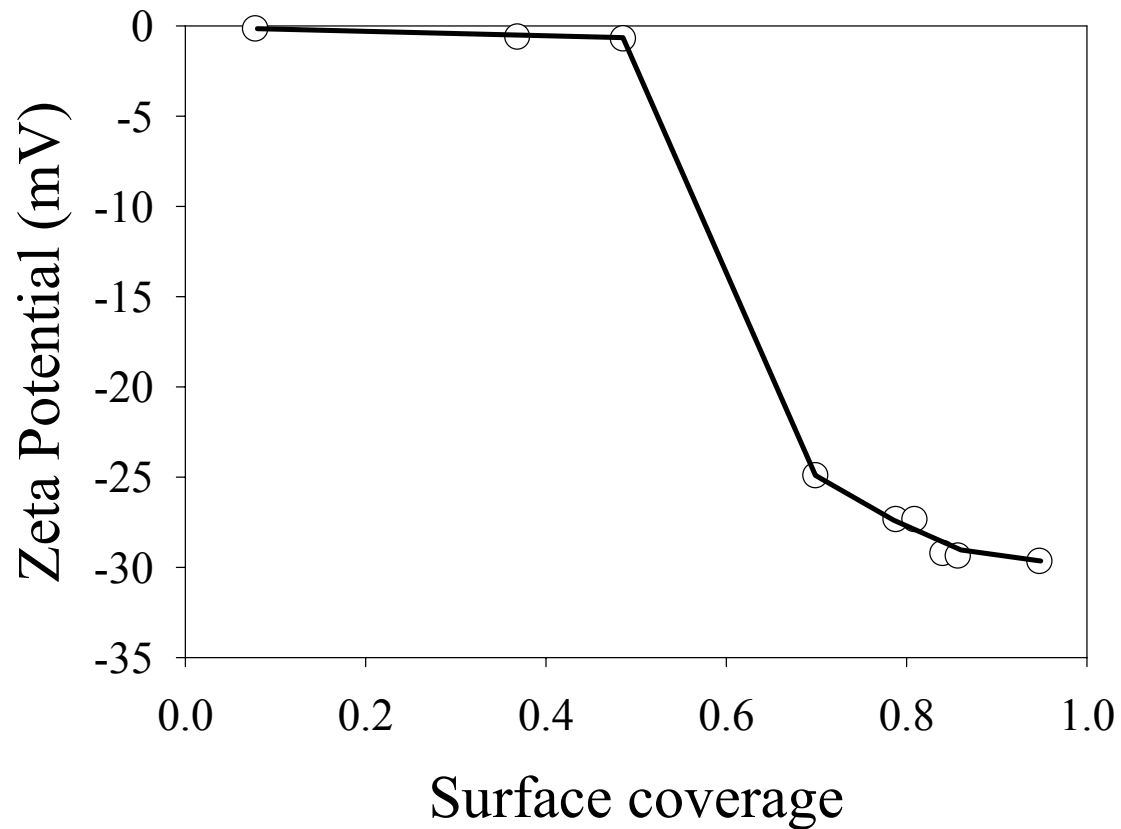
The description of the charged particle contains the zeta potential and a measure of how “thick” is the electrical double layer.

Electric charge on carbon black particles in oil

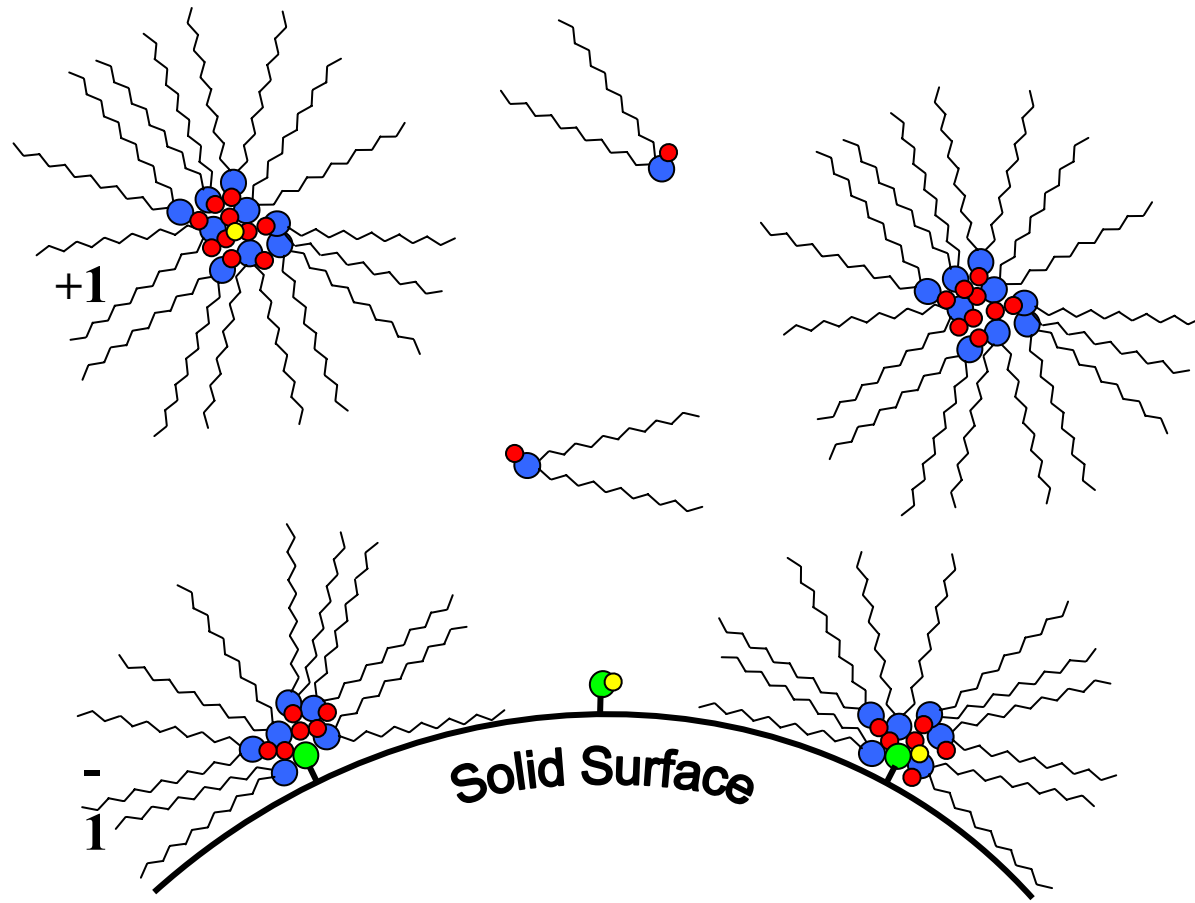


Zeta potential and adsorption

OLOA 1200 on Carbon black (2% vol) in Isopar



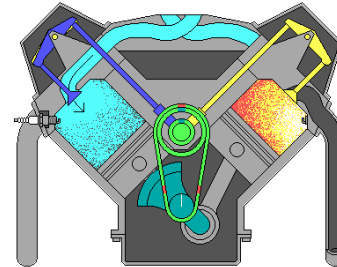
Charging of particles in nonpolar liquids



Nonpolar, electrocratic applications:

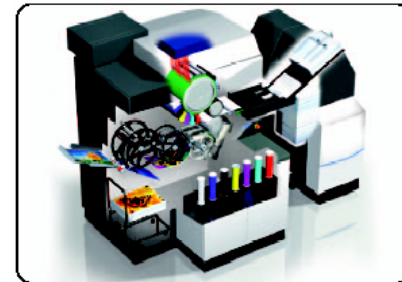
- Carbon in engine oils:

<http://www.autoshop-online.com/auto101/eng1.html>



- Liquid immersion printing:

HP Indigo



- Electrophoretic displays:

E Ink / Philips

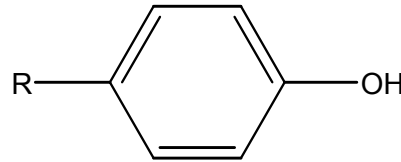


Commonly used surfactants

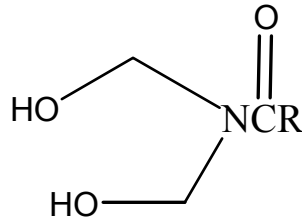
Chemical Class	Application
	1. <i>Anionic</i>
Alkyaryl sulfonates	Detergents, emulsifiers
Fatty alcohol sulfates	Detergents, emulsifiers
Lignosulfonates	Dispersants
Alkali soaps of tall oil	Anionic emulsifiers
Alkali soaps of rosin	Anionic emulsifiers
Dialkylsulfosuccinates	Wetting agents
	2. <i>Cationic</i>
Alkyltrimethylammonium chloride	Emulsifier, corrosion, inhibitor, textile softener, antibacterial agent, detergent
	3. <i>Nonionic</i>
Alkanolamides	Detergents, foam stabilizers
Glyceryl esters	Emulsifiers
Ethylene-oxide condensates of alkylphenols	Emulsifiers
Ethoxylated alkylphenols	Detergents, wetting agents, emulsifiers, dispersants
Ethoxylated fatty esters	Food emulsifiers (oil in water)
Fatty esters	Food emulsifiers (water in oil)
Polyalkylsuccinimides	Oil-soluble dispersants
Lecithins	Oil-soluble dispersants
Metal soaps	Oil-soluble dispersants

Large volume surfactants

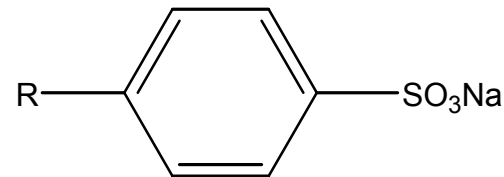
- Fatty alcohols and alkylphenol ethoxylates:



- Alkanolamides:



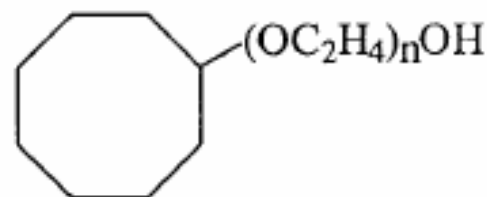
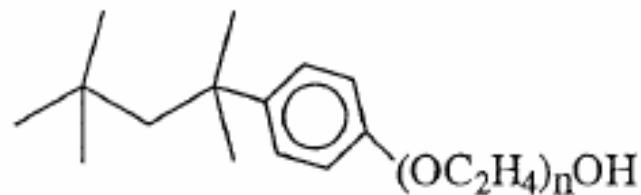
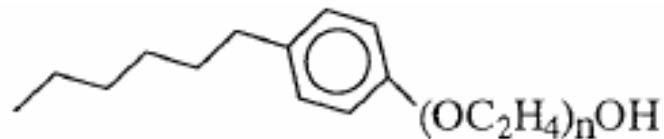
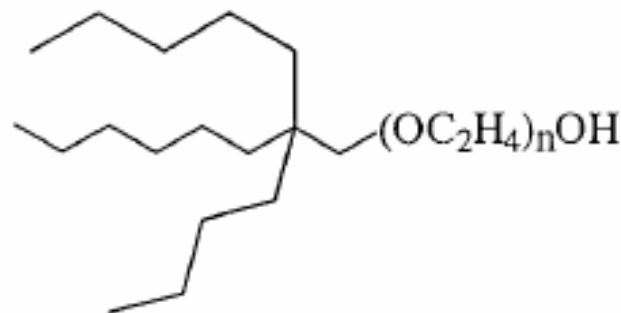
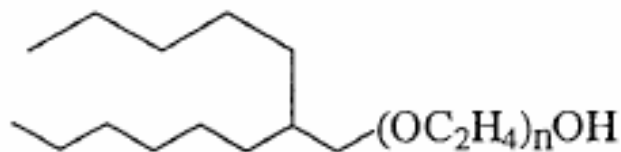
- Alkylbenzene sulphonates



- Fatty alcohol and fatty alcohol ether sulphates:



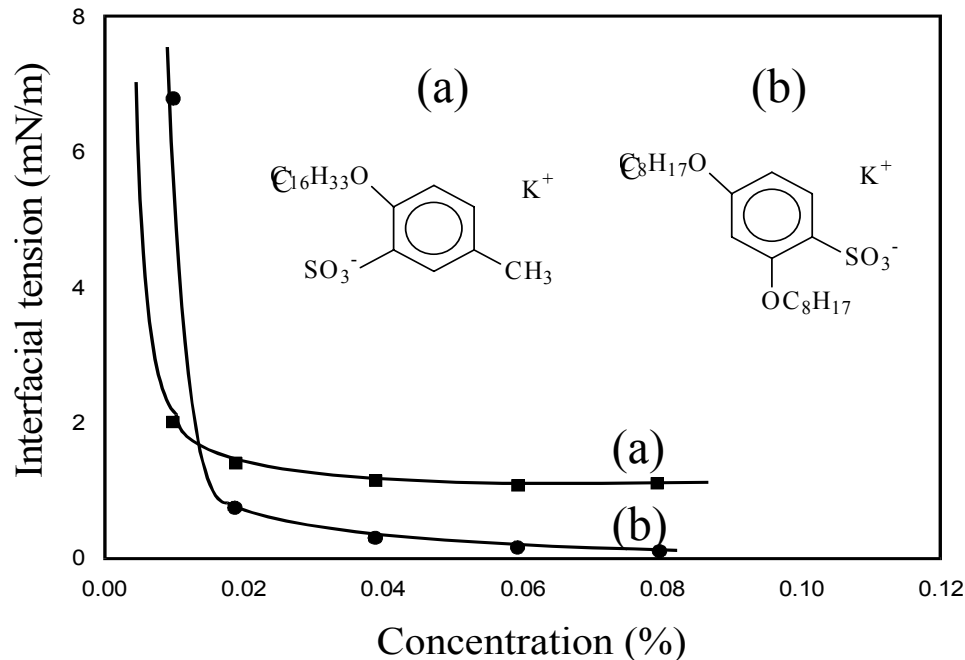
Surfactant structure



Structure affects adsorption, stability, solubility, and temperature dependence, etc.

<http://surfactants.net/huibers/Huibers1997.pdf>

Effect of structure on adsorption and micellization



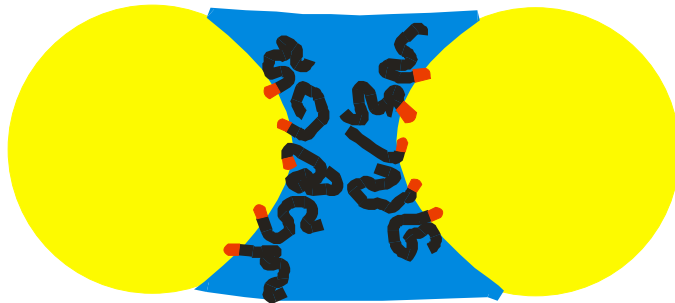
The linear molecule is more effective at lowering interfacial tension at low concentrations, but forms micelles easily.

The branched molecule is not as effective at lowering interfacial tension, but does not form micelles so readily and therefore gets to a higher concentration in solution.

Bancroft's Rule

“The emulsifier stabilizes the emulsion type where the continuous phase is the medium in which it is most soluble.”

A hydrophilic solute in an
O/W emulsion.



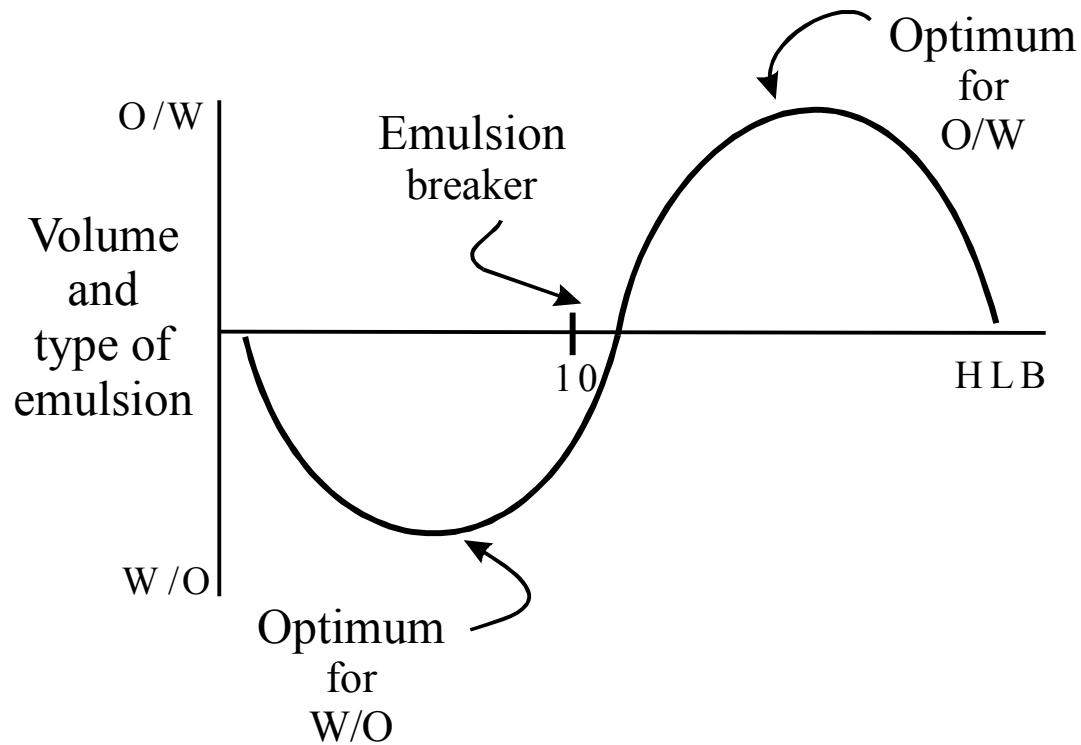
A hydrophilic solute in a
W/O emulsion.



The long tail on the surfactant is to represent the longer range interaction of a “hydrophilic” molecule through water.

The HLB Schema

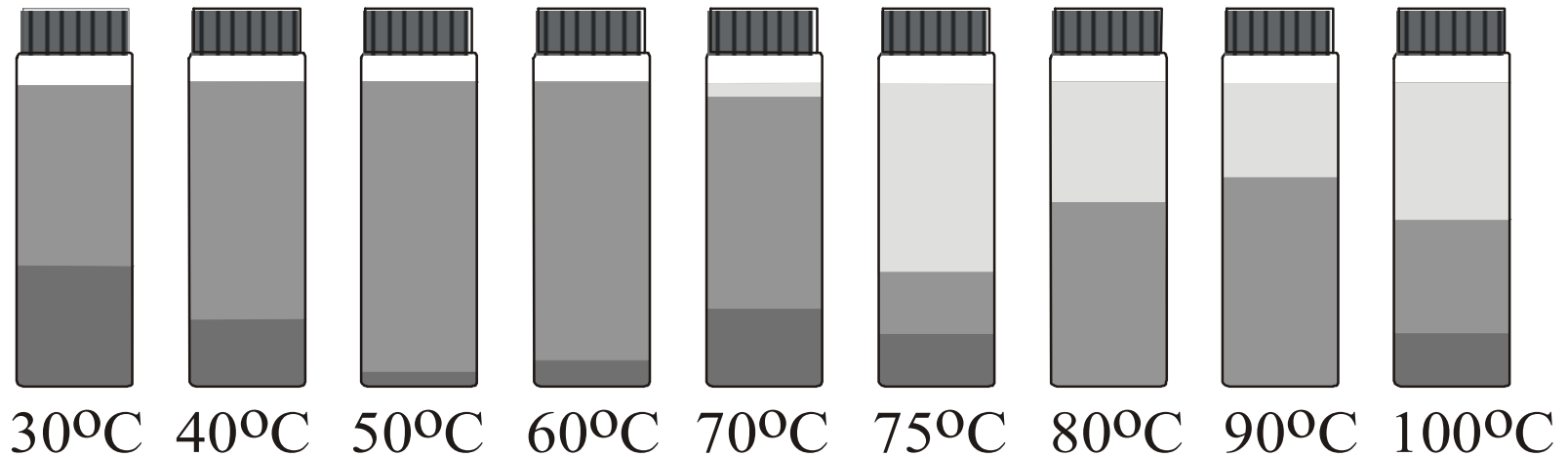
Variation of type and amount of residual emulsion with HLB number of emulsifier.



HLB Scale

Lipophilic End of Scale			Hydrophilic end of scale		
Stearane	Steric Acid	Sodium Stearate	Sodium Laurate	Sucrose	Sodium Sulfate
Soluble in oil; insoluble in water	Soluble in oil; insoluble in water	Soluble in oil; and in hot water	Slightly oil-soluble; soluble in water	Insoluble in oil; soluble in water	Insoluble in oil; soluble in water
Nonspreading on water substrate	Spreads on water substrate	Spreads on water substrate	Reduces surface tension of aqueous solutions	Does not affect the surface tension in aqueous solution	Increases surface tension in aqueous solution
Does not affect interfacial tension at oil-water interface	Reduces interfacial tension at oil-water interface	Reduces interfacial tension at oil-water interface	Reduces interfacial tension at oil-water interface	Does not affect interfacial tension at oil-water interface	Increases interfacial tension at oil-water interface
Does not stabilize emulsions	Stabilizes water in oil emulsions	Stabilizes either type of emulsion	Stabilizes oil in water emulsions	Does not stabilize emulsions	Decreases the stability of emulsions
	1	HLB Scale		20	

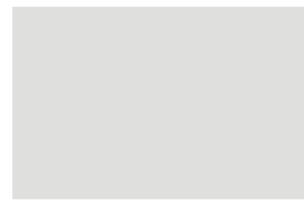
Phase inversion temperature



Water



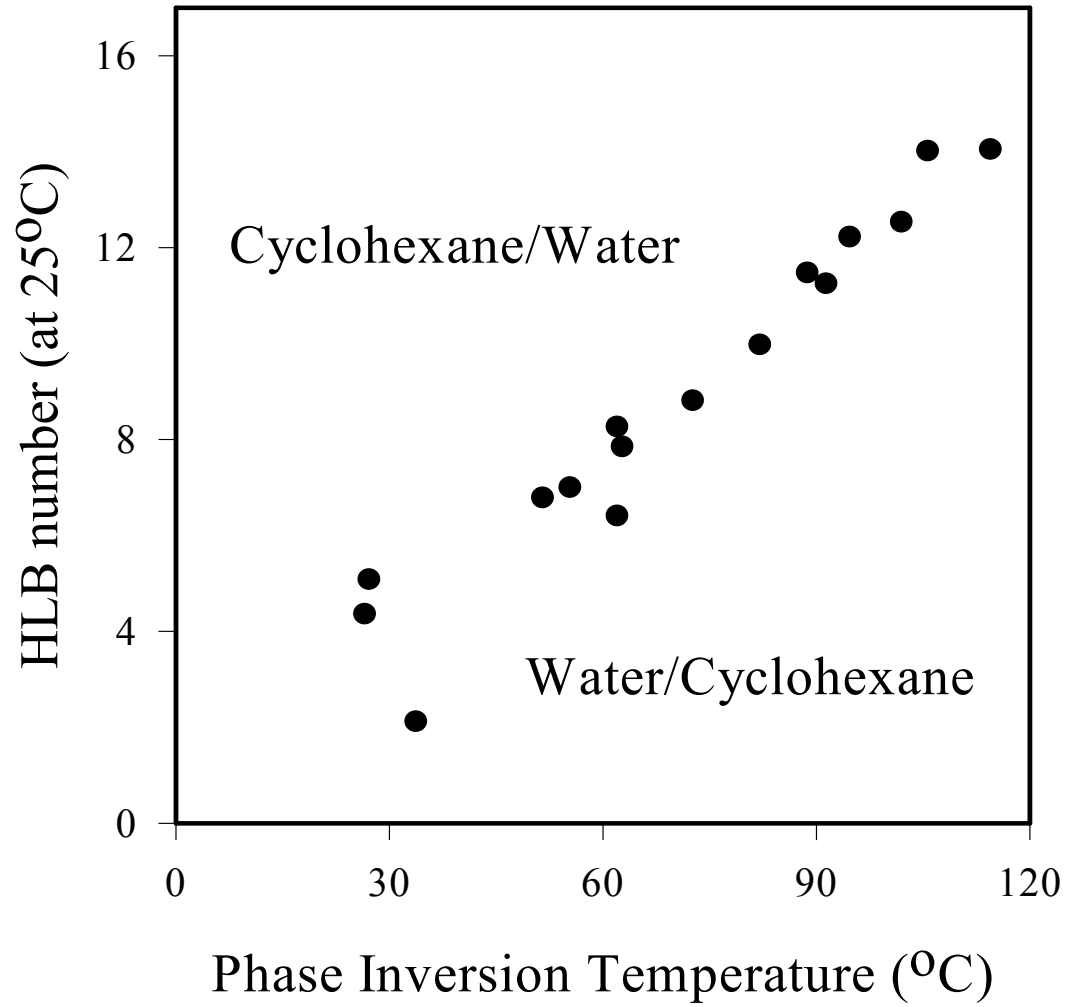
Emulsion



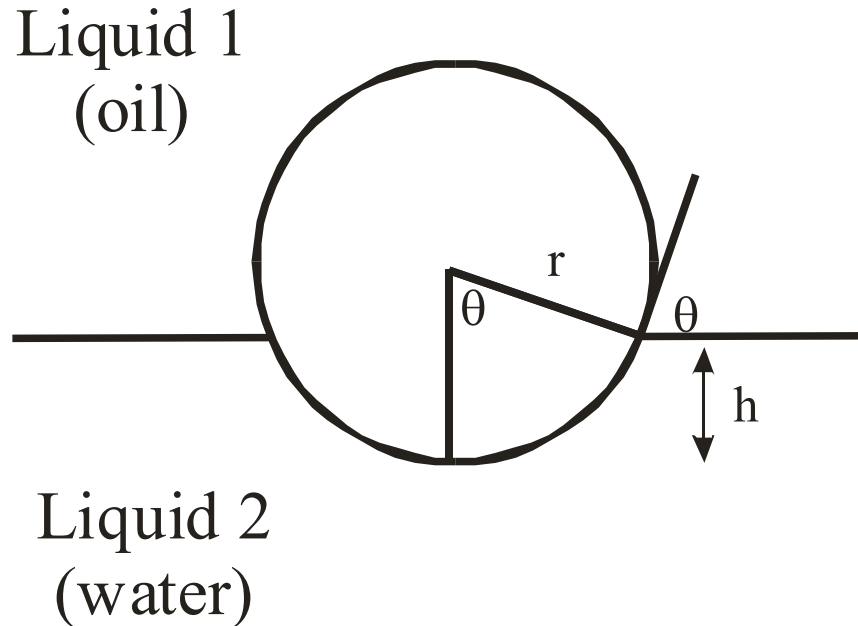
Oil

www.bias-net.com/chimica/pdf/set_baglioni.pdf

HLB and the Phase Inversion Temperature



Particles as emulsion stabilizers

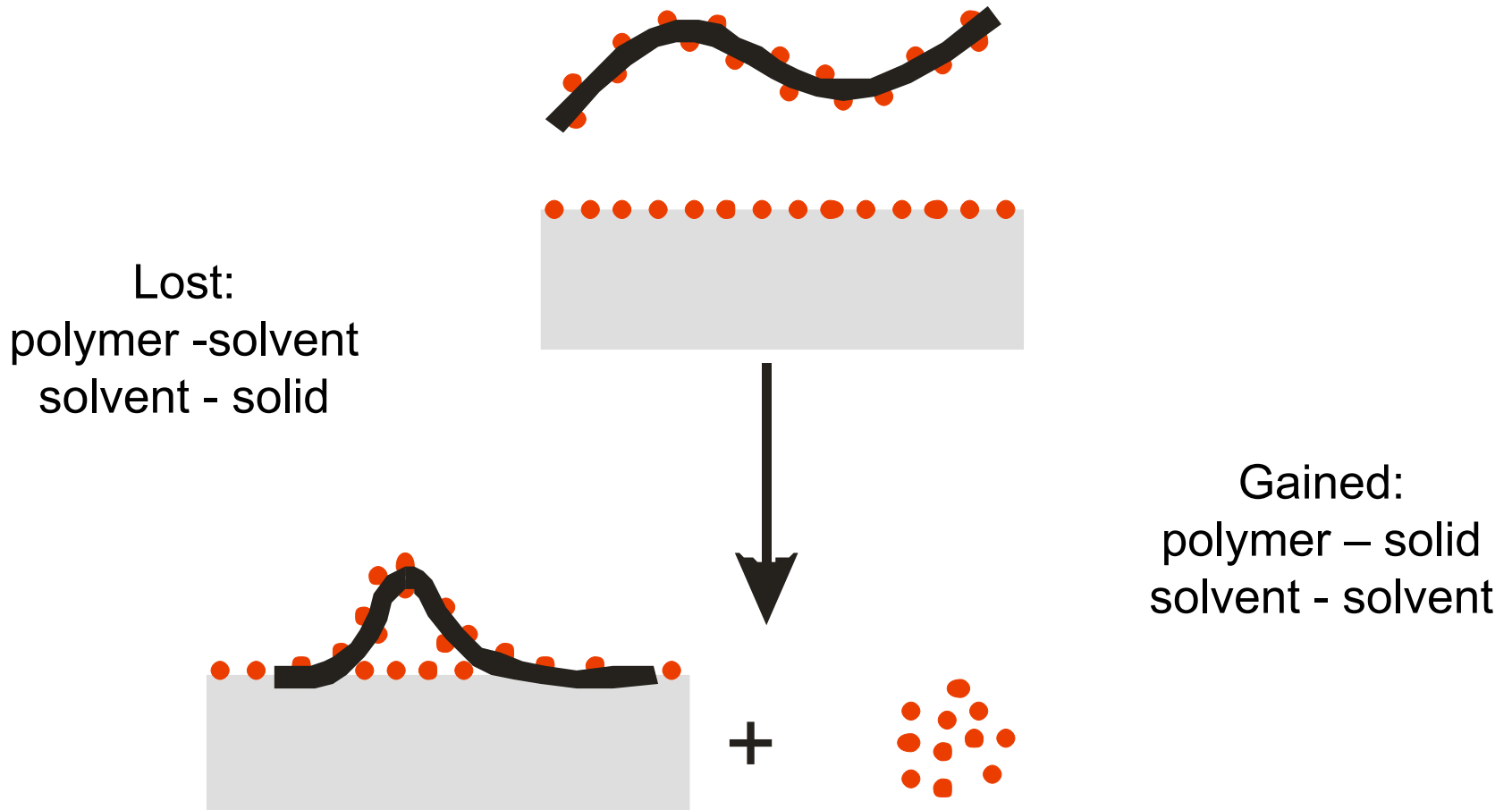


Almost all particles are only partially wetted by either phase.

When particles are “adsorbed” at the surface, they are hard to remove – the emulsion stability is high.

Crude oil is a W/O emulsion and is old!!

Polymer Adsorption



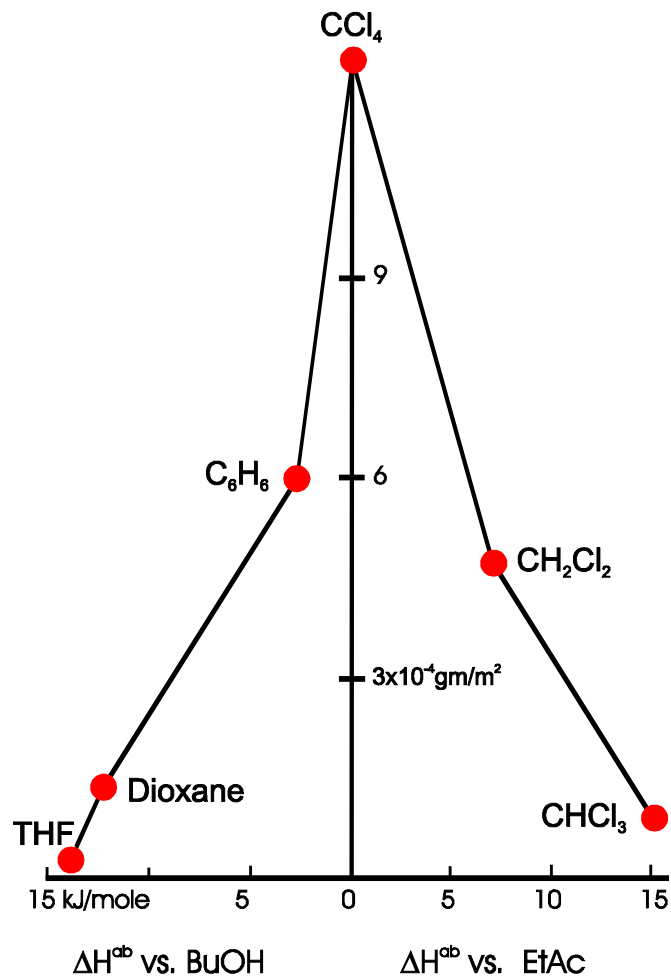
Drago E and C Parameters for a Variety of Molecular Bases

Bases	C_b	E_b
Pyridine	13.09	2.39
Ammonia	7.08	2.78
Methylamine	11.41	2.66
Dimethylamine	17.85	2.33
Trimethylamine	23.6	1.652
Ethylamine	12.31	2.80
Diethylamine	18.06	1.771
Triethylamine	22.7	2.03
Acetonitrile	2.74	1.812
<i>p</i> -Dioxane	4.87	2.23
Tetrahydrofuran	8.73	2.00
Dimethyl sulfoxide	5.83	2.74
Ethyl acetate	3.56	1.994
Methyl acetate	3.29	1.847
Acetone	4.76	2.018
Diethyl ether	6.65	1.969
Isopropyl ether	6.52	2.27
Benzene	1.452	1.002
<i>p</i> -Xylene	3.64	0.851

Drago E and E Parameters for a Variety of Molecular Acids

Acids	C_a	E_a
Iodine	2.05	2.05
Iodine monochloride	1.697	10.43
Thiophenol	0.405	2.02
<i>p</i> - <i>tert</i> -Butylphenol	0.791	8.30
<i>p</i> -Methylphenol	0.826	8.55
Phenol	0.904	8.85
<i>p</i> -Chlorophenol	0.978	8.88
<i>tert</i> -Butyl alcohol	0.614	4.17
Trifluoroethanol	0.922	7.93
Pyrrole	0.603	5.19
Isocyanic acid	0.528	6.58
Sulfur dioxide	1.652	1.88
Antimony pentachloride	10.49	15.09
Chloroform	0.325	6.18
Water	0.675	5.01
Methylene chloride	0.02	3.40
Carbon tetrachloride	0.00	0.00

Adsorption of PMMA on Silica



Gutmann Acceptor-Donor Numbers

Acidic Solvents	AN kcal mol ⁻¹	Basic Solvents	DN kcal mol ⁻¹	Basic Solvents	DN kcal mol ⁻¹
Hexane (reference solvent)	0	1,2-Dichloroethane		Tetrahydrofuran	20.0
Diethyl ether	3.9	Benzene	0.1	Diphenylphosphonic chloride	22.4
Tetrahydrofuran	8.0	Sulfonyl chloride	0.1	Trimethyl phosphate	23.0
Benzene	8.2	Thionyl chloride	0.4	Tributyl phosphate	23.7
Carbon tetrachloride	8.6	Acetyl chloride	0.7	Dimethoxyethane	~24
Diglyme	9.9	Tetrachloroethylene carbonate	0.8	Dimethylformamide	26.6
Glyme	10.2	Benzoyl fluoride	2.3	N-Methyl-2-caprolactam	27.1
HMPA	10.6	Benzoyl chloride	2.3	N-Methyl-2-pyrrolidinone	27.3
Dioxane	10.8	Nitromethane	2.7	N,N-Dimethylacetamide	27.8
Acetone	12.5	Dichloroethylene carbonate	3.2	Dimethyl sulfoxide	29.8
N-Methyl-2-pyrrolidinone	13.3	Nitrobenzene	4.4	N,N-Diethylformamide	30.9
DMA	13.6	Acetic anhydride	10.5	N,N-Diethylacetamide	32.2
Pyridine	14.2	Phosphorous oxychloride	11.7	Pyridine	33.1
Nitrobenzene	14.8	Benzonitrile	11.9	Hexamethylphosphoramide	38.8
Benzonitrile	15.5	Selenium oxychloride	12.2	Hydrazine	44.0
DMF	16.0	Acetonitrile	14.1	Ethylenediamine	55.0
Dichloroethane carbonate	16.7	Sulfolane (tetramethylene sulfone)	14.8	Ethylamine	55.5
PDC	18.3	Dioxane	14.8	Isopropylamine	57.5
CH ₃ CN	18.9	Propanediol 1,2-carbonate	15.1	tert-Butylamine	57.5
DMSO	19.3	Benzyl cyanide	15.1	Ammonia	59.0
Methylene chloride	20.4	Ethylene sulfite	15.3	Triethylamine	61.0
Nitromethane	20.5	Isobutyronitrile	15.4		
Chloroform	23.1	Propionitrile	16.1		
Isopropyl alcohol	33.5	Ethylene carbonate	16.4		
Ethyl alcohol	37.1	Phenylphosphonic difluoride	16.4		
Formamide	39.8	Methyl acetate	16.5		
Methyl alcohol	41.3	n-Butyronitrile	16.6		
Acetic acid	52.9	Acetone	17.0		
Water	54.8	Ethyl acetate	17.1		
CF ₃ COOH	105.3	Water	18.0		
CH ₃ SO ₃ H	126.3	Phenylphosphonic dichloride	18.5		
SbCl ₅ as ref. in DCE	100	Diethyl ether	19.2		

W.B. Jensen
*The Lewis Acid-Base Concepts:
 An Overview*
 Wiley-Interscience: NY; 1980

Common Polymeric Stabilizers

Aqueous dispersions	
Anchor polymer	Stabilizing moieties
Polystyrene	Poly(oxyethylene)
Poly(vinyl acetate)	Poly(vinyl alcohol)
Poly(methyl methacrylate)	Poly(acrylic acid)
Poly(acrylonitrile)	Poly(methacrylic acid)
Poly(dimethylsiloxane)	Poly(acrylamide)
Poly(vinyl chloride)	Poly(vinyl pyrrolidone)
Poly(ethylene)	Poly(ethylene imine)
Poly(propylene)	Poly(vinyl methyl ether)
Poly(lauryl methacrylate)	Poly(4-vinylpyridine)
Nonaqueous dispersions	
Anchor polymer	Stabilizing moieties
Poly(acrylonitrile)	Polystyrene
Poly(oxyethylene)	Poly(lauryl methacrylate)
Poly(ethylene)	Poly(12-hydroxystearic acid)
Poly(propylene)	Poly(dimethylsiloxane)
Poly(vinyl chloride)	Poly(isobutylene)
Poly(methyl methacrylate)	Cis-1,4-poly(isoprene)
Poly(acrylamide)	Poly(vinyl acetate)
	Poly(methyl methacrylate)
	Poly(vinyl methyl ether)

Sources of surfactants

Surfactant Companies

1. Surfactant Producers

[3M Corp.](#)
[Air Products And Chemicals, Inc.](#)
[Akzo Nobel Surfactants America](#)
[Albemarle Corp.](#)
[Arizona Chemical](#)
[BASF Corp.](#)
[BFGoodrich Personal Care](#)
[\(Noveon\)](#)
[CK Witco \(Crompton\)](#)
[Clariant Corporation](#)
[The Cognis Group](#)
[Croda Inc.](#)
[DeForest Enterprises, Inc.](#)
[The Dow Chemical Co.](#)
[Dow Corning](#)
[DuPont](#)
[EAC Chemicals](#)
[Ethox Chemicals](#)
[Goldschmidt AG \(Degussa\)](#)
[Henkel KGaA \(The Henkel Group\)](#)
[Heterene Inc.](#)
[Huntsman Corp.](#)

[ICI in North America](#)
[Jeneil Biosurfactant Company](#)
[Lambent Technologies](#)
[Libra Chemicals Ltd](#)
[LidoChem, Inc.](#)
[Lonza Inc.](#)
[MacDermid, Inc.](#)
[McIntyre Group Ltd.](#)
[Montello Inc.](#)
[National Starch and Chemical](#)
[Company](#)
[Nikko Chemicals](#)
[Novo Nordisk A/S](#)
[Petroferm, Inc.](#)
[PILOT Chemical Company](#)
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Dispersants

DISPERSING POWDERS IN LIQUIDS

RALPH D. NELSON, Jr.,
*Consultant Engineering Services Division,
E.I. du Pont de Nemours & Co., Inc., Newark, Delaware, U.S.A.*



ELSEVIER
Amsterdam — Oxford — New York — Tokyo 1988

Typical Entries

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Dispersing Powders in Liquids

Nonionic and Cationic Class Characteristics

Table C-7

class →	Al	Fa	Fe	Gr	Ge	Ao	Ag	Aa	Pm	So	Pp	Fc	Si	An	Qa	Im	Da
CHARGE OF SURFACTANT IN WATER																	
low pH	0	0	0	0	0	0	0	0	0	0	0	0	0	+	+	+	+
mid pH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	+	Z	+
high pH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.	-	0
SOLUBILITY OF SURFACTANT IN LIQUID																	
acid water	Y	Y	Y	Y	.	Y	.	.	.	Y	.	Y	Y	Y	.	N	.
base water	Y	Y	Y	Y	.	Y	.	.	.	Y	.	Y	N	Y	.	Y	.
H-b org	.	.	Y	Y	Y
polar	Y	.	Y	Y	Y
nonpolar	Y	.	Y	Y	.	Y	.	.	.	Y	Y	Y	Y
fluoroc	Y
DISPERSING AGENT FOR PARTICLE (SURFACE)																	
metal	.	Y	Y	Y	.	.	.
carbon	Y	.	.	Y
salt	Y	Y	.	.
oxide/h	.	Y	Y	Y	.	.	.	Y	Y	.	.
H-b org	Y	.	Y	Y	Y	Y	.
protein	Y	.	Y	Y	.
polar	Y	Y	.	.	Y	Y	.	Y	.
nonpolar	Y	Y	.	Y	Y	.	Y	.
fluoroc	Y
STABILITY AND BEHAVIOR																	
high IS OK	Y	Y	.
di cat OK	Y	.	.	Y
foams	.	N	.	N	.	N	Y	N	Y	.
STABLE TOWARD																	
biodeg	N	N	.	.	Y	.	.	.	N	.	Y	.	.	Y	.	.	.
oxidation	.	N	N	.	Y
reduction	Y
hot acid	.	Y	N	.	.	.	N	.	N	.	Y	.	.	.	Y	.	.
warm acid	.	Y	.	.	.	N	.	N	.	Y	.	Y	.	Y	.	.	.
cold acid	.	Y	.	.	.	N	.	N	.	Y	.	Y	.	Y	.	.	.
cold base	Y	Y	Y	Y	.	Y	.	.	.	N	Y	.	.
warm base	Y	Y	Y	Y	.	Y	.	.	.	N	Y	.	.
hot base	Y	Y	N	.	.	.	Y	Y	.	Y	.	.	.	N	Y	.	.

Properties of Surfactant

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Anionic Class Characteristics

Table C-8

chemical class →	Sf	Sd	To	Ab	Is	Ss	Ta	As	St	Ap	Ip	Ai	Pl
CHARGE OF SURFACTANT IN WATER													
low pH	0	-	+
mid pH	-	-	-	-	-	-	-	-	-	-	-	-	Z
high pH	-	-	-	-	-	-	-	-	-	-	-	-	-
SOLUBILITY OF SURFACTANT IN LIQUID													
acid water	Y	Y	Y	Y	Y	Y	Y	.	.	Y	Y	Y	Y
base water	N	Y	Y	Y	Y	Y	N	.	.	Y	Y	N	Y
H-b org	Y
polar	Y
nonpolar	Y
fluoroc	Y	.	.	Y	.	Y
DISPERSING AGENT FOR PARTICLE (SURFACE)													
metal	Y
carbon
salt
oxide/h	.	.	.	Y	Y	.	.
H-b org	Y	.	Y	Y	Y	Y
proteins	.	.	Y	Y	.	Y	Y	Y	Y
polar	.	.	.	Y	Y	.	Y	Y	Y	Y	Y	Y	Y
nonpolar	.	.	.	Y	Y	.	Y	Y	.	Y	.	.	.
fluoroc
STABILITY AND BEHAVIOR													
high IS OK	N	.	.	Y	.	.	Y	.	.	Y	.	Y	.
di cat OK	N	Y	Y	Y	Y	.	Y	.	.	Y	N	.	.
foams	Y	Y	.	Y	Y	Y	Y	Y	N	N	.	.	.
STABLE TOWARD													
biodeg	.	.	.	N	.	.	.	N	N	.	.	Y	.
oxidation
reduction
hot acid	.	.	.	Y	.	.	Y	N	N	.	N	.	.
warm acid	.	.	.	Y	.	N	Y	.	.	.	N	Y	.
cold acid	.	.	.	Y	.	.	Y	Y	.	.	N	Y	.
cold base	.	.	.	Y	.	.	Y	Y	.	Y	Y	Y	.
warm base	.	.	.	Y	.	.	Y	Y	.	Y	Y	Y	.
hot base	.	.	.	Y	N	N	Y	Y	N	Y	Y	.	.

McCutcheon's Handbook

**1994
McCutcheon's
VOLUME 1:
Emulsifiers & Detergents
International Edition**

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1994 / Emulsifiers & Detergents / International ii

Typical Entry

Span

ICI Surfactants

Span 20

Chemical Description: Sorbitan monolaurate

Form: liquid **Conc. %:** 100 **Type:** nonionic **HLB:** 8.6

Span 40

Chemical Description: Sorbitan monopalmitate

Form: powder **Conc. %:** 100 **Type:** nonionic **HLB:** 6.7

Span 60

Chemical Description: Sorbitan monostearate

Form: powder **Conc. %:** 100 **Type:** nonionic **HLB:** 4.7

Span 65

Chemical Description: Sorbitan tristearate

Form: powder **Conc. %:** 100 **Type:** nonionic **HLB:** 2.1

Span 80

Chemical Description: Sorbitan monooleate

Form: liquid **Conc. %:** 100 **Type:** nonionic **HLB:** 4.3

Span 85

Chemical Description: Sorbitan trioleate

Form: liquid **Conc. %:** 100 **Type:** nonionic **HLB:** 1.8

Remarks: Emulsifiers. Lipophilic surfactants, insoluble or dispersible in water but generally soluble in oils or organic solvents. Used as o/w emulsion stabilizers and thickeners. Used in the textile industry as fiber lubricants and softeners, used as oil additives for corrosion inhibition. Food emulsifiers.

Chemcyclopedia

CHEMCYCLOPEDIA 1995

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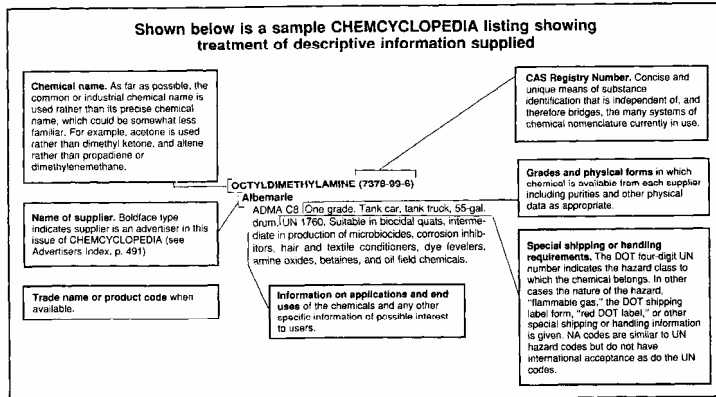
CHEMCYCLOPEDIA provides users and purchasers of chemicals with a unique opportunity to obtain information helpful in making buying decisions. In addition to the listing of a given chemical, suppliers have been asked to furnish trade names (if any), available forms, packaging, special shipping requirements, and potential applications. CAS Registry Numbers are supplied if available. To further aid readers of CHEMCYCLOPEDIA in locating specific products, chemicals are listed in categories consistent with accepted patterns of use. The categories are:

1. Organic Chemicals
2. Oils, Fats, and Waxes
3. Fatty Chemicals
4. Surfactants
5. Inorganic Chemicals
6. Industrial and Specialty Gases
7. Pigments and Dyes
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9. Catalysts and Process Chemicals
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continued on page 6



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Typical Page

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Croda, Inc. INCROMETANT AMEA-70 and -100. Liquids at 70% and 100% active. Clarifying/deterging agents in shampoos, conditioners, and cream rinses; humectants in creams and lotions.

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Pilat Chemical Co. CALFOAM. Liquid forms. Tank car, tank truck, 55-gal drum.

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ALCOHOL-ETHOXYLATED-PROPOXYLATED SURFACTANT DEFOAMER

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McIntyre Chemical

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