

Solutes ...
Surface-active solutes ...
Surface-active agents ...
Surfactants

Lecture 1

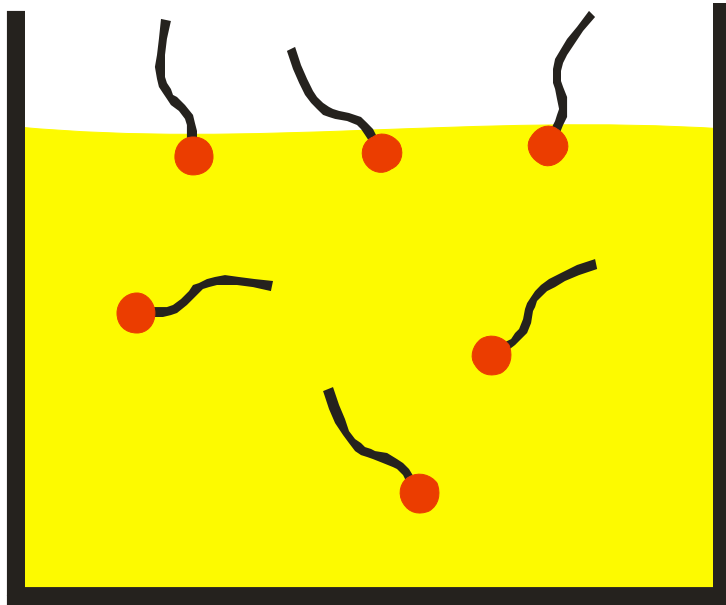
Surface tension is a pull



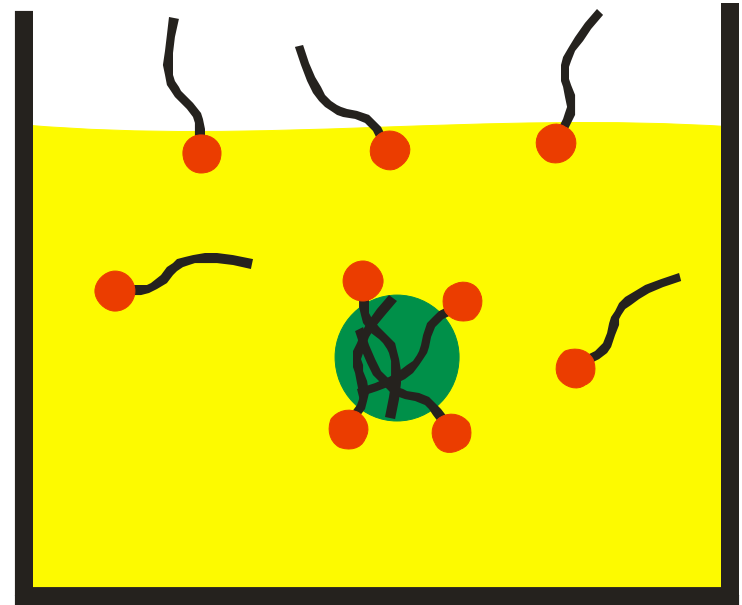
Adsorption lowers the energy

At the air/liquid interface:

And the solid/liquid interface:



Lowers surface tension.



Stabilizes dispersions.

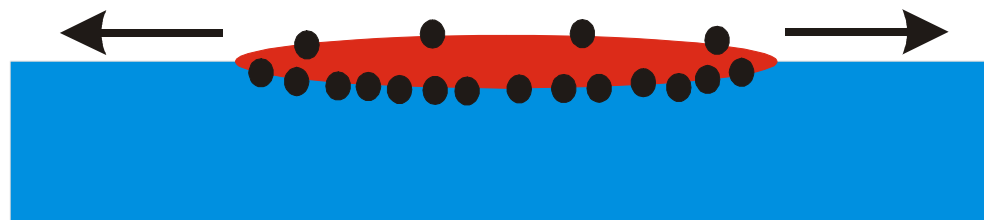
Spreading



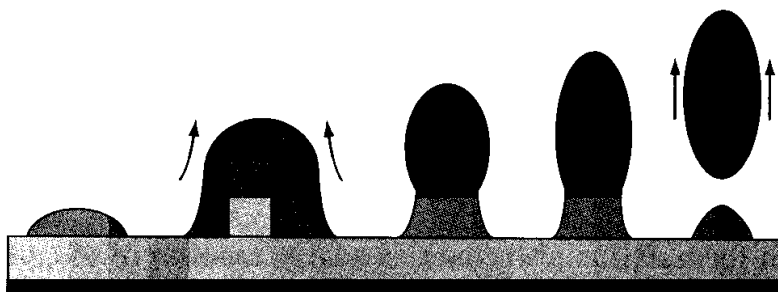
The energy change per unit area for liquid 2 (top) to spread across the surface 1 (bottom) is:

$$\Delta \bar{F} = (\sigma_2 + \sigma_{12} - \sigma_1)$$

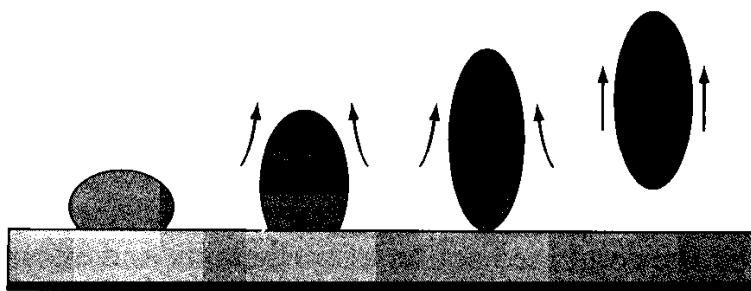
Surfactants reduce the two terms positive terms allowing the drop to spread.



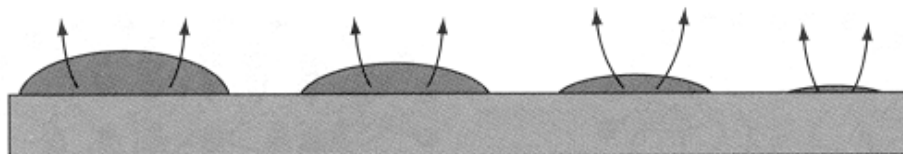
Detergency



The emulsification mechanism of removal of oily soil from a solid surface



The roll-up mechanism of removal of oily soil from a solid surface



The solubilization mechanism of removal of oily soil from a solid surface

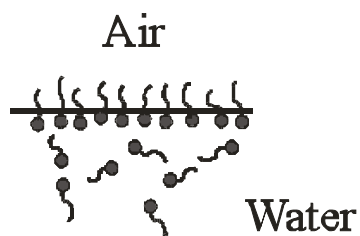
Requires only that the energy of surfactant adsorption is greater than the energy of the new liquid surface created.

Also requires that the surfactant lower the new solid/liquid interface to be less than the previous solid/oil interface.

Requires spontaneous absorption of oil into micelles.

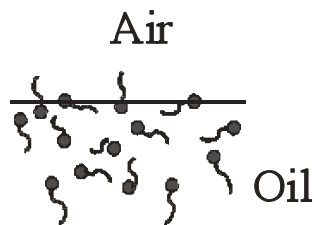
Adsorption at interfaces

Air-water surface



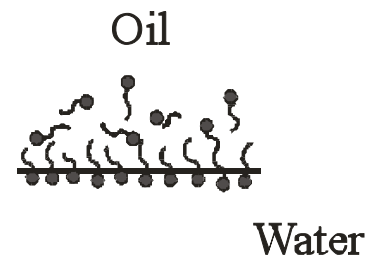
Strong adsorption, substantial lowering of surface tension.

Air-oil surface



Little adsorption, little lowering of surface tension.

Oil-water interface



Strong adsorption, substantial lowering of interfacial tension.

Etymology

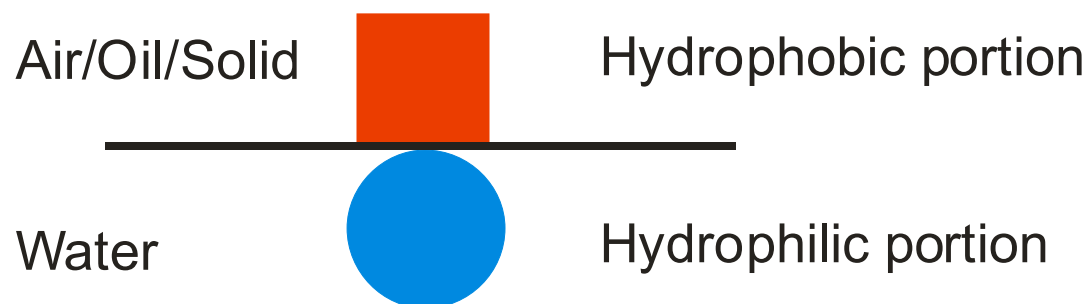
English	Greek	Latin
oil	lipo-	oleo-
water	hydro-	aqua-
solvent	lyo-	solvo-
both	amphi-	
flow	rheo-	
affinity	-philic	
lack-of-affinity	-phobic	
nature	-pathic	
science	-logy	

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:

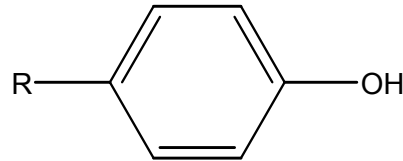
- amphipathic** = combining both natures (oil and water understood)
- amphiphilic** = with affinity for both (oil and water understood)
- hydrophilic** = with affinity for water
- lipophilic** = with affinity for oil
- lyophilic** = with affinity for the solvent
- lyophobic** = lack of affinity for the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

Common surfactants

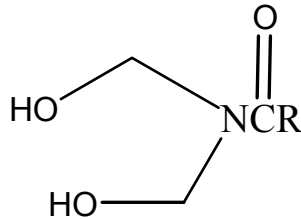


Large volume surfactants

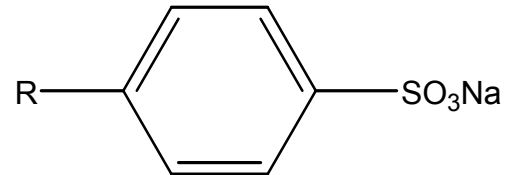
- Fatty alcohols and alkylphenol ethoxylates:



- Alkanolamides:



- Alkylbenzene sulphonates



- Fatty alcohol and fatty alcohol ether sulphates:



Classification of surfactants

- Anionic – The surface-active portion bears a negative charge
 - Alkane carboxylic salts (soap)
 - Alkane sulfonic salts (detergents)
 - Alkyl-aromatic sulfonic salts
 - Others: Phosphates, phosphoric salts
- Cationic – The surface-active portion bears a positive charge
 - Amine salts
 - Quaternary ammonium salts
- Zwitterionic – The surface-active portion bears both charges
 - Long-chain amino acid salts
 - Betaines
- Nonionic – The surface-active portion contains no charge
 - Long chain ethers
 - Fatty acid esters
 - Amides

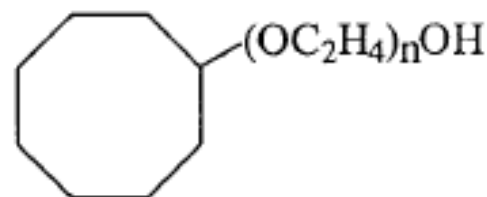
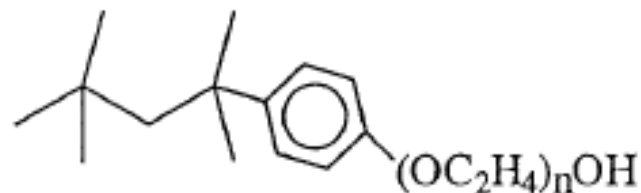
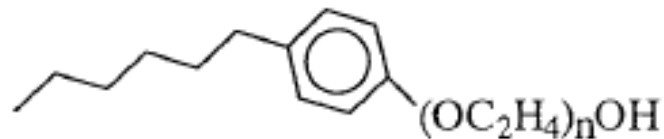
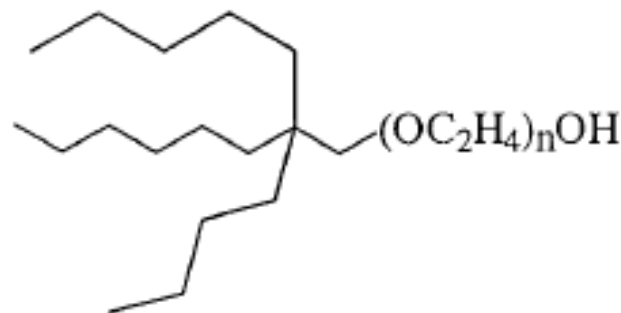
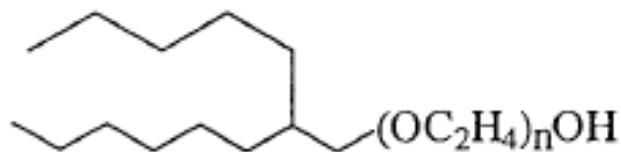
Nature of hydrophobic group

The variation in chemistry of the hydrophobic group is less pronounced than that of the hydrophilic group:*

- Straight chain, long alkyl groups (C8 – C20)
- Branched-chain, long alkyl groups (C8 – C20)
- Long chain (C8 – C15) alkylbenzene residues
- Alkylnaphthalene residues (C3 and greater)
- Rosin derivatives
- High MW propylene oxide polymers
- Long-chain perfluoroalkyl groups
- Polysiloxane groups
- Lignin derivatives.

* Rosen, 3rd ed., p. 4

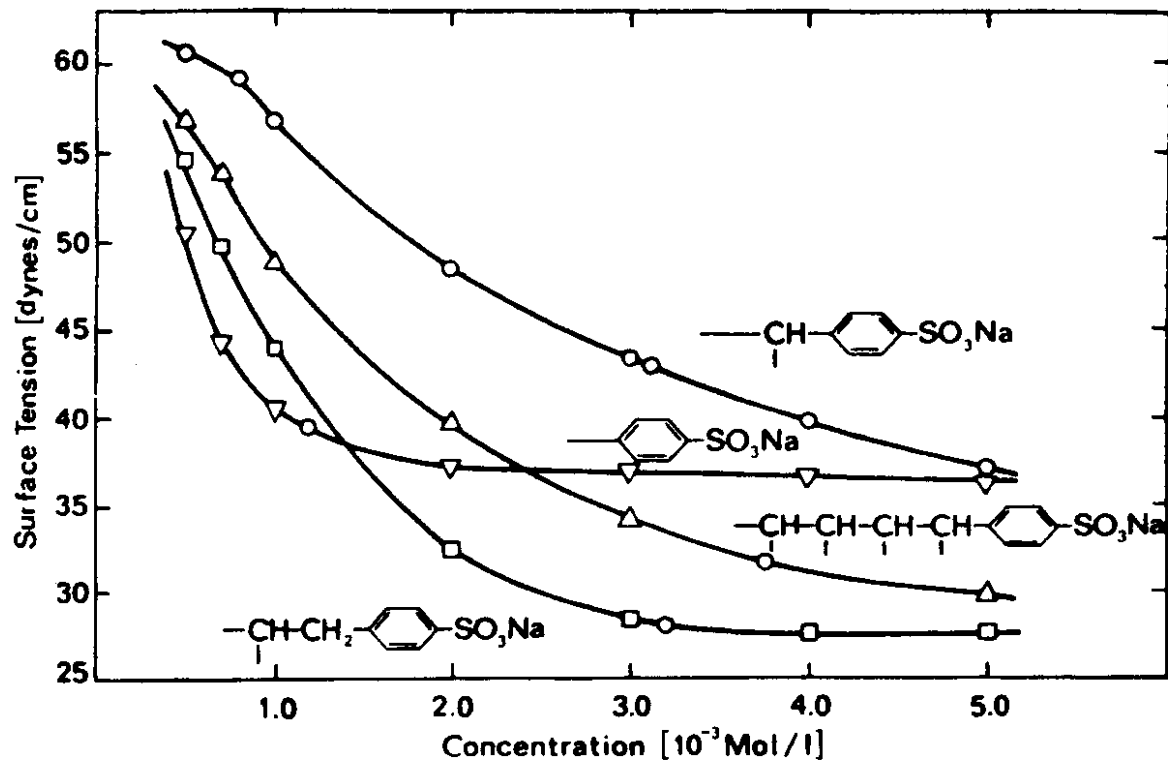
Surfactant structure



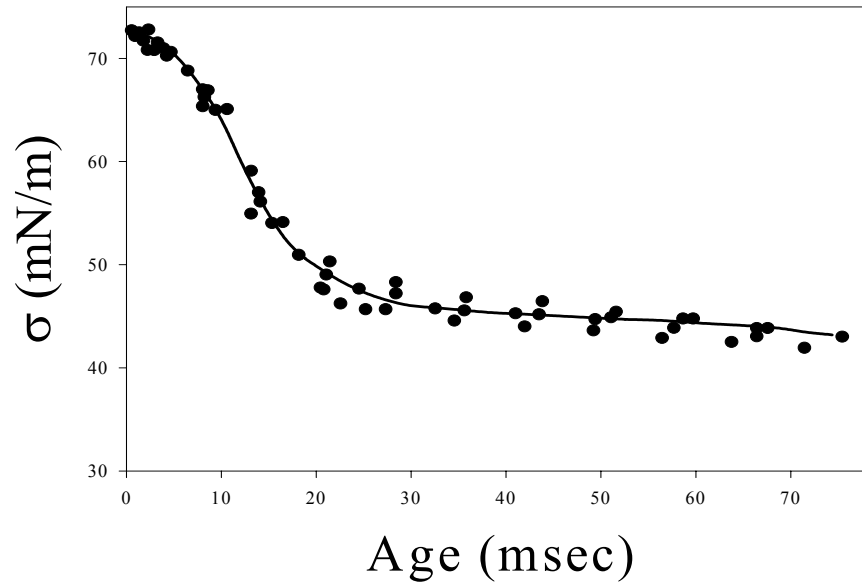
Structure affects adsorption, stability, solubility, and temperature dependence, etc.

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

Effect of structure on surface tension



Dynamic surface tension

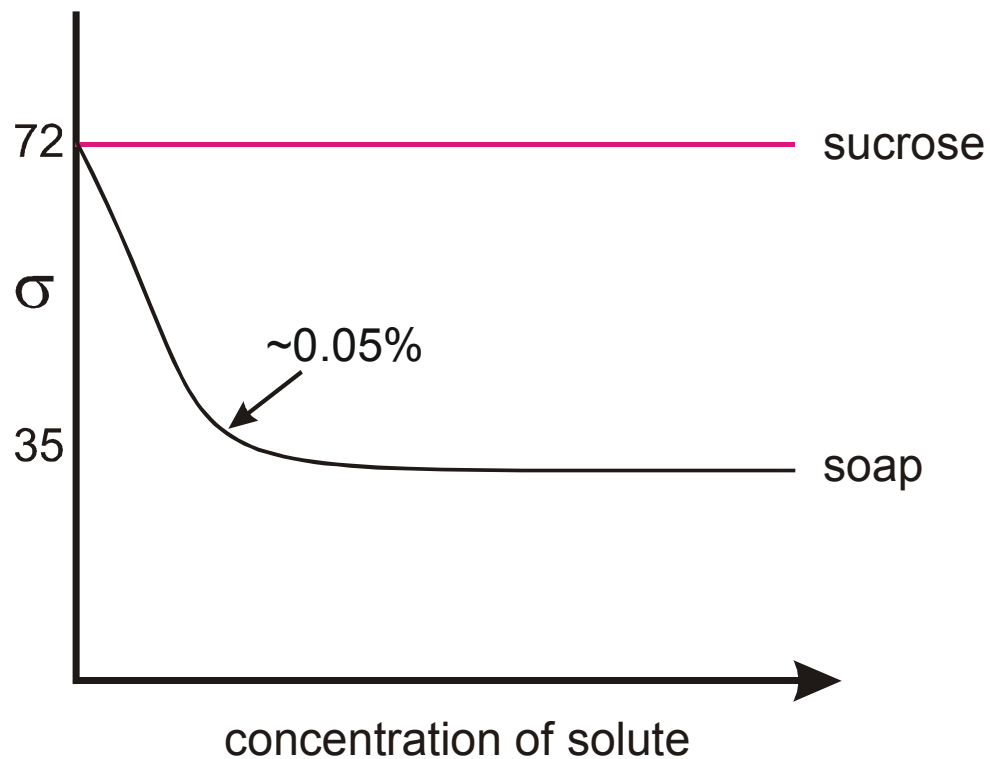


Aerosol OT at 500 mg/l by the vibrating jet.

Micelles and liquid crystals

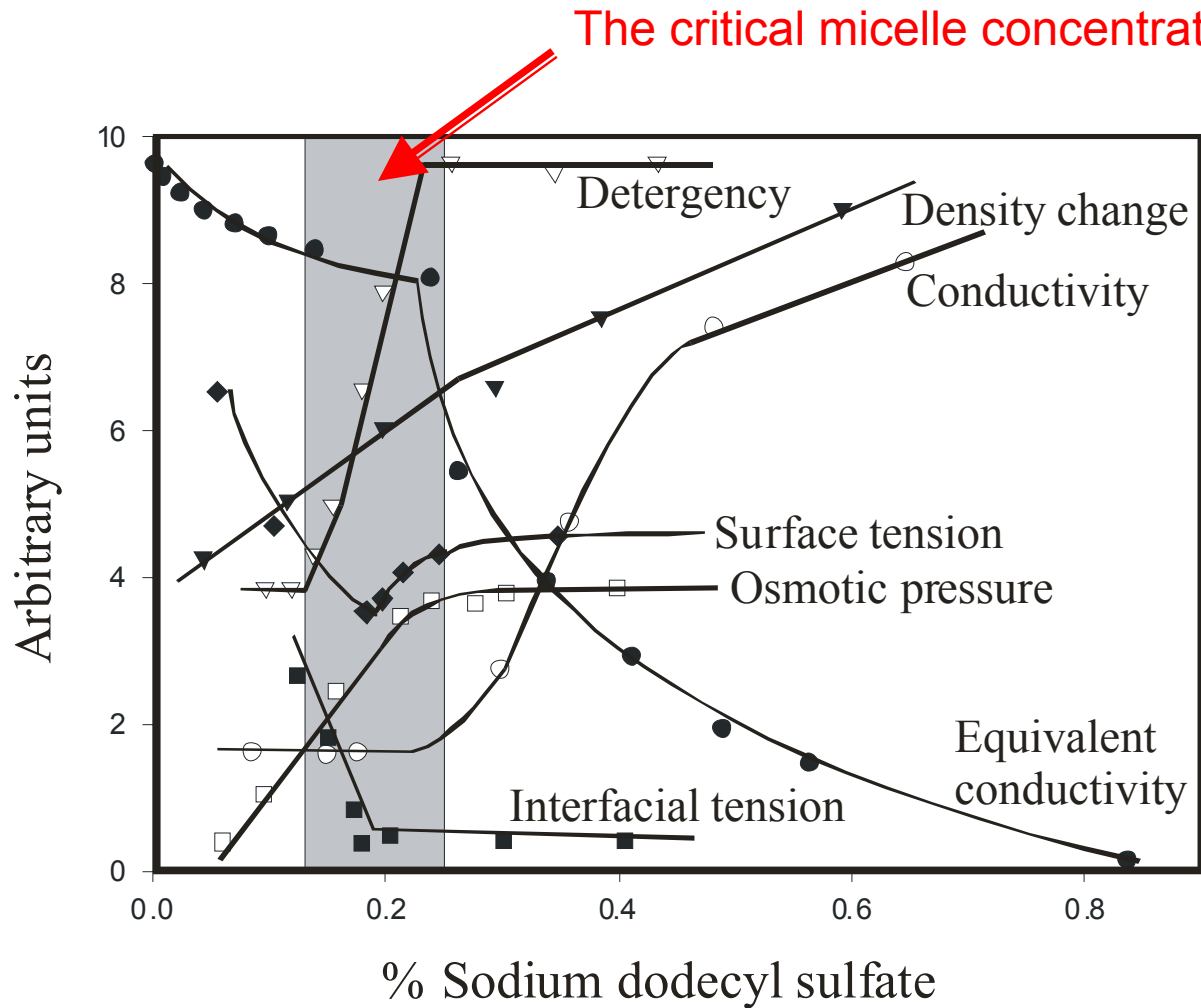
Surfactants “self-associate” at
higher concentrations

Lowering of surface tensions with surfactants

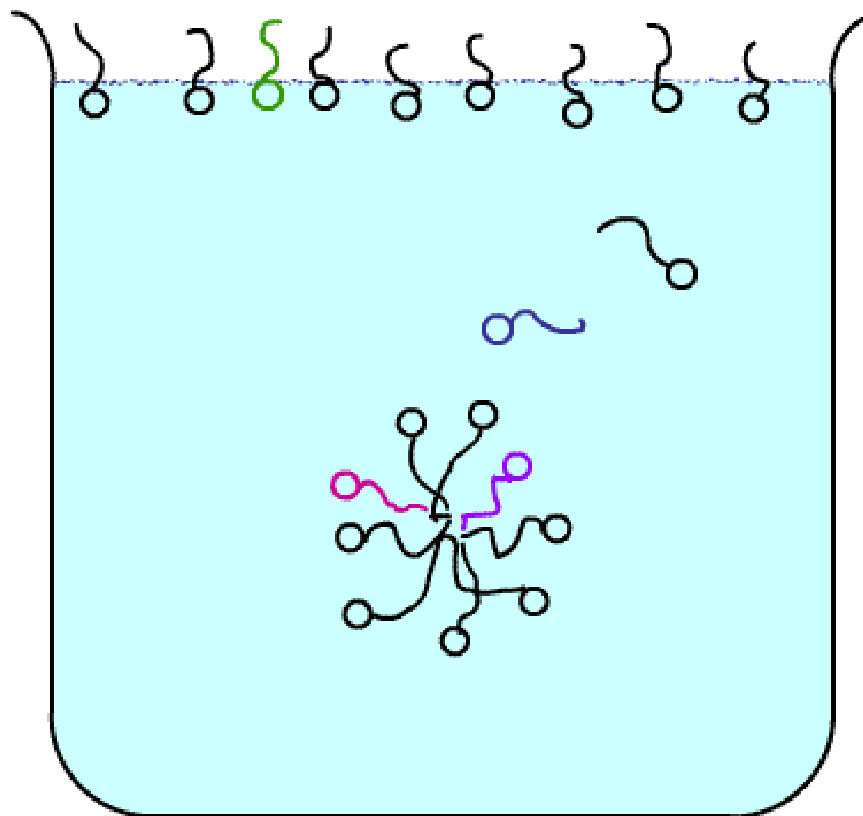


The surface tension drops but reaches a limit.

Physical properties of surfactant solutions

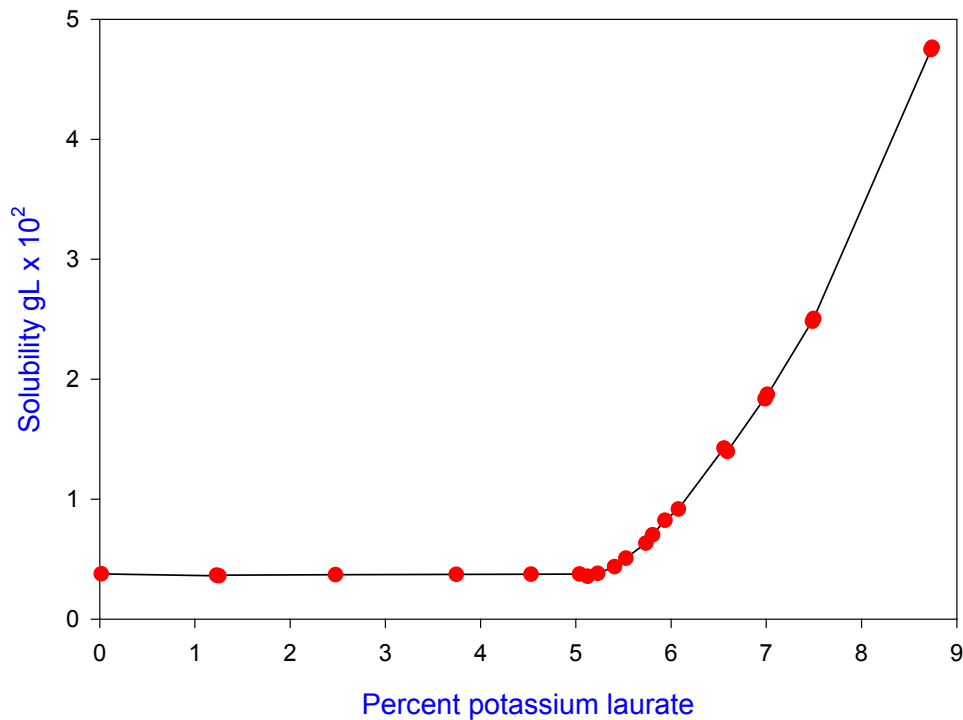


Surfactants can create their own “surface” - Micelles



Adsorption and micellization are competing processes.

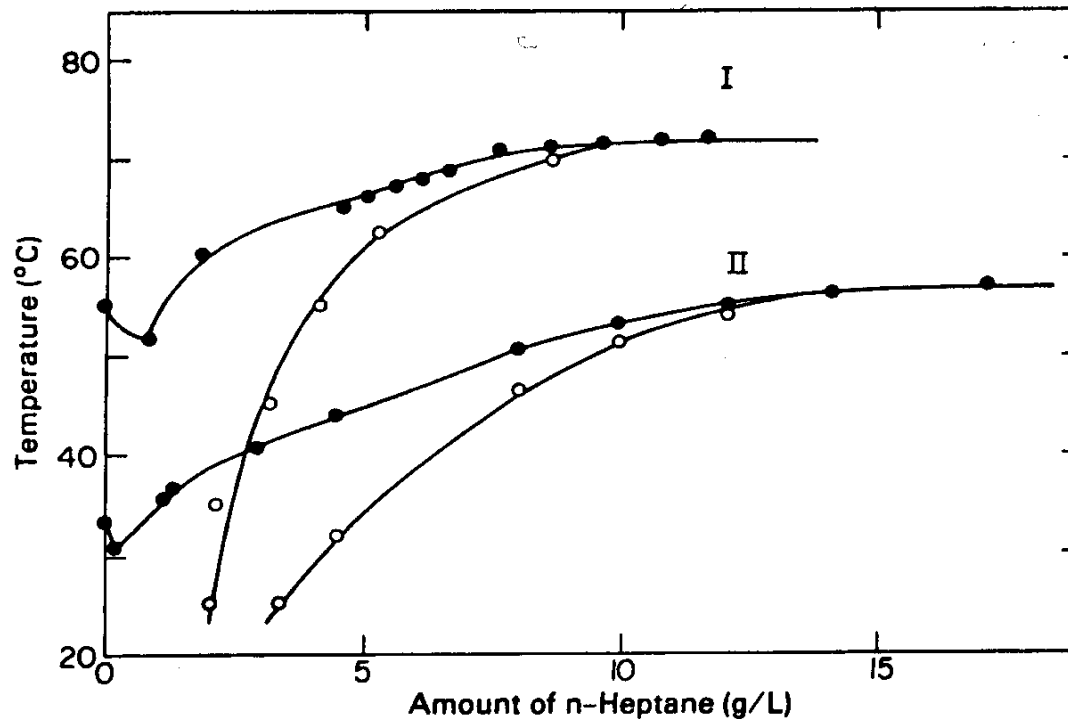
Solubilization below and above the CMC



The solubility of gas increases sharply after micelles form (at the CMC).

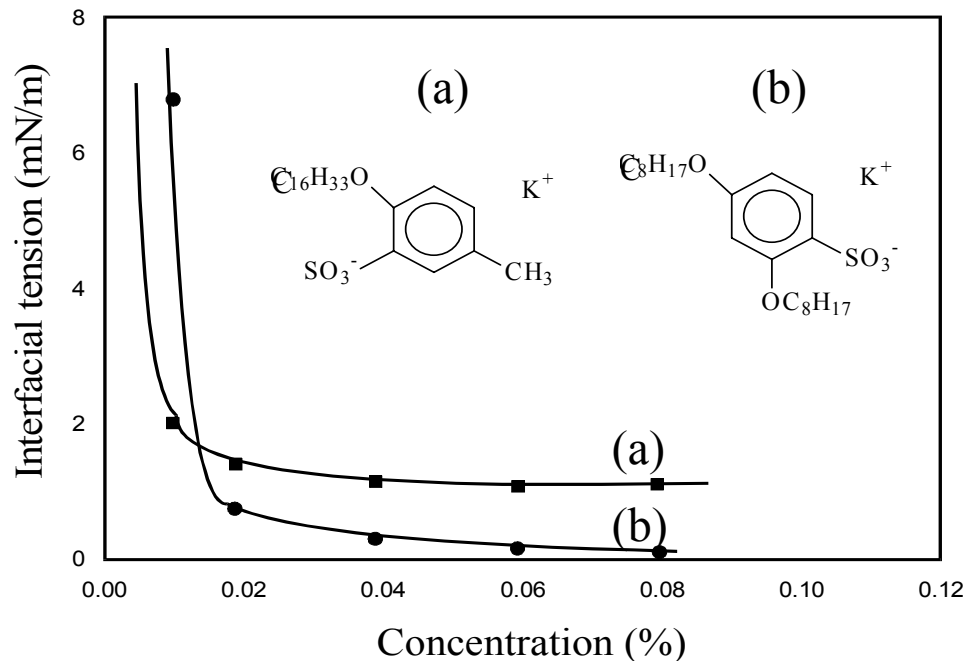
Solubility of 2-nitrodiphenylamine in aqueous solutions of potassium laurate.

Effect of temperature on solubilization for nonionics



Solubilization of n-heptane in 1% aqueous solutions of POE(9.0) nonylphenyl ether (I) and PEO(9.2) dodecylphenyl ether (II). Filled circles are cloud points. Open circles are solubility limits (Rosen, p. 188).

Effect of structure on micelle formation

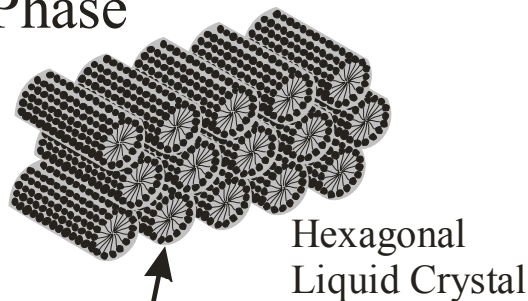


The linear molecule (a) forms micelles easily.

The branched molecule (b) does not form micelles so readily and therefore lowers surface tension more.

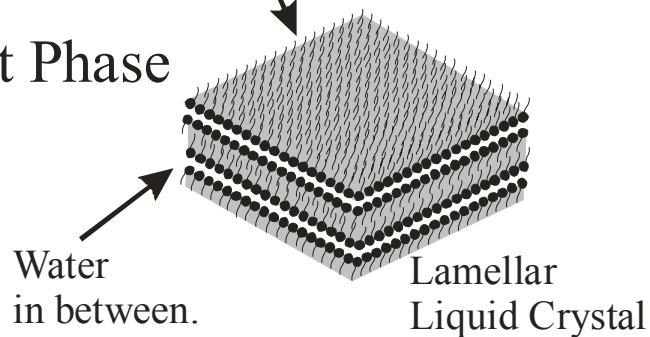
Surfactant “phases”

Middle Phase



Surfactant

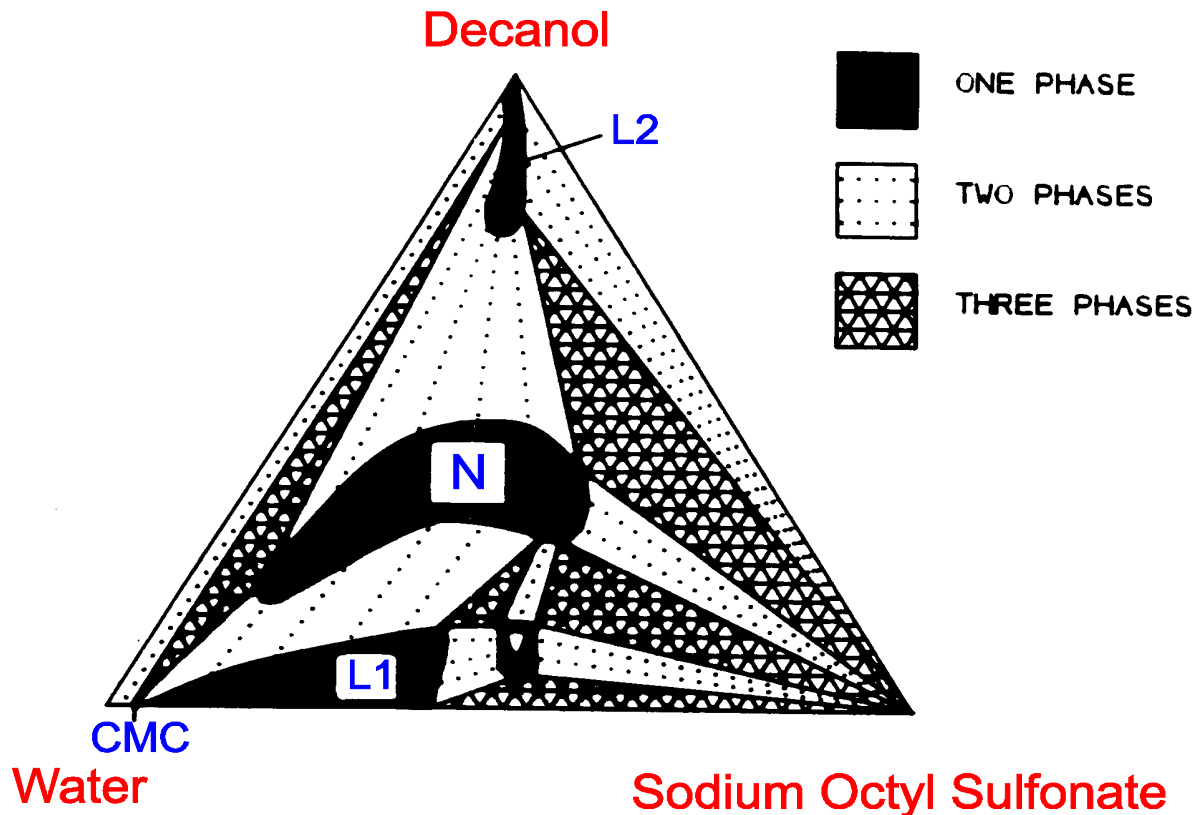
Neat Phase



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.)

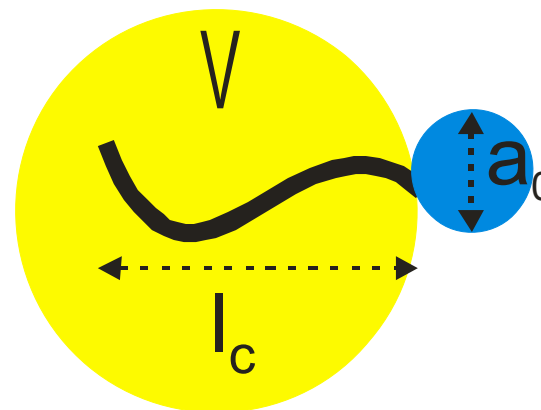
Packing parameters

The “shape” of a surfactant helps determine the “shape” of any structures formed.

V is the volume of the core

l_c is the length of the surfactant

a_0 is the cross sectional at the interface



Value of $\frac{V}{l_c a_0}$

Structure of micelle

0 - 1/3

Spheroidal in aqueous media

1/3 - 1/2

Cylindrical in aqueous media

1/2 - 1

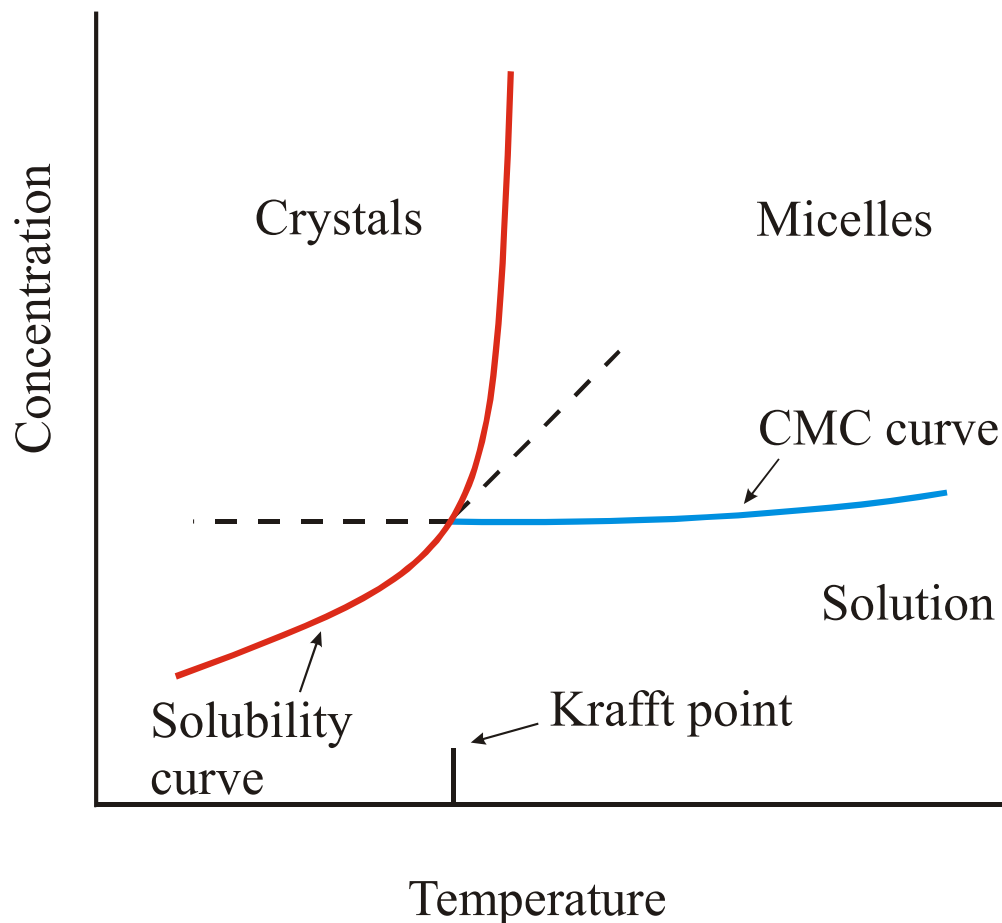
Lamellar in aqueous media

> 1

Inverse micelles in nonpolar media

Solubility of ionic surfactants

The Krafft Point

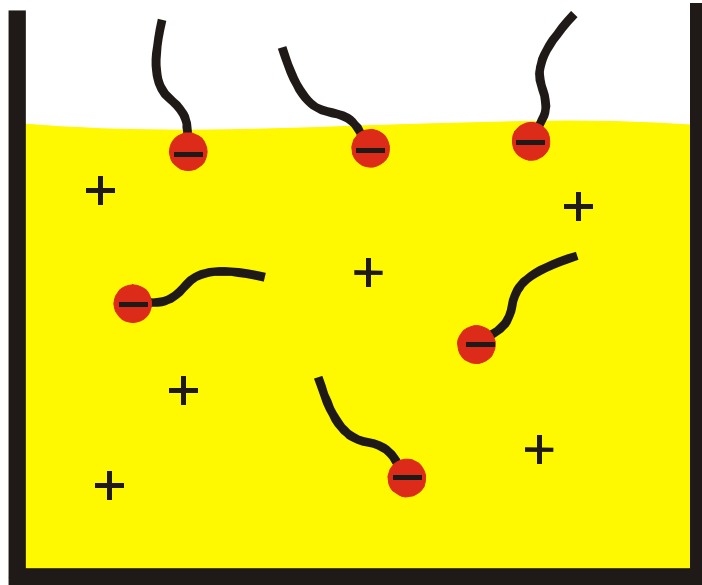


Note: the rapid increase in apparent solubility of the ionic surfactant at a critical temperature!

Micelles form above this temperature.

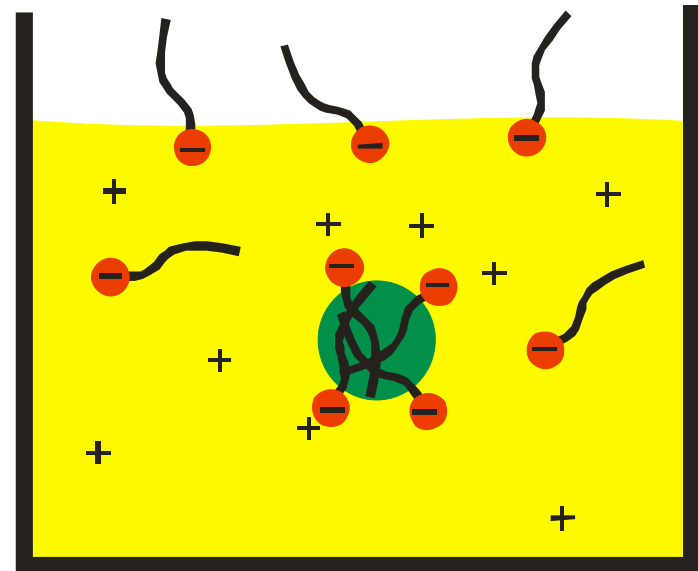
Adsorption of ionic surfactants

At the air/water interface:



Lowers surface tension.

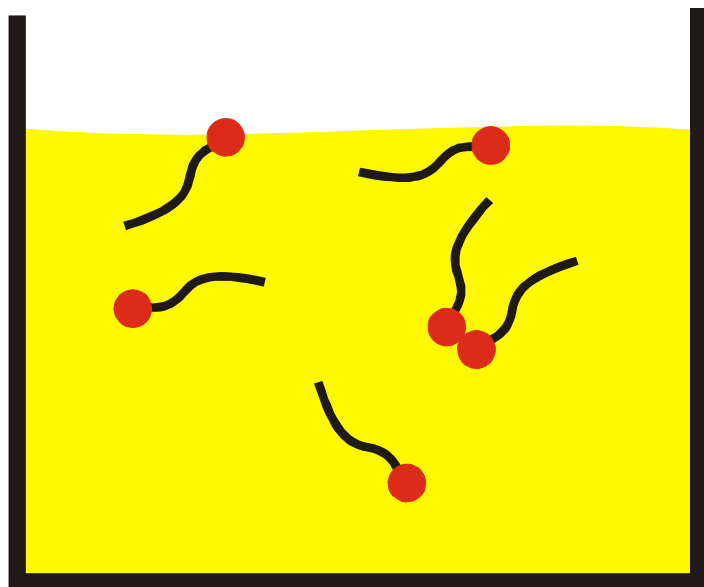
At the solid/water interface:



Charges the particle and stabilizes the dispersion.

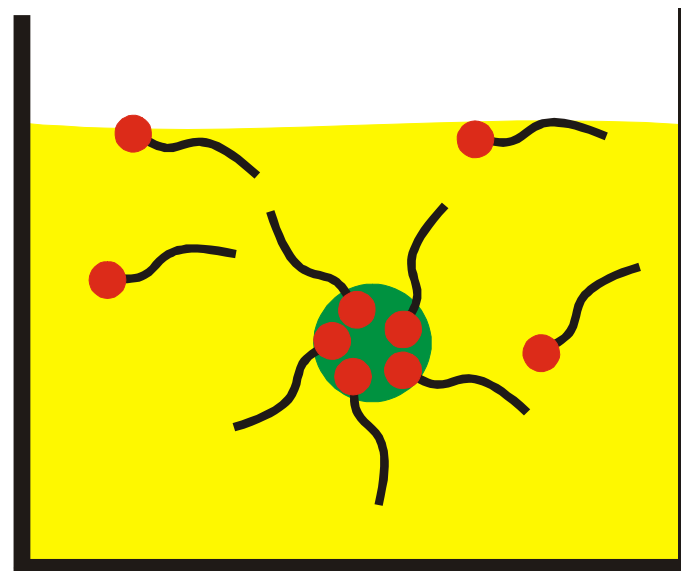
Adsorption of nonaqueous surfactants

At the air/oil interface:



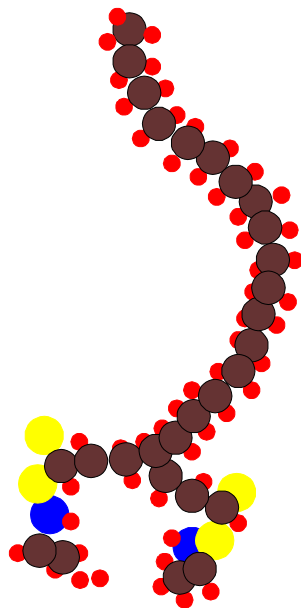
Little effect on surface tension.

At the solid/oil interface:



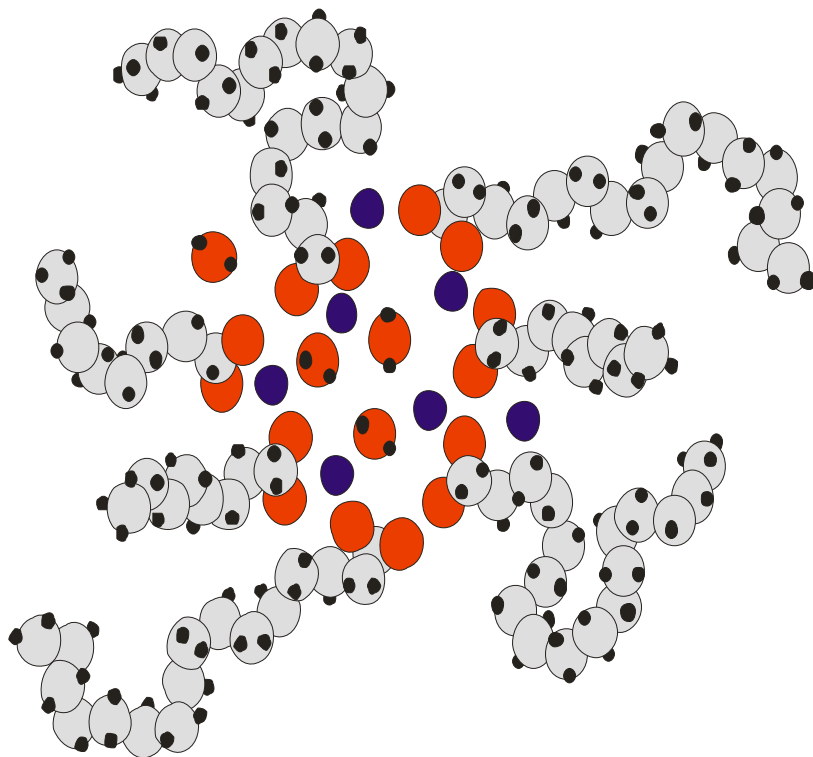
Stabilizes the dispersion.

Oil-soluble detergents



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 “surfactants” form inverse micelles

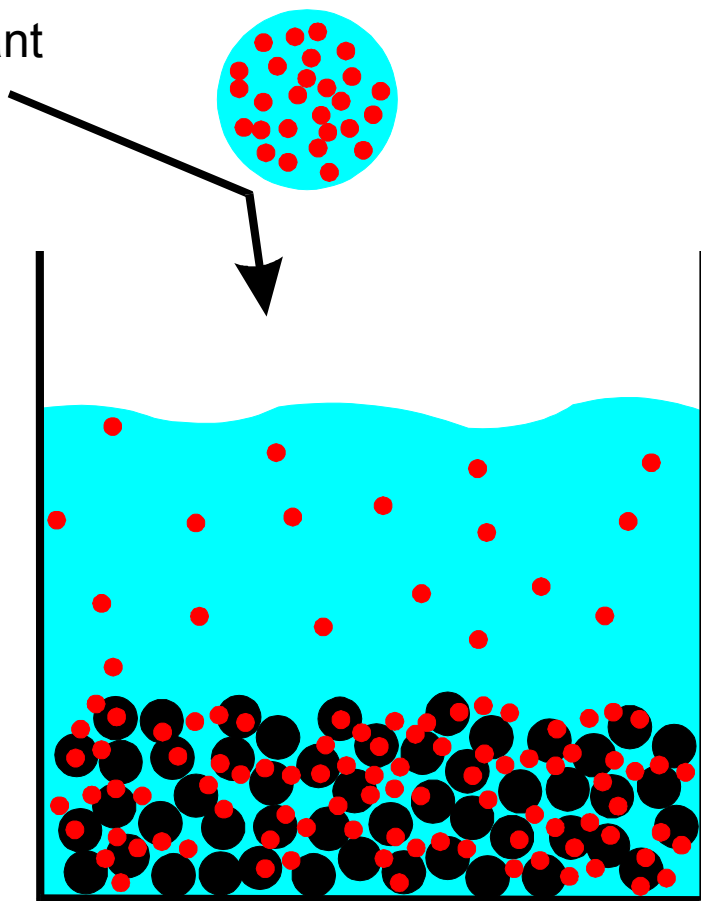


The micelle core is highly polar.

The diameters are 10's of nanometers.

Adsorption from Solution

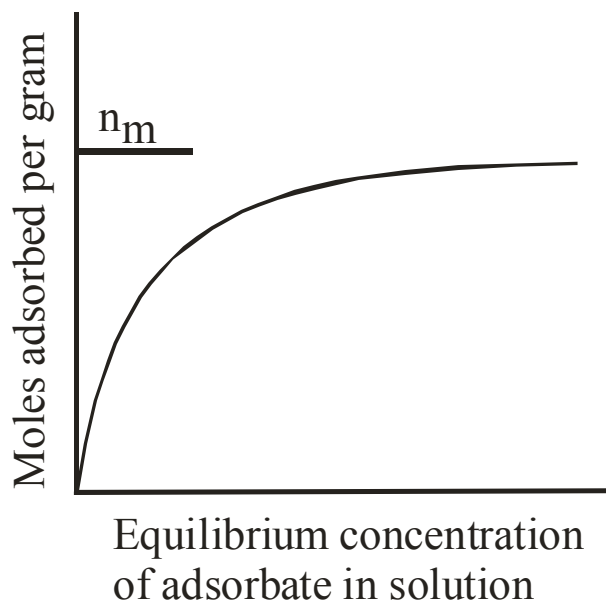
Titrate
surfactant



The moles adsorbed is the total number of moles added minus the concentration in solution after adsorption times the volume of the solution.

Since adsorption is “spontaneous”, the interfacial energies must be lower.

Langmuir Adsorption Isotherm

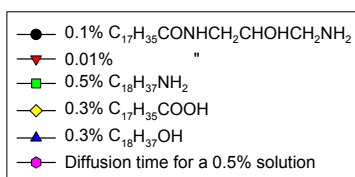
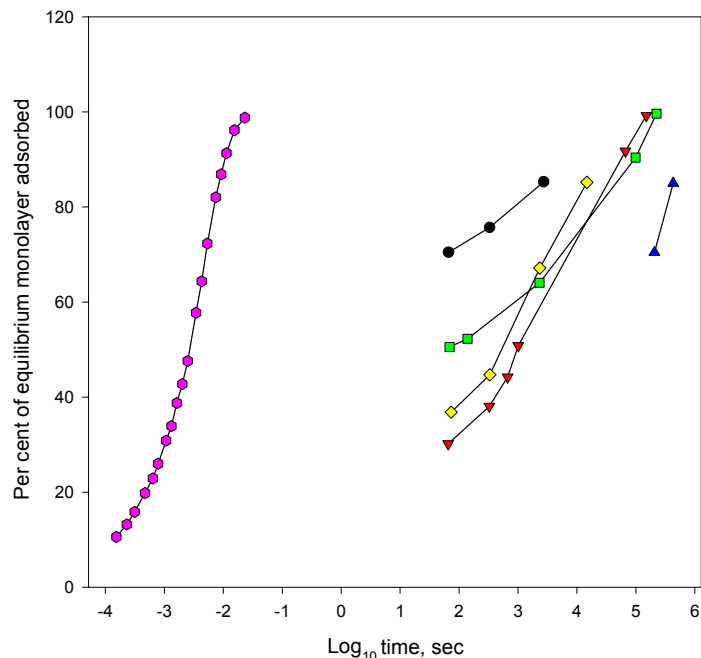


$$\frac{n}{n_m} = \frac{c}{K + c}$$

n_m is called the monolayer capacity and has units of moles per gram of solid.

K is called the Henry's law constant and is a measure of the solid-adsorbate interaction.

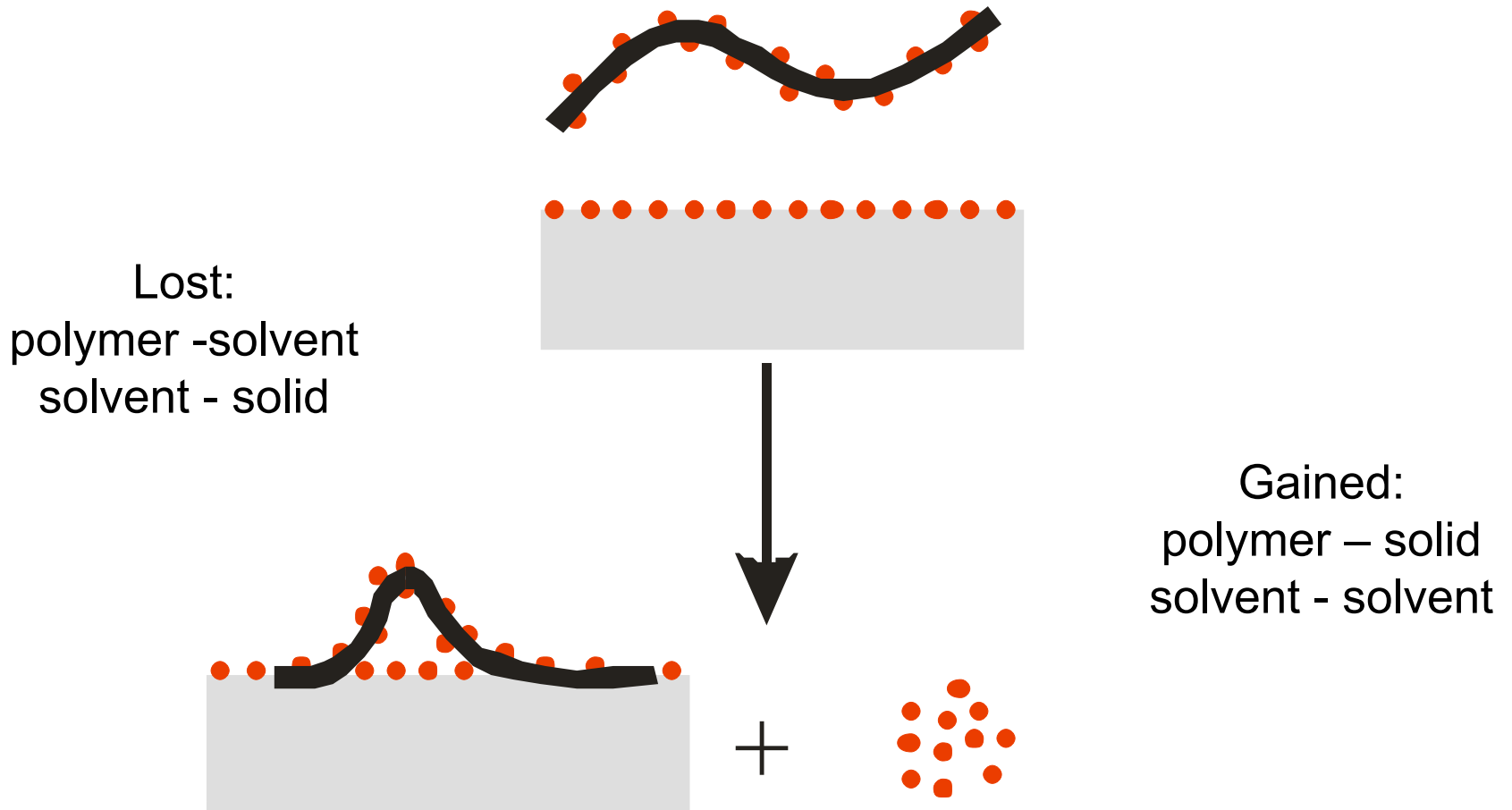
Adsorption at a solid surface is a slow process



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.

Polymer Adsorption

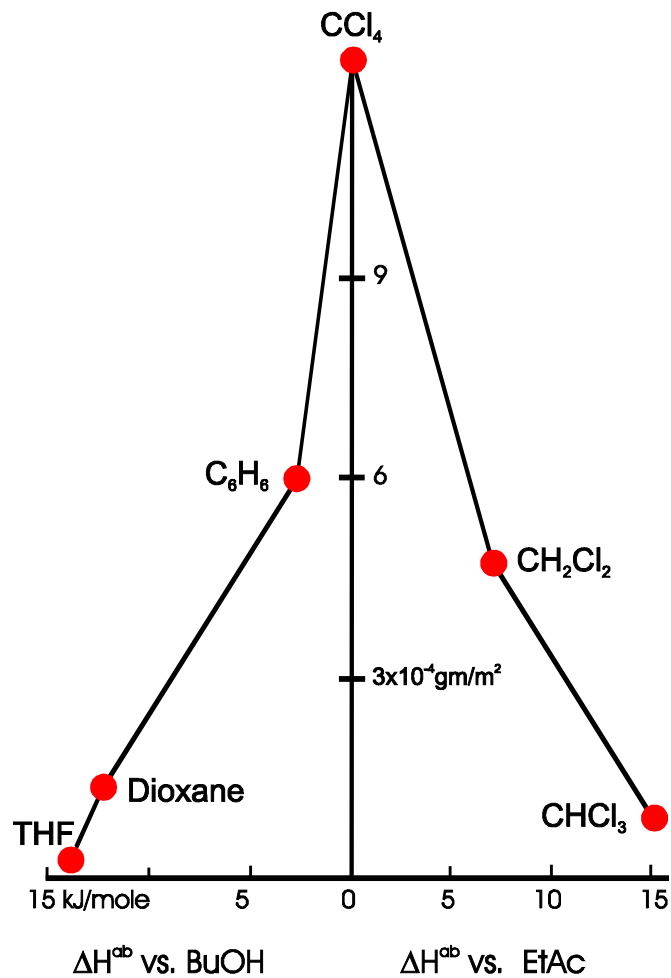


Drago E and C Parameters

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

Acids	C_a	E_a
Iodine	2.05	2.05
Iodine monochloride	1.697	10.43
Thiophenol	0.405	2.02
<i>p-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	Sulfuryl 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	<i>N</i> -Methyl-2-caprolactam	27.1
HMPA	10.6	Benzoyl chloride	2.3	<i>N</i> -Methyl-2-pyrrolidinone	27.3
Dioxane	10.8	Nitromethane	2.7	<i>N,N</i> -Dimethylacetamide	27.8
Acetone	12.5	Dichloroethylene carbonate	3.2	Dimethyl sulfoxide	29.8
<i>N</i> -Methyl-2-pyrrolidinone	13.3	Nitrobenzene	4.4	<i>N,N</i> -Diethylformamide	30.9
DMA	13.6	Acetic anhydride	10.5	<i>N,N</i> -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	<i>tert</i> -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	<i>n</i> -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

ACS© 2005

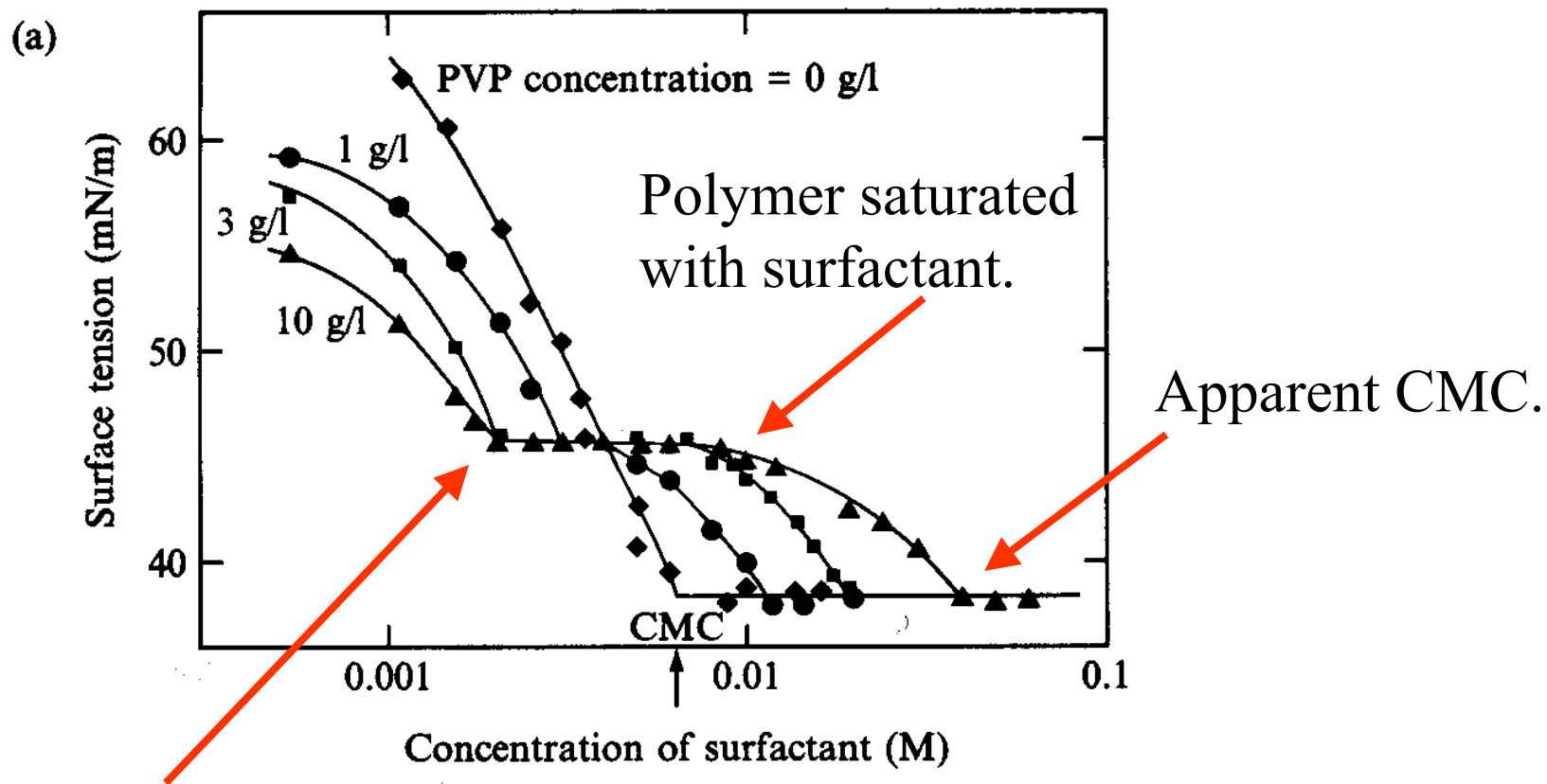
Lecture 1 - Surfactants

35

Common Polymeric Stabilizers

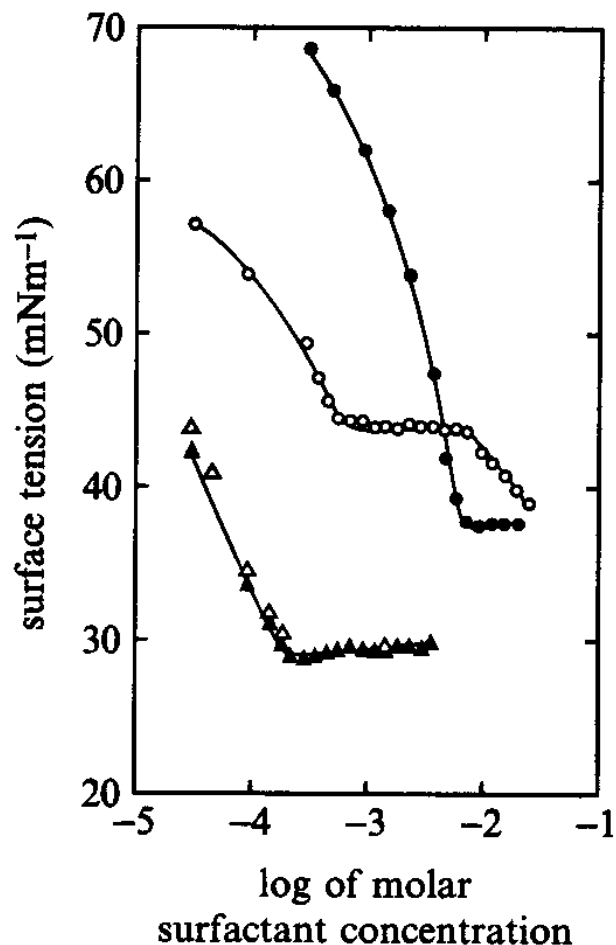
Aqueous dispersions	
Anchor polymer	Stabilizing moieties
Polystyrene	Poly(oxyethylene)
Poly(vinyl acetate)	Poly(vinyl alcohol)
Poly(methyl methacrylate)	Poly(acrylic acid)
Poly(acrylonitrile)	Poly(methacrylic acid)
Poly(dimethylsiloxane)	Poly(acrylamide)
Poly(vinyl chloride)	Poly(vinyl pyrrolidone)
Poly(ethylene)	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)

Surfactant(SDS) – Polymer Interaction



Onset of surfactant/polymer interaction.

Surfactant (SDS) – Protein Interactions



The effect of gelatin on the surface tension of solutions of SDS (circles) and Triton-X100 (triangles). Without gelatin (filled) and with gelatin (open).

For Triton X-100: no interaction with the nonionic.

For SDS: a plateau corresponding to a protein/surfactant association.

Reference material

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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.](#)
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[DuPont](#)
[EAC Chemicals](#)
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[Goldschmidt AG \(Degussa\)](#)
[Henkel KGaA \(The Henkel Group\)](#)
[Heterene Inc.](#)
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[Novo Nordisk A/S](#)
[Petroferm, Inc.](#)
[PILOT Chemical Company](#)
[Procter & Gamble Chemicals](#)
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[Rohm and Haas](#)
[Shell Chemical](#)
[Stapan Co.](#)
[Taiwan Surfactant Co.](#)
[Tomah Products, Inc.](#)
[Uniqema](#)

2. Surfactant Distributors

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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	Y	Y
nonpolar	Y	Y	.	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	.	Y
cold acid	.	Y	.	.	.	N	.	N	.	.	Y	.	Y	.	Y	.	Y
cold base	Y	Y	.	.	.	Y	Y	.	Y	.	Y	.	.	N	Y	.	Y
warm base	Y	Y	.	.	.	Y	Y	.	Y	.	Y	.	.	N	Y	.	Y
hot base	Y	Y	N	.	.	.	Y	Y	.	.	Y	.	.	N	Y	.	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	Y	.
oxide/h	.	.	.	Y	Y	.
H-b org	Y	.	Y	Y	Y	Y
proteins	.	.	Y	.	.	.	Y	.	Y	Y	Y	Y	Y
polar	.	.	.	Y	Y	.	Y	Y	Y	Y	Y	Y	Y
nonpolar	.	.	.	Y	Y	.	Y	Y	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	Y	Y
warm base	.	.	.	Y	.	.	Y	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 iii

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

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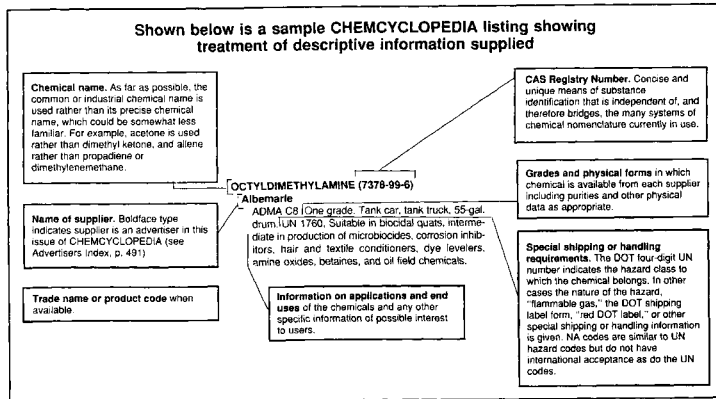
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2. Oils, Fats, and Waxes
3. Fatty Chemicals
4. Surfactants
5. Inorganic Chemicals
6. Industrial and Specialty Gases
7. Pigments and Dyes
8. Plastics, Additives, and Synthetic Elastomers
9. Catalysts and Process Chemicals
10. Environmental Chemicals and Services
11. Pharmaceuticals and Fine Chemicals

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continued on page 6



Typical Page

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Crods, Inc. INCROMECTANT AMEA-70 and -100. Liquids at 70% and 100% active. Clarifying detangling agents in shampoos, conditioners, and cream rinses; humectants in creams and lotions.

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Norman, Fox & Co.
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Vista Chemical Co. ALFONIC, NOVEL II. Wide range