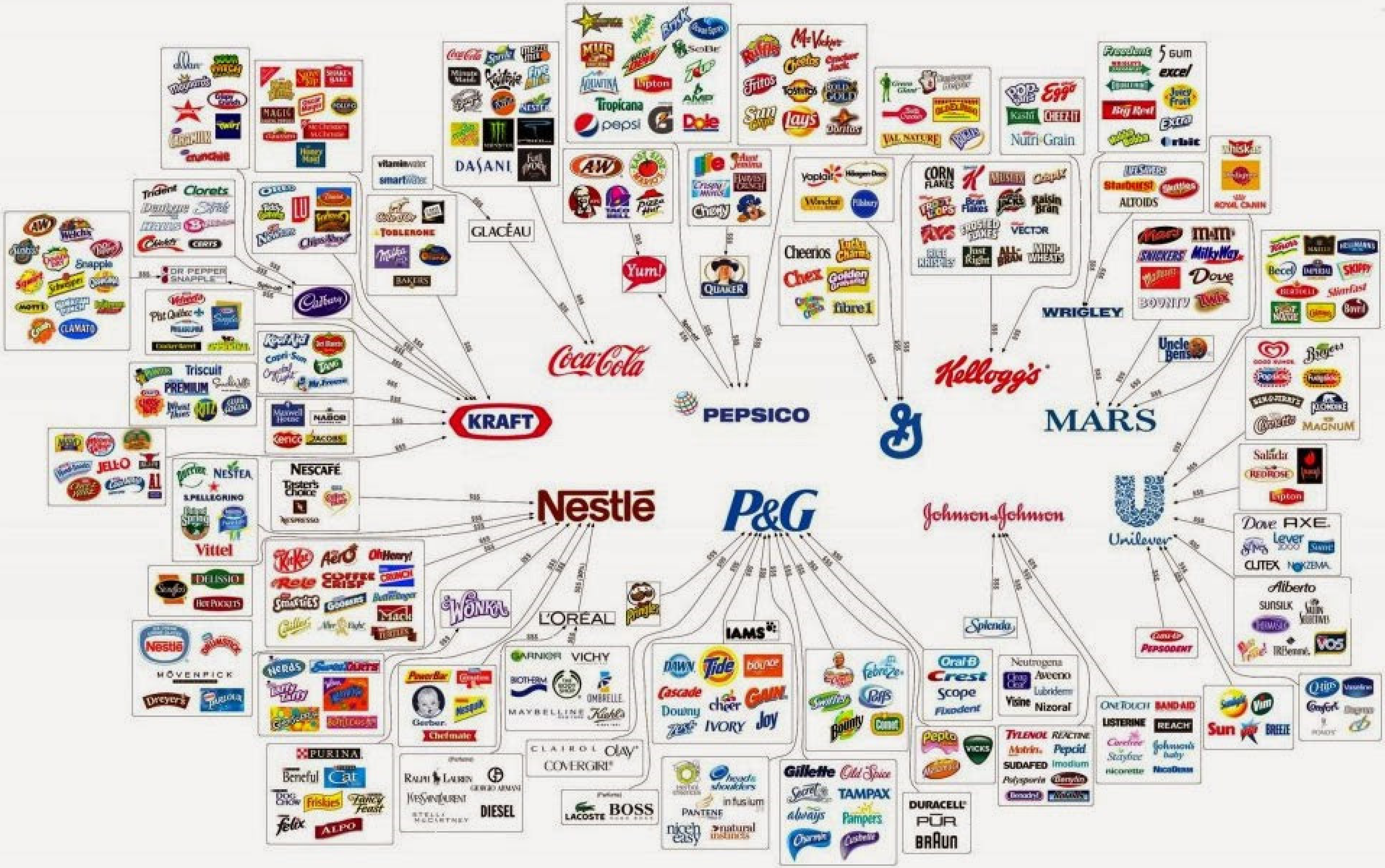
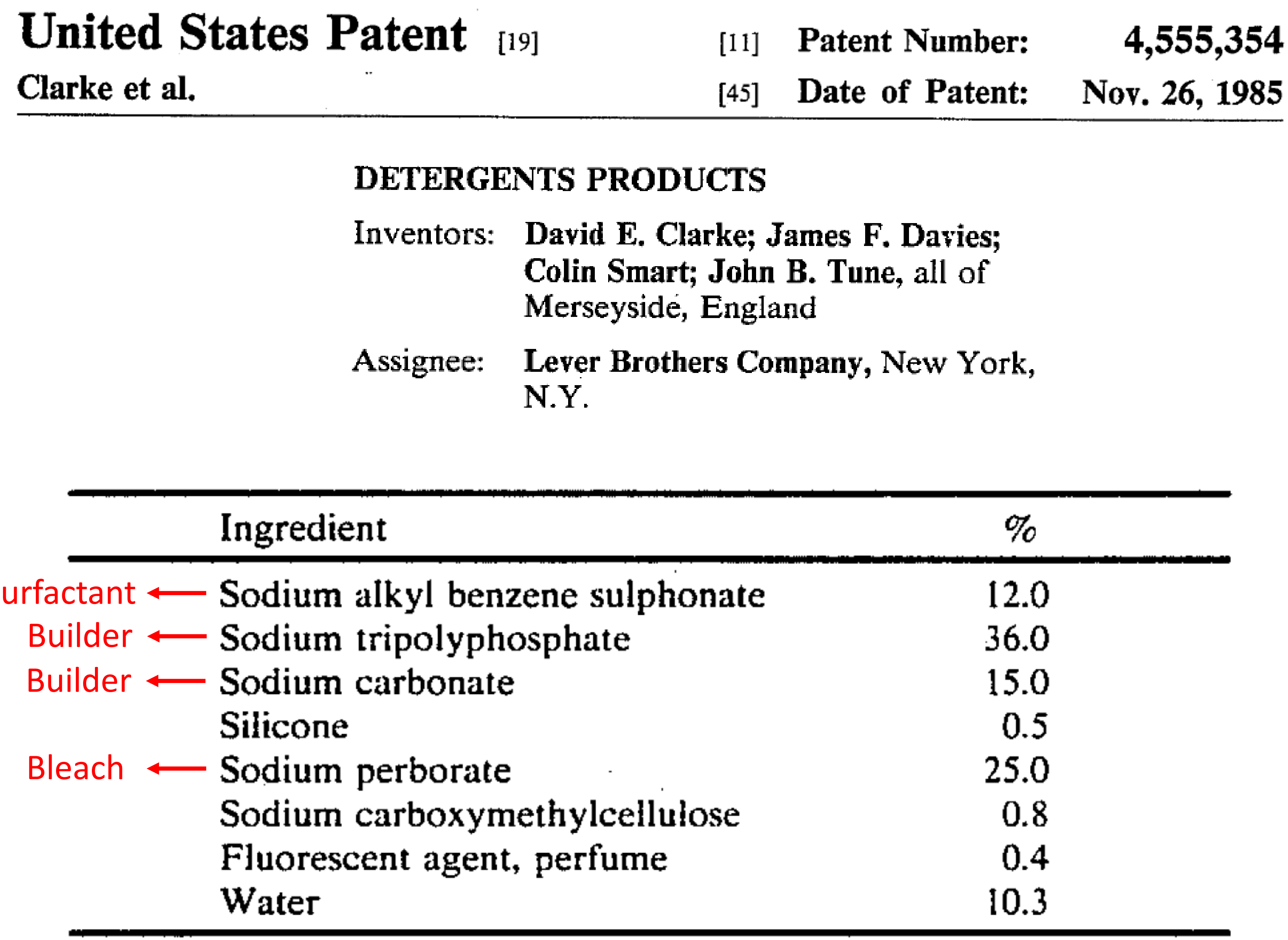
Detergent Chemistry

Owner: P&G

Owner: Henkel AG / Unilever


KRAFT
Coca-Cola
PEPSICO
Kellogg's
MARS
Nestlé
P&G
Johnson & Johnson
Unilever
Yum!
QUAKER
WRIGLEY
GLACÉAU
Cadbury
DR PEPPER SNAPPLE
Uncle Ben's
Wonka
L'ORÉAL
Pringles
IAMS
Splenda
Pepsodent
vitaminwater
smartwater
DASANI
Tropicana
pepsi
Lipton
Dole
Cheerios
Chex
fibre1
Pillsbury
Häagen-Dazs
CORN FLAKES
VECTOR
Nutri-Grain
5 GUM
excel
Orbit
ALTOIDS
Starburst
M&M's
SNICKERS
Milky Way
Dove
BOUNTY
TWIX
WHISKAS
ROYAL CANIN
Knorr
SKIPPY
Bovril
Ben & Jerry's
Magnum
Cornetto
Salada
REDROSE
Lipton
Dove
AXE
Lever 2000
CUTEX
NOXZEMA
Alberto
SUNSILK
TRESemmé
VO5
Sun
BREEZE
Vaseline
PONDS
ONE TOUCH
BAND-AID
LISTERINE
REACH
Johnson's baby
Nicorette
TYLENOL
Motrin
Pepcid
SUDAFED
Imodium
Polysporin
Neutrogena
Aveeno
Nizoral
Visine
Oral-B
Crest
Scope
Fixodent
VICKS
Pepto
Febreze
Bounty
DAWN
Tide
Cascade
Downy
cheer
GAIN
IVORY
Joy
Gillette
Old Spice
Secret
TAMPAX
always
Pampers
Charmin
head & shoulders
PANTENE
infusium
nice'n easy
natural instincts
DURACELL
PUR
BRAUN
CLAIROL
Olay
COVERGIRL
LACOSTE
BOSS
RALPH LAUREN
GIORGIO ARMANI
YVES SAINT LAURENT
STELLA McCARTNEY
DIESEL
GARNIER
VICHY
BIOTHERM
THE BODY SHOP
MAYBELLINE
Kiehl's
PURINA
Beneful
Cat Chow
Dog Chow
Friskies
Fancy Feast
Felix
ALPO
PowerBar
Carnation
Gerber
Nesquik
Chef-mate
Nestlé
MÖVENPICK
Dreyer's
Parlour
Nerds
SweeTARTS
Laffy Taffy
KitKat
Aero
Oh Henry!
Rolo
COFFEE CRISP
CRUNCH
Smarties
Goobers
Butterfinger
Stouffer's
DELISSIO
Hot Pockets
Perrier
NESTEA
S.PELLEGRINO
Poland Spring
Vittel
NESCAFÉ
Taster's Choice
Coffee-mate
NESPRESSO
JELL-O
A1
Maxwell House
NABOB
JACOBS
Triscuit
PREMIUM
Wheat Thins
RITZ
Kool-Aid
Capri Sun
Crystal Light
Del Monte
Velveeta
Philadelphia
TOBLERONE
Milka
BAKERS
OREO
Chips Ahoy!
Trident
Clorets
Dentyne
Halls
Chiclets
CERTS
Stride
Mott's
Snapple
Schweppes
Sunkist
CLAMATO
Honey Maid
Nabisco
$$$



United States Patent [19]

Clarke et al.

[11] **Patent Number:** **4,555,354**

[45] **Date of Patent:** **Nov. 26, 1985**

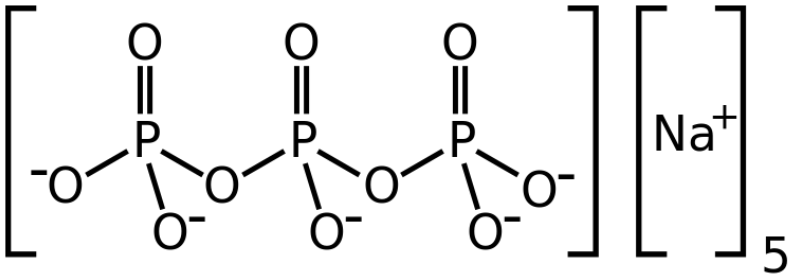
DETERGENTS PRODUCTS

Inventors: **David E. Clarke; James F. Davies; Colin Smart; John B. Tune**, all of Merseyside, England

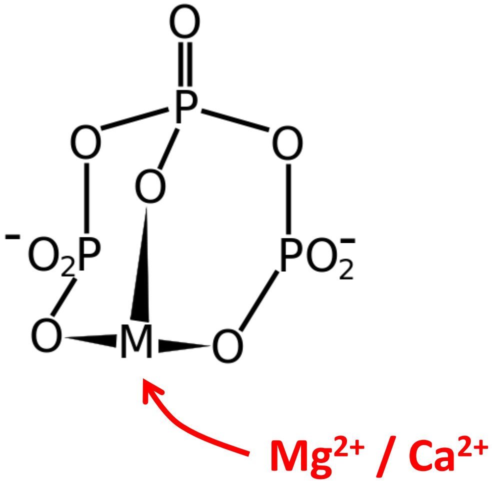
Assignee: **Lever Brothers Company**, New York, N.Y.

	Ingredient	%
Surfactant ⟵	Sodium alkyl benzene sulphonate	12.0
Builder ⟵	Sodium tripolyphosphate	36.0
Builder ⟵	Sodium carbonate	15.0
	Silicone	0.5
Bleach ⟵	Sodium perborate	25.0
	Sodium carboxymethylcellulose	0.8
	Fluorescent agent, perfume	0.4
	Water	10.3

Builder (Wiki:Chelating Agent)



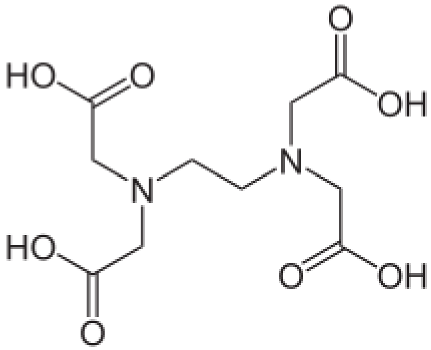
Sodium Tripolyphosphate



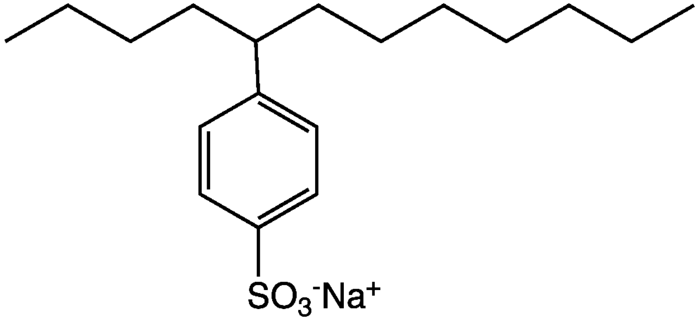
“Chelation” of metal ions by tripolyphosphate.

Act as “softener” to remove Ca and Mg ions from water.

Replaced by phosphate-free compounds such as EDTA



Surfactant



Sodium Alkyl Benzene Sulfonate

The main ingredient to remove dirt from clothes.

What is the science behind surfactant – water system?

Lecture 3

Surfactant Science

The functional chemical components inside detergents are the surfactants, which remove oil from dishes and dirt from clothes. The term *surfactant* is short for *surface active agent*[1] that "activates" the surface by reducing the surface / interfacial tension. In this lecture we will see the chemistry and physics behind the surfactant science.

3.1 Basic mechanism of surfactants

Surfactants are a large group of **amphiphilic** molecules which contains both hydrophobic and hydrophilic groups. Commercially available surfactants usually have a hydrophilic "head" (e.g. small polar or charged group, like -OH, -COOH, -CN, -SO_3^-, -OSO_3^-, etc.) and a hydrophobic "tail" (e.g. long hydrocarbon chains). The typical structure of a surfactant can be seen in Figure 3.1.

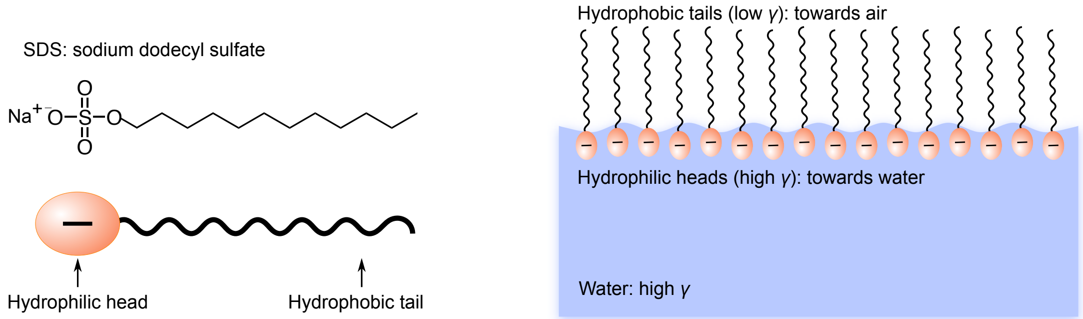

SDS: sodium dodecyl sulfate
Na⁺ ⁻O–S–O
O
O
−
Hydrophilic head
Hydrophobic tail
Hydrophobic tails (low γ): towards air
Hydrophilic heads (high γ): towards water
Water: high γ

Figure 3.1: Scheme of surfactants and its interfacial behavior. Left: chemical structure of a typical industrial surfactant, sodium dodecyl sulfate (SDS), which consists of a hydrophilic head and a hydrophobic tail. Right: assembly of surfactants on the water-air interface. The hydrophilic heads are embedded in water and tails are in air.

The interaction work ΔW_{hw} between the head and water is usually larger than ΔW_{tw} between the tail and water. Due to the large portion of tail, the energy dissolving a surfactant molecule in bulk water is larger than putting the surfactant at the water surface. At the water-air interface, the surfactants tend to have the heads towards water molecules, and the tails toward air (Figure 3.1). Experimentally, it is observed that the water surface tension γ_w of the surfactant solution varies with the surfactant concentration c. By adding surfactants, γ_w drops from the surface tension of pure water $\gamma_{L,0}$, before c reaches a critical concentration c_CMC (Figure 3.2). When $c > c_\mathrm{CMC}$, γ_w no longer decreases with further addition of surfactants. The concentration c_CMC is called the critical micelle concentration.

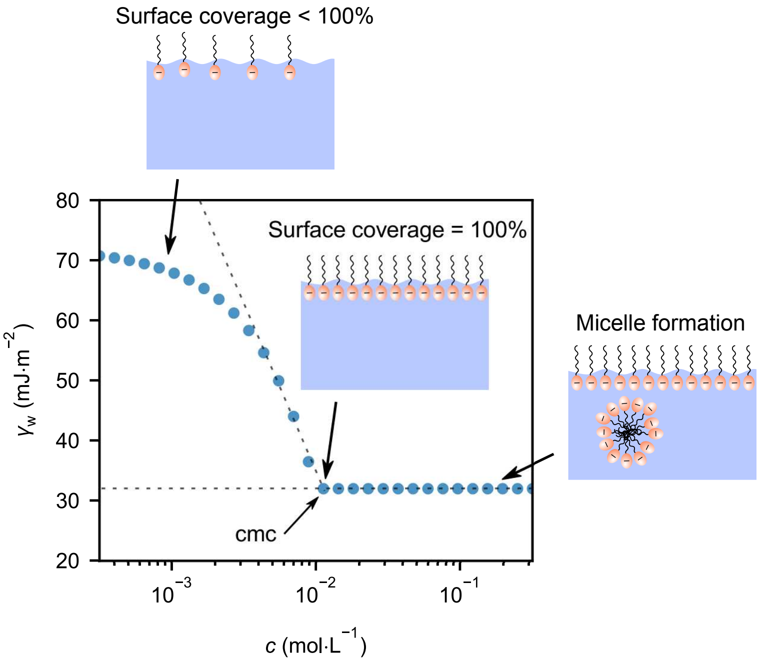


Figure 3.2: Simulated Water surface tension γ_w as a function of surfactant concentration c. When $c < c_\mathrm{CMC}$, γ_w decreases with adding surfactants, due to incomplete coverage of surfactants. When $c > c_\mathrm{CMC}$, γ_w remains constant and micelles form.

The behavior of γ_w with c is related to the microscopic picture of surfactants in water. When $c < c_\mathrm{CMC}$, surface coverage of surfactants is incomplete. Additional surfactants will first occupy the water-air interface and γ_w gradually decreases. When c_CMC is reached, the surface area is fully covered by the surfactants, and extra surfactants will only form micelles in bulk water (see insets of Figure 3.2). Therefore when $c > c_\mathrm{CMC}$, γ_w saturates. A micelle is the aggregate of surfactants in bulk solution, that hydrophilic heads are towards water molecules and the hydrophobic tails are embedded inside.[2]

So how do surfactants in detergents function? From our simple picture in Lecutre 1, the interfacial tension γ_wo between water and oil can be approximated by $\gamma_\mathrm{wo} = (\sqrt{\gamma_\mathrm{w}} - \sqrt{\gamma_\mathrm{o}})^2$. Therefore if γ_w becomes smaller by additing surfactants, γ_wo also decreases. Consider an oil droplet on cloth that immersed in water (Figure 3.3a), the total surface energy is:

$$E_\mathrm{c} = \gamma_\mathrm{wc} f A_\mathrm{c} + \gamma_\mathrm{oc}(1-f)A_\mathrm{c} + \gamma_\mathrm{wo} A_\mathrm{o} \tag{3.1}$$

where $\gamma_\mathrm{wc} \approx \gamma_\mathrm{w}$ is the interfacial tension between water and cloth, A_c is the total area of the cloth, f is the fraction of unstained surface on the cloth, γ_oc is the interfacial tension between oil and cloth, and A_o is the contact area between water and oil. When $c < c_\mathrm{CMC}$, γ_w and γ_wc

gradually drops. which makes it easier to release the oil droplet from the cloth (Figure 3.3b). Increasing c (but not larger than C_{CMC}) improves the cleaning ability. When $c > c_{\mathrm{CMC}}$, the cleaning ability of the surfactant does not further increase, since γ_{w} saturates. However, the capacity of the detergent (the amount of oil stabilized in water) becomes higher due to the formation of micelles which can stablize more oil droplets in water (Figure 3.3c).

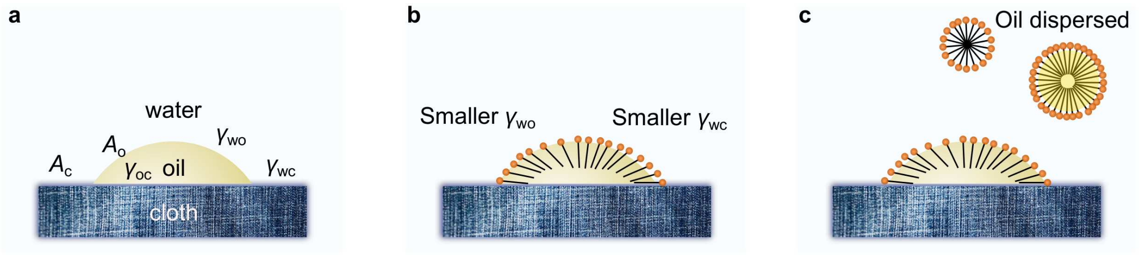


Figure 3.3: The mechanism of surfactants in detergent. (a) A droplet of oil on cloth that immersed in water. The oil droplet adheres to the cloth surface due to relatively low γ_{oc}. (b) Same with (a) but immersed in surfactant solution at cmc, the surfactants assemble at the oil-water interface and reduces both γ_{wo} and γ_{wc}. (c) Further increasing surfactant concentration in (b) does not increasing the cleaning ability. Nevertheless the capacity is higher due to oil-micelles stablized in water.

3.2 Adsorption and surface tension

The $\gamma_{\mathrm{w}} - c$ relation in Figure 3.2 indicates that γ_{w} decreases with higher surfactant coverage at the water-air interface. This phenomenon can be explained by the thermodynamics of surface adsorption. Consider a bulk closed system, the internal energy consists of the contribution from entropy, external pressure-volume work and chemical potential of the species. If interfaces are present in the system, the surface energy should also be considered. The internal energy with all aforementioned contributions is expressed as:

$$U = \underbrace{TS}_{\text{entropy}} - \underbrace{PV}_{\text{work}} + \underbrace{\gamma A}_{\text{surface energy}} + \underbrace{\sum_i \mu_i n_i}_{\text{chemical energy}} \tag{3.2}$$

Where T is temperature, S is entropy, P is pressure, V is volume, γ is surface tension, A is surface area, μ_i and n_i are chemical potential and amount of specie i, respectively. The intrinsic properties of U are T, P, γ, and μ_i, and the extrinsic properties (natural variables) are S, V, A and n_i.[3] The differential form of U with the extrinsic properties is:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \gamma\mathrm{d}A + \sum_i \mu_i \mathrm{d}n_i \tag{3.3}$$

Yet the total differential of U is:

$$\mathrm{d}U = T\mathrm{d}S + S\mathrm{dT} - P\mathrm{d}V - V\mathrm{d}P + \gamma\mathrm{d}A + A\mathrm{d}\gamma + \sum_i \mu_i \mathrm{d}n_i + \sum_i n_i \mathrm{d}\mu_i \tag{3.4}$$

In our system, we set both P and V to be constant. By comparing Equations 3.3 and 3.4, we have:

$$S\mathrm{d}T + A\mathrm{d}\gamma + \sum_i n_i \mathrm{d}\mu_i = 0 \tag{3.5}$$

This is the Gibbs (2D) adsorption equation,[4] which is the 2D analog of the Gibbs Duhem equation. The Gibbs adsorption equation states the interplay between the internal properties of the system. At const T, the surface tension is related to the surface adsorption density:

$$\mathrm{d}\gamma = -\sum_i \frac{n_i}{A} \mathrm{d}\mu_i = -\sum_i \Gamma_i \mathrm{d}\mu_i \tag{3.6}$$

where Γ_i is the (excess) surface adsorption density for specie i compared with the bulk solution. The 2D adsorption assumption is valid when the adsorption layer thickness is much smaller than the characteristic size of the system (i.e. the surfactants at the water-air interface). The change of μ_i can be derived from the thermodynamics of ideal mixtures:

$$\mathrm{d}\mu_i = RT\mathrm{d}\ln a_i = RT\mathrm{d}\ln x_i \tag{3.7}$$

where a_i is the activity of specie i, and x_i is the molar fraction of i. We assume $a_i \approx x_i$ under the ideal solution assumption. Therefore the surface adsorption density Γ_i is written as:

$$\Gamma_i = \frac{n_i}{A} = -\frac{x_i}{RT}\frac{\partial \gamma}{\partial x_i} = -\frac{1}{RT}\frac{\partial \gamma}{\partial \ln x_i} \tag{3.8}$$

$\dfrac{\partial \gamma}{\partial \ln x_i}$ behaves differently depending on the solute:

- Hydrophilic solute: i.e. hydrated ions (Na^+, Cl^-, etc)

  The hydrophilic solute has lower free energy when immersed in the bulk solution compared with the surface. Therefore $\Gamma_i < 0$ and as a result γ_w increases with increasing x_i.

- Amphiphilic molecule: i.e. surfactants discussed here

  As discussed previously, the amphiphilic molecules tends to stay at the interface. Therefore $\Gamma_i > 0$ and the surface tension γ_w decreases with adding salts.

The comparison between the two types of solutes is shown in Figure 3.4. The increase of γ_w due to addition of hydrophilic solutes is usually much smaller than that induced by surfactants.

The adsorption density close to c_CMC can be determined by plotting the slope of $\partial\gamma/\partial \ln x_i$ when $c \approx c_\mathrm{CMC}$ (see Figure 3.2) Since $\Gamma_i = n_i/A$, by knowing the surface area, we can estimate the size of the amphiphilic molecule.

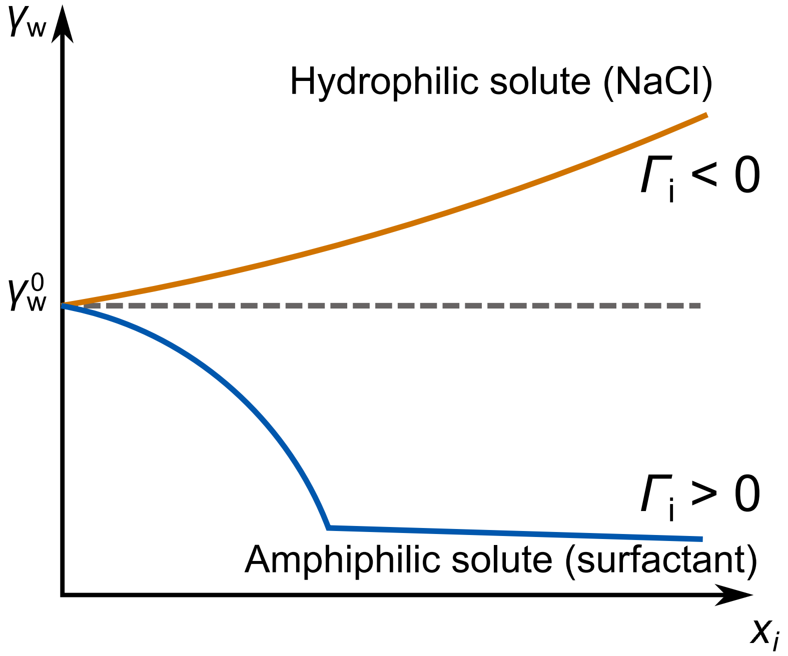


Figure 3.4: Change of surface tension as a function of x_i for different solutes.

3.3 Emulsion

One application of surfactants is to stablize immisible liquids to form a emulsion. We know that phase separation occurs sponatenously between pure water and oil, even after rigorous mixing. However by adding surfactants and mixing, the oil phase splits into microscopic droplets that are stablized in water (emulsion). By mixing and forming emulsion, the interfacial area change ΔA> 0, the free energy of mixing the two phases is then:

$$\Delta G_{\text{mix}} = \Delta H - T\Delta S = \gamma_{\text{ow}} \underbrace{\Delta A}_{>0} - T \underbrace{\Delta S}_{>0} \tag{3.9}$$

Althou γ_{ow} is reduced by adding surfactants, ΔG_{mix} is still dominated by the surface energy, and usually positive. As a result, the mixing and forming emulsion is *always* thermodynamically unfavored.

However we normally observe that the emulsion is *kinetically* stable over a long period of time. The kinetic stability comes from the potential barrier of repulsive forces (usually electrostatic) in the system, when the barrier height is much larger than thermal activation energy (remember at 300 K, $kT \approx 26$ meV). As can be expected, by increasing temperature or reducing the repulsive forces in the emulsion, the stability is reduced and phase separation occurs again. The detailed theory for the kinetic stability of colloidal solution will be discussed in Lecutre 13.

References

(1) Rosen, M. J.; Kunjappu, J. T., *Surfactants and Interfacial Phenomena: Rosen/Surfactants 4E*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2012.

(2) Vert, M.; Doi, Y.; Hellwich, K.-H.; Hess, M.; Hodge, P.; Kubisa, P.; Rinaudo, M.; Schué, F. *Pure Appl. Chem.* **2012**, *84*, 377–410.

(3) Canagaratna, S. G. *J. Chem. Educ.* **1992**, *69*, 957.

(4) Menger, F. M.; Rizvi, S. A. A. *Langmuir* **2011**, *27*, 13975–13977.