

Initial Question:

You have decided that your new hobby will be soap making. You need to decide how much to charge for the luxury soap. How much soap would be produced from a reaction of 100.0g lye and 100.0g of lard? If you charged \$5.00 per bar made from these amounts, how much profit would you make? (Assume your only costs to be the lye and lard.)

The Penn Inquiry Model

Results:

The cost of making the soap is \$2.99 when using the amounts given in the initial question. There is an excess of 85.8g NaOH (2.13mol) used.

Existing Information:

- Basic reaction for soap making/ equation
- Lye is impure NaOH (MW 40g/mol)
- Structure of trioleic acid ($C_{54}H_{104}O_6$), the main component of lard
- Stoichiometric calculations

Organize and Reflect:

- Lard is composed of mainly trioleic acid,
- Set up equation for making soap
- 1mol fatty acid: 3 mol base= 3 mole soap: 1 mole glycerine
- Get respective moles of substances
- Calculate yield
- Calculate cost of 100g NaOH, 100g lard, calculate total cost of materials
- Assume 100% theoretical yield
- (See calculations, attached)

New Info Needed?

- Cost of lard (500g/\$4.49 = \$.0089/g)
- Cost of lye (2.5kg/\$53.65= \$.02146/g)
- Trioleic acid MW 848g/mol

Peer Review:

- Discussion, proving the answer and why the stoichiometry is important
- If you make a lot, you could perhaps get supplies in bulk, cheaper
- Costs of other supplies (fragrance, coloring...) would impact the final costs.

Community Knowledge

It would cost \$2.99 to produce the soap; but using a stoichiometric amount of NaOH would reduce costs by \$1.84, creating a greater profit. In addition, the soap would be too basic, and need to be treated before using if made with such an excess of NaOH. It is important to determine the price for a product after careful consideration and calculation, rather than assuming a price.

Calculations:

$$(100\text{g TOA}*/1)(1\text{mol TOA}/848\text{g TOA})(3\text{ mol soap}/1\text{mol TOA})(304\text{g soap}/1\text{mol soap})=108\text{g soap}$$

$$(100\text{g NaOH}*/1)(1\text{mol NaOH}/40\text{g NaOH})(3\text{mol soap}/3\text{mol NaOH})(304\text{g soap}/1\text{mol soap})=760\text{g soap}$$

TOA is the limiting reagent, 108g of soap are produced

Lard costs \$4.94 for 500g, for a cost of $500/4.94$ or \$.00988/g

For 100g lard, the cost of production is \$.988

$$\text{As } (100\text{g lard}/1)(\$0.00988/1\text{g lard})= \$0.988$$

The cost of NaOH is \$53.65 for 2.5kg, for a cost of $2500/53.65$ or \$.02/g; for 100g

NaOH used here, the cost of production is \$2.00 as

$$(100\text{g NaOH}/1)(\$0.02/\text{g})=\$2.00$$

However, there is a fair amount of excess NaOH being used.

To produce 107g soap:

$$(107\text{g soap}*/1)(1\text{mol soap}/304\text{g})(3\text{ mol soap}/3\text{mol NaOH})(40\text{g NaOH}/1\text{mol NaOH})=14.2\text{g NaOH}$$

$$100\text{g NaOH}-14.2\text{g NaOH}=85.8\text{g NaOH excess}$$

$$(85.8\text{g NaOH}/1)(1\text{mol NaOH}/40\text{g NaOH})=2.13\text{mol NaOH}$$

$$(14.2\text{g NaOH}/1)(\$0.02/1\text{g})= \$0.284 \text{ cost of NaOH used}$$

The production cost as listed is $\$.988 + \$2.00 = \$2.99$, for 2.01 profit per 107g bar soap

However, if stoichiometric amounts are used, the cost would be $\$.988 + \$0.284 = \$1.27$
per 107g bar soap

*TOA= trioleic acid

**Clean-Up on Aisle 5:
The Chemistry of Soaps, Detergents, and
Bleach**

Jennifer Tareila

Thesis

Master of Chemistry Education Program

University of Pennsylvania

August 19, 2004

Clean-Up on Aisle 5: The Chemistry of Soaps, Detergents, and Bleach

Several times during the course of a day, people use chemistry without being aware of it. It is used to style hair, cook food, and to power cars. However, it is often overlooked. One such example of oversight is using chemistry to clean. People often bathe on a daily basis, as well as wash their hair. People wash their hands several times a day. Clothing is likely to be washed weekly. Occasionally bleach is needed to remove soil that stains fabric, or to disinfect a surface or material. However, people seldom pause to consider the chemistry involved with cleaning. In fact, they may not even consider these materials to be chemicals, as they are exposed to them almost daily from a young age.

The past fifty years has been an interesting time in terms of “domestic chemistry”, or chemistry of household substances. It allows almost unlimited freedom to choose products that make infinitely simple, as compared to earlier times in human history. Today, a large industry is based upon cleaning and the production of cleaning materials. Walking down the detergent aisle of a supermarket yields a plethora of choices in how to clean your clothes. A similar set of choices awaits you on the personal care aisle, where countless shampoos and soaps are available.



Fig 1-4: Views down soap, shampoo, detergent, and toothpaste aisles at Genuardi's Supermarkets

History of Soaps and Detergents

Three thousand years ago, life was not so easy. In addition, as compared to today's standards, we would not consider it clean. Most people in the United States today would not consider it sanitary, and would be appalled by the usual state of affairs. To have a sense of what life was like, consider bathing. In ancient Greece and Rome, people cleaned themselves by rubbing themselves with sand, pumice, and ashes. Then, they would pour oil onto the skin. The skin was then skimmed off, removing the excess oil, and presumably, dirt, with an object called a strigil, a piece of metal shaped like the end of a hockey stick. People today, with an obsession for antibacterial soaps, would most likely not consider them to have been clean, although they would admit that it was likely that these people had soft and supple skin ^(18, 28,45).

Washing laundry was equally different, and much more difficult. When it was wash time, the laundry was brought to the river and rubbed against rocks to help remove dirt and soil. One can only presume that the time needed to clean a load of laundry has been greatly reduced with the advent of the washing machine and detergents ^(18, 28,45).

The earliest use of soaps began around 2800BC ⁽¹⁸⁾. Recipes for primitive soaps have been determined to be dated approximately 1500BC. It is credited to the people

living near the Tiber River at the foot of Mount Sapo, who noted that washing downriver was easier. As the story goes, the tallow from the animal sacrifices made on the mountain washed downstream, mixing with water from the basic soils on the banks, making a type of soap that made wash cleaner with less effort than in other areas along the river. It wasn't until the 1600's that soap making became a common affair, but even then it was reserved for the wealthy. Eventually, people began making their own soaps at home, from ash and fat or oil⁽¹⁸⁾. The process of soap making is called saponification.

Saponification: Making a typical Soap

The basic process of making a soap, saponification, can also be called base catalyzed hydrolysis of an ester. Typically, a triglyceride is used, as most naturally occurring fats and oils are triglycerides. Animal fats commonly contain saturated acids, while vegetable oils usually contain a higher portion of unsaturated fatty acids. Most triglycerides are mixed, containing a combination of fatty acids. The percentages of fatty acid composition for three lipids used to make soap are given in the table below (38).

	Sat. <10 Carbons	Sat. 12C	Sat. 14C	Sat. 16C	Sat. 18C	Unsat. 18C	Unsat. 18C
		lauric acid	myristic acid	palmitic acid	stearic acid	oleic acid	linoleic acid
butter	12%	3%	12%	28%	10%	26%	2%
lard			1%	28%	14%	46%	5%
olive oil			1%	5%	2%	83%	7%

Table 1: Fatty acid composition of butter, lard, and olive oil. (38)

To make soap, the fat or oil is heated in the presence of concentrated base(Fig 5). (The reaction is spontaneous, but is sped up considerably by heating the reactants.) Lye, or unpurified sodium hydroxide made from soaking wood ash in water, was used as the base. For each triglyceride molecule consumed, three molecules of soap are produced. Three molecules of base are needed for each molecule of soap produced. One molecule of glycerin results for each triglyceride molecule consumed. The final product, soap, is a salt of the fatty acid.^(11, 18, 38, 57, 71, 75)

In this manner, soap can be made from almost any triglyceride. However, some salts of triglycerides are harsher than others.^(11,51) If excess base remains after formation of the salt, it must be neutralized, or it may be caustic and cause irritation to skin, or damage to materials. Also, some preferences are made as to which triglycerides would be best used to make soap. "Beef tallow makes the hardest soap, but I feel lard has the ideal mix of stearates and oleates to give the best soap characteristics, hardness and adequate solubility."⁽³⁹⁾

It has only been since the 1930s that the commercial availability of soaps and detergents has become so widespread⁽¹⁸⁾, and today we have whole aisles in stores devoted to cleaning. Even that at times is not enough choice, and we have whole stores devoted to presenting an astounding array of personal cleaning products to choose from.

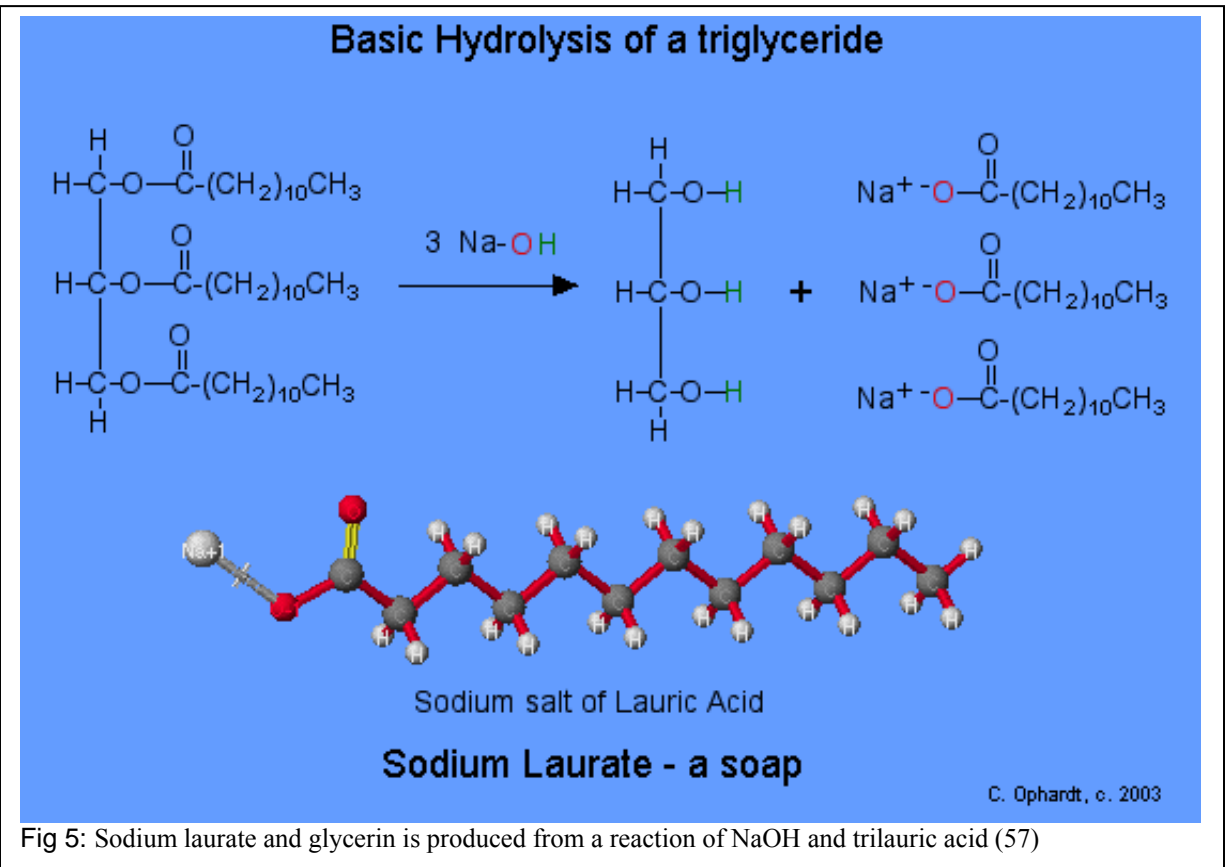


Fig 5: Sodium laurate and glycerin is produced from a reaction of NaOH and trilauroic acid (57)

Soaps found in stores can smell like apples, daisies, or plumaria; shampoos can give hair lift and body, as well as control frizz; laundry detergents can remove stains while leaving fabric soft, bright and in vivid color. However, how different are all soaps and detergents? Can they really fulfill all of their promises? Can they really *clean*? Are soaps and detergents really that different?

The Basics of Clean: Soaps vs. Detergents

Most people would be shocked to discover that many of the “soaps” that they use on a daily basis are actually detergents. In fact, detergents are found in some unlikely places. Detergents are found in toothpastes, as well as in pesticides and glues. But why? And how are they different from soaps?

Soaps and detergents are both classified as surfactants, short for SURFice ACTIVE AgeNTS. Surfactants are substances that change the properties of surfaces or interfaces. Anything that exists as a solid or a liquid has a surface, and where any two or more materials meet is an interface. (When you wash something, the water is a surface, and the material that is being washed is a surface. Where the two meet is an interface. Often, dirt or soil exists at the interface as well.) Both soaps and detergents are excellent surfactants, changing the interface in a way that favors ^(44, 42).

Even though both soaps and detergents act as surfactants, they have a few differences between them. Soaps are usually made from “natural” oils or fats (oleochemicals), rather than from petroleum products (petrochemicals), like detergents usually are. As a result of being produced from oleochemicals, soaps usually contain carboxylic acids, while detergents do not. Also, soaps are typically biodegradable, while detergents are usually not. While this information makes soaps seem natural and great, and detergents are bad chemicals, one must consider the final difference: soaps produce curd, or soap scum, while detergents do not ^(18, 51, 79b).

For the purpose of discussion, the term surfactants will be used in place of the term soap or detergent, unless it is necessary to distinguish between the two classes as discussed above.

How Surfactants Clean

Surfactants clean in four steps:

1. Surfactants alter surface tension
2. Surfactants release or loosen soil
3. Surfactants emulsify water
4. Surfactants hold soil in suspension (42,84, 90)

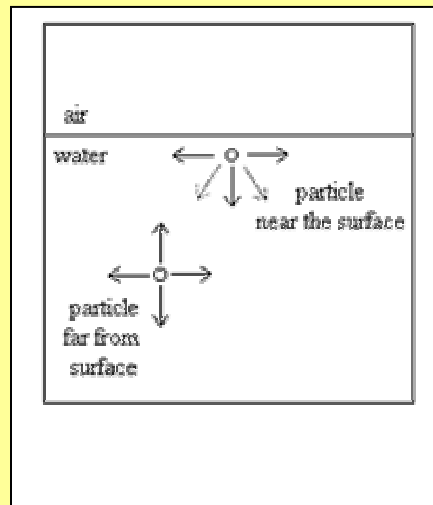
These four steps are common to all types of surfactants; the process of cleaning hair is not very different from laundering your favorite shirt.

Surface Tension (Surface Free Energy)

Surface tension is also known as surface free energy. When materials, such as air and water, or oil and water, come into contact, they form an interface. Every interface has an amount of energy associated with it, related to the free energy of the molecules in each material, as well as an energy change in response to the interaction of the two materials. Some materials have favorable energy changes, and mix freely, such as when alcohol is dropped into water. Other materials do not have as favorable an interaction, and remain separate, such as when oil is dropped into water.

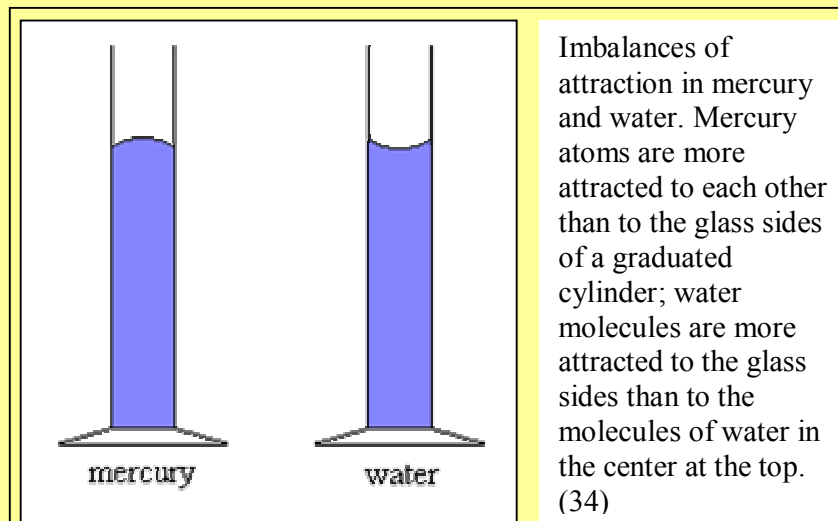
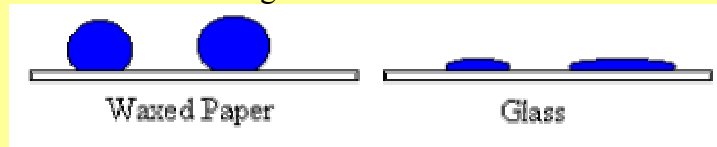
In order to understand why some materials mix well, and others do not, it is important to look at the materials when in contact with air. When thinking of surface tension, one of the first images to come to mind is how water beads up on certain surfaces. This is due to the large attractive forces which water molecules have for each other.

These attractive forces are called hydrogen bonds, and are a result of the partial positive charges on the hydrogen atoms and the partial negatives on the oxygen in the water molecule that result from unequal electronegativities of the atoms. At the surface of a water bead, there is an uneven distribution of these hydrogen bonds. The molecules at the top are attracted to each other the same as those in the middle are, but they are not



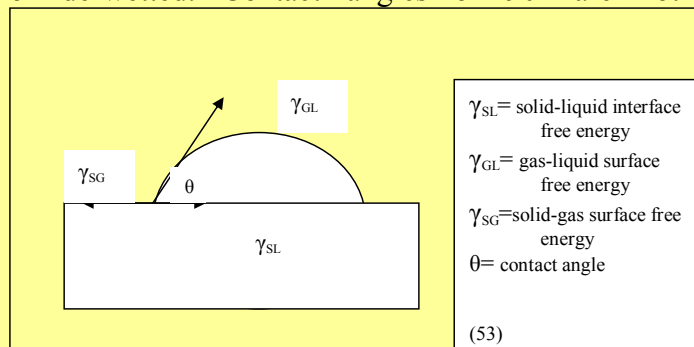
attracted to the air as much as they are attracted to each other. This results in an imbalance of forces at the surface of the water, which keeps the air and the water separate.

Most things aren't floating in air, they are touching a surface. At the interface of the water and the surface that the water is on, for example a piece of wax paper, there is also an imbalance of forces. As such, water beads up, because it is more attracted to the water molecules than it is to the waxy surface. However, if we change the surface to a piece of regular glass, the water does not bead up to the same degree. This is because the water is more attracted to the glass than to the wax paper, and spreads out over the surface of the glass.

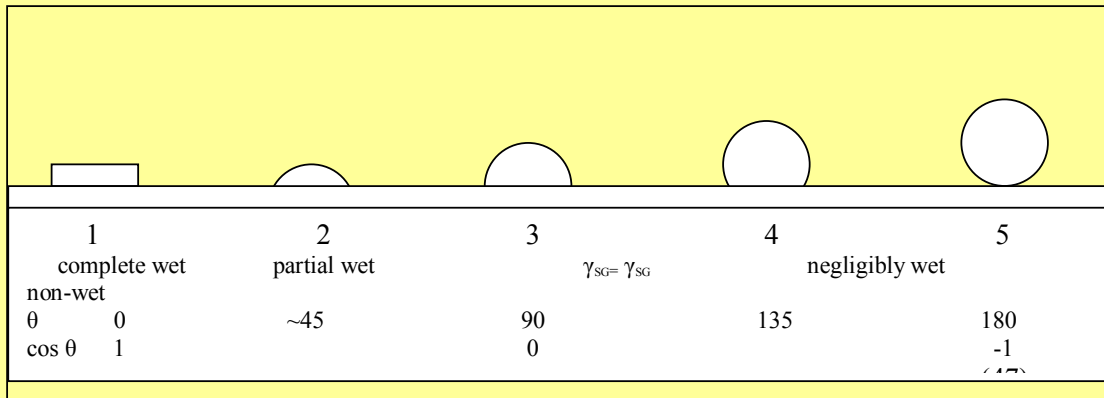


Imbalances of attraction in mercury and water. Mercury atoms are more attracted to each other than to the glass sides of a graduated cylinder; water molecules are more attracted to the glass sides than to the molecules of water in the center at the top. (34)

Surface tension (surface free energy) can be measured in several ways; one of the most common ways is to measure the contact angle (θ) at the interface. When a liquid beads up, there is not a strong attraction to the surface it is sitting on. Conversely, when a liquid spreads out there is a stronger attraction to the surface. Materials with a contact angle less than 90° are said to be wet, while those greater than 90° are non-wet, or de-wetted. Contact angles of 90° are not wet or de-wet. (1, 36, 47, 83)



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(53)

Surface tension can also be reported in mNm^{-1} , by testing the pressure needed to break the surface. Pressure measures in mNm^{-1} correspond closely to the measured contact angles. ^(1, 36, 47, 83)

Temperature, $^\circ\text{C}$	Surface Tension, mNm^{-1}
-5	76.4
0	75.6
10	74.22
20	72.75
50	67.91
100	58.9

Surface tension of water (30, 87)

The surface tension of water changes as temperatures is increased; this is due to the fact that the hydrogen bonds are more transient in the molecules as the temperature is increased, as more of the molecules are moving faster.

Surface tension is referred to as surface free energy because it deals with the amount of energy that is involved with interactions at surfaces, specifically the amount of energy that is involved with increasing the surface area of the material at the interface. If a liquid interacts with a surface by wetting it, the free energy of the

Alteration of surface tension

When surfactants are introduced to water, they alter the properties of the water in a way that aids in cleaning. This is not surprising, as the definition of surfactant tells us that surfactants alter interactions at surfaces, or interfaces. In the case of water, surfactants lower the surface tension of water, making the water “wetter”. “Wetting” refers to the ability of water to spread on a surface. If water is “wetter”, it is able to spread more on a surface. In terms of washing, the water is more able to spread on the material being cleaned, as well as onto the soil that covers the material.

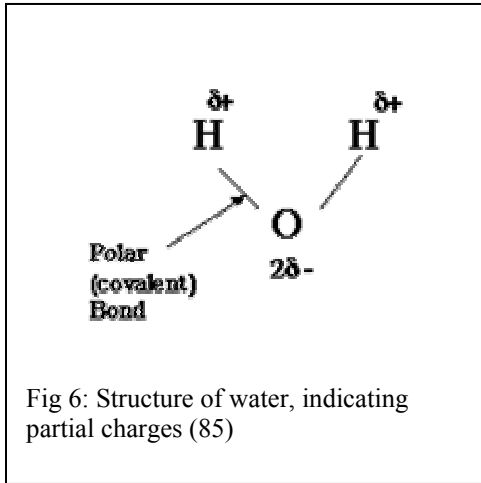


Fig 6: Structure of water, indicating partial charges (85)

This occurs because the forces that hold water molecules together are disrupted. Normally, hydrogen bonds attract one molecule of water to another molecule. Water is referred to as a polar molecule; it has ends that are partially charged (represented by δ^+ and δ^-). The charges are a result of the electronegativities of the atoms involved, as well as the overall shape of the water molecule, which results from the electron configuration of the central oxygen.

Water has a unique way of interacting with other water molecules. The molecules order themselves in a way that allows the positive and negative ends to attract to each other. As the positive ends are hydrogen (and the negative ends are oxygen), this attraction is referred to as hydrogen bonding. Any addition of a substance, especially a polar substance, will break the hydrogen bonds, preventing the water molecules from sticking together in the usual fashion.

As a result of losing “stickiness” to other water molecules, the water can spread out to a much greater degree on a surface, getting the surface “wetter” than plain water alone. This allows the water to coat a surface better, and to come into contact with the soil better.

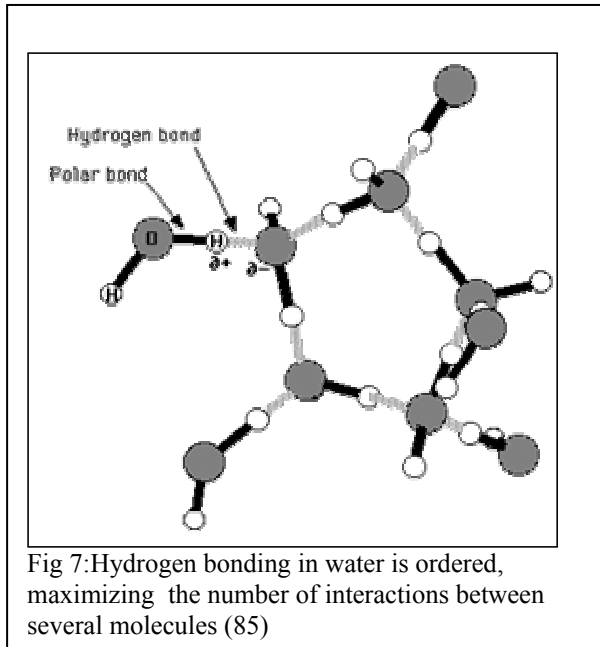


Fig 7: Hydrogen bonding in water is ordered, maximizing the number of interactions between several molecules (85)

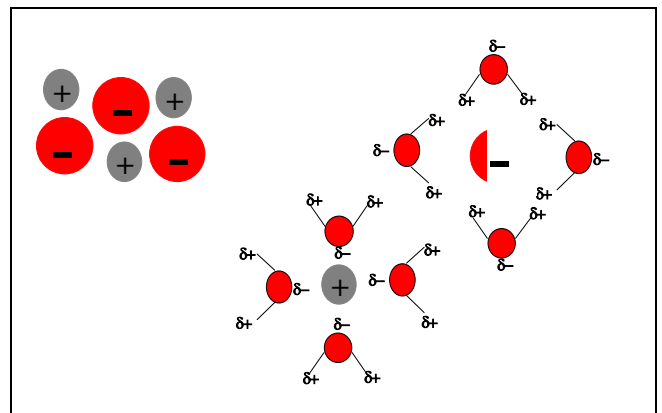
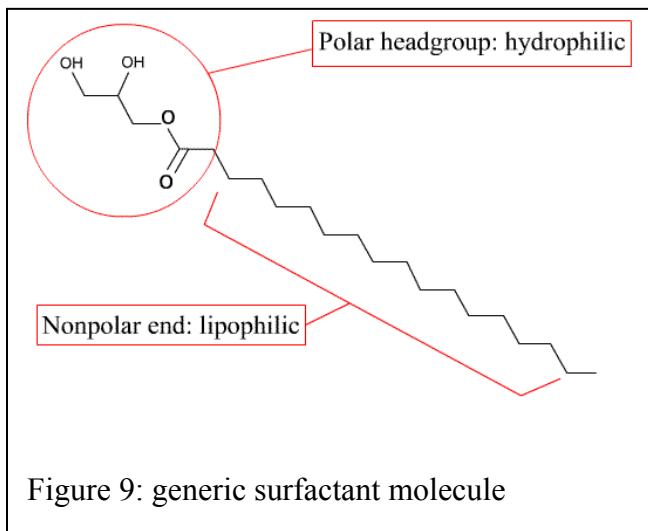


Fig 8: Acceptance of charge into water (86)

This alteration of surface tension can only occur because surfactants

molecules get between the water molecules; they need to be polar in order to mix with the water. However, the surfactants also need to be nonpolar to interact with the lipophilic (fat-loving) soils that cling to surfaces.



A main part of the reason that surfactants work so well is because they are amphipathic- they are attracted to fats and to water, because there are two ends to a long molecule of detergent. There is a polar head group, made from the carboxylic acid of a fatty acid (when the surfactant is soap), and a non-polar tail group, composed of the hydrocarbon tail. The hydrocarbon tail group is hydrophobic, or water fearing, which may also be lipophilic, fat loving. The head group is hydrophilic, or water loving. ^(42 84, 90)

Hydrophilic and Hydrophobic Interactions

The hydrophobic/ hydrophilic nature of a molecule is determined by influence of the atoms that compose the molecule. Molecules that are similar in nature are soluble with each other, while those with opposite natures are insoluble. Therefore, molecules with a nature similar to that of water are soluble in water, and those with a dissimilar nature are insoluble. To determine the nature of the molecule, polarity and shape must be examined.

The polarity, and therefore, electronegativity, of the atoms in a molecule are of importance. The electronegativity of an atom refers to how well the atoms of a given element attract electrons in a chemical bond. Electronegativity is an intrinsic property, and does not change from atom to atom of a particular element. Electronegativity is due in part to the electron configuration of an atom. In general, electronegativity decreases as you go down the periodic table, and increases as you go across the periodic table (with the exception of the noble gases, which have no stated electronegativity). Fluorine has a high electronegativity because fluorine has an electron configuration very similar to that of Neon, and it desires electrons in a bond in order to fill the octet to become like Neon. It has a higher electronegativity than chlorine, an element in the same family with a similar electron configuration. Chlorine also desires one electron, but since it has a larger atomic radius, the chlorine does not pull electrons into a bond as strongly as the smaller fluorine.

Electronegativity of selected elements:

H 2.1 C 2.5 N 3.0 O 3.5 F 4.0

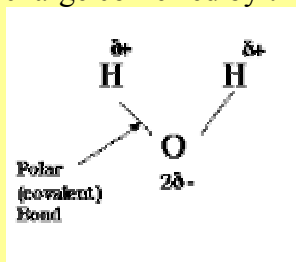
In terms of polarity, bonds between atoms are classified based upon differences in electronegativities, as follows:

0-0.4 nonpolar covalent

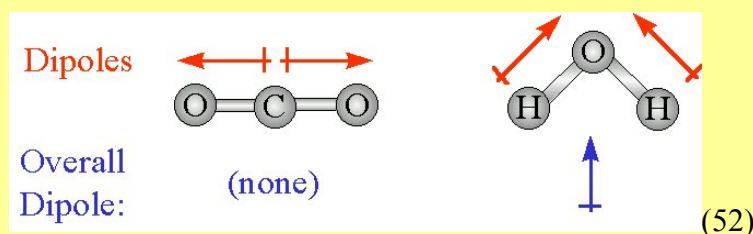
0.5-1.9 polar covalent

>2.0 ionic

Accordingly, a C-H bond would be classified as nonpolar covalent, having an electronegativity difference of 0.4. A C-F bond (difference of 1.5) would be classified as polar. An H-O bond would be classified as polar, and an N-H bond as polar. Polar bonds are indicated with an arrow, pointing in the direction of the most electronegative element. The elements are labeled as partially positive and partially negative, using δ^+ and δ^- , respectively, to indicate partial charge conferred by the electrons.



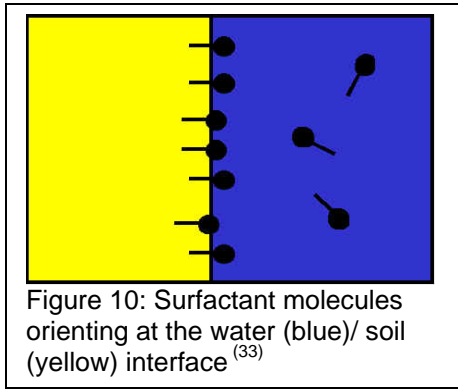
Bond polarity is not the only factor used to determine the polarity of a molecule; shape also plays an important role. If a molecule has all nonpolar bonds, it can be easily determined to be nonpolar. However, some molecules that consist of only polar bonds are nonpolar in nature, as they do not possess an overall dipole moment. In other words, all of the polar bonds are evenly distributed in the molecule, having no net “pull” of electrons in any direction. CO_2 would not be considered to be polar, even though it is composed of two polar bonds, as there is no net dipole. However, water is considered to be polar, as it has a net dipole, pulling the electrons toward the more electronegative oxygen.



Water molecules attract and stick to other water molecules because they are polar. The partially positive hydrogen is attracted to the partially negative oxygen. Water has such strong polar differences between the hydrogen and the oxygen that they attract has its own name- hydrogen bonding. In terms of non-bonding interactions, hydrogen bonding is the strongest. Polar molecules are molecules that mix with water, and are referred to as hydrophilic, or water loving.

Molecules that are nonpolar, such as oils and waxes, do not mix with water because they do not exhibit a net dipole. They are excluded from the interactions of the water molecules, and therefore do not mix with the water. As a result, they separate out. These molecules are considered to be hydrophobic (water fearing) due to this separation.

The release, or loosening, of soil



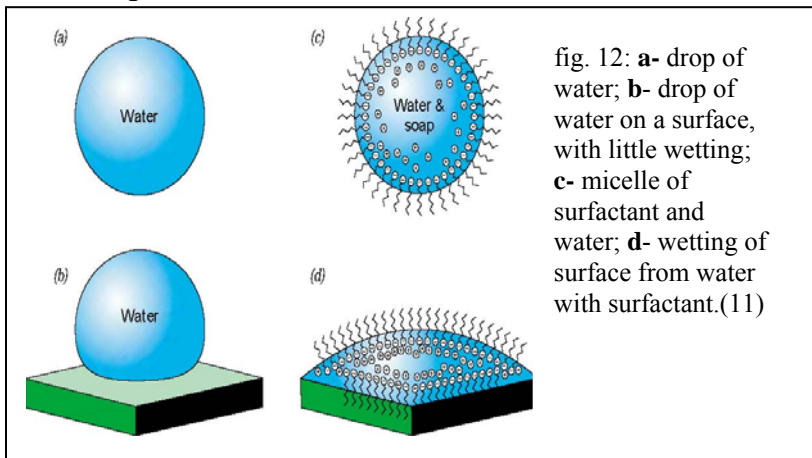
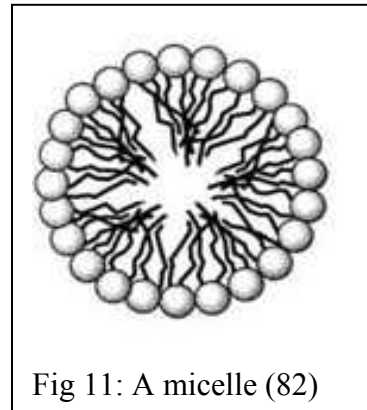
A surfactant must loosen soil from the material to be cleaned. To do so, it must attach to the soil. The surfactant molecules orient their molecules at the interface, with the hydrophobic tail groups of a surfactant against the soil, and the polar head groups in the water. Mechanical agitation during cleaning (such as the motion of a washing machine, or the scrubbing of hands) helps this to occur.

In addition, the molecules of surfactant must begin to remove the soil from the material, pulling the soil molecules into the water/ surfactant mix. For this to occur, there need to be attraction between the oily soil, and the hydrophobic tail end of the surfactant. The hydrophilic ends of the surfactant will remain in contact with the water^(42, 84, 90).

Emulsification of water and soil, and suspension of soil in water

When water and oil are added together, they do not mix well. Usually, the water will settle to the bottom of the mixture, while the oil will remain on the top. When cleaning, this separation is not helpful to clean a surface; pouring water on an oil spot would only allow the water to run off, not doing much in terms of cleaning. Unless there was a way to mix the two materials, not much would happen.

If a surfactant is added to water, the water molecules exclude the hydrophobic tail groups in the process of hydrogen bonding as much as possible. The hydrophobic tail groups are pushed together, and accumulate in the center of micelle, a roundish accumulation made from groups with differing attractions to each other.



The formation of micelles of sodium dodecyl sulfate (also known as sodium lauryl sulfate, the detergent found in many hand soaps, liquid body washes, shampoos, and laundry detergents) occurs with an negative enthalpy change of 6kcal/mol at 28°C, a spontaneous process.

Soils are “held” in the micelle by the hydrophobic tail groups. As the micelles are formed spontaneously, the soil is picked up readily when the micelle is formed. The micelles of surfactant and water do not allow the soil to drop out of suspension, so that the soil may be washed away^(42, 84, 90).

Types of surfactants

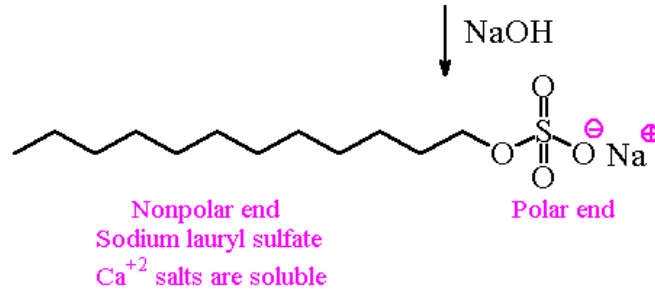
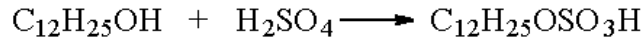
Not all surfactants are created equally. As stated earlier, soaps leave behind curd as they react with ions found in water. Curd, or soap scum, is the insoluble product of a soap reacting with the Mg^{2+} and Ca^{2+} in water. Soaps are salts of fatty acids, and typically have a monovalent ion attached, usually Na^+ , or K^+ . The fatty acid of the soap contains a COO^- group, which is attracted to any positive charge. When in hard water, the Na^+ or K^+ is replaced by Ca^{2+} or Mg^{2+} . The Mg^{2+} and Ca^{2+} salts bind to two fatty acid molecules each, and are insoluble, leaving a deposit behind that we refer to as soap scum. This curd formation can be prevented by using detergents, which do not form insoluble when bound to Mg^{2+} or Ca^{2+} (11,18, 27.)

As a result of these problems, detergents were created. There are several types of detergents, and consequently, there detergents have a wide range of properties as compared to soaps.

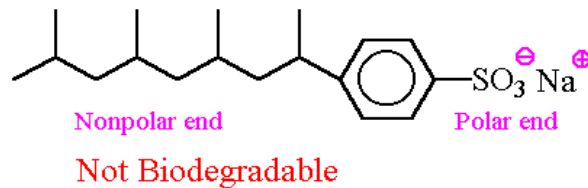
Anionic	linear alkybenzene sulfonates, alkyl sulfate, alcohol ethoxysulfates	foam (suds) well	Laundry and hand dishwashing detergents, household cleaners
Cationic	quaternary ammonium compounds	disinfect, sanitize, and act as fabric softeners and conditioners/ anti-frizz agents in shampoos	fabric softening detergents and shampoos
Amphoteric	imidiazoles, betaines	mild, foam well, stable in acidic and basic water	personal cleaning products, such as liquid soaps
uncharged (non-ionic)	alcohol ethoxylates	low foam, resist hardness, works on most soils	laundry and automatic dishwashing detergents

Table 2: Types, examples, properties and uses of detergents (18, 82)

Synthetic Detergents



Alkylbenzene sulfonates (ABS)



Linear alkyl sulfonates (LAS)

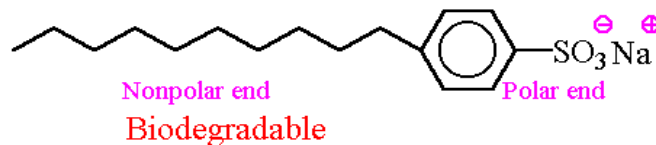


Fig 13: Common synthetic detergents (78b)

Additives: Other Materials in soaps and detergents

As mentioned earlier, there is an amazing variety of soaps and detergents to choose from when going to the store. Since soaps and detergents all clean the same way, how different can one product be from the next? The differences lie in the additives- the materials added to give a detergents unique behavior.

It makes sense that bubble bath does not contain the same ingredients as automatic dishwashing detergent; one would not want the dishwashing detergent to foam up to the same degree. Also, one would not want foamless bubble bath. Other considerations for additives must also be taken into account. How a product smells, feels, and looks must fit the purpose that the consumer has in mind. A brief scan of the MSDS sheets for the Proctor and Gamble Company, manufacturer of many household products, tells the story that many detergents are very similar with the exception of the amount of additives. Dawn, Joy and Ivory dish detergents have the same ingredients⁽⁶⁶⁾.

Fragrance	scent; covers scent of product or packaging	usually secret
Anti-redeposition agents	prevent soil from sticking to surface in the future	Carboxymethyl cellulose, polycarbonates
Anti-Microbial Agents	destroy bacteria by rupturing cell or prevent bacteria from reproductng	quaternary ammonium compounds, bleaches, triclosan
Whiteners & Brighteners	keeps colors and whites bright by absorbing the yellow end of the spectrum	usually secret
Suds Stabilizers/ Suppressors	keep suds / suppresses suds formation	alkanolamides, alkyl phosphates, silicones
Enzymes	help remove soils by digesting them	amylase, lipase, protease, cellulase
Colorants	color product	dyes
Preservatives	keep product fresh; prevent decay from bacteria or oxidation	butylated hydroxytoluene (BHT), ehtylene diamine tetrasacetic acid, gluteraldehyde
Bleaches	disinfect, remove stains	sodium hypochlorite, sodium perborate
Hydrotropes	prevent separation of detergent	cumeme sulfonates, ethyl alcohol
Fabric softeners	prevent static electricity and soften fabrics	quaternary ammonium compounds

Table 3: Additives to detergents ^(18, 51)

Bleach and Color

Bleaches are a unique category of additives; so unique that they merit special attention. Bleaches act as disinfectants, as well as destroy colored molecules. Colored molecules appear colored because they absorb light in the visible range, reflecting back the complementary color. Conjugated systems of molecules (molecules that have many alternating single and double bonds) have a tendency to absorb light in the visible range. It should not be a surprise that many biologically active molecules that are colored find out way onto clothing and other surfaces, as we eat them on a regular basis. Lycopene, β carotene, chlorophylls, and many other brightly colored molecules find their way onto plates, counters, and clothes in the form of fruits and vegetables.

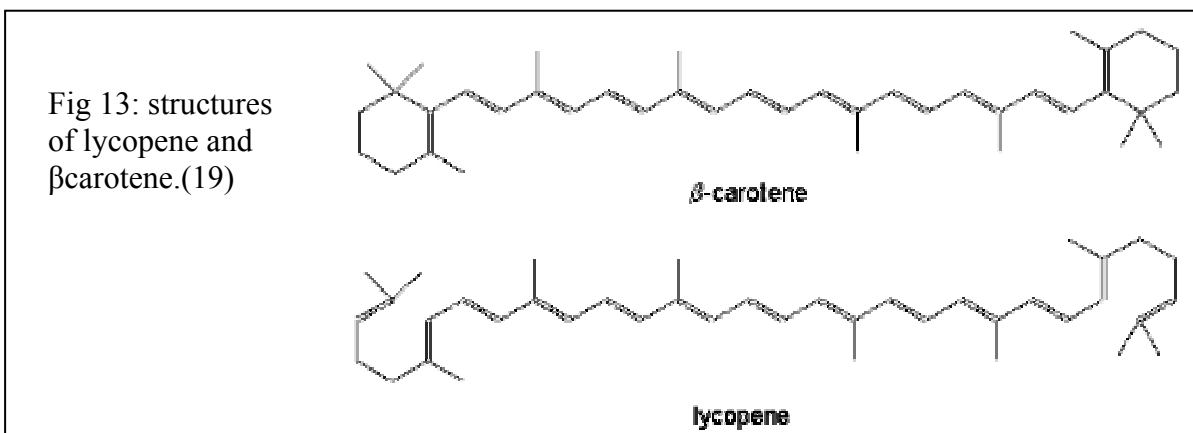
When we have the inevitable stain, we reach for the bleach to remove the stain. But what causes the molecules to be colored in the first place? Any why does bleach remove the stain? Bleaches do this by breaking the bonds in colored molecules,

specifically the double bonds. In order to look at the action of bleach, it is important to look at the chemistry of the molecules that are being altered when reacting with bleach.

Color and wavelength

Wavelength of light, nm	Color of light at that wavelength	Complementary color (observed)
400-430	Violet	green-yellow
430-480	Blue	yellow
480-490	green-blue	orange
490-510	blue-green	red
510-530	Green	purple
530-570	yellow-green	violet
570-580	Yellow	blue
580-600	Orange	green-blue
600-680	Red	blue-green

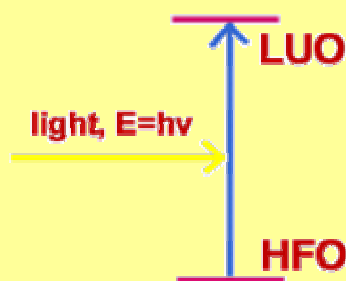
Table 4: Color and wavelength (19)



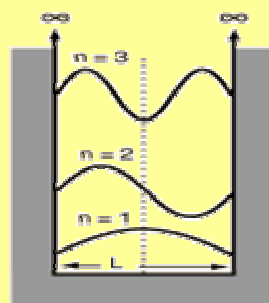
Lycopene, found in tomatoes, and β carotene, found in carrots and other orange foods, are good examples of conjugated systems that absorb light in the visible range. The colors of lycopene and β carotene tell that they absorb at wavelengths of approximately 490-510 (green-blue absorption; red reflection) and 480-490 (blue-green absorption, orange-red reflection) respectively. As the amount of conjugation increases, the absorption spectra is pushed to the red end of the spectrum.

Particle in a Box: Predicting Absorption Spectra

Electrons in molecules are not static; they can and do move rapidly in bonds between atoms. Molecules composed of only single bonds do not exhibit delocalization, while molecules containing multiple bonds do. Molecules containing conjugated systems- alternating double and single bonds- exhibit larger degrees of delocalization. In delocalized systems, the electrons have a larger area in which to move freely, as they can move between all atoms in the delocalized system, rather than between only two atoms. With adequate energy, these electrons can move up an energy level from its ground state.



(24)



$x = 0$ at left wall of box.

(64)

To raise an electron from the highest occupied molecular orbital (HOMO, here the HFO- highest filled orbital) to the lowest unfilled molecular orbital (LUMO, here the LUO- lowest unfilled orbital), an amount of energy must be added. The amount of energy added must exactly correspond to the needed amount of energy to cause the transition. Light energy can cause this transition, provided it is of the the wavelength (λ) corresponding to the energy needed. This energy can be predicted fairly accurately by using the particle in a box model, a simple application of wave theory.

Particle in box treats electrons as a wave function in a one dimensional box of length (L). The energy is quantized, the lowest energy point is unequal to zero, with nodes of unknown energy, as the electron can not exist at the node. The electrons exert no force on the box. The energy of each transition can be determined fairly accurately using:

$$\Delta E = \frac{h^2(N+1)^2}{8m_e L^2} \quad (\text{Eq. 1})$$

$$E = h\nu \quad (\text{Eq. 2})$$

$$\lambda = \frac{8m_e L^2}{h(2N+1)^2} \quad (\text{Eq. 3})$$

where N = number of electrons in π bonds

L = length of box (m)

m_e = mass of electron = 9.109×10^{-31} kg

c = speed of light = 2.998×10^8 m s⁻¹

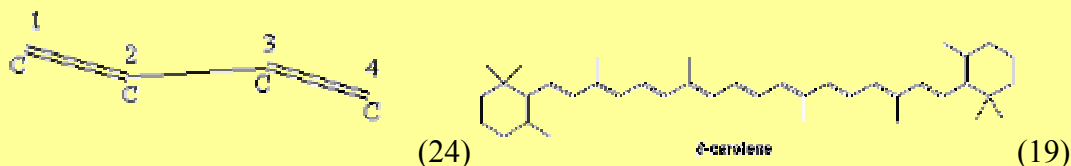
E = energy

ν = velocity

h = Planck's constant = 6.626×10^{-34} Js

The energy of the transition is the wavelength needed to stimulate such change, as transitions occur only at the exact energy needed. The larger the extent of conjugation, the greater the amount of delocalization, and the absorption is shifted to the red end of the spectrum.

As it would stand, it would be assumed that the absorption spectrum of 1,3-butadiene would be less that that of β carotene.



This is the case when calculated, as well as observed experimentally. Using bond lengths of 1.35 Å for double bonds, and 1.46Å for single bonds, the absorption spectrum can be calculated for each using equation 3. 1,3-Butadiene absorbs in the UV spectrum at approximately 290nm, while β carotene absorbs in the blue-green spectrum at approximately 480, reflecting back the red-orange color that we see when we look at it. ^(24, 83,92)

Particle in a box calculations do not exactly correspond to experimental data collected, but can provide a fairly good estimate as to the amount of energy absorbed, and is increasingly more accurate as the box length increases. Inaccuracies arise from error in the actual bond length as compared to the calculated bond length, as well as the electron-electron repulsions that occur in real molecules that are not accounted for with the particle in a box model. ^(24, 64, 65, 83)

The less conjugation, the higher the energy absorbed. For example, cyanin, carbocyanin, and dicarbocyanin are similar in structure, but differ in the number of C-C double bonds connecting the two ring structures, having 4, 6 and 8 bonds in the system. These differences result in difference absorption spectra.

	Particle in a box calculation	Observed wavelength, WebMo
Cyanine- 4 electrons in box	465.7nm (21473cm ⁻¹)	520nm (19231cm ⁻¹)
Carbocyanine- 6 electrons in box	568.7nm (17584cm ⁻¹)	601.5nm (16625cm ⁻¹)
Dicarbocyanine- 8 electrons in box	715.3nm (13980cm ⁻¹)	703.5nm (14215cm ⁻¹)

Table 5: cayanine, carbocyanine, and dicarbocyanine absorption. (80)

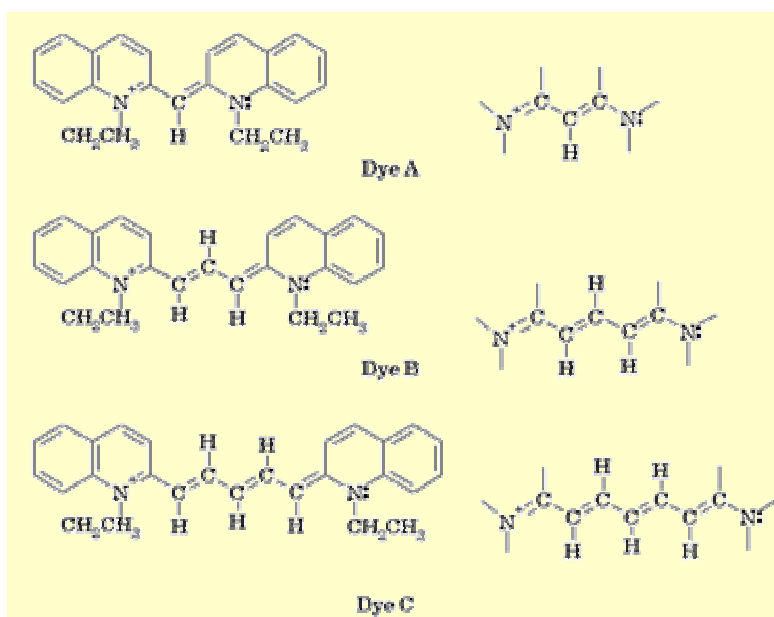


Fig 14: dye A, cyanine; dye B, carbocyanine; dye C, dicarbocyanine.

When absorptive molecules are exposed to bleach, the double bonds are cleaved in a way that conjugation is interrupted to an extent that renders the molecule colorless. However, the molecule may very well still be on the surface of the clothing, just not visible^(19, 41, 46, 60, 77).

In addition to breaking double bonds, there is also evidence that the bleach ionizes, causing the spontaneous formation of soap from oily soils⁽³²⁾.

A few final thoughts...

Soaps, detergents and bleaches are chemicals that are used on a daily basis by almost everybody. However, people seldom stop to think about the complex, microscopic interactions that allow these materials to clean and disinfect the surfaces they come into contact with. The application of surface chemistry, spectroscopy, and organic chemistry are all important aspects of the function of soaps and detergents, as well as the uses of soaps and detergents in products such as pesticides (to allow leaves to be better "wetted" with spray), and glue (to allow the glue to better coat the surfaces)⁽⁴⁰⁾.

Soaps and detergents make our lives more pleasant; people smell better, look better, and this in turn can help people to feel better. One study on the use of soaps in hand washing noted an almost 50% reduction in childhood deaths due to contagious diarrhea when soap was distributed to rural villages in Pakistan⁽⁴⁹⁾.

The choice of cleaning agents presented in stores is astounding, but the basics are the same for all soaps and detergents. Pick confidently, knowing that whatever choice is made, the dirt will be lifted by a swift reduction in surface tension, coupled with a quick suspension of soil in a micelle that will be quickly washed away. If that doesn't do the trick, a few drops of common bleach should "take out" the stain by breaking a few bonds!

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Aisle 5: Soaps, Detergents, and Bleach

Test Questions

1. How much soap would be made by reacting 10.gKOH with 50.g trilauric acid (MW 686g/mol)?

1 mole TLA + 3 mole KOH → 1 mole glycerol + 3 mole soap

(50g TLA*/1)(1mol TLA/686g TOA)(3 mol soap/1mol TOA)(266.1g soap/1mol soap)=
58g soap

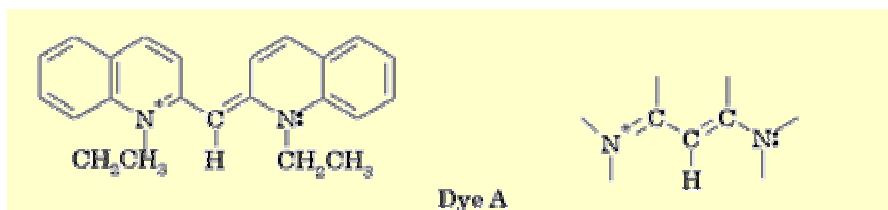
(10g KOH*/1)(1mol KOH/56.1g KOH)(3mol soap/3mol KOH)(266.1g soap/1mol soap)=
47g soap

2. A molecule of dye has a box length of 11.18Å, with 6 electrons in the box. Determine the wavelength absorbed.

$$\begin{aligned}\Delta E &= h^2(N+1) / 8m_e L^2 \\ E &= h\nu \\ \lambda &= 8m_e L^2 / h(2N+1) \\ \lambda &= [8(9.01939 \text{ E}^{-31} \text{ kg})(11.18 \text{ E}^{-10} \text{ m})^2] / [6.626 \text{ E}^{-34} \text{ Js}^{-1}(7)] \\ \lambda &= 5.89 \text{ E}^{-7} \text{ m}\end{aligned}$$

3. Why would treatment of cyanine with bleach make the molecule colorless?

The structure of cyanine contains a delocalized system of conjugated double bonds. When exposed to bleach, the double bonds would be broken, and the molecule would no longer absorb in the visible range.



Cyanine (<http://www.chemistry.nmsu.edu/studntres/chem435/Lab5/intro.html>)

4. LaVerne spilled butter on her new shirt before school while making breakfast. She soaked the shirt in water all day, but the stain still remained. She then treated the shirt with bleach, but it also did not help. Explain to her why the water and bleach treatments would not wash the spot out, and explain why soap and detergents can.

Water is a polar molecule, and oil is nonpolar. Because of this, the water would not dissolve the oil, and would not attach to the oil to remove it. The bleach would only break double bonds, “removing” color from a stain by changing its absorption spectra. Soap is amphiphilic- it has both a polar and a nonpolar end. The soap/ detergent can the “dissolve” the oil in the water by attaching to both at the same time, forming a micelle that would suspend the soil and allow it to be washed away. (Soap/ detergent also would lower the surface tension of the fabric/ water and fabric/oil interface, making the interface

wetter, but this would have a negligible influence on cleaning the oil from the shirt.)

5. What is soap scum, and how is it formed? How can its formation be avoided?

Soap scum, or curd, is the insoluble product of a soap reacting with divalent ions (Mg^{2+} , Ca^{2+}) in hard water. Soaps are salts of fatty acids, and typically have a monovalent ion attached, typically Na^+ , or K^+ . The fatty acid of the soap contains a COO^- group, which is attracted to any positive charge. When in hard water, the Na^+ or K^+ is replaced by Ca^{2+} or Mg^{2+} . The Mg^{2+} and Ca^{2+} salts would bind to two fatty acid molecules each, and are insoluble, leaving a deposit behind that we refer to as soap scum. This can be prevented by using detergents, which do not form insoluble when bound to Mg^{2+} or Ca^{2+} .

6. You go on vacation to an area that has well water. While away, you notice that your shampoo does not lather as well as it does at home. Explain one reason why this could occur.

The water on vacation is “hard water”- it contains Mg^{2+} and Ca^{2+} that bind up detergent/ soap and prevent it from foaming well. Soaps are salts of fatty acids, and typically have a monovalent ion attached, typically Na^+ , or K^+ . The fatty acid of the soap contains a COO^- group, which is attracted to any positive charge, and will take them from the water, releasing the monovalent ion into the water. This can be prevented by using a water softener that removes Mg^{2+} and Ca^{2+} from the water before it comes out of the tap.

7. Compare and contrast soaps and detergents.

Both soaps and detergents act as surfactants and alter surfaces which they are exposed to. They both decrease surface tension of a surface, and are amphipathic, possessing both hydrophilic and hydrophobic ends on the same molecule/.

Soaps are usually made from “natural” oils or fats (oleochemicals), rather than from petroleum products (petrochemicals), like detergents usually are. As a result of being produced from oleochemicals, soaps usually contain carboxylic acids, while detergents do not. Also, soaps are typically biodegradable, while detergents are usually not. Soaps produce curd, or soap scum, while detergents do not, as they pick up divalent ions (Ca^{2+} and Mg^{2+}) from wash water.

8. How do most detergents differ from each other?

Most detergents differ in the additives that give them their unique properties. For example, most liquid hand soaps (or laundry detergents, or dishwashing detergents) contain the same active ingredients, but have different amounts of perfumes, dyes, humectants, preservatives and other additives. In fact, the only differences between some would be the different dyes and fragrances.

9. What are the four general steps that occur when detergents and soaps clean?

1. Surfactants alter surface tension, making water wetter
2. Surfactants release or loosen soil from the surface
3. Surfactants emulsify water, holding the soil in suspension

4. Surfactants hold soil in suspension, preventing them from reattaching to the surface

Hot Process Soap Making

Adapted from: "Hot process soap making" URL

Procedure:

You MUST wear goggles or glasses!

Plug in a hot plate and set it on HIGH. Half fill a 400 ml beaker with hot water from the sink and place on the hot plate. When the water begins to boil, adjust the heat, so that the water boils gently, but continuously. While waiting for the water to boil, weigh a 250ml Erlenmeyer flask on a triple beam balance and add 10g of fat (Crisco, spray, or lard) to it. In a 150ml beaker prepare 100 ml of a 50-50 solution of alcohol-water, by mixing 50 ml of cold water and 50 ml of 95% cold ethanol. Mass another 150 ml beaker on the balance, and add 10g of NaOH pellets to the beaker. **Caution: Handle NaOH with care as NaOH can burn the skin and is especially harmful to the eyes.** In the hood, carefully mix the NaOH with 36 ml of the of the 50-50 alcohol-water solution to it. Stir the mixture until a transparent solution is formed. **Caution: the beaker will get very hot as the lye dissolves;** however, the cold water-ethanol mixture should lower the temperature a bit.

Pour the lye solution into the Erlenmeyer flask containing the fat, and mix well by using a stirring rod or by swirling with a beaker tongs. Clamp the Erlenmeyer in the boiling-water bath, and with occasional stirring, allow it to heat for at least 30 minutes. While the mixture boils, some foam will form (due to soap formation). Try to minimize excessive foaming, by adding small portions of excess alcohol-water solution. The reaction is complete when oil globules are no longer visible after the reaction mixture is stirred.

Half fill a 600 ml beaker with 300 ml of clear (filtered) saturated salt (NaCl) solution, and 50 ml of water. Pour the still hot reaction mixture containing soap, glycerine, excess NaOH, and alcohol into the salt solution. Stir the resulting mixture and allow it to stand for 5-10 minutes. The soap will collect as a white layer on the surface of the salt water in the beaker.

Prepare a suction trap from the vacuum flask, which will be used later to filter the soap preparation. Bend a long piece of glass tubing into a right angle (instructor will demonstrate), and push one leg of the bend through a one-hole rubber stopper fitted for the mouth of the flask. When inserted, the glass tube should extend to about ½ inch from the bottom of the flask. The exposed leg of the bend should be cut off at about 3 inches from the bend, and, by means of a piece of rubber connector tubing, be attached to a 12-inch length of glass tubing. The side-arm of the vacuum flask is now connected to the vacuum outlet with pressure tubing. When the suction is turned on, this device will act like a vacuum cleaner, sucking up liquid instead of dust.

Be sure the suction is OFF, before proceeding. Bring the beaker containing the soap preparation next to the suction trap, and place the “spout” of the trap into the beaker having it touch the bottom. Slowly turn on the suction, and watch the bottom (aqueous) layer being drawn into the vacuum flask. Draw off most, but not all, of the bottom layer. Be ready to stop the suction instantly, if it appears that some of the soap crystals are being sucked up. You can stop the suction quickly by pulling the pressure tubing away

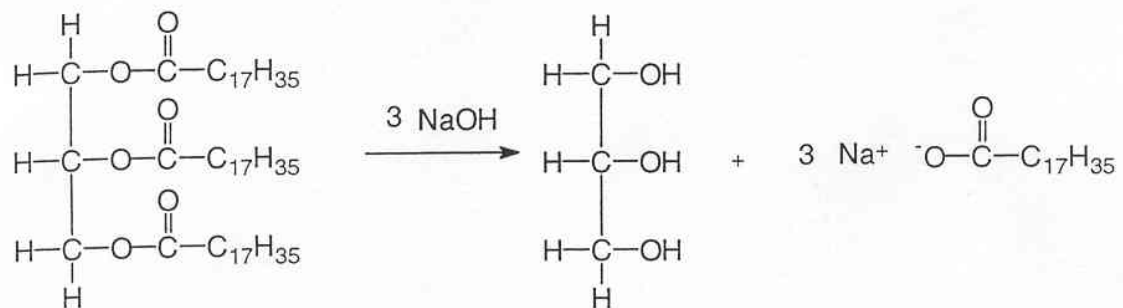
from the outlet, then turning off the vacuum. Caution: At no time should the vacuum flask be allowed to fill more than half the trap, and pour out its contents.

When most of the aqueous layer in the beaker has been drawn off, filter the remaining mixture of soap and liquid through a Buchner funnel (with filter paper attached!) to the suction flask. Wash the crystals on the filter with 5 ml portions of ice-cold water. Press out any remaining moisture from the cake of filtered crystals on the funnel with the flat end of a clean cork, or the clean bottom of a small beaker. Allow the product to dry for 10-15 minutes.

Turn off the suction, detach the Buchner funnel, and with the help of a clean spatula, transfer the soap crystals to a large sheet of smooth paper. Pick up the sheet and slide the crystals into a clean, dry 150 ml beaker. Leave the beaker stand, uncovered for several days to air-dry the product.

Weight the soap powder, determine the yield, and hand it to your instructor.

Saponification Reaction of Glyceryl Tristearate



Report Sheet Hot Process

Name _____ lab section _____ Date _____

Type of fat used _____

Weight of fat taken _____ g

Weight of NaOH used _____ g

Weight of soap formed _____ g

Use the weight of fat taken, assuming pure trilauric acid is used, MW 686g/mol, and the reaction to find the theoretical yield (weight) of soap bar.

Theoretical yield
_____ g

% yield = (actual yield (weight of soap formed)/theoretical yield) X 100=
_____ %

Questions

- 1) Why may you use the same weight of fat in your soap preparation regardless of the type of fat-saturated or unsaturated- employed?
- 2) What is the difference between a detergent and a soap?
- 3) Using the same weights of fat and alkali, would you get more or less soap by using KOH instead of NaOH? Explain!
- 4) Why do detergents typically not form soap scum?
- 5) What is a micelle?
- 6) Indicate the polarity differences that occur in a soap molecule? (Draw a picture.)
- 7) Why can you unclog a kitchen-sink drain filled with fat by pouring lye down into it?