Surfactants and Emulsions:

By James Fox

Dedicated to the tireless work of Dr. Paul Stamberger, Crusader Chemical Founder (circa 1950).

Surfactants are very important for coatings, cosmetics, environmental, and health care applications due to a range of surface-active properties they possess. Additionally, the global surfactant market is expected to be worth approximately US$28.83 billion by 2023 [1], further demonstrating their significance Here, we discuss some basic ideas and techniques that will aid in the selection of surfactants for formulating wetting, defoaming, or cleaning , as well as for simple cosmetics.

Surfactant theory and practice can be seen throughout many disciplines. The name surfactant refers to "surface active agents" and their use is to modify the surface tension between liquid/liquid, gases/liquid, or liquid/solid interfaces. Characteristic to surfactants are their critical micelle concentrations (CMCs) which is defined by the concentration required to promote self-assembly of the molecules into hierarchal structures called micelles (also vesicles or worm-like micelles). The CMC is illustrated in Figure 1.

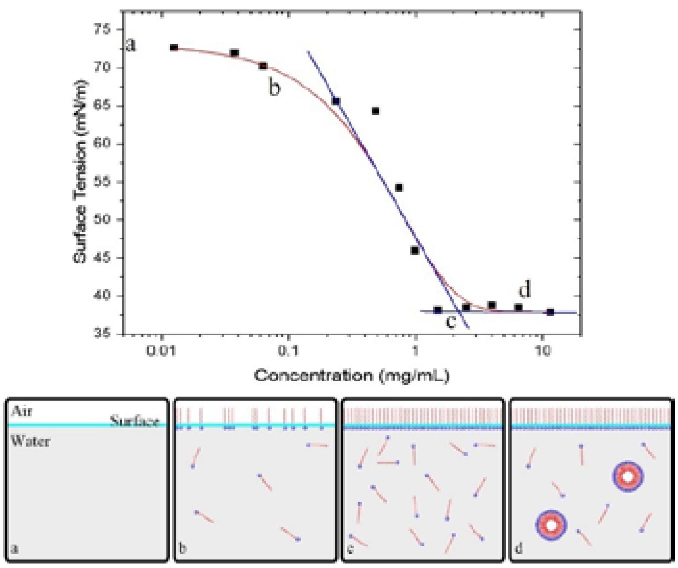

Figure 1. Illustration of critical micelle concentration and its relationship to solution surface tension as a function of surfactant concentration (c_s). a) c_s = 0; 0 < c_s > CMC; c_s = CMC; c_s > CMC.

The CMC of a surfactant can be measured using a surface tensiometer. Other methods make use of light scattering or fluorescent probes to determine CMC. Figure1. demonstrates a typical surface tension measurement as a function of surfactant concentration to determine the CMC (Figure 1, c).

The branch of chemistry involving surfactants is sometimes call "soft colloids" and the earliest known use of this chemistry dates to the Neanderthal cave paintings in Lascaux, France. The Food Industry uses a naturally occurring surfactant, phosphatidylcholine (lecithin) to make emulsions like mayonnaise (liquid/liquid) or meringues (gas/solid). The Printing Industry improves printing resolution on high energy surfaces with the addition of surface modifiers. Foam mattresses use such surface modifying agents to stabilize cells filled with entrained air.

Surfactants also have relevance in biology. In medicine, a condition called Surfactant Dysfunction, is an imbalance of phospholipids (a surfactant) and proteins around the lung alveoli causing difficulty in breathing and eventually death. [2] New surfactant drugs reduce scarring of lung tissue Cystic Fibrosis patients. Finally, surfactants in a grasshopper's regurgitate are used to ward off attacking ants. The low surface tension regurgitate covers the hydrophobic cuticles of the ants causing them to spend most of their time cleaning their cuticles. [3]

In 1949, Griffin [4] assigned a scale to describe a hydrophobic–lipophobic balance (HLB) that predicts the nature of surfactants. This scale assigns a numeric value to the ratio of polar functional group strength relative to the non-polar portion of the surfactant. Surfactants with a hydrophilic head have contributing values for water soluble segments >10 and for lipophilic tails the contributing values for oil soluble segments

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are <10 Combining these contributions produces an overall number for HLB, which is outlined for various surfactant behaviors in Figure 2. For example, given the same hydrophilic head group, a surfactant with a higher molecular weight (MW) alkyd tail length would be more hydrophobic, and thus, lower on the HLB scale.

To calculate HLB of ethoxylated, nonionic surfactants from physical data, one uses the formula, HLB = E / 5, where E is the percentage of the ethoxylated mass in the surfactant. For example, Oleth-20 has 20 ethoxylate repeat units in its hydrophilic portion. Each ethoxylate unit is 44 g/mole. The hydrophobic portion, oleyl alcohol, has a molecular weight = 268 g/mole. The calculation for the HLB of Oleth-20 is as follows:

$$20 \times 44 = 880 \quad (1)$$

$$880 + 268 = 1148 \quad (2)$$

$$880 / 1148 = 76.6\% \quad (3)$$

$$76.6\% / 5 = 15.3 \quad (4)$$

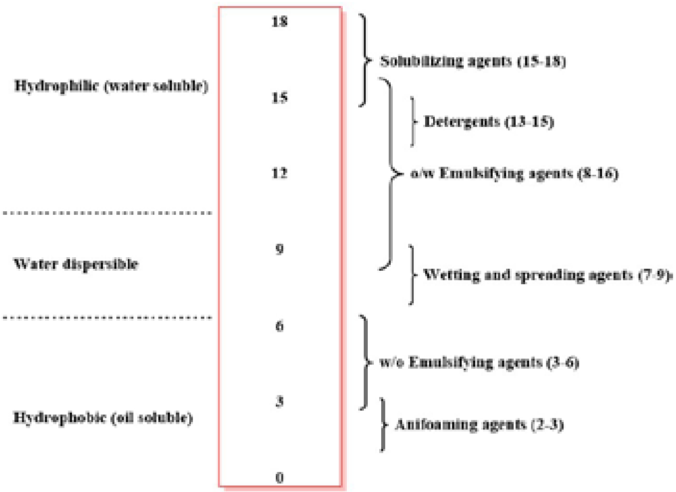

Figure 2. HLB scale showing classification of surfactants.

From Figure 2, one notes that Oleth-20 is quite water soluble (HLB= 15.3). Another method (Davies, 1957) calculates HLB based on chemical groups to assure stronger and weaker hydrophilic groups are accounted for when describing the HLB value. [5]

There are several surfactant categories: ionic, non-ionic, and amphoteric (Figure 3). Ionic surfactants have subgroups that include anionic (negative) alkyl benzyl, sulfonates, or phosphates which are utilized in the cleaning industry. Cationic-based surfactants (positive) are used as water softeners and anti-static agents. Cationic, anionic and amphoteric surfactants may be pH dependent and are often affected by added electrolytes in water, which has implications in formulating coatings when pigments are used that carry a charge.

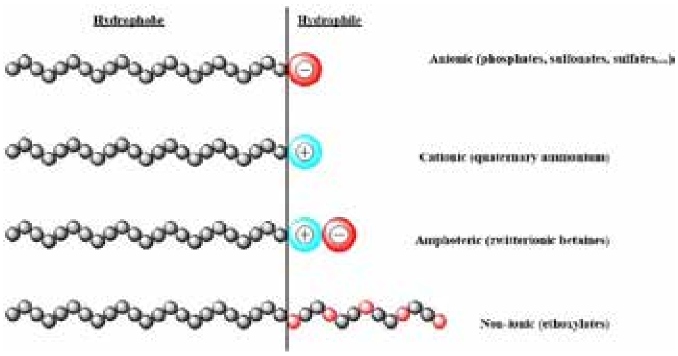

Figure 3. Types of surfactant groups and charges.

As the name infers, non-ionic surfactants are not ionized, and thus are not affected by wide pH swings or free electrolytes in solution. As a result, nonionic surfactants have good compatibility with additives like pigments and clays that may carry a charge. The synthesis of these molecules is carried out via the ring opening polymerization (ROP) of ethylene oxide monomer using an initiating species, often an alkyl alcohol. The reaction results in the formation of a polymeric ether with a degree of polymerization that is dictated by the monomer to initiator molar ratio as representing in the ring opening polymerization of ethylene oxide in Figure 4.

Figure 4. Ethoxylated alcohol formation from an alkyl alcohol and ethylene oxide.

The degree of ethoxylation plays a role in the properties of the final surfactant. One property is cloud point (CP), which varies with molecular weight. As the temperature increases above what is called a lower critical solution temperature (LCST), the ethoxylated chains undergo an extended-to-collapsed conformational change. This LCST behavior results in the solution becoming turbid or cloudy as the temperature increases due to a decrease in the solubility of the ethoxylated chains in water.

Another observation on cloud points is the molecule (CP) is lowered by electrolytes in solution.[6]

The decrease is due to anions weakening the hydrophobic hydration along the alkyd chain length as depicted

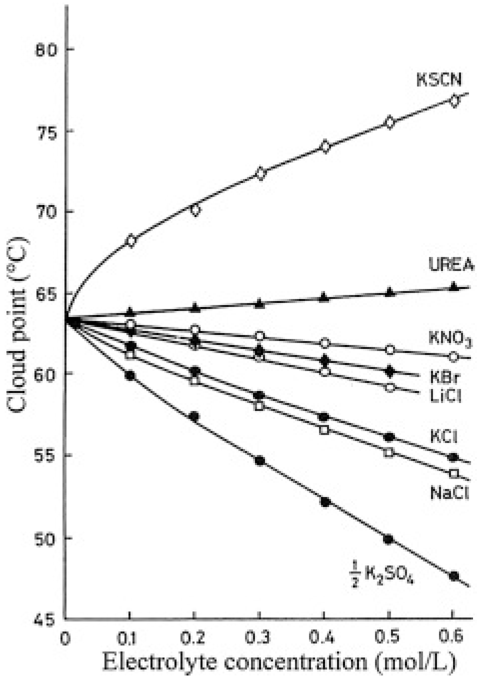

Figure 5. Effect of electrolytes on the cloud point of C12EO7 (5 mmol/L)

When selecting ethoxylated alcohol type surfactants, one should know they come with some precautions. Ethoxylated nonylphenol type (NPE) are banned in textiles by the European Union's REACH Committee. This is because NPE surfactants are removed in the washing cycle of textiles. This displaced nonylphenol molecule causes infertility due to the accumulation in aquatic life. [7]

Some nonionic surfactants are derived from sucrose-base chemistry due to their biocompatible structures. For example, polyglucosides tend to be more environmentally friendly and less toxic for skin care creams. A safer glycoside-derived surfactant, Tween 60, is a polyoxyethylene (20) sorbitan monostearate. The (20) represents the number of polyoxyethylene groups (w+x+y+z) attached to the sorbitan ring (Figure 5). The monostearate group for Tween 60, or as another example, monolaurate for Tween 20, describes the hydrocarbon chain capping a single terminus of the ethoxylate groups (Figure 7)

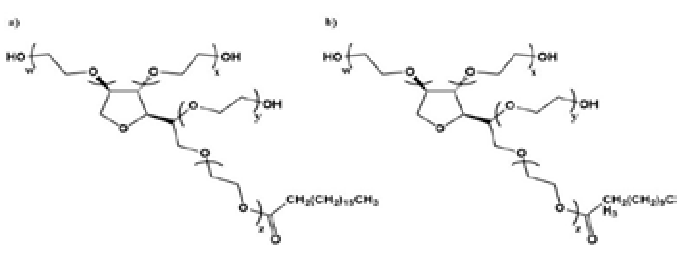

Figure 7. Chemical structure of a) Tween 60 (CAS No. 9005067-8); b) Tween 20 (CAS No. 9005-64-5).

New trends in reducing one's carbon footprint, give rise to new sustainable chemistries. Bio-based ethanol is replacing petroleum-based grades to generate ethylene oxide for surfactant syntheses. These intermediates are used to produce "green" surfactants like the above Tweens (Figure 7). Additionally, the cosmetic industry is not only promoting plant-based creams but EO free ingredients as well. Chemistries with propylene oxide are now added onto the linear alcohol chains to make Tween-type surfactants. Surfactants with both EO/PO copolymers exhibit lower CMCs, lower surface tension, and better dispersing power than the surfactants with only EO groups. Combinations of EO/PO copolymer capped systems can also be synthesized on the alkyl chain to modify HLB, and subsequently, the demulsifying properties of surfactants. (Wu, 2004). [8]

A novel surfactant group called Gemini (twin) entails two hydrophobic tails joined by two hydrophilic heads. In the special case shown in Figure 8, amino acids are used for the head portion, lending itself to a more biocompatible molecule. (Perez 2014) [9]

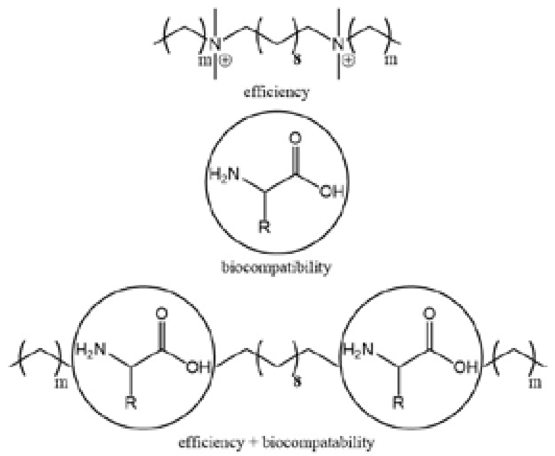

Figure 8. Gemini Surfactants based on hydrophilic amino acid head groups.

The Gemini structure achieves a CMC using less material, which is beneficial when used as additives in the coatings industry. Lowering the surfactant levels will result in less fisheyes, craters, and orange peel surface defects. In clear coats, less surfactant will result in less blushing of high gloss lacquers.

Cosmetic chemists attempt to formulate stable emulsions from specialty oils, surfactants, and water using predictions from a variety of methods. One method used to predict such stability is centrifugation followed by heat cycling. For example, canola oil has an HLB =7 and can be matched with a specific surfactant (HLB = 7) prior to adding water (most of the selection process can be done with a test tube that is shaken by hand).

Over time separation will occur because the dispersed particles tend to migrate towards each other to reduce their interfacial area in the continuous phase. Varying the concentration may result in a stable emulsion, however, one can improve emulsion stability by selecting surfactants with high and low HLB values (e.g. SPAN 80 = 4.3 and Tween 80 = 15.5) until the overall HLB is equal to 7. In the above case, the surfactant mixture calculation is as follows:

Tween 80	15 x 0.255	= 3.825	(5)
SPAN 80	4.3 x0.745	= 3.203	(6)
Adding HLB approx.		= 7.0	(7)

In the final formula, 2.55-part Tween 80 and 7.45 part of Span 80 are used to create a stable emulsion.

Note the chemistry of both surfactants is derived from the same sorbitan monooleate. The fact they are the same improves emulsification of water in oil. Based on Bancroft's rule, the nature of the emulsifying agent determines the emulsions stability.

Typical equipment for emulsifying water and oil mixtures include, shear mixers, Silverson mixers, or even sonication equipment. Sonication has shown that less surfactant is needed since the droplet sizes produced are very small. Homogenization factors include shearing time, shearing blade shape, and temperature. It is critical to maintain the homogenized state to reduce separation of both phases. To overcome this entropic nature, cellulosic derivatives have been added to aid in homogenization; additives like methocel lower the surface tension at the oil/water interface. Stability tests show very little oil migration on top and slight water separation at the bottom. Additionally, a conductivity test can reveal if you have an O/W emulsion (conductive) or a nonconductive W/O system.

In conclusion, most formulating is done countless trial and error. Design of Experiment Software is a useful tool for this field since it will improve product development. One aspect of formulating that should be standardized is a supplier's raw material quality.

Alternative materials used for an ISO 9000 contingency plan can lead to supply chain problems. One should not be surprised when the "so called" same raw materials show different results. There is an old adage "if it isn't broke, don't fix it" can be a useful reminder before changes are made to formulas. Finally, choose surfactants, with good product stability or shelf life in the system. Factors of hydrolysis, compatibility, long term UV stability, service temperatures and regulatory synergies all lead to the success of the product. The formulator should be detail oriented, innovative and most of all love his work.

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