HLB (Hydrophilic–Lipophilic Balance) is an empirical expression for the relationship of the hydrophilic (water–loving) and hydrophobic (water–hating) groups of a surfactant. The higher the HLB value, the more water–soluble the surfactant. The HLB system is particularly useful to identify surfactants for oil and water emulsification. There are two basic emulsion types: Water–in–oil (W/O): water is dispersed in oil, Oil–in–water (O/W): oil is dispersed in aqueous phase. Water–in–oil emulsions (W/O) require low HLB surfactants. Oil–in–water (O/W) emulsions often require higher HLB surfactants. Surfactant selection for an O/W emulsion can be simplified if the HLB system is applied. Oils have required HLB numbers that identify the HLB necessary to give good o/w emulsification. Often the oil supplier can provide the required HLB value. Alternatively, there are a number of compiled lists in the literature on the required HLB for common waxes and oils. Since overall chemical structure (e.g., branched, linear, aromatic) is also a variable, a number of different surfactants with the required HLB should be examined. Not all surfactants having the same HLB value may be acceptable for an o/w emulsion. HLB values for surfactants can be calculated for simple alcohol ethoxylates. If a surfactant is not a simple alcohol ethoxylate, the HLB value must be determined experimentally. HLB values are additive; therefore, if two different surfactants or oils are present, the HLB will be the weighted average of the HLB values for each component.

Keywords: Surfactant, Amphiphilic, Amphoteric, HLB, Hydrophilic, Lipophilic, Anti–foaming agent, W/O (water in oil) emulsifier, Wetting and spreading agent, Detergent, O/W (oil in water) emulsifier, Solubiliser or Hydrotropic, Anionic surfactants, Cationic surfactants, Zwitterionic surfactants, Nonionic surfactants (Tweens & Spans).

Introduction
Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids (emulsions) or between a liquid and a solid (suspensions) to make a monophasic formulation from biphasic unit. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents and dispersants. Surfactants are usually organic compounds that are amphiphilic or amphipathic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains both a water–insoluble (or oil–soluble) component and a water–soluble component (or oil–insoluble). Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The water–insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water–soluble head group remains in the water phase.[1]

<table>
<thead>
<tr>
<th>Hydrophilic Groups</th>
<th>Group Number</th>
<th>Lipophilic Groups</th>
<th>Group Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium sulphate (−SO₄ Na⁺)</td>
<td>38.7</td>
<td>Iso series (−CH−)</td>
<td>−0.475</td>
</tr>
</tbody>
</table>

Table–1: Hydrophilic/Lipophilic Groups with Group Numbers

Classification: The ‘tail’ of most surfactants is fairly similar, consisting of a hydrocarbon chain, which can be branched,
linear, or aromatic. Fluorosurfactants have fluorocarbon chains. Siloxane surfactants have siloxane chains. Many important surfactants include a polyether chain terminating in a highly polar anionic group. The polyether groups often comprise ethoxylated (polyethylene oxide–like) sequences inserted to increase the hydrophilic character of a surfactant. Polypropylene oxides conversely, may be inserted to increase the lipophilic character of a surfactant. Surfactant molecules have either one tail or two; those with two tails are said to be double–chained. Surfactant classification according to the composition of their head: nonionic, anionic, cationic, amphoteric.[1]

Most commonly, surfactants are classified according to polar head group. A non–ionic surfactant has no charged groups in its head. The head of an ionic surfactant carries a net positive or negative charge. If the charge is negative (−), the surfactant is more specifically called anionic (R−); if the charge is positive (+), it is called cationic (R+). If a surfactant contains a head with two oppositely charged groups (+/−), it is termed zwitter–ionic (R+R−). Commonly encountered surfactants of each type include:

**Anionic surfactants:** Sulfate (SO4−), sulfonate (SO3−), phosphate (PO4−) and carboxylate (−COO−). Anionic surfactants contain anionic functional groups at their head, such as sulfate, sulfonate, phosphate and carboxylate. Prominent alkyl sulfates include ammonium lauryl sulfate, sodium lauryl sulfate (sodium dodecyl sulfate, SLS, or SDS).

**Others include:** Docusate (dioctyl sodium sulfosuccinate), Perfluorooctanesulfonate (PFOS), Perfluorobutanesulfonate, Alkyl–aryl ether phosphates, Alkyl ether phosphates.

**Carboxylates:** These are the most common surfactants and comprise the alkyl carboxylates (soaps), such as sodium stearate. More specialized species include sodium lauroyl sarcosinate and carboxylate–based fluorosurfactants such as perfluorononate, perfluorooctanoate (PFOA or PFO).

**Cationic surfactants:** pH–dependent primary, secondary, or tertiary amines: Primary and secondary amines become positively charged at pH<10: Octenidine dihydrochloride. Permanently charged quaternary ammonium salts: Cetrimonium bromide (CTAB), Cetylpyridinium chloride (CPC), Benzalkonium chloride (BAC), Benzethonium chloride (BZT), Dimethyl dioctadecyl ammonium chloride, Diodoctadecyl dimethyl ammonium bromide (DODAB)

**Zwitterionic surfactants:** Zwitterionic (amphoteric) surfactants have both cationic and anionic centers attached to the same molecule. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations. The anionic part can be more variable and include sulfonates, as in the sultans CHAPS (3–[3–Cholamidopropyl] dimethylammonionol –1 –propanesulfonate) and cocamidopropyl hydroxysultaine. Betaines such as cocamidopropyl betaine have a carboxylate with the ammonium. The most common biological zwitterionic surfactants have a phosphate anion with an amine or ammonium, such as the phospholipids (phosphatidylserine, phosphatidylethanolamine, phosphatidylcholine and sphingomyelins).

**Nonionic surfactants:** Many long chain alcohols exhibit some surfactant properties. Prominent among these are the fatty acids, cetyl alcohol, stearyl alcohol and cetostearyl alcohol (consisting predominantly of cetyl and stearyl alcohols) and oleyl alcohol.


Polypropylene glycol alkyl ethers: CH3–(CH2)10–16–(O–C3H7)1–25–OH.

Glucoside alkyl ethers: CH2–(CH2)10–16–(O–Glucoside)1–3–OH: Decyl glucoside, Lauryl glucoside, Octyl glucoside


Glycerol alkyl esters: Glycerol laurate.

Polyoxyethylene glycol sorbitan alkyl esters: Polysorbate (Tweens). Polysorbate 20 (common commercial brand names include Scattics, Alkest TW 20 and Tween 20) is a polysorbate–type nonionic surfactant formed by the ethoxylation of sorbitan before the addition of lauric acid. Its stability and relative nontoxicity allows it to be used as a detergent and emulsifier in a number of domestic, scientific and pharmacological applications. As the name implies the ethoxylation process leaves the molecule with 20 repeat units of polyethylene glycol; in practice these are distributed across 4 different chains leading to a commercial product containing a range of chemical species. Tween and Tween 20 are registered trademarks of Croda Americas.

Sorbitan alkyl esters: Spans. Sorbitan is a mixture of isomeric organic compounds derived from the dehydration of sorbitol and is an intermediate in the conversion of sorbitol to isosorbide. Sorbitan is primarily used in the production of surfactants such as polysorbates; which are important emulsifying agents, with a total annual demand of more than 10000 tons in 2012.

Cocamide MEA, Cocamide DEA, Dodecyl(dimethylamine oxide, Block copolymers of polyethylene glycol and polypropylene glycol: Poloxamers, Polyethoxylated tallow amine (POEA).

**According to the composition of their counter–ion:**

**In the case of ionic surfactants, the counter–ion can be:**

**Monatomic/Inorganic:**

**Cations: metals:** alkali metal, alkaline earth metal, transition metal. Anions: halides: chloride (Cl−), bromide (Br−), iodide (I−).

**Polyatomic/Organic:**

The HLB Scale ranges 1–20. Surfactants with higher HLB numbers (>10) are more hydrophilic (water soluble/lipid insoluble). Surfactants with lower HLB number (<10) are more hydrophobic (lipophilic: lipid soluble/water insoluble). Complete water solubility of a surfactant occurs at and HLB of approximately 7.3. The hydrophilic–lipophilic balance of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic, determined by calculating values for the different regions of the molecule, as described by Griffin in 1949 and 1954. Other methods have been suggested, notably in 1957 by Davies.[2]

Griffin’s method for non–ionic surfactants as described in 1954 works as follows: \[ \text{HLB} = 20 \times \frac{M_\text{h}}{M} \]

Where \( M_\text{h} \) is the molecular mass of the hydrophilic portion of the molecule and \( M \) is the molecular mass of the whole molecule, giving a result on a scale of 0 to 20.

**Conclusion**

HLB Scale is essentially a ranking of how hydrophilic an amphiphilic molecule (surfactant) is. Developed by Griffin (1949), the HLB Scale ranks the tendency of a surfactant to be hydrophilic or hydrophobic (lipophilic). Since a surfactant molecule has both hydrophilic and hydrophobic portions (that’s why it’s a surfactant!), Griffin developed a ranking system to determine ‘how hydrophilic’ and ‘how hydrophobic’ a surfactant is. Surfactants generally have hydrophobic hydrocarbon chains with hydrophilic branches or ends (this scale is for non–ionic surfactants). The HLB scale is very relative scale; the number values of the HLB Scale don’t necessarily give insight into the properties of a surfactant, just their relative hydrophilicity compared to other surfactants. HLB Scale is widely used in industry.

**To summarize:**

The HLB Scale ranges 1–20; Surfactants with higher HLB numbers (greater than 10) are more hydrophilic; Surfactants with lower HLB number (less than 10) are more hydrophobic (lipophilic); Complete water solubility of a surfactant occurs at and HLB of approximately 7.3.

Higher HLB Scale valued surfactants are more hydrophilic and thus are more water soluble. Similarly, lower HLB Scale valued surfactants are more lipophilic and thus more oil soluble. So, higher HLB surfactants will create oil–in–water emulsions and lower HLB surfactants will create water–in–oil emulsions:

Often mixtures of surfactants are used to obtain a desired HLB number. To find the HLB number of a mixture of surfactants, the concentration of each surfactant is multiplied by its HLB number. To find the HLB number of a mixture of surfactants, the concentration of each surfactant is multiplied by its HLB number. To find the HLB number of a mixture of surfactants, the concentration of each surfactant is multiplied by its HLB number. To find the HLB number of a mixture of surfactants, the concentration of each surfactant is multiplied by its HLB number. To find the HLB number of a mixture of surfactants, the concentration of each surfactant is multiplied by its HLB number. Therefore, the HLB number of a mixture is the sum of the HLB values of all the individual surfactants:

\[ \text{HLB}_{\text{mixture}} = \sum (\text{HLB}_i \times \text{C}_i) \]

Where: \( \text{HLB}_i \) is the HLB value of each surfactant, \( \text{C}_i \) is the concentration of each surfactant in the mixture, and \( n \) is the number of surfactants.

**Assigning surfactants to the following desired emulsions:**

(a) Mixing unlike oils together=use surfactants with HLB’s of 1 to 3 (b) Making water–in–oil emulsions=use surfactants with HLB’s of 4 to 6 (c) Wetting powders into oils=use surfactants with HLB’s of 7 to 9 (d) Making self emulsifying oils=use surfactants with HLB’s of 7 to 10 (e) Making oil–in–water emulsions=use surfactant blends with HLB’s of 8 to16 (f) Making detergent solutions=use surfactants with HLB’s of 13 to 15 (g) For solubilizing oils (micro–emulsifying ) into water=use surfactant blends with HLB’s of 13 to 18.

Where: \( n= \)Number of hydrophilic groups in the molecule, \( h_i = \)Value of the \( i^{th} \) hydrophilic groups, \( n= \)Number of lipophilic groups in the molecule. \[4\]

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