Unit III

Surface and interfacial phenomenon

Hydrophilic lipophilic balance scale:

The hydrophilic lipophilic balance (HLB) system is based on the concept that some molecules of surfactants are having hydrophilic groups; other molecules have lipophilic groups and some have both hydrophilic and lipophilic groups called amphiphilic molecules.

Hydrophilic and lipophilic portions dissolve in aqueous and oily phase. It is useful to correlate and measure these characteristics of the surfactants by some means for their applications in various fields such as to formulate various dispersed systems like lotions and emulsions.

A common system, which is used to express the amphiphilic nature as a balance between hydrophilic and lipophilic portion of the molecule is called as HLB system.

Weight percentage of each type of group in a surfactant molecule or in a mixture of surfactants predicts what behaviour the surfactant molecular structure will exhibit. Griffin in 1949 and its latter development in 1954 introduced the HLB system, a semi-empirical method. It is the number on scale of 1 to 40, as shown in Fig.

The HLB value for a given surfactant is the relative degree to which the surfactant is water-soluble or oil soluble. An emulsifier having a low HLB number indicates that the number of hydrophilic groups present in the molecule is less and it has a lipophilic character. For example, spans generally have low HLB number and they are also oil soluble. Because of their oil soluble character, spans cause the oil phase to predominate and form a w/o emulsion.

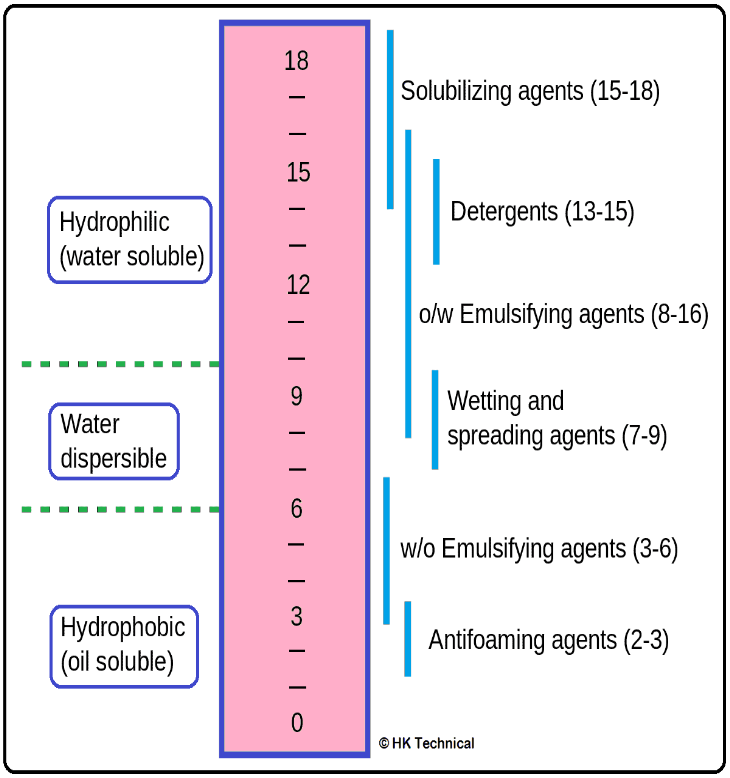

Figure: HLB Scale Showing Functions of Surfactants along with Their HLB Range

A higher HLB number indicate that the emulsifier has a large number of hydrophilic groups on the molecule and therefore is more hydrophilic in character. Tweens have higher HLB numbers and they are also water soluble. Because of their water-soluble character, Tweens will cause the water phase to predominate and form an o/w emulsion.

The usual HLB range is from 1 to 20, while there is one exception to this range as shown in Table at the bottom. Sodium lauryl sulphate, a surfactant dissolves in water very well and is common additive to most of the heterogeneous systems and to almost all common detergents. As HLB value is additive, the blending of surfactants with known HLB values to get a desired one is very easy. The appropriate HLB values are calculated by various methods.

Table: HLB Values of Some Surfactants

Use	**Example**	**HLB**
Antifoaming agent	Oleic acid	1
	Sorbitan tristearate	2
	Glyceryl monostearate	3
Emulsifying agent (w/o)	Sorbitan mon-oleate (Span 80)	4
	Glyceryl monostearate	5
	Diethylene glycol monolaurate	6
Emulsifying (w/o), wetting and spreading agents	(None)	7
	Sorbitan monolaurate (span 20)	8
	Polyethylene lauryl ether (Brij 30)	9
Emulsifying agents (w/o)	Methyl cellulose (Methocel 15 cps)	10
	Polyxyethylene monostearate (Myrj 45)	11
	Triethanolamine oleate	12
Emulsifying agents (o/w) and Detergents	Polyethylene glycol 400 monolaurate	13
	None	14

	Polyxyethylene sorbitan mon-oleate (Tween 80)	15
Emulsifying (o/w), solubilizing agent, detergents	Polyxyethylene sorbitan monolaurate (Tween 80)	16
Solubilizing agents	Polyxylene lauryl ether (Brij 35)	17
	Sodium oleate	18
	None	19
	Potassium oleate	20
Everything	Sodium lauryl sulfate	40

Methods to Determine HLB:

Method I - Alligation or Algebraic manipulations:

If a and b are the HLB values of surfactant A and B, respectively, and the c is desired HLB value then proportional parts required of A and B surfactants are x and y, respectively.

$$x/y = (c - a) / (a - c) \text{ Or}$$

$$HLB_{Blend} = f\ HLB_A + (1 - f)\ HLB_B$$

where, f is fraction of surfactant A and (1 − f) is fraction of surfactant B in the surfactant blend.

Method II - Water dispersibility:

Approximation of HLB for those surfactants and not described by Griffin can be made either from characterization of their water dispersibility.

Table: Estimation of HLB of Surfactants based on Water Dispersibility

HLB range	Water dispersibility
1 – 4	Not dispensible
3 – 6	Poorly dispersible
6 – 8	Milky dispersion only on vigorous agitation
8 – 10	Stable milky dispersion
10 – 13	Translucent to clear dispersion
≥ 13	Clear solution

Method III - Experimental estimation:

From experimental estimations blends of unknown surfactants in varying ratio with an emulsifier of known HLB are used to emulsify oil. The blend that performs best is assumed to have a value approximately equal to the required HLB of the oil.

Method IV – Group contribution method:

Davis and Rideal suggested an empirical calculation of HLB based upon the positive and negative contribution of various functional groups to the overall hydrophilicity of a surfactant. Substituting values given in Table for various group numbers in equation below gives HLB of a surfactant.

$$\text{HLB} = \sum (\text{Hydrophilic group number}) - \sum (\text{Lipophilic group number}) + 7$$

Table: HLB Contribution of Hydrophilic and Lipophilic Groups

Hydrophilic groups	Group number	Lipophilic groups	Group number
$-SO_4' Na^+$	38.7	$-CH =$	0.475
$-COO' K^+$	21.1	$-CH_2-$	0.475
$-COO'Na^+$	19.1	$-CH_3-$	0.475
$SO_3'Na^+$	11.0	$-CH_4$	0.475
R_2N	9.4	$-CF_2-$	0.870
$-COOH$	2.1	$-CF_3$	0.870
$-OH$ (free)	1.9		
$-O-$	1.3		
$-(OCH_2CH_2)-$	0.5		
$-(OCH_2CH)-$	0.33		
$-OH$ (sorbitan ring)	0.15		
Ester (sorbitan ring)	6.8		
Ester (free)	2.4		

Experimental estimations of HLB values of lanolin derivatives like bees wax and wool fat cannot be obtained easily. Each atom or group has assigned a constant and used in calculation of HLB. For example, if surfactant contains Polyoxyethylene chains, the HLB is calculated by equation;

$$HLB = \frac{E+P}{5}$$

Where, E and P are percent by weight of oxyethylene chains and polyhydric alcoholic groups, respectively in the surfactant molecule.

When the molecule contains only oxyethylene groups then, HLB is calculated by equation:

$$HLB = E / 5$$

HLB values of surfactants such as glyceryl monostearate that contain fatty acid esters and polyhydric alcohols is calculated by equation:

$$HLB = 20 \left(\frac{1 - S}{A}\right)$$

where, S is saponification number and A is acid number.

Saponification number is defined as the number of milligrams of potassium hydroxide required to neutralize the acid formed during saponification of one gram of sample.

Acid number is the number of milligrams of potassium hydroxide required to neutralize the free acid in one gram of sample. One part of structure of glyceryl monostearate contains a fatty acid stearic acid, which is lipophilic in nature while other part is alcohol, which is hydrophilic in nature. Therefore, analysis of these parts by saponification gives HLB estimates.

Factors Affecting HLB Value:

1. Nature of immiscible phase
2. Presence of additive
3. Concentration of surfactant
4. Phase volume
5. Temperature

Drawbacks of HLB system:

HLB system provides only information about the hydrophilic and lipophilic nature of the surfactants but concentration of these surfactants is not considered. For optimum stability and therapeutic safety concentrations of the surfactant are equally important. It does not consider the effect of temperature as well as the presence of other additives.

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