Hydrophilic Lipophilic Balance

In 1949 Griffin (1, 2) proposed a method for classification of non-ionic emulsifiers to assist in their selection for producing stable emulsions. His method known as the Hydrophilic Lipophilic Balance is usually abbreviated to HLB (see Table 1).

The HLB value of an emulsifier can be determined by comparing the relative content of the hydrophilic region of the molecule to the molecule as a whole. The formula is as follows:

$$HLB = 20 \times \frac{Mh}{M}$$

Where: $Mh$ = molecular weight of the hydrophilic component of the molecule

$M$ = total molecular weight.

From an experimental standpoint, when referring to ester-derived emulsifiers, the HLB can be determined using the following formula and data that can be measured relatively easily in the laboratory:

$$HLB = 20 \times \left(1 - \frac{Sv}{Av}\right)$$

Where: $Av$ = Acid value

$Sv$ = Saponification value

A further derivation of the HLB equation can assist in the theoretical design of ester-derived emulsifiers of a particular desired HLB value.

$$HLB = 20 \times \left(1 - \frac{Mwa}{Mwe}\right)$$

Where: $Mwa$ = Molecular weight of the carboxylic acid starting material

$Mwe$ = Molecular weight of the esterified final structure

Oils can be assigned compatible HLB values to assist in correctly selecting the emulsifier to partner the specific oil (3). In designing a complete emulsion system, two emulsifiers with differing HLB values (one high and one low) can be used. The resulting HLB of a blend of emulsifiers can be easily calculated using the following formula:

$$HLB = \left(\frac{\%a \times HLBa}{100}\right) + \left(\frac{\%b \times HLBb}{100}\right)$$

Where: $\%a$ = percentage of emulsifier a used

$HLBa$ = HLB of emulsifier a

$\%b$ = percentage of emulsifier b used

$HLBb$ = HLB of emulsifier b

For example, if we had a blend of 70 percent of a HLB 15 emulsifier with 30 percent of a HLB 4 emulsifier, the resulting HLB of the blend will be 11.7. Whilst the HLB system is a good indicator for compatibility of emulsifiers, there are limitations, namely it does not:

- Consider the ratio of oil phase to water phase
The principle of the NAC theory is based on the shape and size of droplet at the critical point when the microemulsion undergoes phase inversion. As it can be seen, the equations are quite complicated and require functions and factors that can only be derived by practical measurements. At the present time there is a growing database providing the relevant factors and coefficients for known emulsifiers however, it is still limited in size and scope.

**The Bancroft Rule**

We have previously mentioned types of emulsion used for the personal care sector, namely oil in water and water in oil. Determining if an emulsion is O/W or W/O cannot simply

- Indicate the level of emulsifier required
- Work well for emulsifying waxes
- Account properly for the use of fatty alcohols
- Consider the effect of temperature on the HLB of ethoxylates
- Consider the effect of salts on the HLB of ethoxylates
- Work well for ionic materials
- Account for the benefits of water phase thickeners
- Account for material interactions/synergy
- Account for the structure of the emulsifier

Give a clear indication of the best emulsifiers to use for W/O emulsions.

**Hydrophilic Lipophilic Difference**

A relatively new theory has been proposed to assist in the selection of emulsifiers, and to overcome the short fallings in Griffin's HLB theory. Hydrophilic Lipophilic Difference – Net Average Curvature (HLD-NAC) theory (4-8) takes a few key parameters and defines the conditions (salinity, temperature, oil) which would produce the minimum interfacial tension and the highest solubilisation of water in oil or oil in water. There are 2 equations that can be used to calculate HLD, one for non-ionic surfactants:

\[
\text{HLD} = \{b \times S\} - \{K \times \text{EACN}\} \times f(A) + C_1 \Delta T + C_{C_i}
\]

Where:
- \( b = 0.13 \) (for sodium chloride) or 0.1 (for calcium chloride)
- \( S \) = Salinity in units of g/100ml water
- \( K = -0.17 \)
- \( \text{EACN} = \) Effective alkane carbon number
- \( f(A) = \) a function of the alcohol type and concentration
- \( C_1 = \) a coefficient describing the effect of temperature change (0.06)
- \( \Delta T = \) difference in temperature from the reference point 25°C
- \( C_{C_i} = \) characteristic curvature specific to the non-ionic surfactant

The \( (b \times S) \) term in the non-ionic equation takes into account of any “salting out” effects of the salinity in the aqueous phase. The value of \( b \) relates to the valency of the type of salt present, either sodium chloride (mono-valent) or calcium chloride (di-valent).

The equation for ionic surfactants:

\[
\text{HLD} = \ln(S) - \{K \times \text{EACN}\} \times f(A) - \alpha_T \Delta T + C_{C_i}
\]

Where:
- \( \alpha_T = \) a coefficient describing the effect of temperature change (0.01)
- \( \Delta T = \) difference in temperature from the reference point 25°C
- \( C_{C_i} = \) characteristic curvature specific to the given ionic surfactant

The NAC component of both equations \( C_{C_i} \) takes into account the size and geometry of the surfactant molecule.
be arrived at by assigning the phase that is in the larger proportion as the continuous phase. For example, a formulation that consists of 70 percent aqueous phase and 30 percent oil phase does not necessarily mean that it is an oil in water emulsion.

The Bancroft rule (9) states: “The phase in which an emulsifier is more soluble constitutes the continuous phase”.

At first sight what the Bancroft rule states appears to contradict common sense, where the emulsion type does not rely on relative percentages of oil or water, but which phase the emulsifier is more soluble in. HLB values can be used to determine the solubility of individual emulsifiers in either the oil or aqueous phase. High HLB emulsifiers are more soluble in the water phase leading to an O/W emulsion, whereas a low HLB emulsifier favours the oil phase thus giving a W/O emulsion. There are some exceptions to Bancrofts rule, where high HLB emulsifiers are compatible with the oil phase however, it’s a very useful rule of thumb for most emulsion systems.

**MANUFACTURE OF EMULSIONS**

The conventional way of forming an emulsion is to heat the two phases separately, then bring them together with vigorous mixing, and continue the mixing until cool to prevent separation. Once cool, the additional temperature and shear sensitive ingredients can be added and mixed into the emulsion.

Whilst this method has been employed for decades, it is not without some drawbacks. It takes time and energy to heat the vessels containing the oils and waxes, and once mixed it takes even more time and resources to cool the product down. Also with highly viscous products, post-cooling addition of ingredients combined with inefficient mixing systems may lead to non-homogeneity in the finished product.

Waxes are widely used in personal care formulations as emollients and they additionally provide a characteristic texture to a finished emulsion, a widely used example of such a wax is petrolatum. These waxes readily solidify at ambient temperatures, therefore a “wax emulsion” can be considered as a dispersion of fine wax particles in the continuous phase. Cold process emulsifiers are now available that enable the formulator to prepare emulsions at ambient temperature with no heating requirement for the duration of the manufacturing process (10). Cold process technology provides an energy efficient means to prepare emulsions and significantly reduces processing times. Because no heating is used in the manufacturing process, any temperature sensitive materials can be combined to their compatible phase prior to forming the emulsion. One critical aspect of cold process emulsion formulation is the selection of viscosity modifier. Only components that are liquid at ambient temperature can be used in cold process preparation, therefore waxes cannot be incorporated into the emulsion as there is no heat to melt them into a molten form. In the absence of waxes the responsibility of developing texture and feel of the emulsion falls upon the viscosity modifier.

**REFERENCES AND NOTES**