The Studies on Hydrophilic-Lipophilic Balance (HLB): Sixty Years after William C. Griffin's Pioneer Work (1949-2009)

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SUMMARY. The Hydrophilic-Lipophilic Balance (HLB)was formally presented by William C. Griffin sixty years ago at a meeting in Chicago for the first time and later on in an article published in the first volume of the Journal of the Society of Cosmetic Chemists. In later publications, Griffin proposed formulas for the HLB value calculation that are satisfactory for non-ionic surfactants of various types. Several experimental methods developed then in order to obtain the HLB values of surfactants and required HLB of oils in a way simpler than with Griffin's original experimental method. Also there were proposed mathematical equations that HLB values of surfactants allows to calculate from its chemical formulae and also from quality control data of surfactants and its components.

Short biography of W.C. Griffin

William C. Griffin was born in October 9, 1914, in Mount Pleasant, Pennsylvania, thirty miles southeast of Pittsburgh. He graduated from Pennsylvania State University in 1936 with a Bachelor of Science degree in Chemical Engineering. Upon graduation, he began to work at the Atlas Powder Company, which later became part of Imperial Chemical Industries. Later, ICI gave the name of Uniqema to the surfactants portion of the business and a few years later sold it to Croda, USA. In 1940 he was co-author of a paper that proposed and demonstrated the utilization of electronic endpoint detection of the Karl Fisher endpoint for water analysis and the method is still in practice. In 1949 his first paper on the use of the HLB system for emulsifier selection was published. In 1953 he was awarded a Master of Science by Penn State University based on a thesis detailing this work. A second paper on HLB was published in 1954.He retired from ICI in 1979 after 43 years. Griffin received the 1999 Maison G. deNavarre Award from the Society of Cosmetic Chemists in recognition of the early HLB studies. In 2008, Croda dedicated a laboratory as the William C. Griffin Innovation Center (Fig. 1).

HLB History (by William C. Griffin)

Atlas Powder Company, my first employer in 1936, manufactured and sold dynamite and also the blasting caps that were required to detonate the dynamite. They were small copper tubes filled with mercury fulminate with attached wires to make them explode. They were sensitive to mechanical shock and if dropped they would explode spreading shards of copper everywhere.

Atlas learned of a person who had found that mannitol hexanitrate was an equally good explosive to detonate dynamite and that it was dramatically safer. In fact, one could drive a nail through them without their exploding. He and Atlas got together and designed a new blasting cap based on mannitol hexanitrate.

Atlas decided to manufacture the caps and to make mannitol for them. Mannitol is a sugar alcohol. In the process, they produced four

water soluble ones with the oil soluble ones and get the same effect as an in-between length of ethylene oxide, so the initial product line consisted of mono and tri esters with added ethylene oxide ranging from zero to twenty molecules.

The next question was how could one decide which product or products to use for the hundreds of different products that our potential customers could produce? We soon found that you could determine the required HLB for the oils and waxes that were in the products. Likewise, with a mixture of different oils and/or waxes the required HLB for the blend could be calculated based on weight percentages.

Of course, at first we blended various amounts of low and high HLB emulsifiers for each product but soon we made an array of test emulsifiers with HLB values of 2, 4, 6, 8, 10, 12, 14 and 16. These became our HLB Kit with which the approximate required HLB for a blend could be easily. Then with final blending of high and low, the best HLB is easily determined. Further, one will choose the composition of the surfactants based on the desired characteristics of the final product.

Our calculations of HLB at that time were crude compared with today's tools. It was basically the percentage of the hydrophilic portion of the molecule multiplied by twenty. This included not only the ethylene oxide but also the sorbitan portion.

Suffice to say, today's methods of determining the HLB of a surfactant is so far beyond my imagination back on those days.

The Studies on Hydrophilic-Lipophilic Balance (HLB)

The Hydrophilic-Lipophilic Balance (HLB) for emulsifier classification and selection was first issued in 1948 in an Atlas Powder Company's brochure [1]. The following year, William C. Griffin, one of the company's chemists, formally presented the HLB concept at a meeting in Chicago for the first time and later on in an article published in the first volume of the Journal of the Society of Cosmetic Chemists [2] (Fig. 2). In this innovative paper, Griffin explained some experimental details for the determination of the numerical HLB values of the emulsifiers and the required HLB for oils. Griffin stated that HLB values for emulsifier mixtures and required HLB values for oil mixtures were obtained by applying the additive property.

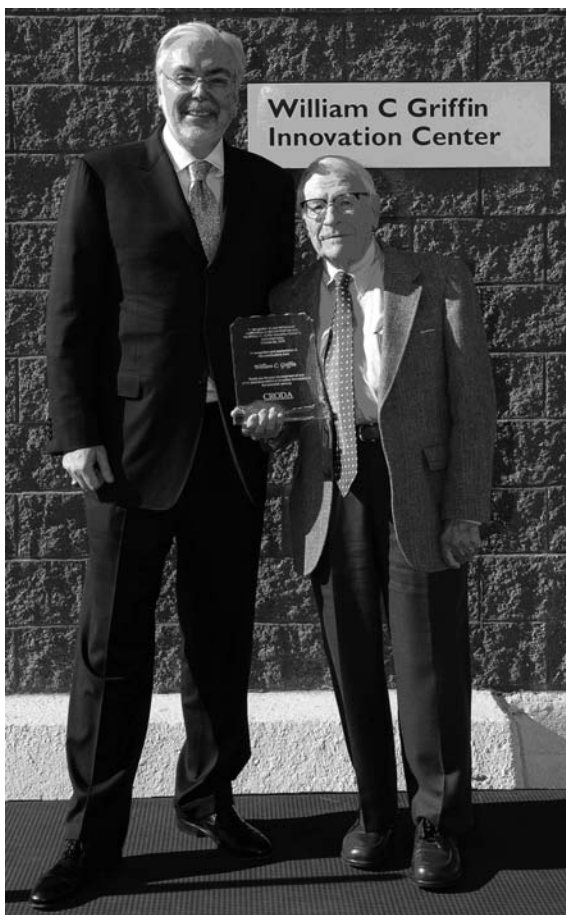In later publications, Griffin [3,4] proposed for-

Figure 1. William C.Griffin with the president of Croda Inc., USA, in the inauguration of the William C. Griffin Innovation Center.

pounds of sorbitol for every pound of mannitol. Our small laboratory group, fewer than a dozen, had the task to find these markets.

Sorbitol was hygroscopic and a possible alternate for glycerin in many products. The fatty acid derivatives of sorbitol were also possible alternates for glycerol monostearate and the like. At the end of World War II one of our staff, Rudolph Maximilian Goepp, was a part of the scientific group that traveled to Germany to assess their scientific efforts. When he returned he suggested that the sorbitan esters be reacted with ethylene oxide. When this was done, their properties changed from oil soluble esters to products dispersible in or eve soluble in water. Here was a true opportunity for new products that were non-ionic and not dependant upon ionic surfactants.

Since you could add one or five or twenty or fifty or more molecules of ethylene oxide to each ester you suddenly had an infinite number of products. We found that you could blend the

CLASSIFICATION OF SURFACE-ACTIVE AGENTS BY "HLB"†

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SINCE THE INTRODUCTION of the "HLB" system of classifying and selecting emulsifiers (6) numerous requests have been received concerning its derivation. The term "HLB" comes from the words hydrophile-lipophile balance. Emulsifiers consist of a molecule that combines both hydrophilic and lipophilic groups (or polar and nonpolar groups) and it is the balance of the size and strength of these two opposing groups that we call HLB.

Surface-active agents have been classified in many ways: including chemical types and according to ionization. Classification by HLB permits some prediction of behavior and reduces the amount of work involved in the selection of an emulsifier, wetting agent, or other type of agent.

Emulsifiers constitute one of the widest used subdivisions of surface-active agents and we will use this group as an illustration of the manipulation of the HLB system, with reference to other applications later.

A complete system for selecting an emulsifier would provide the *best* emulsifier to give the *desired form* of product for the desired *raw materials*. Thus, knowing the materials to be emulsified, the *most efficient* emulsifier could be chosen for the desired type of emulsion.

ACTION OF EMULSIFIERS

An emulsifier has two actions that are distinctly different. The accepted action is that of promoting the formation of an emulsion; making the emulsion easier to prepare; producing a finer particle size; and aiding the stability of the emulsion. The second action, which occurs along with the preparation of the emulsion, consists in controlling the type of emulsion that is to be formed, O/W or W/O. This second action appears to be a function of HLB.

In evolving a system for the selection of emulsifiers, we will first consider briefly the theory of emulsification. For practical purposes, an emulsion consists of two immiscible liquids, one being dispersed as a multitude of small particles in the

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Figure 2. Facimilar copy ot the article "Classification of surface-active agents by "HLB", by William C. Griffin, published in the Journal of the Society of Cosmetic Chemists, vol. 1, pp. 311-26.

mulas for the HLB value calculation that are satisfactory for non-ionic surfactants of various types. However, non-ionic surfactants containing propylene oxide, butylene oxide, nitrogen or sulphur, exhibit a behavior which has not been related to their composition. For these products, an experimental method must be used.

Greenwald *et al.* [5] proposed that the titration by water of a dioxane-benzene solution of an oil or a surface active agent to a cloud end point can be used to determine a value related to the hydrophile-lipophile balance character of the oil or surface active agent.

Moore & Bell [6] introduced the H/L numbers for non-ionic surfactants with polyoxyethylene. This number is defined as 100 by the quotient of the number of ethylene oxide units and the carbon atoms number of the lipophilic moiety. Like HLB value, a high value of H/L number indicates that the surfactant is hydrophilic.

In a study about the coalescence rates of emulsions, Davies [7] found that HLB values for surface active agents can be consistently calculated directly from the chemical formulae, using group numbers. For surfactants with polyoxyethylene as the sole hydrophilic moiety, the Davies scale differs substantially from the Griffin scale in the entire range of practical applications [8].

Robbers & Bhatia [9] developed a technique for the rapid determination of HLB and required-HLB values. In this method, a series of emulsions are prepared which cover the range of HLB values between two stocks emulsions. The desired amounts of each stock emulsion are weighed into a 15 mL graduated centrifuge tube to make a total of 10 g of mixed emulsion. Then, the tubes are centrifuged at 1500 rpm. The HLB value of the emulsifiers in the emulsion showing the least separation is taken to be equal to the required HLB value.

Chun & Martin [10] developed an interfacial tension method for the evaluation of HLB values of water soluble surface-active agents. One-tenth percent aqueous solutions of surfactant were overlayered with toluene and the interfacial tension were measured. A linear relationship resulted when the interfacial tension values were plotted again HLB values.

Huebner [11] developed a rapid method of determining relative polarity of surfactants. This method is based on a comparison of the retention times of methanol and n-hydrocarbons when a surfactant is used as the liquid phase in a gas-liquid chromatography column. Huebner defined the "polarity index", a parameter related to the hydrophile-lipophile properties of the surfactant tested. Based on the study of Huebner, Fineman[12] founded a linear relationship between polarity index and HLB value's of surfactants formed by ethylene oxide adducts.

Gorman & Hall [13] founded a linear relationship with the log dielectric constant of surfactants and its HLB values. These authors also founded a linear relationship with the log dielectric constant and required HLB of oils.

Becher & Birkmeier [14] determined HLB values by gas-liquid chromatography. The different retention times of two liquids, one being polar and the other non-polar, allows for the measurement of the HLB value of a surfactant or a mixture of surfactants, if used as a substrate, via gas-liquid chromatography.

The additivity of HLB values of non-ionic emulsifiers and required HLB of oils was evaluated experimentally by Ohba [15,16] and Becher & Birkmeier [14].

Shinoda [17] developed a phase inversion temperature (PIT) system for selecting an emulsifier and compared with the HLB-value system. The HLB value of a nonionic surfactant changes with the temperature and the inversion of an emulsion type occurs at which these two properties just balance.

Ben-Et & Tatarsky [18] determined HLB values for various commercial nonionic surfactants by means of high resolution NMR. The results obtained are in good agreement with given HLB values. The method is rapid, nondestructive and requires only small samples.

Little [19] proposed a mathematical relationship between solubility parameter and the HLB value, which was tested with anionic and non-ionic surfactants. This equation is not applicable for cationic surfactants.

Schott [20] compared the solubility parameters of various polyoxyethylated nonionic surfactants with their HLB values. The compounds included three homologous surfactant series based on dodecanol, octylphenol, and fatty acid esters of sorbitan, respectively, a polyoxyethylated sorbitol ester, and a polyethylene glycol. Solubility parameters were calculated by Schott from measured heats of vaporization for the polyoxyethylated dodecanol series and from molar attraction constants for all three surfactant series. When the solubility parameter was corrected for hydration by including a hydrogen-bonding component, plots of HLB versus this new solubility parameter were nearly linear and parallel for the three series of surfactants, with slopes of 5.0 ± 0.2. The three lines were spaced apart only 1.2 (cal/cm³)$^{1/2}$ despite structural differences among the surfactants, indicating that the chemical nature of the hydrocarbon moiety exerts only a limited effect on the solubility parameter.

In an interesting paper about the required hydrophilic-lipophilic balance for emulsification, Graciaa et al. [21] propose that the intrinsic stability or lack of stability of an emulsion depends on the HLB number of the emulsifier present in the interfacial regions separating oil from water. This HLB number is generally quite different from the value assigned to the emulsifier system blended with the oil and water to create the emulsion because some of the emulsifier molecules will tend to dissolve into the oil and water as well as be adsorbed at the interface. These authors proposed equations that permit to calculate the HLB number of the emulsifier present in the interfacial region. In this calculations, the authors used incorrectly molar fractions instead of mass (or weight) fractions to express the additively of the HLB values of the surfactant mixtures (adducts with different quantities of ethylene oxide, for example). Moreover, the Poisson equation that expressed the distribution of ethylene oxide in adducts is incorrectly used [22].

Pasquali et al. [23] obtained a correlation between the required HLB values and the solubility parameters of oils, a more precise correlation between the required HLB values and the dielectric constant, than the one obtained by other authors; and new values of the required HLB for o/w emulsions of solid fatty acids and alcohols from the values of the solubility parameters and dielectric constants, that could be more trustful than the ones obtained by the methodology based in emulsion stability studies. Pasquali et al. [24] obtained equations that permit to calculate the HLB value of polyoxyethylene esters from quality control data of the raw materials (fatty acids and polyethylene glycol) and the finished product (surfactant). These data are: acid value of the fatty acid, hydroxyl value of the polyethylene glycol and hydroxyl value of the surfactant. These calculations permit, moreover, to know the mean molecular masses of fatty acids, of polyethylene glycol, of monoester and diester, and the proportion of polyoxyethylene monoester and polyoxyethylene diester.

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