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HLB



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Alternative Concepts

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HLB – Sense or Nonsense?

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abstract

The Hydrophilic/Lipophilic Balance (HLB) concept as introduced by *Griffin* in 1949 means assigning a single number between 0 and 20 to fatty alcohol ethoxylates in order to describe their hydrophilicity/lipophilicity and assuming that this number is useful to predict the applicability as emulsifier. This approach has severe limitations as it ignores crucial parameters such as temperature, presence of the oil phase, pH, salt, or processing during emulsion manufacturing. However, despite these deficiencies, HLB values are still given today by the surfactant manufacturers in their brochures and product documentations. The only meaningful purpose of the HLB value is that it provides (especially in case it has been determined experimentally) a rough guesstimate of the water solubility or dispersability of an emulsifier. All other properties, often a consequence of the molecular architecture especially of polymeric emulsifiers, cannot be predicted by a single HLB value. This paper critically discusses the limitations of the HLB concept in order to avoid misconceptions, especially when dealing with non-fatty-alcohol-ethoxylate amphiphiles.

Introduction

For many years, the quest for HLB values of non-fatty-alcohol-ethoxylate surfactants is a nuisance to physical chemists, as long as they are well aware of the inherent deficiencies of the HLB concept. The original approach by *Griffin* [1] to assign a single number to a fatty alcohol ethoxylate in order to describe its hydrophilicity/lipophilicity and to assume that this number is useful to predict the applicability as emulsifier has severe limitations. It ignores not only crucial parameters such as temperature, presence of the oil phase and the type of oil, pH, salt, or processing during emulsion manufacturing, but also the molecular architecture of (polymeric) emulsifiers. Although these limitations are well-known to surfactant experts, why are HLB values still used today? The main reason seems to be a vicious circle: The customers of the surfactant suppliers are asking for HLB values because the surfactant manufacturers are providing them – most probably only because the customers are asking for them! Even the extensions of the HLB concept which were proposed in the last several decades, often in terms of other or more refined methods to generate HLB values, cannot solve the inherent problems. This is the reason why the CESIO Working Group “Test Methods of Surfactants” and the TEGEWA Working Group “Surface Active Substances” have decided to deal with the topic of HLB, since A) spreading the word about the deficiencies

of the HLB concept and B) discussing alternatives (see part 2 in *sofw journal* 12-2020 [2]) should be of interest to both the manufacturers and/or developers as well as the customers and/or formulators of surfactants.

History – *Griffin and Davies*

Based on theoretical considerations suitable emulsifiers should fulfill two requirements. First, they should have a proper balance between attraction for the water phase and attraction for the oil phase. This first requirement could be met by small molecules like simple alcohols (methanol, ethanol), but these do not meet the second requirement, which is the enrichment at the interface, leading to a reduction in interfacial tension. While the interfacial activity can be measured by determination of interfacial tension, the balance between polar and non-polar portions of a surface-active molecule is much less straight-forward to quantify. According to a rule of thumb in emulsion technology, known as *Bancroft's rule* [3], water-soluble emulsifiers tend to give o/w-emulsions and oil-soluble emulsifiers w/o-emulsions. The first attempt to extend this entirely qualitative rule into some kind of quantitative relationship has been undertaken by *Griffin* [1] at the Atlas Powder

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Company. They have published a systematic ranking of emulsifiers in 1948, based on evaluations of the type of emulsion (o/w vs. w/o) and their stabilities prepared from a series of oils and fatty alcohol ethoxylates as surface-active agents [4]. This experimental approach to generate these HLB numbers was pretty time-consuming – for each value as many as 75 emulsions had to be prepared by the following procedure: Shaking 95 ml of oil and 95 ml of water in the presence of 10 g of emulsifier and observing the result of this procedure after storage for 24 hrs. **Tab. 1** shows *Griffin's* HLB scale and its correlation with water dispersability and potential use of the amphiphiles. Later on, the HLB numbers for fatty alcohol ethoxylates were calculated as weight-% ethylene oxide in the molecule divided by 5 [5]. Using those calculated HLB numbers and performing emulsification tests, the required HLB for a specific oil phase was determined as guidance. Therefore, the HLB concept has helped to reduce random trial-and-error by a more systematic approach, eliminating a large number of otherwise failed emulsification attempts.

Since the calculation of HLB numbers by *Griffin* ($HLB = \text{wt\%EO}/5$) was basically only suitable for fatty alcohol ethoxylates, *Davies* [6] suggested to calculate HLB values by adding so-called group numbers assigned to the different hydrophilic (even ionic!) and lipophilic groups of the amphiphiles. It is hardly ever reported that the *Davies* scale differs substantially from the *Griffin* scale in the entire range of practical applications; unfortunately, for reported HLB values, it is typically not specified how the values have been derived and to which scale they refer to.

Alternative methods to generate HLB values

Experimental determination of HLB values has a chance to capture the influence of molecular architecture, which is not accounted for in case of the calculation methods by *Griffin* or *Davies*. Several approaches have been reported over the years. *Greenwald* [7] could find a reasonable correlation of the HLB numbers with solubility characteristics by titration of

the surfactant dissolved in e.g. 4% benzene in dioxane and titration with water, the end point being the appearance of a second phase. Other experimental methods to derive HLB values are based on interfacial tension between water and toluene [8], gas chromatography [9, 10, 11], dielectric constant [12], NMR [13], Relative Solubility Number (RSN; by titration) [14], or – as a rough guesstimate of HLB – simply the water solubility/dispersability, using the original classification by *Griffin* (**Tab. 1**).

Benefits of the HLB concept – Examples of success

In the typical B2B relation between the surfactant manufacturers and surfactant formulators, it is rarely the physicochemical specialists which are talking to each other. Therefore, it is obvious that a deep dive into different surfactant theories and concepts is rarely part of the negotiations between the salesperson of the surfactant supplier and the purchasing person of the customer. Intentionally developed as a guidance for emulsification, the HLB concept, however, can help even non-experts to categorize surfactants into defoamers, wetting agents, emulsifiers, detergents and solubilizers as depicted in **Tab. 1**. Although the HLB scale is only a rough guesstimate, it is due to its extreme simplicity and ubiquitous use in surfactant product brochures a highly appreciated tool that helps to preselect substitutes from different supplier portfolios. One successful example is the replacement of nonylphenol ethoxylates by environmentally more benign surfactants during the past decade. The next best alternative to a nonylphenol ethoxylate turned out to be in most cases an alcohol ethoxylate with a comparable molecular weight, cloud point and HLB value.

Limitations of the HLB concept – Examples of failure

Even in the preface of a monograph on HLB [15], it is explicitly stated that A) the applicability of the HLB system is often overestimated, and B) *Griffin's* and *Davies'* HLB numbers represent different hydrophilicity scales – but this aspect often seems to get ignored. In the scientific literature, there are several examples demonstrating the deficiencies of the HLB system, e.g. *Balson* gives a number of surfactants with either the same HLB numbers but different phys.-chem. properties or vice versa [16]. He concludes that “HLB remains a scientific curiosity rather than a useful concept”. *Griffin* himself has given oleic acid (used as oil phase!) an HLB value of 1, whereas to sodium oleate he assigned a value of 18. This shows that a single number characterizing a molecule without specifying the conditions such as pH is just not helpful to predict interfacial behavior. Often, the type of emulsion formed is significantly influenced by the process of emulsification; therefore, not even the unambiguous prediction whether an emulsifier is suitable for o/w- or for w/o-emulsions is possible. Moreover, in case of polymeric emulsifiers,

HLB	Dispersability in water	Suitable as
1-4	nil	defoamer
3-6	poor	w/o emulsifier
6-8	milky dispersion upon agitation	wetting agent
8-10	stable milky dispersion	wetting agent o/w emulsifier
10-13	translucent	o/w emulsifier
13-20	clear solution	o/w emulsifier solubilizer detergent

Tab. 1 HLB values, water solubility and potential uses of surfactants.

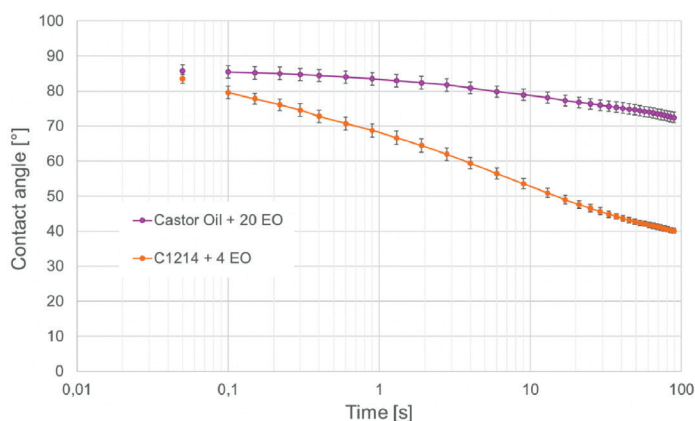


Fig. 1 Contact angle of a 0.1% aqueous solutions of castor oil ethoxylate and a fatty alcohol ethoxylate having the same HLB value of 10 (according to Griffin) on Parafilm (DataPhysics OCA50, 25°C, 50% rel. humidity, droplet volume 3.7 μL ; average of at least 8 droplets).

molecular architecture rather than overall chemical composition determines the interfacial properties, which makes the assignment of a calculated HLB number – independent of the molecule's amphiphilicity – nothing but useless. For example: A random EO/PO-copolymer is not amphiphilic, whereas a corresponding block copolymer, consisting of the very same number of EO and PO units, is known to have emulsifying properties.

Especially for polymeric amphiphiles, the calculated HLB value neglects the effect of molecular size and surfactant architecture. Many technical processes have characteristic times in the order of (milli-)seconds and are dominated by diffusion and/or adsorption kinetics. Diffusion of surfactants towards a surface or interface is directly affected by the size (i.e. hydrodynamic radius) and consequently molecular weight of the surfactants. Differences in diffusion/adsorption kinetics are directly reflected in the application performance of the surfactant. In the following, three examples are shown in which surfactants of identical calculated HLB value, but different molecular structures behave quite differently.

Surfactants with an HLB value between 6 and 10 are categorized as wetting agents according to Griffin's concept. The wetting behavior on Parafilm of solutions of a castor oil ethoxylate with 20 moles of EO and a C12-14 alcohol with 4 moles of EO has been compared (**Fig. 1**). Both surfactants possess a calculated HLB value of 10, but differ significantly in their molecular weight (MW). The much higher MW castor oil ethoxylate performs significantly poorer as compared to the lower MW fatty alcohol ethoxylate. This is not too surprising, since "speed" is known to be crucial for wetting processes. The second example concerns the cloud point of nonionic surfactants [17]: Clear surfactant solutions turn turbid above the cloud point, because the system then forms a surfactant-rich phase dispersed in a surfactant-poor phase. The reason is that the H-bonds, which keep the ethoxylates in solution, break up at elevated temperatures. Above the cloud point, nonionic surfactants cannot really be used any more

for solubilizing or emulsifying purposes, but they can act now as antifoaming agents [18]. Therefore, the cloud point is a pretty good measure of the suitability of a fatty alcohol alkoxy-late for certain applications, and it takes into account one of the most important features of nonionic surfactants, their temperature dependent solubility. Generally speaking, there is some correlation between cloud point and HLB [2]: Hydrophilic, highly ethoxylated, water-soluble ethoxylates have an HLB >10 (Griffin) and a high cloud point, whereas more hydrophobic ethoxylates with an HLB <10 (Griffin) have a cloud point below room temperature. However, there is no strong correlation between calculated HLB and cloud point, as shown in the following example C12-14EO9 vs. i-C13EO9. These two alcohol ethoxylates have identical hydrophilic headgroups (9 EO); there are only

differences in the structure of their hydrophobic tail: either linear C12/C14 with on average of 12.7 methylene groups, or branched i-C13. Both of these nonionic surfactants have the same HLB value, whether calculated according to Griffin (13.7) or to Davies (5.7). However, their cloud points are quite different (**Fig. 2**). Therefore, HLB can hardly be used to predict the application performance of these products.

The third example shows the effect of order of addition of EO and PO onto a C18 alcohol; in a simplified oil/water system, based on a semisynthetic metalworking formulation, the emulsifier efficiency (i.e. the minimum mass fraction $\bar{\gamma}$ of emulsifier needed to form a one-phase microemulsion, for details see [2]) of C18+6PO+6EO is considerably higher as compared to C18+6EO+6PO, although both emulsifiers have the identical calculated HLB values.

Conclusion

The original approach by Griffin of introducing the HLB concept to reduce the number of emulsification trials did make

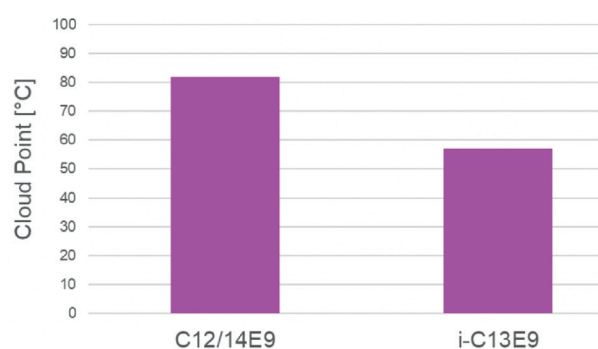


Fig. 2 Cloud points of two alcohol ethoxylates of identical calculated HLB.

sense – but it seems like over the decades the original idea got lost and the HLB number has been taken more seriously than intended originally. The HLB values reflect the result obtained when shaking – at room temperature – equal amounts of water and oil, using a fixed amount of emulsifier. All other extensions to derive either “more precise” HLB values or develop other – less laborious – methods to generate HLB values still suffer from this limitation. Moreover: Calculating HLB values for some modern PEG-free emulsifiers makes even less sense than for the ethoxylates it has been developed for. However, if the formulators would like to get an idea about the dispersability of an emulsifier in water, the HLB value can be used as an indication – especially if it has been determined experimentally. *Steven Abbott* states in his textbook [20] that HLB should be banned, because the concept was not only useless, but has caused huge damage because it has stood in the way of a much better systems. It should be clear that such alternative, better methods should consider parameters such as the type of oil, salt and pH; therefore, these alternatives have to be more complex than a single universal number assigned to an emulsifier alone. An introduction into two of these alternative concepts will be the topic in sofww journal 12-2020 [2].

Remark

This paper is a joint effort of the members of the CESIO Working Group “Test Methods of Surfactants” and the TEGEWA Working Group “Surface Active Substances”: *Roland Borner* (Chemische Fabrik Schärer&Schläpfer AG), *Wolfgang Brennich* (Zschimmer&Schwarz GmbH&Co KG), *Karsten Holtin* (Kolb Distribution Ltd.), *Carmen Pey* (Kao Corporation S.A.), *Arjan Gelissen* and *Renke Rommerskirchen* (Sasol Germany GmbH), *Natascha Schelero* (Clariant Produkte (Deutschland) GmbH), *Kati Schmidt* (BASF SE), *Louis Schwarzmayr* (Nouryon Surface Chemistry AB), *Michael Stappels* (Kao Chemicals GmbH) and *Joachim Venzmer* (Evonik

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Component	Formulation I [g]	Formulation II [g]	$\tilde{\gamma}$
Oil phase	33	33	
Water phase	55	55	
Emulsifier C18+6PO+6EO	3		0.03
Emulsifier C18+6EO+6PO		7.8	0.08

Tab. 2 Comparison of emulsifier efficiency $\tilde{\gamma}$ in an oil/water system with emulsifiers of same calculated HLB, but different molecular architecture (C18PO6EO6 vs. C18EO6PO6). $\tilde{\gamma}$ is defined as the minimal mass fraction of surfactant $\tilde{\gamma} = m_{\text{surfactant}} / (m_{\text{oil}} + m_{\text{water}} + m_{\text{surfactant}})$ which is necessary to form a one-phase microemulsion (see [2]).

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HLB – Alternative Concepts

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abstract

Alternative classification concepts of emulsifiers have to cope with HLB’s main flaw, which is assigning a single, “universal”, calculated number to an emulsifier, as discussed in our previous paper. For emulsions, the influence of the oil phase needs to be considered as well as temperature, pH or salinity. Both alternatives to HLB discussed here make use of a thermodynamic equilibrium state as a reference – in case of oil/water/surfactant this means a microemulsion. The Hydrophilic-Lipophilic Deviation (HLD) describes the deviation of an entire formulation of water, oil, and a surfactant from the optimum, balanced reference state. From this the characteristic curvature (Cc) of surfactants can be determined, which is a number that describes their hydrophilicity or hydrophobicity. In contrast, the PIT-slope method characterizes the hydrophilicity/hydrophobicity of a surfactant in relation to C10E4 in an octane/water system; therefore, it is also able to capture all effects of molecular structure of the surfactant.

Introduction

The limitations of the classic Hydrophilic/Lipophilic Balance (HLB) concept have been discussed in our preceding paper [1]. Alternative, and better approaches should consider important but neglected parameters such as temperature, pH, salinity, as well as the presence and type of the oil phase. Moreover, especially for polymeric surfactants, molecular architecture is ignored by HLB but is crucial for determining the interfacial behavior. It is obvious that all these influences cannot be reflected by a single calculated HLB value assigned to a surfactant alone. As a consequence, the alternative concepts have to be more complex, unfortunately.

The main motivation to classify an amphiphile – apart from a rough guesstimate of its dispersability in water – is often the selection of an emulsifier for a specific task. Depending on the application, there are more criteria than just emulsion stability in terms of prevention of water or oil separation. For cosmetic creams and lotions, for example, the stability criteria are much more challenging, e.g. the viscosity should not change during long-term (6 months?) storage at elevated temperatures (e.g. 40°C) and several freeze/thaw cycles. In addition, there are also other criteria for emulsifier selection beyond stability, such as the chemical basis (e.g. PEG-free, biobased) or certifications (e.g. COSMOS, Ecocert), and – last but not least – the sensory (i.e. skin feel) properties of the emulsions.

For many industrial uses, however, e.g. oil and gas recovery, agrochemicals or metal-working fluids, the focus is on emulsification and/or emulsion stability. For such applications, alternatives to the HLB concept have been developed to predict emulsifier performance. In this paper, two of the

more successful alternative approaches will be discussed: HLD (Hydrophilic-Lipophilic Deviation) and PIT (Phase Inversion Temperature)-slope. Both are useful because besides the surfactant characteristics also salinity, application temperature, oil characteristics and co-solvent (e.g. alcohol) addition are taken into account. In order to discuss and understand both the HLD and the PIT-slope concept, some fundamental knowledge about the phase behavior of surfactant/oil/water systems and the formation of microemulsions is required.

Basics – Emulsions and Microemulsions

Most formulations containing oil, water and emulsifier are emulsions. One of their inherent features is that they are only kinetically stable – sooner or later, water and oil will separate. In contrast, there are thermodynamically stable mixtures called microemulsions, which are neither emulsions nor contain droplets in the µm range. The main differences between (macro-) emulsions and microemulsions are summarized in **Tab. 1**.

	(Macro-)Emulsion	Microemulsion
Appearance	milky	clear
Stability	only kinetically stable	thermodynamically stable
Formation	by applying (high) shear forces	spontaneously
Droplet size	>0.5 µm	1–100 nm [2]
Interfacial tension	1–5 mN/m	10 ⁻² –10 ⁻⁴ mN/m
Emulsifier content	1–3%	3–35% (for Winsor IV)

Tab.1 General differences between (macro-)emulsions and microemulsions [3].

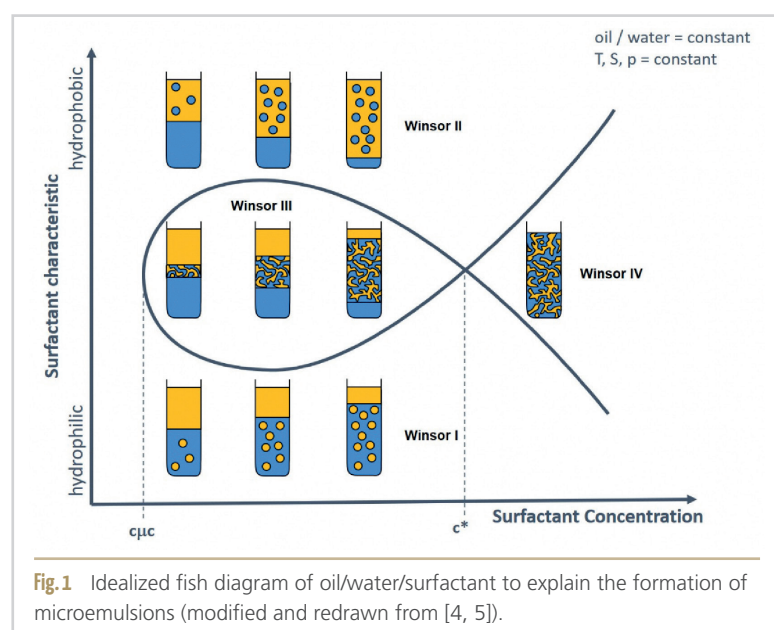
According to the scientific definition, microemulsions are macroscopically homogeneous, nanostructured, and thermodynamically stable mixtures of at least three components, i.e. oil, water, and surfactant. While emulsions look milky because of the presence of droplets in the range of the wavelength of light or larger, microemulsions appear clear because the droplets/structures are in the nm range. Common emulsions are obtained by applying high shear forces to create finely dispersed droplets in the μm range. In contrast, a microemulsion forms spontaneously. This only works if the interfacial tension is extremely low – several orders of magnitude lower than in the case of emulsions. To achieve this, the coverage of the oil/water interface with surfactant must be somewhat ideal. Extremely small droplets mean an extremely large interfacial area which has to be occupied by the surfactant. Thus, a larger amount of surfactant is required for a microemulsion. For a given surfactant, several external factors influence the phase behavior. Besides temperature and the salinity of the water phase, these can be the nature of the oil, pH, presence of co-surfactant, or the ratio of the water and oil phase in the mixture, amongst others. The formation of microemulsions and their relation to emulsions can best be explained by using the so-called fish diagram (Fig. 1). Hence, the phase behavior is illustrated in a system with a given ratio of oil to water and increasing surfactant concentration (x-axis). For phase behavior studies, easily accessible experimental parameters such as temperature or salinity are usually being used. However, in industrial uses most of the external parameters are set by the application itself and a surfactant structure is sought that fulfills the requirements at these pre-defined conditions. Therefore, in Fig. 1 the hydrophilicity/hydrophobicity of the surfactants is used as the tuning parameter on the y-axis, which is determined by the length and branching of its hydrocarbon backbone and the type and structure of its hydrophilic headgroup. A more hydrophilic surfactant prefers the water phase and thereby forms an oil-in-water (o/w) droplet microemulsion

which coexists with an oil excess phase (Winsor I). Here, the interfacial surfactant film is bent around the oil and the curvature is by definition positive. Analogously, a more hydrophobic surfactant has a higher tendency to dissolve in the oil phase and thereby leads to a water-in-oil (w/o) droplet microemulsion which coexists with an excess water phase (Winsor II). The interfacial surfactant film is now bent around the water and the curvature is by definition negative.

If the surfactant's hydrophilicity/hydrophobicity ratio is properly chosen and balanced, a three-phase region (Winsor III) develops in which a microemulsion middle phase coexists with both a water and an oil excess phase. At this point the interfacial tension between oil and water has a distinct minimum. The middle phase comprises a bicontinuous structure where water and oil domains are separated by the interfacial surfactant film. Thereby it is bent around both water and oil domains, resulting in a mean curvature of zero. With increasing surfactant concentration, the excess phases get smaller, until at a concentration c^* both excess phases are completely solubilized and a single-phase microemulsion (Winsor IV) is obtained. The corresponding temperature and salinity, at which the surfactant's hydrophilicity and -phobicity is balanced, are the so-called optimum conditions T^* and S^* of the surfactant. They are characteristic for each surfactant in a given environment.

In this paper we could only briefly touch the basics in microemulsion science (for further details see [6, 7, 8, 9]) to introduce the curvature of the surfactant film in microemulsions, which is the crux of both alternative concepts discussed in the following.

Physicochemically speaking, conventional (i.e. macro-)emulsions are comparably easy to understand: They are being obtained by stirring a Winsor I or II system, i.e. dispersing the excess oil or water phase, respectively, in the continuous phase. By adding thickener or using emulsifiers which effectively prevent coalescence of the droplets, phase separation back to the Winsor I or II situation can be avoided or at least slowed down sufficiently.



HLD

Formulators often need to identify the surfactant with the lowest interfacial tension for a given system. This requires a careful balance between surfactant/oil and surfactant/water interactions. Hence, a surfactant structure should be chosen whose optimum conditions match the application parameters e.g. in terms of choice of oil, application temperature, water salinity. In some cases, co-surfactant or co-oil may be required. The HLD concept helps to narrow down the surfactant selection and reduce the experimental work significantly.

In their work on enhanced oil recovery in the 1970s, *Salager et al.* [10] published quantitative correlations between all necessary formulation pa-

rameters which were neglected by the HLB approach. Later on, the Hydrophilic-Lipophilic Deviation (HLD) theory has been simplified by Acosta [11, 12]. It quantifies the difference to the optimum conditions (balanced Winsor III microemulsion; $HLD = 0$), as a reference:

$$HLD = Cc - k \cdot EACN - \alpha \cdot T + f(S) + f(A)$$

with:

- Cc : Characteristic curvature; characterizes the surfactant and reflects its hydrophilicity/hydrophobicity [13, 14]
- k : Scaling factor; characteristic for the surfactant headgroup
- $EACN$: Equivalent Alkane Carbon Number; characterizes the oil. For alkanes, the EACN equals the number of carbons (Alkane Carbon Number (ACN)). The EACN of other non-linear or unsaturated oil components and of mixtures is equal to the ACN of that n-alkane which exhibits identical optimum conditions for the given environment [15, 16], e.g. for benzene $EACN = 0$, for toluene $EACN = 1$, and for some more polar oils it can even be negative
- α : Scaling factor for temperature dependency; anionic surfactants $\alpha=0.01$; typical ethoxylates $\alpha=-0.06$; APGs (alkyl polyglucosides) $\alpha=0$
- ΔT : Difference between the temperature T of the system and the reference temperature $T_{ref}=25^\circ C$
- $f(S)$: Function of salinity S (in g NaCl/100 mL)
 - nonionic surfactants: $f(S) = b \cdot S$; b : constant; characteristic of salt type, e.g. $b = 0.13$ for NaCl, $b = 0.1$ for $CaCl_2$, ...
 - ionic surfactants: $f(S) = \ln(S)$
- $f(A)$: Function for alcohol as cosurfactant

The crucial parameters to characterize and rank surfactants are Cc and k . The Cc value can range from negative for hydrophilic surfactants (normal micelles) to positive for hydrophobic surfactants (reverse micelles). Cc together with k can be derived from phase behavior studies; k is the slope of the graphs of optimum salinity as a function of oil characteristic (EACN), Cc is the intersection with the y-axis (see Fig. 2). The Cc values for many surfactants and surfactant mixtures were investigated for various systems [17]. In further refinement the HLD concept was also applied to extended surfactants and biosurfactants such as rhamnolipids [18, 19, 20]. Hammond and Acosta were able to identify value contributions of different functional groups to the characteristic curvature of the surfactants and thereby exemplarily demonstrated the use of the HLD concept as a guideline for surfactant selection for microemulsion formulations used in various applications such as detergency, hard surface cleaning, drug delivery, and oil and gas recovery [21].

It is clear that this concept also uses approximations and assumptions. However, the theoretical concept, including these approximations, is broadly accepted and used in both academia and specialized industrial applications. Despite its superior surfactant performance prediction in comparison with the HLB concept, the HLD concept did not lead to a general classification of surfactants using the Cc parameter as an improved HLB value. One reason might be that the tempera-

ture-dependent evaluation of a system containing oil, water, salt, surfactant and co-surfactant is challenging and the interplay between these parameters is not easy to explain to a non-expert in the field. The HLD concept has been designed to identify an optimal formulation and is focused on (micro-) emulsification; a simple and pragmatic categorization of surfactants in defoamers, wetting agents and detergents, for which HLB-values are being used, has never been the aim of the HLD concept.

But why should those who are interested in formulating (macro-)emulsions (rather than microemulsions) care about HLD? Since HLD is a property not of an emulsifier but of an entire emulsion system (Cc , $EACN$, T , S), it is possible to predict a suitable HLD value for creating a stable emulsion. A good starting point for a formulator would be $HLD=-1$ for o/w and $HLD=1$ for w/o. A balanced formulation ($HLD=0$) should be avoided, because a minimum in interfacial tension is just the opposite of what is required to prevent coalescence of colliding drops [22].

PIT-slope

Similar to HLD, this concept is related to the “balanced” state of a microemulsion. Here, the reference formulation is 3% C10E4 in a 1:1 mixture of n-octane and water (containing 10 mM NaCl), which has a three-phase area (Winsor III) in a range between 22 and 29°C. Upon stirring, the transition from an o/w- to a w/o-emulsion happens at 24.8°C, the so-called Phase Inversion Temperature (PIT), as determined by conductometry. The PIT-slope [23] method now monitors the evolution of the PIT of this well-defined reference system as a function of increasing amounts of an additional second surfactant S2. The linear change of the PIT with addition of S2 gives a surfactant characteristic slope, which is used as a simple classification of surfactants in relation to C10E4. Positive and negative values correspond to more or less hydrophilic surfactants compared to C10E4, respectively. The experiment is simple to conduct with both ionic and nonionic surfactants

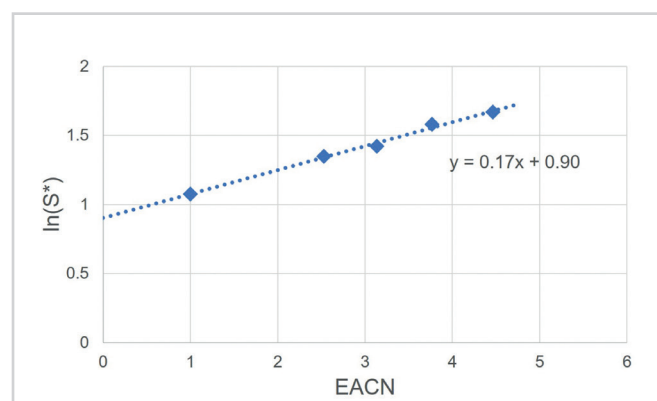


Fig. 2 Optimum salinity of di-hexyl sulfosuccinate sodium salt with varying EACN at 25°C. The parameters k and Cc are derived from the linear fit ($k = 0.17$; $Cc = 0.90$).

and captures the most important deficit of the HLB-concept: the temperature sensitivity of a surfactant. The effects of molecular architecture and characteristics of the hydrophobic tail in terms of unsaturation, branching, or alkyl chain distribution on the interfacial properties of the surfactant are also accounted for. One drawback might be that for very hydrophilic or hydrophobic surfactants the result of the PIT-slope might be biased, because these surfactants mainly partition with the water phase or oil phase, respectively, and not at the interface. As a consequence, the PIT-slope will be closer to 0 and the hydrophilicity (hydrophobicity) is underestimated.

Conclusion

Alternative classification concepts of emulsifiers have to avoid HLB's main flaw of assigning a single, "universal", calculated number to an emulsifier; they rather have to include the influence of the oil phase as well as temperature, pH or salinity. Both alternatives to HLB discussed here make use of a thermodynamic equilibrium state as a reference – in case of oil/water/surfactant this means a microemulsion.

- The Hydrophilic-Lipophilic Deviation (HLD) describes the deviation of an entire system from its optimum, balanced reference state and delivers C_c and k parameters as characteristic numbers of a surfactant.
- The PIT-slope method characterizes the hydrophilicity/hydrophobicity of a surfactant in relation to C10E4 in an octane/water system and therefore is also able to capture all effects of molecular structure of the surfactant.

However, using these concepts in the development of emulsion formulations is rather challenging. Alternatively, a good starting point might be the guideline formulations of the surfactant manufacturers.

Remark

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