Three-Dimensional HLB

This revolutionary development helps formulators choose surfactants for stable oil, water and silicone emulsions

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Today, silicone-soluble materials are an important aspect of emulsion technology. A growing number of silicone-based surfactants contain no hydrocarbon-based hydrophobes.[a] Other silicone-containing surfactants also contain hydrocarbon groups.

The development of the HLB — hydrophile/lipophile balance — system almost 50 years ago both simplified and systematized the selection of the optimal surface-active agent for a specific emulsification application. The system, proposed by Griffin[1] and widely promoted by ICI,[2] has provided formulators very valuable assistance over the years. Despite that, our ability to predict the performance of specific emulsifiers in the preparation of stable emulsions remains a formulating challenge.

Formulators truly need an expansion of the traditional HLB concept that will work with these new surfactants and anhydrous systems. We have developed a system that gives formulators a powerful tool to help them make stable emulsions using combinations of water-, silicone- and/or hydrocarbon-soluble ingredients.

Adding Dimension to HLB

The current HLB system has helped predict the emulsifiers needed for water-in-oil (w/o) and oil-in-water (o/w) emulsions. However, it has predicted the performance of silicone-based molecules less well and fails completely for those surfactants having silicone, hydrocarbon and polyoxyalkylene portions. Any attempt to expand the current HLB system must be able to assign meaningful values to the surfactants that contain all three of these chemical entities, since each is insoluble in the others.

This mutual insolubility led us to design an HLB system that would consider oil, water and silicone solubilities to determine the emulsion properties of surfactants. Because of the three solubility parameters we consider, we call our system "3D-HLB."

Our first efforts to build a new HLB model attempted to use a cube with x, y and z coordinates. However, such a system is conceptually difficult and the mathematics are not easy to handle. Fortunately, experimental data solved our problem. As we worked with selected compounds, some of which appear in Table 1-4, we found that a much less complex system would work.

Because the standard HLB system has proven helpful

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[a] We will use the generic term "hydrocarbon" to designate the oil-soluble portion of the molecule; this generic term encompasses the more specific terms "fatty," "lipid" and "alkyl."

Pour surmonter les faiblesses du système HLB traditionnel dans le choix des surfactants pour des émulsions contenant des silicones, les auteurs développent un système élargi. Leur système HLB 3D aide à déterminer les surfactants appropriés pour préparar des émulsions stables utilisant toute combinaison des phases huile, silicone et eau.

Um Schwächen des traditionellen HLB-Systems bei der Auswahl von Tenside für Emulsionen mit Silikonen zu umgehen, entwickeln die Autoren ein erweitertes System. Ihr 3D-HLB System unterstützt das Auffinden von geeigneten Tensiden zur Bildung stabiler Emulsionen bei Verwendung jeglicher öl-, Wasser- und Silikon-Phasen.

Para evitar los puntos difíciles del tradicional sistema HLB para seleccionar tensioactivos que contienen siliconas, los autores desarrollan un sistema más amplio. Sus sistema 3D HLB permite determinar los tensioactivos para emulsiones estables usando cualquier combinación de fases de aceite, agua y silicona.

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The Original HLB System

The HLB system was originally developed for ethoxylated products and, in fact, predicts emulsification properties best for alcohol ethoxylates — surfactants based on fatty alcohols modified by reaction with ethylene oxide (Figure 2-1). The system is also designed for emulsions containing water.

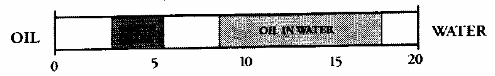

Figure 2-1. Traditional HLB scale

The current HLB system envisions two basic types of emulsions: oil-in-water (o/w) and water-in-oil (w/o). The phase listed first is the discontinuous phase, the phase that is emulsified into the other, continuous phase.

Bancroft postulated that the emulsifier forms a third phase, a film at the interface between the two phases being mixed together.[3] He also predicted that the phase in which the emulsifier is most soluble will become the continuous phase. The continuous phase need be the larger one; emulsions exist in which the discontinuous phase makes up a greater weight percent. A simple test: if the emulsion is readily diluted with water, water forms the continuous phase.

Calculation of HLB

The original system compares the ratio of the oil- to the water-soluble portions of a surfactant molecule. Table 2-1 lists some approximate HLB values for surfactants as a function of their solubility in water. Values assigned based on that table form a one-dimensional scale, ranging from 0 to 20.

Table 2-1. Some approximations for the HLB value for surfactants as a function of their solubility in water

Solubility in water	*HLB*	*Description*
Insoluble	4 - 6	water in oil emulsifiers
Poorly dispersible (milky appearance)	7 - 9	wetting agents
Translucent to clear	13 - 15	detergents
Very soluble	8 - 18	oil in water emulsifiers

In Adamson's *Physical Chemistry of Surfaces*, this statement appears:"The HLB system has made it possible to organize a great deal of rather messy information and to plan fairly efficient systematic approaches to optimize emulsion preparation. If one pursues the concept too far, however, the system tends to lose itself to complexities."[4] We agree with this and believe that a system that helps formulators select an emulsifier is of primary importance. A mathematical model that has been developed allows calculated approximations of HLB.

The HLB system, in its most basic form, calculates HLB using the following formulation:

$$\text{HLB} = \frac{\%\ \text{Hydrophile by weight of molecule}}{5}$$

For instance, oleyl alcohol (5 EO), with a total MW of 489 and a hydrophile MW of (5)(44) = 220, is 45.0% hydrophile. Dividing that by 5, we get 9.0 for the HLB of oleyl alcohol.

Using such calculations, formulators can predict the approximate HLB needed to emulsify a given material and make more intelligent estimates of which surfactant or combination of surfactants are appropriate to a given application (Table 2-2). When blends are used, the HLB can be estimated by using a weighted average of the HLBs of surfactants used in the blend. For materials not listed on Table 2-2, formulators should test the oil using specific blends of known emulsifiers to calculate the HLB needed to emulsify it.

Table 2-2. HLBs needed to emulsify some common cosmetic materials[2]

Acetophenone	14	Lanolin	12
Beeswax	9	Lauric acid	16
Benzene	15	Lauryl amine	12
Butyl Stearate	11	Mineral spirits	10
Carbon Tetrachloride	16	Nonylphenol	14
Castor oil	14	Oleic acid	17
Chlorobenzene	13	Orthodichlorobenzene	13
Chloronated paraffin	8	Petrolatum	7
Cottonseed oil	6	Pine oil	16
Cyclohexane	15	Toluene	15
Kerosene	14	Xylene	14

The appearance of the resultant emulsion depends on the particle size of the discontinuous phase (Table 2-3).

Table 2-3. Emulsion appearance related to particle size

Particle size (nm)	*Appearance*
> 1	White
0.1 -1.0	Blue-white
0.05 - 0.1	Translucent
< 0.05	Transparent

and is widely recognized, we wanted our new system to expand on the existing one. We kept the 0-20 scale used by the standard HLB.

We discovered that we actually needed to calculate only two values, the weight-percentages of the water- and oil-soluble segments for the surfactant in question. Subtracting the sum of those from 100%, we get the % silicone-soluble. The standard HLB uses the calculation of % hydrophile/5; in fact, the standard HLB is the hypotenuse of our new system (Figure 1-1). Molecules with no silicone component will fall on that line.

The three sides making up our 3D-HLB triangle represent the three possible pairs of component types: oil/water, silicone/water and oil/silicone. We originally thought that

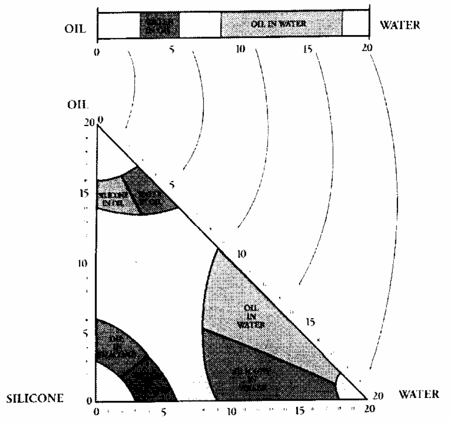

Figure 1-1. 3D-HLB: We calculate the x and y coordinates within our system (Table 1-1). Essentially, the silicone HLB becomes the difference between the x and y values. The corners of the graph are defined by the reference materials shown in Table 1-2.

Table 1-1. Calculation of coordinates for 3D-HLB

	% Water sol./5 (x coordinate)	*% Oil sol./5 (y coordinate)*
Standard hydrocarbon surfactant (standard HLB, on oil/water line)	50%/5 = 10.0	50%/5 = 10.0
Standard silicone surfactant (on silicone/water line)	50%/5 = 10.0	0%/5 = 0.0
Combination surfactant (three-dimensional)	30%/5 = 6.0	20%/5 = 4.0

Table 1-2. Materials defining the 100% soluble states for water, hydrocarbons and silicones.

Material	*x*	*y*	*x,y*
Mineral oil	0/5	100/5	0,20
Silicone oil	0/5	0/5	0,0
PEG 600	100/5	0/5	20,0

the triangle would be equilateral. However, experimental data generated values best accommodated by the right triangle that we propose. You can clearly see that the hypotenuse, representing the standard HLB and connecting the 100% oil-and water-soluble loci, is longer than the other two sides. This difference in length seemed unsettling at first. However, silicone and hydrocarbon compounds are not equally hydrophobic at equal weight-percents. As we worked with the new system, we realized that this inequity explains why the standard HLB does not give useful values for silicone surfactants.

As we said before, the standard, water/hydrocarbon HLB line forms the hypotenuse. It connects the points for 100% oil-soluble (20,0) and 100% water-soluble (0,20) substances. All points on this line represent materials with no silicone portion; traditional surfactants fall on this line.

The silicone HLB line on the bottom of the triangle connects points for 100% silicone-soluble (0,0) and 100%

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Silicone Surfactants

Ethoxylated silicone surfactants: In recent years, ethoxylated silicone surfactants have found a greater acceptance in emulsion preparation. Direct application of the HLB concept to these materials generate only an approximate value. Many manufacturers of silicone surfactants, rather than dealing with the differences between calculated and observed silicone HLBs, have stopped providing specific values and adopted the use of such nebulous terms as "high," "middle" or "low" to classify silicone HLB values. This approach simply begs the issue.

Blends: Most formulations that use silicone-based surfactants also have traditional hydrocarbon surfactants present. These blended systems present a challenge for formulators trying to predict emulsification properties. A recent paper dealing with the difficulties in predicting the behavior of silicone-based surfactants used with hydrocarbon surfactants concluded that, even when using silicone compounds of low molecular weight, there is "varying non-ideal behavior" depending on the type and concentration of the surfactants used.[5] This conclusion, while supported by the data, does not help the formulator.

Mixed silicone/hydrocarbon surfactants: To further complicate the situation, the market has experienced a virtual explosion of new silicone compounds (Table 3-1). These combine water-soluble polyoxyethylene, silicone and oil-soluble hydrocarbon components into one molecule. The introduction of these molecules and our inability to fit them into the classical HLB concept has resulted in confusion on how to use the new compounds.

Table 3-1. Comparison of fatty and silicone derivatives

Hydrocarbon-Based	*Silicone-Based*
Anionics	
Phosphate esters	Silicone phosphate esters
Sulfates	Silicone sulfates
Carboxylates	Silicone carboxylates
Sulfosuccinates	Silicone sulfosuccinates
Cationics	
Alkyl quats	Silicone alkyl quats
Amido quats	Silicone amido quats
Imidazoline quats	Silicone imidazoline quats
Amphoterics	
Amino proprionates	Silicone amphoterics
Betaines	Silicone betaines
Phosphobetaines	Silicone phosphobetaines
Nonionics	
Alcohol alkoxylates	Dimethicone copolyol
Alkanolamides	Silicone alkanolamides
Esters	Silicone esters
Taurine derivatives	Silicone taurine
Isethionates	Silicone isethionate
Free-Radical Polymers	
PVPquats	Silicone free-radical quats
Polyacrylates	Silicone/polyacrylate copolymers
Polyacrylamides	Silicone/polyacrylamide copolymers
Polysulfonic acids	Silicone/polysulfonic acid copolymers

water-soluble (0,20) substances. All points on this line represent molecules or mixtures with no hydrocarbon portion. Traditional dimethicone copolyol compounds fall on this line.

The vertical, oil HLB line connects points for 100% silicone-soluble (0,0) and 100% oil-soluble (20,0) substances. This last line predicts an interesting possibility not previously considered, emulsifying silicone and hydrocarbon oils as anhydrous products. While this clearly makes sense now, we had not originally contemplated such an emulsion definition.

With a triangular system, if one of the three groups is missing from the surfactant molecule or mixture, the calculation produces a point on one of the exterior lines. And, because no system can have less than 0% of an element or more than 100% of the other two, no points will fall outside the triangle.

As one of the three paired component scales represents the standard HLB line, we adopted its 0-to-20 scale for all three sides. As we worked with the system, we clearly saw that predictions of the system qualitatively matched the compounds available. In addition, the system suggests new compounds to synthesize.

Experimental Confirmation

The 3D-HLB system predicts six types of emulsions, so we set up test formulas for each type (Formulas A-F). We evaluated

Formulas A through F. Test emulsions

	A *s/w*	*B* *o/w*	*C* *w/s*	*D* *w/o*	*E* *o/s*	*F* *s/o*
Silicone oil (350 visc)	15.0%	-	80.0%	-	80.0%	15.0%
Mineral oil	-	15.0%	-	80.0	15.0	80.0
Test surfactant	5.0	5.0	5.0	5.0	5.0	5.0
Water	80.0	80.0	15.0	15.0	-	-

Procedure: We added the test surfactant to the internal (discontinuous) phase under good agitation for 5 minutes. We then slowly added the continuous phase.

Table 1-3. Predicted values for test compounds

Compound Tested	*% Water sol.*	*% Oil sol.*	*x,y*
1. Dimethicone copolyol isostearate "A"	47.5/5	24/5	9.5,4.8
2. Dimethiconol stearate	0/5	15/5	0.0,3.0
3. Dimethicone copolyol isostearate "B"	32/5	20/5	8.0,4.0
4. Cetyl dimethicone	0/5	20/5	0.0,4.0
5. Dimethicone copolyol amine	19/5	0/5	3.8,0.0
6. Dimethicone copolyol isostearate "C"	55/5	10/5	11.0,2.0
7. Dimethicone copolyol isostearate "D"	48/5	16/5	9.6,3.2
8. Dimethicone copolyol amine "B"	27.5/5	5/5	5.5,1.0
9. Dimethicone copolyol amine "C"	20/5	75/5	4.0, 15.0
10. Dimethicone copolyol amine "D"	19/5	30/5	3.8, 6.0
Blends			
11. Dimethiconol stearate (and) steareth (2) alcohol	21.5/5	70/5	4.3,14.0
12. Dimethiconol stearate (and) steareth (2) alcohol	6/5	55/5	1.2,11.0
13. Dimethiconol stearate (and) steareth (2) alcohol	0/5	79/5	0.0,15.8

emulsion stability on a scale with 5 representing a stable emulsion and 0, completely unstable.

We then tested the predictive value of the 3D-HLB graph by using a variety of surfactants we synthesized to cover a broad range of the possible silicone/water/hydrocarbon solubilities. We compared our predictions (Table 1-3) to the actual data (Table 1-4). The performance of the surfactants studied helped define the system boundaries.

Table 1-4. Silicone surfactant performance in test emulsions

	Emulsion Formula					
Compound Tested	**A** S/W[a]	**B** O/W[b]	**C** W/S[c]	**D** W/O[d]	**E** O/S[e]	**F** S/O[f]
1. Dimethicone copolyol isostearate "A"	4	5	0	0	0	0
2. Dimethiconol stearate	0	0	0	3	5	0
3. Dimethicone copolyol isostearate "B"	5	2	0	0	0	0
4. Cetyl dimethicone	0	0	0	0	5	2
5. Dimethicone copolyol amine	0	0	5	0	0	0
6. Dimethicone copolyol isostearate "C"	4	2	0	0	0	0
7. Dimethicone copolyol isostearate "D"	5	3	0	0	0	0
8. Dimethicone copolyol amine "B"	0	0	5	0	3	0
9. Dimethicone copolyol amine "C"	0	0	3	4	0	0
10. Dimethicone copolyol amine "D"	0	0	0	0	0	0
Blends						
11. Dimethiconol stearate (and) steareth (2) alcohol	0	0	0	0	4	5
12. Dimethiconol stearate (and) steareth (2) alcohol	0	0	0	0	0	0
13. Dimethiconol stearate (and) steareth (2) alcohol	0	0	0	0	3	5

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[a] Silicone-in-water
[b] Oil-in-water
[c] Water-in-silicone
[d] Water-in-oil
[e] Oil-in-silicone
[f] Silicone-in-oil

Conclusions

The evaluation of silicone and mixed surfactant systems has led us to a practical modification of the standard HLB system. This modified, 3D-HLB system apparently works for a broad range of emulsifiers and emulsion types.

Before devloping this system, we had not thought of making anhydrous emulsions with mineral and silicone oils forming the continuous phase. The 3D-HLB system not only predicts the existence of such emulsions (Formulas E and F), but identifies the surfactant molecules that will work in them.

The 3-D HLB system predicts an overlap in those materials that can make two closely related emulsions. For example, surfactants on the cusp between o/w and s/w emulsions will have properties typical of each. This implies that these materials will be good emulsifiers for systems co-emulsifying both oil and silicone in water.

Using the 3D-HLB system will allow formulators to select the most suitable emulsifiers for w/o, o/w, w/s, s/w, o/s and s/o emulsions. By eliminating much trial-and-error and thus saving laboratory time, the system will be a valuable tool for the formulating chemist.

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