KEY WORDS: SURFACTANT, EMULSION, DIMETHICONE COPOLYOL, SILICONE, 3D-HLB, HYDROPHILIC-LIPO-PHILIC BALANCE, SOLUBILITY, MULTIPLE EMULSION

• *The structure of the surfactant molecule determines the surfactant's functionality. The authors studied the dimethicone copolyol surfactant molecule with five different weight percentages of silicone and both with and without an added fatty group. They observed the effect of these structural changes on the molecule's solubility and on the emulsion stability in six different emulsion types. Then they compared the observed effects with those predicted by 3D-HLB theory. They conclude that the 3D-HLB system can make predictions that will improve the efficiency with which emulsifiers are engineered and complex emulsions are formulated.*

• *La structure de la molécule de tensio-actif détermine les propriétés du surfactant. Les auteurs ont étudié la molécule de surfactant copolyol dimethicone avec cinq pourcentages en poids de silicone différents et simultanément avec et sans ajout d'un groupe gras. Ils étudient l'effet de ces changements structuraux sur la solubilité de la molécule et sur la stabilité des émulsions dans six types d'émulsions différents. Ensuite ils comparent les résultats obtenus avec ceux prédits par la théorie HLB-3D. Ils concluent que le système HLB-3D permet des prédictions capables d'améliorer l'efficacité avec laquelle les émulsifiants sont développés et les émulsions complexes formulées.*

• *Die Struktur des Tensidmoleküls bestimmt die Funktionaliät des Tensids. Die Autoren untersuchen das Dimethicone Copolyol Tensidmolekül mit fünf verschiedenen Gewichtsprozenten an Silikon sowohl mit wie auch ohne hinzugefügter Fettgruppe. Sie beobachteten den Effekt dieser Strukturveränderungen bzl. der Löslichkeit des Möleküls und der Stabilität der Emulsion bei sechs verschiedenen Emulsionstypen. Danach verglichen sie die beobachteten mit den mittels 3D-HLB Theorie vorausgesagten Effekten. Sie fassen Zusammen, dass das 3D-HLB System Voraussagen machen kann, die die Effektivität massgeschneiderter Emulgatoren und komplexer Formulierungen betreffen.*

• *La estructura de la molécula del tensioactivo determina su funcionalidad. Los autores estudiaron la molécula tensioactiva dimeticona copoliol con cinco diferentes porcentajes en peso de solución y con y sin grupo graso adicional. Observaron los efectos de estos cambios estructurales en la solubilidad de la molécula y sobre la estabilidad de la emulsión en seis diferentes tipos de emulsiones. Entonces compararon los efectos observados con los calculados de acuerdo con la teoria 3D-HLB. Llegaron a la conclusión que el sistema 3D-HLB puede predecir como se mejorará la eficiencia en la mejoría de los emulsionantes y en la formulacion de emulsiones complejas.*

Applying the Three-Dimensional HLB System

Tests varying the structure of a dimethicone copolyol surfactant molecule demonstrating the 3D-HLB system's predictive power

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Formulators in the personal-care field have a vast number of traditional surfactants from which to choose in the preparation of new products. There are non-ionic, cationic, amphoteric and anionic products available. Each product class is composed of products with different functional properties. Within each class there are numerous products with specific formulation nuances. A novice formulator might ask, "Why are there so many types of surfactants?" The answer is clear. The structure of the surfactant determines the functionality. It is, therefore, not surprising that when scientists developed a series of surfactants containing silicone, they found that the structure determined the properties of these new materials, just as it did with the traditional surfactants.

Silicone is unique when placed into molecules. It confers substantivity, lowers irritation and alters feel on skin and hair. When silicone is incorporated into a surface-active agent, with polyoxyalkylene and hydrocarbon portions of the molecule, unique emulsifiers result.

Recently, as an expansion to the 50-year-old hydrophile/lipophile balance (HLB) system, we proposed incorporating silicone as one of the components to make up what we call the three-dimensional HLB system, or 3D-HLB system.[1,3,4] In an effort to investigate the system further, we looked at the effect of introducing a fatty ester group onto specific dimethicone copolyols. Specifically, we were interested in the changes in solubility and emulsification properties that result as a consequence of the introduction of the fatty group into the molecule. We studied the following types of emulsions:

- Silicone in water (s/w)
- Oil in water (o/w)
- Water in silicone (w/s)
- Water in oil (w/o)
- Oil in silicone (o/s)
- Silicone in oil (s/o)

In this article, we compare the results of our evaluation against the predictions of the 3D-HLB system. The study tested molecules with no fatty group as well as molecules with a fatty ester group. The standard HLB system has been found to work least well with these types of molecules.[2]

The 3D-HLB System

The 3D-HLB system uses a right triangle to predict the effectiveness of various compounds in making emulsions. The 3D-HLB system assigns an x and y value to a compound. The x coordinate is the old HLB

Table 1-1. The test compounds

Compound	% Silicone soluble	% Fatty soluble	% Water soluble	3D-HLB x, y
DMC A	40.0	0.0	60.0	12, 0
DMC B	60.0	0.0	40.0	8, 0
DMC C	70.0	0.0	30.0	6, 0
DMC D	75.0	0.0	25.0	5, 0
DMC E	80.0	0.0	20.0	4, 0
Ester A	30.0	25.0	35.0	7.5, 5.0
Ester B	48.8	19.2	32.0	6.5, 4.8
Ester C	58.5	16.5	25.0	5.0, 3.3
Ester D	65.2	13.0	21.8	4.4, 3.2
Ester E	72.0	10.0	18.0	3.6, 2.0

Table 1-2. Formulations of the test emulsion systems

Material	S/W	O/W	W/S	W/O	O/S	S/O
Silicone oil (350 visc)	15.0		80.0		80.0	15.0
Test surfactant	5.0	5.0	5.0	5.0	5.0	5.0
Water	80.0	80.0	15.0	15.0		
Mineral oil		15.0		80.0	15.0	80.0
	100.0	100.0	100.0	100.0	100.0	100.0

Table 1-3. Solubility properties of test compounds

Compound	Water	Mineral oil	Cyclo-methicone	Dimethicone (visc 350)
DMC A	sol	disp	disp	ins
DMC B	micro	disp	disp	ins
DMC C	disp	disp	sol	disp
DMC D	ins	disp	sol	disp
DMC E	ins	disp	sol	disp
Ester A	micro	disp	disp	ins
Ester B	disp	trans	disp	disp
Ester C	disp	trans	sol	disp
Ester D	ins	trans	sol	disp
Ester E	ins	disp	sol	disp

Legend: micro = microemulsion; ins = insoluble; disp = dispersible; sol = soluble; trans = translucent

Table 1-4. Stability range of the test compounds

Compound	Emulsion formulation (from Table 1-2) S/W	O/W	W/S	W/O	O/S	S/O
DMC A	3	1	0	0	0	0
DMC B	0	0	0	0	0	0
DMC C	0	0	4	0	0	0
DMC D	0	0	5	0	0	0
DMC E	0	0	4	0	0	0
Ester A	4	3	0	0	0	0
Ester B	0	0	0	0	0	0
Ester C	0	0	4	0	3	0
Ester D	0	0	5	0	4	0
Ester E	0	0	5	0	2	0

Legend: 0 = unstable (split in two layers); 5 = stable emulsion

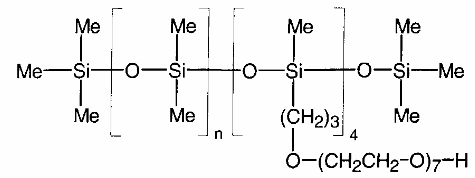

Figure 1-1. Dimethicone copolyol

value. The new y coordinate is calculated using the % oil soluble in the molecule. By definition, the calculations are as follows:

x coordinate = (% water soluble)/5

y coordinate = (% oil soluble)/5

This calculation gives the two values that define a point on the 3D graph. The point will fall into a region that specifies a type of emulsion for which the molecule is predicted to be applicable.

Compounds

Dimethicone copolyol compounds: Compounds evaluated are branched dimethicone copolyols and isostearic esters thereof. The former conform to the structure in Figure 1-1. We varied the "n" value in that structure to get dimethicone copolyols with a variety of molecular weights.

Dimethicone copolyol esters: To obtain the best comparisons, we used esters that were based upon the same polymer backbone as the dimethicone copolyols and also conformed to the structure shown in Figure 1-2, where R is isostearic.[a]

The use of a common silicone backbone for both the dimethicone copolyol and the ester results in molecules that vary only with the presence or absence of the isostearic portion. We will refer to the dimethicone copolyol compounds as DMC A through DMC E and the ester compounds as Ester A through Ester E. The nomenclature allows for a direct comparison. The compounds with the same letter designation are prepared from the same silicone backbone. Therefore, DMC A has the same silicone backbone as Ester A; the only difference is that the ester has the added isostearic portion of the molecule.

We calculated the percentage water soluble, oil soluble and silicone soluble to ascertain the 3D-HLB value for each molecule. Then we compared the observed solubility properties of the resulting molecules, as well as their emulsification properties. Finally, we compared the emulsification properties to the predictions made by the 3D-HLB system.

Compounds

We studied the compounds shown in Table 1-1. The compounds were all clear yellow liquids as prepared.

[a]Lambent Technologies markets compounds of this type under the Silwax trade name.

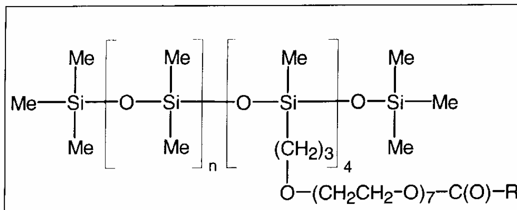

Figure 1-2. Dimethicone copolyol ester

Testing

Solubility testing: We tested the ten compounds in the following solvents for solubility at 5% by weight:

- Water
- Mineral oil
- Cyclomethicone
- Dimethicone

Emulsion testing: The 3D-HLB system predicts the following emulsion types:

- Silicone in water (s/w)
- Oil in water (o/w)
- Water in silicone (w/s)
- Water in oil (w/o)
- Oil in silicone (o/s)
- Silicone in oil (s/o)

We prepared an emulsion system for each of the emulsion types (Table 1-2). In each case, we prepared the formulation by adding the test surfactant to the discontinuous (internal) phase under good agitation for 5 min. Then we slowly added the continuous phase.

We evaluated the emulsions on a scale with 5 being a stable emulsion and 0 being completely unstable.

Results: Table 1-3 summarizes the results for solubilities in various solvents at 5% weight compound in solvent. Table 1-4 summarizes the results of the experimentation on emulsification properties.

Discussion

Solubilities: The tested compounds reveal several interesting trends.

- As the percentage of silicone in the molecule increases, the water solubility decreases. Molecules go from soluble, to micro emulsions, to dispersible and finally to insoluble. This trend occurs both in the dimethicone copolyol compounds and in the ester compounds. However, the presence of the fatty group in the ester further lowers water solubility of the molecule.
- As the percentage of silicone in either set of compounds increases, there is no effect upon solubility in mineral oil. Incorporation of the fatty group into the molecule changes the mineral oil surfactant blend from milky white to translucent stable emulsions. Incorporation of fatty groups into the molecule improves oil compatibility.
- As the percentage of silicone in the molecule increases, the solubility in cyclomethicone increases. Molecules go from dispersible to soluble. This is true in both esters and dimethicone copolyols. One compound (DMC C) is dispersible in water and soluble in cyclomethicone

and another (Ester B) is dispersible in both.

- As the percentage of silicone in the molecule increases, the dispersibility in 350 visc dimethicone increases. Molecules go from dispersible to insoluble. This trend occurs both in the dimethicone copolyol compounds and in the ester compounds. However, the presence of the fatty group in the ester improves dimethicone compatibility.
- The ratio of (a) silicone, (b) fatty and (c) water soluble portion of the molecule alters solubility of compounds in various solvents. The trends are predictable; consequently, it is possible to choose molecules for specific applications.

Emulsification properties: Figure 1-3 presents a graph based on the 3D-HLB theory. The figure shows the lines that are generated by connecting the 3D-HLB values of the dimethicone copolyol and the ester made from the same silicone backbone; that is, we join the 3D-HLB value for a lettered dimethicone copolyol with the 3D-HLB value for a similarly lettered ester.

Figure 1-3 shows that the inclusion of the fatty group not only increases the amount of fatty from zero, it also dilutes the other percentages. This is why the lines slope upward to the left. The slope of the lines decreases as one looks at lines A through E. The reason for this is that as you go from A to E the polymers have an increasing amount of silicone in the molecule. Consequently, there is less isostearic needed to react on a mole-to-mole basis. This is also why the percentage fatty continues to be lower as one progresses from A to E.

Figure 1-3 also predicts the effects of the alteration of structure on the emulsification properties. It is significant to look at what we call the cusp surfactants. In each corner of the triangle there are two regions that have a common line between them. These three pairs share a common border. They are (o/w : s/w), (o/s : w/s) and (s/o : w/o). A surfactant whose 3D-HLB value falls on these border lines is called a "cusp surfactant." Cusp surfactants are predicted to be good as emulsifiers in both types of emulsions that share the common border.

The inclusion of the fatty groups into the molecules and the shifts that occur in the emulsification properties result in some near cusp surfactants. In Figure 1-3, the closest to the border line is Ester A. This material as predicted is good for making both s/w and o/w emulsions, unlike the dimethicone copolyol based upon the same silicone back-

Table 1-5. Effect of esterification on the stability of dimethicone copolyols shown in Figure 1-1

Line	*Connects*	*Predicted*	*Observed*	
A	DMC A to Ester A	Improved S/W Improved O/W	S/W O/W	3 to 4 1 to 3
B	DMC B to Ester B	No change	No change	
C	DMC C to Ester C	Improved O/S	O/S	0 to 3
D	DMC D to Ester D	Improved O/S	O/S	0 to 3
E	DMC E to Ester E	Improved W/S Improved O/S	W/S O/S	4 to 5 0 to 2

bone (DMC A). Esters C, D, and E are all closer to the cusp than the dimethicone copolyol sharing the common backbone. Consequently, they are predicted to be better emulsifiers for o/s than the dimethicone copolyol based upon the same backbone. The way one would make Esters C, D and E true cusp surfactants is to increase the amount of fatty in the molecule to fall on the border line between the o/s and the w/s regions.

Conclusion

We continue to believe that the predictions made by using the 3D-HLB system will be helpful in engineering emulsifiers that will allow for the formulation of complex emulsions. We have learned that if one makes an emulsion using the 3D surfactants, the emulsion can be emulsified into mixed emulsions using our system in two easy steps. This simplified process makes multiple phase emulsions by making two simple emulsions one after another. We expect to address the multiple emulsion aspect of the 3D-HLB system in a subsequent work.

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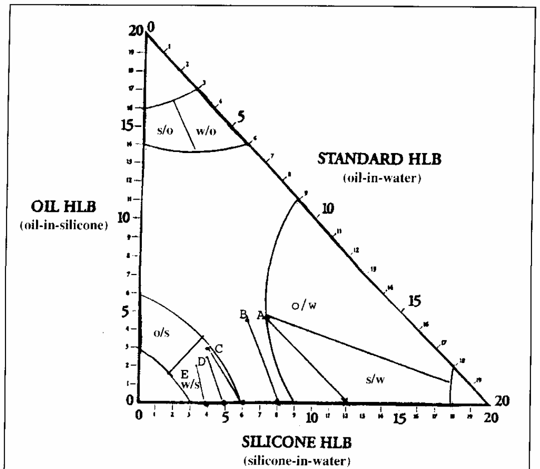

Figure 1-3. 3D-HLB plot of five pairs of a dimethicone copolycol and an isostearic ester with the same polymer backbone

Line A joins DMC A and Ester A
Line B joins DMC B and Ester B
Line C joins DMC C and Ester C
Line D joins DMC D and Ester D
Line E joins DMC E and Ester E

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