Editors Note: This edition of the Silicone Spectator deals with amphilic silicones, that is silicones that are surface active.

Silicone at the Surface

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Originally Published: May 2000

Silicone Spectator®
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Silicones have become a more and more important raw material in the formulation of personal care products. The reason for this is that silicone provides a number of unique properties, including surface tension reduction. Proper selection of the silicone molecule can result in wetting in both oil and water, foam, emulsification, and film formation. The prudent selection of amphilic silicones will aid in efficient utilization of these materials resulting in cost effective formulations. The reason for this is that amphilic silicones are found at the surface in their lowest energy state.

The term amphilic refers to a compound that possesses at least two groups that if present in pure form, rather than in a compound would be insoluble in each other. The groups that are most commonly encountered in amphillic compounds are oil and water. When a molecule contains groups that make it an amphile, the resulting product is surface active. Surface-active materials are a very wide range of compounds that are found in nature (for example surfactants in lungs) and can also be made by man.

There are four types of groups that are mutually insoluble they are described in Table 1.

Table 1 Designation	Description	Example
Oleophilic	Oil Loving	Hydrocarbon
Hydrophilic	Water Loving	Polyoxyethylene glycol (PEG)
Siliphilic	Silicone Loving	Dimethyl polysiloxane
Fluorophilic	Fluoro Loving	Fluoro Alcohol

The ratio of the groups to each other will determine the materials into which the amphile is soluble and the surfactant function of the particular compound. Many compounds contain two of the four, three of the four or all four in a single molecule.

The amphilic compounds of interest in this article are those that contain silicone soluble group and another group. These compounds by virtue of their structure have very interesting physical chemical properties and formulation attributes. These attributes allow the formulator to provide foam, emulsification or wetting to consumer products which are directly related to the activity of the amphile at the surface and in particular the ability to lower surface tension.

Solubility

We can organize our world based upon solubility according to the following simple definitions[1]:

1. A **solution** is a homogeneous mixture composed of one or more substances, known as solutes, dissolved in another substance, known as a solvent.
2. A **suspension** is a colloidal dispersion in which a finely divided species is combined with another species, with the former being so finely divided and mixed that it doesn't rapidly settle out. In everyday life, the most common suspensions are those of solids in liquid water.
3. An **emulsion** is a mixture of two immiscible substances. One substance (the discontinuous phase) is dispersed in the other (the continuous phase).

However, the world of chemistry is rearly so easy to organize. Consider a fully dissolved 1% solution of sodium chloride in water. This simple system has sodium ion (Na^+), chloride ion (Cl^-) and water, roughly equally distributed over the entire mass of the system. The solution is clear and homogeneous.

Now consider a 1% solution of a surfactant. Surfactant, or surface active agent has a water soluble head and a water insoluble tail. A very well known surfactant is sodium lauryl sulfate (CAS 151-21-3). Like NaCl, Sodium lauryl sulfate has a two opposite ions, but sodium lauryl sulfate in water is very different. The presence of a large fatty portion makes the product surface active.

Most systems encountered by formulation chemists are not pure liquids; they are compositions (i.e. mixtures of materials)[3]. The ability to obtain wetting, foaming, and emulsification requires that the compound added lower surface tension. Not all materials that lower surface tension are effective for all of the above surfactant properties, but lowering surface tension is a prerequisite for all of these.

Surface tension reduction requires molecules that have a particular function in solution. Solutions of amphillic molecules are fundamentally different than solutions other type of solutions. Consider NaCl (salt). It is an example of an ionic, non-surface active agent and Sodium Lauryl Sulfate (SLS) an example of a surface active agent. Both are water soluble (i.e. clear in water), but what they do in solution is significantly different and key to their properties.

The term solution relates to the clarity of a liquid and consequently the size of any particle present. Consider a 0.5% solution of salt. NaCl is not a surface-active agent, since it does not have a hydrophobic portion. Consequently, upon dissolution in water at low concentrations, it is present at the same concentration at the top of the beaker as at the bottom, at the left and at the right of the beaker. At this concentration salt can be considered sodium ion and chloride ion. This is a key concept. If sodium chloride and potassium sulfate are mixed in dilute solution, the solution contains all four ions rather than two compounds. As the concentration of ionic material in solution is increased nearing saturation structured systems form due to repulsion of the ions.

Surfactant systems are much different. They contain hydrophobic and hydrophilic portions. SLS has a C12 fatty portion and a water-soluble sulfate portion covalently bonded in one molecule (such molecules are referred to as amphillic). When such molecules are added under dilute solution a clear "solution" results, but the distribution of molecules in solution is not the same. As one adds SLS to water the molecules go to the surface, lowering surface tension. At the air / water interface the water-soluble groups align in the water and the water insoluble material C12 groups point into the air. This is the lowest free energy for the system. As one continues to add more SLS, the ability to pack the surface stops. This is the Critical Micelle Concentration (CMC). At concentrations below the CMC, surfactants are found at the surface. At the CMC point the surfactants assemble to form micelles. Water soluble groups into the water, oil soluble groups in the center associating with each other.

While both beakers contain solutions, the organization of the molecules in the respective liquids is far different. Likewise, the surfactant properties, (surface tension, ability to wet, foam, cleanse or emulsify) are very different.

The ability for surface-active materials to provide desirable properties by lowering surface tension is an important reason to use surfactants. The SLS discussed above is added to water, a solvent that not only has a high surface tension, but also one in which the surfactant is soluble. SLS provides wetting, foam and detergency to the water, by virtue of lowering its surface tension.

Cosmetic formulators work with materials other than water. One major material are the various oil phases (including mineral oil, squalene, esters, and many others). These oil phases have surface tensions values of around 32 dynes/cm^2. This means if we can find a material soluble in the oil, amphillic in nature and having a lower surface tension, the surface tension of the oil can be reduced exactly analogously to the water example with SLS. SLS is not of interest in oil phases because it is not soluble. Alkyl silicones are the amphillic materials of choice for oil phases.

The importance of surface tension reduction cannot be overstated when making personal care products. The application to hair and skin always is based upon the formation of new surface area, lipsticks are spread on the skin, shampoos spread on the hair, and so on. The through and efficient spreading requires a lowering of surface tension. Amphillic molecules because they are active at surfaces are in motion in the dynamic system created by spreading out.

As surfactant is added, demonstrated by the second box, surface tension is falling as dilute surfactant organizing at the surface. As the surface reaches saturation a very significant situation develops. The surface tensions no longer drops, even with additional surfactant. It is at this concentration called critical micelle concentration that micelles become the dominant form of surfactant. This situation is shown in the third box, Figure 1.

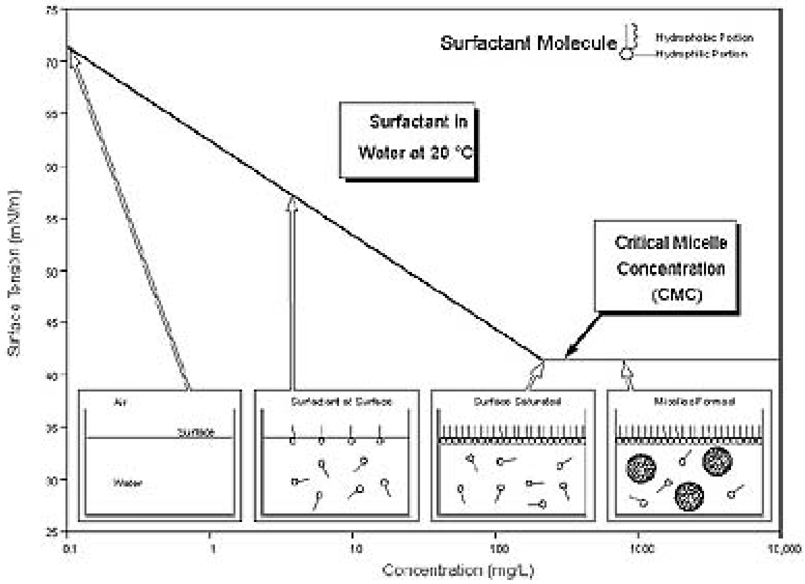
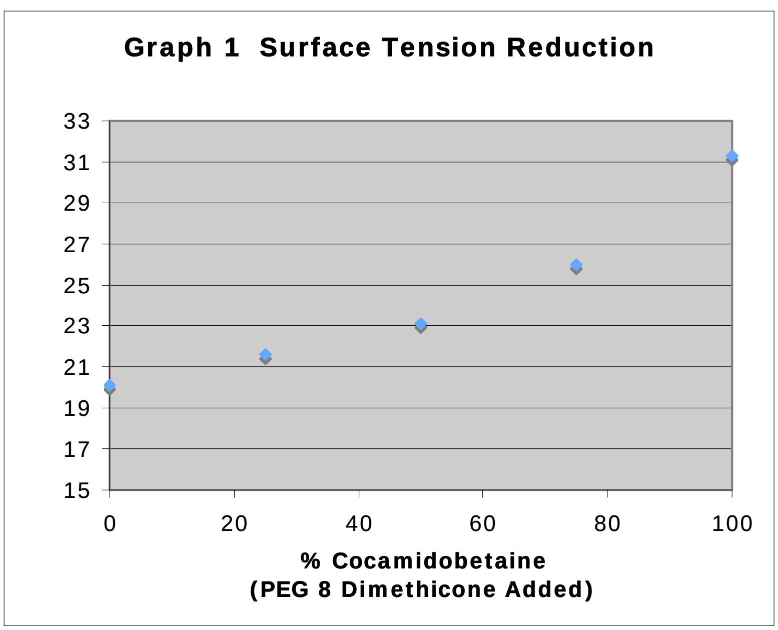
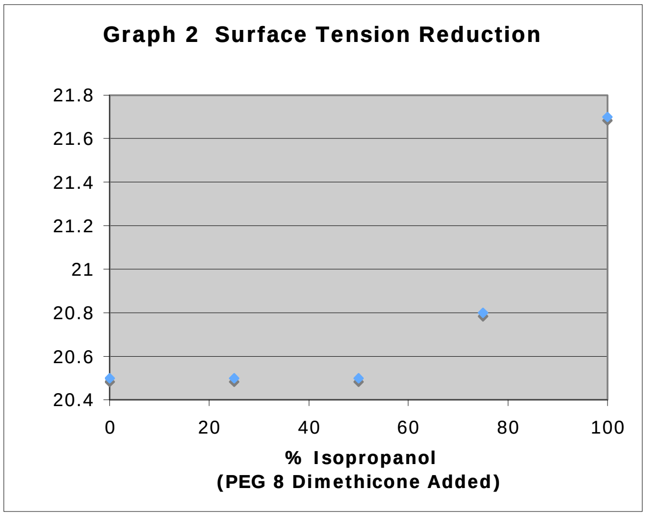


Figure 1 Surfactant Orientation[2]

Concentration Effects on Reduction of Surface Tension with Amphilic Silicone

To show the effect of adding amphilic silicone to a variety of products, blends with several ratios were evaluated for surface tension reduction. The results are shown in Graph 1 and 2.





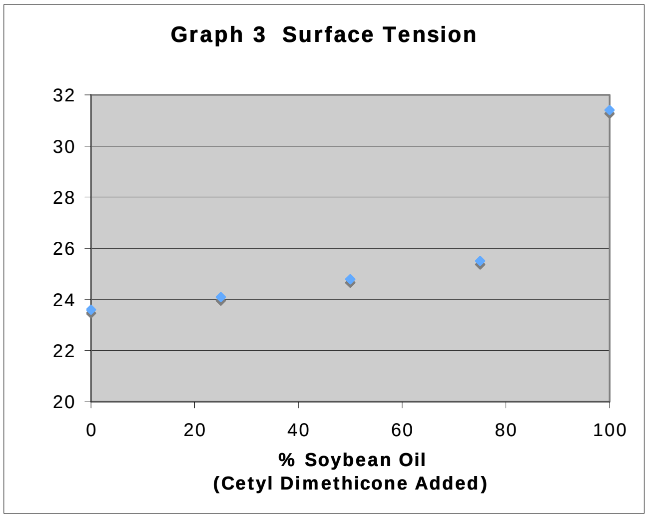
A number of solvents can have their surface tension altered by addition of the proper silicones. Table 2 shows the effect[4]. The ability to lower surface tension of many materials that we commonly find in cosmetic products, allows for the improvement of spreadbility, alters skin feel and provides new cosmetic properties to existing formulations. This approach is useful for both oil phases and polar phases. In fact the addition of 0.5% of a silicone amphilic polymer to a formulation can result in very different consumer perceptions. This approach allows the formulator to make small modifications to existing formulations to meet new product profiles.

Table 2
Reduction of Surface Tension of Oils with Silicone Derivatives

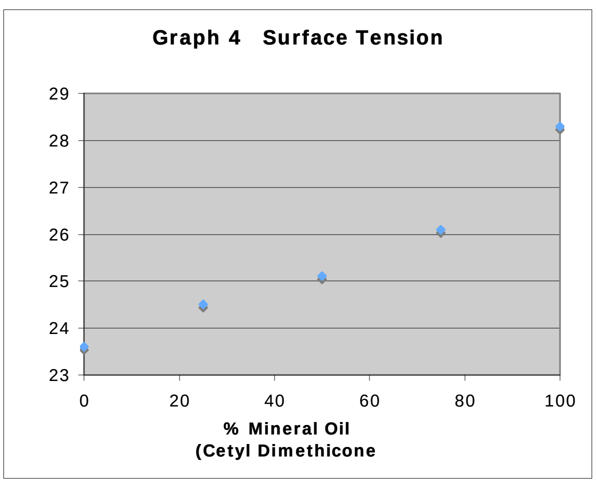
Solvent	Surface Tension (as is) Dynes/cm^2	Silicone Added (0.5% weight)	Surface Tension Dynes/cm^2
Toluene	28.9	C-26 alkyl dimethicone	25.0
2-butoxy ethanol	29.1	Stearyl dimethicone	22.0
Methanol	23.4	Octyl PEG-8 dimethicone	22.2
Water	72.3	PEG-8 dimethicone	20.1

It is perfectly proper to consider the question; What is the CMC of behenyl dimethicone in toluene.

Graph 3 shows the effect of adding cetyl dimethicone to soybean oil.



Graph 4 shows the effect of adding cetyl dimethicone to mineral oil.



Why is the cosmetic formulator interested in surface tension? Surface tension effects spreadbility and cushion. The addition of the proper silicone to a high viscosity ester can improve spreadability without effecting the play time (i.e. the time it takes to spread out). A different silicone can improve spreadability and reduce playtime. The result is an ability to alter aesthetics in personal care products by adding low concentrations of silicones. This allows one to significantly alter the cosmetic feel of a product without dramatic alteration in the formulation!

The addition of the proper silicone can also improve wetting time and alter bubble structure.

Table 3

Effects of Added PEG-8 dimethicone upon Cocamidobetaine

Table 3	Draves Wetting (seconds)	Ross Miles Foam (Initial)	Ross Miles Foam (5 minutes)
Example 3.1	9.6	175	150
Example 3.2	7.5	170	145
Example 3.3	4.8	155	135
Example 3.4	3.6	145	115
Example 3.5	2.0	135	110

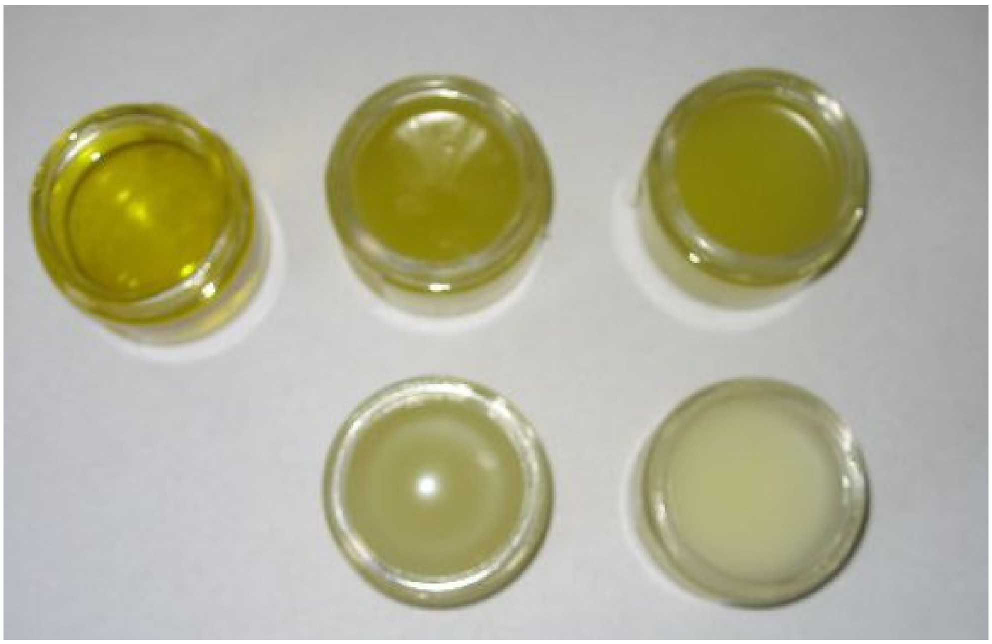
Gellation of Oils

As the concentration of alkyl dimethicone increases micelles form and the oil is gelled. In this case behenyl dimethicone is added to olive oil.

If there is amount of silicone present in the molecule is low, the gel will be essentially clear (as seen in figure 2 for 456 and 476). As the concentration of silicone is increased the clarity is lost (406 and 402), but the silicone feel increases. The optimization of the gel structure is the topic of several pending patent applications.

Figure 2
Olive Oil Thickened with 10% Behenyl Dimethicone

Olive Oil   Behenyl Dimethicone 456   Behenyl Dimethicone 476



Behenyl Dimethicone 406   Behenyl Dimethicone 402

Conclusions

1. Many of the most interesting properties that are founding silicone compounds are found in those molecules that are amphillic.

2. The salient property is surface tension lowering and can include wetting, emulsification, foaming, and gellation, depending upon the specific structure.

3. The specific structure of the compound determines the properties a silicone amphile will have.

4. Since silicone polymers are almost never the sole ingredient in the formulation, it is critically important to consider the interaction of the various components in formulations.

5. The effect of a silicone surfactant in formulation is structure dependant and since INCI

names do nothing to relate structure, far more details are needed to construct meaningful models.

The evaluation of the effect of silicone surfactants in formulation is an ideal candidate for computer-assisted evaluation of many different formulations.

References

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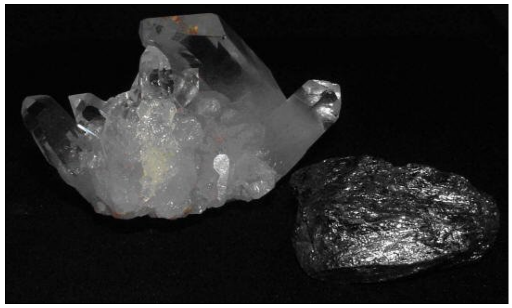
3. O'Lenick, Anthony, *Surfactants Strategic Raw Materials*, Allured Publishing 2004 p. 112.



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