



INNOVATIVE SILICONE SPECIALTIES



Silicone Surfactant Interactions

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Abstract

Cosmetic products are complex mixtures of materials. More and more silicone surfactants and traditional fatty surfactants are used in formulations to provide the aesthetics consumers demand. The physical chemistry of interactions between these two classes of very different materials is a complicated matter. Even clear solutions can be complex in terms of the distribution of species at the surface and within the solution. This article investigates some of the interactions between silicone surfactants and ingredients often found in personal care formulations.

Background

As technical people we want our formulations to be governed by clear technical rules and to use simple concepts to organize our world. If we organize our world according to simple definitions¹, we would observe:

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 cosmetic chemistry is rarely 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. The structure of sodium lauryl sulfate is shown in figure 1.

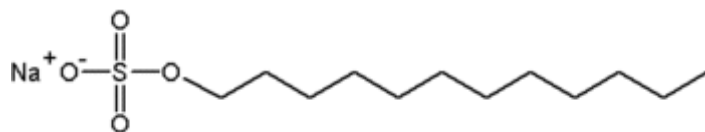


Figure 1 Sodium Lauryl Sulfate

A 1% solution of sodium lauryl sulfate, like that of sodium chloride, is clear but not homogeneous. As one adds sodium lauryl sulfate to water, the orientation of the material in the water is driven by achieving the lowest overall free energy. In this case minimize disrupting hydrogen bonding in water. The sodium lauryl sulfate organizes itself at the air water interface and then begins to self assembly into micelles. Figure 2 shows this². The first box shows pure water, having a surface tension is around 72 dynes/cm². 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 tensios no longer drops even with additional surfactant. It is at this concentration called crirical micelle concentration that micelles become the dominant form of surfactant. This situation is shown by the third box in Figure 2.

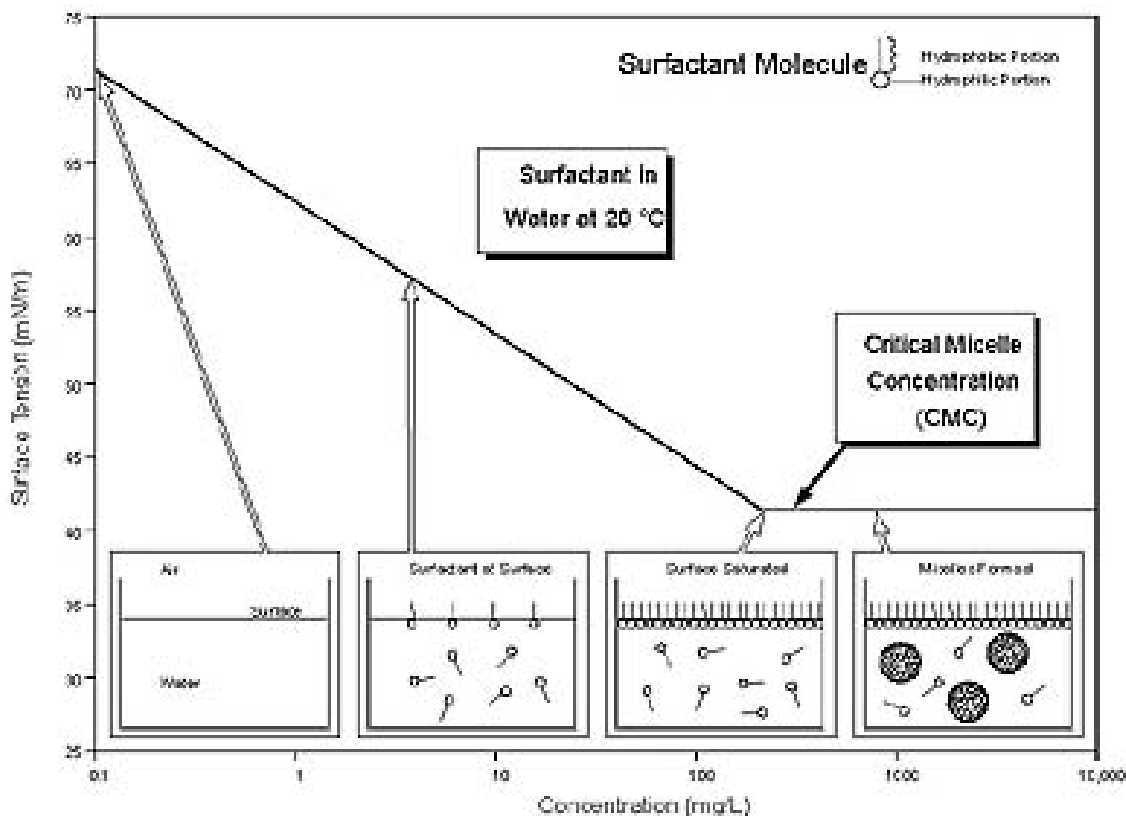


Figure 2 Surfactant Orientation²



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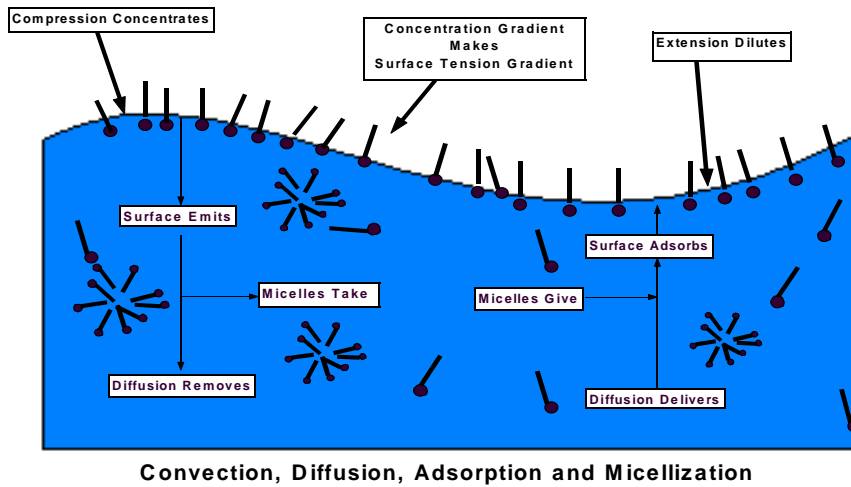
Group Opposites³

The above situation occurs when a surface active material is added to water. The surface active agent, while “soluble” has a structural attribute that causes the lowest free energy level to be at the interface or in micelles rather than uniformly distributed throughout the solution. This very same phenomenon occurs in non-aqueous systems, if the surface active agent is soluble and ” has a structural attribute that causes the lowest free energy level to be at the interface or in micelles rather than uniformly distributed throughout the solution. The world of cosmetic chemistry has water, oil and silicone phases, all mutually immiscible. So is it proper to ask what happens when an alkyl silicone is added to an oil? Or to ask What is the critical micelle concentration of cetyl dimethicone in an ester? These are very proper and important questions for the cosmetic chemist.

The introduction of surfactants based upon silicone hydrophobes offers another dimension to surfactant technology. Often called the 3D HLB system⁴, the altered solubility allows the cosmetic formulator an opportunity to take advantage of silicone’s unique properties to achieve a desired benefit. One such benefit is derived from the fact that the solubility of silicone can be made modified by addition of alkyl groups for water solubility, water soluble groups for water solubility or even fluoro solubility by addition of fluoro groups. Silicone surfactants and fatty surfactants differ fundamentally in their surfactant properties. While fatty surfactants generally have aqueous surface tensions of around 32 dynes/cm², their silicone based cousins have surface tension values of around 20 dynes/cm². Since most organic oils have surface tensions below 30 dynes/cm² only silicone surfactants are able to alter the surface tension, spreadability, cushion and play time of oil phases. Silicones can be engineered to be both soluble in and surface active in oil phases. Table 1 shows that even at 0.5% by weight surface tensions can be reduced by using a properly selected silicone. The use of fatty surfactants is not effective due to insolubility and / or the fact that the fatty surfactant has a higher surface tension than the solvent.

The type of products the cosmetic formulator generally encounters are ones in which dynamic surface tension is important. That is, we are generally creating new surface area as we spread color cosmetics on the lips, spread shampoo on the hair, or spread fragrance on the skin. This means surfactant tension, wetting and cushion and play time are critical to an elegant feel. Dynamic surface tension is a rather complex situation with a number of equilibrium steps. Figure 3 shows some of them.

Figure 3 Dynamic Surface Tension⁵



One part of the study is to look at surface tension reduction. Table 1 shows that silicones can be used to reduce surface tension of several materials, making addition of the proper silicone highly desirable.

Table 1 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

The effect of concentration on surface tension was also studied, with several different systems. Table 2 shows the results.



Table 2

Concentration Effects on Reduction of Surface Tension of Oils with Silicone

Blends of several ratios of different materials was evaluated for surface tension reduction. The results are as follows:

	Cocamidobetaine (% Weight)	PEG-8 Dimethicone (% Weight)	Surface Tension (Dynes/cm ²)
Example 1.1	100%	0%	31.3
Example 1.2	75%	25%	26.0
Example 1.3	50%	50%	23.1
Example 1.4	25%	25%	21.6
Example 1.5	0%	100%	20.1

	Soybean oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm ²)
Example 2.1	100%	0%	31.4
Example 2.2	75%	25%	25.5
Example 2.3	50%	50%	24.8
Example 2.4	25%	75%	24.1
Example 2.5	0%	100 %	23.6

	Mineral oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm ²)
Example 3.1	100%	0%	28.3
Example 3.2	75%	25%	26.1
Example 3.3	50%	50%	25.1
Example 3.4	25%	75%	24.5
Example 3.5	0%	100 %	23.6

	Isopropanol (% Weight)	PEG-8 Dimethicone (% Weight)	Surface Tension (Dynes/cm ²)
Example 4.1	100%	0%	21.7
Example 4.2	75%	25%	20.8
Example 4.3	50%	50%	20.5
Example 4.4	25%	75%	20.5
Example 4.5	0%	100 %	20.5

Why is the cosmetic formulator interested in surface tension? Surface tension effects spreadability 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 presonal 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 Cocamido betaine

	Draves Wetting (seconds)	Ross Miles Foam (Initial)	Ross Miles Foam (5 minutes)
Example 1.1	9.6	175	150
Example 1.2	7.5	170	145
Example 1.3	4.8	155	135
Example 1.4	3.6	145	115
Example 1.5	2.0	135	110

Simple Surfactant Systems

A. Fatty Surfactants

The CMC graph for sodium lauryl sulfate is observed in Figure 4 and the CMC graph for sodium laureth-2- sulfate is observed in Figure 5. These can be easily related to figure 2 to determine what is happening.



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Figure 4

CMC for SLS

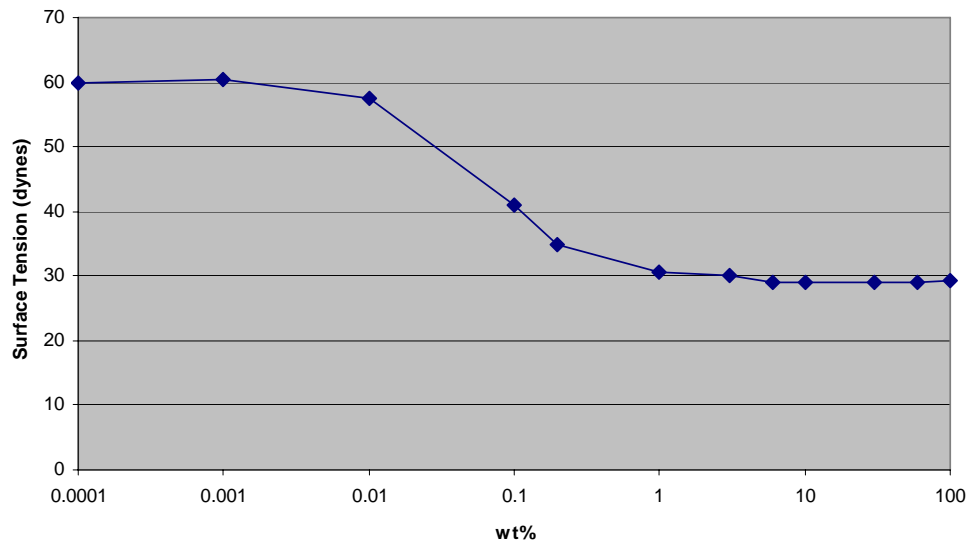
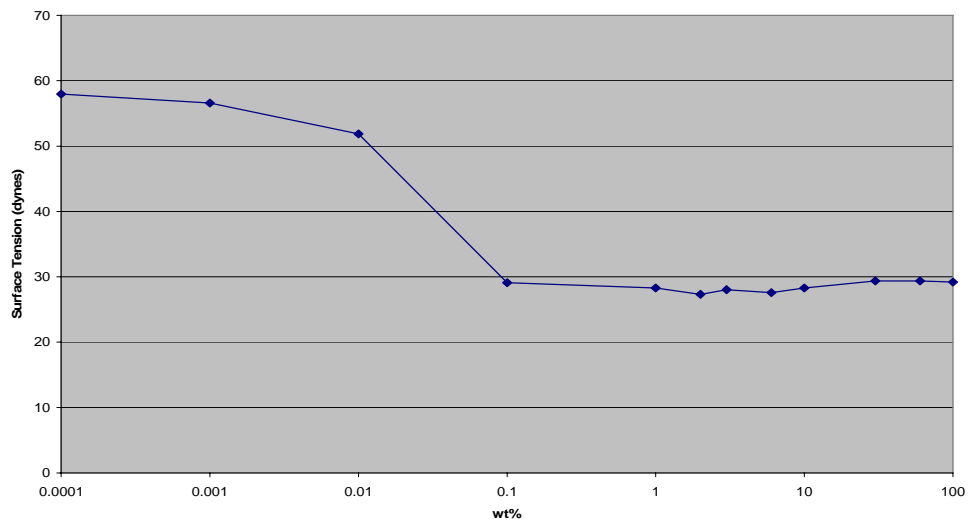


Figure 5

CMC for SLES-2





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B. Silicone Surfactants

Likewise a CMC graph can be generated for silicone surfactants. Figure 6 and Figure 7 show two different molecular weight silicone compounds (INCI name PEG-8-dimethicone).

Figure 6
CMC graph for low molecular weight PEG-8-dimethicone

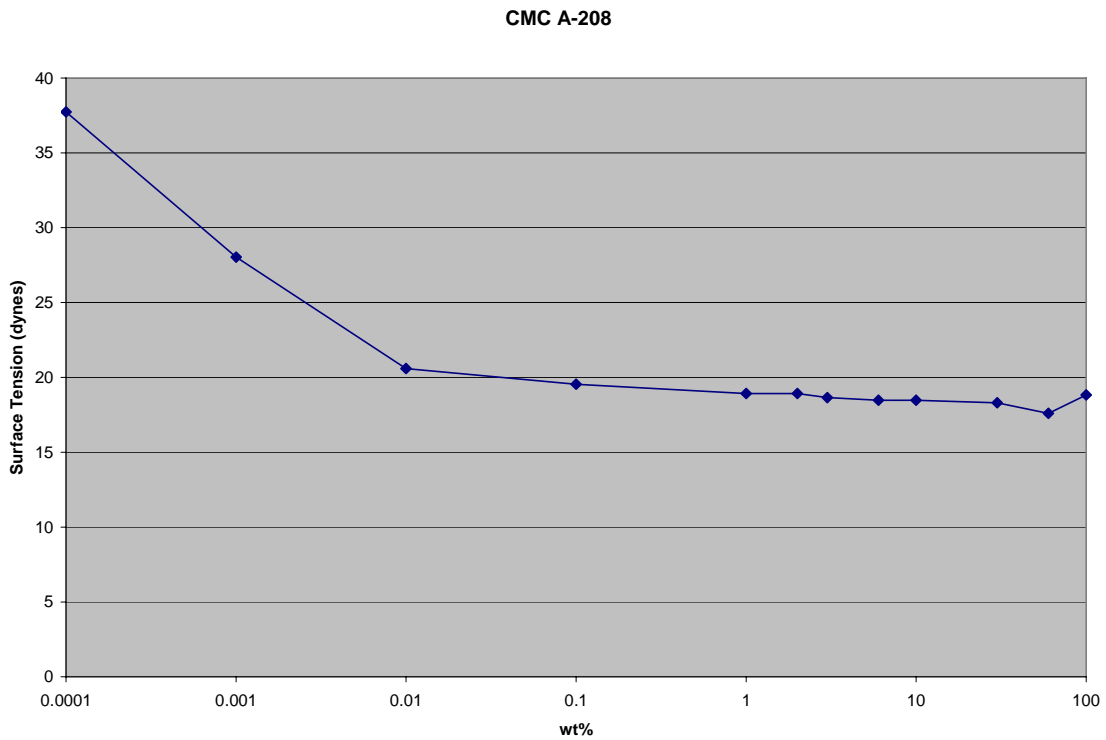
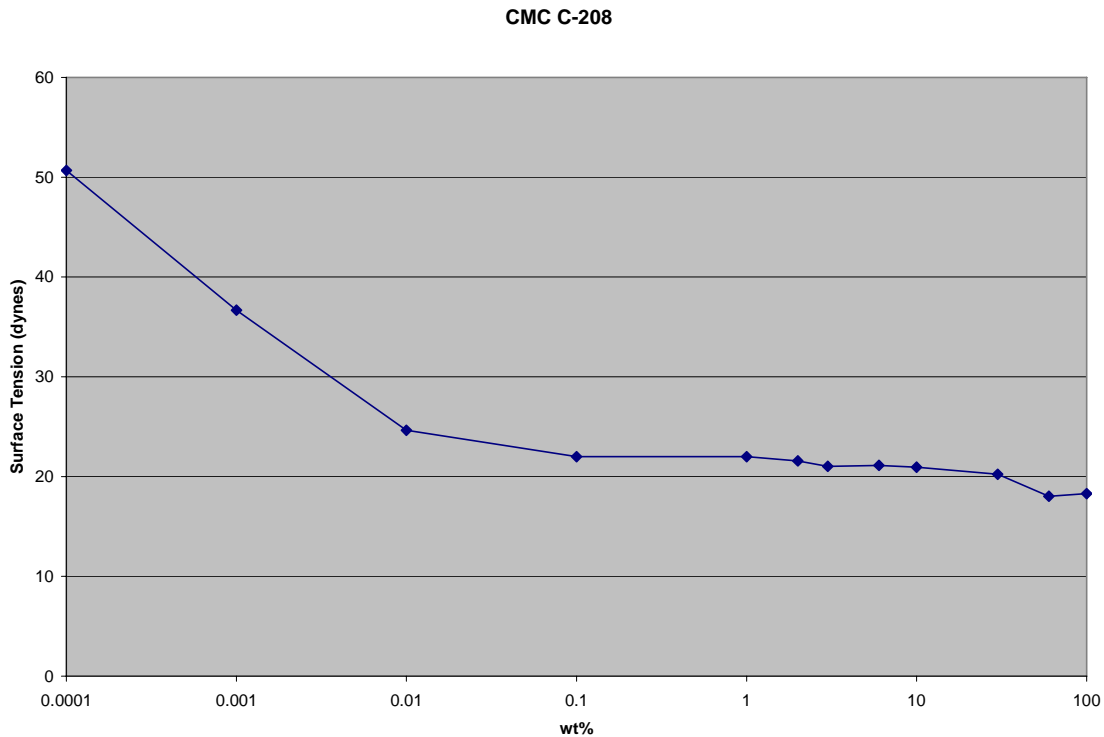


Figure 7
CMC graph for higher molecular weight PEG-8-dimethicone



C. Mixed Systems

However, silicone surfactants are seldom used in systems as the sole material. As stated above “Silicone surfactants and fatty surfactants differ fundamentally in their surfact tension properties. While fatty surfactant generally have aqueous surface tensions of around 32 dynes/cm², their silicone based cousins have surface tension values of around 20 dynes/cm².” What happens to mixed systems?

One can pretty well predict the starting surface tension with no added silicone surfactant (the surface tension of the fatty surfactant) and the ending surfact tension (the surface tension of the silicone surfactant). The shape of the intermediate points (that is the surface tension of the blends) was not predictable.

Test Methodology

In order to study the effect of adding silicone surfactant to fatty surfactant it was decided to take a 1% solution of either sodium lauryl sulfate or sodium laureth sulfate and use it as the solvent, replacing water in running standard CMC analysis. To a 1% solution of the fatty surfactant was added different amounts of silicone surfactant and the surface tension was measured. The starting surface tension was around 30 (the surface tension of the pure fatty surfactant) and the surface tension of the pure silicone surfactant was around 20.

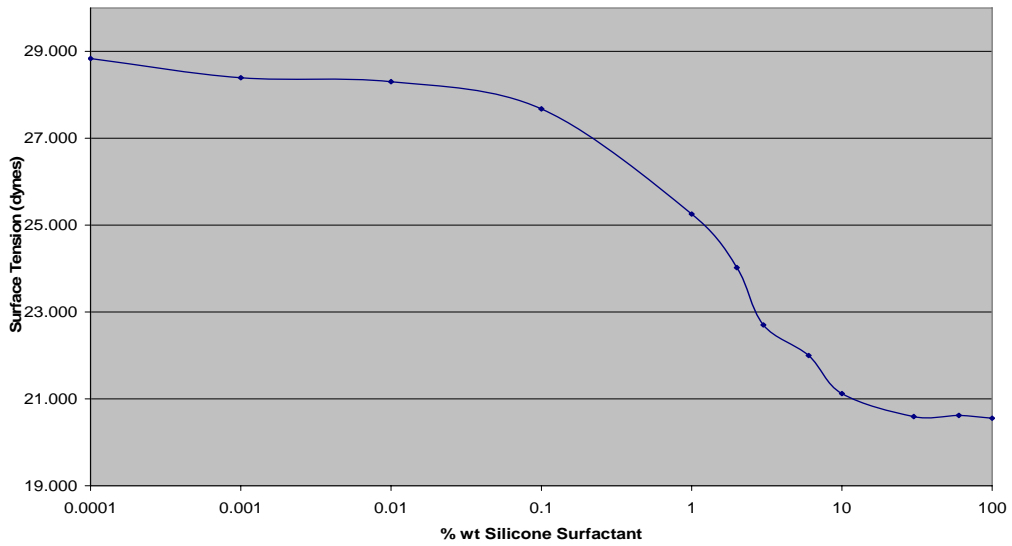


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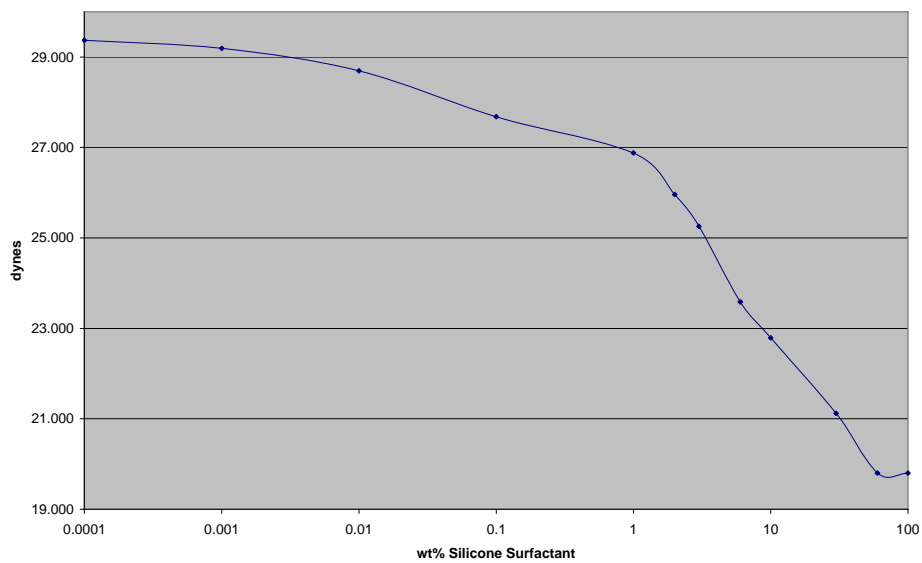


Result:

Surface Tension of blends of SilSurf A-208 and SLS



Surface Tension of Silsurf C-208 and %SLS

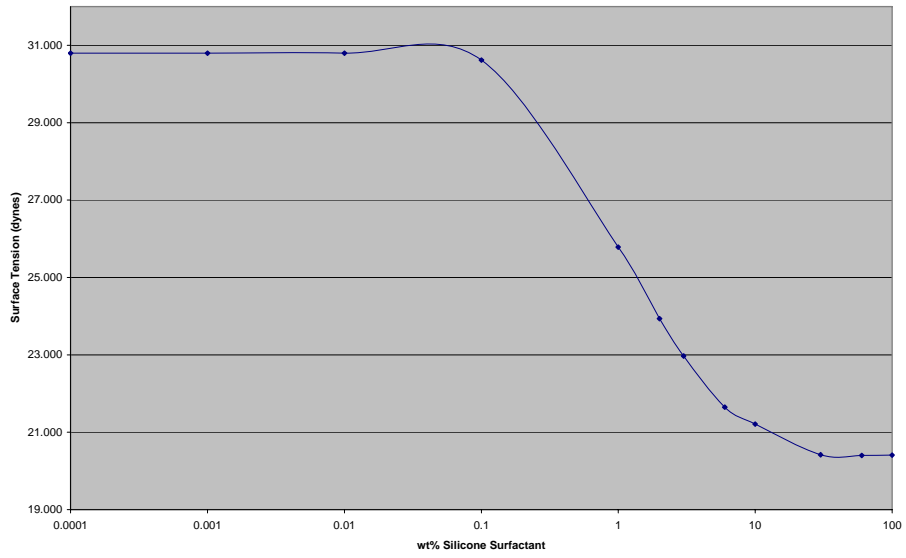


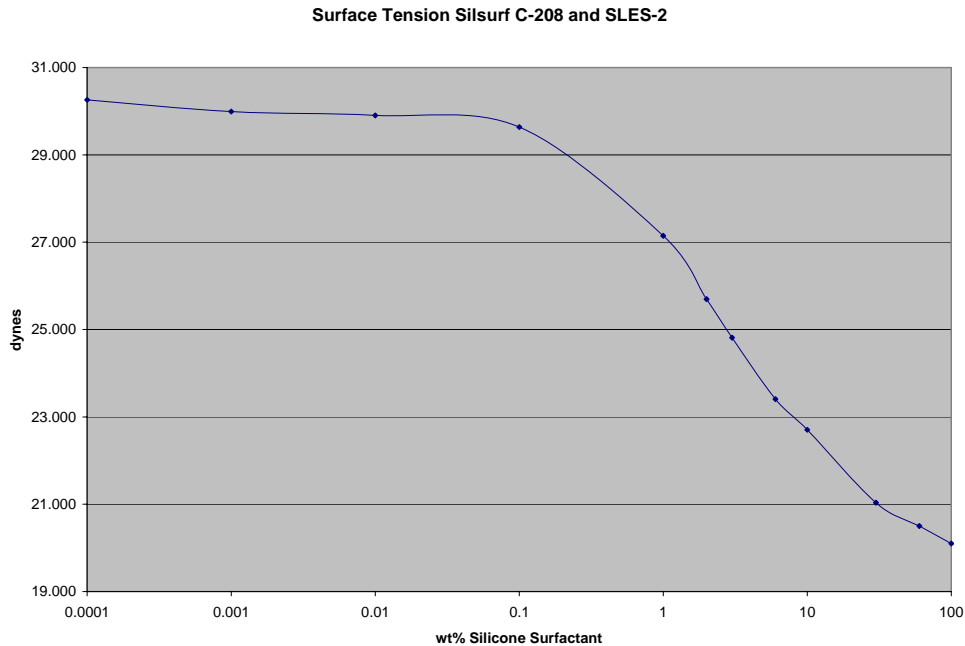


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Surface Tension Silsurf A-208 and SLES-2





The concentration of SLS and SLES in the system exceeds the CMC for those material in all evaluations. In fact the 1% solution of fatty surfactant is significantly over the CMC. This situation was chosen because the surface is saturated with surfactant at this concentration. Any reduction in surface tension beyond the CMC surfactant tension for the fatty surfactant is a direct result of competition between the fatty surfactant and the silicone surfactant. The fact that there is a significant lowering of the surface tension by addition of low concentration of silicone surfactant, indicates the silicone surfactant competes well with the fatty surfactant for surface at the interface.

We suggest looking at what we call the RF_{50} that is the *Reduction Factor 50%* for each silicone surfactant in each system. The definition is as follows:

RF_{50} = the concentration of silicone surfactant added to reduce the surface tension half of the difference between the fatty surfactant's surface tension and the silicone surfactant's surface tension.

The lower the RF_{50} the better able is the silicone surfactant to compete with the fatty surfactant for surface and the more efficient the silicone surfactant will be. This technique allows one to design molecules that will be optimized for a particular formulation. Not only can surfactant systems be evaluated but complex formulations can be evaluated, by simply defining the Fatty Surfactant's Surface tension as the formulation's initial surface tension. Not only surface tension, but also foam and the like can be tested and optimized by evaluating foam as the property rather than surface tension.



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Silicone Surfactant	Fatty Surfactant	RF ₅₀
A-208	SLS	1.2
A-208	SLES-2	1.2
C-208	SLS	1.5
C-208	SLES-2	3.5

For SLES-2 systems the A-208 and C-208 models have about the same RF₅₀, meaning the molecular size is not the controlling issue in the system. We assume the interaction between the polyoxyalkylene groups is controlling. In SLS systems, removing the polyoxyalkylene interactions, molecular size is most important.

Conclusions

1. By understanding the properties obtained by mixing different ratios of silicone surfactants with traditional surfactants, one can maximize the effect in formulation and minimize cost. This property can be defined by RF₅₀ a technique which allows for the evaluation of effectiveness of silicone surfactants in a variety of formulations for a variety of applications.

2. It is also quite possible to use surface active silicone compounds in oil phases to alter surface tension, spreadability, cushion and play time in formulations. These oils can be used as is or in emulsions.

3. The alteration of surface tension of products offered by incorporating the proper amount of silicone into products allows the formulator to obtain altered aesthetics from formulations that are already developed, minimizing development time and maximizing lab efficiency.

Acknowledgements

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