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TONY O'LENICK Siltech L.L.C., 1625 Lakes Parkway, Suite N., Lawrenceville, GA 30043, USA



Surfactant Interactions in Formulations *Part 2 Amphoteric / Anionic Interactions

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Abstract This is the second of a series of review articles on the interactions that occur in our formulations as a simple consequence of combining the raw materials used in the formulation of personal care products. These interactions are largely ignored but the functionality of the formulation is the sum of the properties and ratios of each of the raw materials added. There are a number of interactions, which include formation of self-assembling complexes. These complexes can either enhance or detract from the functional attributes of the formulation. Since most of today's high performance formulations are very complex containing a plethora of ingredients, it is difficult to predict the effect of changes in those formulations. In an attempt to understand these interactions we have gone back to simple systems. The results of these interactions can then be used to help formulate more effective products.

The first article investigated the interaction between anionic and cationic surfactants in aqueous systems1. This article will investigate the interaction between amphoteric surfactants and anionic surfactants. Viscosity when combined, foam and salt curve will all be evaluated. Choice of amphoteric is very important to determine the best combination for optimizing properties (2).

The interaction between ingredients in a formulation is almost always the most important factor in determining the properties of the formulation. Simply put, the formulator adds a number of ingredients to a formulation with the intention of altering viscosity (that include salt, alkanolamid and others), increasing or stabilizing foam, or altering foam structure, and altering rinse off are but a few. This article will show data that indicates that the selection of amphoteric type and concentration in a formulation is a very powerful technique to alter formulations.

FORMULATION TIP

It is recommended that the formulator look at a basic formulation, leaving out the ingredients with the exception of the anionic and amphoteric components. By looking at variation in the ratio of these two ingredients and varying the ratio, very important differences in this simple formulation can be determined. One of these is irritation, which is an important concern as lower and lower irritation scores are highly prized in formulations.

Surfactants Chosen

The surfactants chosen were the most traditional surfactants in the cosmetic industry.

| Designation | Description | CAS ³ |
|-------------|-------------|------------------|
| S-1 | SLS | 151-21-3 |
| S-2 | SLES-2 | 3088-31-1 |

Anionic Surfactants

The anionic surfactants chosen for this study are designated in Table 1.

Amphoteric Surfactants

The amphoteric surfactants chosen for the evaluation were selected to cover a number of different types of surfactants as well as those with different alkyl groups. They are described in Table 2.

| Designation | Description | Abbreviation (COAB) (DAB) (PB) | |
|-------------|-------------------------------|---|--|
| A-1 | Cocamidopropyl betaine | | |
| A-2 | Dimer amido propyl betaine | | |
| A-3 | Cetyl Betaine | | |
| A-4 | Lauric Myristic Amido Betaine | (LMAB) | |
| A-5 | Lauramphopropionate | (LP) | |

 Table 2. Amphoteric Surfactants Evaluated (4).

I Anionic Interaction Study

The protocol used to evaluate the interaction is shown in Table 3.

Test Methodology:

- 1. A 10% solution of anionic was prepared.
- 2. A 10% solution of amphoteric was prepared
- 3. A blend 50/50 by weight was prepared.
- 4. Viscosity was run at 6 rpm using a Brookfield viscometer LV Spindle 4.

Table 3. Anionic / Amphoteric Interaction.

The first study was to evaluate the viscosity to determine the viscosity of the 50/50 blends. The results are shown in Table 4.

| | SLS/Amphoteric 50/50 | SLES-2 /Amphoteric 50/50 | |
|--------|----------------------|--------------------------|--|
| | Viscosity | Viscoisty | |
| | 6RPM | 6RPM | |
| A1 CAB | 31,500 | 3,500 | |
| A2 DAB | 14,000 | 14,500 | |
| A3 PB | Not Soluble | 3,500 | |
| A4 LAB | 4 | 13,400 | |
| A5 LP | 14,500 | 13,500 | |

Table 4. 50/50 Blend of Anionic / Amphoteric (10% Active each).

There are significant differences in the degree if interactions that occur between anionic surfactants and amphoteric surfactants depending upon the nature of the amphoteric surfactant studied. Alkyl betaines exhibit interaction but some become insoluble as the concentration approaches stoichiometric. Amidobetaines have strong interactions and better solubility often producing gels.

There are likewise differences in the degree and direction of the interactions that occur between amphoteric surfactants and SLS or SLES-2. The effect of going from SLS to SLES-2 is variable and determined by the exact solubility of the amphoteric evaluated.

VISCOSITY BY ADDITION OF SALT

One of the most interesting interactions that can be studied is the interaction between a surfactant and salt. The addition of salt to a surfactant results in a so-called "salt curve" (5). The salt curve relates to a graph on which salt added is plotted on the x axis and viscosity plotted on the y-axis. The concentration at which the highest viscosity reached is the concentration at which there is the greatest interaction. The mechanics of generating a "salt curve" is added salt in increments to an aqueous solution of surfactant and tracking the viscosity with each add. There will be an increase, but at a certain point the maximum viscosity will be reached, then the viscosity will drop. This is why the addition of water to a shampoo formulation might actually increase viscosity. Two salient attribute of the salt curve are important, the maximum viscosity and the amount of salt needed to reach it.

Test Methodology:

- 1. A 10% solution of anionic was prepared.
- 2. A 10% solution of amphoteric was prepared
- 3. A blend 75 anionic $\ensuremath{/} 25$ amphoteric by weight was prepared.
- 4. Viscosity was run at 6 rpm using a Brookfield viscometer LV Spindle 4.
- 5. NaCl was added in increments to build to peak viscosity.
- Both the peak viscosity and % NaCl added were recorded.

Table 5. Anionic / Amphoteric Interaction – Salt Addition.

Salt additions were made to the 10% active blends consisting of 75% anionic and 25% betaine to determine peak viscosity. This ratio was chosen for two reasons, first the viscosity of the 50 / 50 was already high in mot instances, and second the 25% amphoteric 75% anionic was more commercially interesting in terms of formulation cost. Increments of 0.5% salt were added at a time to a 10% active solution of the specified blend. The viscosity was measured after every addition @ 22.0 \pm 0.3° C using a Brookfield Synchro-lectric^R Viscometer.

| | SLS Materials | | SLES 2 Material | | | |
|----------|----------------|-----------------|-----------------|-------------------|-----------------|--|
| Material | Peak Viscosity | % NaCl Added | Material | Peak Viscosity | % NaCl Added | |
| DAB-SLS | 37,500 | 3.0 | SLES-2 | 25,000 | 5.5 | |
| COAB-SLS | 37,000 | 3.5 | LMAB-SLES-2 | 24,000 | 3.0 | |
| LMAB-SLS | 23,000 | 3.5 | DAB-SLES-2 | 19,250 | 2.5 | |
| PB SLS | 22,500 | 2.5 | COAB-SLES-2 | 15,750 | 2.0 | |
| SLS | 19,500 | 4.5 | PB-SLES-2 | 15,200 | 2.5 | |

Table 6. Salt Curve Summary.

The addition of betaine and salt to the SLS resulted in improved peak viscosity in all cases. Additionally, in all instances addition of betaine shifted the salt curve to the left. That is the amount of salt needed to reach peak viscosity dropped when betaine is present. In many instances the curve was also broadened. The presence of the conditioning betaine DAB actually increased peak viscosity and lowered the amount of salt needed to reach it in SLS systems.

The addition of amphoteric and salt to the SLES-2 resulted in lowering of the peak viscosity in all cases. LMAB decreased peak viscosity least. In all instances the addition of betaine shifted the salt curve to the left. That is the amount of salt needed to reach peak viscosity dropped when betaine is present. The inclusion of the conditioning betaine DAB provided good viscosity along with conditioning.

Formulation Tip

The formulator should always be on the outlook for unrecognized synergies between and among the ingredients in formulations. These interactions can drive formulation and cost.

B. FOAM DATA

Since in all instances the 50/50 had the highest viscosity, a 1% active solution of the 50/50 blend was subjected to the Ross miles test (6). The results are shown in Table 7.

INITIAL FOAM (FROM HIGHEST TO LOWEST)

The initial foam data is shown in Table 7.



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It was a surprise that SLS and SLES-2 alone have lower foam except for those mixtures with DAB, a conditioning material. This means there is a positive synergistic effect upon foam for all other amphoteric compounds except DAB. This result means there is a wide possibility to formulate products that have outstanding foam using blends of anionic and amphoteric. It also implies that the complex so formed has different foam properties than the SLSD or SLES alone.



This explains why amphoterics and in particular betaines are so commonly used in personal care formulation. They improve foam an attribute that is very important to the consumer.

Formulation Tip

The formulator is encouraged to investigate the properties of amphoteric and anionic surfactants including sulfosuccinates. Sulfosuccinate surfactants are becoming more prevalent as replacements for sulfates.

C. WETTING (FROM FASTEST TO SLOWEST)

Draves wetting (7) is a test that measures the amount of time it takes for a 1% solution of surfactant to cause a cotton skein to sink. Consequently, the lower the time required sinking, the better the wetting. The 50/50 blend of anionic to amphoteric was cut with water to 1% active. The wetting times are shown in Table 8.

The wetting times of the blends vary quite a bit depending upon the betaine used. The addition of all but the DAB material increased the wetting time of both SLS and SLES-2. The DAB products are much slower in terms of wetting time. This is not unexpected, since they are the most substantive products evaluated and provide outstanding conditioning not seen in combinations of anionic and other betaines. All SLES blends and SLS alone wet better than the SLES counter parts. In fact the type of sulfate drives wetting almost entirely.

Formulator Tip

The formulator should never underestimate the importance of

wetting to shampoo performance. Shampoos need to spread in an aesthetically appealing way on the hair, and wetting helps that spreading. Additionally, hair that has been shampooed with a formulation having a fast wetting time will blow dry more efficiently and the water is more easily removed (8).

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