Anionic/Cationic Complexes

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ABSTRACT: *Understanding the interactions of surfactants is important to optimizing their properties in formulations. The author describes how the anionic/cationic interaction is critical to properties such as foam, viscosity, conditioning properties and minimal irritation.*

There have been a multitude of approaches to the formulation of hair care products that provide multifunctional benefits. This partially is because the various functions expected from products do not coexist well in one formulation. Consumers demand cleansing, viscosity, foam, wet conditioning (antistat and wet comb) and longer-term conditioning (dry-property conditioning). It would be ideal if a universal surfactant existed that had just the right amount of each property so formulation would be easy, but there is none. Any step toward increasing the level of understanding related to the interaction of surfactants and providing optimized properties in formulation is desirable.

One major area in which interactions are critical is the anionic/cationic interaction. Most formulators of 2-in-1 shampoos understand that indiscriminate mixing of anionic and cationic materials can result in undesired insoluble "gunky" solids. Anionic and cationic materials that are incompatible when mixed together have been classified as *hard complexes.* As the expression implies, the cationic and anionic compounds possess properties that when added together form insoluble complexes such as salts. In contrast, anionic and cationic compounds that can be mixed over a wide range of ratios and provide a clear, viscous, high-foaming complex are defined as *soft complexes.* Optimized soft complexes have many desirable properties including high levels of foam, viscosity build without alkanolamides, conditioning properties, and low levels of eye and skin irritation.

The terms used for quats and anionic materials are an adaptation of the work of R. G. Pearson used to describe acids and bases. Pearson proposed that "hard acids bind strongly to hard bases and soft acids bind softly to soft bases;"[1] the anionic and cationic interactions of surfactants are exactly analogous.

Structural changes can "soften" cationic surfactant molecules, making them more compatible with anionic systems. The compatibility of specific quats with sodium lauryl sulfate (SLS) and sodium laureth-3-sulfate (SLES-3), the foam properties of the combinations with SLS and SLES-3, and the substantivity of these combinations with SLS and SLES-3 are key factors in understanding the function of conditioners.

In order to understand the interaction, several quats were studied (see Figure 1) in combination with SLS and SLES-3 (see Table 1). The entire work is published.[2]

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\begin{array}{c}
R^2 \\
| \\
R^1\text{-}N^+\text{-}R^3 \qquad Cl^- \\
| \\
R^2
\end{array}
$$

R^1:
1. Alkyl (C12)
2. Ricinoleylamidopropyl
3. Dilinoleylamidopropyl
4. Cocamidopropyl

R^2:
1. Methyl (CH_3)
2. 2-hydroxy ethyl (CH_2CH_2OH)

R^3:
1. Methyl (CH_3)
2. Benzyl (CH_2-C_6H_5)
3. Glyceryl (CH_2-CH(OH)-CH_2-OH)

Figure 1. Several quats were studied.

Test Methodology

A determination of compatibility of a variety of quats with the anionic surfactants, SLS and SLES-3 was made. A 100g sample of 10% active solution of SLS and SLES-3 was prepared, as was one for each of the quats evaluated. The 100g solution of sulfate was added to a 250-ml beaker and under good agitation the solution was titrated with the 10% quat solution. The endpoint was the first sign of (a) an insoluble complex, (b) haziness, or (c) viscosity build.

Results

The quats that were compatible with SLS or SLES-3 are shown in Table 2. All others in the study group were incompatible. The use of the proper quat with a given anionic will allow the formulator to maximize the performance of formulations.

Foam Testing

The solutions shown above were cut

Table 1. Compounds studied

Name	R^1	R^2	R^3	Description
AMB	Alkyl (C12)	CH_3	Benzyl	Coco dimethyl benzyl ammonium chloride
AME	Alkyl (C12)	CH_2CH_2OH	CH_3	Coco di-2 hydroxyethyl methyl ammonium chloride
AMG	Alkyl (C12)	CH_3	Glyceryl	Coco dimethyl glyceryl ammonium chloride
AMM	Alkyl (C12)	CH_3	CH_3	Coco tri-methyl ammonium chloride
AEB	Alkyl (C12)	CH_2CH_2OH	Benzyl	Coco di-2 hydroxyethyl benzyl ammonium chloride
AEG	Alkyl (C12)	CH_2CH_2OH	Glyceryl	Coco di-2 hydroxyethyl glyceryl ammonium chloride
CaMB	Castor Amido	CH_3	Benzyl	Ricinoleylamidopropyl dimethyl benzyl ammonium chloride
CaMG	Castor Amido	CH_3	Glyceryl	Ricinoleylamidopropyl dimethyl glyceryl ammonium chloride
DMB	Dimer Amido	CH_3	Benzyl	Dilinoleylamidopropyl dimethyl benzyl ammonium chloride
DMG	Dimer Amido	CH_3	Glyceryl	Dilinoleylamidopropyl dimethyl glyceryl ammonium chloride
DMM	Dimer Amido	CH_3	CH_3	Dilinoleylamidopropyl trimethyl ammonium chloride
MMB	Cocamido	CH_3	Benzyl	Cocamidopropyl dimethyl benzyl ammonium chloride
MMG	Cocamido	CH_3	Glyceryl	Cocamidopropyl dimethyl glyceryl ammonium chloride
MMM	Cocamido	CH_3	CH_3	Cocamidopropyl trimethyl ammonium chloride

Table 2. Soft quats—gel formers

Quat Sample	Soft quats in SLS (viscosity of gel)	Quat Sample	Soft quats in SLS-3 (viscosity of gel)
MMB	14,000	AME	7,000
MMM	13,400	DMM	6,200
DMM	6,000	MMM	50,000
CaMB	1,000	CaMB	1,000
MMG	19,200	AMG	1,000
DMG	12,000	MMB	9,800
		MMG	40,000
		DMG	6,800
		AEG	1,000
		CaMG	1,000

Table 3. Foam heights (cylinder shake foam test)

Quat sample	Foam height (ml) (SLS)	Foam height (ml) (SLES-3)
AMB	Does not foam	Does not foam
AME	190	90
AMG	500	400
AMM	600	500
AEB	300	200
AEG	200	100
CaMB	250	150
CaMG	200	100
DMB	400	300
DMG	300	200
DMM	250	150
MMB	400	300
MMG	400	300
MMM	400	300
Control (no quat)	600	450

with water to 1% active and evaluated in cylinder shake foam tests. The foam data is shown in Table 3.

Conclusions

Quaternium compounds can be classified as hard or soft by their ability to form gelled systems with anionic systems. Cationic systems that form a gel at near stoichiometric amounts are classified as *soft* quats; those that form precipitates of haze without appreciable viscosity build-up are classified as *hard* quats. Soft quats can produce foam in the systems they gel, albeit at levels below the volume of foam generated by the anionic, per se.

Quaternium compounds titrated with SLES-3 produced greater viscosities with amido quats. The exception was amido quats containing a benzyl group that exhibited a low viscosity in SLES-3.

Good foaming results also were seen with a number of complexes. Additional work needs to be performed to expand the testing to a variety of compounds including silicone-based compounds.

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References

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