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Anionic/cationic interactions

Abstract As formulators we are told that "oil and water don't mix" and "anionic and cationic compounds are incompatible". While these broad statements are generally helpful, they should neither be taken as absolute truth or limit creativity in formulation research. We know that oil and water can mix, if the proper emulsifier is added and the right homogenization process is followed. As for the incompatibility of anionic and cationic compounds, this rule is not absolute. Properly chosen cationic and anionic surfactants when combined will not only produce clear systems, but systems that have good foam and good substantivity to hair.

Formulator Tip

Use general rules as guidelines, none are absolute truths.

It is always amazing that cosmetic formulators can put together very sophisticated products that contain many different raw materials. These materials all interact with each other sometimes in unpredictable ways. The interactions that occurs when combining the raw materials used in the formulation of personal care products is more than the sum of the properties of each of the raw materials.

There are a number of complex interactions that occur in the most simple formulation. These interactions 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 interactions of ingredients in those formulations.

SURFACTANT INTERACTIONS

Surfactants are present in almost all formulations, in reasonably high concentrations, generally between 5 and 25% actives by weight. The types of surfactants based upon charge are shown in Table 1(1). Surfactants interact with each other and other ingredients present in formulation including salt, preservatives and others.

Perhaps, the most commonly understood interaction between surfactants are anionic and cationic interactions. A dilute aqueous solution of stearalkonium chloride mixed with sodium lauryl sulfate a white, pasty gunk. This observation is why one generally avoids putting an anionic and cationic

surfactants together. However, there are instances where one might well want the effect of having both an anionic and cationic present in the same formulation, for example a two in one shampoo, where the anionic cleans and the cationic conditions.

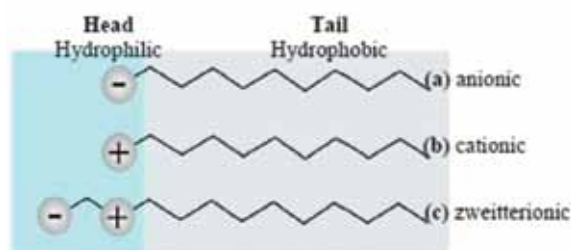


Table 1. Types of Surfactants¹.

There are some cationic surfactants mixed with anionic / cationic surfactants that are soluble (visually clear combinations), even at stoichiometric concentrations (2). This observation allows for classification of two types of quats, one hard and the other soft. Hard quats were those products which were incompatible with anionic surfactants. Soft quats on the other hand, were defined as those quats that formed thick, clear, high foaming complexes with anionic surfactants.

Surfactant molecules interact with the solvent molecules around them. Typically when discussing surfactants, the

solvent is water. In order to be soluble in water, the surfactant molecules need to hydrogen bond with the water molecules. Ionic surfactants contain a charge, either positive or negative, that is capable of forming these hydrogen bonds with water molecules. When mixing ionic surfactants, it is important to consider the interactions of not only surfactant / water but also surfactant / surfactant interactions. When there is a mixture of positive and negative surfactants, the positive and negative charges on the surfactants can interact with one another. If the positive / negative interaction is strong (greater than the interaction of surfactant / water), the two surfactant molecules will prefer to interact with each other and not with the surrounding water molecules. This creates "shielding" of the charges from the water molecules and the surfactant can lose solubility in water. This is seen in Hard Complexes (HC), the turbidity of the solution is a result in the positive / negative interaction being stronger than the surfactant / water interactions (hydrogen bonds). As the solubility decreases, the particles start to scatter light leading to turbidity. The turbidity is clearly shown under laser light. If the positive / negative interaction is weak (less than the interaction of surfactant / water) the solution will remain clear and no surfactant precipitation will occur. The difference between the two is shown in Table 2.

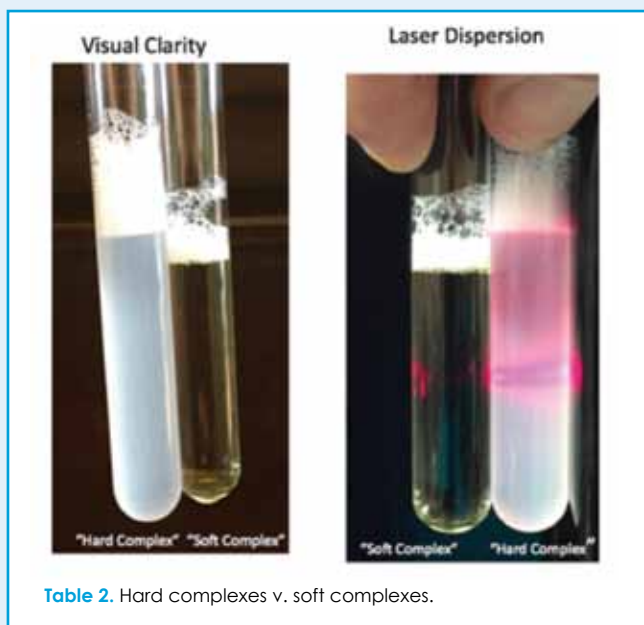


Table 2. Hard complexes v. soft complexes.

The difference between the two types of complex is the "solubility" of the particular anionic and cationic materials when paired up. It will be understood that when a blend of anionic and cationic surfactant is made, all ions of the combination dissociate in solution and the overall effect is a broad mix of the ions. Each will organize in the lowest free energy, and if that arrangement is soluble in water, a clear solution that does not disrupt a laser will occur.

It is the nature of this complex rather than the properties of the surfactants themselves that determines how the formulations function. As ionic materials are added to water, opposite charges attract and the same charges repel.

As the concentration of point charges are increased, the solution becomes so ordered that either (a) the solubility

product of the salt is exceeded and a precipitate occurs, (b) The viscosity of the solution increases or (c) the complex becomes turbid showing insolubility. This type of insolubility needs to be distinguished from the solubility of the raw materials themselves in water. That is the insolubility is the insolubility of the combination of ingredients not pure the ingredients. The insolubility is due to the so called shielding of charges that occurs.

The white sticky solid that results in blending stearylamine chloride and sodium lauryl sulfate gives an example of what we refer to hard complexes. As the expression implies the cationic and anionic compound possess properties which when added together form insoluble complexes (salts).

1963 : Ralph Pearson introduced the hard-soft-acid-base (HSAB) principle.

"Hard acids prefer to coordinate the hard bases and soft acids to soft bases".

This very simple concept was used to rationalize a variety of chemical information, as an attempt to unify inorganic and organic reactions.

1983 : By Ralph Pearson and Robert Parr, the qualitative definition of HSAB was converted to a quantitative one by using the idea of polarizability.

A less easily polarized atom or ion is "hard" and a more easily polarized atom or ion is "soft"

Table 3. Pearson hard and soft acids and bases³.

The terms used here for quats and anionic materials are an adaptation of the work of Pearson² used to describe acids and bases. Pearson proposed that "hard acids bind strongly to hard bases and soft acids bind softly to soft bases". Table 3 provides a time line for the development of Pearson's theory.

If different structures could be more developed that have increased solubility in anionic / cationic combinations such surfactants could have functionality in formulations.

The chemical structure of each determines the hardness or softness of the complex. As a 10% active cationic surfactant is titrated into a 10% active solution of an anionic, like sodium lauryl sulfate, more and more of the cationic surfactant complexes with the anionic. As the number of anionic and cationic species becomes equal, the number of interaction complexes will be greatest and at the same point, the concentration of uncomplexed surfactant becomes lowest. It is for this reason that the highest viscosity of the blends of anionic and cationic surfactant occurs at roughly equal amounts based upon molecular weight.

ANIONIC CATIONIC INTERACTIONS

The structural changes that can be made to cationic molecules can "soften" them, making them more compatible with anionic systems. Alternatively, there should also be the possibility of developing an anionic material that has increased compatibility with cationic surfactants, perhaps a more highly ethoxylated sulfate or a sulfosuccinate.

However, this concept of modifying the anionic, is a topic for another investigation.

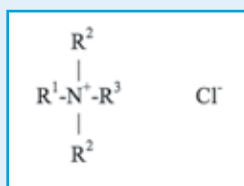
A study was undertaken to determine (1) compatibility of specific quats with SLS and SLES, (2) foam properties of the combinations with SLS and SLES (3) substantivity of these combinations with SLS and SLES and (4).

The quats studied are outlined in Table 4.

The generic chemical structure of the cationic compounds studied are:

Name	R ¹	R ²	R ³	Description
AMB	Alkyl (C12)	CH ₃	Benzyl	Coco dimethyl benzyl ammonium chloride
AME	Alkyl (C12)	CH ₂ CH ₂ OH	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 ₂ CH ₂ OH	Benzyl	Coco di-2 hydroxyethyl benzyl ammonium chloride
AEG	Alkyl (C12)	CH ₂ CH ₂ OH	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 4. Compounds Studied².



The preferred definitions for the study groups are:

- R¹
1. Alkyl (C12)
 2. Ricinoleylamidopropyl
 3. Dilinoleylamidopropyl
 4. Cocamidopropyl

- R²
1. Methyl -CH₃
 2. 2-hydroxy ethyl - CH₂CH₂OH

- R³
1. Methyl -CH₃
 2. Benzyl -CH₂-C₆H₅
 3. Glyceryl -CH₂-CH(OH)-CH₂-OH

(A) COMPATIBILITY WITH ANIONIC SURFACTANTS

A determination of compatibility of a variety of quats with two anionic surfactants, sodium lauryl sulfate and sodium laureth-3-sulfate was made. The compatibility is determined by titration. The point at which an anionic solution containing 10% anionic either became hazy formed a precipitate was determined.

CALCULATIONS

$$\% \text{ QUAT ADDED} = \frac{\text{GRAMS OF QUAT ADDED}}{(50 + \text{GRAMS OF QUAT ADDED})} \times 100$$

The quats that showed the best compatibility and gellation properties with sodium lauryl sulfate were the amido quats. The only exception was the amido quat that contained an aromatic group (DMB).

There was improved compatibility with sodium laureth-3-sulfate when compared to sodium lauryl sulfate. This leads to the conclusion that SLES is a softer anionic than SLE

All quat compounds reached a cloud point when titrated into anionic. However, the amount necessary to reach the haze point was different and the nature of the end point were different. The so-called hard quats have very little tolerance for anionic, forming insoluble precipitates with very little addition. Quaternary compounds having intermediate hardness show compatibility with anionic surfactants at near stoichiometric amounts, but do eventually haze. Soft quats do not exhibit a haze, but rather show a clear gel.

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AMB	9.75	<10	Did not form a gel
AME	6.28	<10	Did not form a gel
AEB	14.58	<10	Did not form a gel
AMM	17.63	<10	Did not form a gel
DMB	18.33	<10	Did not form a gel
AEG	29.53	<10	Did not form a gel
AMG	30.49	<10	Did not form a gel

Table 5. Titration data (SLS) soft quats gel in sodium lauryl sulfate.

Quat Sample	Notes
AMB	Did not form a gel
AMM	Did not form a gel
AEB	Did not form a gel
DMB	Did not form a gel

Table 6. Titration data (SLS) hard quats no gel in sodium lauryl sulfate.

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AME	4.47	7,000	Formed a gel
DMM	20.00	6,200	Formed a gel
MMM	20.23	50,000	Formed a gel
CaMB	24.31	1,000	Formed a gel
AMG	25.04	1,000	Formed a gel
MMB	25.00	9,800	Formed a gel
MMG	26.68	40,000	Formed a gel
DMG	28.37	6,800	Formed a gel
AEG	38.72	1,000	Formed a gel
CaMG	46.23	1,000	Formed a gel

Table 7. Soft quats - Gel in sodium laureth-3-Sulfate.

Quat Sample	Notes
AMB	Did not form a gel
AMM	Did not form a gel
AEB	Did not form a gel
MMG	Did not form a gel
DMB	Did not form a gel
AEG	Did not form a gel
AMG	Did not form a gel

Table 8. Titration data (SLES) hard quats – no gel in sodium laureth-3-sulfate.

(B) FOAM HEIGHT AND STABILITY



Table 9. Cylinder Shake Foam Test (5).

The foam evaluation studies were done using the cylinder shake foam test (5)

It has been generally assumed that a gel made using anionic and cationic in combination would not foam due to incompatibility. An evaluation of the gelled system mentioned above was undertaken.

Quat solutions titrated with sodium lauryl sulfate (SLS) produced higher levels of foam than those titrated with sodium laureth sulfate (SLES). However, the quat solutions that were titrated with SLES exhibited greater foam stability than those titrated with SLS. In some cases the quats titrated with SLES had a half-life greater than 24 hours (1440 minutes), including the control. After running all controls, it can be concluded that the

addition of quaternium compound had a negative effect on the foaming capabilities of SLS and SLES. Stock SLS produced a foam height of 600mL, while the average foam height produced from quat/SLS was around 250mL.

Quat AMB (SLS) produced no foam. Unlike all the other quats that were titrated with SLS, which formed translucent, cloudy, gels at their respective cloud points, quat AMB produced a white, opaque paste. This is evidence that a complex is forming between this quat and SLS. This did not occur when quat AMB was titrated with SLES.

Quat AMM and MMM performed superior in SLS and SLES compared to all the samples tested, including the controls. AMM showed superior foaming capabilities, by achieving the

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

Table 10. Foam of complexes cationic / SLS or SLES (1% Active).

greatest foam height in SLS, as well as having one of the best foam stabilities in SLES. This stability was roughly ten times greater than all other quats and controls tested, with the exception of AEG, CaMB, MMG, and MMM, which all had foam stabilities. It can be concluded that these quaternium compounds did not have a great effect on the expected foaming capabilities of SLS or SLES, with the exception of AMM and MMM. These two quat solutions increased foam stability by a factor of ten without suppressing foam height.

CONCLUSION

Quaternium compounds can be classified as hard or soft by their ability to form clear systems with anionic systems. Cationic systems that form a gel at near stoichiometric amounts are classified as "soft", those that form precipitates of haze without appreciable viscosity build 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 sodium laureth sulfate (SLES) produced greater viscosities with amido quats. The exception was amido quats containing a benzyl group, which exhibited a low viscosity in SLES. Compounds that contained a benzyl group, or were an alkyl rather than amido, (i.e. AMB, AME, AMG, AMM, AEB, AEG), precipitated at lower levels of titration and are consequently classified as "hard quats".

Overall, all quat/anionic solutions tested had less foam than when the anionic itself was tested. This was true for both SLS and SLES. With the exception of quats AEG, AMG, and CaMG, and the negative control, all 0.5% active, aqueous solutions of quaternium compounds produced positive results for cationic substantivity, when evaluated per se.

Quat MMM concluded to be the best performer, yielding a thick, translucent gel with a viscosity well over 10,000 cps for both SLS and SLES titrations. MMM/Anionic Solutions produced an above average foam height without suppression and extended foam stability well over 24 hours or, ten times greater than SLS and SLES, controls, and positive controls (polyquaternium 10 and SLS/SLES). MMM performed equally as well in substantivity tests when delivered from an aqueous system. Like all other quat solutions, no substantivity was observed when delivered from an anionic mixture.

Because of its performance, MMM was chosen for subjective and combing analysis.

Like quats DMG and MMG, quat MMM performed poorly in the wet combing test. However it did perform slightly better in the dry combing test. Quat MMM turned out to perform the best in the instrumental analysis of combing force, part VI. The average performance of quat MMM was superior to all quats in this study.

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