Synergistic Interactions of Shampoo Ingredients

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ABSTRACT

Certain pairs of surfactants interact in relatively concentrated aqueous solutions to give unexpectedly high viscosity. When nonsurfactant substances are added to such a surfactant pair, there may be either a further increase in viscosity or a decrease. Results of detergency tests of one surfactant pair in varying proportions are given.

INTRODUCTION

Most useful preparations for critical applications such as hair shampoos are made up of a number of ingredients, and usually each ingredient performs a different, specialized function, i.e., cleaning, foam boosting, hair conditioning, etc. Other ingredients may be added to impart or enhance certain pre-use properties of the product. These include clarity, color, fragrance and viscosity.

Formulators of shampoos must deal with the problem of incompatibility or antagonism between ingredients, which often makes it difficult to achieve a high level of performance in all properties simultaneously. The antagonism may result in precipitation or separation, at which point the formulator may add yet another ingredient to restore compatibility. The antagonism may result in the nullification of a desirable property, as in the case of the negative effect of an anionic surfactant on the germicidal activity of a quaternary ammonium surfactant (1).

There are also cooperative interactions of ingredients, as when the activity of one ingredient is increased by the addition of another, different ingredient which by itself does not possess this power. Such a case is the increased surface activity of an ionic surfactant when electrolytes are added.

It is usually preferable that the number of ingredients be held to a minimum and it is therefore advantageous when two ingredients, each added for a specific purpose, interact to produce a third desirable effect without the need to add a third ingredient. This paper discusses the interaction of pairs of surfactants of different chemical types often used in shampoos where the combination gives a much higher viscosity than is given by either separate surfactant. This extra property advantage, provided by the cooperation of two ingredients which had been selected for another property, may be considered a type of synergism.

VISCOSITY EFFECTS OF SURFACTANT PAIRS

The effect of increased viscosity was first noticed in these laboratories for combinations of Sandopan TFL Conc.® and sodium lauryl sulfate. Sandopan TFL Conc. is a sulfonated fatty amideamine surfactant which has in its chemical structure both basic (amine) and acidic (sulfonate) functions. Solutions of equal concentrations of the two surfactants show a maximum viscosity, as seen in Figure 1. Solutions containing 18% active substance Sandopan TFL Conc. are slightly more viscous than those with 16.5% or 15%; but as sodium lauryl sulfate is added in place of Sandopan TFL, the viscosity of mixtures of constant total concentrations of combined surfactants rises to a maximum in the range of 40-50% sodium lauryl sulfate, and then rapidly falls to a low level for 100% sodium lauryl sulfate. The magnitude of the viscosity increase is 6.7 times for the solutions of 15% concentration, 43 times for 16.5% and 167 times for 18%.

This viscosity synergism effect varies somewhat with the brand of sodium lauryl sulfate used, as shown in Table I. One of the reasons for this is that there may be different amounts of salt in the commercial sodium lauryl sulfates used. This was tested by adding varying amounts of sodium chloride or sodium sulfate to a solution of Sandopan TFL Conc. and sodium lauryl sulfate. As shown by the data given graphically in Figure 2, each salt produces a pronounced thickening action, increasing with added salt up to a point, after which the viscosity again is less. Less sodium chloride (1%) than sodium sulfate (2.8%) is required for the maximum effect.

Other possible sources of variation of composition of commercial sodium lauryl sulfate were not investigated. These include differences in carbon chain length, carbon chain distribution and the presence of small amounts of unsulfated alcohol.

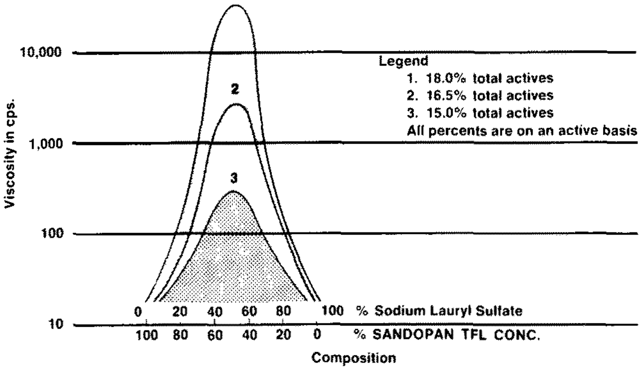

FIG. 1. Synergistic viscosity build-up of Sandopan TLF Conc. with sodium lauryl sulfate.

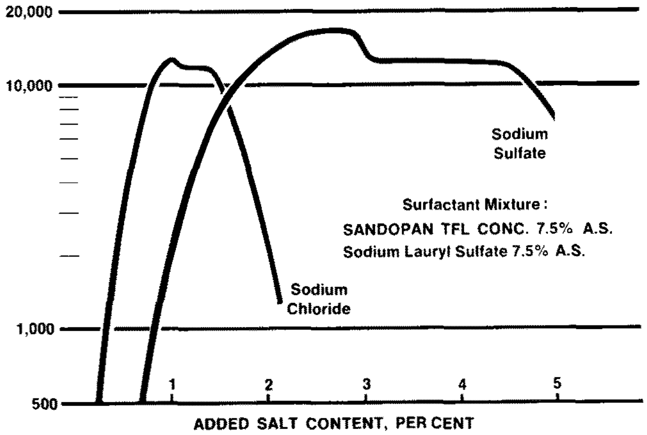

FIG. 2. Effect of added salt on viscosity (in centipoises).

TABLE I

Viscosity of Solutions of Surfactant Pairs

Surfactant	Composition, % active substance A	B	C	D	E	F
SANDOPAN TFL CONC.	8.25	8.25	8.25	8.25	---	16.5
Sodium lauryl sulfate						
Brand M	8.25	---	---	---	---	---
Brand R	---	8.25	---	---	---	---
Brand CN	---	---	8.25	---	---	---
Brand CS	---	---	---	8.25	16.5	---
Viscosity, centipoise	6,500	560	740	5,360	15	16

TABLE II

Viscosity Increase of Surfactant Pairs
SANDOPAN TFL CONC. With Various Surfactants

Surfactant	Viscosity increase
Sodium lauryl sulfate	Large
Ammonium lauryl sulfate	Large
Sodium dodecylbenzene sulfonate	Large
Triethanolamine lauryl sulfate	Small
Sodium coco methyl taurate	Very small
Sodium lauryl ether sulfate	Very small
Ammonium lauryl ether sulfate	None
Sodium lauroyl sarcosinate	None

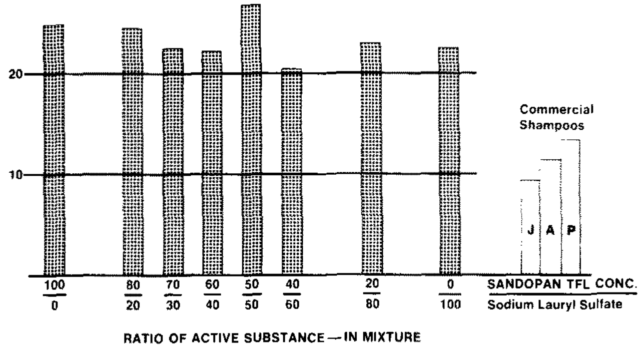

FIG. 3. Detergency of surfactant pair; per cent wool grease removal.

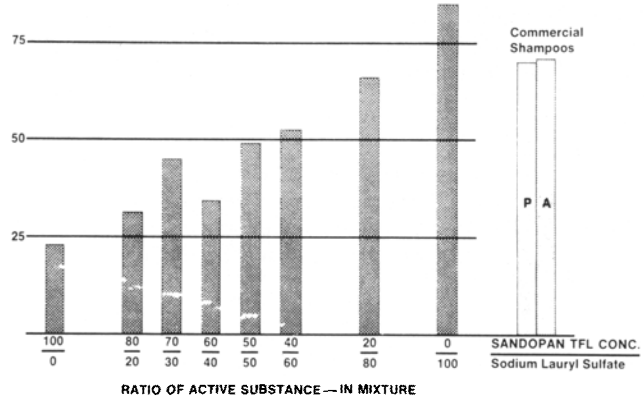

FIG. 4. Detergency of surfactant pair; per cent soil removal from wool soil cloth.

TABLE III

Viscosity Increase of Surfactant Pairs
Sodium Lauryl Sulfate With Various Surfactants
(8.25% A.S. of each surfactant)

Surfactant	Viscosity increase
SANDOPAN TFL CONC.	Large
Coco-imidazoline carboxymethylate	Large
Coco-imidazoline dicarboxymethylate	Very large
Coco-diethanolamide 1:1	Small
Betaine	Incompatible
N-Coco-beta-amino propionate	Incompatible

Other pairs of surfactants were investigated for viscosity synergism. Replacement of sodium lauryl sulfate by another surfactant gave a similar viscosity increase in some cases and not in others, as shown in Table II. Table III shows that other surfactants in combination with sodium lauryl sulfate sometimes show a large viscosity increase, whereas some do not make clear solutions.

DETERGENT PROPERTIES OF SURFACTANT PAIRS

It might be expected that any interaction between Sandopan TFL Conc. and sodium lauryl sulfate capable of causing such a great change in viscosity could affect other properties. As these two ingredients are both detergent surfactants and would be used in a shampoo for their cleaning power, it was of interest to investigate the detergency of mixtures. As the results in Figure 3 show, there is very little difference in the detergency, as measured by removal of wool grease from unscoured sheep's wool, of either surfactant or any of their mixtures. Grease content, before and after washing, was determined by solvent extraction. At this low concentration of 0.1%, the detergency of three commercial shampoos was about half as strong.

Testing detergency by another method (soil removal from wool fabric printed with standard soil) gave a different pattern but still no indication of a synergistic effect of the two ingredients. As is shown in Figure 4 sodium lauryl sulfate is a stronger detergent than Sandopar TFL Conc. in this test, but mixtures of the two surfactant

TABLE IV

Effect of Third Ingredients on Mixture of
SANDOPAN TFL. CONC. With Sodium Lauryl Sulfate

Ingredient	Composition, % (Balance: Water)							
SANDOPAN TFL	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Sodium lauryl sulfate	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Hexylene glycol	---	9.9	---	---	---	---	---	---
Propylene glycol	---	---	9.9	---	---	---	---	---
PEG 600	---	---	---	9.9	---	---	---	---
Pentaerythritol	---	---	---	---	9.9	---	---	---
Glycerol	---	---	---	---	---	9.9	---	---
Sucrose	---	---	---	---	---	---	9.9	---
Sorbitol	---	---	---	---	---	---	---	9.9
Viscosity, centipoise	380	8	60	24	388	950	4,300	3,520

gave detergency roughly proportional to the compositions. Detergency of two commercial shampoos was about equal to sodium lauryl sulfate, when measured by this method.

EFFECT OF A THIRD INGREDIENT

The surfactant pair Sandopan TFL Conc.-sodium lauryl sulfate may be made into a complete shampoo by the addition of other ingredients for such purposes as foam boosting, hair control, fragrance, etc. In addition it may be necessary to add cosolvents or other inert ingredients as well as components to lower the cost. Formulations with equal amounts of Sandopan TFL Conc. and sodium lauryl sulfate were made which contained various diols and polyols. As shown in Table IV, the polyols glycerine, sorbitol and sucrose produce a further rise in viscosity, whereas the diols propylene glycol, hexylene glycol and polyethylene glycol drastically interfere with the viscosity synergism between Sandopan TFL and sodium lauryl sulfate. It has not been possible to predict with certainty the viscosity effect of a third ingredient, but the following produced an increase: hexachlorophene, lauryl isoquinolinium bromide, N-alkyl, dimethylbenzyl ammonium chloride and N-(stearyl colamino formyl methyl) pyridinium chloride.

THEORETICAL ANALYSIS

An attempt should be made to explain the viscosity behavior of surfactant pairs, even though it is apparent from the foregoing report that the situation is not simple. Evidently the viscosity increase observed for Sandopan TFL and sodium lauryl sulfate involves formation of a complex or aggregate involving pairing of the two surfactants of different chemical structure. Although the structure of surfactant micelles in very dilute solution has been well studied by X-ray diffraction and other means, little is available concerning the structure of concentrated solutions. It may be that relatively concentrated solutions (10-20% w/w) of surfactants are composed of noninteracting micelles with hydrophobic cores and hydrated, ionically charged surfaces, repelling one another by reason of like charges; and that when micelles of two types of surfactant have a weak affinity for one another, they form aggregates without precipitating and increase the viscosity. If the attraction is too strong, incompatibility is observed. If too weak, there is no viscosity increase.

To explain the effect of diols on synergistic viscosity build-up we suggest that the diol associates with the surfaces of the micelles of one or both of the surfactants, reducing its availability to associate with the other type of micelle. It is highly likely that both types of micelle are involved because of the observed fact that glycerol and other polyols seem to increase the degree of aggregation, suggesting that the polyols form "bridges" from one micelle to another.

ACKNOWLEDGMENT

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REFERENCE

1. Lawrence, C.A., and M. Bond, J. Amer. Pharm. Ass. Sci. Ed. 37:57 (1948).

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