Alcohol Ether Sulfates in Shampoos[1]

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Abstract

Mono-, di- and triethanolamine sulfates of several different molecular weight alcohol ether sulfates were formulated into shampoos. The ethylene oxide content of the alcohol ethoxylates varied from about 20 to 60%, although 40% was usual. The shampoo formulation was 20% active ether sulfate and 5% foam stabilizer. Lauric diethanolamide and amine oxides were used as foam stabilizers.

The shampoos were tested for quality and quantity of foam, viscosity and cloud point. Although no "hair effects" tests were run, a limited home use test was made.

Alcohol ether sulfate shampoos are equal or superior to several popular commercial products on the basis of a laboratory foam test. They are comparable in foam to alcohol sulfates in similar formulations. Cloud points of these shampoos were generally good. Amine oxide foam stabilizers reduced the cloud point more than the amide. Viscosities of the shampoos were readily controllable. Although the choice of alkanolamine, alcohol molecular weight and degree of ethoxylation had some effect on these properties, none were highly critical; this allows considerable leeway in their selection. The home use tests assured us that these shampoos were not obviously deficient in the desired "hair effect" properties. The literature records that alcohol ether sulfates are preferred to alcohol sulfates for low skin and eye irritation.

By varying the free oil (unsulfated ethoxylate) content and making the proper choice of ether sulfate and foam stabilizer, bright and clear liquid shampoos with viscosities from about 10 centipoise to over 50,000 centipoise were made. The latter are essentially gels. Paste shampoos were also made from these ether sulfates.

Introduction

THIS WORK EVALUATES the potential use of ether sulfates in place of alcohol sulfates in shampoos. The effect on foam, cloud point and viscosity from different amines, i.e., mono-, di- or triethanolamine as the base, the ethylene oxide content of the ethoxylate, alcohol molecular weight changes in the hydrophobe, the foam stabilizer used and the unsulfated matter level were studied. The reported lower skin irritation of ether sulfates (1,2) suggests that this basic information will be useful in designing improved shampoo formulations.

Experimental Procedures

Test Procedures

Foam is of primary interest in evaluating shampoo formulations. Our foam test is run by stirring 200 ml of a 5% solution of the shampoo in a liter beaker for 1 min with the revolving brush. If hair clippings are to be used, 2 g are placed in the solution before stirring. A qualitative and quantitative evaluation of the foam is made immediately and another is made after the foam stands for several minutes. The evaluation comprises visual paired comparisons among products tested within a short period of time.

Originally we ran the foam test by stirring a 5% solution of the shampoo with a mixmaster. Then in an attempt to get quantitative foam measurements, a method using a revolving brush in a graduated cylinder was used. It soon became evident that foam quantity was less meaningful than quality. Consequently, the graduate was replaced with a beaker and we were essentially right back where we started. Although foam testing is somewhat subjective by this method, reasonable estimates of both foam quality and quantity can be made.

Soil in the form of hair clippings can be added to observe its effects on foam. In addition, the hair clippings serve to increase the sensitivity of the test. The hair clippings have a strong foam depressing effect and exaggerate differences between samples. This means that if differences are not noted between samples run without hair the addition of hair may show differences. Thus samples are usually tested without hair clippings first and then rerun with the hair clippings if no differences are seen.

A major disadvantage to the use of hair clippings is the lack of homogeneity which makes replicate runs necessary. This defect can be somewhat reduced by chopping and mixing the hair as much as practical. The use of a synthetic soil might be even more practical.

In addition to foam, we measured viscosity and cloud point of the shampoo. Viscosity measurements were made with a Brookfield Viscometer. Cloud point, a measure of solubility, was determined by cooling in a jacketed tube in an isopropanol-dry ice bath with constant agitation until a cloud formed.

Although no "hair effect" tests were run, a limited home use test elicited favorable reports, assuring us that these shampoos were not obviously deficient.

Sample Preparation

The mono-, di- and triethanolamine sulfates used in this work were made by sulfating the ethoxylate with chlorosulfonic acid and neutralizing with the desired alkanolamine. 1.03 mole of the acid is added to a mole of ethoxylate in a three-neck Morton flask equipped with a stirrer. The reaction product is poststirred and blown with dry air or nitrogen 10

TABLE I

Foam of Shampoos Containing 20% Ether Sulfate, 5% Foam Stabilizer

Hydrophobe[a]	Base	Foam stabilizer: None	Foam stabilizer: Lauric diethanolamide	Foam stabilizer: C_{14} Alkyldimethyl amine oxide
C_{1014}	TEA	....	Very good	Excellent
C_{1214}	TEA	....	Very good	Excellent
C_{1412}	TEA	Good	Very good	Excellent
C_{1412}	DEA	Good	Very good	Excellent
C_{1412}	MEA	Good	Very good	Excellent
C_{1412}	MEA	C_{12} alkyldimethyl amine oxide		Very good
Commercial shampoo "P"			Excellent	
Commercial shampoo "H"			Very good	
Commercial shampoo "B"			Fair to good	

[a] All ethoxylates had 40% ethylene oxide.
1014 is 30% C_{10}, 40% C_{12}, 30% C_{14} alcohol blend.
1214 is 55% C_{12}, 45% C_{14} alcohol blend.
1412 is 35% C_{12}, 65% C_{14} alcohol blend.

[1] Presented at the AOCS Meeting, Chicago, October 1967.
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TABLE II

Effect of Ethylene Oxide Content on Foam of 20% Active/5% Foam Stabilizer Shampoo

% EO	TEA C_{1214} alcohol ether sulfate	
	Foam stabilizer	Foam with soil
11	LDEA	Excellent
28	LDEA	Very good
40	LDEA	Very good
60	LDEA	Good
11	C_{14} amine oxide	Excellent
28	C_{14} amine oxide	Excellent
40	C_{14} amine oxide	Excellent
60	C_{14} amine oxide	Excellent

min to facilitate the removal of HCl. The acid is neutralized by pouring into the selected alkanolamine, observing the usual precautions.

The ether sulfates had a pH from 7.0–7.5 and were 30% aqueous solutions or 40% active pastes. The unsulfated compounds, except where noted, were 3.5–5.0% based on active content.

The shampoo formulation contained 20% active sulfate and 5% foam stabilizer. The ingredients were combined and stirred until dissolved. Heat is helpful in effecting solution.

Discussion

Foam

The foam of three popular commercial shampoos were run to provide a basis for comparison. Differences among the commercial products could be observed by feel, bubble size, stability, thickness and viscosity of the foam.

Among the first objectives in evaluating ether sulfates in shampoos was to observe differences caused by the foam stabilizer and compare experimental formulations with commercials.

The data in Table I show that the foam stabilizer has a significant effect on foam. The use of lauric diethanolamide showed a noticeable improvement in foam quality. Tetradecyl dimethyl amine oxide is even more effective, giving an extremely luxurious foam, comparable to the foam produced by the best commercial shampoo we observed. Dodecyldimethyl amine oxide is only about as effective as the lauric diethanolamide. The term "very good" describing the amide stabilized samples is descriptive of the second best commercial shampoo as based on our foam preference. These data show that the use of different alkanolamine as the cation has no effect on foam stability or less than can be detected by the foam test used. Similarly the alcohol base used for the ether sulfate had no effect on foam. Thus from the foam quality standpoint there is considerable latitude in the selection of the alkanolamine ethoxy sulfate and such a selection could be based on factors outside of foam performance.

The ethylene oxide content of the ethoxysulfate affects the foam of the shampoo. The data in Table II show that increased ethoxylation has an adverse effect on foam when lauric diethanolamide is the stabilizer but not when tetradecyl dimethyl amine oxide is used. This points out the importance of considering the entire formulation when evaluating one variable.

TABLE III

Effect of Foam Stabilizer on Shampoo Cloud Points, °F

Hydrophobe[a]	Alkanolamine	Foam Stabilizer		
		None	LDEA	C_{14} Amine Oxide
C_{1014}	TEA		30	56
C_{1214}	TEA		30	68,64
C_{1214}	DEA		30	55
C_{1214}	MEA		30	50
C_{1412}	TEA	30	30	70
C_{1412}	DEA	30	30	56
C_{1412}	MEA	30	32	47
	Commercial "P"	40		
	Commercial "H"	23		
	Commercial "B"	22		

[a] All ethoxylates had 40% ethylene oxide. See Table I for alcohol distribution in blends.

TABLE IV

Effect of Free Oil on Cloud Point of Shampoo

Hydrophobe[a]	Alkanolamine to neutralize ES	Foam stabilizer	Cloud point, °F	
			High free oil[b]	Low free oil[b]
C_{1014}	TEA	LDEA	29(14.0)	30(5.0)
C_{1014}	TEA	C_{14} Amine oxide	63(14.0)	56(5.0)
C_{1214}	TEA	LDEA	27(40.5)	30(4.7)
C_{1412}	DEA	LDEA	24(14.5)	30(10.4)
C_{1412}	DEA	C_{14} Amine oxide	58(14.5)	56(10.4)

[a] All ethoxylates have 40% ethylene oxide. See Table I for alcohol distribution of blends.
[b] Values in parentheses are free oil/active levels for the ether sulfates.

Solubility

The foam stabilizer used has a great effect on the cloud point of the shampoo. All of the shampoos made with lauric diethanolamide have cloud points below 32F. There is no apparent effect from the other variables. Tetradecyl dimethylamine oxide stabilized shampoos have cloud points above freezing and effects of the other variables on cloud point can be seen. In Table III we see that monoethanolamine sulfate shampoos have the lowest cloud point while the triethanolamine gives the highest. Also there is an increase in cloud point with an increase in the molecular weight of the base alcohol.

The free oil content has very little effect on the cloud point as shown in Table IV. This means that cloud point specification will not restrict the use of free oil to adjust viscosities of the finished shampoo.

As is generally known, increased ethylene oxide content helps solubility. This applies to the shampoos containing amine oxide foam stabilizer as shown in Table V.

Viscosity

The choice of the alkanolamine has a noticeable effect on the viscosity of the shampoo. The data in Table VI show that triethanolamine sulfate gives the least viscous and the monoethanolamine sulfate gives the most viscous shampoo.

Amine oxide stabilized shampoos are more viscous than the lauric diethanolamide stabilized shampoo. Therefore this can be another advantage in the use of amine oxide over lauric diethanolamide.

These differences can be drawn with assurance from the data, but the apparent difference in viscosity between alcohol bases should not be given significance.

TABLE V

Effect of Ethylene Oxide Content on Cloud Point of Shampoo from C_{1214} Alcohol TEA Ether Sulfates

% EO	Cloud point, °F	
	LDEA	C_{14} Amine oxide
17	28	70
28	28	66
40	30	62
60	28	54

TABLE VI

Effect of Alkanolamine on Viscosity of Shampoos

Hydro-phobe[a]	Alkanol-amine	Viscosity in cp. foam stabilizer		
		None	LDEA	Amine oxide
C_{1412}	TEA	10	17	63
C_{1412}	DEA	12	20	154
C_{1412}	MEA	12	90	960
C_{1214}	TEA	....	15,22	120,246
C_{1214}	DEA	....	59	633
C_{1214}	MEA	....	170	2930
C_{1014}	TEA	....	13	18

[a] All ethoxylates had 40% ethylene oxide. See Table I for alcohol distribution of blends.

TABLE VIII

Shampoo Viscosity as a Function of Free Ethoxylate in Ether Sulfate

Shampoo composition				Viscosity, cp.
%[a] Ether sulfate	% Unsulfated ethoxylate added[b]	% Nonionic in total active	LDEA	
16	1.1	6.4	5	15
13.6	3.9	22.3	5	175
12.4	5.4	30.4	5	1580
11.2	6.8	37.8	5	>5000

[a] Ether sulfate is monoethanolamine neutralized sulfate of 1214 alcohol plus 40% ethylene oxide.
[b] Ethoxylate is that used to make the ether sulfate.

Although very large, the difference could be due to variables in ethoxylation or sulfation as well as alcohol hydrophobe. The unsulfated material is lower on the series with the C_{1214} and C_{1014} alcohols than on the C_{1412} alcohol series (Table IV). This only confuses the analysis of viscosity/alcohol or free oil relationship. We must assume that there may be an alcohol/free oil effect which we cannot define without more data.

We also feel that the ethoxylation level of the ether sulfate could have an effect on the shampoo viscosity. Two series made at varying levels of ethylene oxide in the ether sulfate are shown in Table VII. The free oil analysis of the ether sulfate is also shown. While these products all have low levels of unsulfated ethoxylate it does suggest that free oil may affect viscosity.

There is no consistent relationship between ethylene oxide level and viscosity as shown. In some cases free oil appears to have an effect on the results and in general the lower levels of ethylene oxide give higher viscosities. We would not be able to predict, however, the viscosity effect for any projected series.

We have seen that free oil (unsulfated ethoxylate) very likely affects viscosity of the shampoo.

Some high free oil products were prepared and evaluated for foam. No obvious differences were seen between the high and low free oil samples. These tests inferred that as much as 15% of the active content can be unsulfated nonionic without detracting from foam. Table VIII shows intentional blends of ether sulfate and unsulfated nonionic and demonstrates the continued increase in viscosity with higher ratio of nonionic to ether sulfate.

The relationship of free oil and foam stabilizer on viscosity is shown in Table IX.

Observe that the viscosity increase caused by the high free oil is dependent on the presence of a foam stabilizer. Neither the extra free oil nor lauric diethanolamide causes a marked increase in viscosity with this ether sulfate, but a combination of the two produces a substantial increase. On the other hand, a high free oil is not needed to get the viscosity boost from amine oxide.

While it is possible to increase the viscosity of these shampoos with sodium chloride, most of the shampoos so thickened did not remain clear and bright—they developed a slight haze. While this would not be a disadvantage in an opacified type shampoo, it would be a prohibitive disadvantage in the clear liquid type.

A shampoo should have excellent foam and as low as possible cloud point. Viscosity may vary with sales objectives. Upon reviewing our data we find that with an amine oxide stabilizer we can obtain excellent foam at any of several levels of ethylene oxide in the ether sulfate. With an amide stabilizer, foam is better as the ethylene oxide level decreases.

Cloud point with the amide stabilizer is not a problem. With an amine oxide we prefer a monoethanolamine ether sulfate and a higher ethylene oxide level. Free oil up to about 15% on the total active should not cause a problem with either foam or cloud point.

Table X lists compositions using each foam stabilizer to give the maximum range of viscosity consistent with satisfactory foam and cloud point. It is obvious that a commercial product of any desired viscosity should be obtainable using either of the foam stabilizers and an ether sulfate from an appropriate combination of alcohol, ethylene oxide, alkanolamine to neutralize and free oil.

TABLE VII

Effect of Ethylene Oxide Content on Viscosity of Shampoo

% EO	% Free oil	Viscosity, cp.	
		LDEA	A014
	TEA C_{1214} Alcohol ether sulfates		
17	3.88	27(18)[a]	400
28	2.02	60	1,100
40	5.24	28(20)	350
60	5.91	28(52)	50
	MEA C_{12} Alcohol ether sulfates		
0	6.5	5,800	26,000
11	4.9	12,400	54,000
26	2.7	3,200	15,200
40	7.0	450	2,100

[a] Figures in parentheses are from duplicate products.

Paste Shampoo

A cursory investigation was made into the suitability of using ether sulfates in paste shampoos. They were made as 20% active with stearic acid and sodium hydroxide to form sodium stearate as the hardening agent.

The foam response of these shampoos gave comparatively the same differences among products that the liquid shampoos gave. Differences due to foam stabilizer or degree of ethoxylation were of the same visual order as on liquids. However, the paste shampoos gave less foam volume and higher density with smaller bubble size.

Ethoxy sulfates were basically no different from the alcohol sulfates in forming a paste. The texture of the ethoxy sulfate shampoos was different from

TABLE IX

Free Oil and Foam Stabilizer Effect on Viscosity

Formulation number	1	2	3	4	5
TEA-"ALFONIC" 1412-40 ES, %	20	20	20	17	20
Unsulfated Ethoxylate, %	....	....	5	3	....
LDEA, %	....	5	....	5	....
Dodecyldimethyl Amine Oxide, %	....	....	....	....	5
H_2O, %	80	75	75	75	75
Viscosity, cp.	10	50	45	1015	750

TABLE X

Predicted Optimum High and Low Viscosity Shampoos

Alcohol	E.O. level	Alkanol-amine	% Free oil in E.S.	Foam stabi-lizer	Cloud pt. °F	Vis-cosity cp.
1214	17	TEA	5	LDEA	28	24
1214	17	MEA	16	LDEA	33	3450
1014	40	MEA	5	AO	35	36
1214	40	MEA	14	AO	49	8000

those of the alcohol sulfate shampoos but could not be described as being necessarily better or worse.

In the formation of these paste shampoos the cation of the sulfate has a very significant effect. The mono- and diethanolamine and sodium sulfates formed pastes while the triethanolamine sulfate did not do so consistently. The sodium sulfate seems to work best followed by the diethanolamine sulfate and monoethanolamine in that order. The amine sulfate shampoos are inclined to be gummier than the sodium.

Penetration tests were run on some of these samples to determine difference in hardness as a function of the sulfate and amount of soap. As the results in Table XI show, it is possible to attain a hardness about equal to those of commercial paste shampoos by adjusting the soap content. The test used was the Shell modification of the Cone Penetration Test, ASTM D217, using a half scale cone.

TABLE XI

Penetration of Paste Shampoos, 0.1 mm[a]

Type sulfate[b]	Foam stabilizer	Amount sodium stearate in shampoo		
		10%	5%	2.5%
Na C_{1412} Ether Sulfate	None	141	295	Too soft
Na C_{1412} Alcohol Sulfate	None	185	237	
Na C_{1412} Ether Sulfate	5% LDEA	171		
TEA C_{1214} Alcohol Sulfate	None	Liquid		
TEA C_{1214} Alcohol Sulfate	5% LDEA	Liquid		
TEA C_{1214} Ether Sulfate	5% A014	Liquid		
DEA C_{1214} Ether Sulfate	None	245		
Commercial Paste Shampoo HC			325	
Commercial Paste Shampoo LC			325	
Commercial Paste Shampoo NT			295	

[a] Value is depth of penetration, so low value is stiffest.
[b] Ether sulfates have 40% ethylene oxide, alcohol blends are described in Table I.

REFERENCES

1. Thomas Hedley & Co., Ltd., British 791,704 (1958).
2. Thomas Hedley & Co., Ltd., British 797,119 (1958).