Detergent Alcohols. I. The Effect of Alcohol Structure and Molecular Weight on Surfactant Properties[1]

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Abstract

A large number of aliphatic alcohols have been studied to relate performance of the derived surfactants to structure and molecular weight. The alcohols were examined as sulfates, ethoxylates, and ethoxysulfates in heavy- and light-duty compositions. Clear points and surface tensions of aqueous solutions were determined. Cotton detergency was evaluated in a bench-scale test by using artificially soiled test cloths. Foam performance was measured in a soil titration test. In general, excellent performance is observed with derivatives which have 70% or greater n-primary alcohol content. The odd-numbered alcohol derivatives contribute significantly to optimum performance.

Introduction

THE WIDESPREAD INTEREST in reducing the pollution of water resources has led the detergent industry to seek sources of biodegradable surfactants. In this context an investigation was undertaken to assess the influence of structure and molecular weight of 100% primary alcohols on some surface properties and some performance responses of surfactants readily derived from them. These primary alcohols, which were considered accessible for commercial development, were prepared on a laboratory scale. For convenience in comparing and clarifying the influence of changes of molecular structure on the various properties, the derivative alcohol sulfates, ethoxysulfates, and ethoxylates have been considered to arise from parent alcohols classified in three groups: a) the normal primary alcohols C_{11} through C_{18} (PAI); b) the normal primary alcohols C_{11} through C_{18} plus the corresponding 2-alkyl isomers (predominantly 2-methyl) in the ratio 75 normal to 25 isomeric (PAII); and c) a mixture of C_{12} through C_{15} primary alcohols (in the ratio 20/30/30/20), in which the ratio of normal alcohol to 2-alkyl isomer varied. For comparison, surfactants were prepared from some C_{13} and C_{15} primary alcohols of different structure as well as some secondary alcohols. Although a large number of studies of surfactants derived from normal primary alcohols have appeared (1,3,4), similar results are included for direct comparison with those obtained on compounds for which data are not reported.

Experimental Procedures

Preparation of Straight-Chain and Isomeric Alcohols

The data in Table I summarize the analyses which were obtained on the straight-chain and isomeric alcohols used in this investigation. The majority of the alcohols were purchased or synthesized by unequivocal routes using well-recognized procedures. Two materials require further comment.

C_{13} Guerbet Alcohols. C_{13} Guerbet alcohols were prepared by the Guerbet condensation of equimolar amounts of 1-hexanol and 1-heptanol. GLC analysis showed the resultant mixture to contain: 2-butyl-1-octanol, 3%; 2-pentyl-1-octanol, 47%; 2-butyl-1-nonanol, 49%; and 2-pentyl-1-nonanol, 1%.

C_{15} Guerbet Alcohols. C_{15} Guerbet alcohols were made by the Guerbet condensation of equimolar amounts of 1-heptanol and 1-octanol. GLC analysis showed the resultant mixture to contain: 2-pentyl-1-nonanol, 1%; 2-hexyl-1-nonanol, 49%; 2-pentyl-1-decanol, 48%; and 2-hexyl-1-decanol, 2%.

Preparation of Alcohol Derivatives

Sulfates and Ethoxysulfates. These were prepared by allowing the alcohols and ethoxylates to react with chlorosulfonic acid. Conversions were better than 98% with primary alcohols. Excessive amounts of unreacted organic matter were removed from the secondary alcohol sulfates and ethoxy-sulfates by petroleum ether extraction of water/isopropanol solutions. Anionic surfactant was determined by methylene blue titration (2). Petroleum ether extracts were analyzed for unreacted hydroxyl by using an acetic anhydride technique.

Ethoxylations. Ethoxylations were carried out by using NaOH catalyst with primary alcohols and BF_3 with secondary alcohols. GLC analyses of the $(EO)_3$ ethoxylates show that the primary and secondary alcohol ethoxylates both contain 12–15% unethoxylated alcohol. Average ethylene oxide (EO) content was determined by weight and by NMR analysis.

Preparation of Detergent Solutions

Unformulated surfactant solutions were made by using distilled water. Built detergent solutions were prepared with water having a hardness of 150 ppm as $CaCO_3$ (Ca/Mg = 60/40) to correspond to the following compositions.

Heavy-Duty, High-Foaming Solids (HDHFS). HDHFS consists of sodium alcohol sulfate/sodium

TABLE I

Analyses of C_{11} Through C_{18} n-Primary and C_{13} and C_{15} Isomeric Alcohols

Alcohol	GLC purity %	Hydroxyl value eq/100 g		Boiling point	
		Calc.	Found	°C	mm Hg
n-Primary					
1-Undecanol	97	0.582	0.585		
1-Dodecanol	99	0.537	0.538	147–148	15
1-Tridecanol	99.5	0.500	0.500	170	20
1-Tetradecanol	99	0.467	0.465	170–172	15
1-Pentadecanol	99	0.438	0.436	133	0.8
1-Hexadecanol	96	0.413	0.429		
1-Heptadecanol	95	0.397	0.403		
1-Octadecanol	98	0.370	0.367		
Isomeric C_{13}					
2-Methyl-1-dodecanol	98	0.500	0.498	92	0.5
6-Methyl-1-dodecanol	99	0.500	0.508	140	6
C_{13} Guerbet alcohols		0.500	0.493	101–102	0.2
2-Tridecanol	98	0.500	0.520	147–151	10
7-Tridecanol	97	0.500	0.507		
Isomeric C_{15}					
2-Methyl-1-tetradecanol[a]	99				
C_{15} Guerbet alcohols		0.438	0.440	148	3
2-Pentadecanol	98	0.438	0.439	133	0.4
7-Pentadecanol	98	0.438	0.437	128–130	0.6

[a] MP, 31.5C.

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[1] Presented at the AOCS Meeting, Chicago, October 1964.

tripolyphosphate (STPP)/sodium silicate ($SiO_2/Na_2O = 2.40$)/sodium sulfate (20/45/7/23). The remaining 5% consists of unsulfated alcohol (2% based on alcohol sulfate for C_{11} through C_{15}; 5% for C_{16} through C_{18}) and water.

Heavy-Duty, Low-Foaming Solids (HDLFS). This consists of alcohol ethoxylate/STPP/sodium silicate ($SiO_2/Na_2O = 2.40$)/sodium sulfate/water (10/55/5/20/10).

Light-Duty Liquid (LDL). Light-duty liquid consists of ammonium alcohol $(EO)_3$ sulfate and water.

Determination of Properties

Surface tensions were determined by the ring method (ASTM D 971). Clear points were measured by cooling 25 g of solution to 5C below the previously determined approximate clear point and then warming (0.1 deg/min) while gently stirring with a thermometer until the solution cleared.

Determination of Performance

Cotton Detergency. This test was run in a Terg-O-Tometer for 20 min at 50C and 150 rpm, using four 10-cm × 10-cm pieces of cotton fabric (one soiled; three unsoiled Indian Head Muslin) in 500 ml of built detergent solution. Washed-minus-soiled (W-S) reflectances (four replicates) were obtained by using three cotton soiled cloths (Foster D. Snell, Testfabrics Inc., 51S47, and United States Testing Company), and the over-all average was computed. The detergency rating is this average expressed as a percentage of the corresponding quantity for a reference compound which is used at a concentration of 0.040% active matter. In the case of alcohol sulfates a linear alkylbenzene sulfonate (LAS, average alkyl group $C_{12.6}$) was used in the HDHFS composition; for alcohol ethoxylates a 40/36/24 mixture of n-$C_{14}/C_{16}/C_{18}$ $(EO)_9$ in the HDLFS composition was used. A difference of 5% in detergency rating is required for two detergents to differ at the 95% confidence level.

Foam Performance. The Dynamic Foam test developed by Spangler (8), with Crisco on cotton terry cloth swatches and a 46C initial detergent solution temperature, was used. Foam performance (four replicates per datum) is expressed as a percentage of a reference compound at a concentration of 0.025% active matter. For alcohol sulfates the linear alkylbenzene sulfonate was used in the HDHFS composition; for the ethoxysulfates, ammonium coconut alcohol $(EO)_3$ sulfate in the LDL formulation was used. A difference of 7% in performance rating is required for two detergents to differ at the 95% confidence level.

TABLE II
Effect of Alcohol Carbon Number on Cotton Detergency of PA I[a] and PA II[b] Sulfates in HDHFS and Ethoxylates in HDLFS

Alcohol carbon number	Detergency Rating[c]			
	Sulfates[d]		Ethoxylates[e, f]	
	PA I	PA II	PA I	PA II
11	59	56	111	110
12	61	65	112	112
13	96	94	112	111
14	113	115	111	114
15	117	117	108	111
16	119	114	111	111
17	121	110	106	108
18	114	116	107	105

[a] n-Primary alcohols.
[b] 75% n-Primary alcohols + 25% 2-alkyl isomers.
[c] Terg-O-Tometer test, 150 ppm hardness. References—HDHFS: LAS($C_{12.6}$) ≡ 100; HDLFS: $C_{14/16/18}$ $(EO)_9$ ≡ 100; conc., 0.040% active matter.
[d] Concentration, 0.040% alcohol sulfate.
[e] 62% Ethylene oxide in ethoxylate.
[f] Concentration 0.040% alcohol ethoxylate.

TABLE III
Effect of Alcohol Carbon Number on Clear Point and Surface Tension of Unbuilt Alcohol Sulfate[a] Solutions

Alcohol carbon number	Clear Point, °C						Surface Tension dynes/cm at 50C			
	PA I[b]			PA II[c]			PA I		PA II	
	1[d]	5	10	1	5	10	1	5	1	5
11	11	13	14	8	11	13	35.4	33.4	34.8	30.3
12	16	18	18	14	16	17	33.1	29.9	33.1	29.5
13	27	31		25	27	29	33.1	29.9	33.9	31.3
14	31	34	35	28	31	32	32.6	30.6	34.6	30.7
15	40	43	44	38	40	42	33.4	30.3	32.5	30.1
16	45	46	47	41	44	45	31.7	29.6	31.7	30.1
17	51	52	52	49	49	50	31.2	30.4	31.7	28.2
18	(52)[e]		(57)	(54)		(50)	31.4		32.2	

[a] Extracted with petroleum ether to remove unsulfated alcohol. Less than 0.5% inorganic salts (Na_2SO_4, traces of Na_2CO_3), based on alcohol sulfate (except C_{18} PA II sulfate which has 0.9% inorganic salts).
[b] n-Primary alcohol.
[c] 75% n-Primary alcohol + 25% 2-alkyl isomers.
[d] Percentage solution.
[e] Approximate values.

In both of these tests the performance of the reference materials has been replicated at least 20 times.

Results and Discussion

Effect of Varying Carbon Number

Cotton Detergency. The cotton-washing performance (relative to the linear alkylbenzene sulfonate) in the Terg-O-Tometer test is shown in Table II for the series of straight-chain alcohol PAI and PAII sulfates. For both series of compounds, the C_{11} and C_{12} members are notably less effective in soil removal than the higher members. The C_{13} compounds in both series are intermediate in performance, and for C_{14} through C_{18} the performance becomes independent of chain length. Within the statistical limits of the testing procedure, the PAII sulfates, containing 75% n-primary and 25% 2-alkyl isomers, are indistinguishable from the PAI sulfates in this HDHFS formulation. The surface-tension lowering at concentrations where the surface tension is relatively independent of concentration, i.e., above the critical micelle concentration (CMC), is shown in Table III for these two series of compounds, from which the unreacted alcohol had been removed by extraction with petroleum ether. PAI and PAII sulfates with the same carbon number are essentially equal in surface activity at 50C for concentrations exceeding the CMC. The surface tensions of the built solutions for these series are shown in Table IV. With the possible exception of the C_{11} and C_{12} compounds, the built solutions are initially above the CMC at washing temperature. The surface tension of the built PAI and PAII solutions (which include the inorganic salts and unsulfated alcohol)

TABLE IV
Effect of Alcohol Carbon Number on Surface Tension of Built[a] PA I[b] and PA II[c] Sulfate Solutions

Alcohol carbon number	Surface Tension dynes/cm at 50C		
	PA I		PA II
	0.025[d]	0.040	0.025
11	48.0	37.8	39.5
12	46.3	38.4	34.1
13	28.5	31.6	30.2
14	24.2	28.4	29.1
15	27.3	27.6	28.1
16	28.9	26.8	27.7
17	30.5	29.1	27.9
18	33.3	30.4	28.2

[a] In the HDHFS composition.
[b] n-Primary alcohol.
[c] 75% n-Primary alcohol + 25% 2-alkyl isomers.
[d] Percentage alcohol sulfate in built solution.

are also substantially equal. Clear-point data for the purified compounds show the PAII derivatives to be more soluble than the corresponding PAI compounds. The Kraft point (the temperature at which the solubility begins to increase rapidly) for the n-primary alcohol sulfates, as determined by Raison (5), increases linearly for the even-carbon-numbered compounds. A plot of the data of Table III for the PAI sulfates shows some curvature and suggests that the even and odd members of the PAI series lie on different curves. This is also apparent in the clear-point data of Table III for the PAII sulfates. These unexpected findings will be the subject of further investigation.

The cotton detergency of the ethoxylates of the PAI and PAII series at a constant 62% ethylene oxide content is also given in Table II. At each carbon number the PAI and PAII derivatives show essentially equivalent behavior. In contrast to the performance in the two series of sulfates, the inferior soil-removing ability of the C_{11} and C_{12} compounds is not apparent in the ethoxylates. Further, at this level of ethoxylation, the performance is independent of hydrocarbon molecular weight.

Foam Performance. The foam performance (measured by using a Terg-O-Tometer test and expressed relative to the LAS) of C_{11} through C_{18} PAI and PAII sulfates is shown in Figure 1. These tests were conducted by using the HDHFS composition which was modified by the replacement of 10% of the active matter with lauric isopropanolamide (LIPA). Both series exhibit optimum performance at C_{15} with a sharp rise between C_{13} and C_{14} and a sharp drop-off between C_{16} and C_{17}.

The foam performances (in light-duty liquid application and expressed relative to coconut alcohol $(EO)_3$ sulfate) of the C_{11} through C_{18} PAI and PAII $(EO)_3$ sulfates are essentially equal at a given alcohol carbon number (Figure 2). As a result, the optimum performance for both series is the same and occurs between C_{13} and C_{14}. In addition, there is a definite influence of carbon number on performance, but it is less pronounced than in the alcohol sulfate case (Figure 1). Ethoxylation, prior to sulfation, has made the foam performance less dependent on carbon number near the optimum.

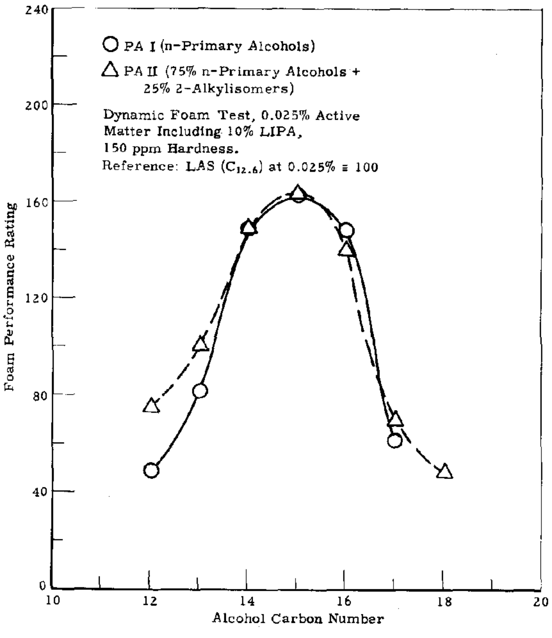

FIG. 1. Effect of alcohol carbon number on foam performance of alcohol sulfates in HDHFS.

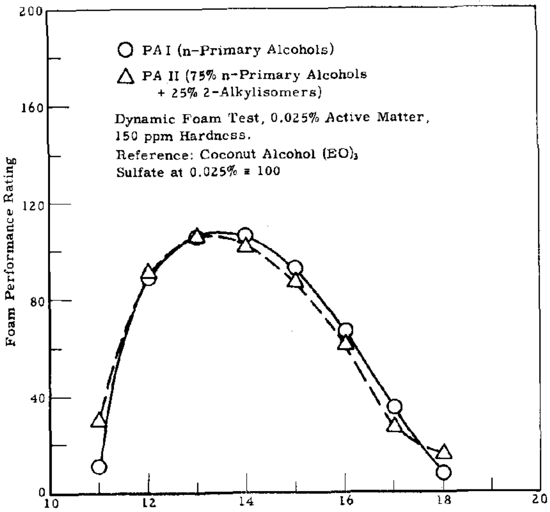

FIG. 2. Effect of alcohol carbon number on foam performance of alcohol $(EO)_3$ sulfates in LDL application.

Effect of Varying Normal/Iso Ratio

The effect of normal alcohol content on the performance of mixtures of straight-chain and 2-alkyl isomers was determined. For this purpose, a series of C_{12-15} ($C_{12}/C_{13}/C_{14}/C_{15} = 20/30/30/20$) primary alcohols was prepared by blending the various isomers. Compositions with normal alcohol content from 5 to 98% were studied.

Cotton Detergency (Figure 3). As the normal alcohol content increases, the cotton detergency of the C_{12-15} alcohol sulfates in the HDHFS composition increases slowly, reaching a level independent (within

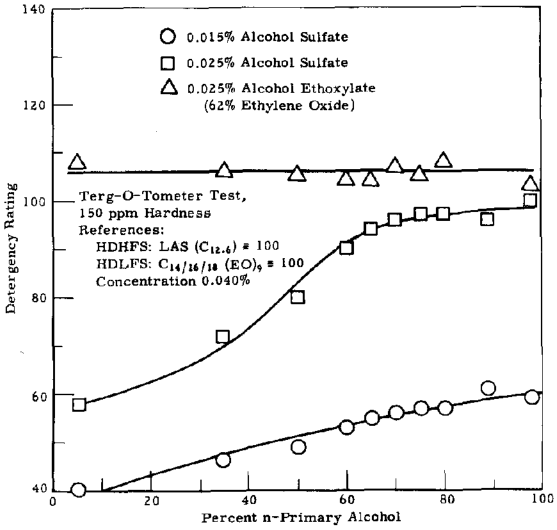

FIG. 3. Effect of normal/iso ratio on cotton detergency of C_{12-15} alcohol sulfates in HDHFS and ethoxylates in HDLFS.

the statistical limitations of the Terg-O-Tometer test) of the amount of straight-chain alcohol present. The ultimate level of performance increases, of course, with the concentration of surfactant. The data also suggest that the normal alcohol content required to reach essentially the performance level of the pure straight-chain compound depends on the surfactant concentration and/or the builder concentration. Even at the 0.015% level, where the STPP content is insufficient to sequester the 150 ppm hardness, an n-primary alcohol level of about 65% is necessary. At 0.025%, where the STPP is equivalent to the hardness, an n-primary alcohol content of about 65% is again needed.

The series of alcohols with varying normal alcohol content were also used to prepare ethoxylates that contained 62% ethylene oxide for studying their performance in the HDLFS composition. Figure 3 shows that the soil removal, as measured in the Terg-O-Tometer, is independent of the straight-chain content of the parent primary alcohol blend. Thus, as with ethoxylates of primary alcohols of varying chain-length, the influence of the hydrocarbon moiety of the primary alcohols is not apparent at this level of ethoxylation.

These results show that a sulfate and ethoxylate based on a $C_{12\text{-}15}$ alcohol with 75% straight-chain content have equivalent cotton detergency to the corresponding 100% straight-chain alcohol derivatives.

Foam Performance (Figure 4). The foam performance in the HDHFS composition of this series of $C_{12\text{-}15}$ alcohol sulfates of varying straight-chain content increases with increasing normal content, and the ultimate performance level depends on surfactant concentration. Replacement of 10% of the alcohol sulfate with lauric isopropanolamide at the 0.025% level shifts the performance curve upwards. And, above 70% straight-chain content, the performance becomes independent of normal/iso ratio within the statistical limits of this test. This apparently results from the increased efficiency of LIPA in improving the foam performance of compositions that contain lower amounts of straight-chain alcohols and agrees with earlier observations with amide-type foam promoters (6).

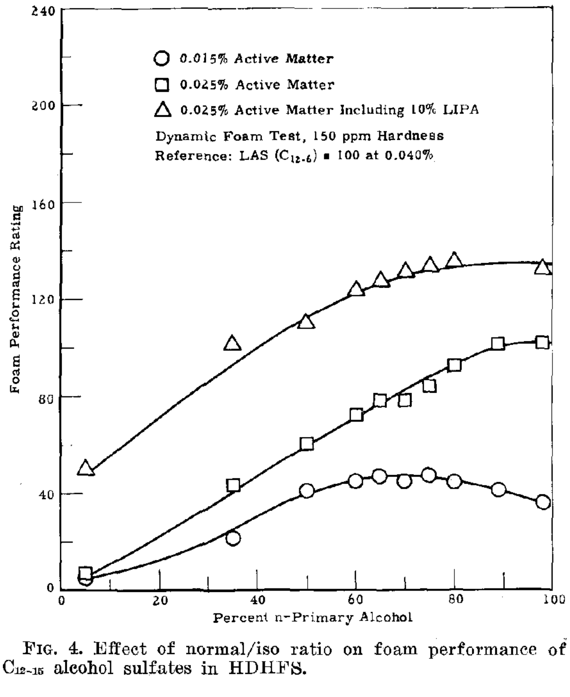

FIG. 4. Effect of normal/iso ratio on foam performance of $C_{12\text{-}15}$ alcohol sulfates in HDHFS.

TABLE V

Effect of Normal/Iso Ratio on Surface Tension and Foam Performance of $C_{12\text{-}15}$ Alcohol Ethoxysulfates

n-Primary alcohol %	Surface tension dynes/cm at 25°C		Foam performance rating[b]
	0.025[a]	1.0	0.025
5			99
35	30.0	31.8	98
50			98
60	31.0	33.0	102
65			99
70	30.8	33.0	102
75			105
80	31.6	32.0	103
98	34.0	34.5	105

[a] Concentration of ethoxysulfate in 150 ppm hard water.

[b] Dynamic Foam Test. Reference—coconut alcohol. $(EO)_3$ sulfate ≡ 100; concentration 0.025%.

The role of STPP in foam performance has been discussed by Burgess et al. (1), who have shown that performance increases rapidly as STPP content increases for constant water hardness and alcohol sulfate concentration. This effect of STPP on foam performance presumably accounts for the decline in performance with increasing normal alcohol content at 0.015% surfactant concentration. At this concentration, the STPP present in the composition is insufficient to sequester the 150 ppm hardness, thus permitting the less-soluble calcium and magnesium salts of the higher straight-chain compounds to exert a deleterious effect.

The $C_{12\text{-}15}$ $(EO)_3$ sulfates in LDL application exhibit a slight, but not statistically significant, upward trend in foam performance as the straight-chain content increases from 5 to 98% (Table V). With the exception of the composition containing the highest amount of straight-chain alcohols, the surface tension of the solutions is also essentially independent of normal content. In contrast to the study of chain-length variation on the performance of the sulfated parent alcohols (Figure 1), the influence of normal/iso ratio is completely obscured by ethoxylation prior to sulfation.

Effect of Varying Structure

The effect of alcohol structure on performance was further studied with C_{13} and C_{15} isomeric alcohols in which the degree and position of branching and the position of the hydroxyl group were varied. The data

TABLE VI

Effect of Alcohol Structure on Cotton Detergency of Alcohol Sulfates in HDHFS and Ethoxylates in HDLFS

Alcohol	Detergency Rating[a]	
	Sulfate[b]	Ethoxylate[b, c]
C_{13}		
1-Tridecanol	96	112
2-Methyl-1-dodecanol	66	113
6-Methyl-1-dodecanol	68	111
C_{13} Guerbet alcohols[d]	54	114
2-Tridecanol	63	103
7-Tridecanol	47	98
C_{15}		
1-Pentadecanol	117	108
2-Methyl-1-tetradecanol	110	103
C_{15} Guerbet alcohols[d]	92	110
2-Pentadecanol	111	98
7-Pentadecanol	78	85

[a] Terg-O-Tometer test, 150 ppm hardness. References—HDHFS: LAS($C_{12.6}$) ≡ 100; HDLFS: $C_{14/16/18}$ $(EO)_9$ ≡ 100; concentration, 0.040%.

[b] Concentration, 0.040% active matter.

[c] 62% Ethylene oxide in ethoxylate (i.e., $C_{13}(EO)_{7.4}$ and $C_{15}(EO)_{8.5}$).

[d] Isomer distribution and structure as described in Experimental Procedures.

TABLE VII

Effect of Alcohol Structure on Foam Performance of Alcohol Sulfates in HDHFS and Ethoxysulfates

Alcohol	Foam Performance Rating[a]	
	Sulfates[b]	Ethoxysulfates[b]
C_{13}		
1-Tridecanol	43	106
2-Methyl-1-dodecanol	16	86
6-Methyl-1-dodecanol	10	114
C_{13} Guerbet alcohols[c]	4	121
2-Tridecanol	12	67
7-Tridecanol	5	76
C_{15}		
1-Pentadecanol	166	93
2-Methyl-1-tetradecanol	110	84
C_{15} Guerbet alcohols[3]	8	103
2-Pentadecanol	110	86
7-Pentadecanol	4	108

[a] Dynamic Foam Test, 150 ppm hardness. References—HDHFS: LAS($C_{12.0}$) ≡ 100; ethoxysulfate in LDL: coconut alcohol $(EO)_3$ sulfate ≡ 100; concentration, 0.025%.

[b] Concentration, 0.025% active matter.

[c] Isomer distribution and structure as described in Experimental Procedures.

obtained for cotton detergency and foam performance are shown in Tables VI and VII respectively.

Alcohol Sulfates. Table VIII presents some results of the performance of the isomeric alcohol sulfates as well as clear points and surface tensions well above the CMC. For a given number of carbon atoms, either a) changing the $-OH$ group away from the terminal position or b) moving the methyl group from the terminal position (i.e., the linear primary alcohol) to more central positions in the chain decreases the cotton detergency and foam performance, as shown in Table VII. This decrease is less pronounced for the C_{15} compounds, suggesting that the principal chain-length is the dominant factor which influences these performances. The observations are consistent with the data of Table II and Figure 1, which show that cotton detergency and foam performance of the HDHFS compositions are more dependent on chain length at C_{12} and C_{13} than at C_{14} and C_{15}. The clear point of these compounds decreases in a regular manner as the methyl group or hydroxyl group is moved to a more central position. However the surface tension is not strongly influenced by these isomeric changes with the exception of the compounds with a central hydroxyl group (7-pentadecanol and 7-tridecanol), which have appreciably lower values. For these compounds the observations on surface tension and cotton detergency are consistent with those made by Shedlovsky (7); however in a pour-foam test this author found superior foam performance for the compounds with central hydroxyls. This latter result is not borne out in the Dynamic Foam Test, involving the continuous destruction of the foam while the soil load is increased.

Long branches (e.g., Guerbet and 7-hydroxyl alcohols) have a much larger deleterious effect on the performance of alcohol sulfates than does a methyl branch. The decrease in cotton detergency (relative to PAI sulfates) for long branches vs. a methyl branch is ca. 45% vs. 35% for C_{13}, and 25% vs. 5% for C_{15}. The corresponding decreases in foaming are >90% vs. 75% for C_{13} and >95% vs. 35% for C_{15}.

Alcohol Ethoxylates. With the exception of the 7-hydroxy isomers, cotton detergency of the ethoxylates shown in Table VI is essentially independent of alcohol structure. This again shows the equalizing effect of ethoxylation on performance.

Alcohol Ethoxysulfates. The ethoxysulfate foam performance shows no discernible trends with respect to branch length or location (Table VII). In some cases, movement of OH or CH_2OH (Guerbet alcohols) groups to a central location appears to be beneficial.

Conclusions

The results of this investigation with particular test methods, conditions, and practical formulations show that variations in alcohol structure can have important influences on the performance of derived detergents.

Carbon-Number Variation

The cotton detergency of primary alcohol sulfates reaches a maximum about C_{14} and remains constant through C_{18}. Primary alcohol ethoxylates, containing 62% ethylene oxide, have the same cotton detergency from C_{11} through C_{18}.

The foam performance of primary alcohol sulfates in heavy-duty compositions exhibits a pronounced peak at C_{15}. Primary alcohol $(EO)_3$ sulfates show a broad maximum in foam performance about C_{13}-C_{14}. The odd-numbered primary alcohol derivatives contribute significantly to these performances.

Derivatives of primary alcohols which contain 25% 2-alkyl isomers in the carbon-number range C_{11} through C_{18} have equivalent performance to the corresponding n-primary alcohol derivatives.

Variation of Normal/Iso Ratio

The amount of n-primary alcohol in blends of C_{12-15} alcohols with 2-alkyl isomers does not influence the cotton detergency of ethoxylates (62% ethylene oxide) or the foam performance of ethoxysulfates.

TABLE VIII

Effect of Hydroxyl and Methyl Group Positions on the Performance and Properties of C_{13} and C_{15} Isomeric Alcohol Sulfates

Position	C_{13}				C_{15}			
	Surface tension[1] dynes/cm at 50C	Clear point[a] °C	Decrease[b]		Surface tension dynes/cm at 50C	Clear point °C	Decrease	
			Cotton detergency[c]	Foam performance[d]			Cotton detergency	Foam performance
Hydroxyl group								
1	33.1	27	0	0	33.4	40	0	0
2	35.0	21	34	72	34.3	34	5	34
7	28.2	<0	51	88	24.5		33	98
Methyl group								
n-Primary alcohol	33.1	27	0	0	33.4	40	0	0
1[e]	35.0	21	34	72	34.3	34	5	34
2	35.7	17	31	63	34.0	30	6	34
6	34.2	<0	29	77				

[a] 1% Solution in distilled water, using alcohol sulfates that had been extracted with petroleum ether to remove unsulfated alcohol. The sulfates contain less than 0.45% inorganic salts (Na_2SO_4; traces of Na_2CO_3), based on alcohol sulfate.

[b] Percentage decrease in performance = 100 (A − B)/A: A = n-primary alcohol derivative response (Tables VI, VII); B = isomeric alcohol derivative response (Tables VI, VII).

[c] Concentration, 0.040% alcohol sulfate (HDHFS).

[d] Concentration, 0.025% alcohol sulfate (HDHFS).

[e] Tridecanol-2 and pentadecanol-2.

However greater than 65% n-primary alcohol is required for alcohol sulfates to reach maximum detergency and foam performance.

Gross Structural Changes

The following structural changes are deleterious to the performance of alcohol sulfates. Moving the $-OH$ from the terminal position toward the central position has a large effect. Placing a $-CH_2OH$ near the center (Guerbet alcohol) also has a large effect. Correspondingly moving a $-CH_3$ has a small effect.

The effect of these structural changes is more pronounced for the C_{13} alcohols than for the C_{15} alcohols. Further, it appears in general that ethoxylation (62% ethylene oxide) tends to eliminate the effect on performance of these structural variations in the hydrocarbon chains. In certain cases an alcohol with a centrally located $-OH$ or $-CH_2OH$, when ethoxylated and sulfated, displays a relatively high foam performance.

Clear-point data indicate that the presence of 25% 2-alkyl isomers in blends with n-primary alcohols increases the solubility of the alcohol sulfates and has little effect on the surface tension above the critical micelle concentration. Further, the odd-numbered alcohol sulfates appear to be somewhat less soluble than the even-numbered compounds.

ACKNOWLEDGMENTS

Synthesis of certain of the pure alcohols provided by R. F. Mason, N. R. Roobol and J. L. Van Winkle; aid in analytical determinations by A. E. O'Donnell, G. A. Stenmark and H. W. Daeschner; preparation of many of the alcohol blends by R. I. Thomas.

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[Received October 19, 1964]