The Effect of Homolog Distribution on Sodium Alcohol Sulfate Solution Viscosity

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ABSTRACT

Several compositional factors influence the viscosity of fatty alcohol sulfate solutions. The effects of free oil and inorganic salts on viscosity are known by most sulfators. Each builds viscosity as its level is increased. The relation between viscosity and alkyl sulfate homolog distribution is more subtle and often overlooked. Some synthetic alcohol manufacturers have the flexibility within the coconut alcohol range to vary the lauryl, myristyl, and cetyl alcohol composition. Mixtures containing high lauryl and cetyl alcohol content yielded alkyl sulfates having low viscosities. Mixtures of lauryl and myristyl alcohol gave high viscosity alkyl sulfates. When restricted to compositions containing all three alcohols, the viscosity of the sodium alkyl sulfate derivative was shown to be dependent on the myristyl sulfate content. Solutions having high myristyl sulfate levels had high viscosities. A. limited solubility study of different sodium lauryl, myristyl, and cetyl alcohol sulfate solutions was made.

INTRODUCTION

Sulfates fatty alcohols are widely used in the detergent industry in a variety of products including hair shampoos (1,2), carpet shampoos (3,4), cosmetics (5), and emulsion polymerization (6). These alcohol sulfates are generally manufactured and handled as concentrated aqueous solutions rather than as solids or slurries. The viscosities of these solutions are important to the manufacturers and users of these products. Frequently, the ultimate product end use determines these viscosity requirements. For this reason, lauryl alcohol sulfate manufacturers produce a variety of different sulfates meeting different viscosity specifications.

The viscosity of an alcohol sulfate solution can be altered. Such viscosity adjustments are generally accomplished by addition of organic solvents to reduce viscosity or by addition of certain inorganic salts to build viscosity (7). Inorganic salts such as alkali metal sulfates and chlorides are present as reaction products from the sulfation process. These salts obviously affect solution viscosity as does the free oil (primarily unconverted alcohol) remaining after alcohol sulfation. The effects of these constituents on viscosity, while generally recognized in the industry, are not well documented in the literature.

Another parameter affecting alcohol sulfate viscosity which has not been previously studied is alcohol sulfate homolog distribution. The purpose of this paper is to show the effect of changing the distribution of C_{12}, C_{14}, and C_{16} homologs in a "lauryl range" alcohol on product viscosity. The effect of homolog distribution of sodium alcohol sulfate solubility is also discussed.

Facility to change alcohol homolog distribution is available to some commercial fatty alcohol producers. For this reason this approach to controlling alcohol sulfate viscosity is an area where alcohol raw material suppliers can participate in controlling viscosity.

EXPERIMENTAL PROCEDURES

Starting Materials

1-Dodecanol, 1-tetradecanol, and 1-hexadecanol were ALFOL 12, ALFOL 14, and ALFOL 16 Alcohols as produced by Continental Oil Company. Analyses of these alcohols are presented in Table I.

Chlorosulfonic acid was iron-free, 100% sulfating strength obtained from MCB Manufacturing Chemists. All inorganic salts used were reagent grade.

Preparation of Pure Alcohol Sulfate Homologs

Typically, 4.0 moles of the appropriate alcohol was mixed with 4.0 moles of chlorosulfonic acid at 30-40 C, similar to the manner described previously by Sosis and Dringoli (8). After addition of the chlorosulfonic acid, the reaction vessel was purged for 15 min with dry nitrogen, then neutralized with aqueous sodium hydroxide. The

TABLE I

Compositions of Alcohols and Sodium Alcohol Sulfates Used

Starting alcohol	1-Dodecanol	1-Tetradecanol	1-Hexadecanol
Homolog distribution, wt %[a]			
C_{10} and less	nil	nil	nil
C_{12}	99.8	0.2	nil
C_{14}	0.2	99.7	0.2
C_{16}	nil	0.1	99.2
C_{18} and greater	nil	nil	0.6
Alcohol sulfate			
Total solids, wt %	99.4	99.2	99.2
Active, wt %[b]	99.3	99.0	98.7
Free oil, wt %[c]	0.02	0.10	0.31
Na_2SO_4, wt %[d]	nil	nil	0.15
NaCl, wt %	<0.05	< 0.05	<0.05

[a] Determined by GLPC. A 12 ft X ¼ in. OD column packed with 20% UCW-98 silicone gum rubber on 45/60 mesh Chromosorb W-AW-DMCS was used.

[b] Determined by MCAS. Hyamine cationic titration.

[c] Determined by petroleum ether extraction from water-alcohol solution.

[d] Determined by amperometric titration.

[e] Determined by $AgNO_3$ titration using a modification of the Volhard method.

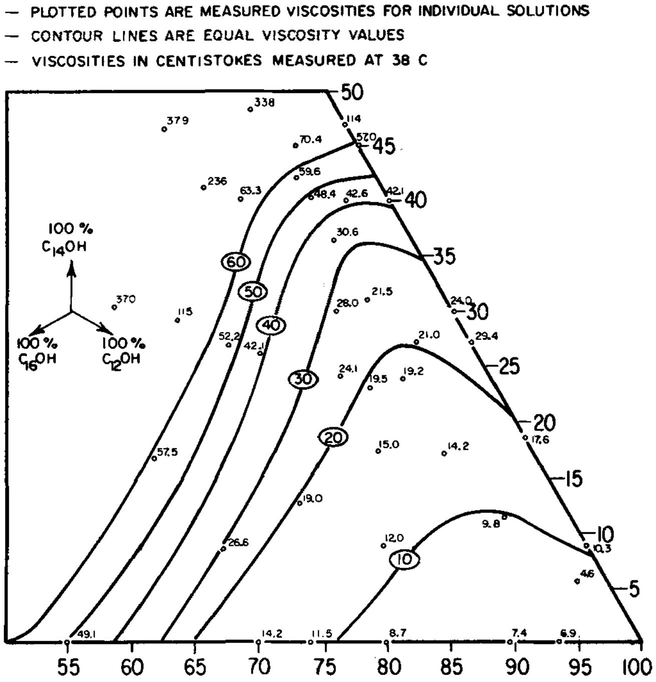

FIG. 1. Relationship of sodium alcohol sulfate viscosity to alcohol homolog distribution.

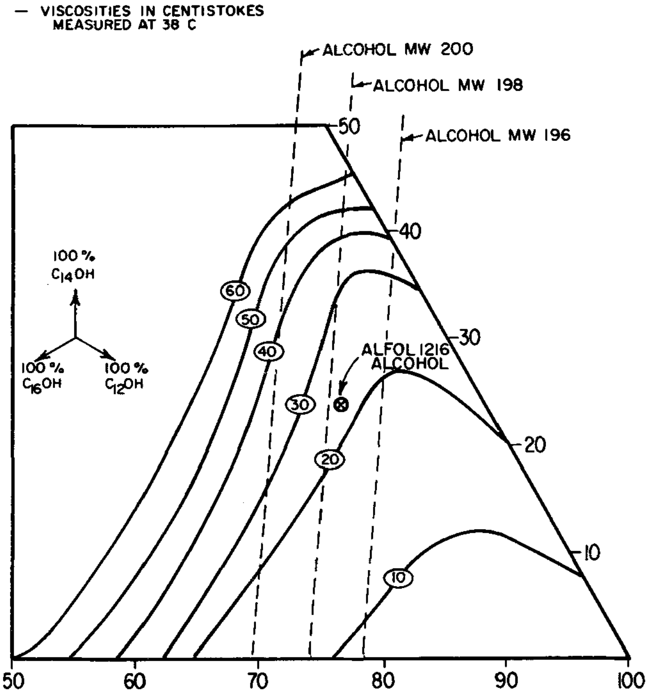

FIG. 2. Relationship of alcohol molecular weight to sodium alcohol sulfate viscosity.

resulting sodium alcohol sulfates were then recrystallized from lower alcohol solution. Sodium dodecyl and tetradecyl sulfates were recrystallized from isopropyl alcohol. Sodium hexadecyl sulfate was recrystallized from ethyl alcohol. The isolated white crystalline solids were dried in a vacuum oven to remove residual quantities of solvent. Analyses of the purified sodium alcohol sulfates are presented in Table I.

Isolation of Free Oil from a Commercial Sodium Lauryl Sulfate

Free Oil was isolated from a commercially chlorosulfated lauryl alcohol (ALFOL 1216 FCA Alcohol) to provide reagent for preparing sodium alcohol sulfate solutions of fixed compositions. Sodium lauryl sulfate (4139 g) was dissolved in 16 liters of 50% aqueous ethanol. This solution was extracted twice with 8-liter portions of petroleum ether. The combined petroleum ether extracts were carefully heated on a steam bath to remove solvent. The procedure yielded 38.1 g of free oil.

Preparation of 28% Active Sodium Alcohol Sulfate Solutions

From the previously described reagents, several 28% active sodium alcohol sulfate solutions were prepared having the following composition: 28.0% active, 1.0% free oil, 0.8% Na_2SO_4, 0.3% NaCl, 0.2% Na_2CO_3, q.s. water. These solutions differed one from the other only in the homolog distributions of the sodium alcohol sulfates.

Viscosity Measurements

Kinematic viscosities were measured at 38 C according to ASTM D 445.

RESULTS AND DISCUSSION

The viscosities of a number of sodium alcohol sulfate solutions each differing in C_{12}, C_{14}, and C_{16} homolog distribution were measured. Compositions of these solutions were adjusted as described in the Experimental Procedures section to contain a fixed level of active ingredient, free oil, sodium sulfate, and sodium chloride. A composition typical of what one would expect from a commercial chlorosulfation operation was selected as standard.

The results of our viscosity measurements are presented graphically in Figure 1. A grid was constructed representing the possible C_{12}, C_{14}, and C_{16} alcohol homolog compositions. Results are shown for the corresponding 28% active, sodium alcohol sulfate homolog. Only that portion of the triangle of interest to commercial sulfators is shown in Figure 1. Individual sodium alcohol sulfate solution viscosities were then plotted for 40 different alcohol homolog distributions. Lines of equal viscosity, isovis lines, were then constructed. The isovis lines clearly show that alcohol sulfate viscosity is affected by starting alcohol homolog distribution.

One would expect that alcohol molecular weight would have an effect on resulting alcohol sulfate viscosity. Figure 2 demonstrates that higher average molecular weight alcohols do tend to give higher viscosity sodium alcohol sulfate solutions. A typical lauryl-range ALFOL 1216 Alcohol is included in Figure 2 as a reference point. However, since the isovis lines do not parallel the lines of equal alcohol molecular weight, other factors are involved.

An analysis of the data presented in Table II may help

TABLE II

Effect of C_{14} Alcohol Content on the Viscosity of 28% Active Sodium "Lauryl" Alcohol Sulfate Solutions[a]

C_{14} alcohol content, wt %	Viscosity, cSt. @ 38 C
46	57.0
40	42.6
30	28.0
24	24.1
0	11.5

[a] The starting alcohol molecular weight was held constant at 198 molecular weight units. Alcohol sulfate solutions contained 1.0% free oil, 0.8% Na_2SO_4, 0.3% NaCl, 0.2% Na_2CO_3.

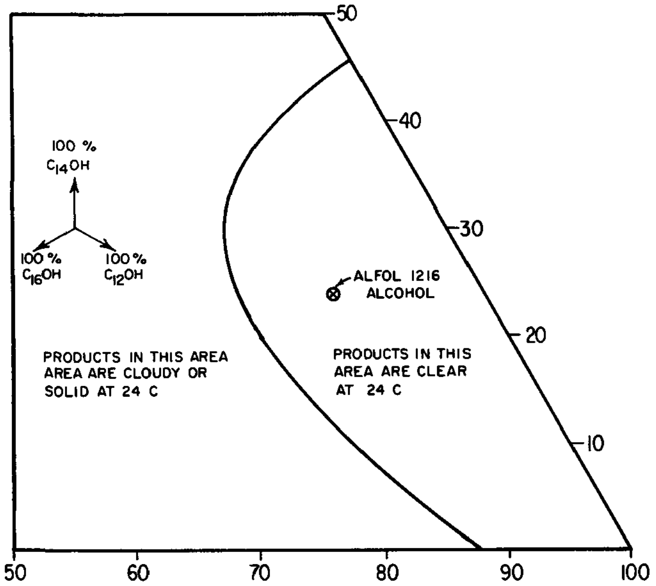

FIG. 3. Sodium alcohol sulfate clear point as a function of alcohol homolog distribution.

to explain some of these other factors. The results in Table II show that for a starting alcohol of molecular weight 198, alcohol sulfate viscosity is related to C_{14} alcohol content. Alcohol molecular weight was held constant in this experiment by adjusting the ratio of C_{12} to C_{16} alcohol as the C_{14} alcohol content was varied. The highest viscosity solution was obtained at 46% C_{14} alcohol – a composition containing 46% C_{14}, 54% C_{12}, and no C_{16} alcohol. Viscosity decreased as C_{16} alcohol content is increased until the minimum viscosity is realized in a composition containing 74% C_{12}, 26% C_{16}, and no C_{14} alcohol. The minimum viscosity is realized by a mixture of the two most diverse molecular species – a situation reminiscent of melting points of pure compounds and mixtures. Since 28% active lauryl sulfate solutions are micellar colloids, the arguments of Tanford can be applied in describing their physicochemical properties (9). Replacement of the C_{14} alcohol sulfate with C_{12} and C_{16} alcohol sulfate produces micelles with mixed hydrophobes of significantly different chain lengths. In a mixture containing all three types of molecules, increasing the component with the largest critical micelle concentration (CMC), C_{12} in this case, raises the CMC of the mixture (9) and concomitantly reduces the sizes of the individual micelles (10). These smaller micelles also have less surface area per unit volume since they are more nearly spherical (11). With both reduced cross-sectional area and reduced surface area, the micelles pass each other in solution with greater facility. The result is colloidal solutions with reduced viscosities.

Figure 3 contains results of investigations of sodium alcohol sulfate solution clear points. The 28% active products used in the viscosity studies were allowed to stand at 24 C for several weeks. These products were then checked for clarity. Compositions giving clear solutions as opposed to cloudy or solid products are illustrated in Figure 3. A typical lauryl-range ALFOL 1216 Alcohol is shown for reference. This product composition, as expected, yields a clear aqueous solution. An overlay of Figure 3 onto Figure 2 allows one to select a sodium alcohol sulfate homolog distribution with acceptable viscosity and solubility properties.

The work reported here clearly shows that alcohol homolog distribution effects both alcohol sulfate viscosity and solubility. Quite drastic changes in alcohol homolog distributions are, however, required to make significant changes in either property. The effect of changes in homolog distribution allowed in typical manufacturing specifications for a particular commercial alcohol would, however, be minimal compared to the effects of free oil and inorganic salts on these properties.

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