Sulfation of Synthetic Linear Primary Alcohols With Chlorosulfonic Acid[1]

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Abstract

This laboratory optimization program was undertaken to describe a method for sulfating linear primary synthetic alcohols with chlorosulfonic acid. Several alcohol blends, containing carbon lengths from C_{12} to C_{16}, were studied. These products find applications in cosmetic and shampoo formulations. A number of quality factors (color, odor, free unsulfated alcohol), demanded by this market, are discussed and comparisons to industry wide standards are made. Some of the operating parameters detailed in this work are: mole ratio of alcohol to acid; rate of reaction; reaction temperature; post reaction sparge time; sparging conditions and reaction time. It was shown that the color, of a finished triethanolamine salt based on Alfol 1216 SP alcohol, was significantly improved by proper sparging of the reaction mixture. Further, the color passed through a maximum during this final step. It was also demonstrated that dry air is functional in this quality improvement, while nitrogen seems to be inert.

Introduction

For many years fatty alcohols derived from natural sources and composed of various linear carbon chain lengths have been converted into alkyl sulfates by treating the alcohols with chlorosulfonic acid to yield the sulfate ester:

$$\mathrm{RCH_2OH + ClSO_3H \rightleftharpoons RCH_2OSO_3H + HCl}$$

followed by neutralization with either a metallic hydroxide or an amine

$$\mathrm{RCH_2OSO_3H + NaOH \rightarrow RCH_2OSO_3Na + H_2O}$$

$$+\ \mathrm{HN}\begin{array}{l}\diagup\ \mathrm{C_2H_4OH}\\ \diagdown\ \mathrm{C_2H_4OH}\end{array} \rightarrow \mathrm{RCH_2OSO_3H \cdot HN}\begin{array}{l}\diagup\ \mathrm{C_2H_4OH}\\ \diagdown\ \mathrm{C_2H_4OH}\end{array}$$

The products produced have wide applications as surfactants for cosmetics, shampoos, emulsion polymerizations and other household and industrial formulations.

The introduction of sulfation grade synthetic normal primary alcohols have presented attractive raw material economics to the market, and precipitated interest in sulfation technology for these materials.

TABLE I

Homolog Distribution and Physical Properties of Lauryl Range Alcohols

Conditions	Alfol 1214 SP	Alfol 1216 SP	Coconut derived alcohol
Per cent C_8	0.1	0.1	0.3
Per cent C_{10}	0.7	0.2	1.7
Per cent C_{12}	55.2	64.3	65.0
Per cent C_{14}	42.7	24.0	26.0
Per cent C_{16}	1.3	11.4	7.0
Per cent C_{18}	....	....	....
Hydroxyl number	279	276	276
Saponification number	0.2	0.2	0.3
Melting point (C)	25	20	22
Viscosity at 20 C	25 cps	25 cps	27.5 cps

All of the alcohol sulfates were analyzed according to the following methods: active, Methylene Blue Cationic Titration; free oil, Petroleum Ether Extraction; chloride, Volhard Silver Nitrate Titration; sulfate, Amperometric Titration; color, Klett-Summerson Photoelectric Colorimeter Model 900-3 equipped with blue filter No. 42 (400–465 mμ) and a 4 cm cell.

Materials

The alcohols used in this program were obtained from commercial sources and were not further purified. The synthetic products were derived from the polymerization of ethylene by the conventional Ziegler process, and the natural product was derived from coconut oil. They contained the following typical homolog distributions and physical properties (Table I).

Chlorosulfonic acid continues to be an important and contemporary sulfation reagent in spite of the fact that considerable sulfur trioxide sulfation plant capacity is on stream. Conventional Ziegler process synthetic normal primary alcohols lend themselves equally well to processing with sulfur trioxide or chlorosulfonic acid.

The general sulfation reaction has been studied by previous workers (1–6). This laboratory concentrated on the more important reaction parameters as they relate to the sulfation of synthetic normal primary alcohols with chlorosulfonic acid.

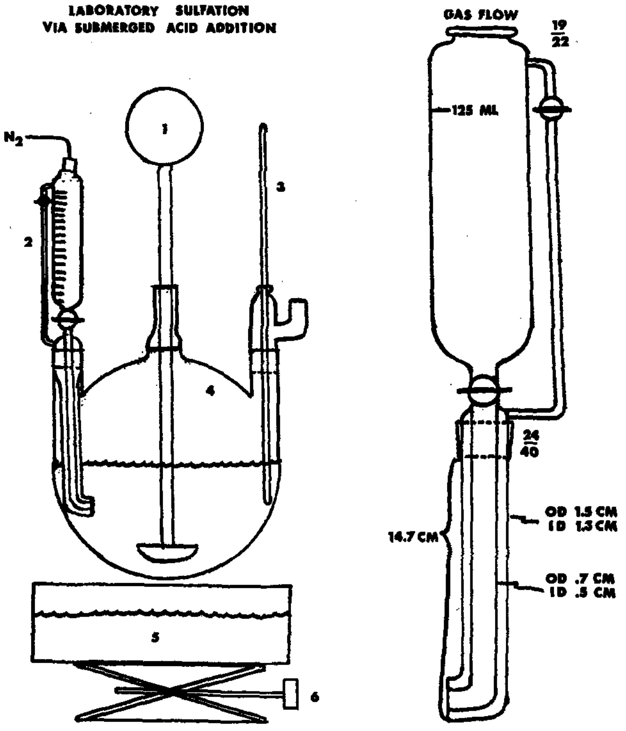

FIG. 1. Apparatus for submerged acid addition. 1, motor; 2, side arm dropping funnel with tube extension; 3, thermometer; 4, threee-neck creased Morton flask; 5, cooling bath; 6, lab jack.

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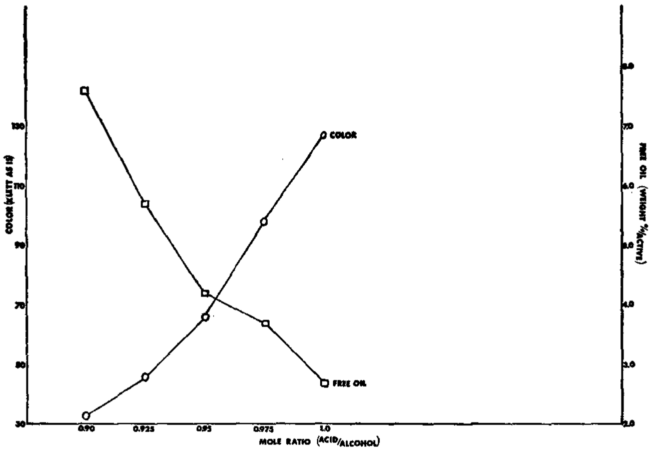

FIG. 2. Effect of mole ratio on color and free oil, TEA salt of Alfol 1216 alcohol sulfate: ○ color; □ free oil. Run conditions: Temperature, 25 C; time, 20 min; sparge time, 10 min; carrier gas, dry air.

Experimental Procedures

Methods

During the course of this project, an improved laboratory sulfation acid addition method was developed. The apparatus is designed to affect rapid dispersion of the chlorosulfonic acid in the alcohol. This is important in helping to avoid local overconcentrations of acid and subsequent darkening of the finished product. Figure 1 shows a diagram of this unit.

The chlorosulfonic acid is gravity fed down the inner concentric tube and dry air is conveyed through the outer concentric tube. At the outlet of these tubes, beneath the surface of the liquid in the reaction flask, the air bubbles vigorously and rapidly disperses the chlorosulfonic acid into the reaction mass. This action provides immediate intimate mixing of the chlorosulfonic acid and greatly reduces the likelihood of local high concentrations. Another advantage inherent in this design is the continuous sparging, thereby removing coproduct HCl as it is formed during the reaction.

The improvement in product quality resulting from this dispersed acid addition technique is demonstrated by comparing a conventional acid addition laboratory sulfation and our new procedure. Table II contains these data on triethanolamine (TEA) sulfate, and the most important difference is the color of the product.

The TEA salt is prepared by slowly adding the sulfate ester into a TEA/water neutralizing solution. A high speed laboratory blade mixer should be used to mix the solution and prevent the formation of gelled droplets of sulfate ester as the material drops into neutralizing solution. The final pH should be 7.2–7.6.

A summary of optimum run conditions, as illustrated by this work appears in Table III.

TABLE II

Comparison of Conventional and Dispersed Acid Addition Laboratory Sulfation

Conditions	Conventional	Dispersed
Activity, % (as TEA alcohol sulfate)	40.0	40.0
Free oil per 100% active, %	4.3	4.1
Chloride, %	0.4	0.2
Sulfate, %	1.2	1.2
Color Klett (as is)	120	50

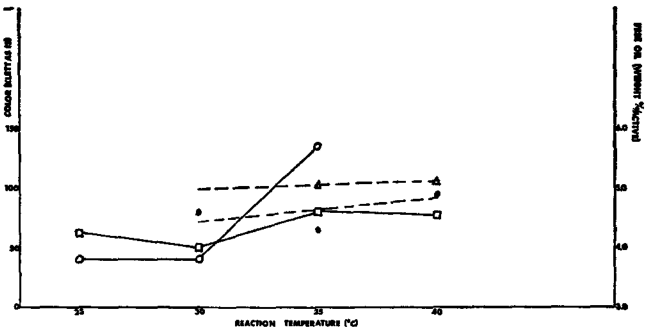

FIG. 3. Effect of reaction temperature on color and free oil: ○ color TEA Alfol 1216 alcohol sulfate; □ free oil TEA Alfol 1216 alcohol sulfate; △ free oil TEA Alfol 1214 alcohol sulfate; ● free oil TEA natural coconut alcohol sulfate. Run conditions: Mole ratio, acid-alcohol, 0.95; time, 20 min; sparge time, 10 min; carrier gas, dry air.

Discussion

The quality requirements for alkyl sulfates vary considerably, depending on the application, past acceptance criteria and convention. For example, the detergent industry generally prefers lower free oil values at the expense, if necessary, of other values, while emulsion polymerization people insist upon exceptionally low salt. The cosmetic industry, on the other hand, is quite concerned with very low colors.

Each of these different and apparently contradictory requirements can be, and are now being met at lower costs, with synthetic normal primary alcohol derivatives. Other special needs for alcohol sulfates are in food technology and as pharmaceutical emulsifiers.

Figure 2 demonstrates the effect of acid to alcohol mole ratio on free oil. It is evident that, as we approach stoichiometric proportions, the reaction approaches theoretical conversion of the alcohol. The free oil consists of unsulfated alcohol and any unsulfatable compounds in the original alcohol. Both Ziegler processed synthetics and naturally derived material of comparable molecular weights contain exceptionally low unsulfatable components.

Mole ratio also has a strong influence on the color of the finished alcohol sulfate. The higher acid to alcohol mole ratios lead directly to darker products. Figure 2 illustrates this phenomenon, and it becomes evident that in order to select on optimum mole ratio for sulfation, one must consider both free oil and color factors.

The effects of reaction temperature on free oil is not as pronounced as that of mole ratio. It is necessary, however, to consider this parameter because of its significant effect on the color of the sulfate. Figure 3 is a plot of reaction temperature vs. per cent of free oil and color. It is evident that the effect on free oil is negligible, while the color factor is quite

TABLE III

Optimum Run Conditions

Conditions	Alfol 1214 SP alcohol	Alfol 1216 SP alcohol	Natural Coconut alcohol
Mole ratio	0.95	0.95	0.95
Temperature, C	30	25	25
Time, min	30	20	30
Sparge time, min	0	0	0
Carrier gas	Dry air	Dry air	Dry air
Gas flow rate, L/min	16	16	16
Activity, % TEA salt	40.0	40.0	40.0
Free oil per 100% Active, %	4.1	4.0	4.0
Chloride, %	1.0	1.0	1.0
Sulfate, %	1.2	1.2	1.2
Color Klett (as is)	70	50	30

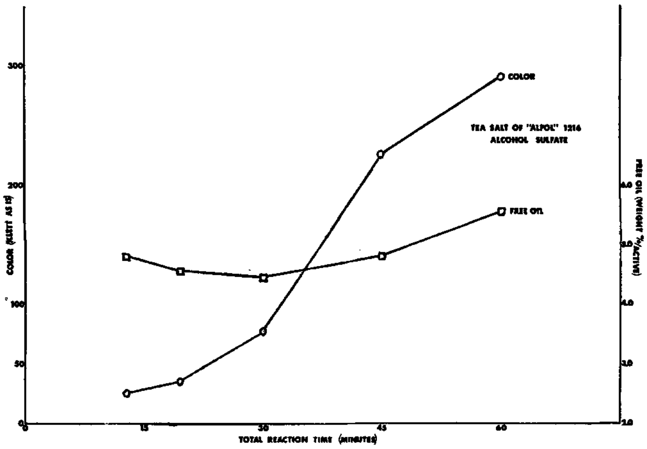

FIG. 4. Effect of reaction time on color and free oil, TEA Alfol 1216 alcohol sulfate: ○ color; ☐ free oil. Run conditions: Mole ratio, acid-alcohol, 0.95; temperature, 25 C; sparge time, 10 min; carrier gas, dry air.

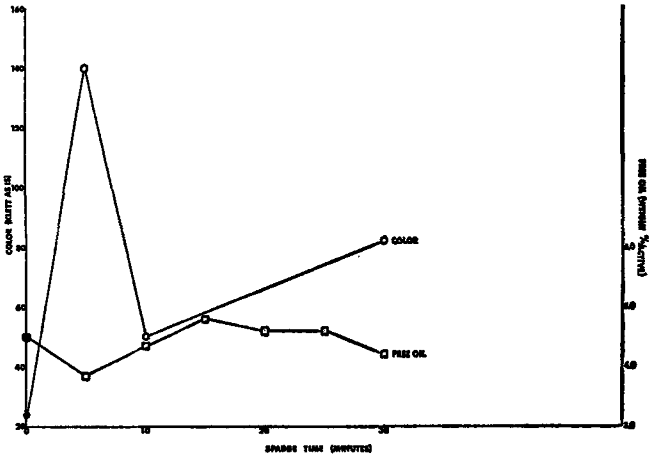

FIG. 6. Effect of sparge time on color and free oil: ○ color TEA salt of natural coconut alcohol sulfate; ☐ free oil TEA salt of Alfol 1216 alcohol sulfate.

seriously affected. The reaction temperature throughout this program was maintained at the nominal value ± 1.5 C.

The third reaction variable investigated in this work was reaction time. This was defined for the purposes of our program, as the elapsed time required to introduce the full charge of chlorosulfonic acid into the alcohol reaction flask. Each point on the following set of graphs, as were those presented previously, represents a separate sulfation run during which we modified the point under study. The effect of reaction time on free oil and color, as seen in Figure 4, is of interest because the plot seems to go through a minimum. This phenomenon may be explained by the fact that very rapid acid addition rates tend to char the alcohol at the point of entry. If this does indeed occur, then we would expect to degrade the alcohol somewhat by dehydration and carbon chain splitting. This condition would lead to a higher free oil caused by the increase in unsulfatables. Free oil can also be increased by running the reaction very slowly, thereby allowing for some hydrolysis of the sulfate ester. Reaction time has also been shown to be detrimental to the color of the alkyl sulfate as shown in Figure 4.

One of the more interesting and novel conclusions drawn from this work was related to the post reaction sparging of the reaction mixture. It is well known that post reaction sparging is beneficial to the finished product because of the removal of dissolved and dispersed hydrogen chloride in the ester. This step reduces the amount of chloride in the alcohol sulfate product. Figure 5 shows this rapid drop in salt content with increased sparge time. This result is accomplished by removal of the HCl gas. It is evident

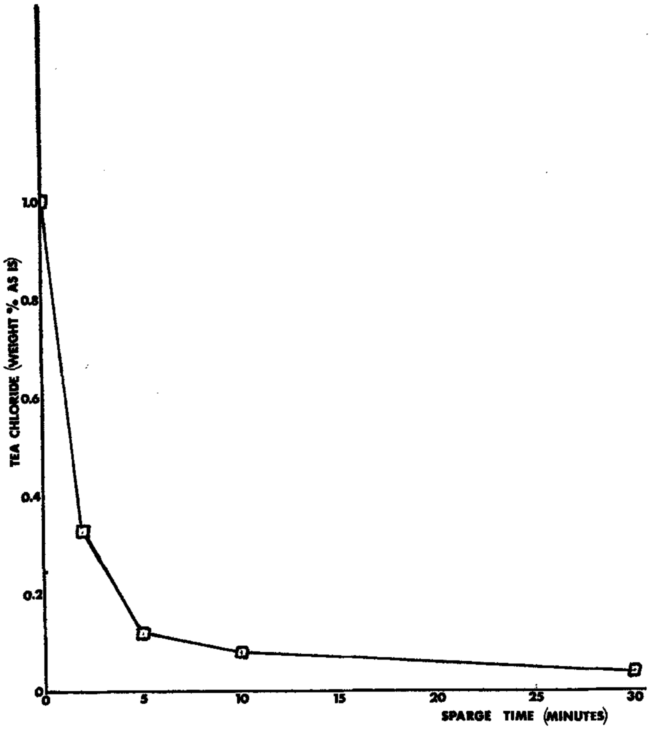

FIG. 5. Effect of sparge time on TEA Chloride, TEA salt of Alfol 1216 alcohol sulfate. Run conditions: Mole ratio, acid-alcohol, 0.95; temperature, 25 C; time, 20 min; carrier gas, dry air.

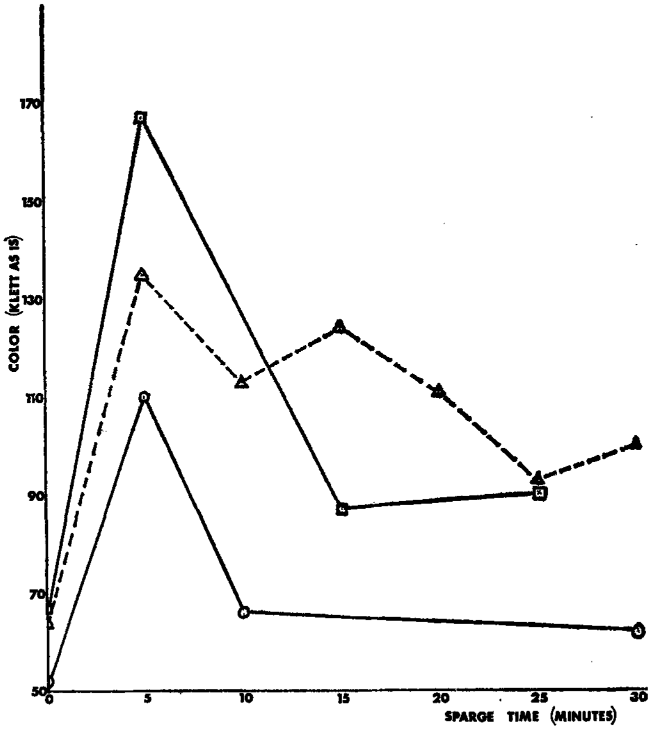

FIG. 7. Effect of sparge time and type of carrier gas on color, TEA salt of Alfol 1216 alcohol sulfate: ○ dry air; ☐ Nitrogen; △ Carbon Dioxide. Run conditions: Mole ratio, acid-alcohol, 0.95; temperature, 25 C; reaction time, 20 min.

that there is little to be gained in this area by continuing to sparge beyond 10 min.

The effect of sparge time on free oil, on the other hand, was found to be essentially inconsequential. Figure 6 is a plot of this type of data developed using dry air as the sparge gas. Similar trends were also observed with nitrogen and carbon dioxide.

The color response to sparge time was found to be more pronounced. In addition an unexpected but consistent increase in color was observed during the first 5 min of the post sparge period. This darkening effect occurred with all three sparge gases tested, dry air, nitrogen and carbon dioxide, although at varying rates (Fig. 7). Continued gas sparging produced a sharp decrease in color and, in the case of dry air, the color after 10 min approached the initial value at time 0. The color did not, at any time, return to the low initial point when the reaction mass was sparged with either nitrogen or carbon dioxide. The apparent functional quality of the dry air in this effect was not thoroughly investigated and remains a point of interest for a future study at our laboratory.

The discussion up to this point centered on the sulfation of one particular synthetic alcohol blend, Alfol 1216 SP alcohol. The effects studied appear to be more general in nature. A plot of free oil vs. reaction temperature for natural coconut alcohol and Alfol 1214 SP (a different homolog distribution) is shown in Figure 3. A family of parallel curves confirm that the effects are similar for these other alcohols.

The effect of sparge time and gas type on color are also carried forth to the other alcohol blends. Figure 6 shows the familiar color plot with natural coconut alcohol.

We recognized that this laboratory sulfation study was only indicative of trends in controlling commercial alcohol sulfate quality, but our laboratory has recently undertaken a pilot plant project to scale up this laboratory technique to produce high quality sulfates on plant scale. Our initial work in this area produced low colored alkyl sulfate (150 Klett). This work is continuing, and we hope to report on this in the future.

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