Anionic Surfactants: Lauric Products

KENSUKE TAKEI, Kao Corporation, R&D Division (Wakayama), **KEIICHI TSUTO**, **SHIGEYUKI MIYAMOTO** and **JUNYA WAKATSUKI**, Kao Corporation, Wakayama Research Laboratories, 1134, Minato, Wakayama, 640, Japan

ABSTRACT

Lauryl sulfate and lauryl ether sulfate obtained by the sulfation of lauryl alcohol and lauryl alcohol ethoxylate are representative of anionic surfactants and are used as a formable detergent or an emulsifier. For the sulfation of lauryl alcohol and lauryl alcohol ethoxylate, SO_3 gas, it was found that the quality of products was significantly influenced by the reaction conditions. In order to obtain good quality products we developed a new technology by using a new type of reactor called a "climbing film reactor," in which SO_3 gas and liquid raw material flow ascendingly.

INTRODUCTION

The sulfation of fatty alcohols and fatty alcohol ethoxylates gives fatty alcohol sulfates (AS) and fatty alcohol ether sulfates (ES), respectively (Fig. 1). These sulfates are representative of the anionic surfactants, and their detergencies depend on alkyl chain length, oxyethylene chain length and nature of the cations.

Lauryl sulfates have good foaming ability and biodegradability, so they have been widely used as detergents or emulsifiers. Sodium lauryl sulfate is superior in detergency and has been used for household products and industrial applications. It is often used as a foaming agent or a dispersant for cosmetics and as an emulsifier for emulsion polymerization. Triethanolamine lauryl sulfate possesses good foaming ability against sebaceous soil and it is used in liquid dishwashing detergents or in cosmetic products, especially in shampoos. Ammonium lauryl sulfate is used in liquid dishwashing detergents and shampoos as a good foaming agent. Lauryl ether sulfates are more soluble in water and less irritative to the skin or eyes than lauryl sulfates. Sodium lauryl ether sulfate is used in liquid dishwashing detergents and liquid shampoos, and triethanolamine lauryl ether sulfate used in shampoos.

THE SULFATION OF FATTY ALCOHOLS AND FATTY ALCOHOL ETHOXYLATES

In the sulfation of fatty alcohols and fatty alcohol ethoxylates, there are four representative sulfating agents.

1. Sulfur trioxide (SO_3)
   $R(OC_2H_4)_nOH + SO_3 \quad R(OC_2H_4)_nOSO_3H$
2. Chlorosulfonic acid ($ClSO_3H$)
   $R(OC_2H_4)_nOH + ClSO_3H \quad R(OC_2H_4)_nOSO_3H + HCl$
3. Oleum (fuming sulfuric acid, $SO_3 + H_2SO_4$)
   $R(OC_2H_4)_nOH + SO_3 \quad R(OC_2H_4)_nOSO_3H$
   $R(OC_2H_4)_nOH + H_2SO_4 \quad R(OC_2H_4)_nOSO_3H + H_2O$
4. Sulfamic acid (H_2NSO_3H);
   $R(OC_2H_4)_nOH + H_2NSO_3H \quad R(OC_2H_4)_nOSO_3H\,NH_3$

Table I lists examples of the industrial sulfation reactions with each sulfating agent. In sulfation with chlorosulfonic acid and sulfur trioxide, reactions proceed quantitatively and good quality products can be obtained, so these sulfating agents are usually used in the industrial sulfation. But in case of chlorosulfonic acid, the removal of HCl is necessary and a small amount of NaCl remains in the products. Further, as the molar ratio of chlorosulfonic acid to fatty alcohols or fatty alcohol ethoxylates is a little high compared with that of sulfur trioxide, the quantity of inorganic salt increases. Consequently SO_3 is the most advantageous with respect to reactivity, product quality and cost. With

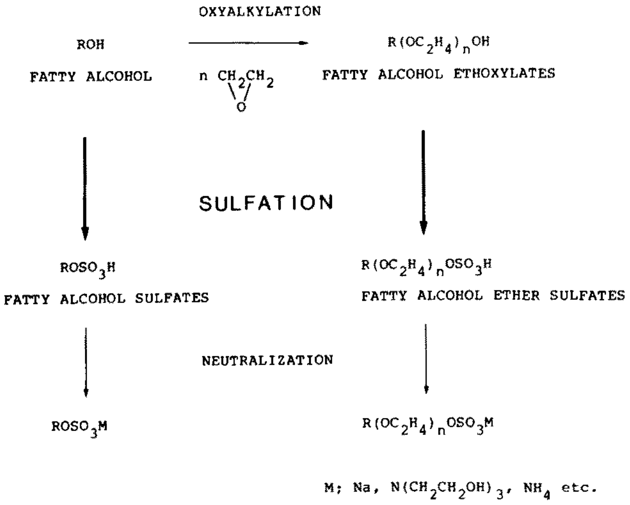

FIG. 1. Sulfation of fatty alcohols and fatty alcohol ethoxylates.

TABLE I

Examples of Industrial Sulfation Reactions of Fatty Alcohols and Fatty Alcohol Ethoxylates

Sulfating agent	Product	Molar ratio[a]	Reaction temperature (C)	Reaction yield (%)	Quality of product: Active/inorganic salt	Quality of product: Color and odor
SO_3	AS ES	- 1.0 -	35	98	100/ 2 100/ 1	○
$ClSO_3H$	AS ES	1.0 - 1.1	35	96	100/ 4 100/ 5	○ - △
Oleum	AS ES	2.0 - 3.0	35	92	100/85	X
NH_2SO_3H	ES	1.0 - 1.1	130	98	100/ 5	△

[a] Molar ratio of the sulfating agent to fatty alcohol or fatty alcohol ethoxylate.
[b] ○: good, △: fair, X: poor.

sulfamic acid, the manufacturing cost is high, and if a product other than the ammonium salt is required, salt exchange is necessary. So this method is employed only for special use. The disadvantage in oleum sulfation is that a large quantity of inorganic salt remains in the products as a result of addition of excess oleum to move the equilibrium to the right side, and in addition, the quality of the products is inferior.

RATE OF REACTION BETWEEN LAURYL ALCOHOL OR LAURYL ALCOHOL ETHOXYLATE AND SO_3 GAS

The rate constant of reaction between lauryl alcohol and SO_3 gas was determined by measuring the relative reaction rates of sulfation of alcohol and sulfonation of alpha olefin. As references, relative reaction rates in the sulfonation of alpha olefin and alkylbenzene, which are the representative detergent raw materials of sulfonate, AOS (alpha olefin sulfonate) and LAS (linear alkylbenzene sulfonate), were measured. Materials used were lauryl alcohol (Kalcohl-20, Kao Corp., hydroxy number=300), 1-hexadecene (iodine number=113) and dodecylbenzene prepared from benzene and 1-dodecene by conventional Friedel-Crafts reaction. In order to facilitate the analysis we assumed that the sulfation or the sulfonation was of first order with respect to both SO_3 and substrates to be sulfated or sulfonated, and the initial relative reaction rates were measured.

In addition the rate constant of the reaction between lauryl alcohol ethoxylates and SO_3 gas was determined by measuring the relative reaction rates of lauryl alcohol ethoxylates and lauryl alcohol. Here, lauryl alcohol ethoxylate, $C_{12}H_{25}(OC_2H_5)_3OH$, of average three oxyethylene units per molecule (EO $\bar{p}=3$, Emulgen-103, Kao Corp., hydroxy number=180) was used. We assumed that the sulfation was of first order with respect to both SO_3 and lauryl alcohol or each of the ethylene oxide adducts similarly.

Sulfation of Lauryl Alcohol and the Sulfonation of 1-Hexadecene

To the mixture composed of equimolecular amounts of lauryl alcohol and 1-hexadecene, in which octadecane was added as an internal standard, was introduced SO_3 gas. The resulting products were neutralized with NaOH, and their solution in ethanol was treated with a cationic and an anionic ion-exchange resin according to Ginn and Church (1). From the purified products unreacted materials were extracted with petroluem ether, and unreacted lauryl alcohol and 1-hexadecene were determined by the relative peak area of the chromatogram in comparison with that of the internal standard. Results are given in Table II.

On the basis of the assumption, the rate equations are:

5. $dx_1/dt = k_1(a_1-x_1)(b-x_1-x_2)$
6. $dx_2/dt = k_2(a_2-x_2)(b-x_1-x_2)$

where a_1, a_2 and b are the initial concentration of lauryl alcohol, 1-hexadecene and SO_3 respectively, x_1 and x_2 are the concentration of the converted substrates (AS and AOS), and k_1 and k_2 are the rate constant of the sulfation of lauryl alcohol and the sulfonation of 1-hexadecene. Dividing equation 5 by equation 6 yields:

7. $dx_1/k_1(a_1-x_1) = dx_2(a_2-x_2)$

Integration of equation 7 yields:

8. $\ln[a_1/(a_1-x_1)] = k_1/k_2 \times \ln[a_2/(a_2-x_2)]$

Consequently, the relative reaction rate, $k_1/k_2=k_{alcohol}/k_{olefin}$, was determined to be 4.6 by the slope of linear plot of $\ln[a_1/(a_1-x_1)]$ vs. $\ln[a_2/(a_2-x_2)]$ (Fig. 2).

TABLE II

Sulfation of Lauryl Alcohol and Sulfonation of 1-Hexadecene with SO_3 Gas

(mole)	Run 1	Run 2	Run 3
Sulfation and sulfonation			
Lauryl alcohol	0.247	0.247	0.247
1-Hexadecene	0.247	0.247	0.247
SO_3	0.0425	0.0924	0.160
Recovered materials after sulfation and sulfonation			
Lauryl alcohol	0.156	0.125	0.101
1-Hexadecene	0.222	0.214	0.202

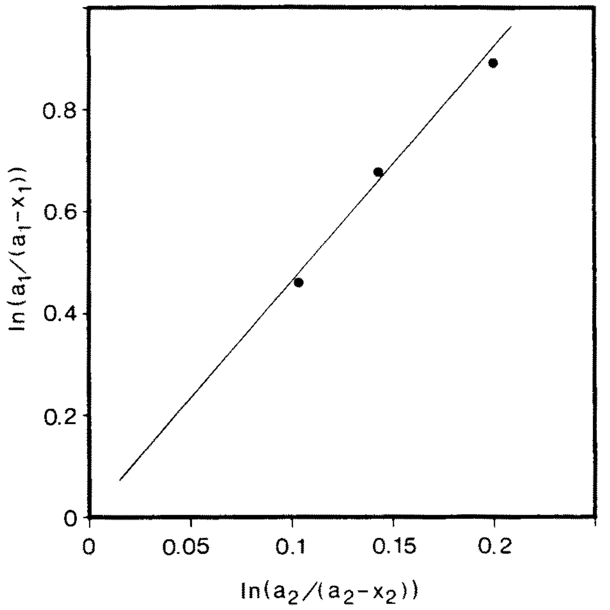

FIG. 2. Plot of $\ln[a_1/(a_1-x_1)]$ vs. $\ln[a_2/(a_2-x_2)]$, in which a_1 and a_2 are the initial concentration of lauryl alcohol and 1-hexadecene, respectively, and x_1 and x_2 are the concentration of the converted substrates (AS and AOS), in the sulfation of lauryl alcohol and the sulfonation of 1-hexadecene with SO_3 gas.

TABLE III

Sulfonation of 1-Hexadecene and Dodecylbenzene

(mole)	Run 1	Run 2
Sulfonation		
Dodecylbenzene	0.797	0.797
1-Hexadecene	0.0163	0.0163
SO_3	0.0138	0.0163
After sulfonation		
Total sulfonate	0.01384	0.01384
LAS	0.00498	0.00485
AOS = Total - LAS	0.00886	0.00899

Sulfonation of 1-Hexadecene and Dodecylbenzene

To one mole of a mixture composed of 98 mol% dodecylbenzene and 2 mol% 1-hexadecene was added 0.02 mole of SO_3 gas. The sulfonation products were then neutralized with excess NaOH, and the sultones produced with 1-hexadecene and SO_3 were hydrolyzed by heating the mixture at 150 C for one hr. From the resulting products, unreacted substrates were removed by extraction with petroleum ether. Total anionic surfactant was determined by methylene blue titration analysis, and alkylbenzene sulfonate was determined by UV analysis. The difference is the amount of alpha olefin sulfonate. The results are given in Table III. In a similar manner as in the sulfation reactions, the ratio of $\ln[a_2/(a_2-x_2)]/\ln[a_3/(a_3-x_3)]$, in which a_2 and a_3 are the initial concentrations of 1-hexadecene and dodecylbenzene, respectively, and x_2 and x_3 are the concentrations of converted substrates (AOS and LAS), gave the relative reaction rate, $k_{olefin}/k_{alkylbenzene}$, to be 130.

Sulfonation of Lauryl Alcohol Ethoxylate

To calculate relative reaction rates based on gas chromatographic data before and after sulfation, lauryl alcohol ethoxylate, EO p=3, was separated into each composition of ethylene oxide units ranging from 0 to 7 as acetate derivatives. After sulfation with SO_3 gas, the product was neutralized with NaOH and ionic materials were removed in ethanol solution by treating with ion exchange resin as described with Ginn and Church (1). The unreacted substrates were weighed and their compositions were determined by gas chromatography as acetate. From the amount of each reaction product, the relative reaction rate, $k_{R(EO)_pOH}/k_{ROH}$ (p=1-7) could be calculated. They are listed in Table IV. The relative reaction rate, $k_{R(EO)_nOH}/k_{ROH}$ is about 0.3 (EO $\bar{p}$=3).

All reactions are summarized in Table V. The rate constant of the reaction between 1-hexadecene and SO_3 gas was reported by Miyauchi et al. (2) to be 4.8×10^2/mol·sec^{-1}. This value was used to estimate the values for lauryl alcohol and lauryl alcohol ethoxylate. As shown in Table V, the rate constant of the reaction between lauryl alcohol and SO_3 gas is 2.2×10^3/mol·sec^{-1}, and the reaction time for 99% sulfation is calculated to be about 0.04 second. It is understandable that the sulfation of lauryl alcohol with SO_3 gas is extremely rapid.

TABLE IV

Relative Reaction Rates of Sulfation of Lauryl Alcohol and Lauryl Alcohol Ethoxylate with SO_3 Gas

	Relative reaction rate, $k_{R(EO)_pOH}/k_{ROH}$	
p	Reaction temperature = 25 C	Reaction temperature = 45 C
1	0.40	0.40
2	0.27	0.29
3	0.27	0.27
4	0.27	0.28
5	0.26	0.29
6	0.26	0.30
7	0.28	0.30

TABLE V

Comparison of Reaction Rate of Sulfation of Lauryl Alcohol and Lauryl Alcohol Ethoxylate and Sulfonation of Dodecylbenzene and 1-Hexadecene with SO_3 Gas

Raw material to be sulfated or sulfonated	Ratio of rate constant	Rate constant k/mol·sec at 50 C
Dodecylbenzene	1	(3.7)[a]
1-Hexadecene	130	4.8×20^2[b]
Lauryl alcohol ethoxylate	180	6.6×10^2
Lauryl alcohol	600	2.2×10^3

[a] We assumed that the reaction was of first order with respect to SO_3.
[b] This was measured by Miyauchi et al. (2).

HEAT OF REACTION OF SO_3 AND LAURYL ALCOHOL OR LAURYL ALCOHOL ETHOXYLATE

The heats of reaction between SO_3 gas and chlorosulfonic acid with lauryl alcohol or lauryl alcohol ethoxylates (EO $\bar{p}$=1, 2 and 3) were measured. In the calorimetry apparatus, lauryl alcohol or lauryl alcohol ethoxylate was dissolved in dichloroethane, and SO_3 or chlorosulfonic acid in amounts of equimolar with lauryl alcohol or lauryl alcohol ethoxylates was added to the solution in a moment, and the temperature rise was measured. The solubility heat of the sulfates was corrected. The results are shown in Table VI. The reaction heat of sulfation with SO_3 gas is about 2-2.5 times higher than that of sulfation with chlorosulfonic acid.

RELATIONS BETWEEN THE MOLAR RATIO AND THE REACTION YIELD OR THE COLOR OF PRODUCTS

In the sulfation of lauryl alcohol or lauryl alcohol ethoxylate (EO p=$\bar{2}$) with SO_3 gas, the relations between the molar ratio and the reaction yield or the color of the products were examined as shown in Figures 3 and 4. The reaction yield increased linearly and quantitatively until the molar ratio of SO_3 to the substrates was 1.02-1.05, but decreased very rapidly when the molar ratio exceeded it in either case. The products colored abruptly when the molar ratio exceeded about 1.0, which is called "over-reaction." It is clear, therefore, that strict control of the molar ratio is important in sulfation with SO_3 gas.

TABLE VI

Heat of Reaction between Lauryl Alcohol or Lauryl Alcohol Ethoxylate and SO_3 Gas or Chlorosulfonic Acid

	Heat of reaction[a] (Kcal/mol)	
	SO_3 gas as a sulfating agent	$ClSO_3H$ as a sulfating agent
Lauryl alcohol	42.7	17.6
Lauryl alcohol ethoxylate		
EO $\bar{p}$ = 1	43.9	20.4
EO $\bar{p}$ = 2	44.6	22.3
EO $\bar{p}$ = 3	43.7	23.0

[a] Molar ratio of SO_3 or chlorosulfonic acid to lauryl alcohol or lauryl alcohol ethoxylate is 1:1.

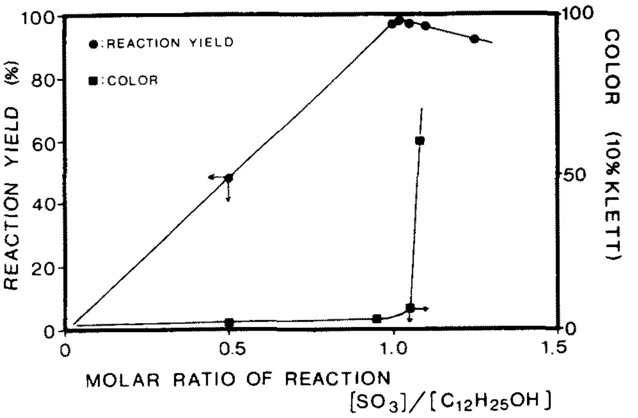

FIG. 3. Relations between the molar ratio and the reaction yield or the color of product in the sulfation of lauryl alcohol with SO_3 gas.

REACTION TEMPERATURE AND COLOR FORMATION

The effect of the reaction temperature on the color formation of the products in sulfation of lauryl alcohol or lauryl alcohol ethoxylates (EO $\bar{p}=2$) with SO_3 gas was examined. The results are shown in Figure 5. In sulfation of lauryl alcohol, the product colored remarkably when the reaction temperature was higher than 70 C. In sulfation of lauryl alcohol ethoxylate, the color of product was minimum when the temperature was about 60 C. The reason for this was that when the temperature was lower than 60 C, the viscosity of the reaction mixture increased, so the substrate could not be mixed with SO_3 gas sufficiently to prevent over-reaction locally, and when it was higher than 60 C, the product colored like sulfation of lauryl alcohol.

THE THERMAL DECOMPOSITION OF LAURYL HYDROGEN SULFATE AND LAURYL ETHER HYDROGEN SULFATES

Thermal decompositions of lauryl hydrogen sulfate at 40, 60, 80 and 100 C, and that of lauryl ether hydrogen sulfates (EO $\bar{p}=3$) at 80, 100 and 120 C were examined. The decrease of the active component was followed as a function of time at each temperature. As shown in Figures 6 and 7, the decomposition proceeded greatly as temperature increases. Figure 8 shows the decomposition of lauryl hydrogen sulfate and lauryl ether hydrogen sulfates (EO $\bar{p}=1$, 2, and 3) at 100 C. Lauryl hydrogen sulfate is more easily decomposed than lauryl ether hydrogen sulfates while lauryl

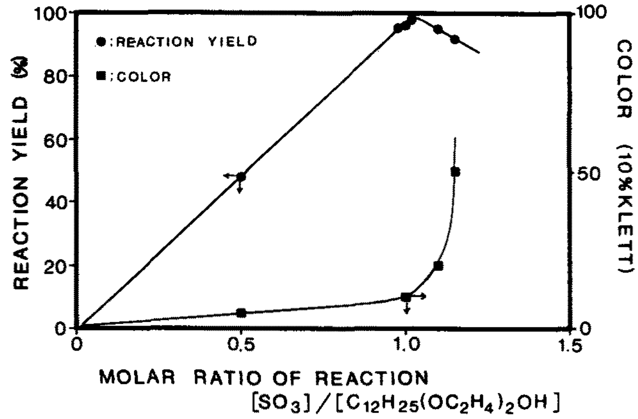

FIG. 4. Relations between the molar ratio and the reaction yield or the color of product in the sulfation of lauryl alcohol ethoxylate with SO_3 gas.

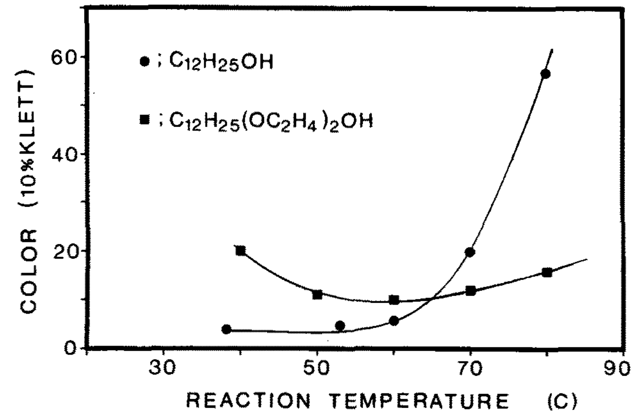

FIG. 5. Relations between reaction temperature and color formation in sulfation of lauryl alcohol and lauryl alcohol ethoxylate with SO_3 gas.

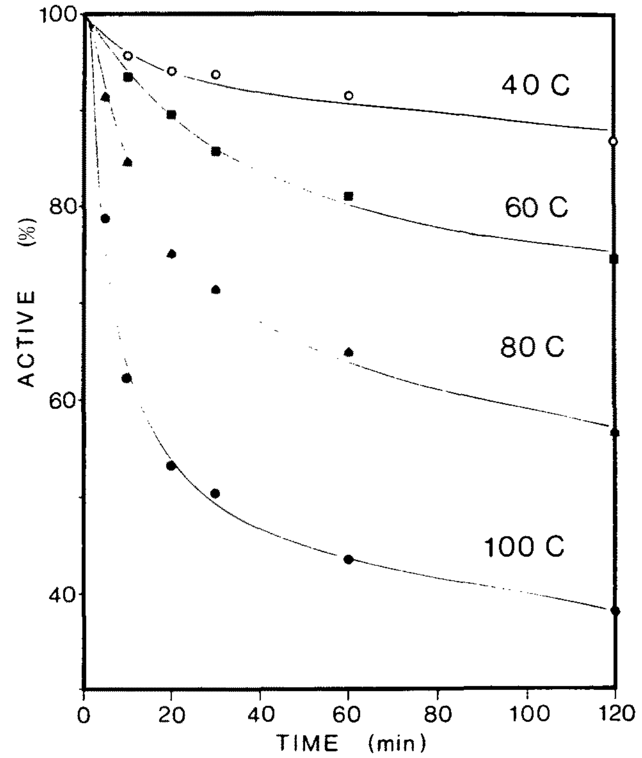

FIG. 6. Thermal decomposition of lauryl hydrogen sulfate $C_{12}H_{25}OSO_3H$.

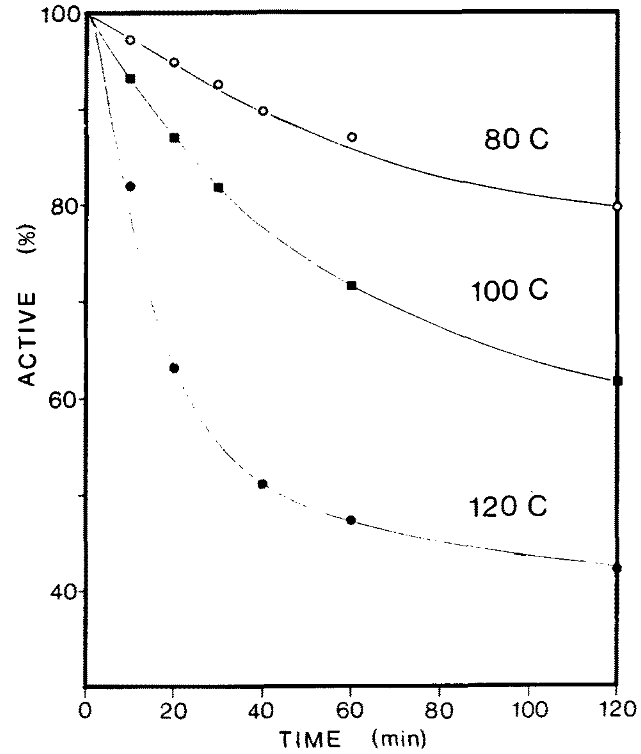

FIG. 7. Thermal decomposition of lauryl ether hydrogen sulfate $C_{12}H_{25}(OC_2H_4)_3OSO_3H$.

ether hydrogen sulfates which have more ethylene oxide units are fairly stable.

DEVELOPMENT OF THE REACTOR

The characteristics of the reaction between lauryl alcohol or lauryl alcohol ethoxylates and SO_3 gas are:

- The heterogeneous reaction between gas and liquid.
- The rate of the reaction is very fast (especially in the sulfation of lauryl alcohol).
- The heat of the reaction is high.

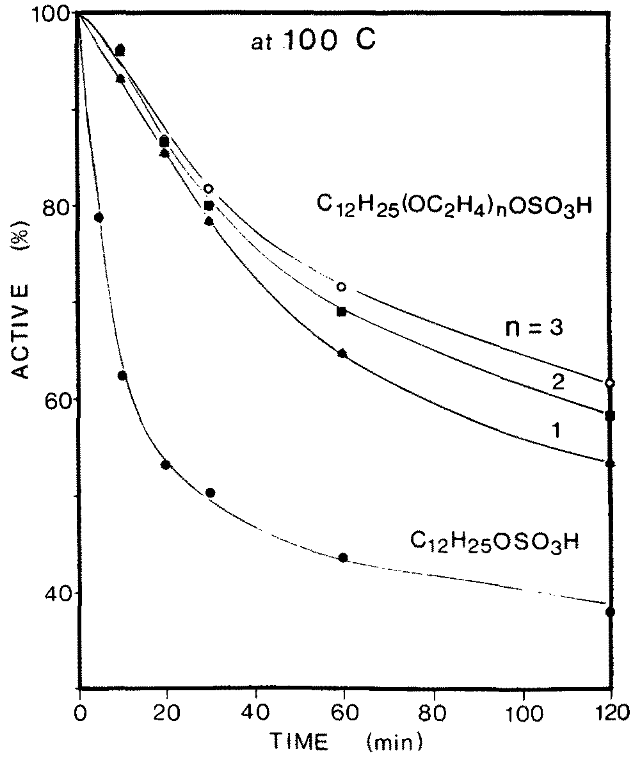

FIG. 8. Thermal decomposition of lauryl hydrogen sulfate and lauryl ether hydrogen sulfates at 100 C.

Characteristics of the products are:

- Lauryl hydrogen sulfate and lauryl ether hydrogen sulfates are liable to decompose at high temperatures to give colored product of lower active content. The sulfated products therefore need to be neutralized as quickly as possible.
- Products are liable to be colored when reaction temperature is high.
- They color with excess SO_3, so it is necessary to control the molar ratio of SO_3 to the substrates strictly.

Accordingly, the requirements for a reactor for sulfation of lauryl alcohol or lauryl alcohol ethoxylates with SO_3 gas are:

- To complete reaction immediately and uniformly with sufficient mixing,
- To remove the reaction heat efficiently,
- To simplify the structure to prevent a reaction mixture from remaining locally in the reactor and to shorten the residence time of the reaction mixture.

Reactors of gas-liquid reaction are classified according to the types of reactor and reaction conditions, which are summarized in Table VII. We first examined conventional reactors commonly used in order to make the reaction efficient and obtain good quality products, but we were not successful. This difficulty lay in the fact that the mixing of a large quantity of gas, in which SO_3 gas was diluted with dried air at between 1 and 10% by volume, and a small amount of liquid—the feed volume ratio of diluted SO_3 gas to liquid material was from 500 to 5000—depends on ordinary gas-liquid contacting and mixing techniques, such as those applied in agitating vessel type, falling film type and combination type reactors. Furthermore, to achieve uniform mixing, a stirring device was attached to all of the reactors, but this made the reactors very complicated, and the mechanical complexity caused localized nonuniform mixing. From the viewpoint of the simplicity of the reactor and the use of kinetic energy of a large amount of gas as an agitation power, we decided to use gas-liquid two phase flow of the vertical ascending type (3). We call the reactor of this type "climbing film reactor." Figure 9 shows the change in the flow pattern when air is injected upward into a stream of ascending water in a vertical tube (4). The situation of the sulfation of lauryl alcohol and lauryl alcohol ethoxylates with SO_3 gas is the annular flow region as

TABLE VII

Classification of Two-Phase (Gas-Liquid) Reactors

Type of reactor / Condition	Tubular reactor: Up flow type (or horizontal flow)	Tubular reactor: Down flow type	Tubular reactor with stirrer	Stirred tank reactor	Others
Ratio of volume flow rate gas/liquid: low	Bubbling-column reactor (bubble-liquid)	Wetted-wall column reactor (gas-liquid)		Gas-liquid stirred tank reactor	Packed-bed reactor Plate tower reactor
	Rising film reactor (gas-liquid)	Falling film reactor (gas-liquid)	Parallel current type (up flow horizontal flow down flow)		Ejector type (Liquid jet type)
high	Spray tower reactor (gas-liquid droplet)	Spray tower reactor (gas-liquid droplet)			Spray chamber type

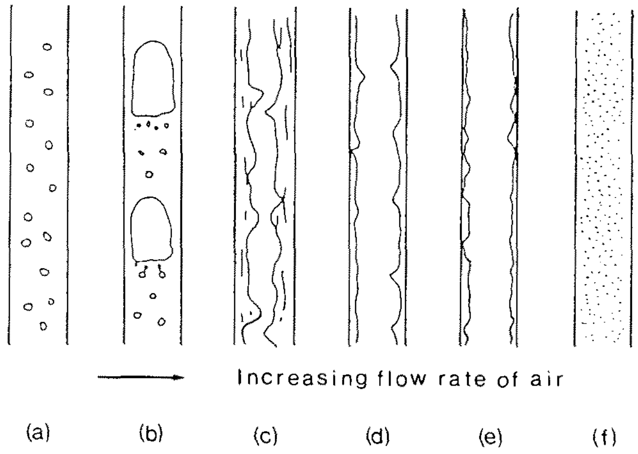

FIG. 9. Flow patterns of upward two-phase flow.

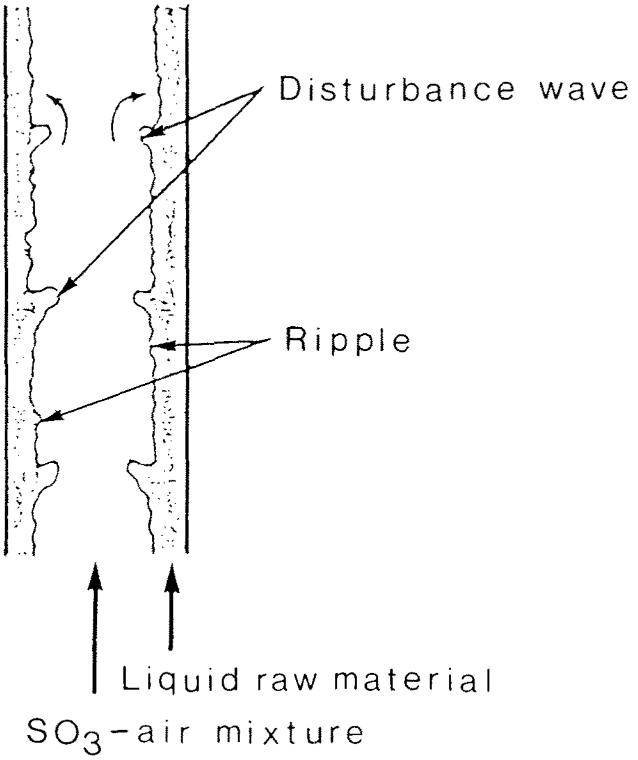

FIG. 10. Behavior of annular upward flow.

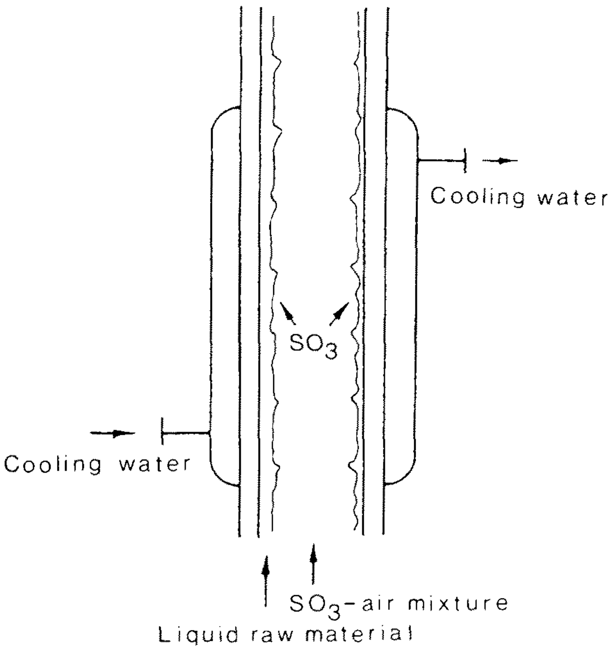

FIG. 11. Model of climbing film reactor.

shown in Figure 9(d), and the characteristic of this region is the lateral striped pattern of the annular flow. Rings of the lateral striped pattern are called "disturbance waves" and indicate a different behavior from that of the small wave "ripple" in the falling film type (Fig. 10). This big wave moves on the climbing film several times faster than the average climbing speed of the film. These rings move in a pulse-like motion and accompany a rotational movement to remove the film from the surface of the wall. Thus this wave seems to act as a mixer.

The fundamental climbing film reactor is schematically shown in Figure 11. A reaction tube is kept vertical and an SO_3-air mixture and lauryl alcohol of lauryl alcohol ethoxylate are continuously introduced from the bottom of the tube. When the molar ratio of SO_3 to the liquid material is adjusted to about 1 and SO_3 is diluted with dried air at between 1 and 10% by volume, the liquid moves up along the wall of the reaction tube, forming a thin film by the driving force of the gas. SO_3 diffuses in a radial direction and reacts with the substrates, and the heat of reaction is removed by the cooling jacket on the tube. The climbing speed (1 to 2 m/sec) of liquid film changes with the diameter of the tube and the quantity of gas and liquid supplied. Then the velocity of gas is adjusted to from 10 to 100 m/sec. In the industrial application of this reactor, several types are considered. As shown in Figure 12(a), this single-tube type reactor is easily applicable industrially. This type has economical advantages in that the plant cost is low and the maintenance is easy. But it has disadvantages in that if the diameter of the reactor tube increases while keeping the molar ratio of SO_3 to lauryl alcohol or lauryl alcohol ethoxylate constant for the purpose of increasing the amount of feeding, the color of the products darkens and the reaction yield decreases. The reason for this is that the quantity of the introduced substrate can be increased in proportion to the square of the tube diameter, but the cooling surface of the tube increases only in proportion to the diameter. Therefore, the temperature in the reactor tube becomes higher because of insufficient cooling capacity. To overcome this difficulty, an improved method was developed that decentralizes heat generation in a single tube by using fractional gas feeding. Figure 12(b) shows an example of this type of reactor. A further improved system is shown in Figure 12(c). In this third system, the reaction is also done in two steps. The first step is done in several small tubes arranged in parallel, and the second step is done in one large tube. We call this type of reactor "multi-tube climbing film reactor." The advantage of this system is that most of the reaction can be completed in the small tubes, and strict control of the molar ratio of SO_3 to the substrate to be sulfated is not necessary in the first step as long as it is precisely controlled in the second step. The structure of the multi-tube climbing film reactor is shown in Figure 13. Using the reactor with 39 tubes (tube diameter 28 mm, tube length 4 m) and feeding the law material at 5-7 kmol/hr, good quality lauryl sulfate and lauryl ether sulfate have been manufactured as shown in Table VIII.

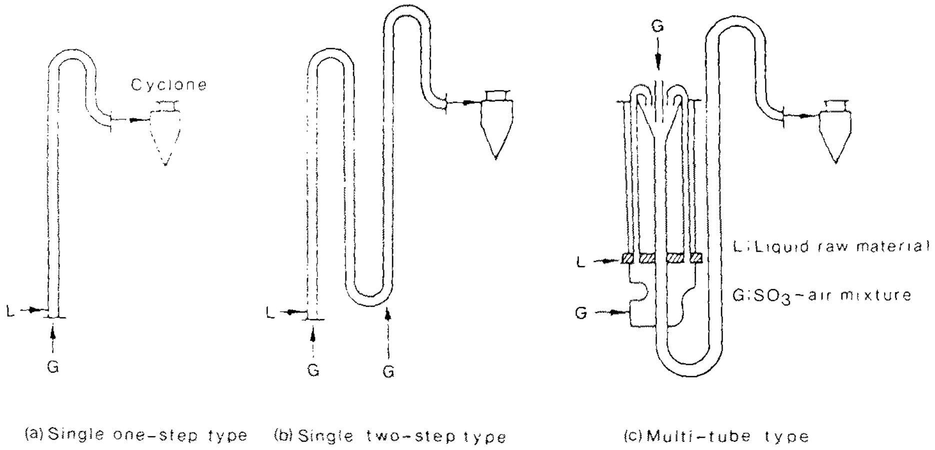

FIG. 12. Types of climbing film reactor.

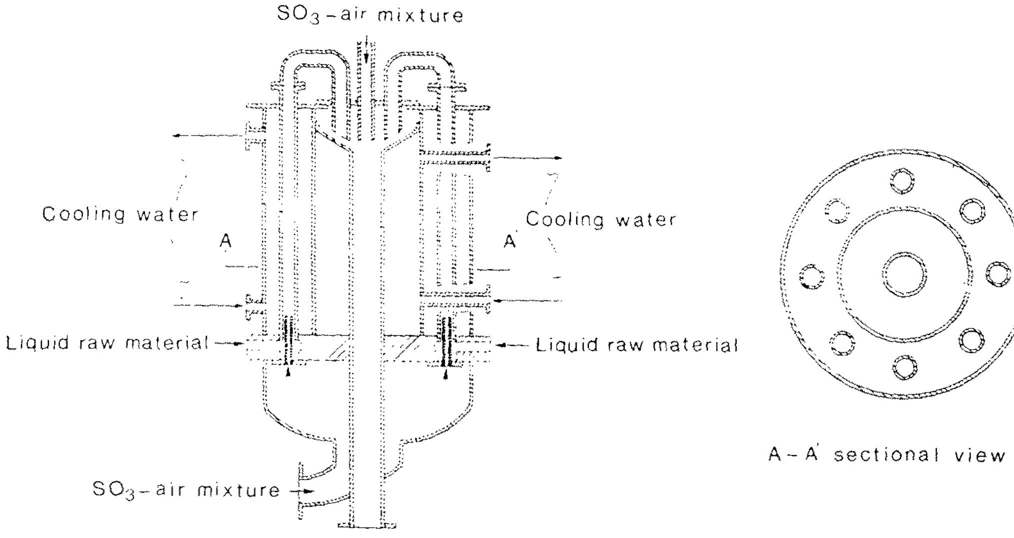

FIG. 13. Structure of multi-tube climbing film reactor.

TABLE VIII

Quality of Lauryl Sulfate and Lauryl Ether Sulfate by Using Climbing Film Reactor

Product	Reaction yield (%)	Na_2SO_4/Active (%)	Color (10% active Klett)
Lauryl sulfate	98	< 1	- 5 -
Lauryl ether sulfate	98	< 1	- 10 -

ACKNOWLEDGMENTS

S. Sasaki, Director of Research Laboratories, permitted publication of this paper. H. Kasai, H. Yamada and T. Kusumi ran the experiments.

REFERENCES

1. Ginn, M.E., and C.L. Church, Anal. Chem. 31:551 (1959).
2. Miyauchi et al., 3rd Autumn Meeting, The Soc. of Chem. Engrs., Japan (1969).
3. Kao Corporation, Japan. Patent 47-37407 and U.S.P. 4086256.
4. Sekoguchi, Y., "Dennetu Kogaku no Shinten 1," Yokendo, Japan (1973), p. 173.