A Mechanistic Approach to the Thermal Degradation of α-Olefin Sulfonates

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Determination of the thermal stability of α-olefin sulfonates (AOS) via the conventional activation energy approach was found to be impractical because of the difficulties arising from the fact that α-olefin sulfonates are mixtures of hydroxyalkane sulfonates and alkene sulfonates. Each of these components of AOS was studied independently and found to follow a complicated thermal degradation path.

We found that the thermal degradation of hydroxyalkane sulfonate is a base-catalyzed process. At elevated temperatures, hydroxyalkane sulfonates are first converted into an intermediate which is still surface active before degrading further to a non-surface active product by a second mechanism. The rate-determining step of the degradation process was found not to involve a cleavage of the C-S bond as observed for other types of sulfonates.

Our work indicates that the first step of the thermal degradation of alkene sulfonates involves isomerization of double bonds followed by cleavage of the C-S bond. The thermal degradation of alkene sulfonates is catalyzed by acids.

Application of α-olefin sulfonates (AOS) in household laundry and cleaning products has been a reality for many years. More recently, the use of AOS to enhance the recovery of heavy oil by means of steam injection has gained in popularity.

Good thermal stability is one of the more important properties required of surfactants for enhanced oil recovery processes. In micellar/polymer floods, the surfactant systems can be exposed to very high natural reservoir temperatures for long periods of time, even years. In steam enhanced oil recovery processes, a surfactant may be exposed to even higher temperatures for shorter time periods. It is generally accepted that the thermal stability of sulfonates is much greater than that of sulfates at elevated temperatures. We are not aware of any detailed mechanistic study of the thermal stability of α-olefin sulfonates being reported in the literature. Furthermore, we found only a few publications addressing the thermal stability of alkylaryl sulfonates (1,2).

The most common approach utilized for measuring the thermal stability of a surfactant has been the determination of the activation energy involved in the degradation process. Once the activation energy is known, it is possible to estimate the rate of thermal degradation under various conditions by making certain reasonable assumptions.

The literature indicates that thermal degradation of aryl sulfonates is a hydrolytic desulfonation process resulting in the formation of sulfuric acid. Also, the hydrolytic desulfonation is reported to be an acid-catalyzed process resulting in the desulfonation being autocatalytic (2).

AOS is composed primarily of two major components, alkene sulfonate and hydroxyalkane sulfonate, in a ratio of approximately three to one. In addition, the olefins used to produce AOS may contain significant levels of vinylidene olefins as well as linear internal olefins, especially at higher molecular weights. Counting both alkene sulfonate and hydroxyalkene sulfonate isomers, AOS is a mixture containing about a dozen identifiable surfactants (3,4).

In view of the complexity of the AOS system it was suspected that the determination of the activation energy for the thermal degradation of AOS might be very difficult, especially if the thermal stabilities of the AOS components were found to differ substantially and/or the degradation of the various structures followed different mechanisms. The objective of this work was to examine the thermal degradation of AOS and to determine the degradation path followed by the two major components of AOS alkene sulfonate and hydroxyalkane sulfonate.

EXPERIMENTAL

All thermal degradation studies were carried out in 15-ml 304 stainless steel cylinders. The sealed cylinders, containing 7 ml of surfactant solution under a nitrogen atmosphere, were marked and placed in a constant temperature oven. The surfactant concentration was 1.0 wt% in all cases. A number of cylinders containing the surfactant solution was placed in the oven at the same time and, after the desired time, a cylinder was removed from the oven, cooled to room temperature and analyzed for active composition.

For the studies carried out in buffered solutions, sodium dihydrogen phosphate was used to regulate the pH to around 7. Sodium borate was used to control solution pH to around 9, and a sodium acetate/acetic acid mixture was used for a pH of 4. Samples were analyzed for active content using a two-phase titration with Hyamine® 1622, according to ASTM method D 1681. High pressure liquid chromatography was used to monitor changes in composition as well as in activity. Ion chromatography was used to determine concentration of sulfate ions produced during the thermal degradation process. Thermal degradation proceeding by C-S cleavage results in formation or less polar material, much of which will be measured as free oil in the surfactant solution. Consequently, the free oil extracted, according to ASTM method D 3673, from a few selected surfactants after thermal degradation was analyzed by GC/MS for composition. The degradation products in the free oil identified by GC/MS provided strong support for the proposed degradation mechanisms.

AOS used in this study was prepared by sulfonation of Ethyl Corporation's α-olefins. The various individual AOS components tested were prepared according to published methods (4,5). Hydroxyalkane sulfonates used were specifically 3-hydroxyalkane-1-sulfonates. Individual alkene sulfonates used were tetradec-2-ene-1-sulfonate and hexadecene-1-sulfonate. The latter was a mixture of alkene sulfonate isomers.

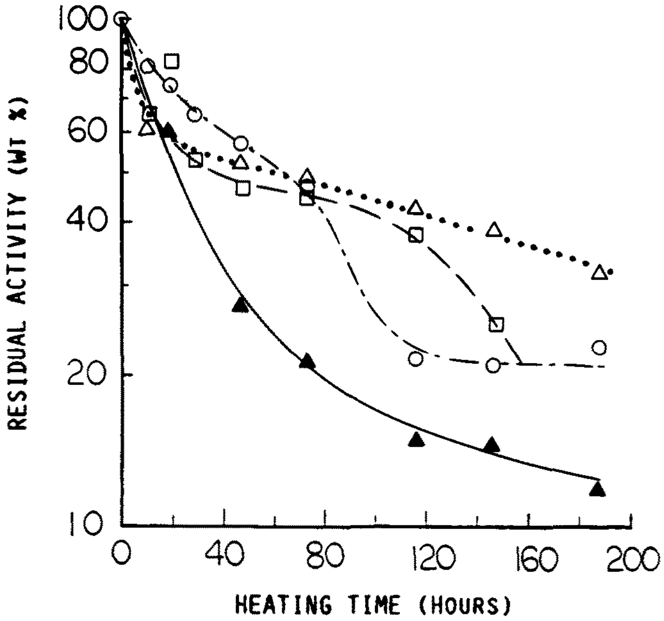

FIG. 1. Thermal degradation of C_{16} AOS at various initial solution pHs (287 C). △, pH10; ○, pH11; □, pH 12; ▲, pH 12.5.

RESULTS AND DISCUSSION

The data obtained for the thermal degradation of a sulfonate prepared from 1-hexadecene are shown in Figure 1. Different symbols are used to represent the initial solution pH of the four surfactant solutions. The residual activity vs. aging time is plotted in a semi-logarithmic scale. Consequently, if the degradation process were to follow first order kinetics with respect to the sulfonate, the data would be expected to be represented by a straight line. Figure 1 shows that under these experimental conditions, none followed first order kinetics with respect to sulfonate. The rate of thermal degradation is shown to be very sensitive to the initial solution pH which resulted in a large scatter for the data obtained at a solution pH of 11 to 12.

In a previous report (1) using aryl sulfonate, it was claimed that a stoichiometric relationship existed between the amount of sulfonate degraded and the amount of acid produced, as measured by pH determinations. However, in this case no such correlation was found, as demonstrated by the data in Table 1. It is seen that the lowest solution pH of 2.8 was recorded with samples having an initial solution pH of 10 and heated at 287 C for 10 hr. A pH of 2.8 corresponds to a hydrogen ion concentration of 1.58×10^{-3} mol/l. On the other hand, the decrease in Hyamine determined active content is equal to 1.2×10^{-2} mol/l. This comparison indicates that only around 8% of the AOS that decomposed produced acid.

To explore the possible reason for the difference between acid production and reduction in active content measured by Hyamine activity, the samples were analyzed for sulfate ion. In addition, the possibility that pH was buffered by the wall of the reactor was also studied. Cylinders containing dilute sodium hydroxide and dilute sulfuric acid were prepared and placed in the oven. It was observed that after heating to 287 C the pH of the dilute sodium hydroxide solutions decreased from 11.7 to 9.7 in 16 hr and to 6.7 after 126 hr. Under the same conditions, the pH of the acid solutions increased from the initial 2.3 to 5.5 in 16 hr and to 6.3 in 126 hr. These data suggest that the type 304 stainless steel cylinders used have substantial pH buffering capacity and tend to stabilized pH at around 6.5. This pH buffering phenomenon can be reduced by maintaining a very small surface area to solution volume ratio. Nevertheless, it is clear that part of the acid generated during the thermal degradation process of α-olefin sulfonate could be neutralized by the wall of the reactor used.

Figure 2 shows plots of residual activity versus time on a semi-logarithmic scale to compare the residual active contant as determined by Hyamine titration and by sulfate analysis. The sulfate analysis is a valid monitoring tool only when sulfate is the thermal degradation product of all the AOS components and a stoichiometric relationship exists between the amount of sulfonate decomposed and the amount of sulfate produced. If degradation of any of the AOS components does not follow the desulfonation path, the rate of thermal degradation determined by sulfate data would be expected to be smaller than the rate determined by Hyamine analysis. The data in Figure 2 clearly demonstrate that desulfonation is not the only mechanism involved in thermal degradation of AOS under the conditions used for this study. It was concluded that

TABLE 1

Change in Solution pH During Thermal Degradation of C_{16} AOS at 287 C

Heating time (hr)	Residual[a] (%)	pH	Residual[a] (%)	pH	Residual[a] (%)	pH	Residual[a] (%)	pH
0	100	10.0	100	11.0	100	12.0	100	12.5
10	61	2.8	64	3.6	81	11.6	62	12.5
19	62	3.9	81	8.2	74	11.2	48	12.5
29	52	5.5	52	5.3	65	11.2	—	—
47	53	4.3	46	8.4	57	11.9	27	12.5
73	49	4.4	45	6.4	47	11.9	21	12.3
116	43	4.5	38	7.3	21	8.5	15	12.5
147	39	4.0	25	8.9	20	8.9	14	12.5
189	34	4.7	22	7.9	24	12.0	12	12.3

[a] Determined by a two-phase Hyamine titration.

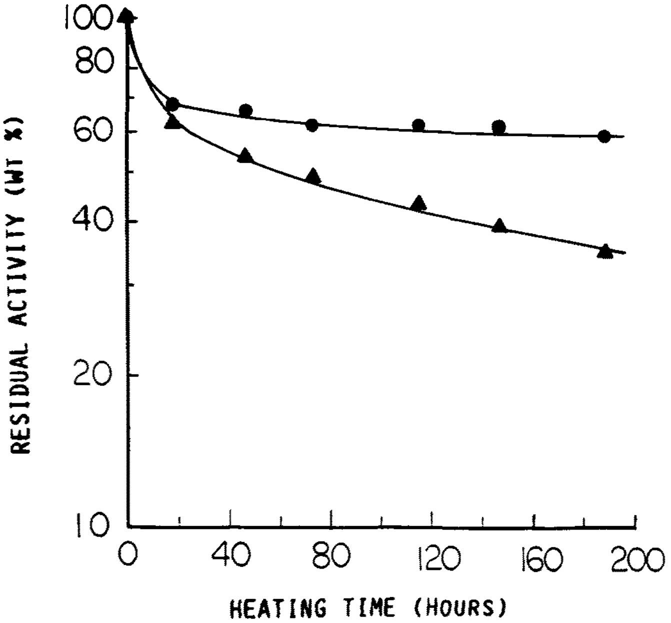

FIG. 2. Thermal degradation of 1-hexadecene sulfonate at 287 C with an initial solution of pH 10. ●, residual surfactant concentration determined by $SO_4^=$ analysis; ▲, residual surfactant concentration determined by Hyamine titration.

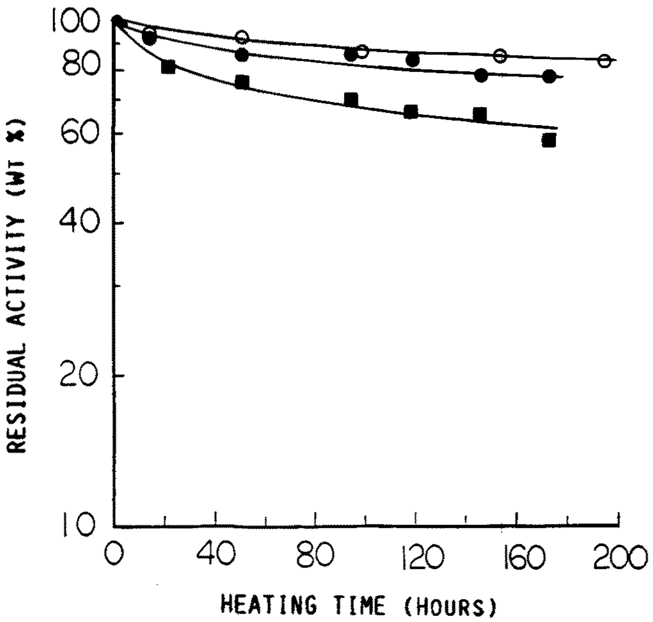

FIG. 4. Thermal degradation of alkene sulfonate and 2-alkene sulfonate at solution pHs of 4 and 7 (287 C). Residual concentration of hexadecene-1-sulfonate at ○, pH 7, and ●, pH 4. Residual concentration of tetradec-2-ene-1-sulfonate at ■, pH 7.

the degradation process for AOS can be established only by studying each AOS component individually.

Three relatively pure AOS components were selected for this study. The alkene sulfonate was prepared by fractional crystallization of γ-sultone from AOS sulfonic acid followed by ring opening under anhydrous conditions to result in hydrolysis with elimination of H_2O. The hydroxyalkane sulfonate was also prepared from γ-sultone by hydrolysis under conditions resulting in addition of H_2O. The third sample was also an alkene sulfonate except that the double bond was located primarily at the 2-position as opposed to a broader double bond distribution for a typical alkene sulfonate (3).

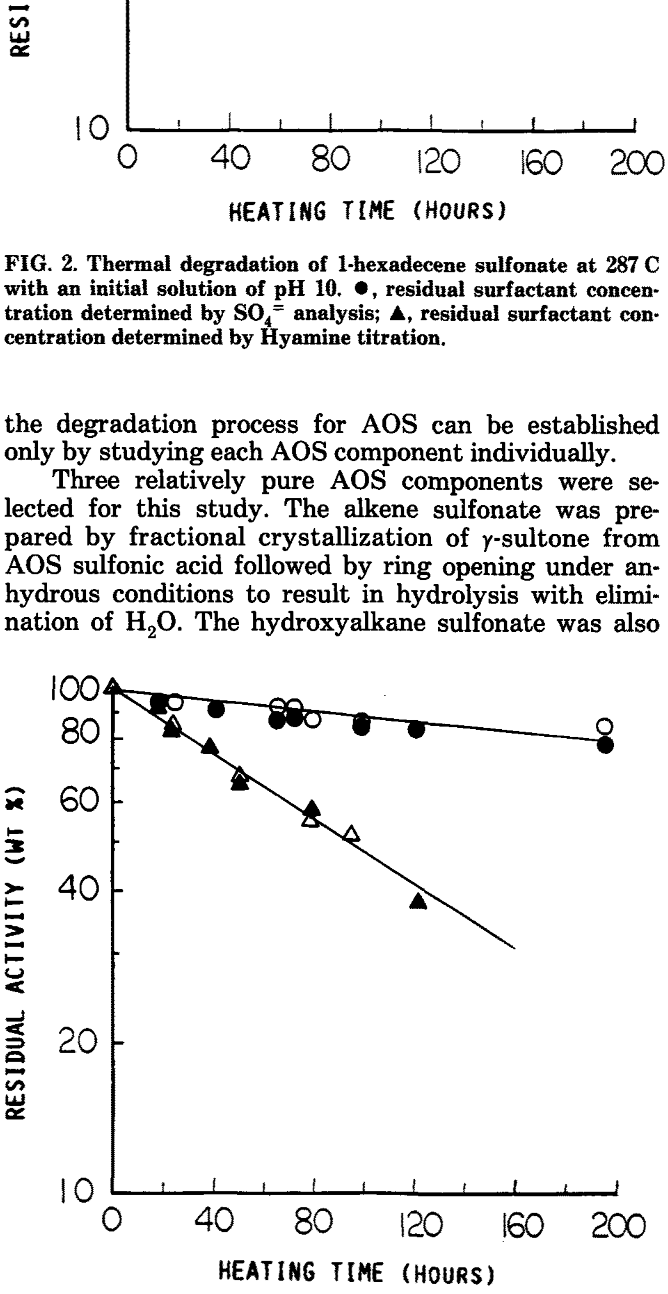

FIG. 3. Thermal degradation of alkene sulfonate and 2-alkene sulfonate at pH 9 (287 C). Residual hexadecene-1-sulfonate concentrations: ●, determined by Hyamine titration: ○, determined by $SO_4^=$ analysis. Residual tetradecec-2-ene-1-sulfonate: ▲, determined by Hyamine titration; △, determined by $SO_4^=$ analysis.

Figure 3 represents the thermal degradation of the alkene sulfonate and the 2-alkene sulfonate with solution pH buffered at 9. The good agreement between the active content as determined by sulfate analysis and by Hyamine titration indicates that desulfonation is the thermal degradation mechanism followed by the alkene sulfonate under the conditions applied. The observation that the mixture of alkene sulfonates is more stable than the 2-alkene sulfonate suggests that location of the double bond is an important factor determining thermal stability. We believe the presence of the double bond actually weakens the C-S bond, and the closer it is to the C-S bond the weaker the C-S bond becomes. This hypothesis is supported by the observation that a paraffin sulfonate (or alkane sulfonate) is considerably more thermally stable than an alkene sulfonate. Inspection of the HPLC chromatogram showing the active decomposition of an alkene sulfonate heated at 287 C for 15 hr also lends support to this hypothesis. With reverse phase HPLC, the closer the double bond to the sulfonate group, the longer is the retention time of the alkene sulfonate. The change in ratio of peak areas having the RT of 9.8 and 10.5 from 0.16 to 0.60 after the sample was subjected to degradation conditions supports this hypothesis.

Thermal degradation data determined by Hyamine titration of hexadecene-1-sulfonate and tetradec-2-ene-1-sulfonate are shown in Figure 4. It appears that even though relatively pure AOS components were used, first order kinetics were not always observed and, surprisingly, hexadecene-1-sulfonate appears to be more stable than tetradec-2-ene-1-sulfonate, and hexadecene-1-sulfonate is more stable at a pH of 7 than at pH 4. So far we have observed that variations of solution pH during degradation and the fact that AOS is a mixture are two factors leading to the thermal degradation of AOS not being represented by first order kinetics. The nonlinear semi-logarithmic plots of the data shown by Figure 4 suggest that there is at least one more factor influencing the degradation of alkene sulfonate. The existence of an additional factor is also illustrated by comparing the two HPLC chromatograms shown in Figure 5. The chromatograms were generated after the pH buffered tetradec-2-ene-1-sulfonate samples were heated at 287 C for 51 hr and 99 hr, respectively. Figure 5 shows that tetradec-2-ene-1-sulfonate (RT of 6.96) transformed into a more stable species having an HPLC retention time comparable to that for tetradec-3-ene-1-sulfonate and tetra-dec-4-ene-1-sulfonate (13). Consequently, it is not surprising to find that the rate of thermal degradation was reduced after an initial heating time, as illustrated in Figure 4.

GC/MS results obtained on the extracted free oil from thermally degraded alkene sulfonates showed that olefin with the same carbon number as the olefin used to prepare the surfactant was the predominant component. However, methyl ketone with one carbon less than the starting olefin also was detected.

Figure 6 represents the data for the thermal degradation of a hydroxyalkane sulfonate at three different pH levels. The rate of thermal degradation of the hydroxyalkane sulfonate increases rapidly with increasing pH. Degradation of the hydroxyalkane sulfonate did not correspond to first order kinetics.

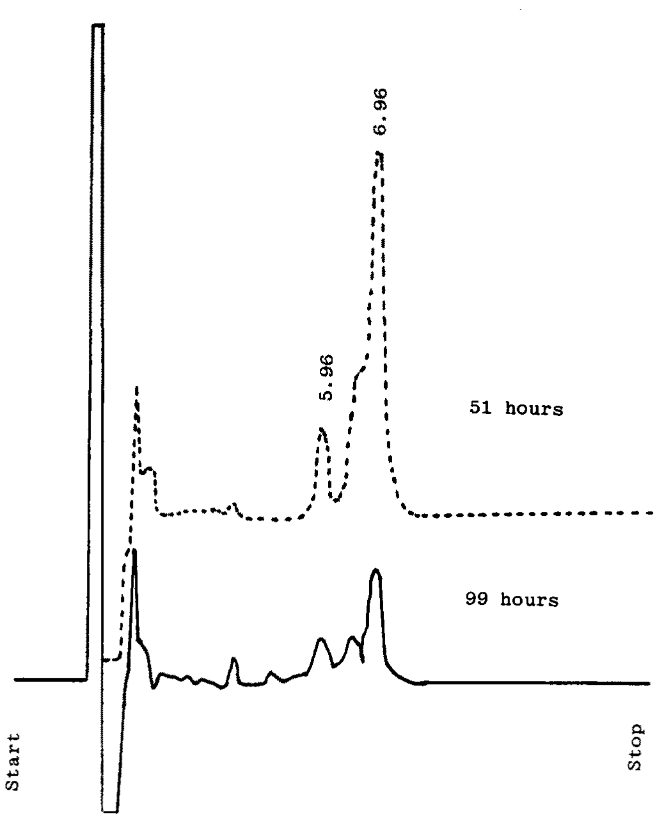

FIG. 5. HPLC chromatograms of tetradec-2-ene-1-sulfonate buffered at pH 7 and heated at 287 C for 51 hr and 99 hr. Column, ZORBAX C-8. Mobile phase—MeOH (27.5)/CH$_3$CH-(37.5)/H$_2$O(35) + 0.4M Na acetate +0.3% acetic acid.

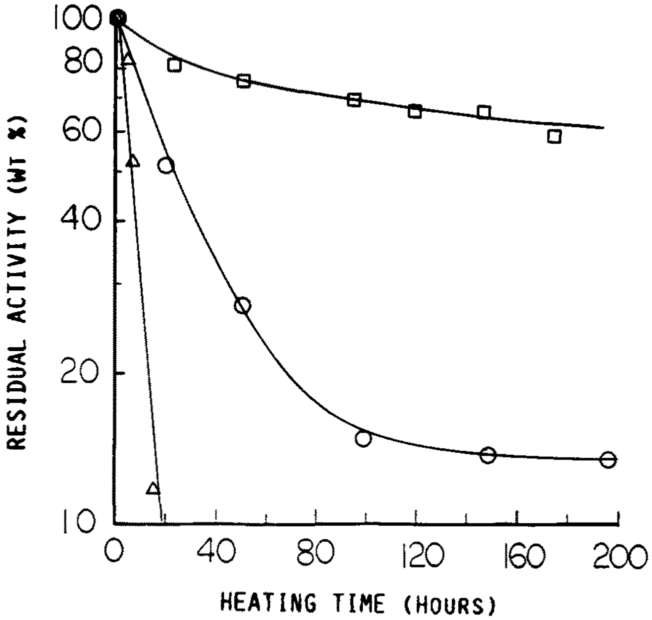

FIG. 6. Thermal degradation of hydroxytetradecane-1-sulfonate at solution pHs of 4, 7 and 9 (287 C). Residual surfactant concentration at □, pH 4; ○, pH7, and △, pH 9.

The quantity of sulfate produced during the thermal degradation of the hydroxyalkane sulfonate was observed to be a function of the pH. No detectable sulfate ion was formed when the hydroxyalkane sulfonate was thermally degraded at a low pH. At pH 9, the amount of sulfate produced represented only a small fraction of the reduction in Hyamine activity. Furthermore, GC/MS analysis of the free oil after degradation revealed that a methyl ketone with one less carbon than the starting olefin sulfonate was the predominant degradation product. This observation suggests that cleavage of carbon/sulfur bonds may not be a significant degradation mechanism in the thermal degradation of hydroxyalkane sulfonates at higher pH.

The pH-dependent degradation is shown again in Figure 7, where the HPLC chromatogram for a sample of 3-hydroxytetradecane-1-sulfonate aged for 22 hr at 287 C at a pH of 9 is compared with the results obtained under the same conditions but at a pH of 4. On comparing the chromatograms, it is clear that at pH 4 at least part of the hydroxyalkane sulfonate, RT of 4.25, was converted into a different surfactant having an HPLC retention time comparable to that of an alkene sulfonate of the same carbon number. The conversion of hydroxyalkane sulfonate into more stable intermediate species during thermal degradation was not observed at a pH of 9.

The observation that hydroxyalkane sulfonate is less thermally stable than alkene sulfonate and the absence of a stoichiometric relationship between sulfate analysis and reduction in Hyamine activity can be postulated as evidence that the formation of an alkene sulfonate intermediate by dehydration of the

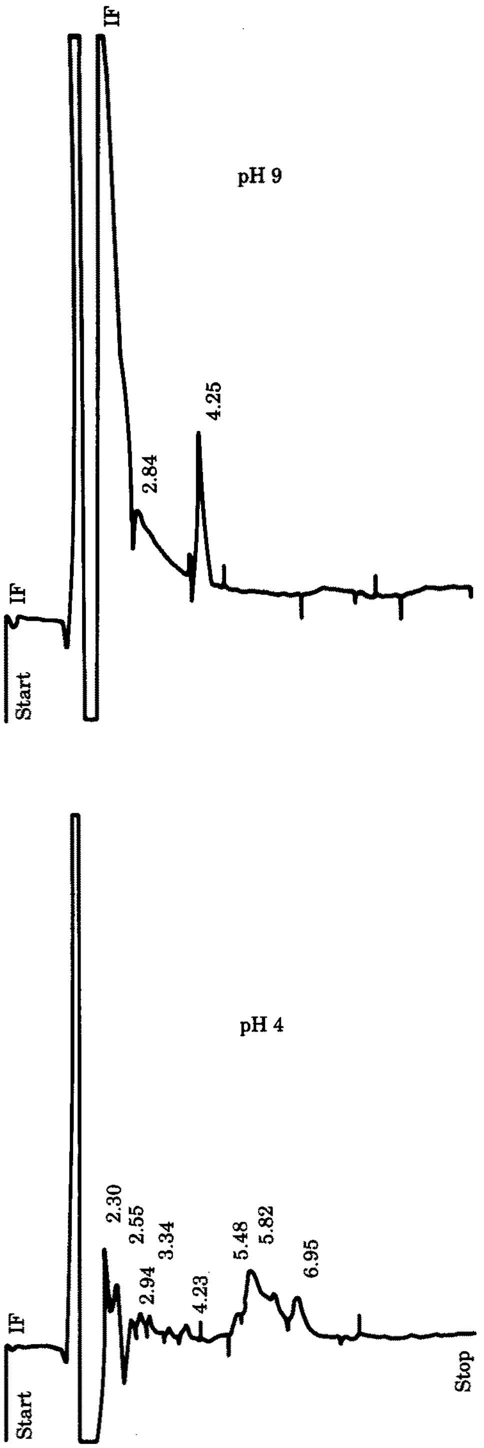

FIG. 7. HPLC chromatogram of 3-hydroxytetradecane-1-sulfonate heated at 287 C for 22 hr. Column—ZORBX C-8. Mobile phase—MeOH(27.5)/CH_3CN(37.5/H_2O(35 + 0.4 M Na acetate + 0.3% acetic acid.

hydroxyalkane sulfonate occurs. The study of alkene sulfonate thermal degradation showed the alkene species having longer HPLC retention times (i.e., being less polar) were less thermally stable than those having shorter retention times (i.e., being more polar). By comparing the retention times for the intermediates produced in the thermal treatment of hydroxyalkane sulfonates to the retention times of alkene sulfonates having the same carbon number, it appears highly probable that the intermediate species formed from thermal degradation of hydroxyalkane sulfonates are the less polar alkene sulfonates having the least thermal stability.

In an attempt to gain a better understanding of the reaction, a methoxyalkane-1-sulfonate was prepared and evaluated for thermal stability. It was observed that this material was much more stable than the corresponding hydroxyalkane-1-sulfonate, suggesting that the formation of a sultone intermediate may be involved in the thermal degradation of hydroxyalkane sulfonates.

Our study of the thermal degradation of AOS shows that the popular practice of defining the activation energy for the thermal degradation of a surfactant based on well defined laboratory experiments with subsequent use of the activation energy to predict the thermal degradation of the surfactant under other conditions is not a practical approach for AOS. AOS is a mixture in which each component was found to follow a different degradation mechanism, depending upon the conditions of the evaluation.

Hydroxyalkane sulfonates were found to degrade into the product starting olefin and methyl ketone having one less carbon number than that for the starting olefin, with the methyl ketone being the predominant degradation product. The observation that hydroxyalkane sulfonates are more stable at low pH than at higher pH leads us to believe that at least one of the steps involved in the degradation is base-catalyzed. The rapid conversion of hydroxyalkane sulfonates to species having HPLC retention times corresponding to those of alkene sulfonate of the same carbon number strongly indicates dehydration is part of the thermal degradation process. Coupled with the observed much greater thermal stability of the methoxyalkane-1-sulfonate than the corresponding hydroxyalkane sulfonates strongly indicates that sultone formation may also be involved.

It appears that alkene sulfonates follow a desulfonation mechanism similar to that reported for aryl sulfonates. However, various alkene sulfonate isomers were observed to have differing thermal stabilities and, in general, it appears that alkene sulfonates having the double bond located farther from the sulfonate group tend to be more thermally stable. The thermal degradation of alkene sulfonates was found to be acid-catalyzed.

Our study of the thermal stability of AOS provides a comparison between the thermal stabilities of the two major AOS components, namely, hydroxyalkane sulfonate and alkene sulfonate. Our work also identifies some of the factors affecting the thermal stability of AOS components, and partially elucidates the mechanism involved in the degradation process. Significant additional effort will be required before the thermal degradation of AOS is completely understood.

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