New Nonionic Detergents Based on Epoxidized Oils. II[1]

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Abstract

The physical and surface-active properties of alkylolamides prepared from methyl-9,10-epoxystearate are discussed. These materials are prepared by reacting methyl-9,10-epoxystearate with a polyoxyethylene alcohol to produce the methyl ester of the hydroxyalkoxypolyoxyether substituted carboxylic acid which is subsequently subjected to aminolysis with diethanolamine.

The properties of the derivatives as a function of the molecular weight of the polyoxyethylene alcohol are explored and appear to exhibit critical changes at a value of about 500. All the materials thus prepared exhibit higher water solubility than corresponding N,N-di(2-hydroxyethyl) amides and foam somewhat less.

Possible applications for materials such as these include formulation of low-foam, heavy-duty cleaning compounds, both of a liquid and dry type. This would, of course, be especially important in the growing field of automatic liquid dishwasher formulations. A need for such materials also exists in heavy-duty metal cleaning, floor washing, and other heavy-duty cleaning applications.

Introduction

THE UTILITY OF ALKYLOLAMIDES as surface-active compounds has been explored to a great degree since the work of Kritchevsky some 30 years ago (1). Such materials find uses in today's detergent compositions both in industrial applications and in the light-duty liquid materials generally associated with household use. These materials usually are N-substituted or N,N-disubstituted amides of fatty acids generally having an average of about 12 carbon atoms in the fatty chain. Their industrial applications include the production of fire-fighting foams, concrete air-entraining agents and go so far as to include compounds designed to remove undesirable water from air-drilled, oil and gas wells.

Saturated materials having in excess of 12 or so carbon atoms in the fatty chain are generally of limited solubility, but their surface-active properties and their ability to form colloidal solutions that are indefinitely stable lead to their use in combination with other materials as opacifiers and pearlescing agents in light-duty household detergent formulations. Introducing unsaturation into the fatty chain generally results in slightly increased water solubility on the part of the hydrophobic portion of the molecule. This disrupts the structure of the compound so that it is generally unable to form the type of solution that is useful as an opacifier, but these materials have increased oil solubility and are well known for their ability to produce emulsions especially of the invert or water-in-oil type. These materials also act as emulsion stabilizers when used in conjunction with more hydrophilic detergents to produce emulsions of the oil-in-water type.

The inherent nature of many of the alkylolamides has, however, hindered or in some cases completely prevented their use in applications where they might otherwise exercise utility. The two outstanding such properties are the high viscosity of their aqueous solutions and the limitations imposed on their solubility especially in the presence of salts or builders. Some modifications have been attempted in an effort to alleviate the disadvantages with some success. One of these modifications designed to increase the solubility of these materials is their production via a route involving ethoxylation of fatty amides or fatty alkylolamides. These materials, while having increased water solubility, do in fact lose their basic nature as alkylolamides, so that the performance characteristics are not always what is desired. Control of the high viscosity of solutions of these materials can be effected by a variety of techniques generally involving the use

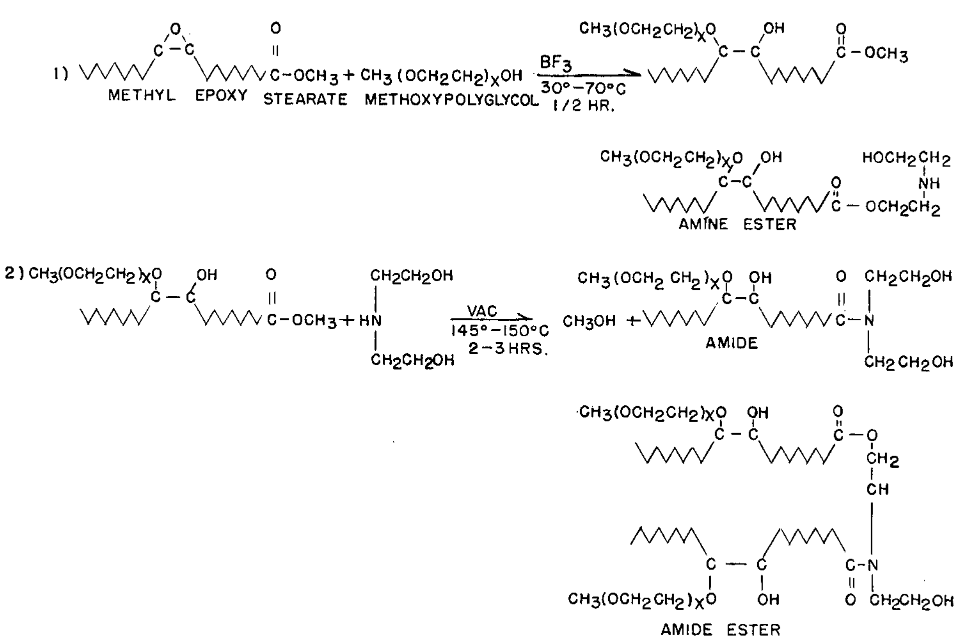

FIG. 1. Reactions studied.

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TABLE I

Physical-Chemical Properties

Molecular weight of Polyoxyethylene side chain	Specific gravity @ 30C	PR of 3% solution @ 30C	Amine soap[a] (corrected)	Titrable amine	Ester amide ratio[b]
320	1.0542	9.35	0.5%	13.2%	0.27–0.30
550	1.0676	9.35	1.0%	9.2%	0.23–0.24
750	1.0776	9.30	Nil	8.3%	0.46

[a] As diethanolammonium oleate.
[b] Determined by infrared spectroscopy after 4 months' aging.

of short-chain alcohols such as ethanol or isopropanol or materials of the commonly encountered glycol ether type. These modifications often are, however, unsatisfactory due to considerations involving flash point, odor, effect on various organic coatings, etc. It is felt that the class of compounds under discussion enlarges the scope of the application of the alkylolamides to such a degree so as to permit their use in applications previously considered inappropriate.

The alkylolamides described herein were synthesized using the methyl ester of 9,10-epoxystearic acid (Fig. 1). The materials could have equally well been prepared from fatty epoxides, but it was found that the benzene cosolvent necessary in the polyoxyalcoholysis of fatty triglycerides was not necessary in the polyoxyalcoholysis of the methyl esters (2). The methyl ester route was thus selected as being the most commercially expedient. In general, the alcoholysis of fatty epoxides is carried out under moderate conditions in the presence of a Friedel-Craft catalyst such as tin-tetrachloride, boron trifluoride or antimony pentachloride, etc., with the catalyst being dispersed in the alcohol prior to the addition of the fatty epoxide. In these studies the monofunctional methyl-9,10-epoxy stearate was reacted with monofunctional polyoxyethylene alcohols. Prior unpublished work in Swift & Company's laboratories has shown that while the adducts of polyoxyethylene glycols and polyols were indeed as would be expected, amphipathic, their utility as surface-active agents was somewhat lacking. The use of these monofunctional materials also avoided any polymerization of the materials beyond that of the condensation as manifested by the performance and physical properties of the products.

Methoxy polyoxyethylene alcohols having molecular weights of 350, 550 and 750 (a), were reacted with commercial methyl-9, 10-epoxystearate (b) in the presence of 0.3% boron trifluoride (c) (as its dihydrate). The reactions were initiated at ambient room temperature and were allowed to proceed without cooling to the maximum temperature obtained by the exothermic reaction.

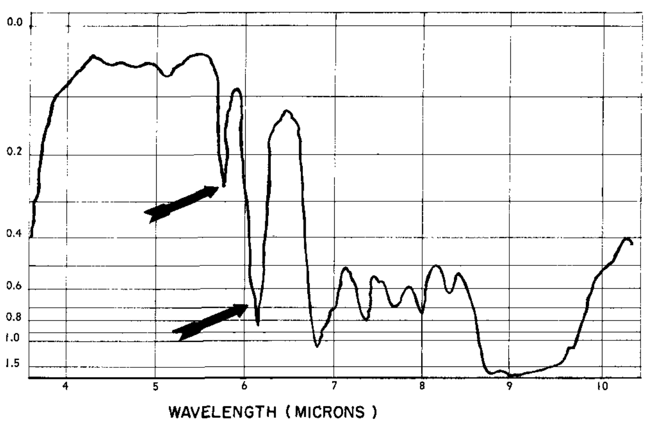

FIG. 2. Infrared absorption spectrum, 350 adduct.

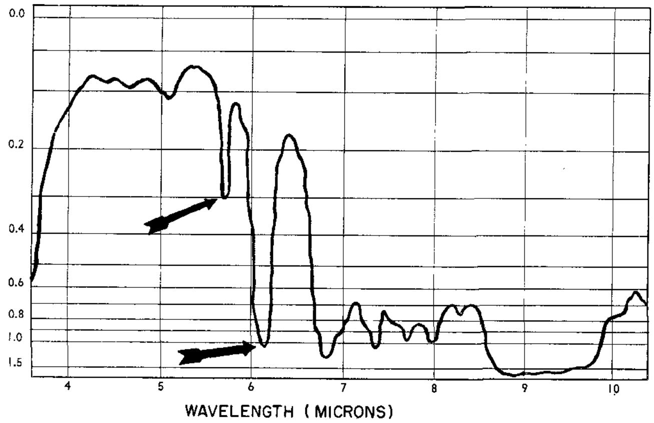

FIG. 3. Infrared absorption spectrum, 550 adduct.

(a) Carbowax 350, 550 and 750 as obtained from Union Carbide Chemicals Company.
(b) Epoxidized methyl oleate obtained from Swift & Company, Chemicals for Industry Department.
(c) General Chemical Division, Allied Chemical Corporation.

This varied from sample to sample inversely as the molecular weight of the polyoxyethylene alcohol, but was generally somewhat less than 80C at the apparent completion of the reaction. This temperature was then maintained for a period of one-half hour followed by the addition of diethanolamine to effect an aminolysis of the ester. This aminolysis was carried out over a three-hour period noncatalytically at a temperature of 150C. This resulted in a so-called low active type amine condensate characterized by the presence of not only the fatty diethanolamide but also the fatty amine ester and the fatty ester amide (3). Materials exhibiting higher amide contents can probably be prepared by the use of sodium methylate or other alkali metal alcoholates as alkaline catalysts at lower temperatures (4). An excess of such a material would, however, have to have been added in order for it to consume the acidic boron trifluoride and filtration of the final product or other refining steps would probably have been necessitated.

The materials thus synthesized were then analyzed to determine their physical properties and their chemical constitution. The results of the analysis were summarized in Table I. It can be seen that specific gravity increased slightly and that the titratable

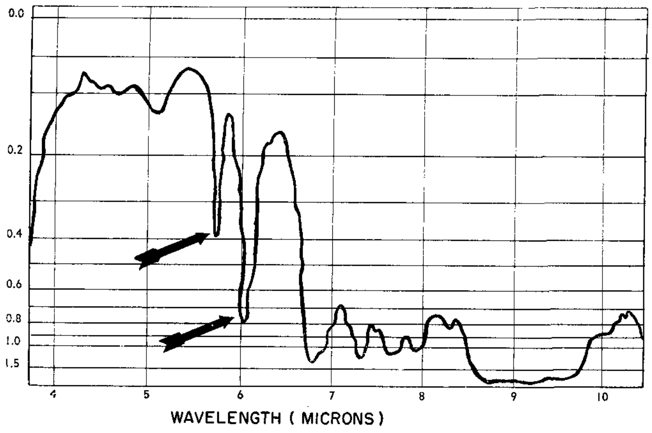

FIG. 4. Infrared absorption spectrum, 750 adduct.

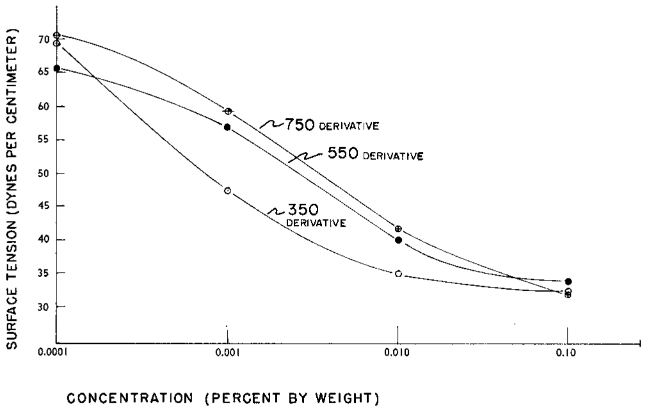

FIG. 5. Surface tension at 25C (ASTM D-1331-56).

amine remained essentially constant at roughly 50% of the original amine. The ester amide ratio which was computed from the infrared spectrum of each of the samples showed some interesting variation. The infrared absorption spectra of the samples shown in Figures 2, 3 and 4 were determined approximately four months after their preparation and the relative absorption ratios at 5.75 μ and 6.15 μ were determined and used to estimate the ester/amide ratio of the condensate (5). The sample having no detectable amine soap retained its original expected high ester/amide ratio, while the samples having detectable quantities of amine soap left in the compound showed a marked decrease in the ester/amide ratio, the decrease being greater with the higher amine soap level. This confirms earlier work that indicated the ester/amide ratio of compounds in this general class decreased upon aging in the presence of amine soap (6).

The performance characteristics of these materials were also quite interesting. The surface tension of the materials in distilled water (7) did as would be expected, decrease with increasing concentration, as shown in Figure 5, but it was interesting to note that the surface-tension-depressing effect was significantly greater in the case of the derivative having the lowest molecular weight polyoxyethylene side chain. This effect was also reflected in the interfacial tension between hexane and the water as shown in Figure 6, but the interfacial tension between benzene and water (Fig. 7) showed no detectable difference between the lowest and highest molecular weight polyoxyethylene side chain with the intermediate molecular weight showing higher interfacial tensions at the same concentration. In all cases the interfacial tensions were quite low and indicated that the materials may show utility as oil-in-water emulsifiers.

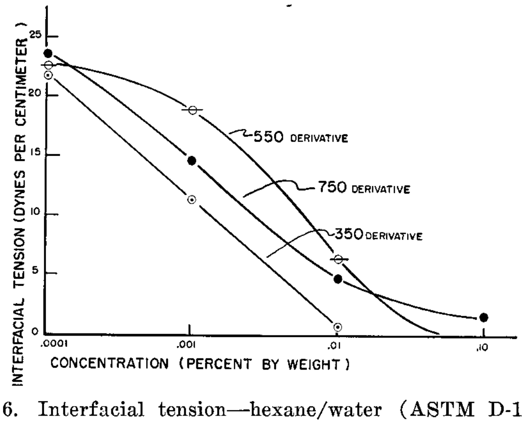

FIG. 6. Interfacial tension—hexane/water (ASTM D-1331-56).

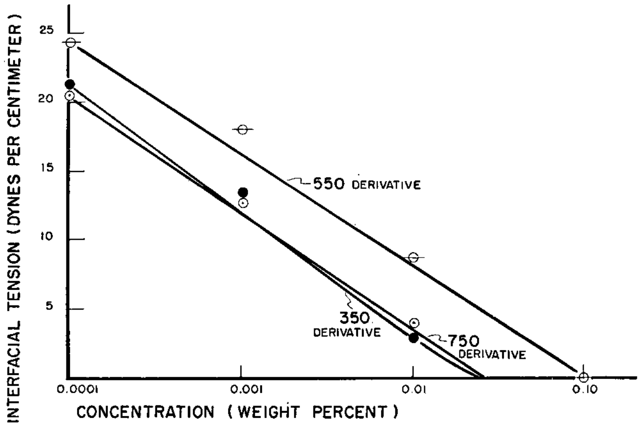

FIG. 7. Interfacial tension—benzene/water (ASTM D-1331-56).

The materials were also subjected to standard wetting tests as described by the American Association of Textile Chemists and Colorists (8). These tests are summarized in Figure 8. Here as with the interfacial tension between benzene and water the intermediate value of molecular weight deviated from both the lowest and the highest value in the same direction, especially at higher concentrations where it gave appreciably faster wetting times. It was noted, however, that at lower concentrations not only did the curve for the intermediate material fail to maintain the advantage it held at high concentrations, but its solutions became cloudy at concentrations of less than 0.2.%

These materials were also evaluated as foaming agents using the pour foam test as originally suggested by Ross and Miles (9) and currently described by the American Society for Testing Materials. The results of these tests are shown in Figure 9. Here again the apparent anomaly in surface characteristics appearing between the molecular weights of 350

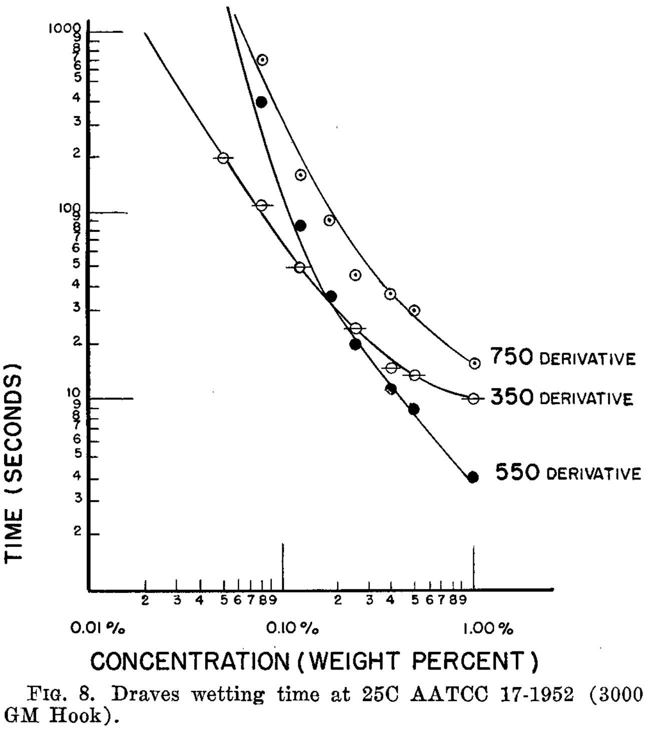

FIG. 8. Draves wetting time at 25C AATCC 17-1952 (3000 GM Hook).

and 750 with respect to the polyoxyethylene chain, manifested themselves in the characteristics of the materials. The foam height values showed a minimum at the intermediate molecular weight. It is possible, though unlikely, that the change in ester/amide ratio or the very small differences in soap level accounted for this anomaly. It is more likely that the molecular weight range between 450 and 650 represents an infection in the characteristics of the materials.

It was also qualitatively ascertained that the products exhibit infinite water solubility at room temperature except in the case of the slight turbidity developed in the intermediate molecular weight range at low concentration. Their solubility at normally encountered detergent concentrations (i.e., in the neighborhood of 2–5%) was good even in the presence 1–5% electrolyte.

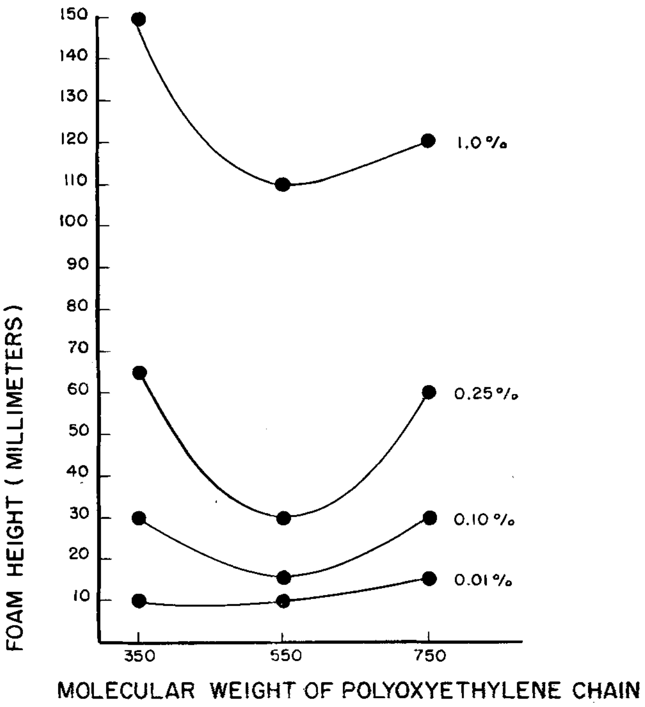

FIG. 9. Ross Miles pour foam test at 25C (ASTM-D-1173-53).

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