

# Effect of Alkyl Carbon Chain Length and Ethylene Oxide Content on the Performance of Linear Alcohol Ether Sulfates

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A series of linear alcohol ether sulfates varying in alkyl carbon chain length and ethylene oxide content was evaluated with respect to surface activity, viscosity, foaming, and detergency. Performance data agree well with surface property data. A low level of EO is best in terms of effectiveness and efficiency in lowering surface tension, which is why a low-mole ether sulfate salt-thickens better, produces foam which is more tolerant of soil, and gives good detergency performance. A lauryl-range alkyl carbon chain length is best for foaming and salt-thickening, but a higher carbon chain length appears to be better for detergency performance.

Approximately 45% of the 800 MM lbs of linear alcohol ethoxylates (AE) produced annually in the United States is converted to alcohol ether sulfates (AES). These are used in various household products, including shampoos, dishwashing liquids, and laundry detergents, as well as in industrial applications, such as wall-board manufacturing.

The purpose of this study was to examine the effect of alkyl carbon chain length and ethylene oxide content on the surface activity, viscosity, foaming, and detergency characteristics of linear alcohol ether sulfates. A similar study dealing with alcohol ethoxylates is reported elsewhere (1).

## EXPERIMENTAL

**Surface Tension Measurements (Gibbs' Plots).** Surface tension measurements were obtained using spinning drop tensiometers (University of Texas, Model 300). Measurements were made at 38°C (100°F).

**Viscosity Measurements.** Viscosity measurements were performed at 25°C (77°F) using a Brookfield (Model LVTCP 115/60) digital viscometer.

**Flash Foam.** Flash foam was measured using a mechanical foam generator (Fig. 1) which was constructed in-house and is based on the German DIN test method no. S3 902. Foam is produced by passing perforated disks through 100 ml solutions of each test surfactant. An eccentric drive system is employed which varies the speed of the pistons so that the disks pass quickly through the test solutions but slowly through the foam. Tests were performed at 100°F. Foam volume was monitored as a function of time.

**Detergency Testing.** Detergency tests were performed using the materials and procedures outlined in Table 1. Tests were performed in duplicate for statistical treatment of data. Performance was determined by measuring reflectance (in Rd units) of the washed cloths.

**Alcohol Ethoxylate Samples.** Compositional data

for the alcohol ether sulfates examined in this study are given in Table 2. For brevity, each test surfactant is described by its carbon chain length and its EO content. For example, 12-1 AES represents a C<sub>12</sub> alcohol with approximately 1 mole of ethylene oxide; 16-3 AES represents a C<sub>16</sub> alcohol with approximately 3 moles ethylene oxide, and so on. All sulfates were prepared using linear, primary alcohols, NaOH-catalyzed ethoxylation, and sulfur trioxide sulfation.

When evaluating alcohol ether sulfates, it is important to remember that the level of ethoxylation determines more than just the average amount of EO placed on the alcohol. It also determines the amount of unethoxylated alcohol that is converted to alcohol sulfate during the sulfation process (Fig. 2). For example, A C<sub>12</sub> 1-mole ethoxylate contains approximately 42% unethoxylated alcohol. Sulfation of this ethoxylate will produce a mixture consisting of approximately 42% alcohol sulfate and 58% alcohol ether sulfate. A C<sub>12</sub> 16-mole ethoxylate, however, has less than 0.3% unethoxylated alcohol, so more than 99% of the sulfation product is AES. To evaluate the effect of alcohol sulfate on performance, dodecyl sulfate (designated 12 AS) was included in all tests as a reference.

## RESULTS AND DISCUSSION

**Surface activity.** Surface activity was evaluated by obtaining Gibbs' plots (surface tension as a function of surfactant concentration) for each AES. All test solutions were made 0.01 M in sodium sulfate in order to buffer differences in salt content. The results are given in Table 3.

With alcohol ethoxylates, increasing EO content increases water solubility by increasing hydration (the interaction of the EO chain with water molecules). Increased hydration results in an increase in the amount of energy required to dehydrate the molecule during its incorporation into the micelle. Increasing EO con-

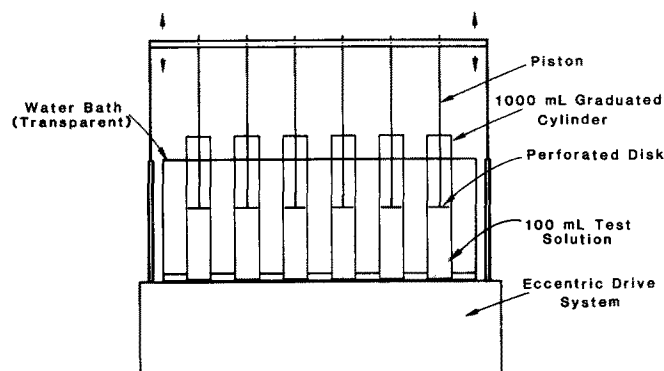


FIG. 1. Illustration of foam generating apparatus.

TABLE 1

**Detergency Test Materials and Procedures**

Testing Apparatus	Terg-O-Tometer
Wash Cycle	10 minutes
Rinse Cycle	5 minutes
Wash Temperature	60°C, 100°F, 140°F
Water Hardness	0
Soil/Substrates	Sebum/Cotton and Sebum/P. Press — manufactured in-house using synthetic sebum*; Cotton (Test Fabrics S/419); P. Press (Test Fabrics S/7406 — 65% Dacron/35% cotton with p. press finish) Mineral Oil/P. Press — manufactured in-house using mineral oil with oil-soluble red dye to aid with detection; P. Press (Test Fabrics S/7406) Clay/P. Press (Scientific Services, Inc.)
No. Soiled Cloths	Three 4.5" × 3.25" swatches of sebum/cotton & sebum/p. press cloths washed together with three clean cotton cloths added for ballast; three 4.5" × 3.25" swatches of mineral oil/p. press cloth washed with six clean cotton cloths added for ballast; three 4" × 3" swatches of clay/p. press cloth washed with six clean cotton cloths added for ballast
Reflectance Measuring Device	Gardner (Model XL20) Colorimeter

Soil recipe<sup>a</sup> consists of 67.6% synthetic sebum (below), 16.2% particulate dust, 10.8% triethanol amine, and 5.4% oleic acid.

Synthetic Sebum Component	Source	Wt. %
Palmitic Acid	Kodak	10.0
Stearic Acid	Kodak	5.0
Coconut Oil	Sargent-Welch	15.0
Paraffin Wax	Paraseal	10.0
Spermaceti Wax	Sargent-Welch	15.0
Olive Oil	Pompeian	20.0
Squalene	Kodak	5.0
Cholesterol	Kodak	5.0
Oleic Acid	Kodak	10.0
Linoleic Acid	Kodak	5.0

<sup>a</sup>Originally based on Spangler's recipe [Spangler, W.G., H.D. Cross, and B.R. Schaafsma, *J. Am. Oil Chem. Soc.* 42:723 (1965)].

TABLE 2

**Compositional Data on Alcohol Ether Sulfates used In Study**

Surfactant	Alcohol <sup>a</sup>	Ethylene Oxide Content		Approximate Alcohol Sulfate Content (wt. %) <sup>b</sup>
		(moles)	(wt. %)	
8-3 AES	Octanol	2.9	49.6	10.1
12 AS	Dodecanol	0	0	100
12-1 AES	Dodecanol	1.1	21.0	42.2
12-3 AES	Dodecanol	2.9	40.9	15.5
12-7 AES	Dodecanol	6.6	60.8	3.4
12-16 AES	Dodecanol	16.1	79.2	0.3
16-3 AES	Hexadecanol	3.3	37.9	12.3

<sup>a</sup>Linear, primary alcohols.

<sup>b</sup>Free alcohol content in feedstock prior to sulfation.

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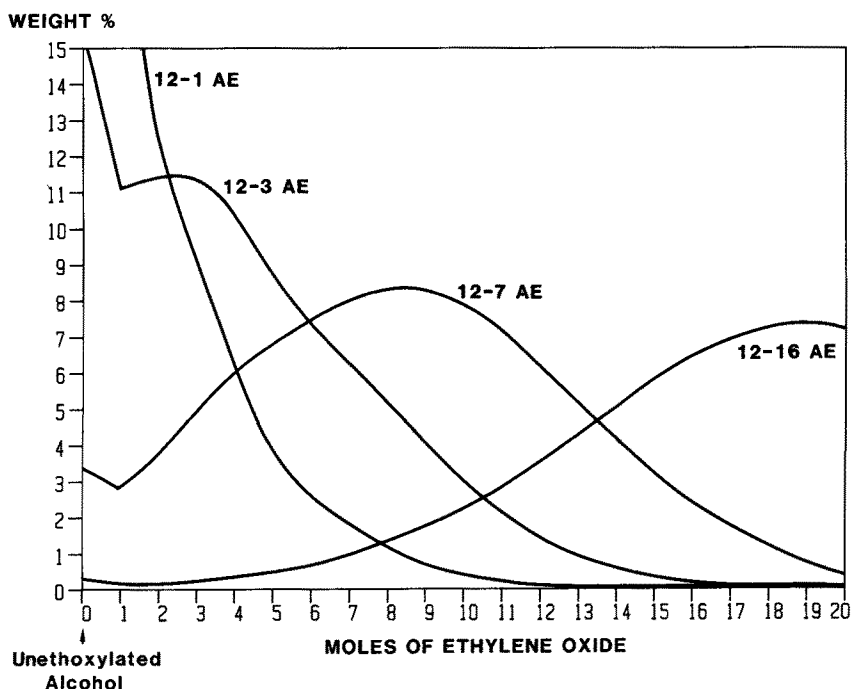


FIG. 2. Ethylene oxide distributions for dodecanol ether sulfates containing 1, 3, 7, and 16 moles ethylene oxide.

TABLE 3

Surface Property Measurements of Alcohol Ether Sulfates (38°C, Test Solutions 0.01 M in  $\text{Na}_2\text{SO}_4$  to Buffer Ionic Strength)

Surfactant	Critical Micelle Concentration		Surface tension at CMC (dynes/cm)
	(ppm)	( $\text{M} \times 10\text{E}4$ )	
Effect of EO Content			
12 AS	630	21.9	23.7
12-1 AES	121	3.6	23.0
12-3 AES	132	3.2	28.7
12-7 AES	135	2.4	34.0
12-16 AES	133	1.3	33.8
Effect of alcohol			
Carbon Chain Length			
8-3 AES	9000	249	30.0
12-3 AES	132	3.2	28.7
16-3 AES	3.3	.07	34.4

tent therefore increases critical micelle concentration (CMC).

With alcohol ether sulfates, however, CMC is observed to decrease with increasing EO. Schwuger (2), who also observed this same effect, has shown that increasing EO content and alkyl carbon chain length both increase aggregation number (micelle size). Both aggregation number and CMC data suggest that a higher EO content increases the hydrophobic portion of the molecule, not the hydrophilic portion. The picture is complicated, however, by Krafft point data assembled by Rosen (3), which show that increasing EO content increases water solubility.

Changes in molecular structure that increase water

solubility normally translate into an increase in CMC and a decrease in aggregation number. The opposite trend observed with AES may be due to differences in the behavior of AES as monomer vs behavior of AES in micelles. As free monomer, lengthening the EO chain logically increases water solubility by increasing hydration, which results in a lower Krafft point. During micellization, however, the degree of hydration is decreased in order to allow more efficient packing of the molecule in the micelle. Since the presence of the sulfate group would place the EO chain farther into the interior of the micelle, the degree of dehydration that must occur is likely to be significantly greater than with alcohol ethoxylates. If the degree of dehydration

is such that the addition of ethylene oxide contributes more to the hydrophobic character of the molecule than the hydrophilic portion, then CMC would logically decrease with increasing EO content.

The effect of EO content on the ability of the surfactant to lower surface tension is the same for both alcohol ethoxylates and ether sulfates. In general, a higher EO content results in a larger molecule, which is less capable of packing at the air-water interface. The ability to lower surface tension is therefore reduced as EO content is increased. The only minor exception occurs with the 12 AS which has a slightly higher surface tension than the 12-1 AES.

The effect of alkyl chain length is demonstrated by comparing surface properties of the 8-3, 12-3, and 16-3 AES. As expected, a longer carbon chain length increases hydrophobic character, which results in a lower CMC. The 12-3 AES gives the lowest surface tension of the three at their respective CMCs, which indicates that it has the best combination of HLB and size.

In summary, surface property data suggest that a lauryl-range AES containing approximately 1 mole of ethylene oxide is best at lowering surface tension. Although lauryl alcohol sulfate is also effective, it is not as efficient as the 1-mole AES (it requires a substantially higher concentration to be as effective as the 1-mole AES). These trends correlate well with performance data discussed below.

*Viscosity.* The viscosity of an AES solution is often increased by simply increasing surfactant concentration or by adding salt (increasing ionic strength). The relationship between ionic strength and viscosity will be discussed first since it is important in understanding how AES composition affects viscosity.

At concentrations below about 25% active, AES is present in spherical micelles because a spherical shape maximizes separation of the negatively charged head groups. Micelle size is fixed because once a certain size is reached, the charge density of the micelle surface itself repels other molecules, which effectively prevents them from entering the micelle. Increasing salt or surfactant concentration increases the concentration of cations available to interact with the negatively charged micelles. A higher concentration of cations in the electric double layer results in better shielding of the negative charges. This, in turn, reduces head group repulsion and lowers the charge density of the micelle surface which allows the micelle to enlarge and deform into cylindrical micelles. Formation of these larger cylindrical micelles increases viscosity dramatically.

If surfactant concentration or ionic strength continues to increase, however, other changes in molecular geometry will occur which will eventually reverse the trend so that viscosity will be observed to decrease (4). This is why a 30% sodium lauryl 3-mole AES is a gel while a 70% solution is a flowable liquid. It also explains why the addition of salt will first thicken, and then thin an AES solution.

With respect to manufacturing AES, the effect of concentration on viscosity is important because it affects the ease at which the product is handled and the concentration at which it can be shipped. Without hy-

drotrope, a lauryl-range 3-mole AES will form a viscous gel at about 28-30% active. Most commercial products contain 12-14% ethanol as hydrotrope to produce a 60% active solution with reasonable (<200 cps) viscosity. Products are also available that achieve a 40% active concentration with the addition of sodium sulfate.

The effect of EO chain length on viscosity as a function of surfactant concentration is shown in Figure 3A. Increasing EO chain length reduces the concentration required to reach high viscosity. This suggests that viscosity is affected by the degree of hydrogen bonding that can occur between adjacent EO chains.

The effect of alcohol carbon chain length on viscosity as a function of surfactant concentration is shown in Figure 3B. Increasing alkyl chain length also reduces the concentration required to reach high viscosity. Higher viscosity likely results from the increase in van der Waal interactions that can occur between hydrophobes when chain length is increased. A longer alkyl chain also results in larger micelles which may be easier to deform into structures which contribute to high viscosity.

Consumers often relate viscosity to efficacy, particularly in personal care products (shampoos, hand soaps, etc.). This is why the ability to be thickened with salt is an important property of ether sulfates. The effect of ethylene oxide content on salt-thickening of 20% AES solutions is shown in Figure 4A. With alcohol sulfate (12 AS), the addition of up to 10% sodium chloride has little effect of viscosity. With 12-1 AES, however, the addition of 3% NaCl boosts viscosity to over 25,000 cps. Viscosity of 12-3 AES is also strongly dependent on NaCl concentration, but more salt is required to reach its maximum viscosity, and its maximum viscosity (approximately 8500 cps) is also substantially less than that observed with 12-1 AES. As EO chain length is increased, salt response decreases to the point where a 12-7 AES is relatively unaffected by salt.

The relationship observed between EO content and salt response is related, at least in part, to differences in molar concentration. With 20% solutions, a longer EO chain means that fewer molecules are available to build structures which contribute to viscosity. The only exception is the alcohol sulfate which does not salt-thicken well at all. This suggests that the presence of ethylene oxide (which promotes hydrogen bonding) is important to salt-thickening.

The effect of alkyl chain length on salt-thickening is shown in Figure 4B. The 12-3 AES is the easiest to salt-thicken, followed by the 16-3 AES. The 8-3 AES does not salt-thicken well at all. These trends are again likely related to differences in molar concentration and micelle size.

*Foaming.* Alcohol ether sulfates are generally excellent foamers. Foaming is the principal reason they are used in shampoos, dishwashing liquids, and wall-board manufacturing.

Foam was evaluated under a variety of test conditions. Foam levels and stability were found to be affected by ionic strength, water hardness, and surfactant concentration. Increasing ionic strength boosts foaming because it increases surface activity by reduc-

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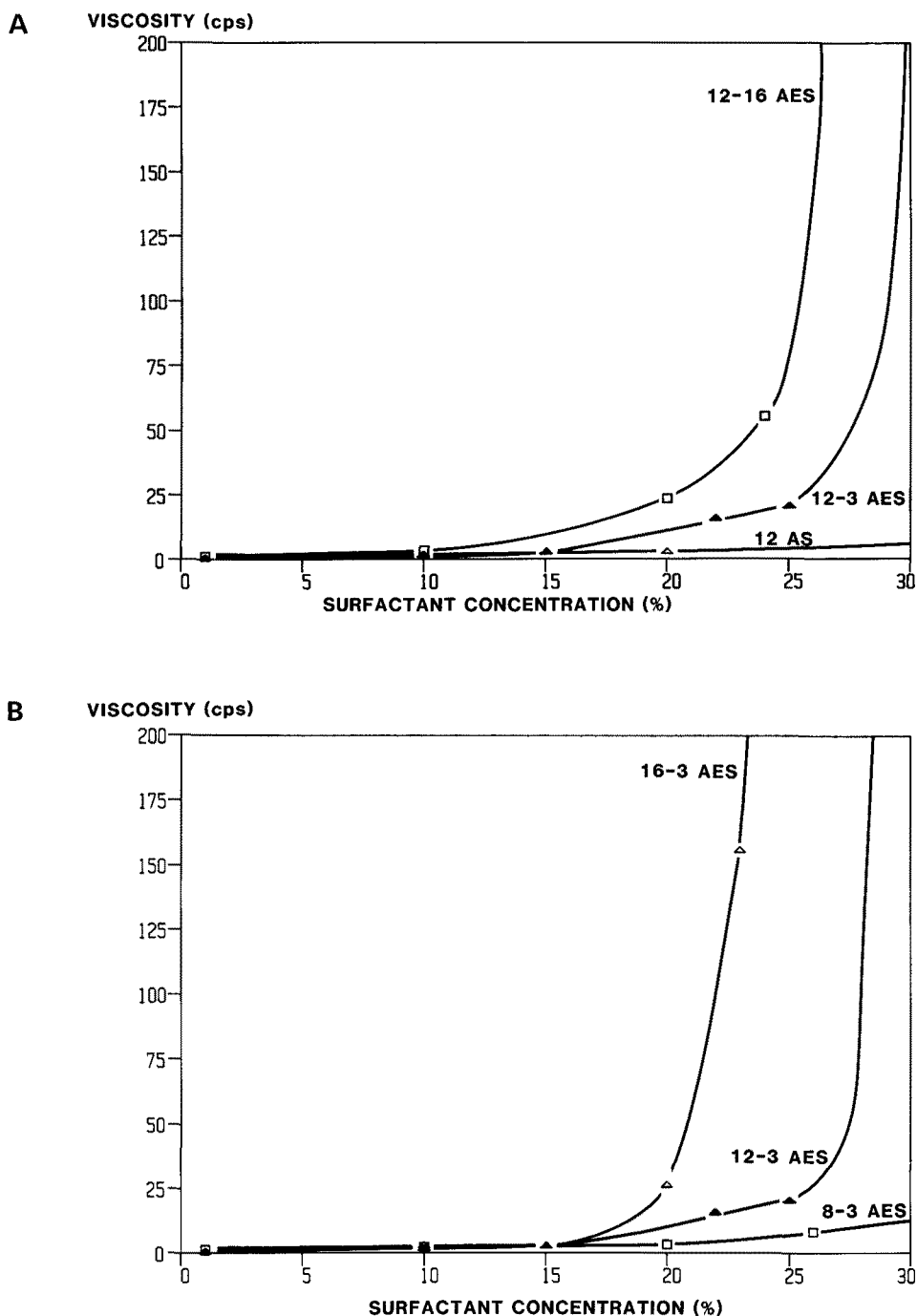


FIG. 3. Viscosity as a function of surfactant concentration for A) dodecyl alcohol ether sulfates containing 0, 3, and 16 moles ethylene oxide, and B) 3-mole alcohol ether sulfates made with hexyl, dodecyl, and hexadecyl alcohol (25°C).

ing surfactant solubility (salts help drive the surfactant to the air-water interface). In addition to contributing to ionic strength, water hardness also helps boost foam by stabilizing the surfactant at the interface via interaction of the surfactant head groups with divalent cations.

No significant differences in foam stability were observed within the AESs series. In comparison to the AESs, however, the 12 AS produced significantly less stable foam than the AES when tested at 200 ppm.

This is presumably due to its relatively poor surface activity at this concentration.

A longer EO chain appeared to increase foam bubble size (measured visually) although differences were small. The 12 AS, however, clearly produced a richer foam (more dense/smaller bubbles) than the AESs. Perhaps the most important factor in evaluating foam is the ability to stabilize foam in the presence of soil. The presence of soil is important because of the stress it puts on foaming by acting as a sink for surfactant. The

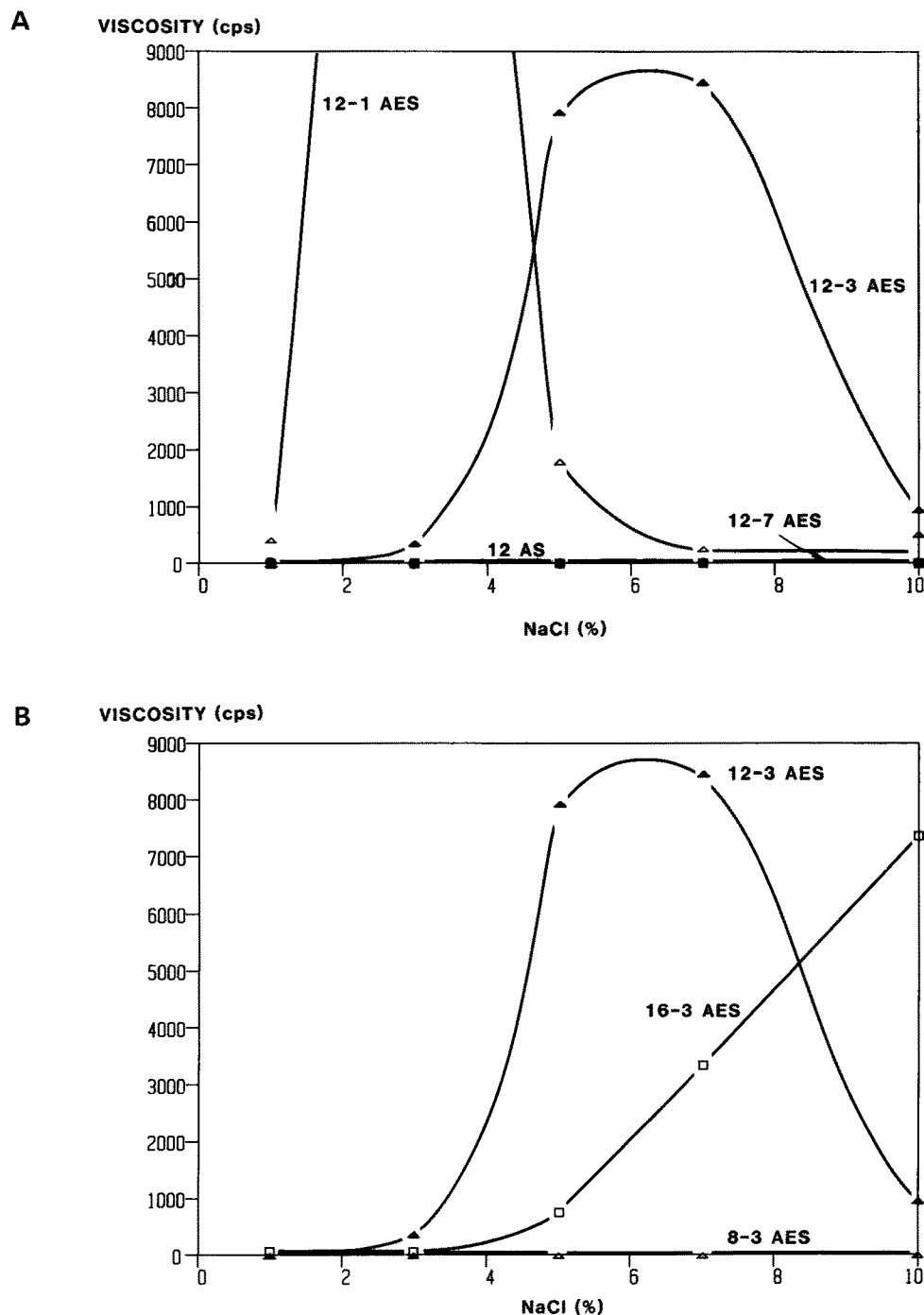


FIG. 4. Viscosity of 20% alcohol ether sulfate solutions as a function of sodium chloride content for A) dodecyl alcohol ether sulfates containing, 0, 1, 3, and 7 moles ethylene oxide, and B) 3-mole alcohol ether sulfates made with hexyl, dodecyl, and hexadecyl alcohol (25°C).

effect of soil was evaluated by monitoring foam while titrating test solutions with soil.

The effects of EO content and alkyl chain length on AES foam performance using 200 ppm solutions (typical use concentration for a dishwashing liquid) are shown in Figures 5A and 5B, respectively. Results demonstrate the importance of surface activity and molar concentration. The surfactants best able to handle soil are clearly the 12-1 and 12-3 AESs. The 12

AS and 8-3 AES suffer because of their relatively poor surface activity at 200 ppm. The 12-16 and 16-3 AESs also suffer because there are fewer molecules available to saturate both the air-water and soil-water interfaces. (The increase in foam volume obtained during the first few additions of oil may be due to localization of the oil in the foam lamella. This could stabilize foam, but would only occur with low concentrations of soil).

Different results, however, were obtained with

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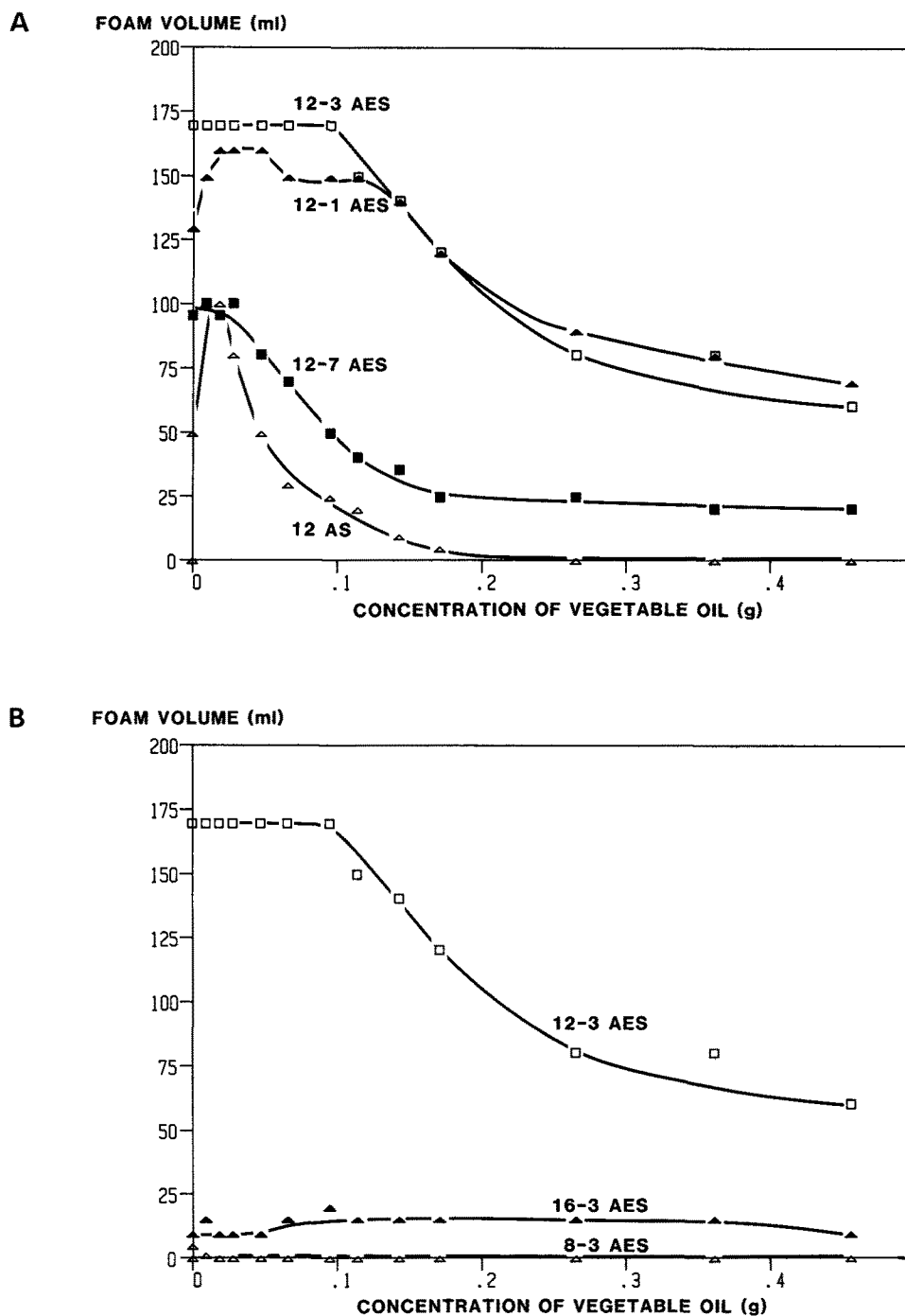


FIG. 5. Volume of foam produced by 200 ppm alcohol ether sulfate solutions as a function of soil (vegetable oil) for A) dodecyl alcohol ether sulfates containing, 0, 1, 3, and 7 moles ethylene oxide, and B) 3-mole alcohol ether sulfates made with hexyl, dodecyl, and hexadecyl alcohol (100°F).

10,000 ppm solutions (typical use concentration for a shampoo), as shown in Figures 6A and 6B. Surfactant concentration is no longer a factor, so the ability to handle soil depends on surfactant effectiveness (surface tension at CMC) and molar concentration (number of molecules available to adsorb at the air-water and oil-water interfaces). The 12-0 and 12-20 AESs are clearly best at handling soil under these conditions because they are the most surface active and they have

higher molar concentrations. In summary, AES foaming appears to correspond directly to the ability to lower surface tension under the conditions at hand.

It should be noted that foam performance is defined differently in other applications. For example, in wallboard manufacturing, the ability to generate foam in the presence of high concentrations of gypsum (calcium sulfate) is important. A shorter carbon chain length and moderate EO content are generally preferred.

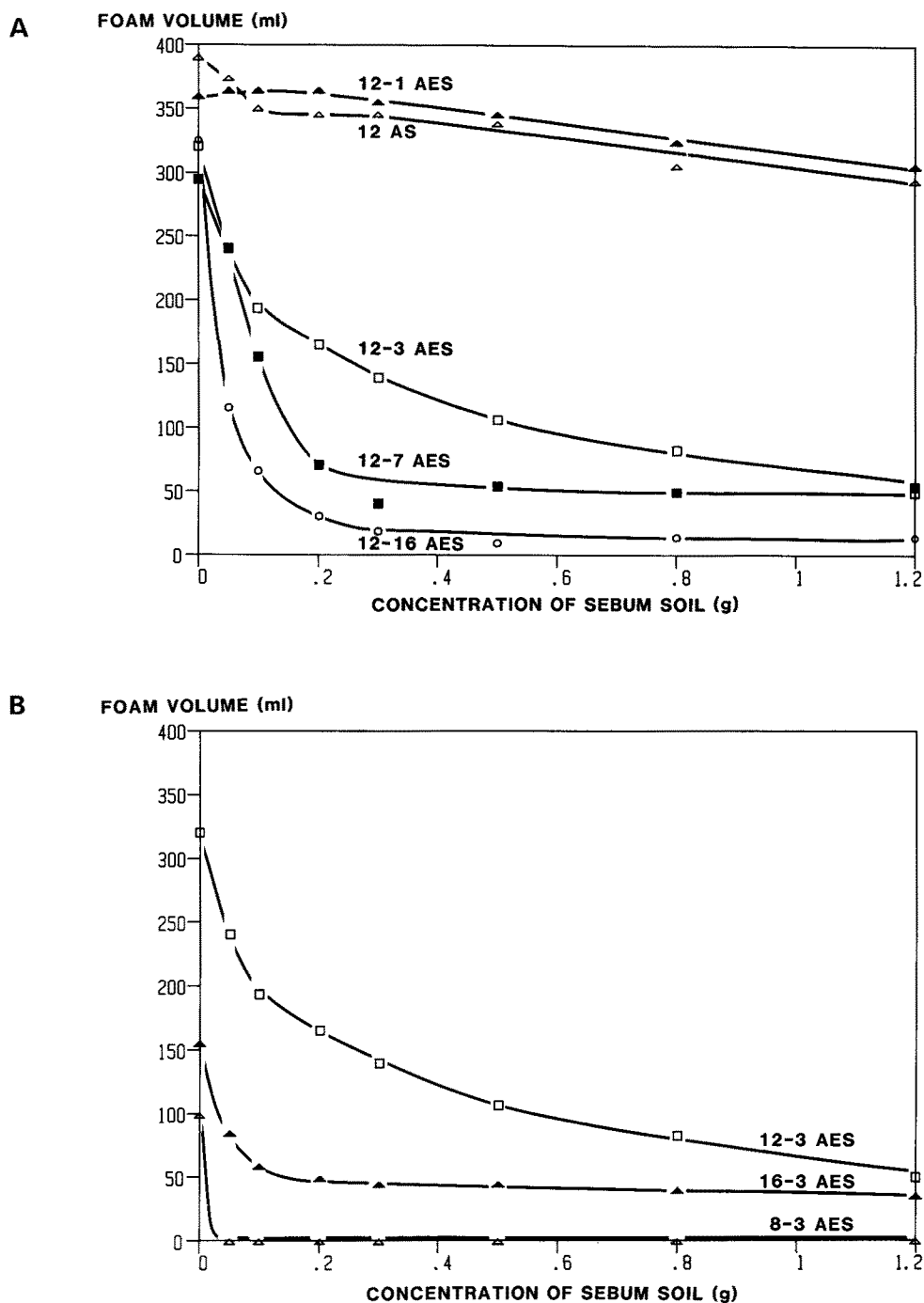


FIG. 6. Volume of foam produced by 10,000 ppm alcohol ether sulfate solutions as a function of soil (sebum) for A) decedyl alcohol ether sulfates containing, 0, 1, 3, and 7 moles ethylene oxide, and B) 3-mole alcohol ether sulfates made with hexyl, dodecyl, and hexadecyl alcohol (100°F).

*Detergency.* The ability of each test surfactant to remove soil from fabric was examined using traditional Terg-O-Tometer test procedures (see Table 1). All test solutions contained 200 ppm surfactant, 0.01 M sodium sulfate (to buffer ionic strength) and 25 ppm NaOH (to adjust pH to 8). Although commercial detergent formulations typically contain other ingredients (builders, antiredeposition agents, optical brighteners,

etc.), they were excluded in order to concentrate on the performance characteristics of the surfactants. Detergency was evaluated using sebum, clay, and mineral oil soils.

Only small differences were observed in detergency performance unless the system was stressed by either adding water hardness, lowering the wash temperature, or by reducing surfactant concentration. When



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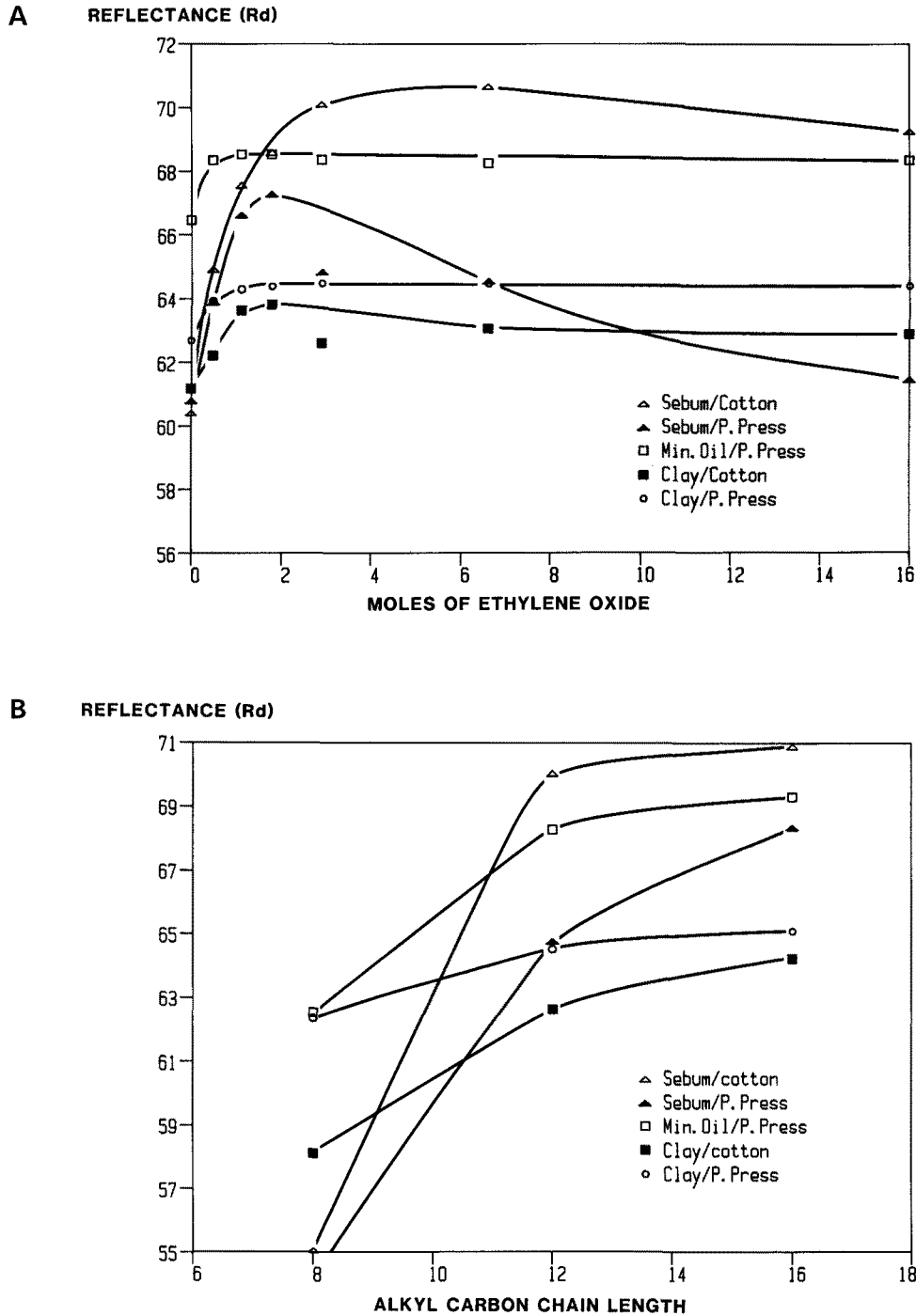


FIG. 7. detergency performance of alcohol ether sulfate as a function of A) ethylene oxide content and B) alkyl carbon chain length at 100°F with 100 ppm water hardness (Rd of unsoiled cotton = 89.2, unsoiled p. press = 86.8).

differences were observed, similar trends were obtained regardless of how the system was stressed.

The effect of EO content on detergency performance is shown in Figure 7A. Optimum detergency performance is obtained with an intermediate level of ethylene oxide. Specific optima depend strongly on the soil/substrate used. This is presumably due to differences in the hydrophilicity of the various cloth substrates.

The effect of alkyl chain length is shown in Figure 7B. Optimum detergency is obtained with the 16-3 AES, although there is not a great deal of difference between it and the 12-3 AES. Although the 16-3 AES is not as effective in lowering surface tension, it does require a significantly lower concentration to reach its minimum surface tension. Since a significant amount of surfactant is lost due to interaction with the soil and substrate, the 16-3 AES is better able to lower surface

tension than the 12-3 AES. Both are significantly better in lowering surface tension than the 8-3 AES.

Best overall detergency appears to be obtained with an AES containing approximately 3 moles of EO and a carbon chain length of about C<sub>16</sub>. This agrees well with studies reported by Matson (5), which showed that an AES made from a C<sub>14</sub>-C<sub>16</sub> alcohol with 25-45% EO gave optimum detergency performance.

Keep in mind that the performance of alcohol sulfate depends strongly on carbon chain length, temperature, and water hardness (6). Although the performance of the 12 AS was generally poorer than the 12-1 AES, the opposite could be true under conditions favoring alcohol sulfate performance.

Alcohol ether sulfates have also been shown to be useful in reducing the water hardness sensitivity of linear alkylbenzene sulfonates (7). This is thought to be accomplished by lowering the critical micelle con-

centration and by helping solubilize Ca(LAS)<sub>2</sub> and Mg(LAS)<sub>2</sub>. A higher EO content has been shown to improve performance along these lines.

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