

SURFACTANTS & DETERGENTS

The Effect of "Peaking" the Ethylene Oxide Distribution on the Performance of Alcohol Ethoxylates and Ether Sulfates

Michael F. Cox

Vista Chemical Company, P.O. Box 200135, Austin, TX 78720-0135

In comparison to conventional ethoxylates, a "peaked" ethoxylate has less unethoxylated alcohol, is more soluble, and has a higher concentration of the more desired homologs. A "peaked" ethoxylate therefore has a lower odor, is easier to formulate into liquids, and can perform better in terms of detergency and wetting performance. Since "peaked" ethoxylates have less unethoxylated alcohol, less alcohol sulfate is formed during sulfation. Decreasing the content of alcohol sulfate increases the capacity to salt-thicken and can potentially improve skin mildness.

KEY WORDS: Alcohol ethoxylate, alcohol ether sulfate, ethylene oxide distribution, peaked ethylene oxide distribution, performance, physical properties, salt thickening.

Ethoxylation of alcohol involves the addition of ethylene oxide (EO), one unit at a time, to the hydroxyl oxygen of the parent alcohol molecule. The chemistry is straightforward but results in the formation of homologs which vary significantly in the number of ethylene oxide units they contain. For example, when n-dodecanol is ethoxylated with an equal weight of ethylene oxide (using conventional caustic catalyst), the resultant ethoxylate consists of a mixture of homologs containing from 0 moles of EO (unethoxylated alcohol) to more than 20 moles (Fig. 1). Even though the mixture contains an average of 4.4 moles of EO, less than 10% (by wt) of the homologs actually have 4 moles of EO.

Conventional ethoxylates are produced with sodium or potassium hydroxide as the ethoxylation catalyst. Differences in the relative reactivity between the alcohol and the ethoximers towards EO cause the broad distribution of homologs. "Peaked" ethoxylates (sometimes called "narrow-range" ethoxylates) are produced

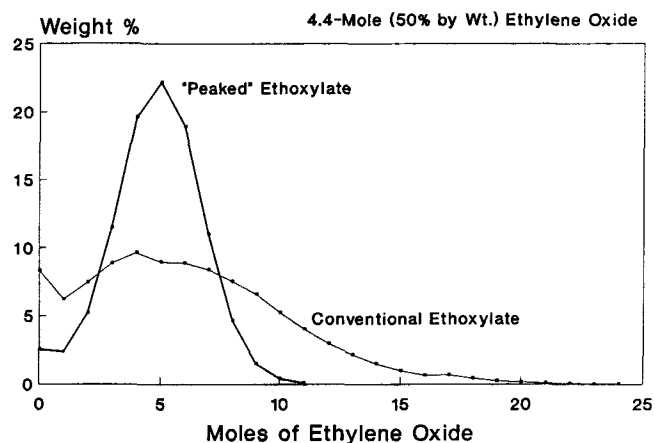


FIG. 1. Ethoxylate homolog distribution for conventional and "peaked" n-dodecyl ethoxylates containing an average of 4.4 moles ethylene oxide.

using sophisticated catalysts that alter this reactivity such that a more peaked distribution of homologs is achieved. For example, the same ethoxylate described above made with a state-of-the-art peaked ethoxylation catalyst also averages 4.4 moles in EO, but contains more than double the amount of the 4-mole homolog (Fig. 1).

The first peaked ethoxylate was introduced in 1982 by Conoco Chemicals (now Vista Chemical Company). It was developed jointly with a major detergent manufacturer to help reduce the pluming associated with spray-drying an ethoxylate-based laundry powder (1). Since then, both Vista and Union Carbide have developed and commercialized peaked ethoxylates that are significantly more peaked than the initial product offered in 1982. Several excellent studies have also been reported which discuss various benefits for peaked ethoxylates (2,3). The purpose of this paper is to present a more complete picture on peaked ethoxylates, and to discuss the effect of peaking on the performance of ether sulfates. The "bottom line" utility for peaked ethoxylates and ether sulfates is also discussed.

EXPERIMENTAL PROCEDURES

Alcohol ethoxylate samples. Samples were prepared from n-dodecanol (ALFOL 12 alcohol—Vista Chemical, Houston, TX) or lauryl (ALFOL, 1412 alcohol = 60% n-tetradecanol/40% n-dodecanol—Vista Chemical, Houston, TX) alcohol using sodium hydroxide (conventional) or a proprietary ("peaked") catalyst (4,5). Ether sulfate samples were sodium salts prepared using sulfur trioxide.

Cloud point. Cloud point was measured by lowering the temperature of individual formulations and visually observing the temperature at which each formulation became opaque.

Detergency testing. Equipment and procedures are described elsewhere (6).

Ethylene oxide distributions. Distributions were obtained using high performance liquid chromatography (HPLC) (7). Unethoxylated alcohol content was measured using gas chromatography.

Surface tension measurements. Equilibrium surface tension measurements were obtained using Spinning Drop Tensiometers (University of Texas, Model 300). Dynamic surface tension measurements were made using Sensadyne Tensiometer Model 5000 (nitrogen bubble rate = approximately 1/sec). All measurements were made at 38°C (100°F). All test solutions contained 0.01 M sodium sulfate to buffer ionic strength.

Viscosity measurements. Viscosity measurements were performed at 25°C (77°F) using a Brookfield (Model RVTDCP-II) viscometer equipped with a CP-51 cone.

Cotton wetting. Wetting was evaluated by measuring the time required to wet cotton fabric at various surfactant concentrations in order to calculate a 25-sec

wetting concentration. Test methodology is described elsewhere (6).

RESULTS AND DISCUSSION

Ethoxylates: effect of peaking on physical properties. Although peaking is usually considered a process which increases the composition of the most important homologs, differences observed in physical properties between peaked and non-peaked ethoxylates are best understood by considering how peaking affects the concentrations of the *less* desirable homologs. As shown in Figure 1, peaking reduces the concentrations of three key groups of homologs found in the ethoxylate mixture: the free alcohol (unethoxylated alcohol), the low-mole homologs, and the high-mole homologs. Changes in physical properties are directly related to the reduction of one or more of these groups. Keep in mind, however, that the effect of peaking on these key groups is dependent on the degree of ethoxylation, as shown in Figure 2.

Reduction in free alcohol content. The extent of this reduction is dependent on the amount of EO added to the alcohol (Fig. 3). Significant reductions are achieved

with all ethoxylates except those containing very high or very low amounts of EO. For example, current state-of-the-art peaking reduces the free alcohol content of n-dodecyl 6.5-mole ethoxylate from 3.9% to about 0.5%. Reducing free alcohol content has the obvious benefit of reducing free alcohol odor.

Another benefit related to a reduction in free alcohol is the corresponding reduction in the capacity of the ethoxylate to plume during spray-drying. Less free alcohol means that less volatile material is present in the exhaust gas of the spray dryer. Less material is therefore available to plume (form a cloud) during cooling of the gas exiting the stack. The desire for a more easily spray-dried ethoxylate is what led to the initial development of peaked ethoxylates (1).

Reduction in low-mole homologs. Solubility of an ethoxylate homolog is directly related to its EO content: the higher the EO content, the greater its water solubility. This is why reducing the concentration of low-mole homologs (including the free alcohol) via peaking results in a substantial increase in water solubility. This increase in water solubility can be beneficial in the formulation of liquid products. For example, when manufacturing a liquid laundry detergent, one exam-

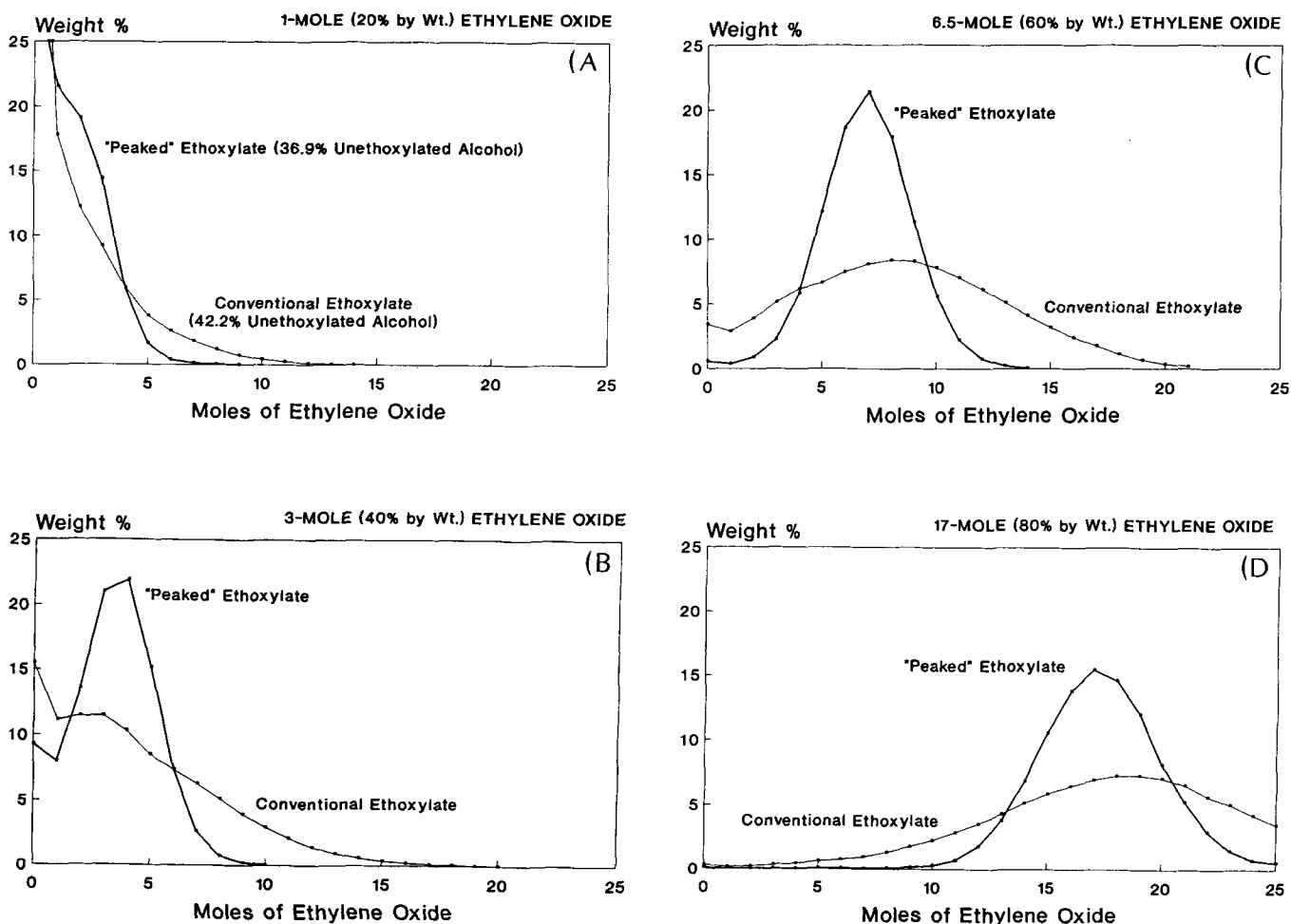


FIG. 2. Ethoxylate homolog distribution for conventional and "peaked" n-dodecyl ethoxylates containing an average of A) 1-mole EO, B) 3-moles EO, C) 6.5-moles EO, and D) 17-moles EO.

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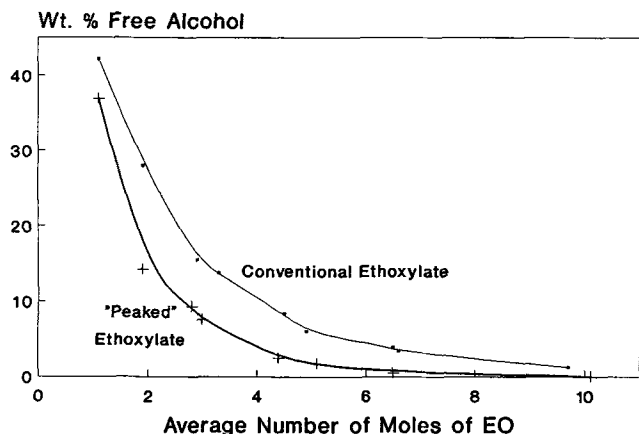


FIG. 3. Unethoxylated alcohol content as a function of EO content for conventional and "peaked" n-dodecyl ethoxylates.

ines temperature stability (e.g., cloud point) as a function of hydrotrope (solubilizer). As shown in Figure 4, a peaked ethoxylate can decrease the amount of hydrotrope required to reach acceptable temperature stability (generally below 40°F). This is one advantage that can translate directly into dollars and cents.

Reduction in high-mole homologs. The ethylene oxide chain of an ethoxylate molecule is thought to exist in two configurations: a "zig-zag" form where the EO chain is more-or-less stretched out in a linear fashion, and a condensed "meander" form where the EO chain is curled around itself (8). Only chains having 9 or more EO units condense into this meander configuration, which is a higher density, lower energy state. Increasing EO content of an ethoxylate results in an increase in ethoxylate melting point because more of the homologs can exist in the meander configuration. Similarly, since peaking reduces the concentration of

high-mole homologs, peaked ethoxylates have lower melting points (Fig. 5).

A longer EO chain also increases the capacity of the molecule to interact in solution with other molecules via hydrogen bonding. Peaking reduces the concentration of high-mole homologs which, in turn, reduces the degree of this type of interaction. This is why peaked ethoxylates generally have lower solution viscosities (Fig. 6).

Another phenomenon observed with peaked ethoxylates that is associated with a reduction in high-mole homologs is an increase in dissolution rate for solid ethoxylates in water. If conventional and peaked dodecyl-17 mole ethoxylates are placed in water and surface tension is monitored as a function of time, the peaked ethoxylate is observed to lower surface tension at a faster rate (Fig. 7). This suggests that a peaked ethoxylate would have a performance advantage over conventional ethoxylates when used in a laundry powder. So far, however, we have been unable to demonstrate any significant improvement. (This is one of those cases where we have a solution in search of a problem.)

Ethoxylates: effect of peaking on performance properties. Although peaking does not greatly affect critical micelle concentration (CMC), it does appear to significantly reduce the ability of the ethoxylate to lower surface tension (Fig. 8). This reduction in surfactant performance is directly related to the fact that peaked ethoxylates are more water-soluble than conventional ethoxylates. Higher water solubility generally decreases the ability to lower surface tension because more surfactant concentrates in bulk solution rather than at the air-water interface.

Although static surface measurements are generally very useful in understanding how structure affects performance, in this case they are misleading. If surface tension is re-examined as a function of time, we see almost the opposite trend (Fig. 9). Under dynamic conditions, peaked ethoxylates are as good or better than conventional ethoxylates in lowering sur-

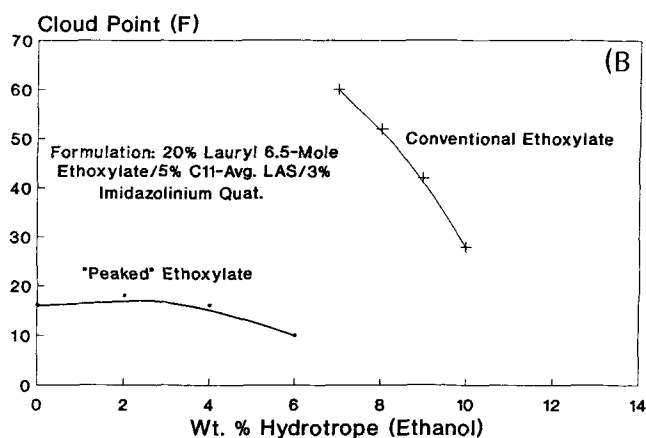
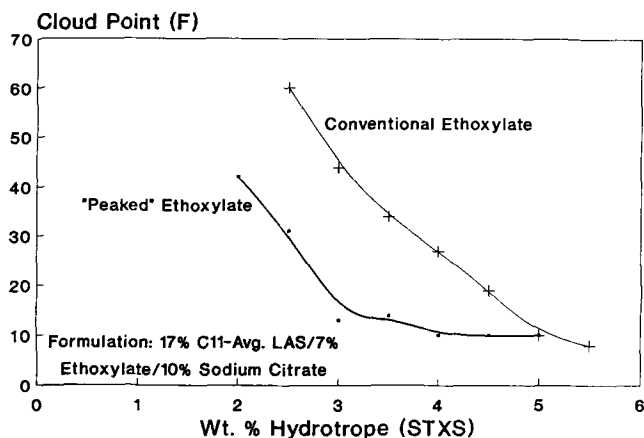


FIG. 4. Cloud point of liquid laundry detergent formulations as a function of hydrotrope level for conventional and "peaked" lauryl ethoxylates.

face tension. Although peaking reduces the concentration of the more surface active low-mole homologs, it also reduces the concentration of the less mobile high-mole homologs. While conventional ethoxylates appear to be better suited for static (equilibrium) conditions, peaked ethoxylates might be better suited for dynamic conditions.

Since wetting is usually measured as a function of time, dynamic surface properties are obviously important. As would be expected, based on dynamic surface tension data, peaked ethoxylates are better at wetting cotton cloth than conventional ethoxylates (Fig. 10).

Unlike wetting, detergency performance is difficult to predict because it is influenced by a multitude of factors. After running a battery of tests, however, we conclude that peaking *can* improve performance provided that the EO content is properly optimized. For example, Figure 11 shows detergency performance of peaked and conventional ethoxylates as a function of EO content. The data presented represent the for-

mulations and conditions that showed the largest differences. In either case, if one chooses an EO content near the optimum, then peaking will appear to improve performance. If one selects an EO content that is not at the optimum, then differences may not be observed, and under certain conditions, peaking may be observed to even hurt performance. Peaking requires that EO content be considered.

Peaking does not appear to significantly affect the ability to generate foam, but it does appear to decrease foam stability. Differences, however, are small.

Ether sulfates: effect of peaking on physical properties. The addition of a sulfate group greatly increases the solubility of the molecule. Sulfation consequently buffers many of the trends observed with peaked vs conventional ethoxylates. Differences are observed, however, with low-mole ether sulfates. Differences between peaked and conventional ether sulfates relate directly to differences that exist in the relative concentrations of the O-mole and the low-mole homologs. Although

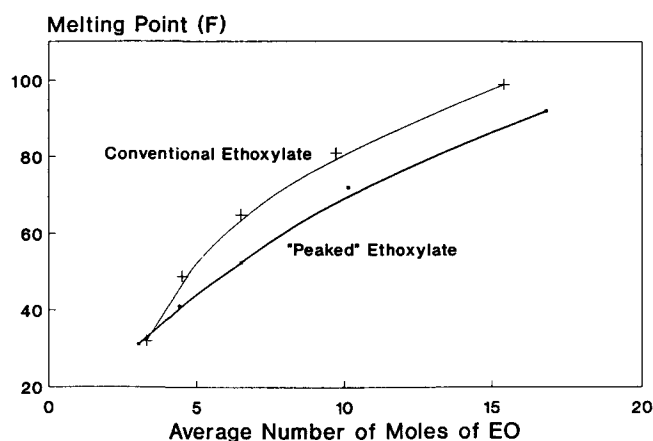


FIG. 5. Melting point (F) as a function of EO content for conventional and "peaked" n-dodecyl 6.5-mole ethoxylates.

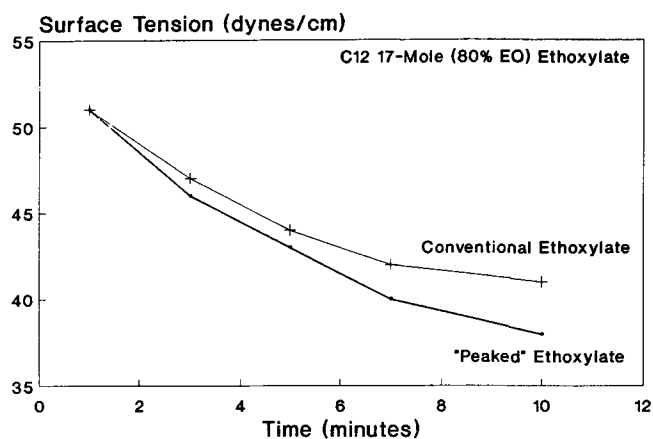


FIG. 7. Surface tension (cps) as a function of time after addition of conventional and "peaked" n-dodecyl 17-mole ethoxylates (100°F).

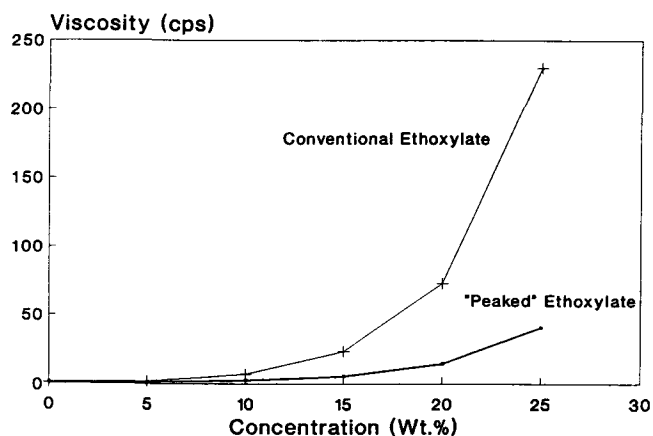


FIG. 6. Viscosity (cps) as a function of surfactant concentration for conventional and "peaked" n-dodecyl 6.5-mole ethoxylates (25°C).

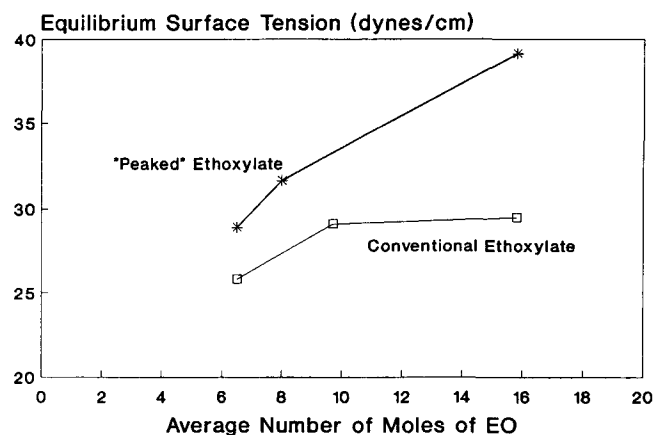


FIG. 8. Surface tension (at equilibrium) as a function of EO content for conventional and "peaked" n-dodecyl ethoxylates (100°F).

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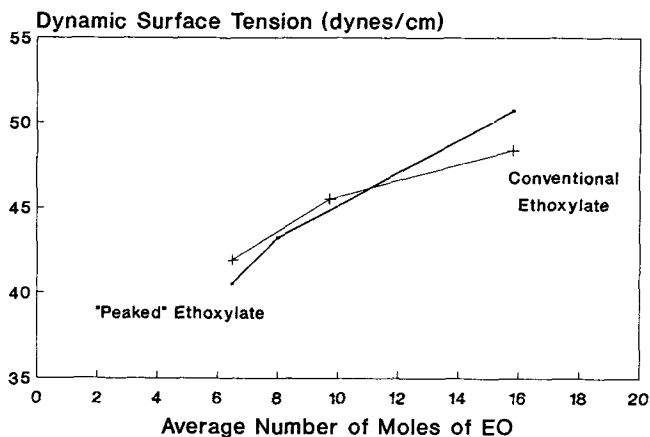


FIG. 9. Surface tension (dynamic) as a function of EO content for conventional and "peaked" n-dodecyl ethoxylates (100°F).

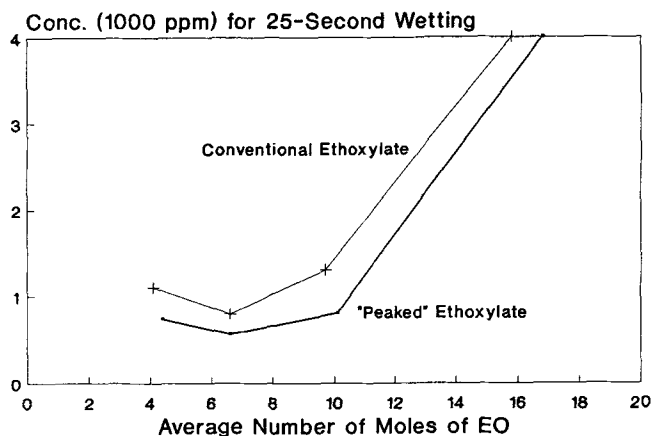


FIG. 10. Concentration to achieve 25-sec wetting of cotton twill as a function of EO content for conventional and "peaked" n-dodecyl ethoxylates (100°F).

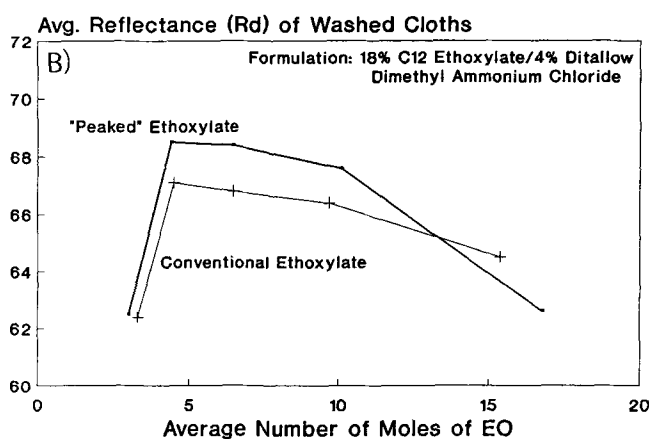
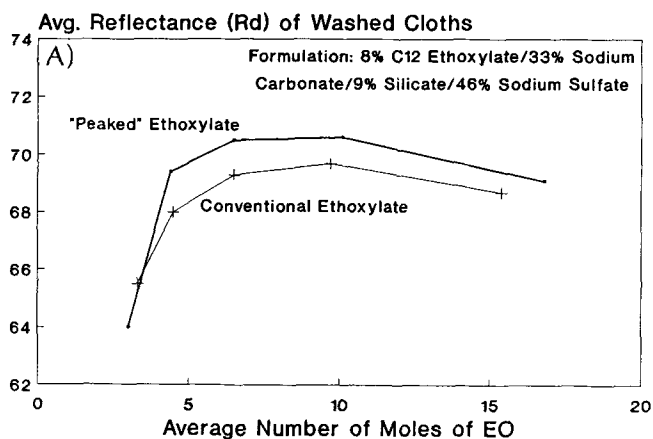


FIG. 11. Detergency performance as a function of EO content for conventional and "peaked" n-dodecyl ethoxylates in laundry detergent formulations: A) mineral oil soil; 100°F, 0.2% use level; 100 ppm water hardness; B) sebum/cotton, 100°F, 0.15% use level, 150 ppm water hardness.

both are adjacent parts of a homologous series, there are clear performance differences between alcohol sulfate (sulfated free alcohol) and the 1-mole ether sulfate (9). It is these differences that allow peaking to have any influence on ether sulfates at all.

The most dramatic effect of peaking on ether sulfate performance is with respect to viscosity—especially the ability to salt-thicken. The effect of peaking on the ability to salt-thicken 15% solutions of conventional and peaked 1-mole and 3-mole ether sulfates is shown in Figure 12. Peaking clearly lowers the amount of salt needed to achieve a certain level of viscosity. It also increases the maximum viscosity that can be reached.

Since peaking reduces the concentration of alcohol sulfate, which is considered more irritating than ether sulfate, peaking could potentially improve skin mildness.

Ether sulfates: effect of peaking on performance. Peaking does not appear to greatly affect detergency or foam performance.

Are these differences significant? Peaked ethoxylates are more soluble, have lower odor, can improve detergency performance, have a lower melting point, are less viscous, and so on. Peaked ether sulfates are easier to salt-thicken and are potentially more mild. Whether or not these benefits are significant depends entirely on whether they solve a problem. For example, peaked ethoxylates can cut hydrotrope costs when formulating a laundry liquid, but if hydrotrope costs are not important, neither is the benefit. The real benefit of peaked ethoxylates and ether sulfates is that they are available to solve some of the problems that can occur when formulating products.

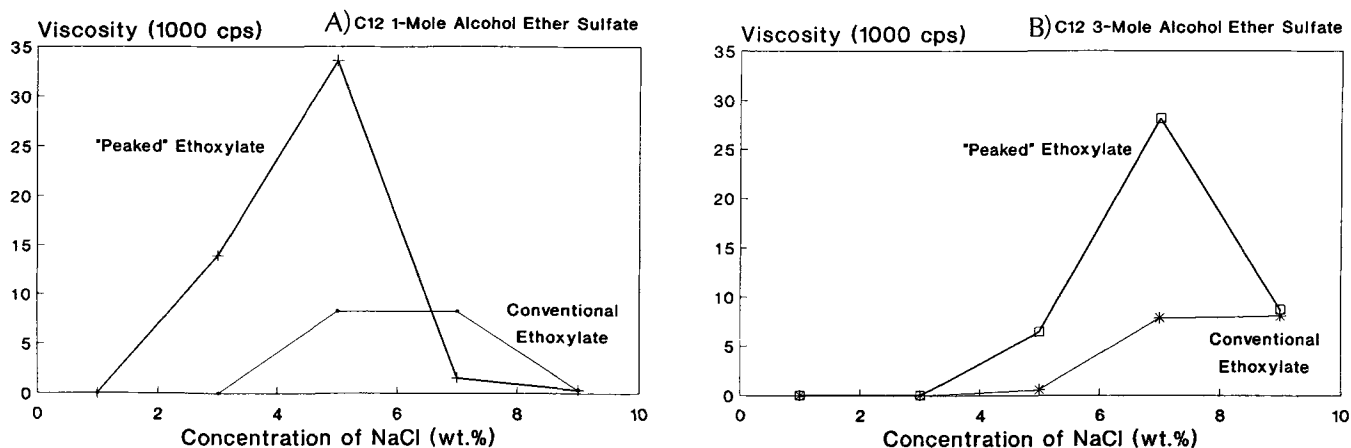


FIG. 12. Viscosity (1000 cps) as a function of NaCl concentration for conventional and "peaked" n-dodecyl A) 1-mole ethoxylates, and B) 3-mole ethoxylates (25°C).

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