Foam Enhancement by Short-Chain Hydrophobe Alcohol Ethoxylates in Light-Duty Liquids

Brian D. Condon*
Vista Chemical Company, Austin, Texas 78726

This study examined linear alcohol ethoxylates as foam-enhancing agents in light-duty liquids. The ethoxylates were formulated as supplementary surfactants to an anionic main surfactant system. The relationship between ethoxylate structure and performance was elucidated, comparisons were made between ethoxylates and other recognized foam-enhancing agents, and a representative light-duty liquid formula was optimized. Performance evaluation focused on manual plate washing capacity but also included agitation foam volume, surface activity, cloud and clear temperatures, viscosity and grease cutting. Short-chain alcohol ethoxylates with a high degree of ethoxylation (such as C_8 with 70% or 7 moles of ethylene oxide) gave optimum performance that was comparable to or better than acknowledged foam-enhancing agents. The substitution of an alcohol ethoxylate for a fatty acid ethanolamide in the test formulation resulted in substantially lower formulation viscosity.

KEY WORDS: Booster, designed experiment, dishwashing, enhancement, ethoxylate, foam, light-duty liquids, nonionic, synergism.

Lauryl-range detergent-type alcohol ethoxylates have historically been formulated into light-duty liquids (LDLs) (manual dishwashing liquids), sometimes as a component of the main surfactant system but mostly in a supporting surfactant role (1). However, formulation trends over the last decade have produced effective products that are based mainly on anionic surfactant systems supported by fatty acid ethanolamide and alkyl dimethyl amine oxide surfactants as foam-enhancing agents (boosters). Generally, these supporting surfactants are formulated at a ratio of about 1:5 with respect to the main anionic surfactant system and serve to create more foam with greater product stability.

The abovementioned surfactant systems arose through extensive formulation and testing work. Such work toward deciding upon the viability of a formulation component is guided by many basic requirements, including ingredient contribution to performance, compatibility with other formulation components, environmental safety and cost effectiveness. It is toward examining their contribution to performance that we have investigated the ability of alcohol ethoxylates to serve as foam-enhancing agents in anionic surfactant-based LDLs. However, in contrast to the abovementioned lauryl-range detergent-type ethoxylates, our testing centered around alcohol ethoxylates that are generally associated with hard-surface cleaning, namely those based on short-carbon chain hydrophobes (2,3). Various factors, such as ethoxylate structure, ethoxylation oligomer distribution and use level in the formulation, were tested for their effect on LDL performance, which was measured by means of agitation foam volume, manual plate washing, surface activity, formulatability, viscosity and grease cutting. The results of this study will present new and substantially different options in LDL systems with potential benefits in cost, performance, skin mildness and formulation flexibility.

EXPERIMENTAL PROCEDURES

Alcohol ethoxylate samples. All of the ethoxylates used in this study were made according to commercial procedures. They were Vista Chemical Company's (Austin, TX) ALFONIC® (conventional distribution) and NOVEL II (narrow-range distribution) alcohol ethoxylate. The degree of ethoxylation is designated by weight percent of ethylene oxide (EO) incorporated into the ethoxylate. Thus, for example, all 60% EO ethoxylates have a hydrophile–lipophile balance (HLB) of 12. This is in spite of the fact that a C_8-60% EO ethoxylate has 4.5 moles of EO incorporated, while a C_{14}-60% EO ethoxylate has 7.3 moles of EO incorporated. The ethoxylate nomenclature first states the carbon chainlength of the alcohol used to make the ethoxylate and then the weight percentage of EO incorporated. For example, 14–60 refers to an ethoxylate produced by adding EO to tetradecanol such that the product weight is composed 60% by EO.

Surface tension (Gibbs' plots). Gibbs' plots were obtained with spinning drop tensiometers (University of Texas Model 300; University of Texas, Austin, TX). Measurements were taken at 118°F (48°C), and solutions were made in water of 100 ppm hardness (as calcium carbonate). The hard water resulted in low numerical values for the surface tension measurements. The conditions were chosen to replicate plate washing tests.

Agitation foam. Agitation foam was measured with an in-house-produced foam generator. The device is based on the German DIN test method S3 902, in which air quickly passes perforated disks through 100 mL of test surfactant solution to produce the foam. An eccentric drive system varies the speed of the plunger disk such that the disks move quickly through the test solution and slowly through the foam. Tests were carried out at 118°F (48°C), 100 ppm hardness as calcium carbonate and 300 ppm total surfactant concentration. Data are reported as the volume of foam 1 min after agitation was stopped.

Viscosity. Viscosity measurements were obtained from a Brookfield model LVTCP 115/60 viscometer (Brookfield Instrument Co., Stoughton, MA) at 25°C and 2 s^{-1} shear rate.

Cloud/clear. Cloud/clear temperatures were measured by slowly cooling 60 g of liquid sample with slow agitation until cloudiness appeared. The cooled sample was then slowly warmed until cloudiness disappeared. The rate of temperature change was controlled to less than 1°F per min.

Plate washing. Manual plate washing performance was evaluated as LDL formulations at 118°F, 0.05% formula concentration in 6 L of water of 100 ppm hardness (as calcium carbonate). The formulations were dissolved into a filled wash basin, and foam was generated by passing compressed air through a fitted disk submerged in the wash solution. Plates were cleaned of vegetable shortening

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*Address correspondence at 4331 Chesapeake Dr., Charlotte, NC 28216.

until the foam no longer covered more than half of the surface of the wash solution.

Grease cutting. Grease cutting was assessed by a method outlined in PCT/US91/06977 (4) whereby weighed samples of a standard grease are placed into beakers. The test solution of 118°F, 0.05% formula concentration and 100 ppm hardness (as calcium carbonate) was then added on top of the solid grease. After one minute, the test solutions were removed from the beakers along with any grease that was removed from the bottom layer. The weight percentage of grease removed was recorded.

Design of experiments. All designed experiments included herein were carried out with the aid of the computer program Design-Expert™ (STAT-EASE Inc., Minneapolis, MN). The graphic data presented results from the computer-generated model for the data acquired. All mathematical models agreed well with experimental data and gave R^2 values above 0.90. The models were also evaluated for significance and gave high F values with "<5% probability of a greater F value." The F value test evaluates the null hypothesis that the model terms are actually part of the error population wherein the variation (response) observed in the design space is comparable in magnitude to the variation due to chance. If this is true, low F values mean that the model has no predictive value beyond chance. If this is false, high F values mean that the model does predict reliably beyond chance. So, the models generated account for 90% or greater of the variance observed within the design space, and there was less than a 5% probability that the variance observed was caused by chance.

RESULTS AND DISCUSSION

The base LDL formulation upon which our performance testing was carried out is: 16% $C_{11}C_{12}$ linear alkylbenzene sulfonate (LAS); 11% C_{12}–C_{14} 3-mole alcohol ether sulfate (AES); 5% foam-enhancing agent; 4% sodium oxylenesulfonate; 3% ethanol; 2% glycerin; 59% water. The foam-enhancing agent was varied according to each test's objectives, and the resultant formulas were compared for various performance characteristics. The formulation represents current anionic surfactant-based LDLs (5). Figure 1 shows the results of a designed experiment wherein the ethoxylate structure was varied from C_8 to C_{14} (vertical axis), and the degree of ethoxylation was varied from 50 to 70%. The various ethoxylates were substituted into the test LDL formulation and tested for agitation foam volume at typical United States manual dishwashing conditions. The response is the volume of foam generated. As can be seen, ethoxylates with short-chain hydrophobes and a high degree of ethoxylation gave the most foam. We did not expect this result: Until this time, these short-chain ethoxylates had been associated with hard-surface cleaning applications and not with foam enhancement (2).

An important attribute of LDL performance is the ability to resist the foam-breaking activity of soils. Thus, the same experiment just described was carried out with the modification of adding 2 mL corn oil. Figure 2 shows that the foam volume was greatly reduced in all cases but that the same trend in performance was observed: Ethoxylates with short-chain hydrophobes and a high degree of ethoxylation lent the best foaming characteristics to the test LDL formulation.

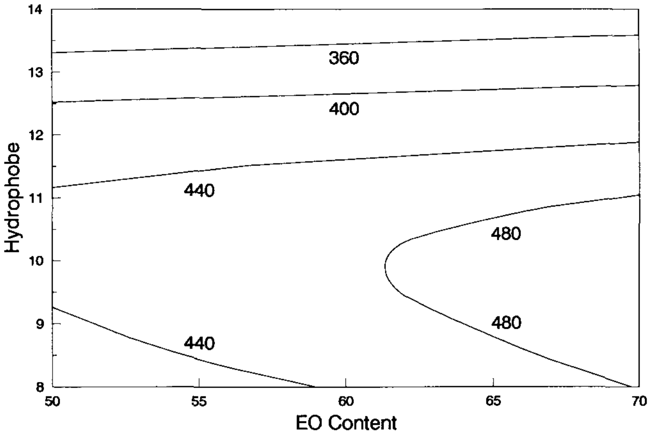

FIG. 1. Designed experiment on agitation foam volume with no soil added. The test light-duty liquid that incorporated an ethoxylate with a short-chain hydrophobe and a high degree of ethoxylation gave the most foam. EO, ethylene oxide.

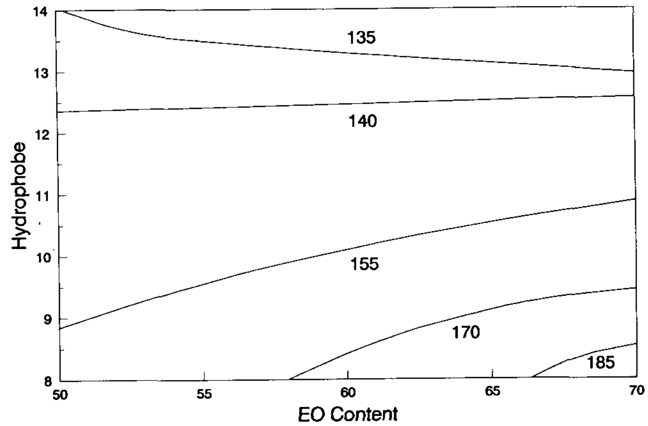

FIG. 2. Designed experiment on agitation foam volume with 2 mL of soil added. The test light-duty liquid that incorporated an ethoxylate with a short-chain hydrophobe and a high degree of ethoxylation gave the best foaming characteristics. See Figure 1 for abbreviation.

While agitation foam volume is an indicator of LDL performance, manual plate washing measures it directly. Thus, Figure 3 illustrates the results of manual plate washing tests with the same formulations described in the agitation foam volume experiments. The response in this case was the number of plates washed. The relationship between an ethoxylate's structure an its efficacy as the foam-enhancing agent in the LDL formulation was consistent throughout all foaming and dishwashing tests. An ethoxylate with a short-chain hydrophobe and a high degree of ethoxylation produced optimal results.

The ethoxylates in the above experiments had 70% EO as their upper limit for degree of ethoxylation, and all had conventional distribution ethoxylates. However, the data displayed in Figures 1–3 suggest that perhaps even better performance could be attained by using an ethoxylate with an even higher degree of ethoxylation. Thus, plate-washing experiments were carried out under the same conditions previously outlined with two modifications:

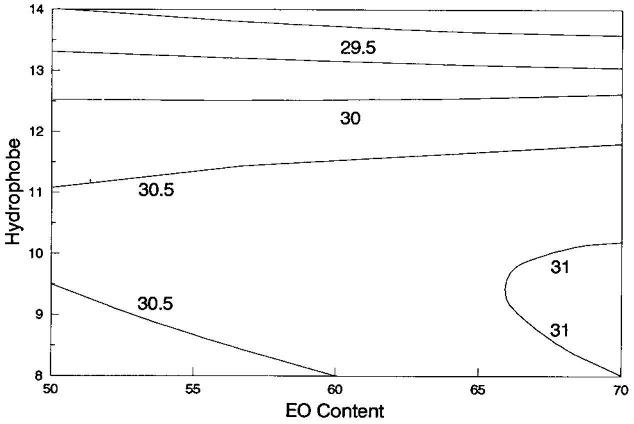

FIG. 3. Designed experiment on manual dishwashing. Results confirm those observed for agitation foaming. See Figure 1 for abbreviation.

Narrow-range distribution (6,7) and higher degrees of ethoxylation were employed. Table 1 shows the results. Evidently, degrees of ethoxylation above 70% did not enhance dishwashing performance, and there was no foam enhancement performance difference between a conventional and a narrow-range ethoxylate. Strictly speaking, these conclusions hold true only for the C_8 type ethoxylates tested directly. However, it is probable that the above two conclusions will hold true for a wider array of hydrophobe chainlengths because these short-chain hydrophobe ethoxylates were the optimally performing structures.

Having arrived at the surprising conclusion that these short-chain hydrophobe ethoxylates enhanced foaming performance of the anionic-based LDL, we then compared their performance to other recognized foam-enhancing agents (1). The following are the results of plate-washing tests carried out on the test LDL formulation that included various common foam-enhancing agents (Note: the foam-enhancing agent is listed followed by the number of plates washed in brackets.): conventional 8–70 [32]; narrow range of 8–70 [31]; C1214 amide [26]; C1214 amine oxide [28.5]; C810 alkylpolyglycoside (APG) [29]; none [26]. The formulations that incorporated the alcohol ethoxylates demonstrably washed more plates than those formulations incorporating other materials as foam enhancers.

While the test formulation (see the first paragraph of the Results and Discussion section of this paper) was chosen to represent a typical current LDL, such formulations were optimized with foam-enhancing agents other than alcohol ethoxylates. Thus, we sought to optimize an anionic surfactant-based LDL with a narrow-range distribution C_8-70 alcohol ethoxylate as the foam-enhancing agent. Figure 4 illustrates the results. Contrary to the previous experiments, the alcohol ethoxylate structure was held constant while the ratio of LAS to AES (vertical axis) and the amount of ethoxylate (horizontal axis) incorporated into the formula were varied. The total of LAS and AES remained constant at 27%. Therefore, each data point within the design space resulted from testing a different LDL formulation, corresponding to the parameters on each axis. These LDLs were assessed for plate-washing performance, so the data displayed are the numbers of plates washed.

One can draw several conclusions from this experiment. Firstly, there exists a fairly broad range of optimally performing formulations encompassing a ratio of LAS to AES of 2:1 or higher and a nonionic content of 1–10%. Secondly, the test LDL is within the optimal region. This lends credence to comparisons between performance results found for the test formula that contained various foam-enhancing agents: All of the formulas are on equal footing as "optimal" formulas (see paragraph 5 of Results and Discussion section of this paper). And finally, plate-washing performance proceeds through a maximum upon addition of nonionic for a given ratio of anionics. This last conclusion addresses a particularly important point. Because alcohol ethoxylates are surfactants, one could propose that their mode of action in foam enhancement is merely that their inclusion in LDLs simply raises the total "active surfactant" level of the formulation. This potential explanation falls short in light of the performance maximum observed.

In an effort to shed more light on the mode of action by which short-chain ethoxylates enhance foaming performance, we examined the surface activity of model surfactant systems. One system contained only LAS and AES in the ratio described by the test formulation while

TABLE 1

Fine-Tuning the Ethoxylate Structure for Optimal Plate-Washing Performance[a]

Ethoxylate structure		% EO	
Alcohol ethoxylate type	70	80	85
Conventional C_8	32	31	31
Narrow-range C_8	32	31	31

[a]Degrees of ethoxylation beyond 70% and the ethylene oxide (EO) oligoner distribution did not affect the plate-washing performance.

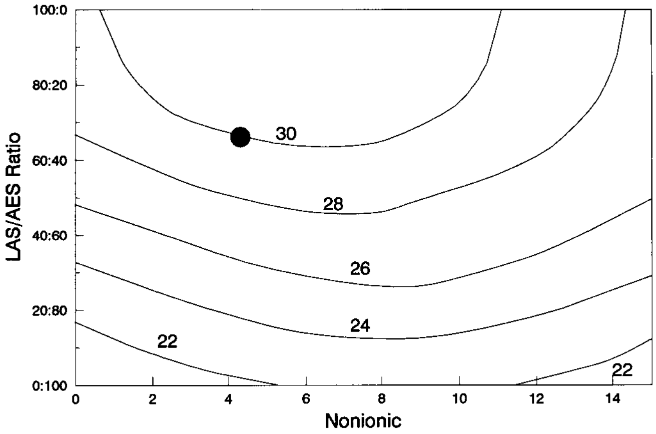

FIG. 4. Light-duty liquid formulation optimization. A fairly broad range of optimal formulations was discovered. The test formulation is within the optimum region (see darkened dot). LAS, linear alkylbenzene sulfonate; AES, alcohol ether sulfate.

TABLE 2

Surface Chemical Data for Model Surfactant Systems with and Without C_8-70 Ethoxylate[a]

Model formula	CMC/ppm (total surfactant)	Surface tension at CMC (dyne/cm)	Interfacial tension at 300 ppm vs. corn oil (dyne/cm)
Anionic only	9.2	29.5	0.58
Anionic and nonionic	11	29.1	0.63

[a]Abbreviation: CMC, critical micelle concentration.

the other contained the anionics and nonionic (narrow range C_8-70) in the amounts outlined in the test formulation. Table 2 lists the surface and interfacial properties of the two systems—they are nearly identical. The fact that the critical micelle concentration of the C_8-70 ethoxylate in question is 3200 ppm (ten times higher than the test concentration) makes the findings regarding surface activity for these two systems seem reasonable.

The literature (8) outlines many mechanisms by which foaming by anionics may be enhanced, and these include increasing the surface film elasticity, lowering the equilibrium surface tension of the system, increasing the bulk viscosity of the system and increasing the ability of the system to solubilize foamacidal soils. The data in Table 2 eliminate equilibrium surface tension differences between the two systems as the cause for the enhanced foaming seen with the nonionic-containing system. Similarly, the similar interfacial tension values for the two systems indicate (but do not prove) that a greater ability to solubilize foamacidal soils is not responsible for the enhanced foaming observed for the nonionic-containing system.

Further, the foaming and plate-washing tests were carried out at 300 ppm total surfactant concentration, and even though we have taken no direct measurements of the viscosity of these two formulations at test level concentrations, we have simply observed that at 300 ppm they are both indistinguishable from water. Thus, an increase in the bulk viscosity due to the presence of the ethoxylate is unlikely.

Therefore, by elimination, we are left with an increase in the surface film elasticity as the mechanism by which these ethoxylates enhance the foaming ability of anionic surfactant systems. Greater surface elasticity can be brought about by moderating the rate of attainment of equilibrium surface tension, reducing the ionic repulsion between the anionic head groups at the surface and increasing the effective hydrogen bonding in the surfactant matrix at the surface. Though we have no direct evidence for these effects, time-dependent surface tension measurements would be an appropriate starting place for such investigations.

In addition to the foaming and plate-washing performance aspects of anionic surfactant-based LDL systems, the physical properties of these formulations present an area of keen interest to formulators. Toward this end, we studied the cloud and clear temperature of the test formulation by incorporating various foam-enhancing agents (Table 3). As one can see, the formulations incorporating short-chain alcohol ethoxylates exhibit excellent solubility properties.

TABLE 3

Cloud and Clear Temperatures of Test Formulations with Various Foam-Enhancing Agents

Foam-enhancing agent	Cloud temperature (°F)	Clear temperature (°F)
Conventional 8-70	9	23
Narrow Range 8-70	7	22
C1214 Amide	39	52
C1214 Amine oxide	12	15
C810 APG	9	21

Another physical property of interest to formulators is formulation viscosity and its manipulation by added sodium chloride. We studied formulation viscosity as a function of salt concentration for LDLs made with various foam-enhancing agents. Several interesting trends were observed (Fig. 5). However, the conclusions most appropriate to the subject of this study are that the formulations made with short-chain alcohol ethoxylates are substantially less viscous and less responsive to added salt than those made with other foam enhancers. This property may in fact become beneficial if one's intent lies in formulating a more concentrated LDL. The loss of viscosity upon replacing an amide or amine oxide with a short-chain ethoxylate is not altogether unexpected because a noted property of amides and amine oxides in LDL systems is viscosity boosting (1).

Finally, including an alcohol ethoxylate in an anionic surfactant-based LDL suggests potentially enhanced grease-cutting ability. This stems from the widely known general efficacy of nonionic surfactants in cleaning oily soils. Toward this end, we carried out grease-cutting evaluations on the test LDL formulation made with various foam-enhancing agents. The results are listed as foam-enhancing agent and percentage of grease removed in brackets, respectively: conventional 8-70 [8.6]; narrow range 8-70 [10.1]; C1214 amide [9.4]; C1214 amine oxide [35.3]; C810 APG [12.5]. Somewhat surprisingly, the formulations that included the C_8-70 alcohol ethoxylates did not show greater grease-cutting ability than those formulated with the other foam boosters. This is probably due to the fact that a C_8-70 ethoxylate is not an efficient surfactant with its critical micelle concentration above 3000 ppm. Thus, the test solution's concentration was far below that necessary for effective surfactant action by the ethoxylate. This result lends further credence to the previous tentative conclusion that enhance solubilization of foamacidal soils was not the mode of action for foam enhancement by these short-chain hydrophobe ethoxylates.

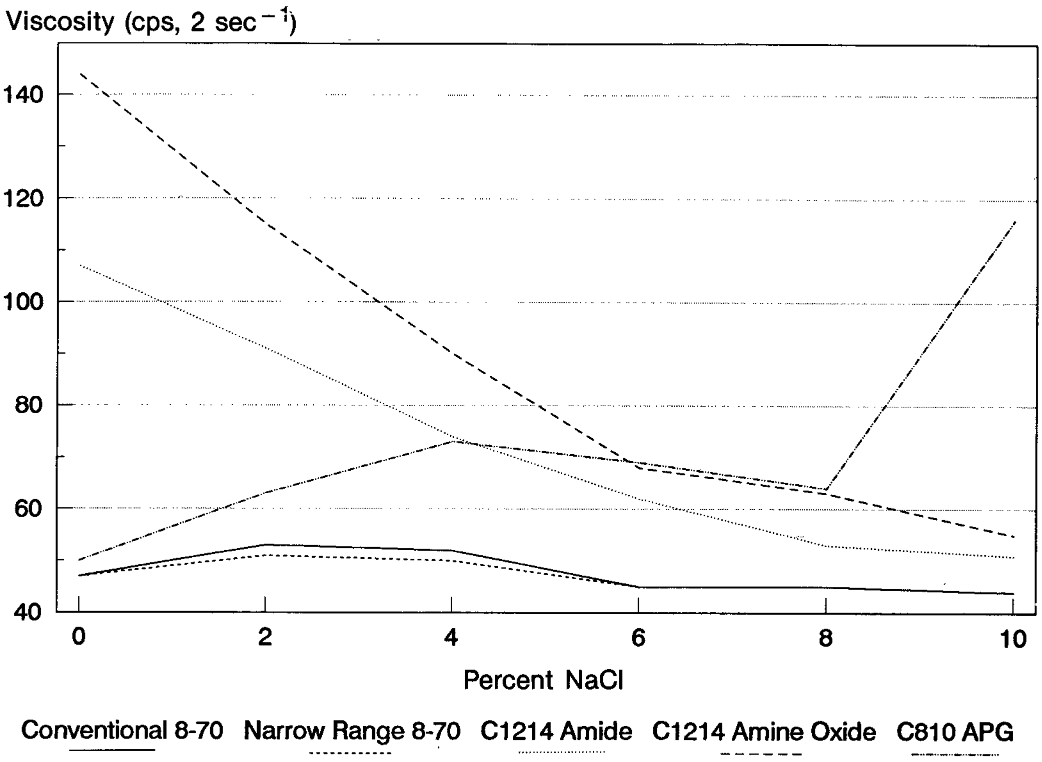

FIG. 5. Viscosity of formulated light-duty liquids at 25°C and 2 s^{-1}. APG, alkylpolyglycoside.

With this study, we have elucidated some of the factors influencing the foam-enhancing ability shown by short-chain hydrophobe alcohol ethoxylates in an anionic surfactant-based LDL and how inclusion of these nonionics in LDLs may affect physical properties. We have also presented some evidence aimed at explaining the mechanism by which this foam enhancement occurs. Further areas of interest currently under investigation include formulation hydrotrope requirement, odor, skin mildness, long-term storage stability and highly concentrated formulations. We suspect that narrow-range ethoxylates present unique opportunities for LDL performance in many of these areas.

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