HIGH-ACTIVE ALCOHOL ETHOXYSULFATE/ALCOHOL ETHOXYLATE BLENDS: A COST-EFFECTIVE ALTERNATIVE FOR DETERGENT FORMULATORS

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High-active alcohol ethoxysulfate/alcohol ethoxylate (AES/AE) blends solve many of the common challenges inherent in the production, transportation and use of alcohol ethoxysulfates. These liquid blends, in which alcohol ethoxylate serves as the solvent for alcohol ethoxysulfate in place of water, are produced using conventional sulfation equipment, typically have activity levels greater than 90% by weight, and contain no preservatives or other organic solvents. Alcohol ethoxysulfates of improved quality, e.g., reduced color, 1,4-dioxane, and sodium sulfate levels, are easily obtained using the technology. The effects of surfactant structure and anionic/nonionic ratio on physical properties are also illustrated. Viscosity and pour point decrease with decreasing anionic surfactant content, decreasing EO-content of the AE, and increasing EO-content of the AES. Typically, the blends are easily pumpable liquids at relatively low temperatures and are stable for several months at shipping and storage conditions. In addition, these blends are shown to be well-suited for use in household laundry powders and liquids as well as industrial cleaning compositions in which both AES and AE are major surfactant components.

WHY STUDY HAM AES/AE BLENDS?

Alcohol ethoxysulfates (AES) are an increasingly important surfactant type for use in household laundry powders and liquids. They provide good detergency in mixed-active formulations with alcohol ethoxylates (AE) due to their high tolerance to water hardness ions.[1] They are high-foaming anionic surfactants that are particularly mild to the skin and provide high levels of enzyme stability in heavy duty laundry liquids.[2]

AES have traditionally been sold as low-viscosity 28%-active aqueous solutions containing preservatives or flammable 60%-active solutions with approximately 14% ethanol as a hydrotrope. More recently, they have been marketed in a viscous 70%-active form. Viscosities of these high-active fluid gels are typically greater than 10,000 cp at shear rates below 10 sec^{-1}. [3] AES surfactants cannot, however, be produced and transported as a dry powder or flake due to their inherent stickiness. Also, the instability of the ethoxysulfuric acid prevents shipping and storage in that form.[4]

Previous publications describe initial studies of high-active matter (HAM) alcohol ethoxysulfate/alcohol ethoxylate blends.[4-6] These blends have greater than 90% total surfactant content and are prepared by neutralization of the sulfuric acid form of the AES in a blend of alcohol ethoxylate and a concentrated base such as 50% NaOH. Intriguing results were obtained in the initial studies as low-viscosity liquids were found to form over a wide range of AES/AE ratios and structures. In this study, these structural effects are described as well as other factors including effects of AES counterion type and production technique on product quality of high-active blends. Also, the use of high-active AES/AE blends in heavy-duty laundry powders and liquids is discussed.

PREPARATION OF HAM AES/AE BLENDS IS STRAIGHTFORWARD

Sulfation of AE to prepare AES is a two-step procedure. In the case of SO_3 sulfation, liquid AE and gaseous SO_3 are first contacted in the reaction zone of a falling film sulfator to yield the acid form of AES. The acid exits the falling film column and is neutralized with the appropriate base. **Figure 1** shows a schematic diagram of the modified procedure in which AE is introduced to the neutralization system with the concentrated base to produce the 90+%-active HAM blend.

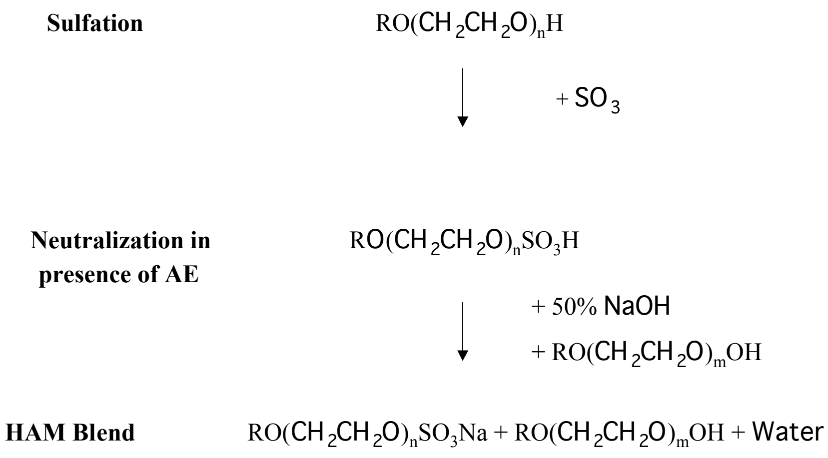

FIGURE 1 : Production process for High Active Matter (HAM) AES/AE surfactant blends

For preparation of a variety of small AES/AE HAM samples of varying structures and ratios, a laboratory-scale falling film sulfation unit was utilized in which one gram/minute gaseous SO_2 is converted to SO_3 over a hot vanadium oxide catalyst bed. The resulting acid was neutralized in a batch mode in glass jars by stirring into a blend of alcohol ethoxylate and 50% NaOH or monoethanolamine. The alcohol ethoxylates used to prepare the HAM systems were derived from modified oxo alcohols. This type of alcohol is approximately 80% linear with 20% two-alkyl branching.

A WIDE RANGE OF HAM AES/AE SYSTEMS ARE OBTAINABLE

Effects of AES/AE Ratio on Viscosity

Viscosities of various HAM AES/AE systems were measured with a temperature-controlled Brookfield Model LVTD viscometer using a number 18 spindle. Shown in **Figure 2** is the viscosity of a 1/1 AES/AE HAM blend consisting of the sodium salt of the ethoxysulfate prepared from a predominantly linear C_{12-15} alcohol with an average of three EO groups (AES 1215-3S) and a C_{12-15} alcohol ethoxylate with an average of nine EO groups (AE 1215-9). At this ratio, approximately 6% water from the 50% NaOH and neutralization reaction is contained in the system. A liquid system with fairly low viscosities is obtained down to the pour point temperature of 38°C. As expected, viscosity decreases as temperature is increased.

A slight non-Newtonian, pseudoplastic behavior is shown in **Figure 2** with increased viscosity exhibited at lower shear rates. However, above the melting temperature, a typical HAM product shows little tendency to cling to the sides of its container. It is important to note that 70% AES 1215-3S solution without the addition of AE exhibits a viscosity of approximately 7000 cp and 5000 cp at a shear rate of 10 sec^{-1} at temperatures of 20°C and 50°C, respectively. The viscous 70% gel is also highly pseudoplastic resulting in product loss when it is transferred from a container even at high temperatures.

Shown in **Figure 3** are the corresponding viscosity data for the same surfactants at a higher AES/AE ratio and at a slightly higher water content. In this case, a liquid system was obtained only at temperatures greater than 63°C. The effects of anionic/nonionic ratio are further demonstrated in **Figures 4 and 5** where the pour point temperatures and high-shear viscosity at 50°C of the HAM blends are plotted versus the wt% level of AES in the HAM blend. Liquid systems below 40°C are noted over a wide range of AES content with a minimum in pour point temperature occurring at approximately 33% AES.

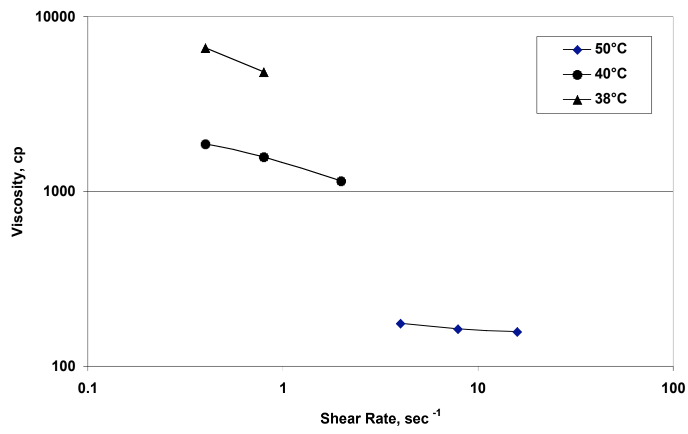

FIGURE 2: Viscosity profile of 47% AES 1215-3S/47% AE 1215-9/6% water HAM system

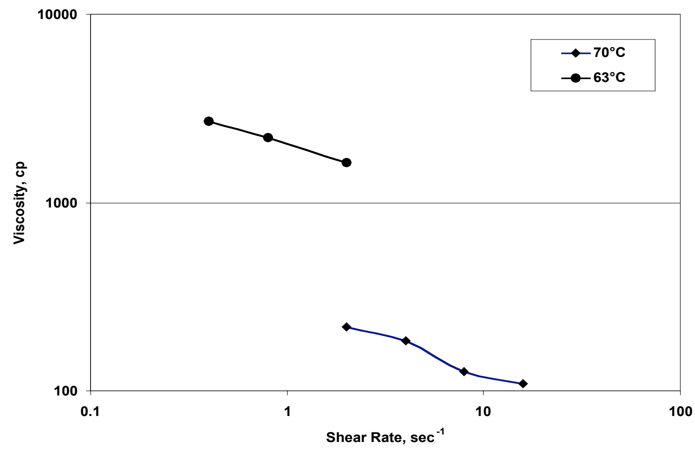

FIGURE 3: Viscosity profile of 57% AES 1215-3S/35% AE 1215-9/8% water HAM system

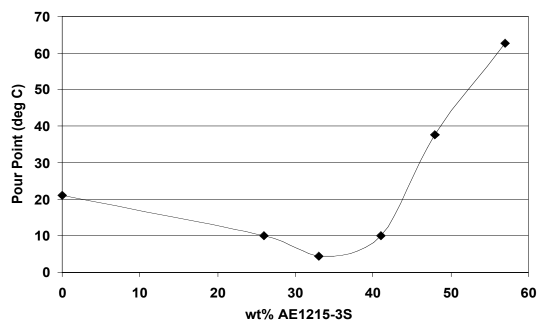

FIGURE 4: Pour point temperatures of AES 1215-3S/AE 1215-9 HAM systems as a function of AES content

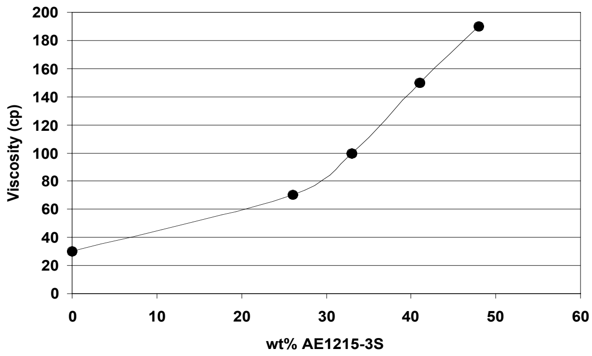

FIGURE 5: Viscosity of AES 1215-3S/AE 1215-9 HAM systems at 50°C and 15.84 sec^{-1}

Effects of AES and AE Structure on Viscosity

Shown in **Figure 6** are viscosity data at a fixed shear rate for HAM systems consisting of AES 1213-6.5S and a variety of alcohol ethoxylates based on the same $C_{12,13}$ alcohol at a 2/1 AES/AE weight ratio. In contrast to the system represented in **Figures 2-5**, the high-EO AES provides fluid blends at temperatures as low as 35°C even at a high AES/AE weight ratio. In contrast, the AES 1215-3S system at the same AES/AE ratio has a pour point temperature in excess of 60°C as illustrated in **Figure 4**. These results point out that viscosity behavior of HAM systems is quite sensitive to the EO-level of the AES with higher levels of ethoxylation resulting in more fluid systems. Similarly, use of alcohol sulfate in place of AES provides quite viscous HAM blends. Additional data for other anionic/nonionic systems can be found in the previous publication.[4]

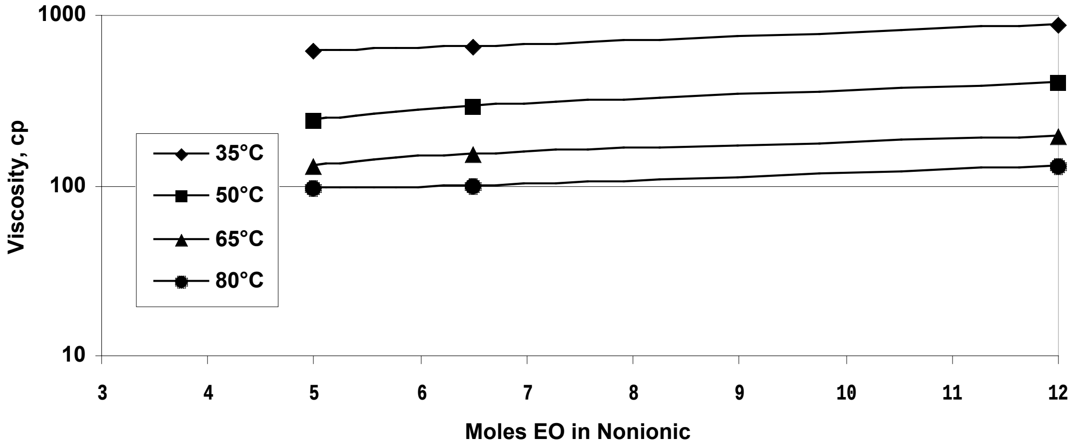

FIGURE 6: Effect of nonionic EO-content on viscosity of 2/1 AE 1213-6.5S/AE 1213-X high active matter blends; Shear rate = 3.96 sec^{-1}

Also illustrated in **Figure 6** are the effects of changes in AE ethoxylation level on viscosity. In contrast to the effect of AES structure, effects on HAM viscosity due to changes in the level of ethoxylation of the alcohol ethoxylate are relatively minor. As would be expected, the use of waxy high-EO ethoxylates having high melting points, e.g., AE 1213-12, tends to slightly increase the viscosity of HAM blends while more liquid low-EO ethoxylates, e.g., AE 1213-5, lower viscosity and pour point temperatures slightly.

Effects of AES Counterion on Viscosity

In addition to the effects of changes in surfactant hydrophobe and hydrophile structure, the effects of AES counterion on HAM physical properties are also of interest. Specifically, the use of monoethanolamine (MEA) as the neutralizing base was investigated. Because this base is anhydrous, water levels in the HAM systems can be controlled and minimized. However, some added water is necessary to provide efficient neutralization of the AES acid.

Shown in **Figure 7** is the viscosity profile of the MEA salt of AES 1215-3 with AE 1215-9. Comparison to **Figure 2** shows that at the same anionic/nonionic ratio, presence of the MEA salt results in a high-active blend with a much lower pour point temperature and reduced viscosity relative to properties of the HAM blend containing the corresponding sodium salt of the AES. Also, this attractive rheology is achieved in the presence of only 1% water versus approximately 6% water for the sodium salt system. Similar reductions in viscosity and pour point temperature were obtained when triethanolamine (TEA) was used as the neutralizing agent.

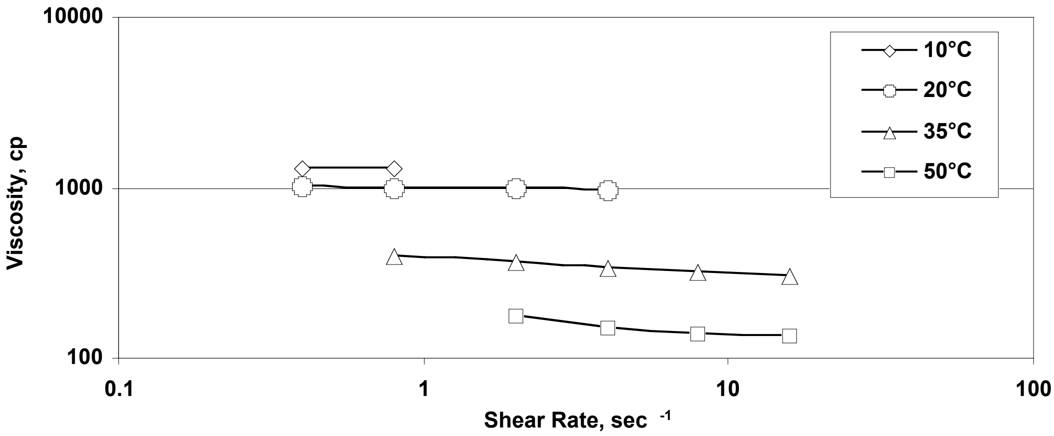

FIGURE 7: Viscosity profile of 49% AES 1215-3(MEA)/49% AE 1215-9/1% water HAM system

HAM AES/AE SYSTEMS EXHIBIT GOOD PRODUCT QUALITY AND THERMAL STABILITY

AES product quality can be profoundly affected by sulfation conditions including reactor temperature and SO_3/AE molar feed ratio. Typically, a feed ratio is maintained at approximately 1.00 to maximize feedstock conversion and minimize free oil formation while minimizing inorganic salt, 1,4-dioxane, and color formation.[3,7,8] The use of HAM technology allows the opportunity to sulfate at more mild conditions, i.e., < 1.00 molar feed ratio, since alcohol ethoxylate is an expected component of the final product. In other words, a low conversion of the alcohol ethoxylate feed in the sulfation unit can be easily tolerated as long as the effect of the presence of unsulfated AE feedstock in the final HAM blend is taken into account. Also, by sulfating at a low SO_3/AE ratio, one could conceivably increase the rate of production without compromising product quality by increasing the concentration of sulfur trioxide in the air reaction mixture.[3]

Table 1 shows composition data for AES 1213-6.5S/AE 1213-6.5 systems prepared using the small-scale batch sulfation method. Although the sodium sulfate and 1,4 dioxane levels at this scale are undoubtedly higher than would be obtained using a continuous commercial sulfation process, the trend toward lower sulfate and 1,4-dioxane levels with reduced SO_3/feed molar ratio while maintaining the same surfactant composition and viscosity properties is clearly demonstrated. Although not quantified in this study, similar reductions in color formation were obtained as a result of sulfation at the milder reaction conditions.

TABLE 1: Effect of SO_3/Feed Molar Ratio on HAM Product Composition and Properties

SO_3/Feed Molar Ratio	% AE 1213-6.5S	% AE 1213-6.5	% Water	% Sodium Sulfate	1,4-Dioxane, ppm[a]	Viscosity, cp[b]
1.03	50	45	4.6	0.89	231	145
0.83	50	45	4.7	0.55	4	130
0.64	52	43	4.5	0.23	1	137

a) Basis AES

b) Shear Rate = 7.92 sec^{-1}; Temperature = 50°C

In addition to finished product quality, the thermal stability of HAM AES/AE systems is also of high importance. AES can degrade when subjected to high temperatures for extended periods of time. In this regard, samples of the system described in **Figure 3** with initial pH 9 were stored under air at 50 and 65°C. The system was stable at both temperatures for greater than six months of storage time as indicated both by stable pH and anionic active matter levels.

HAM AES/AE SYSTEMS ARE WELL-SUITED FOR USE IN LAUNDRY POWDERS

As noted above, AES is a high-performing anionic surfactant well-suited for laundry powders and liquids. It typically is used in conjunction with alcohol ethoxylates to provide both good particulate and oily-soil detergency properties. However, the use of AES in laundry powders has typically been limited to spray tower production processes due to the presence of water and/or other solvents in the neutralized surfactant system. HAM technology provides the opportunity to easily incorporate AES/AE blends into laundry powders by other processes. Specifically, the low viscosities exhibited at relatively low temperatures and high shear rates (see **Figure 5**) allow a wide variety of blends to be easily sprayed onto conventional builder particles at high surfactant levels.[9]

The pseudoplastic behavior of the HAM blends, i.e., increased viscosity at low shear rates, is beneficial in reducing long-term "bleeding" of the surfactant mixture from detergent particles into cardboard packaging. This effect is illustrated in **Figures 8 and 9** for powders prepared from a carbonate builder and 1:1 zeolite/carbonate builder, respectively, and containing 20% total surfactant. The procedures for preparing the powders and measuring surfactant bleeding are reported elsewhere.[9] In this situation, bleeding refers to the percentage of total surfactant available which was transferred from the detergent powder sample to a paper specimen after a specified time of contact. As compared to the all-nonionic powder products, reduced migration of surfactant was observed for systems prepared from HAM AES/AE blends.

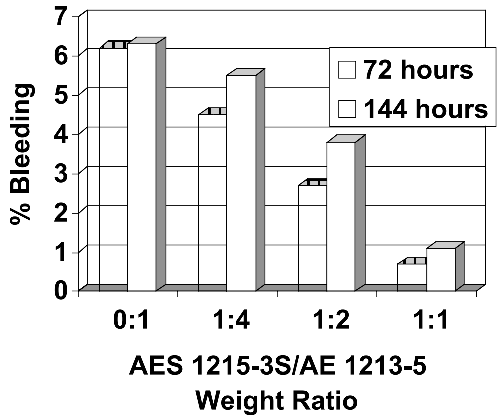

FIGURE 8: Bleeding of AES/AE-containing powders at room temperature; 20% surfactant on carbonate builder

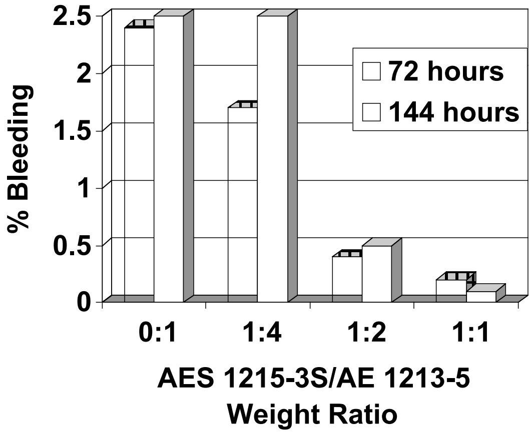

FIGURE 9: Bleeding of AES/AE-containing powders at room temperature; 20% surfactant on 1:1 zeolite/carbonate builder

HAM TECHNOLOGY IS USEFUL FOR PRODUCING CONCENTRATED LAUNDRY LIQUIDS

Heavy-duty laundry liquids (HDL) are the leading detergent market segment in the US and are a growing product form in Europe.[10] Typically, heavy duty liquids contain substantial quantities of both AE and anionic surfactants such as AES. Also, as noted above, AES is a particularly effective surfactant for use in enzyme-containing liquids due to its good compatibility with most types of enzymes. Typically, high-active AES solutions such as 60% AES with ethanol or 70% AES gels are used to produce the HDL's. However, the use of the former product requires handling of a flammable material and inclusion of ethanol in the final formulation. Also, the high viscosities exhibited by the 70% solution can cause handling problems during shipping and storage; specifically, a significant quantity of the AES may cling to the sides of storage containers when the containers are emptied.

Due to their low water content, combined ingredients, and attractive physical properties, HAM AES/AE blends can serve as a non-flammable liquid concentrate for heavy-duty liquid production. For example, a detergent formulator could prepare a HAM blend at a centrally located sulfation facility and ship the concentrated blend to satellite packaging facilities where water, enzymes, perfumes, etc., could be added at the appropriate levels prior to packaging. This process scheme would provide the opportunity for reduced shipping and storage costs throughout the supply chain.

Upon dilution into water, HAM blends exhibit gelling tendencies intermediate between the rigid gels of AES and the more fluid AE gels. One option to mitigate gel formation upon dilution into a HDL formulation is to incorporate a non-flammable solvent such as propylene glycol during production of the HAM blend. The propylene glycol serves two purposes at this point: it reduces the pour point temperature and viscosity of the HAM blend allowing production at higher AES/AE ratios, and it also reduces or eliminates gelling upon dilution into water. Shown in **Figure 10** are viscosity data for a system containing propylene glycol but having the same AES/AE ratio as the system represented in **Figure 2**. The use of propylene glycol at this level reduces the pour point temperature of the HAM system from 63°C to below 10°C and provides an easy-to-handle low-viscosity concentrate for shipping and dilution into a HDL product. In the final HDL product, the propylene glycol serves both as an effective enzyme stabilizer as well as viscosity and clear point modifier.[11]

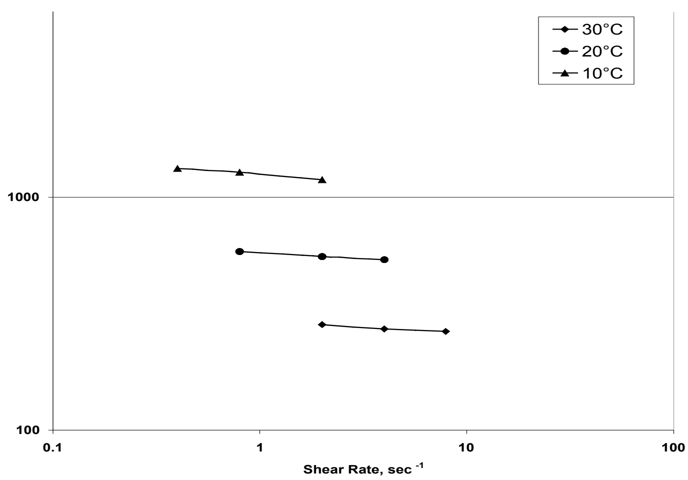

FIGURE 10: Viscosity profile of 48% AE 1215-3S/29% AE 1215-9/17% propylene glycol/6% water HAM system

COMMERCIAL PRODUCTION OF HAM SYSTEMS REQUIRES LITTLE CAPITAL INVESTMENT

HAM systems have been successfully produced on both a pilot and commercial scale using conventional sulfation and neutralization equipment. No modification to sulfation conditions is necessary unless milder reaction conditions are desired for improved product color and reduced 1,4-dioxane production as illustrated above. Typical continuous neutralization systems can easily accommodate HAM production due to the low viscosities exhibited by the blends. Optimally, the neutralization loop is first filled with the nonionic surfactant rather than water to avoid gel formation, and then sulfation of AES is initiated. Typically, the only capital expenditure required for HAM production is conversion or addition of a line to allow direct introduction of the alcohol ethoxylate to the neutralization loop.

HAM AES/AE SYSTEMS PROVIDE MANY LOGISTICAL AND APPLICATION BENEFITS

Table 2 summarizes some of the benefits of using HAM AES/AE systems in household detergent applications. Others may be realized depending on the specific logistical and formulation requirements confronting a detergent formulator.

TABLE 2: Benefits of HAM AEA/AE systems in household detergent applications

Manufacturing	Distribution	Formulation
Easy to handle – Pumpable with low viscosities at temperatures near or slightly above room temperature, e.g., 20-50°C	Lower shipping and storage costs due to low water content versus 28%-active, 60%-active, and 70%-active AES	Enables incorporation of AES in dry blended or agglomerated detergent powders – No spray tower is necessary to remove excess water
Can be manufactured at a single location for widespread distribution to formulators	No preservatives or flammable organic solvents required due to low water content and low pour points	Well-suited for incorporation in superconcentrated laundry liquids and powders and in LDL's containing AES and AE
Blends can be tailored to customer requirements – Wide range possible in component carbon number, EO levels and anionic/nonionic ratios	Serves as reconstitutable base formulation to reduce or eliminate import duties on individual components	Contains reduced levels of AES by-products such as 1,4-dioxane, sodium sulfate, and color
Allows possibility of manufacturing AES at faster rates while maintaining desired product quality	Facilitates use of AES for customers who have flammability concerns or storage limitations and reduces product loss in transport	Provides improved cleaning performance in hard water and increased enzyme stability versus LAS-containing liquid detergents

CONCLUSIONS

A trend toward increased use of AES in laundry detergents and other cleaning products is expected over the next several years driven by consumer and regulatory requirements. In this regard, new technologies for production, transport and application of AES are required to facilitate this trend. Based on the above data, HAM AES/AE technology is clearly one alternative that should be considered by both surfactant producers and detergent formulators.

ACKNOWLEDGEMENTS

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