

Solvent-Free High Active Matter Alcohol Ethoxysulfate/Alcohol Ethoxylate Blends: Preparation and Effect of Surfactant Structure on Rheological Properties¹

L. Kravetz and H.L. Benson

Shell Development Company, Westhollow Research Center, P.O. Box 1380, Houston, TX 77251-1380

Blends of alcohol ethoxysulfates (AES) and alcohol ethoxylates (AE) at high active matter content (90%) have been prepared. These blends contain no solvents other than water and have sufficiently low viscosities enabling the pumping of them from storage vessels to mix tanks. In addition, they may be diluted into aqueous solutions with less gel formation tendencies than shown by AE or AES alone. Specific AE/AES blend ratios, alkyl and polyoxyethylene chain lengths are important selection parameters for achieving desired rheological properties.

Alcohol ethoxysulfates (AES) are finding increasing use in household laundry powders and liquids as part of mixed active surfactant systems (1-3). AES provide good detergency in mixed active formulations and their performance is not affected appreciably by the presence of water hardness ions. In laundry liquids (HDL), AES generally are present with nonionic surfactants, where each of these surfactant types act as mutual hydrotropes, thereby permitting liquid concentrates containing active matter levels as high as 50%. In addition, the use of AES permits the formulation of enzyme-stable HDL (4).

A drawback to the use of AES in formulated products is their strong gel forming tendency as they are diluted into formulations from concentrations greater than 30%. Lauryl-range, 3-mol AES products are generally sold as a 60% active matter solution containing approximately 14% ethanol as the hydrotrope. This relatively high active matter solution lowers shipping costs. However, the presence of ethanol in AES prevents their use in spray-dried or dry-blended laundry powders where the flammability and combustibility of ethanol are significant processing hazards.

In addition to using solvents like ethanol to increase active matter, nonflammable hydrotropes like Na₂SO₄ (5) and carboxylic acid salts like sodium citrate (6) have been used successfully to generate concentrated AES solutions. These approaches result in pumpable aqueous, nonflammable AES solutions having a maximum of 50% active matter. More recently, 70% active matter AES solutions are commercially available at relatively high viscosity, but without flammable solvent. These 70% AES solutions take advantage of the interesting phenomenon of a viscosity minimum which occurs in the concentration range of 65-75% for AES.

In this paper, a new approach to preparing AES solutions with less than 5% water and no solvent is suggested. To accomplish this, an alcohol ethoxylate (AE) is used as hydrotrope, thereby leading to at least 90% active

matter blends of AE and AES which can be used directly in laundry liquid or powder formulations. The preparation of these high active matter blends and the effect of surfactant structure on their rheological properties are discussed.

EXPERIMENTAL

Nonionic and anionic surfactants tested are listed in Table 1 and Table 2, respectively.

Preparation of 90% active matter AE/AES blends. A modification of a continuous SO₃ sulfation procedure (7) was used to prepare AE/AES blends. In this modification, AES in the acid form obtained from the SO₃ sulfation unit was added to the appropriate level of nonionic surfactant and 50% NaOH. The resulting solution contained the indicated sodium salt of AES plus AE at a total active matter content of approximately 90%, 3-5% H₂O, with the remainder being low levels of Na₂SO₄ and unreacted organic matter from sulfation of the AE. In this manner, blends of AE/AES in which the AE and AES differed in alkyl chain and polyoxyethylene (POE) chain length could be prepared.

AES active matter analysis. AES active matter was determined by mixed indicator titration according to ASTM Test Method D3049-83.

Sulfate determination. Sulfate was determined by ion chromatography. Samples were injected, using a Waters

TABLE 1

Nonionic Products Tested

Product	Hydrophobe	Ave. EO/mol alcohol
C ₉₋₁₁ alcohol ethoxylates ^a	C _{9,10,11}	6, 8
C _{12,13} alcohol ethoxylates ^a	C _{12,13}	5, 6.5, 9
C ₁₂₋₁₅ alcohol ethoxylates ^a	C _{12,13,14,15}	5, 7, 10

^aPrepared by KOH-catalyzed ethoxylation of NEODOL® 91, NEODOL 23 or NEODOL 25 alcohols (NEODOL is a registered trademark of Shell Chemical Co.).

TABLE 2

Anionic Products Tested

Product	Hydrophobe	Avg. EO/mol alcohol
C ₁₂₋₁₅ alcohol sulfate ^a	C _{12,13,14,15}	0
C ₁₂₋₁₅ alcohol ethoxysulfates ^b	C _{12,13,14,15}	1, 2, 3, 5, 10
C _{14,15} alcohol ethoxysulfates ^b	C _{14,15}	7

^aPrepared by SO₃ sulfation of NEODOL® 25 alcohol.

^bPrepared by KOH-catalyzed ethoxylation of NEODOL 25 or NEODOL 45 alcohol followed by SO₃ sulfation.

¹This paper was presented at the 79th American Oil Chemists' Society Annual Meeting, May 1988, Phoenix, Arizona.

Autosampler Model 710B, into a Dionex ion chromatography column connected to a gradient pump. Sulfate ion was determined by conductivity detection followed by data acquisition using a Hewlett-Packard Model 300 computer.

Unulfated organic matter analysis. Unulfated organic matter (UOM) was determined by passing the sample dissolved in 50/50 isopropyl alcohol/H₂O through consecutive 50W × 4 cationic and 1 × 4 anionic exchange columns and weighing the resulting eluates after concentration at 65°C under 200 mm Hg vacuum.

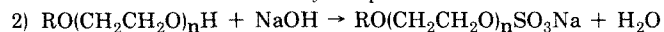
Viscosity measurement. Viscosities of AE/AES solutions from 15° to 50°C were determined using a Brookfield Digital viscometer, Model LVTD, and a number 18 spindle.

RESULTS AND DISCUSSION

Preparation of 90% active matter AE/AES blends. Sulfation of AE to prepare AES is a two-step procedure. In the case of SO₃ sulfation, liquid AE and gaseous SO₃ are contacted in the reaction zone of a falling film sulfator (7) to yield the acid form of AES as the first step. The acid form of AES exits the falling film column and is neutralized with appropriate base in the presence of hydrotrope and H₂O to form AES salts as the second step:



Hydrotrope



In preparing nominal 90% active matter AE/AES blends, a molar ratio of 1.05/1 SO₃/nonionic was used. The acid form of AES was neutralized by addition to a mixture of aqueous NaOH in which appropriate levels of AE had been added to yield approximately 90% active matter AE/AES blends. It is important to neutralize the acid form as quickly as possible after exiting the falling film sulfator. This tends to minimize AES hydrolysis which is accelerated by temperature (8) as shown in Figure 1. Also, short storage time of AES acid prior to neutralization is desirable in order to minimize formation

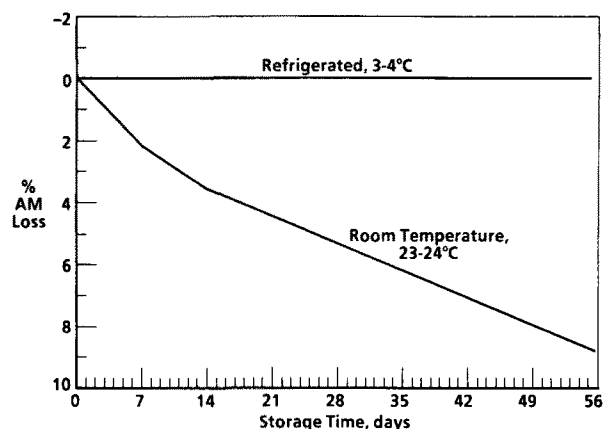


FIG. 1. Hydrolysis of C₁₂₋₁₅AES(3 EO) free acid from SO₃ sulfator.

of 1,4-dioxane. In preparation of these high active matter AE/AES blends, we have found it convenient to receive the AES acid from the falling film sulfation column directly into a stirred mixture of 50% NaOH and the appropriate AE.

Effect of nonionic/AES ratio on viscosity of 90% active matter AE/AES blends. Figures 2 and 3 illustrate the effect of AE/AES weight ratios on viscosity of 90% AE/AES blends at 25°C. As shown, increased AE content results in decreased viscosities. For AE/AES (3EO) blends in which the polyoxyethylene (POE) chain of AES is relatively short, pourable 90% active matter solutions (those having viscosities of less than 4000 cps) could only be achieved by AE/AES in which AE was present at greater than 50% weight. It is believed that the gel-forming structures of the ether sulfates are being disrupted due to the solubilizer properties of the alcohols. Studies on changes in the gel contents and properties of these products with changes in composition and temperature using crossed polarizers are planned.

Effect of AE POE chain length on viscosities of 90% active matter AE/AES blends. Figure 2 illustrates that for C₉₋₁₁ AE, POE content in the range studied has very little impact on the viscosity of 90% active matter AE/C₁₂₋₁₅ AES (3EO) blends. However, as shown in Figure 3, POE content for C_{12,13} AE, having a longer chain hydrophobe than C₉₋₁₁ AE, has appreciable impact on viscosity. For C_{12,13} AE decreasing the POE chain length results in decreasing viscosity, probably due to the lower pour point of the 5-mol AE (7°C) relative to that of the 9-mol nonionic (21°C).

Figure 4 shows the effect of AE structure on viscosity using AE/C_{14,15} AES(7EO) blends. Apparently, the use of AES having longer POE chain length favors lower viscosity. For example, C_{12,13} AE-5/C_{14,15} AES(7EO) blends exhibit lower viscosities compared to C_{12,13} AE-5/C₁₂₋₁₅ AES(3EO) blends (Figure 3) even though the C_{14,15} AES(7EO) alkyl chain is longer than that of C₁₂₋₁₅ AES(3EO). It appears that longer POE chain lengths of AES are more important factors than alkyl chain lengths in their influence on decreasing gel structure formation and lowering viscosity.

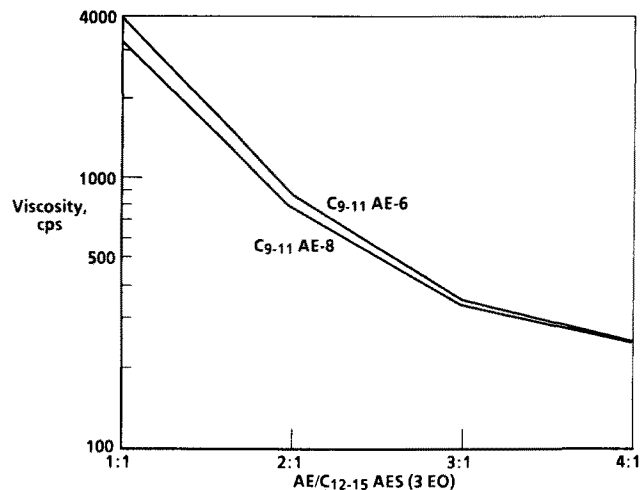


FIG. 2. Viscosity at 25°C of C₉₋₁₁AE/C₁₂₋₁₅AES(3 EO) blends at 90% active matter.

SOLVENT-FREE HIGH ACTIVE MATTER BLENDS

Effect of AES POE chain length on viscosities of 90% active matter AE/AES blends. Figures 5 and 6 further illustrate the effect on viscosity of increasing the C_{12-15} AES POE chain length in 90% active matter blends with $C_{12,13}$ AE-5 and C_{12-15} AE-7, respectively. As shown, lower viscosities are favored by higher POE-containing AES; the reverse of the POE chain length effect on viscosity observed with AE.

Shear rate studies on 90% active matter AE/AES blends. Viscosity as a function of shear rate is plotted in Figure 7 for a 90% active matter 1:1 $C_{12,13}$ AES (6.5 EO)/ $C_{12,13}$ AE-5 blend. The results show non-Newtonian behavior for these blends at this high active matter level. Shear rate data for 90% active matter blends at differing AE/AES ratios also show similar non-Newtonian behavior.

Non-Newtonian behavior has been reported for greater than 30% active matter AES solutions (9). However, below 30% active matter, AES exhibits Newtonian behavior when shear rate is plotted as a function of viscosity.

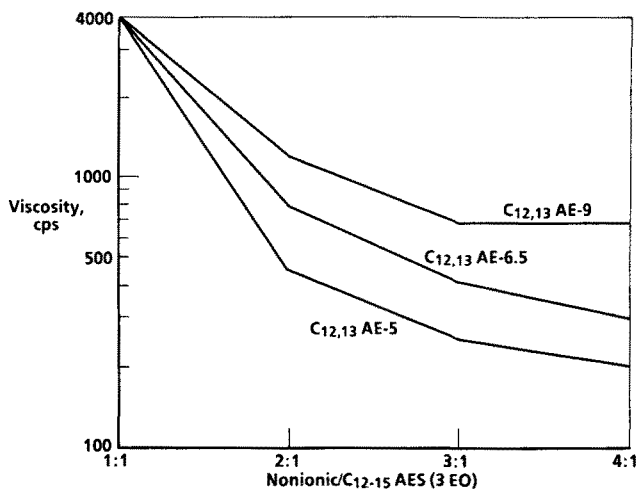


FIG. 3. Viscosity at 25°C of $C_{12,13}$ AE/ C_{12-15} AES(3 EO) blends at 90% active matter.

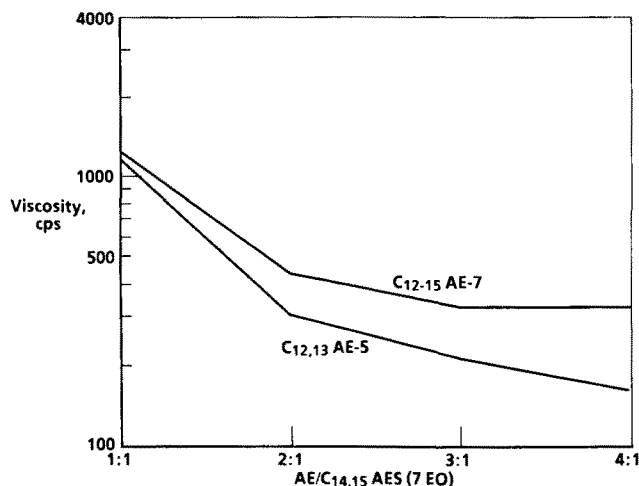


FIG. 4. Viscosity at 25°C of AE/ $C_{14,15}$ AES(7 EO) blends at 90% active matter.

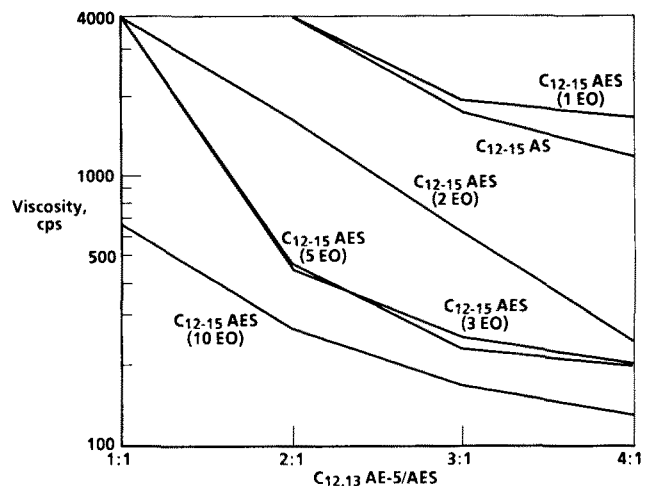


FIG. 5. Viscosity at 25°C of $C_{12,13}$ AE-5/ C_{12-15} AES blends at 90% active matter.

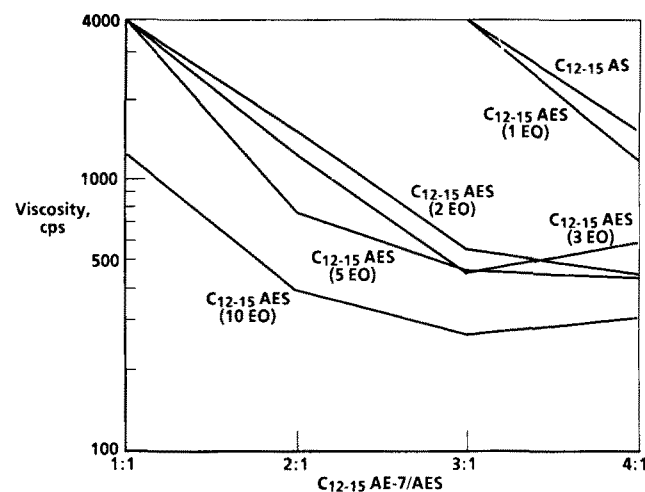


FIG. 6. Viscosity at 25°C of C_{12-15} AE-7/ C_{12-15} AES blends at 90% active matter.

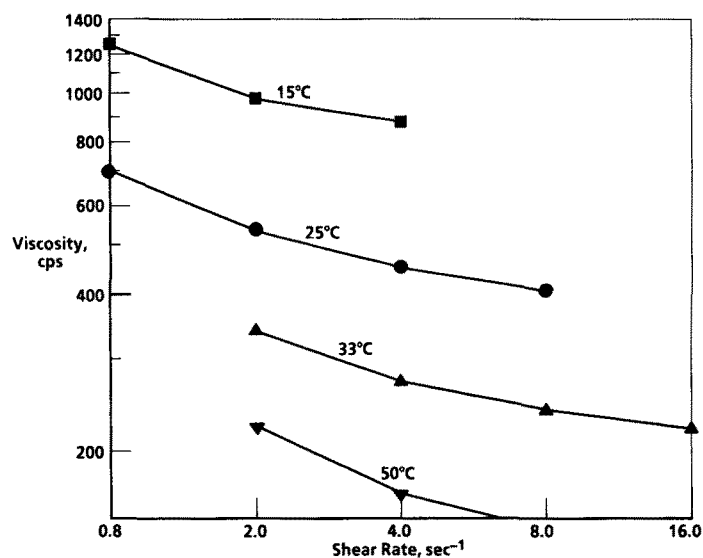


FIG. 7. Viscosity profile for 90% AM $C_{12,13}$ AES(6.5 EO)/ $C_{12,13}$ AE-5 blends (weight ratio = 1:1).

TABLE 3

High Active Matter Alcohol Ethoxysulfate/Ethoxylate Blends:
Correlation of Viscosity with Active Matter

Blend ratio	C ₁₂₋₁₅ AES (7 EO)/C _{12,13} AE-5		
	1:4	1:1	4:1
% Active matter anionic			
Nominal	18.0	45.0	72.0
Found	18.4	41.5	3.5
% UOM			
Nominal	72.0	45.0	18.0
Found	68.5	44.1	67.9
% H ₂ O	3.4	8.5	15.2
% Na ₂ SO ₄	1.1	2.6	5.0
Viscosity, cps	75	2600	>4000 ^a

^aToo viscous to measure on Brookfield viscometer.

These observations of shear-thinning viscosity for the high active matter blends lend strong support to AES-ordered liquid structures being the cause of the high viscosities. The results reported in this paper show that these structures can be partially overcome by AE addition, temperature, and shear.

Effect of viscosity on active matter and UOM of AE/AES blends. Table 3 lists analytical and viscosity data for 1:4, 1:1 and 4:1 C₁₂₋₁₅ AES (7EO)/C_{12,13} AE-5 blends. As shown nominal (calculated) and found (analyzed) results were in good agreement for the 1:4 and 1:1 AES/AE blends. However, for the 4:1 AES/AE blend, nominal and found levels are very different. We attribute this disparity to poor ion transport during the neutralization step for the very viscous 4:1 AES/AE blend. Poor ion transport results in "hot" acid spots with attendant hydrolysis of AES to produce the low anionic active matter, high UOM, and increased H₂O and Na₂SO₄ found. It is likely that for high AES/AE blends, hydrolysis can be prevented by conducting neutralization at higher temperatures than at the 25–30°C used in these studies. Higher neutralization temperatures should decrease solution viscosity to levels where ion transport can be effected rapidly.

Dilution of 90% active matter AE/AES blends. Dilution of well-stirred 90% active matter AE/AES blends with H₂O was achieved with minimal gel formation at or slightly above room temperature. Gelling tendencies were less than occurred with high actives in which AE or AES was sole surfactant. Higher AE/AES ratios favored dilution without extensive gelation at lower temperatures. It is apparent that AE and AES act as mutual hydrotropes when blended at high active matter. This mutual hydrotrope effect persists during dilution into aqueous formulations.

Suggested uses of high active matter AE/AES blends. Although high active matter AE/AES blends can be diluted into any liquid formulations where the physical and performance properties of the blends are desired, the following two end uses appear particularly attractive:

1. Dry-blended laundry powders—The use of AES in dry-blended powders has been difficult due to the high

levels of water and/or flammable solvents which have characterized commercial grade AES. At 90% active matter with less than 5% H₂O, AE/AES blends should readily be adsorbed onto builder beads in a dry-blending or agglomeration procedure to levels of at least 15% total surfactant content on the weight of the builder. Thus, the excellent detergency properties imparted by an AE/AES blend can be achieved in a dry-blended pourable powder.

2. Spray-dried laundry powders—A high active matter AE/AES blend could readily be pumped into the crutcher mix of a spray tower. However, the AE used in the studies discussed above have average POE chain lengths ranging from 5–10. These AE contain volatile components (lower POE-containing AE) which would plume excessively at the high temperatures in effect in spray towers. AE with higher average POE chain length may be useful in minimizing nonionic pluming in spray towers (10) thereby allowing use of high active matter AE/AES blends in spray-dried laundry granules. Narrow range ethoxylates (NRE), made either by "topping" (distillation) of the more volatile components of AE (3) or by direct ethoxylation using catalyst systems different from conventional KOH, should be particularly useful in this application. NRE made by "topping" should be preferred since "topping" reduces free alcohol and other low POE chain components to a greater degree than found in NRE made by the current catalytic routes.

ACKNOWLEDGMENTS

The authors are grateful to S. N. Papitto and E. J. Denton for SO₃ sulfation and preparation of AE/AES blends, to T. D. Hoewing and J. N. Reynolds for viscosity and shear rate studies and to K. F. Guin for arranging for analysis of high active matter blends.

REFERENCES

- Kravetz, L., D.H. Scharer and H. Stupel, *Household Pers. Prod. Ind.* 14:55 (1977).
- Cox, M.F., and T.P. Matson, *J. Am. Oil Chem. Soc.* 61:1270 (1984).
- Kravetz, L., *Chemical Times and Trends* 8:29 (1985).
- Kravetz, L., and K.F. Guin, *J. Am. Oil Chem. Soc.* 62:943 (1985).
- U.S. Patent No. 3,786,003 (1974) assigned to Shell Oil Company, Houston, Texas.
- U.S. Patent No. 3,893,955 (1975) assigned to Albright and Wilson Ltd., West Midlands, England.
- Hurlbert, R.C., R.F. Knott and H.A. Cheney, *Soap & Chemical Specialties* 43:122 (1967).
- Shore, S., and D.R. Berger in *Anionic Surfactants*, part 1, p. 143, edited by W.M. Linfield, Marcel Dekker, Inc., New York and Basel (1976).
- Ekwall, P. in *Advances in Liquid Crystals*, vol. I, p. 1, edited by G.H. Brown, Acad. Press, New York (1975).
- Wharry, D.L., E.L. Sones, S.E. McGuire, G. McCrimlisk and J. Lovas, *J. Am. Oil Chem. Soc.* 63:691 (1986).

[Received October 18, 1988; accepted July 19, 1989]
[J5585]