

Effect of Alkyl Carbon Chain Length and Ethylene Oxide Content on the Performance of Linear Alcohol Ethoxylates¹

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A grid of 30 surfactants varying from C₈ to C₁₈ in carbon chain length and from 40 to 80% in ethylene oxide (EO) content were examined to determine the effect of molecular structure on the physical properties (density, melting point, solution viscosity) and performance properties (surface activity, detergency, hard-surface cleaning, foaming, wetting) of linear alcohol ethoxylates. Results show that while physical properties are influenced primarily by EO content, both carbon chain length and EO content are important to performance. Optimum carbon chain length is also shown to depend strongly on surfactant concentration.

The level of technical expertise needed to achieve success in the marketplace is growing. Products are becoming more complex, and greater efforts are being made to optimize the performance of each component. This requires a better understanding of the relationship between component structure and performance.

This study examines the effect of molecular composition on the physical properties and performance of even carbon chain length (C₁₂, C₁₄, etc.) linear alcohol ethoxylates. The effects of carbon chain length and ethylene oxide (EO) content on density, melting point, solubility, viscosity, surface activity, detergency, hard-surface cleaning, foaming and wetting are discussed.

EXPERIMENTAL

Cotton wetting. Wetting was evaluated by measuring the time required to wet cotton fabric at various surfactant concentrations in order to calculate a 25-second wetting concentration. The basic test methodology used is similar to the Draves test (1) except that cotton twill tape (Elizabeth Webbing Mills, Pawtucket, Rhode Island) was used instead of cotton skeins. Tests were performed at room temperature.

Density measurements. Density measurements were obtained at 25°C (77°F) by measuring weight and volume after each ethoxylate was drawn into a plastic syringe. Solid ethoxylates were melted, drawn into the syringe and then allowed to cool slowly to 25°C. Because the volumes of the solid ethoxylates decreased upon cooling, a plastic syringe was used so the volume could adjust during cooling.

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

Flash foam. Flash foam was measured using a mechanical foam generator (manufactured in-house) which produces foam by repeatedly beating each test solution with a perforated disc. It is based on the German DIN test

TABLE 1

Detergency Test Materials and Procedures

Testing apparatus	Terg-O-Tometer
Wash cycle	10 min
Rinse cycle	5 min
Wash temperature	60°F, 100°F, 140°F
Water hardness	0
Soil/substrates	Sebum/cotton and sebum/permanent press—manufactured in-house using synthetic sebum ^a ; cotton (Test Fabrics S/419); permanent press (Test Fabrics S/7406—65% dacron/35% cotton with permanent press finish) Mineral oil/permanent press—manufactured in-house using mineral oil with oil-soluble red dye to aid with detection; permanent press (Test Fabrics S/7406) Clay/permanent press (Scientific Services, Inc.)
No. soiled cloths	Three 4.5" × 3.25" swatches of sebum/cotton and sebum/permanent press cloths washed together with three clean cotton cloths added for ballast; three 4.5" × 3.25" swatches of mineral oil/permanent press cloth washed with six clean cotton cloths added for ballast; three 4" × 3" swatches of clay/permanent press cloth washed with six clean cotton cloths added for ballast
Reflectance measuring device	Gardner (Model XL20) Colorimeter

^aSoil recipe consists of 67.6% synthetic sebum, 16.2% particulate dust, 10.8% triethanolamine and 5.4% oleic acid (1). The synthetic sebum consists of, with figures indicating wt percent, 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, and linoleic acid (Kodak), 5.0.

method no. S3 902. Tests were performed at 38°C (100°F) using 100-ml solutions of 0.1% surfactant.

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 RVTDCP-II) viscometer equipped with a CP-51 cone.

Preparation of plots. STATGRAPHICS (Statistical Graphics Corp.) software was used to prepare contour and response surface plots.

Alcohol ethoxylate samples. Compositional data for the 30 alcohol ethoxylates examined in this study are given in Table 2. Each ethoxylate is described by both its carbon chain length and its approximate EO content. For example, the 8-40 ethoxylate consists of a C₈ alcohol with approximately 40% (by weight) ethylene oxide, the 12-80 ethoxylate consists of a C₁₂ alcohol with approximately 80% ethylene oxide, and so on. All ethoxylates

¹Presented at the AOCs meeting in New Orleans in May 1987.

TABLE 2

Composition of Test Alcohol Ethoxylates

Alcohol ethoxylate	Free alcohol (via GLC)	Mol wt	Moles EO	Wt % EO
8-40	20.4	227	2.2	42.7
8-50	10.8	266	3.1	51.2
8-60	5.7	332	4.6	60.9
8-70	2.3	438	7.0	70.3
8-80	0.6	671	12.3	80.6
10-40	15.3	272	2.6	42.0
10-50	8.4	325	3.8	51.4
10-60	4.5	400	5.5	60.5
10-70	1.3	510	8.0	69.0
10-80	0.3	778	14.1	79.7
12-40	13.7	331	3.3	43.8
12-50	8.3	380	4.4	51.0
12-60	3.9	472	6.5	60.6
12-70	1.2	613	9.7	69.6
12-80	0.2	859	15.3	78.4
14-40	13.7	368	3.5	41.8
14-50	6.5	443	5.2	51.7
14-60	2.5	544	7.5	60.7
14-70	0.9	698	11.0	69.3
14-80	0.3	1076	19.6	80.1
16-40	8.0	400	3.6	39.6
16-50	5.0	528	6.5	54.2
16-60	2.2	612	8.4	60.4
16-70	0.6	810	12.9	70.1
16-80	0.2	1272	23.4	81.0
18-40	8.3	486	4.9	44.4
18-50	4.3	556	6.5	51.4
18-60	3.5	657	8.8	58.9
18-70	0.6	886	14.0	69.5
18-80	0.2	1278	22.9	78.9

TABLE 3

Surface Properties of Alcohol Ethoxylates Varying in Carbon Chain Length and Ethylene Oxide Content

Ethoxylate	Critical micelle concentration (cmc)		Surface tension at cmc (dynes/cm)
	ppm	M × 10 ⁴	
8-60	1739.0	52.0	24.9
10-60	205.6	5.1	24.8
12-60	22.1	0.5	25.7
14-60	5.5	0.1	27.1
16-60	2.8	0.1	28.9
18-60	4.8	0.1	30.0
12-40	11.6	0.4	24.1
12-50	12.9	0.3	25.2
12-60	22.1	0.5	25.7
12-70	43.1	0.7	27.0
12-80	107.2	1.2	31.2

were produced from linear, primary alcohols using caustic-catalyzed ethoxylation. Ethylene oxide contents of all but the C₁₂-C₁₈ 80% EO ethoxylates were determined using HPLC (2). Because HPLC gives slightly lower values when EO content exceeds 70% (approximately 15 mole), the EO contents of these samples were determined via titration with sodium thiosulfate after cleavage of the ethoxylate with hydriodic acid.

Free alcohol content (Table 2) and EO-homolog distribution (Fig. 1) vary depending on the degree of ethoxylation. This is due to differences in reactivity between the alcohol and the one-mole adduct toward ethylene oxide (3).

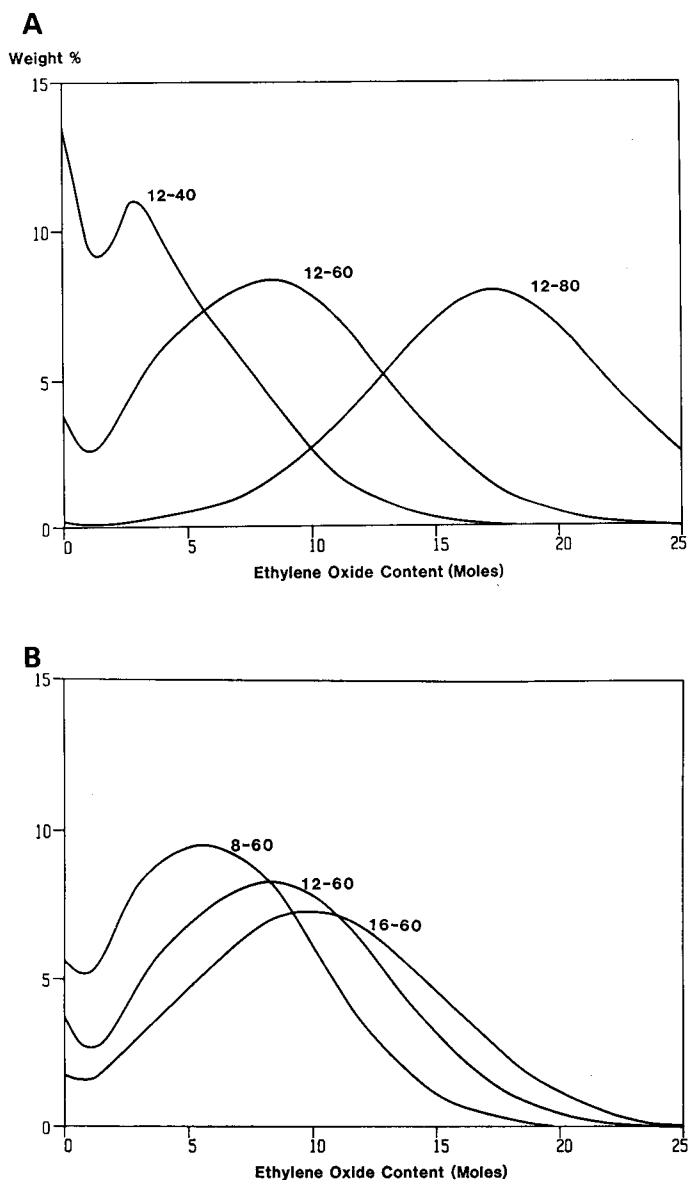


FIG. 1. Distribution of EO adducts obtained with A, dodecyl alcohol ethoxylates containing 40, 60 and 80% ethylene oxide, and B, octyl, dodecyl and hexadecyl ethoxylates containing 60% ethylene oxide.

Tests performed in this study were designed to evaluate the effect of ethylene oxide as a function of weight percent EO (instead of moles EO). Weight percent was chosen because it relates directly to an ethoxylate's solubility character (<50% = oil-soluble; 50% = borderline water-soluble; >50% = water-soluble) and to its emulsification behavior ($HLB = \%EO/5$). Although the nomenclature describing the ethoxylates used in this study denotes weight percent EO, data in terms of both weight percent and moles are given in Table 2. Keep in mind that the relationship between weight percent and moles is nonlinear (Fig. 2). This is why the 8-60 ethoxylate contains 4.6 moles of EO while the 18-60 ethoxylate contains 8.8 moles EO. The mathematical relationship between weight percent EO content and moles of EO is given below:

$$\text{wt \% EO} = \frac{(\text{moles EO})(44)}{(\text{moles EO})(44) + (\text{mol wt of alcohol})} \times 100$$

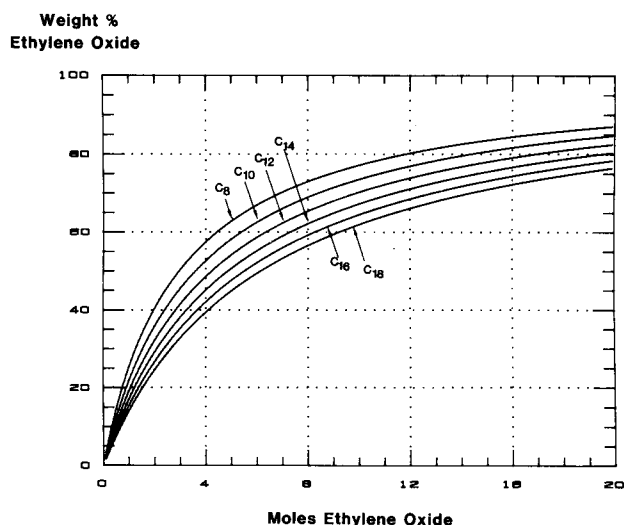


FIG. 2. Curves showing the relationship between wt % EO and moles EO for linear alcohol ethoxylates.

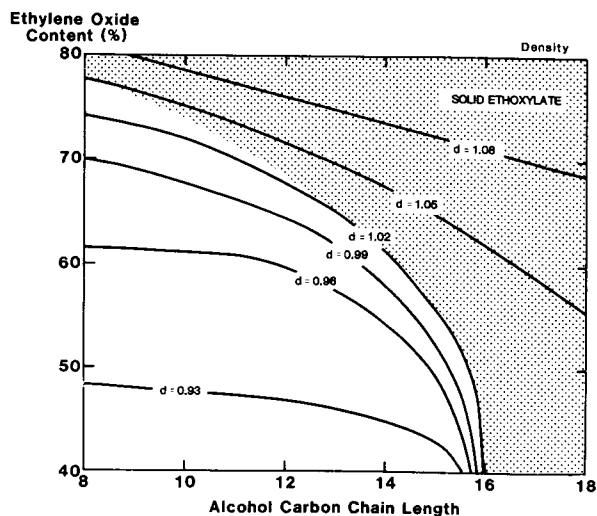


FIG. 3. Density of alcohol ethoxylates as a function of ethylene oxide content and carbon chain length (77°F/25°C).

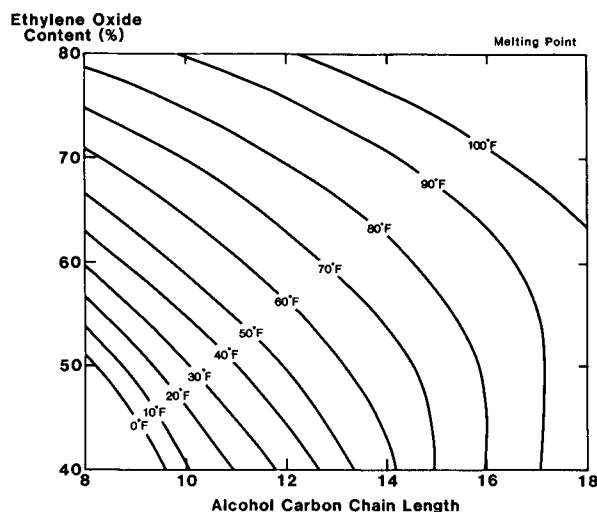


FIG. 4. Melting point range of alcohol ethoxylates as a function of ethylene oxide content and carbon chain length.

RESULTS AND DISCUSSION

Physical properties. The effects of ethoxylate composition on density and melting point range are shown in Figures 3 and 4. Increasing ethoxylate molecular weight results in an increase in both density and melting point due to a corresponding increase in Van der Waal interactions. EO content appears to be more important than carbon chain length, particularly with respect to density.

Pour point was also measured and was found to correspond closely to melting point.

Water solubility of an alcohol ethoxylate is a measure of the ability of the ethylene oxide chain to interact (via hydrogen bonding) with water molecules. When heat is applied to an aqueous solution of an alcohol ethoxylate, the surfactant becomes less soluble due to a reduction in the degree of hydration of the EO chain. As temperature continues to increase, the solution eventually will turn turbid. The temperature at which this occurs is referred to as the cloud point or inverse cloud point.

The effect of ethoxylate composition on cloud point is shown in Figure 5. As expected, increasing EO chain length increases water solubility as evidenced by an increase in cloud point. Less clear trends, however, are observed with changing alkyl chain length. Overall, increasing carbon chain length increases cloud point because of differences in the EO distributions of the ethoxylates. For example, both the 8-60 and 12-60 ethoxylates have an average of 60% EO, but 5.7% of the 8-60 ethoxylate is unethoxylated alcohol while only 3.9% of the 18-60 ethoxylate is unethoxylated alcohol (Fig. 1B). Increasing alkyl chain length logically increases solubility because less alcohol is present in the ethoxylate. This argument breaks down, however, with the 16-60 and 18-60 ethoxylates, which are both cloudy at room temperature. This results from formation of liquid crystals. Lengthening the alkyl chain increases the tendency to form liquid crystals because it increases Van der Waal interactions between hydrophobes. In the case of the 16-60 and 18-60 ethoxylates, it appears that liquid crystals form below

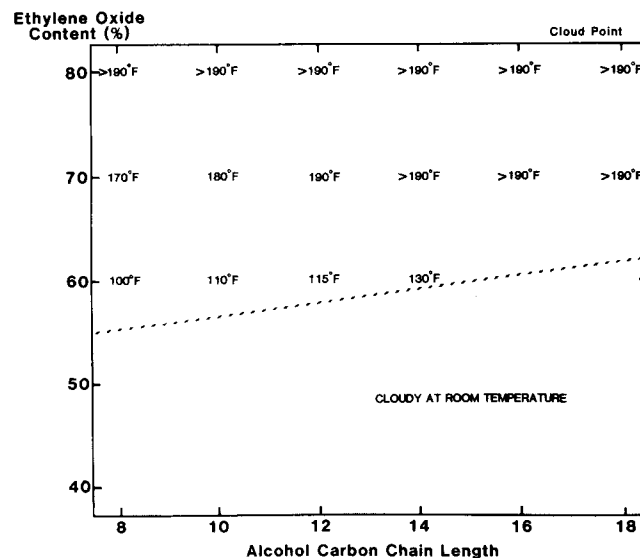


FIG. 5. Cloud point of 1% aqueous solutions of alcohol ethoxylates as a function of ethylene oxide content and carbon chain length.

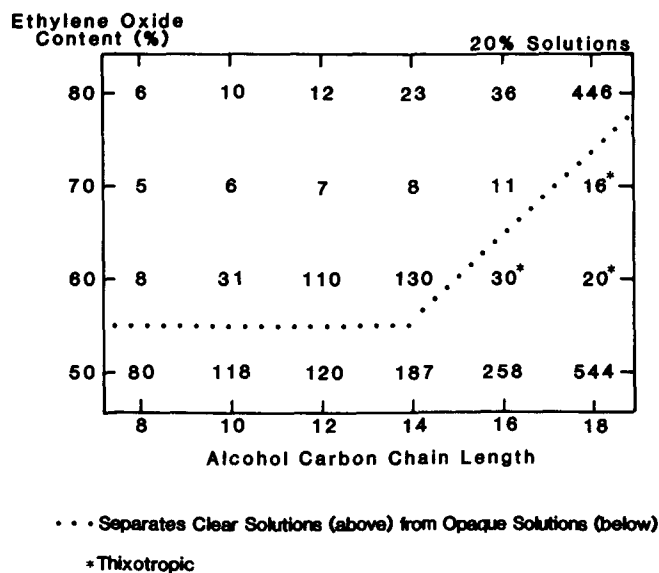


FIG. 6. Viscosity (cps) of 20% aqueous solutions of alcohol ethoxylates as a function of carbon chain length and ethylene oxide content (77°F/25°C).

the temperature at which dehydration occurs. This suggests that liquid crystal formation should be considered when evaluating cloud point measurements.

The effect of molecular composition on solution viscosity is shown in Figure 6. With 50% EO, ethoxylates are borderline water-soluble, so solutions exist in mesomorphic phases which contribute to viscosity. As EO content is increased to 70%, viscosity decreases because more of the surfactant is solubilized by water. The opposite trend, however, is observed when EO content is increased to 80%. Increasing EO content eventually increases viscosity because it increases the ability of the ethoxylate to create water structure via hydrogen bonding. This phenomenon has been observed with other types of ethoxylates as well (4). As would be expected, the magnitude of the effect depends on both EO chain length and surfactant concentration.

Data in Figure 6 also show that increasing alkyl carbon chain length increases viscosity. This is likely due to an increase in the tendency (due to greater hydrophobe-hydrophobe interactions) to form structures which contribute to viscosity. Although the 16-60 and 18-60 ethoxylates were first thought to contradict this trend, further examination showed that they were very thixotropic. Although they were clearly gel-like in consistency, under shear they gave relatively low viscosities.

An excellent discussion on the phase behavior of alcohol ethoxylates is given by Mitchell and co-workers (5).

Surface activity. Gibbs' plots (surface tension as a function of surfactant concentration) showing the effects of carbon chain length and EO content are shown in Figures 7A and B. Critical micelle concentration (cmc) and surface tension values at the cmc are listed in Table 3.

Increasing alkyl carbon chain length increases the degree of Van der Waal interactions that can occur between hydrophobes. This in turn increases stability in the micelle, which results in a lower critical micelle concentration. Although the 18-60 ethoxylate appears to be the

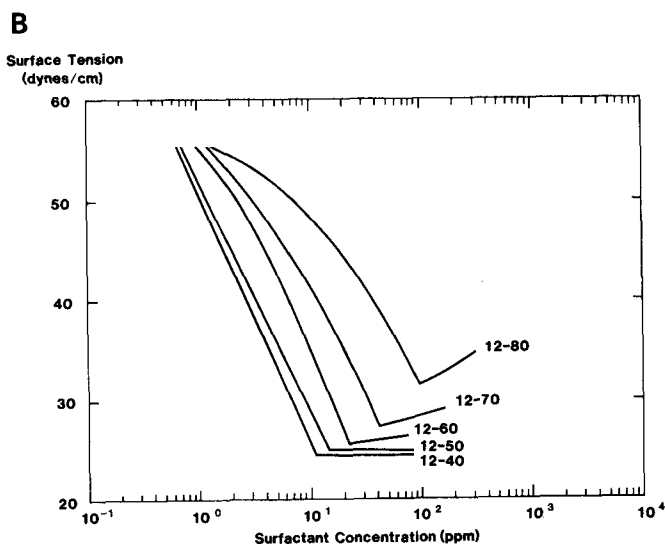
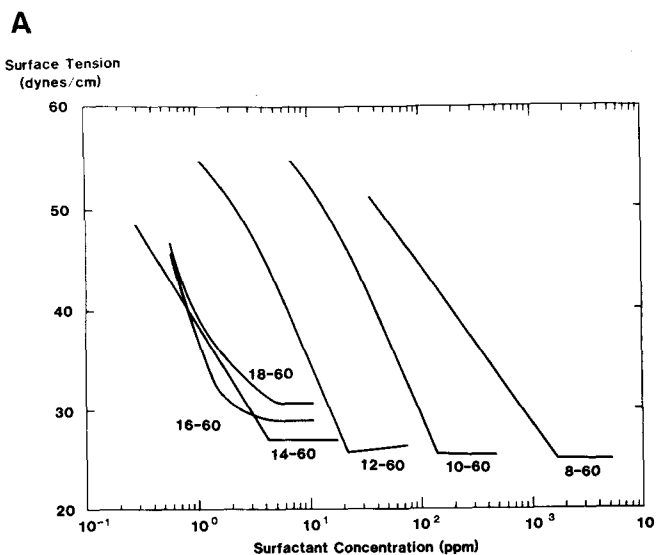


FIG. 7. Gibbs' plots of alcohol ethoxylates varying in A, alcohol carbon chain length, and B, ethylene oxide content (100°F).

exception to the rule in that it has a higher cmc than the 16-60 ethoxylate, the large amount of curvature found in the plots makes cmc data questionable. The cause of this curvature is unclear, but it may be related to difficulty in determining when equilibrium was reached. Because the length of time needed to reach equilibrium (surface tension constant as a function of time) was observed to increase with increasing alkyl chain length, it is possible that when readings were taken for the 16-60 and 18-60 ethoxylates, surface tension was changing so slowly that true equilibrium may not have been reached. This increase in the length of time needed to reach equilibrium may be related to the poor solubility of the C16 and C18 low-EO homologs.

Although a longer carbon chain length results in a lower cmc, a shorter carbon chain length improves surfactant effectiveness (minimum surface tension that can be reached regardless of concentration). For example, as shown in Table 3, the 8-60 and 10-60 ethoxylates are better than the other ethoxylates in lowering surface tension even though they require substantially higher concentrations to reach their minimum surface tension

PERFORMANCE OF LINEAR ALCOHOL ETHOXYLATES

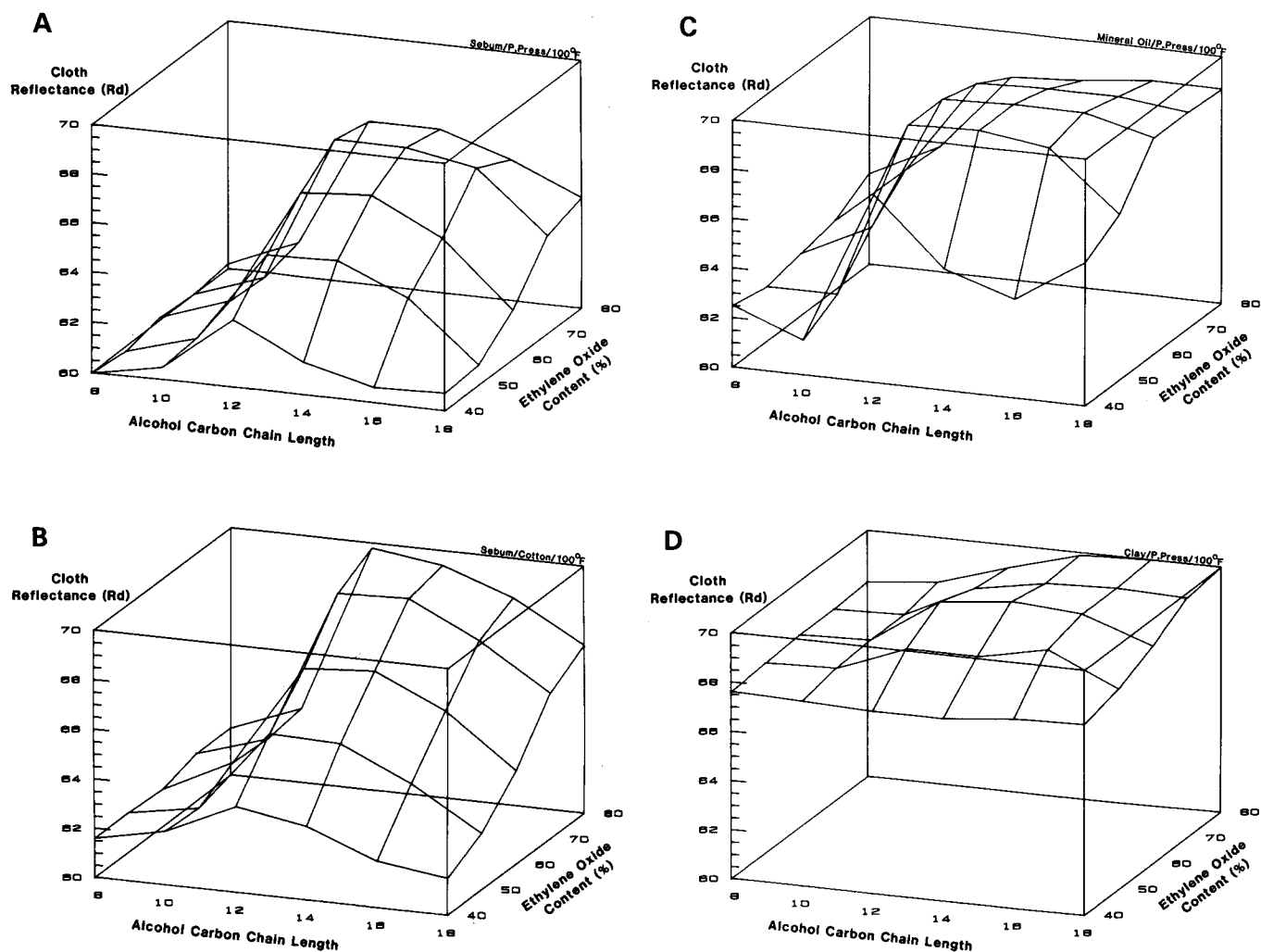


FIG. 8. Detergency performance of alcohol ethoxylates as a function of carbon chain length and ethylene oxide content using A, sebum/permanent press; B, sebum/cotton; C, mineral oil/permanent press, and D, clay/permanent press cloths (100°F, 100 ppm surfactant).

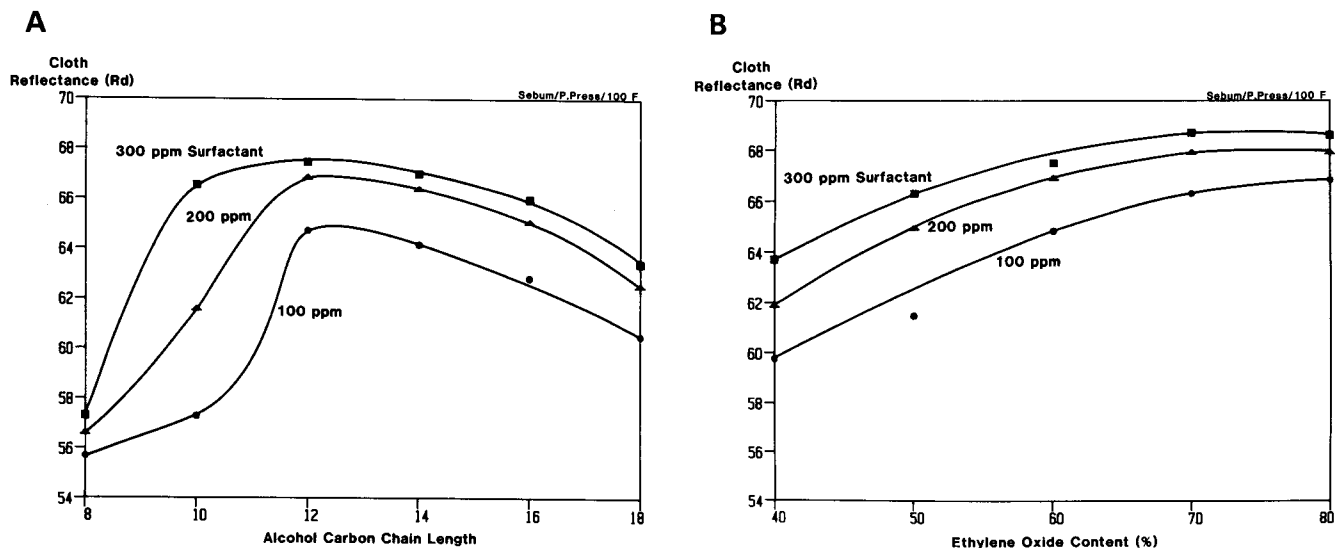


FIG. 9. Detergency performance of alcohol ethoxylates as a function of A, carbon chain length (with 60% EO), and B, ethylene oxide content at 100, 200 and 300 ppm surfactant concentrations (sebum/permanent press cloth, 100°F).

values. This suggests a strong relationship between surfactant concentration and surfactant performance.

Increasing EO chain length 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 content therefore increases critical micelle concentration.

Increasing EO chain length also increases molecular size, which makes it more difficult for the ethoxylate to pack at the air-water interface. The ability to lower surface tension (surfactant effectiveness) is therefore reduced as EO content is increased.

Ethylene oxide content also appears to affect the shape of the Gibbs' plot (Fig. 7B). This may be related to the capacity of the EO chain to interact (via hydrogen bonding) with other molecules.

Intrinsic detergency. The ability of each test ethoxylate to remove soil from fabric was examined using traditional Terg-O-Tometer test procedures (Table 1). Although commercial detergent formulations typically contain other ingredients (builders, alkalinity agents, etc.), they were not included in order to eliminate their effects on detergency performance.

Response surface plots showing detergency performance as a function of alcohol ethoxylate composition are shown in Figures 8A (sebum/permanent press), 8B (sebum/cotton), 8C (mineral oil/permanent press) and 8D (clay/permanent press). Although the magnitude of the differences observed depends on soil type, the same general trends are observed with all soils. Optimum detergency performance is reached with ethoxylates consisting of an intermediate (C_{12} - C_{14}) alcohol with a 60% or greater ethylene oxide content. These surfactants presumably have the greatest surface activity under the conditions tested.

The relationship between composition and performance, however, depends on surfactant concentration. For example, if the 60% EO ethoxylates are compared at 100, 200 and 300 ppm (Fig. 9A), the performance of the 10-60 ethoxylate is observed to increase significantly in comparison to the others as surfactant concentration is increased. This is due to its higher critical micelle concentration (cmc). At 100 ppm, the C_{12} , C_{14} , C_{16} and C_{18} ethoxylates have already reached their cmc, so increasing surfactant concentration does not greatly change the concentration of surfactant monomers which carry out soil removal processes. The cmc of the 10-60 ethoxylate, however, is greater than 100 ppm but less than 300 ppm. Increasing surfactant concentration from 100 to 300 ppm increases monomer concentration, which results in improved performance. The performance of the 8-60 ethoxylate, on the other hand, is not significantly improved because 300 ppm is still far below its cmc (>1700 ppm).

Correlation of surface properties to performance is difficult because a significant amount of surfactant is lost due to adsorption onto soil and substrate surfaces. This is why the detergency performance of the 10-60 ethoxylate increases as concentration is increased from 200 to 300 ppm even though its cmc is only 200 ppm. Detergency data, however, do appear to correlate well with surface properties. When above the cmc, detergency correlates with the ability of the surfactant to lower surface tension.

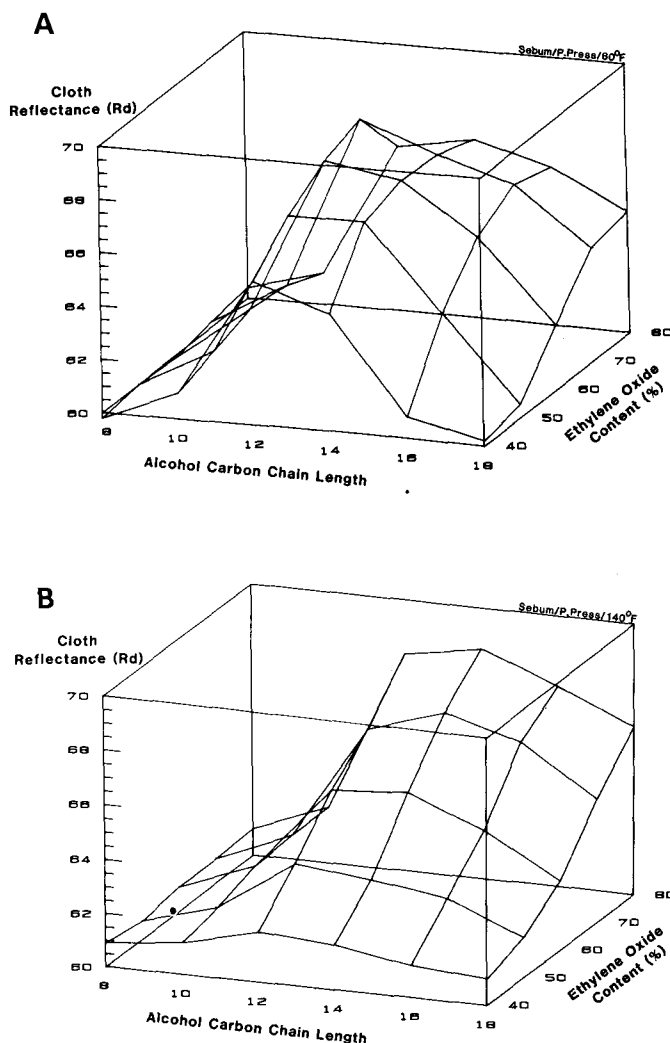


FIG. 10. Detergency performance of alcohol ethoxylates as a function of carbon chain length and ethylene oxide content at A, 60°F, and B, 140°F (sebum/permanent press, 100 ppm surfactant).

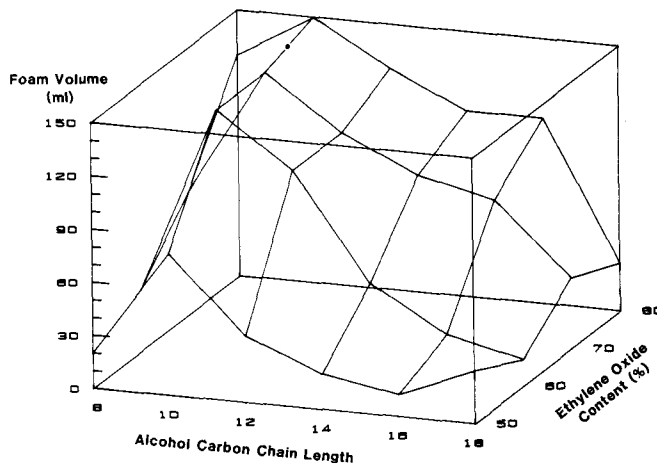


FIG. 11. Foam volume of alcohol ethoxylates as a function of carbon chain length and ethylene oxide content (100°F).

PERFORMANCE OF LINEAR ALCOHOL ETHOXYLATES

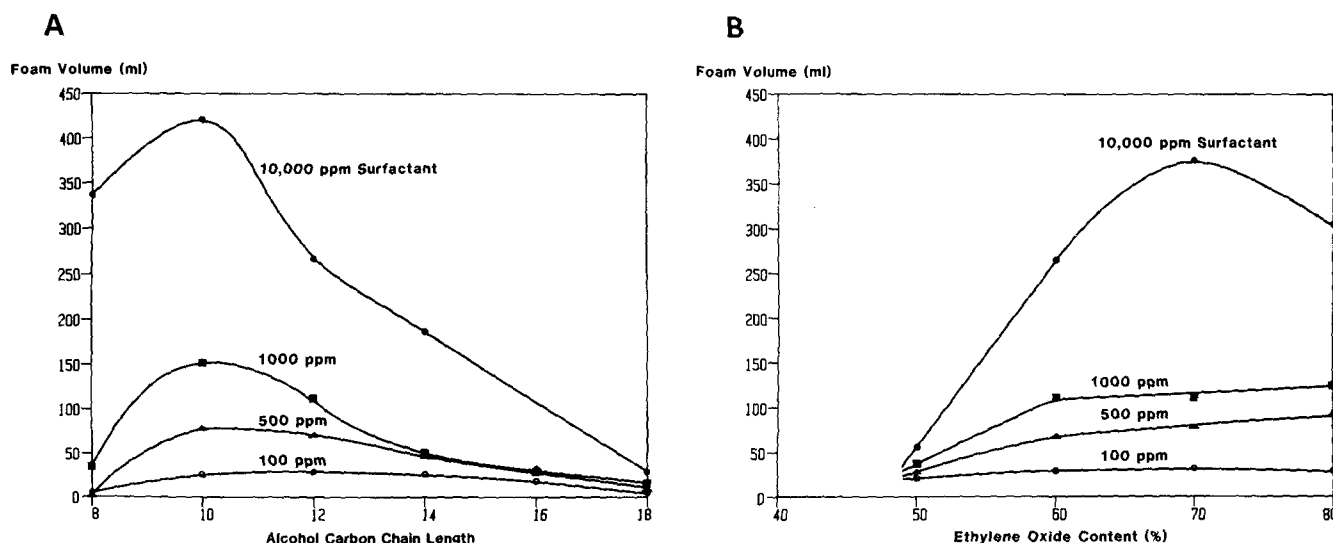


FIG. 12. Foam volume of A, 60% EO ethoxylates as a function of carbon chain length, and B, C₁₂ alcohol ethoxylates as a function of EO content at 100, 500, 1000 and 10,000 ppm surfactant concentrations (100°F).

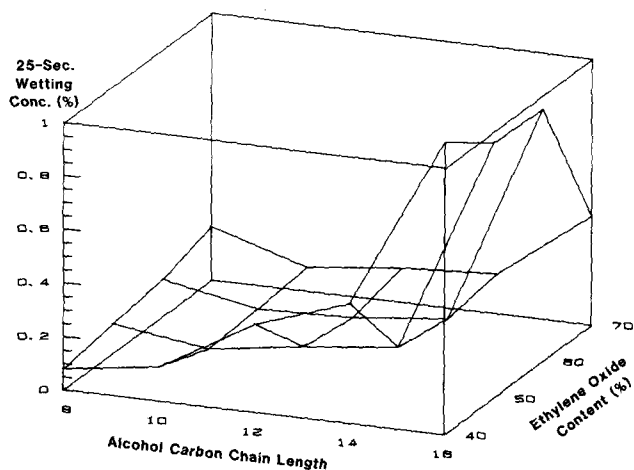


FIG. 13. Wetting performance (surfactant concentration needed to obtain 25-second wetting) as a function of carbon chain length and ethylene oxide content (at room temperature).

When below the cmc, both surface activity and surfactant concentration are important.

As shown in Figure 9B, surfactant concentration does not significantly affect the relative performance of C₁₂ ethoxylates varying in EO content.

Optimum surfactant composition also depends on temperature because of its effect on solubility. As shown in Figures 10A and 10B, a higher temperature enhances ethoxylate performance because it helps drive the surfactant to the soil-water interface by lowering its water solubility. This is why detergency performance of the high EO-containing ethoxylates improves at the higher temperature. However, if surfactant solubility is already low, increasing temperature can reduce performance by effectively removing surfactant from solution. This is why detergency performance of the low EO-containing ethoxylates (e.g., 12-40) decreases at the higher temperature.

Alcohol ethoxylates have also been shown to be useful in reducing the water hardness sensitivity of linear

alkylbenzene sulfonates (6-9). This is accomplished by lowering the cmc and by helping solubilize Ca(LAS)₂ and Mg(LAS)₂. Because of the importance of the latter, high EO-containing ethoxylates are found to be best.

Hard-surface cleaning. The effect of ethoxylate composition on hard-surface cleaning performance is detailed elsewhere (10,11). In summary, reducing carbon chain length appears to increase the solvency properties of the surfactant by improving its ability to penetrate soil. Performance therefore depends on both surface activity of the surfactant and its ability to penetrate the soil. Because surface activity is concentration dependent, so is hard-surface cleaning. At relatively high concentrations (>1%), optimum performance is obtained with a C₆/C₈ alcohol. At lower concentrations (0.1–1%), optimum performance is obtained with a C₈/C₁₀ alcohol. At very low concentrations, a C₁₀/C₁₂ alcohol is best. Optimum performance is obtained with a 50–60% EO content, regardless of carbon chain length.

Foaming. The effect of molecular structure on the ability of alcohol ethoxylates to generate flash foam is shown in Figure 11. C₁₀ ethoxylates with 60–80% EO produce the most foam. As shown in Figures 12A and 12B, surfactant concentration affects the magnitude of the differences observed in foam volume but does not affect relative foam performance.

Cotton wetting. The effect of molecular composition on the ability of alcohol ethoxylates to “wet” cotton cloth is shown in Figure 13. Wetting also appears to correlate with surfactant “effectiveness.” At the relatively high surfactant concentrations needed to obtain wetting during the 25-second time frame, the shorter carbon chain length ethoxylates perform best because they are best at lowering surface tension. At lower surfactant concentrations, however, a higher carbon chain length is likely to give optimum wetting.

Effect of “peaking” EO distribution. Alcohol ethoxylates having “peaked” EO distributions have been available commercially since 1983. Peaking reduces the tendency of the ethoxylate to plume during manufacture of a spray-dried laundry product by lowering the concentration of unethoxylated alcohol (12). Peaking also has

been reported to reduce liquidity and viscosity and increase solubility (13,14). Peaking, however, should not alter the general relationships discussed above between ethoxylate composition and performance.

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ERRATUM

The caption for Figure 2 of "Automated Quantitative Analysis of Isolated (Nonconjugated) *trans* Isomers Using Fourier Transform Infrared Spectroscopy Incorporating Improvements in the Procedure" which appeared on page 121 of the January issue of *JAOCs* contained an incorrect number. The figure, with the correct number, is reproduced below. The paper was written by Ronald T. Sleeter and Mark G. Matlock, Lakeview Technical Center, Archer Daniels Midland Co., Decatur, Illinois.

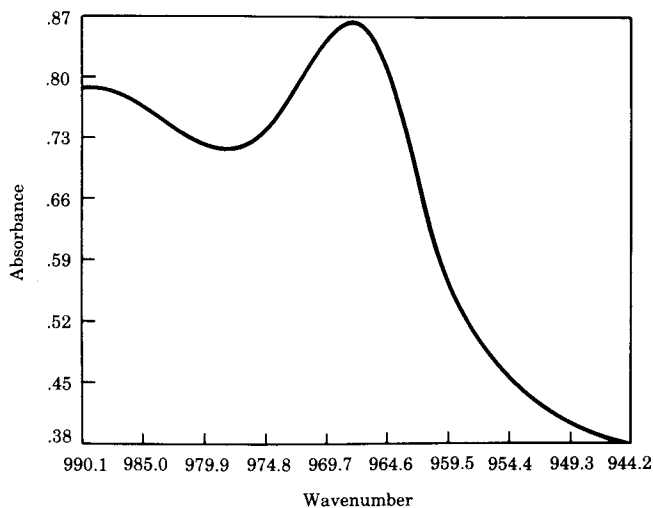


FIG. 2. 10% Methyl elaidate, 90% methyl linoleate.