♣Effects of the Ethylene Oxide Distribution on Nonionic Surfactant Properties

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ABSTRACT

Detergent-range primary alcohols are readily converted into nonionic surfactants by reaction with ethylene oxide. Optimum performance properties for these surfactants generally are attained by varying the number of moles of ethylene oxide reacted with each mole of alcohol or by altering the structure of the primary alcohol. However, variations in the ethoxylate-adduct distribution also affect surfactant properties in such a way that products with relatively narrow distributions possess features which are highly desirable in many household and industrial applications. For a given cloud point narrow-range ethoxylates have lower molecular weights and therefore lower pour points than broad-range surfactants. Because narrow-range ethoxylates contain less unreacted alcohol and other water-insoluble species, they are capable of forming aqueous solutions with much lower cloud points than their broad-range counterparts. Aqueous solutions of narrow-range products have lower viscosities, exhibit lower gel temperatures and remain fluid over a wider concentration range than solutions of broad-range surfactants. While the foams obtained with narrow-range surfactants in the Ross-Miles test are higher initially, they are less stable than those produced by conventional nonionic surfactants. Draves wetting data show that narrow-range products wet cotton substrates more efficiently than normal-distribution materials. Narrow-range ethoxylates exhibit higher aqueous surface tension and higher polyester adhesion tension values than their broad-range counterparts. In addition, narrow-range surfactants reduce the interfacial tension against paraffin oil more efficiently and more effectively than broad-range products. These results, along with laboratory detergency data, suggest that the use of narrow-range ethoxylates may lead to cleaning systems with improved performance and/or physical properties.

INTRODUCTION

Primary alcohols react with ethylene oxide in the presence of a suitable catalyst to produce nonionic surfactants (1-3). Due to their versatile formulating characteristics (4), insensitivity to water hardness ions (5-6), outstanding detergency action on oily soils (7-8) and rapid biodegradation in the environment (9-12), these surfactants are used widely in household, industrial and institutional cleaning products (13). Optimum performance and/or physical properties generally are attained by varying the number of moles of ethylene oxide reacted with each mole of alcohol or by altering the structure of the primary alcohol (14). Variations in the ethoxylate adduct distribution also affect surfactant properties (15-30), but technical difficulties associated with obtaining a narrow distribution have heretofore limited the commercial viability of this approach (26). However, since many of the obstacles to producing narrow-range ethoxylates are rapidly being overcome by advances in catalysis and processing technologies (31-40), surfactant manufacturers and formulators have developed an increased interest in the effects of the ethylene oxide distribution on surfactant properties. Consequently, in this study, two series of primary alcohol ethoxylates, one having typically broad distributions and the other possessing uncommonly narrow distributions, have been used to investigate the effects of the ethylene oxide distribution on some of the chemical, physical, surface-chemical and practical performance properties of nonionic surfactants.

EXPERIMENTAL

All of the nonionic surfactants were prepared in full-scale commercial equipment employing a linear primary alcohol feedstock consisting of 55% dodecanol and 45% tetradecanol. Conventional ethoxylation techniques (41) were used in preparing broad-range ethoxylates, while a proprietary process was utilized to produce narrow-range ethoxylates. Each series of surfactants contained eight products with 1.0 wt% aqueous cloud points of 25, 35, 45, 50, 60, 75, 92 and 98 C. All of the results depicted in the figures in this paper were generated using these 16 products.

Ethoxylate distributions were determined using a Perkin-Elmer "Sigma II" gas chromatograph with a flame ionization detector. A DB-1 methyl silicone fused column, 25 meters by 0.25 millimeters with a film thickness of 0.25 micron, was used. The initial temperature was set at 100 C, with a programmed temperature rise of 8°/min to 330 C. Undecanol was used as an internal standard. To decrease their polarity and lower their boiling point, the ethoxylates were silylated with Sylon HT from Supelco, Inc. Percent weights for the 1-8 mole adducts were calculated using the response factors of undecanol versus monodisperse 1-8 mole dodecyl ethers from Nikko Chemical Company. The response factor for the 9 mole adduct, which was approximated by extrapolating from the response factor curve for the 1-8 mole adducts, was used to calculate the amounts of all of the higher ethoxylates present. While the weight percent values associated with the adducts having greater than 9 moles of ethylene oxide thus may be slightly understated, these data are in good agreement with results obtained using a high pressure liquid chromatography technique which does not make use of response factors. The errors associated with the weight percent of unreacted alcohol and each ethoxylate adduct are ±5 and ±10% of the amount present, respectively.

Table I lists experimental methods. Details are included in the discussion section and/or the corresponding figures.

TABLE I

Experimental Methods

Determination	Procedure
Hydroxyl number	ASTM E 326-69
Cloud point	Adaptation of SMS-ASTM D 97
Pour point	ASTM D 97-66
Foaming	ASTM D 1173-53
Kinematic viscosity	ASTM D 2515
Wetting	AATCC 17
Surface tension	Wilhelmy Plate (7)
Adhesion tension	Wilhelmy Plate (7)
Oil/water interfacial tension	Spinning Drop Technique (42)
Detergency performance	Terg-O-Tometer (43)

RESULTS AND DISCUSSION

Effects of the Ethylene Oxide Distribution on Chemical/Physical Properties

Figure 1 compares the ethoxylate distributions of narrow- and broad-range surfactants exhibiting 50 C aqueous cloud points. Both products have a peak in the distribution at the 7-mole adduct, but while nearly 90 wt% of the narrow-range ethoxylate lies within the 7 ± 2 range, only about

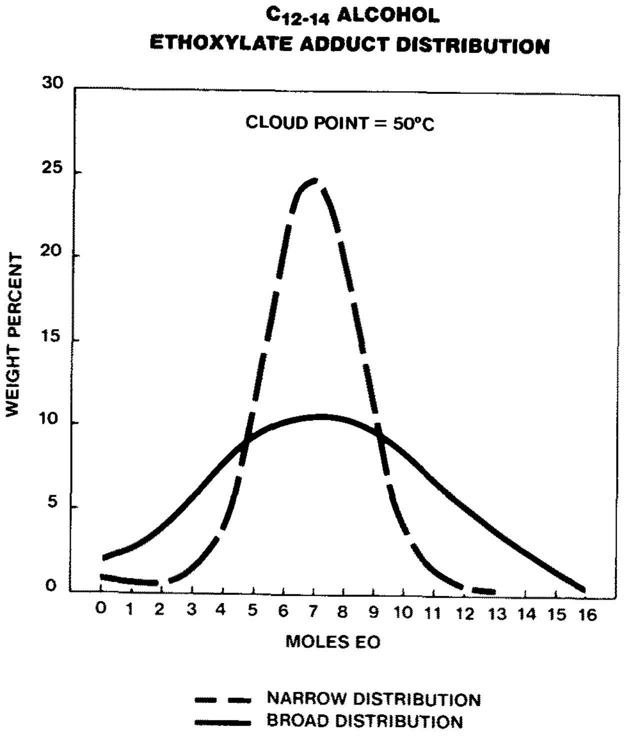


FIG. 1. Comparison of the ethoxylate adduct distributions of C_{12-14} alcohol ethoxylates with 50 C cloud points.

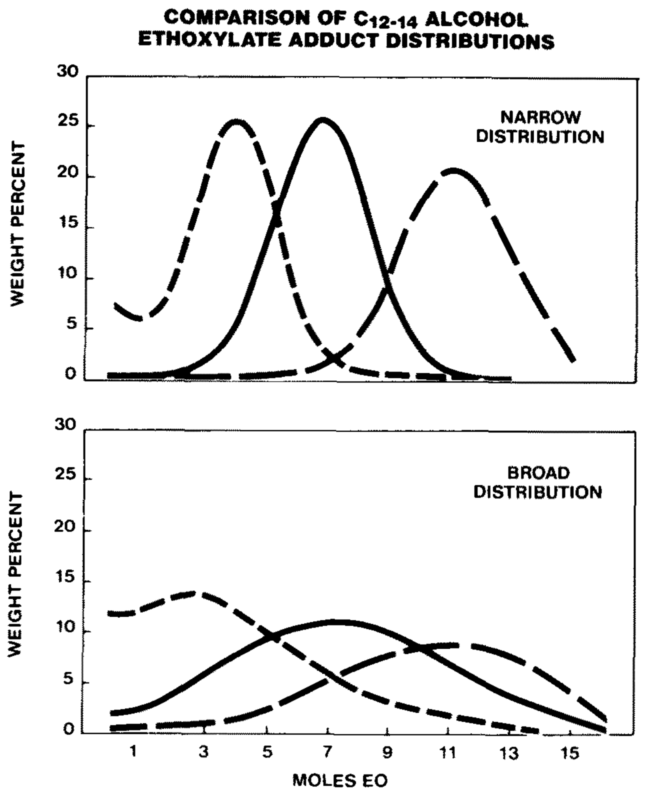


FIG. 2. Comparison of the ethoxylate adduct distributions of narrow- and broad-range ethoxylates with similar cloud points.

50 wt% of the conventional surfactant falls within this range. Differences in unreacted alcohol content also are evident, with the narrow and broad-range products containing 0.5 wt% and 2.0 wt%, respectively. Figure 2 reveals that significant differences in the ethoxylate distribution are noted when other members of the two series are compared as well. Due to the statistical nature of the ethoxylation process (44), however, these differences tend to vary as the degree of ethoxylation increases.

One consequence of the reduced unreacted alcohol and low-mole ethoxylate content of narrow-range surfactants is that fewer moles of ethylene oxide are required per mole of alcohol to achieve a given cloud point. This is illustrated in Figure 3, where molecular weight and moles of ethylene oxide are plotted as a function of cloud point for each of the two series. As the cloud point increases, the difference in molecular weight for members of the respective series decreases, until the curves eventually meet at a cloud point of about 95 C. This is due to the fact that all of the surfactants with greater than about 10 moles of ethoxylation contain relatively few water-insoluble species. Nonetheless, these data suggest that narrow-range ethoxylates have an inherent efficiency advantage in practical applications where surfactants generally are used on a weight basis. That is, for a given cloud point narrow-range ethoxylates offer more molecules per unit weight and a higher percentage of the molecules are within the preferred ethoxylation range.

Another potential benefit derived from the reduced unreacted alcohol and low-mole ethoxylate content of narrow-range products is illustrated in Figure 4, where transmittance is plotted as a function of temperature for aqueous solutions of narrow- and broad-range 5-mole ethoxylates. The narrow-range product exhibits a sharp, well-defined cloud point at about 22 C, with the solution remaining clear below this temperature. Conversely, the broad-range ethoxylate does not form clear solutions regardless of the temperature. This represents a potential practical advantage for surfactants with narrow distributions, i.e., the ability to form clear aqueous solutions with relatively low cloud points. Such solutions will have utility in detergent applications, for C_{12-14} alcohol ethoxylates in the 5 ± 2 moles of ethoxylation range are very effective in removing oily soils from various substrates (7,8,16,28,29). Currently, 5-mole ethoxylates are not widely used in cleaning products because the performance and formulating problems resulting from the relatively high amounts of unreacted alcohol and low-mole ethoxylates in broad-range surfactants more than offset the beneficial attributes of the 5-mole species. Many of these problems may be eliminated, however, by using narrow-range ethoxylates.

In light of the uniform molecular structure of narrow-range ethoxylates and their lack of low-mole species, they are expected to exhibit higher pour points than broad-range surfactants with an equivalent average degree of ethoxylation. However, if the pour points are compared on an equal cloud point basis, Figure 5 reveals that these factors are more than offset by the lower molecular weights of narrow-range surfactants and their lack of high melting ethoxylate tails (44). As the cloud point increases, the difference in pour point between narrow- and broad-range products decreases, and the curves actually cross at a cloud point of approximately 85 C. This is attributable to the loss in molecular weight advantage noted for narrow-range ethoxylates with high cloud points. Nonetheless, the lower pour point associated with narrow-range ethoxylates in the 25 to 75 C cloud-point range represents a practical handling advantage, especially in geographical regions where ambient temperatures often are near the pour point of conventional ethoxylates currently in use.

An important property of nonionic surfactants intended for use in liquid cleaning formulations is aqueous viscosity. Figure 6, therefore, illustrates the relationship between cloud point and aqueous viscosity for 20 wt% and 30 wt% solutions of narrow- and broad-range ethoxylates. For both series of surfactants, viscosity generally decreases as the cloud point increases, and 30 wt% solutions are more viscous than 20 wt% solutions. At any given cloud point, narrow-range ethoxylates consistently provide lower aqueous viscosities than their broad-range counterparts. Furthermore, while not evident in Figure 6, narrow-range surfactants have lower gel temperatures at any given concentration and they have more restricted gel concentration ranges at any given temperature. At concentrations above the gel range, viscosity generally decreases with concentration up to about 95 wt%, and ethoxylate distribution has little effect on viscosity. Similar results have been reported by others (25). These data suggest that narrow-range ethoxylates may provide a cost-saving benefit when used in highly concentrated liquid cleaning products, where hydrotropes and/or salts often are required to reduce viscosity and maintain pourability at low temperatures.

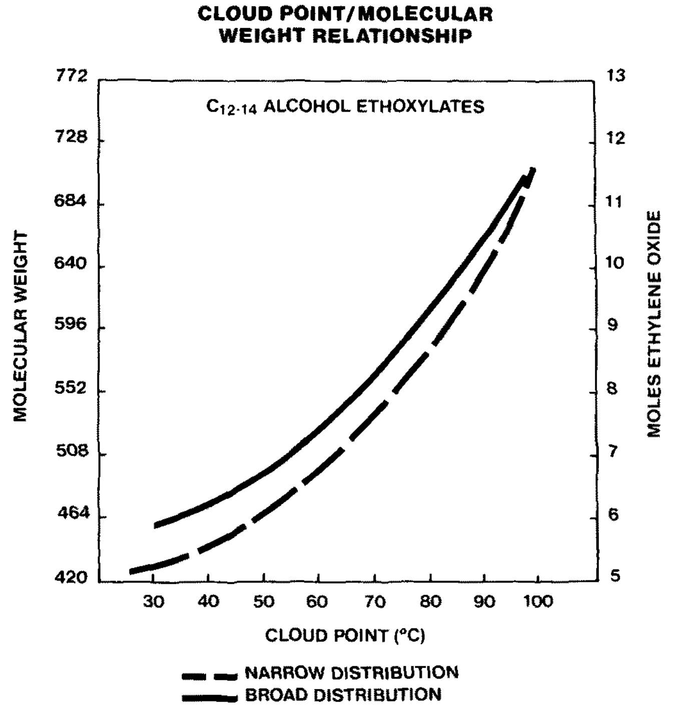
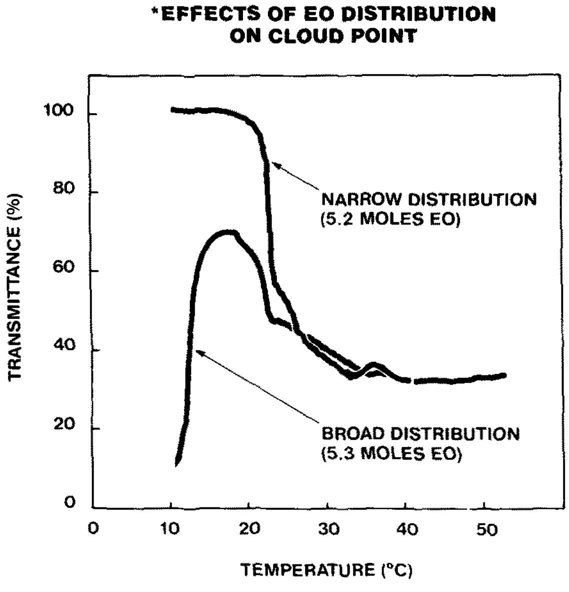


FIG. 3. Relationship between cloud point and molecular weight for narrow- and broad-range ethoxylates.



*1.0% AQUEOUS SOLUTIONS

FIG. 4. Effects of ethylene oxide distribution on cloud point for 5-mole ethoxylates.

Effects of the Ethylene Oxide Distribution on Performance Properties

Because the Ross-Miles foaming test (46) is widely recognized as a means of characterizing the foaming properties of surface-active agents, the effects of the ethoxylate distribution on foaming properties have been examined using this method. Figure 7 shows initial and 5-min foam heights as a function of cloud point for 0.05 wt% solutions of narrow and broad-range ethoxylates at 50 C. Regardless of the distribution, initial foam height increases markedly as the cloud point of the surfactant approaches the use temperature. In general, narrow-range products produce slightly higher initial foams, but the foams are significantly less stable than those displayed by broad-range ethoxylates. Similar trends have been observed at other concentrations, in the presence of water hardness ions and at ambient temperatures. Crook, Fordyce and Trebbi (23) reported similar results for normal distribution and homogeneous octylphenoxyethoxyethanols, and attributed the lower initial foam heights of normal-distribution ethoxylates to the preferential adsorption of inherently lower-foaming short-chain adducts (22) at the air/water interface. No conclusive explanation for the greater foam stability noted with normal-distribution materials is readily apparent, but more efficient healing (47) due to the variety of molecules

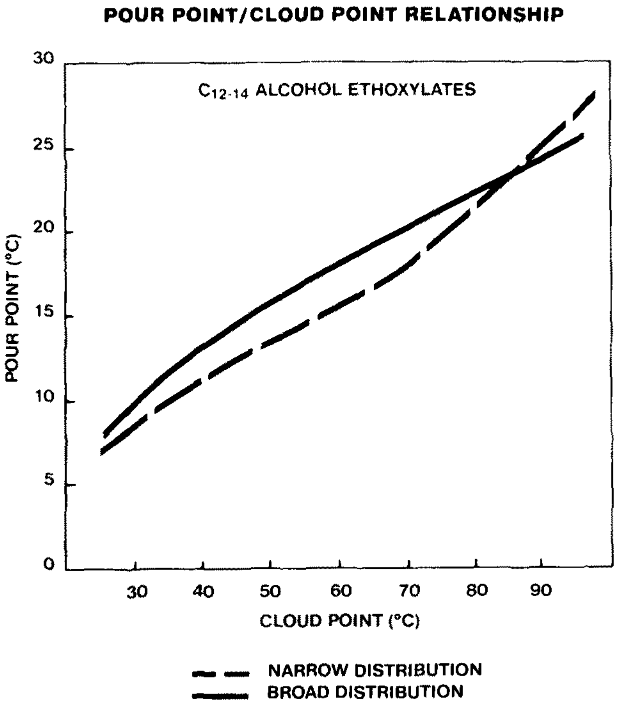


FIG. 5. Effect of cloud point on pour point for narrow- and broad-range ethoxylates.

available to alleviate strains in the interfacial film has been suggested (23). These differences in foaming properties are expected to be of little consequence in most household product applications, where the mechanical energy input is relatively low and foam stabilizers and/or high-foaming anionic surfactants are commonly present. However, the lower foam stability of narrow-range ethoxylates may be beneficial in industrial applications where the mechanical energy input and surfactant use concentrations are relatively high, such as textile wet-processing and newsprint deinking operations.

Another important performance property of nonionic surfactants is their ability to promote rapid wetting of textile substrates. Figure 8 shows 5- and 20-second Draves wetting concentrations (48-49) as a function of cloud point for narrow and broad-range ethoxylates at 25 C. Since these data represent the concentrations of surfactant required to achieve complete wetting of cotton skeins in 5 and 20 seconds, respectively, the lower the concentration the more efficient the surfactant is as a wetting agent. In general, narrow-range ethoxylates are more efficient than broad-range surfactants, especially as measured by the 5-second wetting concentration. This trend also was noted at elevated temperatures and in the presence of water hardness ions. Similar findings have been reported by others working with distilled and normal-distribution nonylphenol ethoxylates (17) and with distilled and normal-range primary alcohol ethoxylates (25). The performance advantage of the narrow-range ethoxylates is due in part to the inherent *efficiency* advantage previously mentioned, i.e., narrow-range ethoxylates contain more molecules per gram and a higher percentage of the molecules is within the optimum ethoxylation range. This advantage could translate into a significant cost savings in industrial applications where relatively high surfactant concentrations normally are required to ensure rapid wetting.

Perhaps the most universally recognized performance property of a surfactant is its ability to reduce the surface

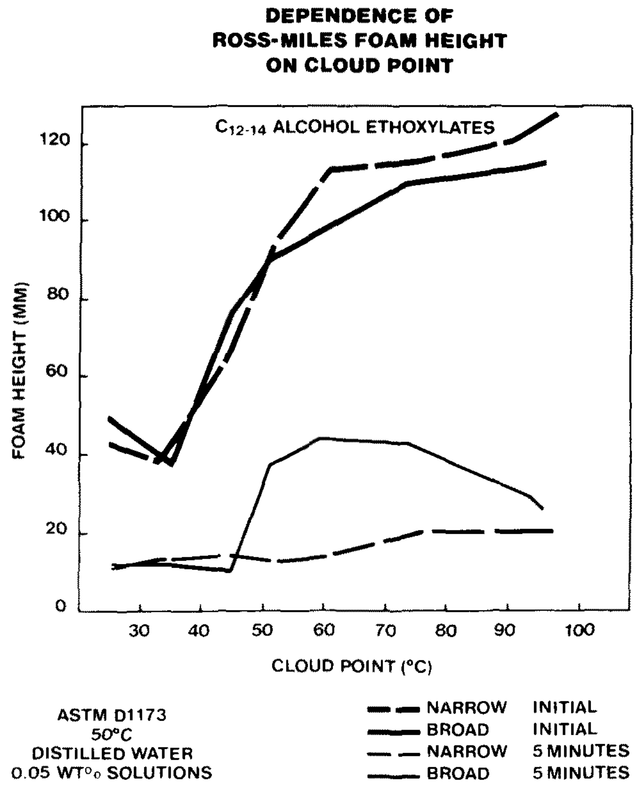


FIG. 7. Dependence of foam height on cloud point for narrow- and broad-range ethoxylates.

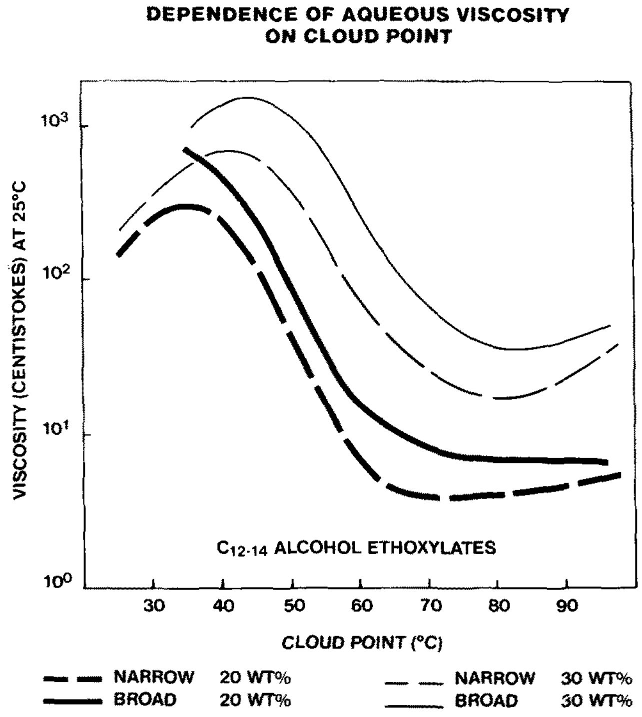


FIG. 6. Dependence of aqueous viscosity on cloud point for narrow- and broad-range ethoxylates.

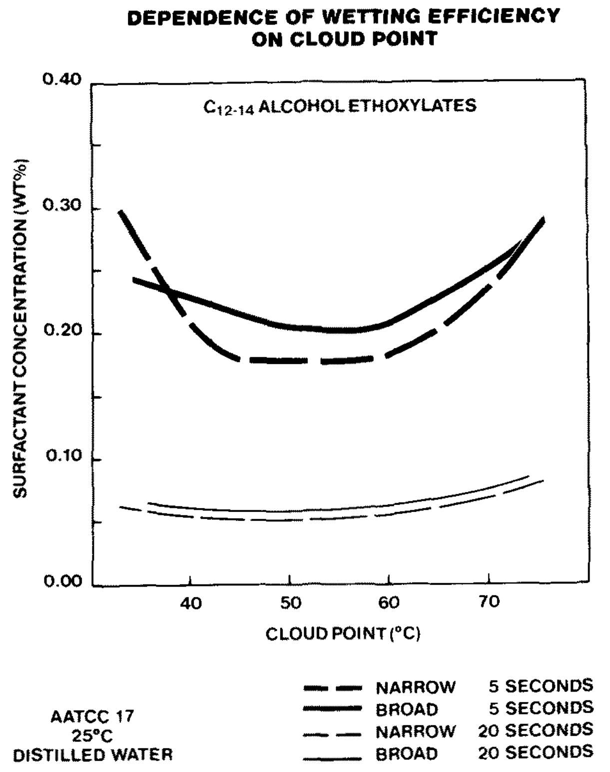


FIG. 8. Dependence of 5- and 20-second Draves wetting concentrations on cloud point for narrow- and broad-range ethoxylates.

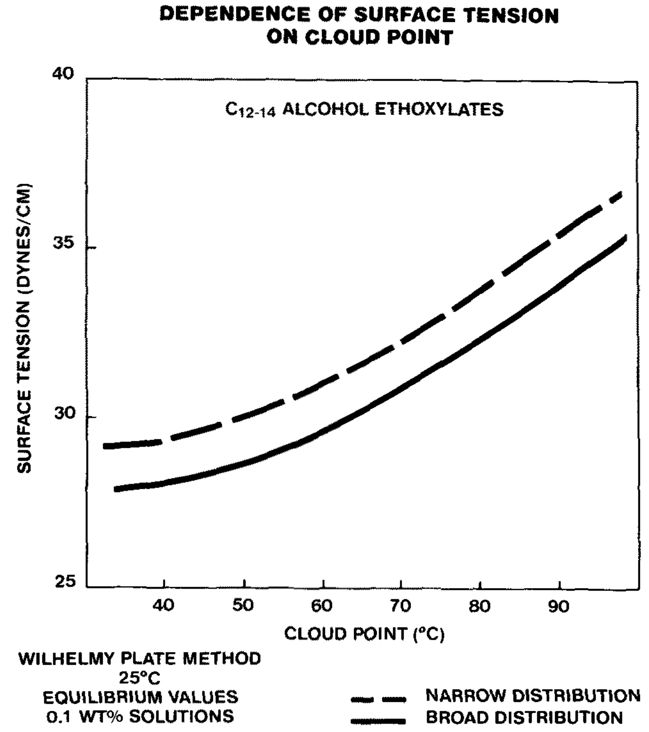


FIG. 9. Dependence of aqueous surface tension on cloud point for narrow- and broad-range ethoxylates.

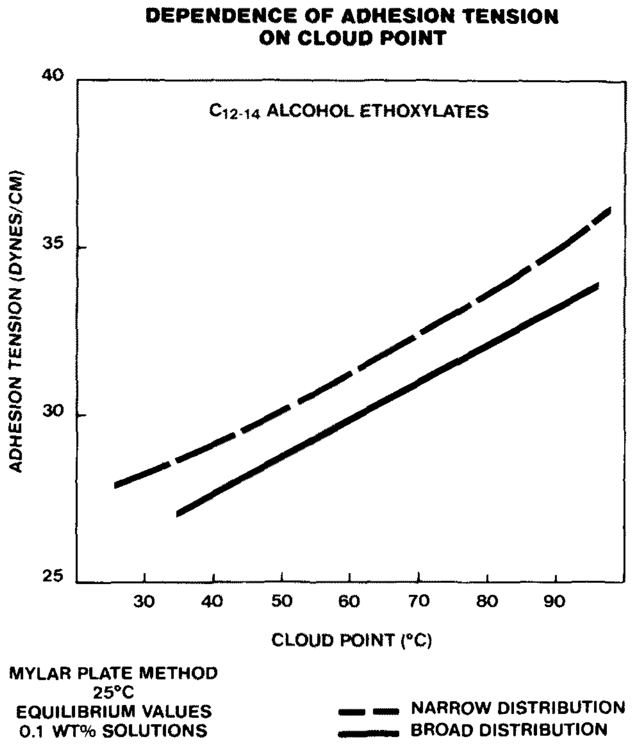


FIG. 10. Dependence of polyester adhesion tension on cloud point for narrow- and broad-range ethoxylates.

tension of water. Accordingly, the relationship between surface tension and cloud point is illustrated in Figure 9 for aqueous solutions of narrow- and broad-range ethoxylates. As observed in previous studies (7-8,15,50-52), surface tension increases with cloud point regardless of the distribution, due to the accompanying decrease in surface activity. For a given cloud point, narrow-range ethoxylates yield higher surface tensions than broad-range surfactants. Similar trends noted using p,t-octylphenoxyethoxyethanols (15) have been attributed to the preferential adsorption of short-chain adducts which are present in relatively high amounts in broad-range products, at the air/water interface. These species are highly surface active and thus are very effective in reducing surface tension. Although technically interesting, the differences in surface tension between narrow- and broad-range surfactant solutions is expected to be of little practical consequence in and of itself. However, as subsequently will be demonstrated, surface tension affects other surface-chemical parameters which have a much greater influence on surfactant performance.

Another important surface-chemical property of nonionic surfactants is the ability to reduce the solid/water interfacial tension (γs/w). Although not directly measurable, certain deductions concerning γs/w can be made by determining the adhesion tension for the surfactant solution on a solid surface. For a drop of aqueous solution on a solid surface, the Young equation (53) can be cast in the form:

$$\gamma w/a \mathrm{COS}\theta w/a = \gamma s/a - \gamma s/w \qquad [1]$$

where γs/a, γs/w and γw/a represent the solid/air, solid/water and water/air interfacial tensions, respectively, and θw/a is the contact angle in the aqueous phase. Using polyester Wilhelmy plates the adhesion tension, γw/a COSθw/a, for a nonionic surfactant solution on polyester can be measured directly (8). Since γw/a is known from similar measurements with platinum plates, where COSθw/a = 1, COSθw/a for polyester substrates can be obtained. On the assumption that γs/a is a constant (54), i.e., no (change in) spreading pressure is registered at the solid/air interface, any change in (γs/a − γs/w) actually reflects a change in γs/w.

Figure 10 depicts the change in polyester adhesion tension values with cloud point for 0.1 wt% aqueous solutions of narrow- and broad-range ethoxylates. Adhesion tension increases with cloud point regardless of the distribution, but for any given cloud point, narrow-range ethoxylates exhibit higher values than broad-range products. These findings closely parallel those previously delineated for surface tension, suggesting that changes in surface tension account for most of the variation in adhesion tension. In other words, COSθw/a for polyester is nearly 1 for all of the surfactant solutions. This result is reasonable, since the critical surface energy of polyester is significantly higher than the surface tension of the various surfactant solutions (55). The practical implications of these results may be deduced by considering the expression relating the extent of oil roll-up during the detergency process (56), i.e., the equilibrium contact angle in the aqueous phase (θw/s), to the solid/water (γs/w), solid/oil (γs/o), and oil/water (γo/w) equilibrium interfacial tensions (53):

$$\mathrm{COS}\theta w/s = \frac{\gamma s/o - \gamma s/w}{\gamma o/w} \qquad [2]$$

Clearly as adhesion tension increases, that is, as γs/w decreases, COSθw/s increases. Thus, since a high value for COSθw/s has been shown to promote efficient nonpolar oil removal from polyester substrates (7-8), narrow-range ethoxylates are expected to be more effective than broad-range ethoxylates in deterging such soils from synthetic strates. Detergency data which are in agreement with this contention have been reported (28-29).

While equation 2 reveals that the resultant force acting at the 3 phase point of contact ultimately determines the value of the contact angle in the aqueous phase and therefore the efficiency of the detergency process, changes in the contact angle usually result from changes in the oil/water interfacial tension (7-8). In addition, practical detergency studies have demonstrated excellent correlation between cleaning efficiency and oil/water interfacial tension (28-29). Thus, in view of the theoretical and established practical significance of the oil/water interfacial tension, the effects of cloud point, time, temperature and surfactant concentration on this parameter have been examined for narrow- and broad-range ethoxylates.

Figure 11 illustrates the relationship between interfacial tension and cloud point for 0.05 wt% solutions of narrow- and broad-range ethoxylates against paraffin oil at 25 C. The data were recorded after 10 min of phase contact, which corresponds to the wash time in a normal home laundering operation. As has been reported previously for other nonionic surfactants (57), interfacial tension increases with cloud point for both series of surfactants. This occurrence is attributable to the decrease in surface activity accompanying an increase in the degree of ethoxylation. Changes in the molecular orientation of the surfactant at the oil/water interface as the ethylene oxide chain length increases may also affect the interfacial tension (58). For a given cloud point, narrow-range ethoxylates lower interfacial tension more effectively than their broad-range counterparts, especially in the low cloud point region. Similar results have been obtained by others working with monodisperse and normal-distribution octylphenol ethoxylates (15,20) and with distilled and normal-distribution primary alcohol ethoxylates (28-29). Differences in the degree of fractionation of the nonionic surfactant, due to partitioning between the oil and water phases, are at least partially responsible for these findings (15,20). Because the short-chain adducts in broad-range ethoxylates are so oil soluble, there is little driving force for them to orient at the oil/water interface. Consequently, the average molecular weight of the surfactant remaining in the aqueous phase increases, and only relatively long-chain adducts are appreciably adsorbed at the interface. Since narrow-range ethoxylates contain a significantly lower percentage of low-mole species at a given cloud point, there is less of a change in the molecular weight of the surfactant in the aqueous phase due to partitioning. Thus, narrow-range ethoxylates provide more highly surface-active species at the interface. The fact that a normal-distribution 5-mole ethoxylate was found to correspond to a single-species 7-mole ethoxylate in terms of interfacial tension lowering has been cited as supporting evidence for this explanation (15).

Representative data illustrating the effects of time and temperature on oil/water interfacial tension values are shown in Figure 12 for 0.01 wt% solutions of narrow- and broad-range ethoxylates with cloud points of 50 C. Due to partitioning of the various nonionic surfactant components between the oil and water phases (15,20,57), the approach to equilibrium is very slow, regardless of the ethoxylate distribution or temperature. However, because the narrow-range product provides a greater concentration of the most highly surface-active adducts at the interface, it reduces interfacial tension more effectively at any given time and temperature. Consistent with the generally accepted principle that surface activity increases with temperature, both surfactants produce lower equilibrium interfacial tension values at the higher temperature. Furthermore, the decrease in interfacial tension with time is more appreciable at 50 C than it is at 25 C for both surfactants, with the most significant change in interfacial tension with time being observed

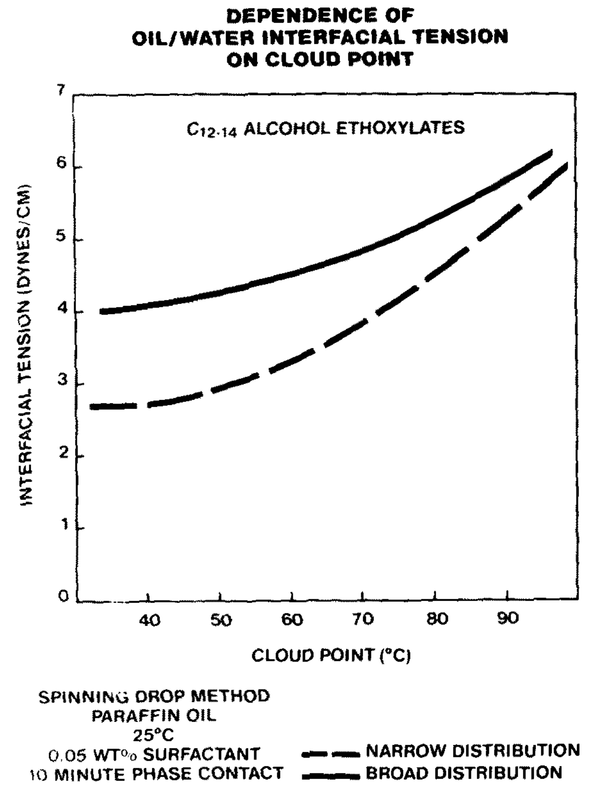


FIG. 11. Dependence of oil/water interfacial tension on cloud point for narrow- and broad-range ethoxylates.

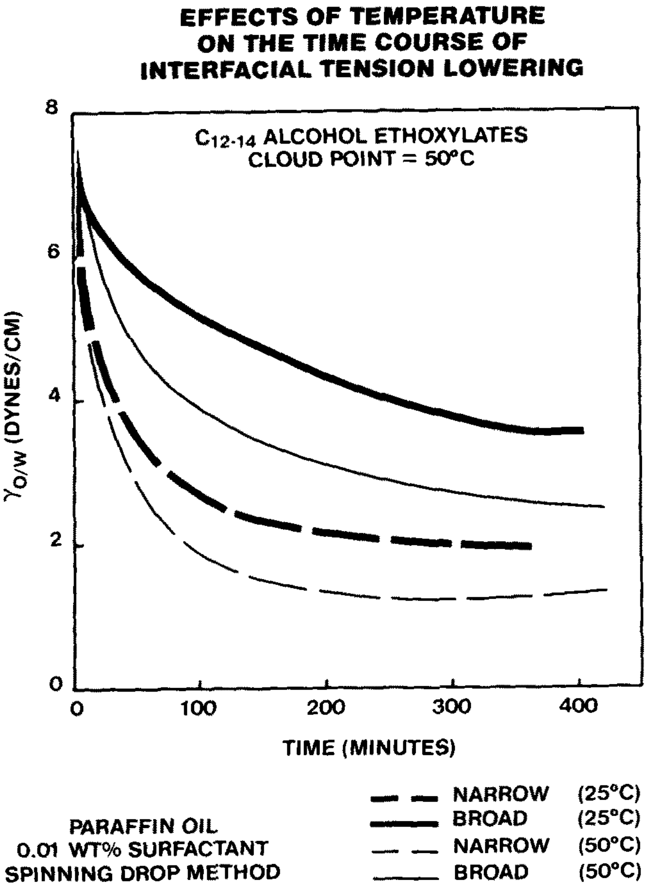


FIG. 12. Effects of time and temperature on oil/water interfacial tension values produced by narrow- and broad-range ethoxylates.

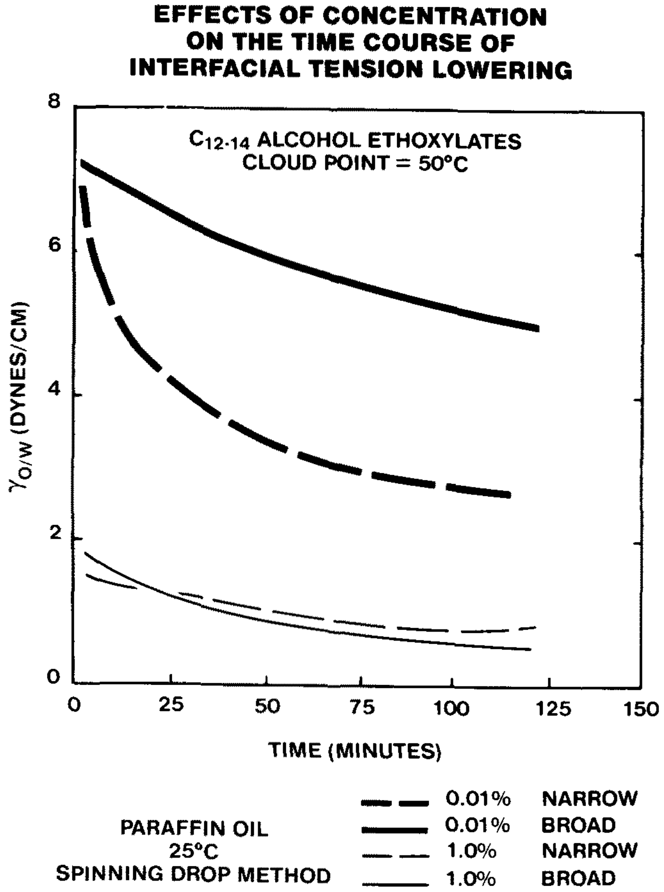


FIG. 13. Effects of concentration on the time course of interfacial tension lowering for narrow- and broad-range ethoxylates.

for the narrow-range ethoxylate at both temperatures. These data are in agreement with the generally accepted principle that transfer of the nonionic surfactant into the oil phase increases near the cloud point. Similar trends have been noted with other nonionic surfactant families (57).

The effects of surfactant concentration on the relative abilities of narrow- and broad-range ethoxylates to reduce interfacial tension are illustrated in Figure 13 for 50 C cloud point products. While little difference in the time course of interfacial tension lowering is noted at 1.0 wt%, the narrow-range ethoxylate reduces interfacial tension more rapidly and to a greater extent at a typical end-use level of 0.01 wt%. In fact, narrow-range ethoxylates are more effective over the entire useful concentration range of 0.005 wt% to 0.1 wt%. Similar results obtained previously for monodisperse and normal-distribution primary alcohol ethoxylates (57) have been explained in terms of inherent efficiency differences. At any given concentration narrow-range ethoxylates provide a greater quantity of the most surface-active species to the interface per unit time and, thereby, reduce interfacial tension more rapidly and effectively. At very high surfactant concentrations both narrow- and broad-range ethoxylates are able to provide excessive quantities of the most highly surface-active species at the interface, so little difference in interfacial tension lowering capability is evident.

Previous studies (7-8, 28-29,57) have established a correlation between the ability of a nonionic surfactant to remove oily soils from synthetic substrates and its ability to reduce the oil/water and solid/water adhesion tensions. Such a correlation also is predicted by equation 2. Thus, it is of interest to consider the relative detergency properties of narrow- and broad-range ethoxylates on oily soils. Detergency experiments were conducted in a Terg-O-Tometer (59). Each beaker contained 4 (4″ x 3″) nylon swatches impregnated primarily with mineral oil and carbon black (60), 4 (4″ x 3″) clean 65% polyester/35% cotton bulking cloths and one liter of a 0.03 wt% surfactant solution. A 10-min wash and a 2-min rinse were conducted at 17 C. Performance was evaluated via the reflectance technique (61) using a Hunter D-25 color/difference meter (62-64). Percent detergency was calculated using the equation (65):

$$\text{Percent Detergency} = (Rw\text{-}Rs)/Ro\text{-}Rs) \qquad [3]$$

where Rw is the reflectance of the laundered swatches; Rs is the reflectance of the soiled swatches; and Ro is the reflectance of the swatches before soiling. At the 95% confidence level the least significant difference is two detergency units.

Table II lists detergency data for selected narrow- and broad-range ethoxylates. Under the cold-water laundering conditions of this test, low cloud point ethoxylates perform better than high cloud point materials, regardless of the ethoxylate distribution. For a given cloud point, narrow-range ethoxylates exhibit superior detergency performance. Similar results have been reported by others (16,28-29). These findings suggest that narrow-range ethoxylates may impart improved performance properties to practical cleaning systems, such as laundry detergents, prewash spotters and hard surface cleaners. It must be recognized, however, that the type of soil encountered can greatly affect the relative performance properties of nonionic surfactants, and that the nonpolar soil used here is not a typical consumer soil. Moreover, fully formulated products contain many ingredients in addition to nonionic surfactants, and the overall product performance is determined by the total of the individual component contributions plus antagonistic or synergistic interactions.

TABLE II

Cold-Water Detergency Performance

	C_{12-14} alcohol ethoxylates	
Ethoxylate distribution	Cloud point (°C)	*Average percent detergency
Narrow	32	33
Broad	34	26
Narrow	49	23
Broad	51	16

*Testfabrics soil on nylon; 17 C; 150 ppm hardness (Ca^{2+}:Mg^{2+} = 3:2); 10-min wash; 2-min rinse; 0.03 wt% surfactant; least significant difference = 2.

ACKNOWLEDGMENTS

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