Glyceryl *Bis*ether Sulfates. II: Performance Properties

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Traditional structure vs. performance relationships have been thoroughly investigated for alcohol ether sulfates (AES) wherein hydrophobe chainlength and degree of ethoxylation served as variables for structure variance. Therefore, a series of molecules, 1,3-*bis*-(alkylethylenoxy)-propane-2-yl sodium sulfates or glyceryl *bis*ether sulfates (GBES), analogous to AES but with a centrally located hydrophile structure, was synthesized and evaluated for its cloth detergency, foaming and wetting properties. Performance test results are presented as response surfaces in the two variables mentioned in addition to comparisons to common surfactants. The centrally located hydrophile structures exhibited varying surfactant and performance properties, with increasing detergency performance shown by higher-molecular weight GBES molecules: Optimum foaming and wetting performance was produced by a range of structures roughly given by C_nEO_{n-6} for n = 6–8.

KEY WORDS: Centrally located, designed experiments, detergency, epichlorohydrin, foam, glyceryl *bis*ether sulfates, performance, wetting.

Surfactant manufacturers and closely allied industries engage in ongoing research toward new surfactant structures from which enhanced finished-product performance may result. During the course of one such investigation, the question arose of "moving" the hydrophilic portion of an alcohol ether sulfate (AES) to the center of the molecule and its effect on surfactant performance. A literature survey (1,2) indicated several general effects that resulted from shifting the hydrophilic portion of an anionic surfactant from the terminal to a central position when all other factors were kept constant. These included higher water solubility, lower efficiency and higher effectiveness of surface tension reduction, faster wetting, higher flash foam volume and potentially better cloth detergency performance.

The literature also showed that surface chemical and performance properties generally improve with increasing molecular weight of the surfactant up to the solubility limit of the surfactant in the medium. Therefore, given the higher water solubility limit of the centrally located hydrophile structure, potentially increased performance may be found for examples of this type of structure with higher molecular weights, where traditional surfactants of equal molecular weight would lose their solubility and performance would fall (3). Therein lies the impetus for this study.

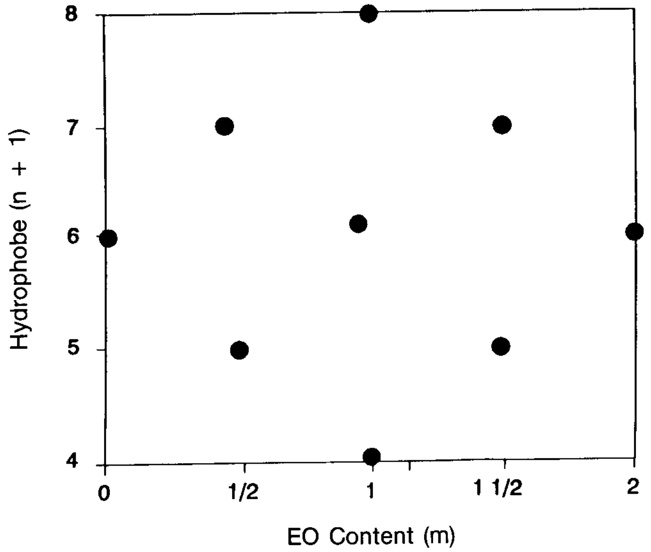

FIG. 1. Glyceryl *bis*ether sulfate structures and their place in the design space wherein $CH_3(CH_2)_nO(C_2H_4O)_mCH_2(CHOSO_3Na)CH_2(OC_2H_4)_mO(CH_2)_nCH_3$ n = 3–7 and m = 0–2. EO, ethylene oxide.

With these factors in mind, the subject molecules (Fig. 1), 1,3-*bis*-(alkylethylenoxy)-propane-2-yl sodium sulfates or glyceryl *bis*ether sulfates (GBES), were synthesized (4) as the centrally located hydrophile analogy of AES. Nine GBES samples filled a central composite design space wherein the hydrophobe carbon chainlength varied from butyl to octyl (on each side), and the number of ethylene oxide (EO) residues ranged from zero to two (on each side). This report details the cloth detergency, foaming behavior and textile wetting properties exhibited by GBES as a function of structure. Comparisons were made to $C_{1214}EO_2$ AES to demonstrate the effect of "moving" the hydrophile to the center of the molecule. In particular, comparison between $C_{1214}EO_2$ AES and its closest GBES counterpart (C_6EO_1, the design space center point) holds relevant information concerning the centrally vs. the terminally located hydrophile structural effect. Comparisons were also made to $C_{11.5}$ linear alkylbenzene sulfonate (LAS) because it is a commercial surfactant with a centrally located hydrophile despite the distribution of phenyl isomers.

EXPERIMENTAL PROCEDURES

Cloth detergency. Standard testing was carried out as detailed elsewhere (5).

Agitation foam. Agitation foam was measured with an in-house produced foam generator. Its design is based on the German DIN test method S3 902 in which perforated disks are quickly passed through 100 mL of test surfactant solution for 30 strokes to produce the foam. An eccentric drive system varies the speed of the plunger disk such that the disks move quickly through the test solution and slowly through the foam. Tests were carried out at 118°F, 100 ppm hardness as calcium carbonate and 300 ppm and 1% total surfactant concentration. Data are reported as the volume of foam 1 min after agitation was stopped. Soil addition tests were carried out by adding corn oil in 0.5-mL increments, followed by ten agitation strokes, which was repeated until 2.5 mL of oil had been added. Foam remaining 1 min after the last agitation was reported.

Cotton wetting. Wetting speed was evaluated by measuring the time required to wet cotton tape at various surfactant concentrations, and the concentration needed to wet in 12.5 s was calculated. Equipment and methods are described elsewhere (5).

Design of experiments. All of the designed experiments included herein were carried out by means of the computer program Design-Expert® produced by STAT-EASE Inc. (Minneapolis, MN). The graphic data presented are the

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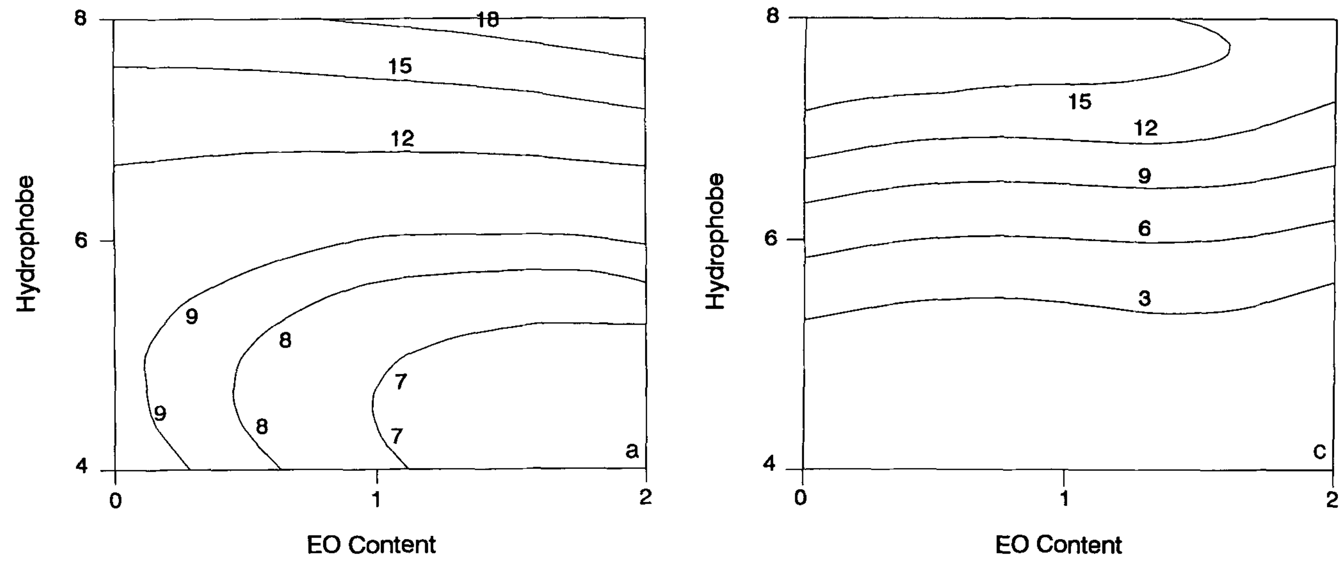


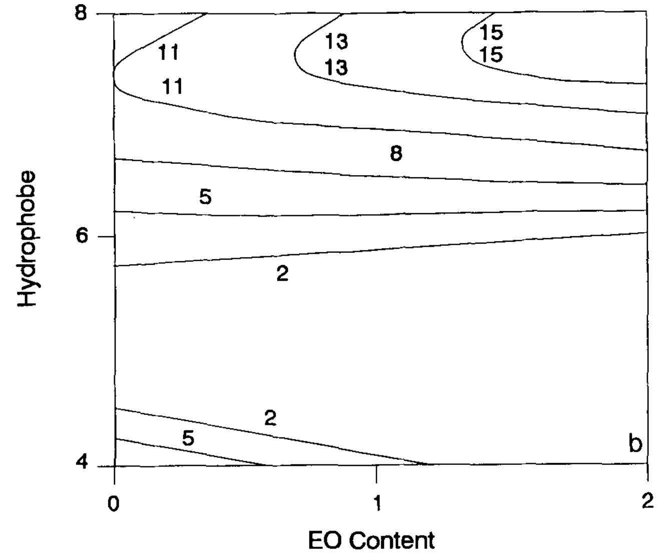


FIG. 2. (a) Detergency performance of glyceryl *bis*ether sulfate (GBES) [reflectance (Rd) washed–Rd soiled] on sebum- and dust-soiled cotton as a function of hydrophobe chainlength and ethylene oxide (EO) content: $C_{11.5}$ linear alkylbenzene sulfonate (LAS) = 13.4, $C_{1214}EO_2$ alcohol ether sulfate (AES) = 18.5. (b) Detergency performance of GBES [reflectance (Rd) washed–Rd soiled] on sebum- and dust-soiled permanent press as a function of hydrophobic chainlength and EO content: $C_{11.5}$ LAS = 13.0, $C_{1214}EO_2$ AES = 14.9. (c) Detergency performance of GBES (Rd washed–Rd soiled) on mineral oil-soiled permanent press as a function of hydrophobe chainlength and EO content: $C_{11.5}$ LAS = 15.3, $C_{1214}EO_2$ AES = 14.2.

computer-generated models for the data acquired. All mathematical models agreed well with experimental data and gave R^2 values above 0.90. The models were also evaluated for significance and gave high F values with "<5% probability of a greater F value." So, the models generated account for 90% or more of the variance observed within the design space, and there was less than a 5% probability that the variance observed was caused by chance.

Alcohol ethoxylate samples. The ethoxylated primary linear alcohols used as starting materials for GBES synthesis were of two types—pure homolog and not pure homolog. For performance testing to produce meaningful results that indicate optimum structures, the samples tested must be as distinct and chemically pure as possible. This highlights rather than dilutes performance differences between structures. Every effort was made to minimize the number of individual compounds used to make the nonpure homolog alcohols such that each GBES sample would then be as chemically distinct as possible. For example, the $C_5EO_{1.5}$ GBES was derived from an alcohol mixture that contained equal parts by weight of C_4-EO_1, C_4-EO_2, C_6-EO_1 and C_6-EO_2 ethoxylated alcohols.

GBES samples. The GBES samples were prepared as described in the companion paper in this issue of the *Journal of the American Oil Chemists' Society* (4).

Commercial surfactants. LAS ($C_{11.5}$ LAS) and AES ($C_{1214}EO_2$ AES) were representative of commercially available materials. The $C_{11.5}$ LAS had 28.6% 2-phenyl content and an average chainlength of $C_{11.5}$. The $C_{1214}EO_2$ AES was based on a C_{1214} alcohol ethoxylated with two moles of EO.

Nomenclature. The GBES molecules were named for the ethoxylated alcohol from which they were made. For example, C_6EO_2 GBES refers to 1,3-*bis*[2-(*n*-hexyloxyethoxy)ethoxy]propane-2-yl sodium sulfate. Even though this compound was made from hexyloxyethoxyethanol (C_6EO_2), the total hydrophobe chainlength is C_{12} and the total number of EO units incorporated is 4.

RESULTS AND DISCUSSION

The GBES samples (Fig. 1) were prepared to fill a central composite design space so that performance results could be displayed as contour maps over the design space.

Cloth detergency. Cloth detergency tests were carried out under typical United States conditions (300 ppm surfactant, 150 ppm hardness as $CaCO_3$, pH 9.5, 0.01M Na_2SO_4) on sebum- and dust-soiled cotton and permanent press and on mineral oil-soiled permanent press. The results in units of reflectance (Rd) change from soiled to washed cloth are shown in Figure 2. A larger change in cloth Rd indicates better detergency performance. For sebum-soiled cotton and permanent press, a higher carbon chainlength and a higher degree of ethoxylation in the GBES molecule gave rise to enhanced detergency when compared to $C_{1214}EO_2$ AES. Not surprisingly, under these conditions with no builder present, $C_{1214}EO_2$ AES performed better than $C_{11.5}$ LAS due to LAS's well-known hardness sensitivity (2).

In the detergency tests on mineral oil-soiled permanent press, the optimum GBES structure contained a high carbon chainlength but one or less EO units per ethoxylate subunit. This stemmed from the hydrophobicity of the cloth and soil combination. In this case, $C_{11.5}$ LAS outperformed $C_{1214}EO_2$ AES, a phenomenon previously described wherein $C_{11.5}$ LAS cleans oily soils quite well under medium hardness conditions (6).

Comparing the results in all three soiled cloth systems between the C_6EO_1 GBES (the design space center point) and its $C_{1214}EO_2$ AES counterpart clearly demonstrates that the linear surfactant structure outperforms the centrally located hydrophile structure of (nearly) the same molecular weight. Indeed, adequate detergency performance was observed only for GBES structures larger than C_6EO_1. However, for all three test systems, higher-molecular weight GBES structures were identified that showed detergency performance comparable to $C_{1214}EO_2$ AES and $C_{11.5}$ LAS. Unfortunately, the performance contour maps also indicated that the expected fall in detergency performance due to increasing GBES molecular weight and lower water solubility did not lie within the range of this design space, and thus, the optimum GBES structure was not identified.

Low water temperature and high water hardness adversely affect the cloth detergency process by many mechanisms, including the limitation of the surfactant's solubility. Therefore, under these stressed conditions, the solubility characteristics of centrally located hydrophile surfactants may result in higher detergency performance compared to $C_{1214}EO_2$ AES, which is commonly incorporated into commercial home detergents. In addressing this possibility, we conducted detergency testing on the two best performing GBES structures, $C_{1214}EO_2$ AES and $C_{11.5}$ LAS, as previously described, except at low temperature (40°F) and high water hardness (300 ppm hardness as $CaCO_3$). The results in Table 1 lead to several conclusions. First, in all test systems, the C_8EO_1 GBES outperforms the $C_7EO_{1.5}$ GBES, thus indicating that even under these stressed conditions, the best performing GBES may have an even higher molecular weight structure than those tested. Also, the C_8EO_1 GBES gives enhanced oily soil removal under stressed conditions, but both GBES structures revealed inferior detergency performance on sebum- and dust-soiled cotton and permanent press. While no conclusive explanation for this observation has been formed, surfactants similar in structure to GBES find use in enhanced oil recovery applications where low interfacial tensions are required (7). These low interfacial tensions occur under conditions of high electrolyte content in the water, which is similar to the high hardness conditions studied here. Low interfacial tensions have been linked to enhanced detergency on oily soils (2).

TABLE 1

Cloth Detergency [reflectance (Rd) washed–Rd soiled] Under Stressed Conditions[a]

Surfactant	Sebum cotton	Sebum permanent press	Mineral oil permanent press
$C_7EO_{1.5}$ GBES	6.1	9.0	10.7
C_8EO_1 GBES	7.0	11.5	13.2
AES	12.2	14.7	8.5
LAS	4.0	7.0	10.9

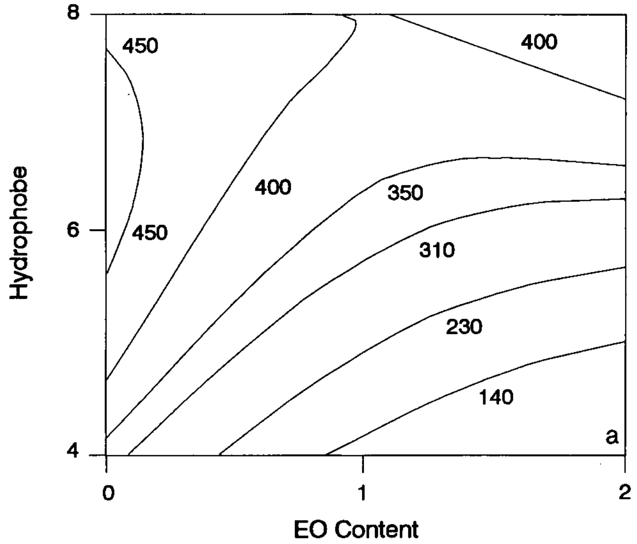
[a] Abbreviations: AES, alcohol ether sulfate; LAS, linear alkylbenzene sulfonate; EO, ethylene oxide; GBES, glyceryl *bis*ether sulfates.

Foaming. Figure 3 shows GBES's high foaming characteristics at 300 ppm and 1% surfactant concentration, both with and without added soil. The optimum overall foaming performance occurred with GBES structures incorporating a medium carbon chainlength (C_{5-7}) and a low degree of ethoxylation. A slightly shorter hydrophobe delivered maximum foaming at the higher surfactant concentration. Except for the low foam stability upon soil addition, exhibited by the high-molecular weight GBES at 300 ppm, the GBES structure displaying maximum foaming did not shift significantly with the addition of soil to the test system. The results (especially at 1% concentration) also revealed a trend similar to the hydrophile–lipophile balance concept (1) wherein similar surfactant performance occurred among GBES structures containing similar ratios of EO to hydrophobe carbon number. This appears graphically as a diagonal region of maximum foaming in the design space.

The C_6EO_1 GBES foamed comparably to its $C_{1214}EO_2$ AES counterpart in all tests except under the conditions of low surfactant concentration with no soil added. Overall, the GBES structures displayed high foaming characteristics with greater resistance to foam breakdown in the presence of soil as compared to $C_{1214}EO_2$ AES and $C_{11.5}$ LAS.

Wetting. A surfactant's wetting speed often determines its applicability to textile and fiber processing; faster wetting is usually preferred. Figure 4 reveals the textile wetting performance of GBES as a function of structure. The concentration needed to wet a cotton tape in 12.5 s measures the wetting speed; a lower concentration indicates faster wetting. Figure 4 bears many similarities to Figure 3, wherein a diagonal band of optimally performing structures stretches across the design space. A possible explanation for this observation lies with the balance between two factors that influence wetting speed (2), molecular size and surface activity. On the one hand, smaller (lower-molecular weight) molecules diffuse more rapidly in solution, leading to faster wetting, but their lower surface activity can moderate this effect. On the other hand, higher-molecular weight molecules are more surface-active, thus increasing wetting speed, but their slower diffusion can moderate this effect. As the result of these two influences, a range of GBES structures produced the fastest wetting speeds, the C_6EO_0 GBES because of its compact size, and the C_8EO_1 GBES (the actual structures tested) because of its enhanced surface activity.

Comparing the wetting performance shown by $C_{1214}EO_2$ AES to the corresponding C_6EO_1 GBES reveals similar wetting abilities. However, GBES structures



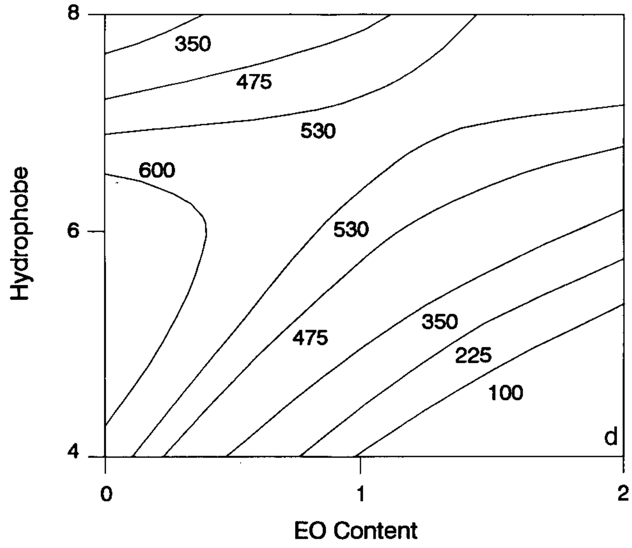
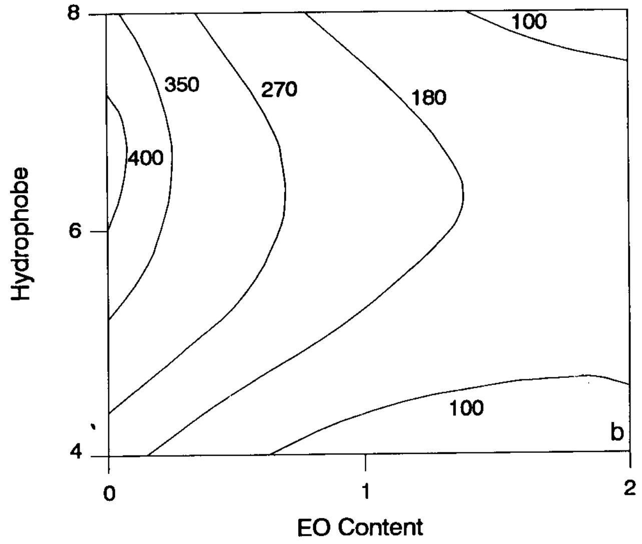
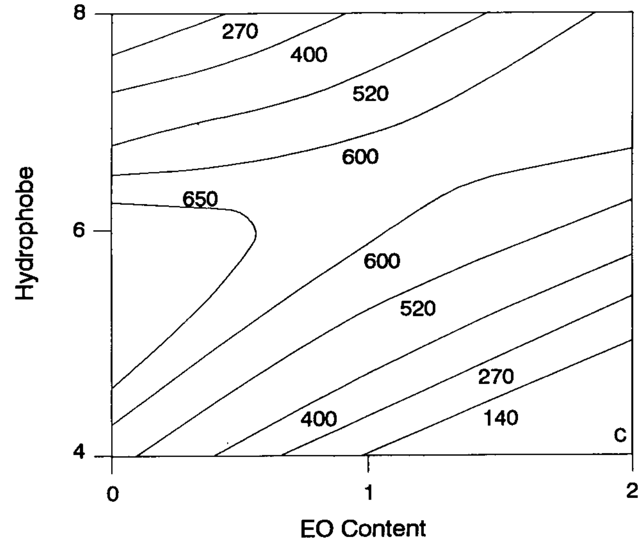


FIG. 3. (a) Foaming performance of GBES (mL of foam) at 300 ppm with no soil added as a function of hydrophobe chainlength and EO content: $C_{11.5}$ LAS = 590, $C_{1214}EO_2$ AES = 450. (b) Foaming performance of GBES (mL of foam) at 300 ppm with soil added as a function of hydrophobe chainlength and EO content: $C_{11.5}$ LAS = 325, $C_{1214}EO_2$ AES = 150. (c) Foaming performance of GBES (mL of foam) at 1% with no soil added as a function of hydrophobe chainlength and EO content: $C_{11.5}$ LAS = 450, $C_{1214}EO_2$ AES = 475. (d) Foaming performance of GBES (mL of foam) at 1% with soil added as a function of hydrophobe chainlength and EO content: $C_{11.5}$ LAS = 500, $C_{1214}EO_2$ AES = 500. See Figure 2 for abbreviations.





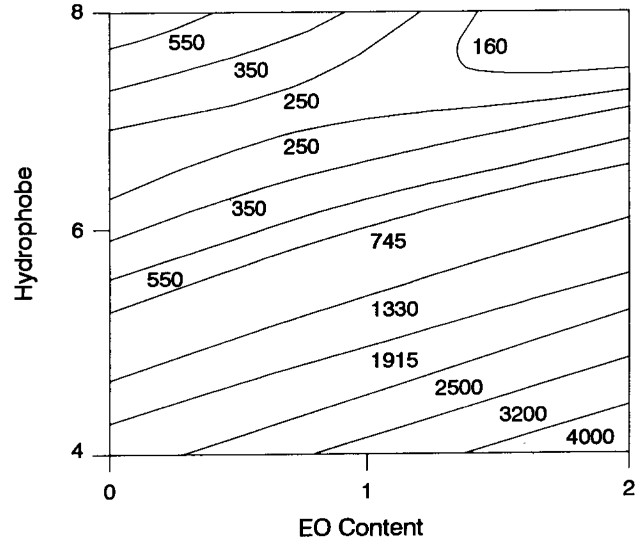


FIG. 4. Wetting performance of GBES (ppm) as a function of hydrophobe chainlength and EO content: $C_{11.5}$ LAS = 500, $C_{1214}EO_2$ AES = 500. See Figure 2 for abbreviations.

within the region of fastest wetting showed wetting speeds significantly faster than $C_{1214}EO_2$ AES or $C_{11.5}$ LAS. This probably stems from GBES's highly symmetrical structure that allows both hydrophobic tails to "fold back" on themselves, thus resulting in a smaller effective molecular size relative to the corresponding linear structure. This leads to faster wetting.

ACKNOWLEDGMENT

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