Committee for the second consecutive year did not accept the procedure for isolated *trans*-isomers as a tentative method.

After considerable discussion of this situation, a modification of the diazomethane method described by Chipault for esterification of fatty acids on a small scale was adopted as the most satisfactory procedure by unanimous vote of the seven members present (5).

An abbreviated version of the experimental procedure will be incorporated into the method for isolated *trans*-isomers and, along with the changes to make the method directly applicable to long-chain fatty acids where the *trans* content is above 15%, will be revised and resubmitted to the Uniform Methods Committee. With these two additions the approved method is as published with last year's report (1).

Other Committee Discussions and Future Planning. Discussions of future activities of the Spectroscopy Committee were centered on investigations of the recently published methods involving the near-infrared region. Suggestions were made by various members that the committee collaboratively investigate near-infrared method for hydroxyl number, for epoxy value, and for direct determination of *cis*-isomers and the combination of such values with the established method for *trans*-isomers to afford an infrared method for total unsaturation. It was decided that recommended procedures for these determinations would be sent to the chairman and that during the coming year one or two of these methods be collaboratively tested for possible recommendation for establishment as tentative official methods.

Cooperation with Coblentz Society

At a meeting in New Orleans, April 21, 1959, the Spectroscopy Committee decided that cooperation with the Coblentz Society in the collection and dissemination of infrared spectra would provide the simplest and most feasible means of making infrared spectra of fatty acids and their derivatives available to any member of the Society and to the entire fat and oil industry. It was decided that spectra should be submitted to the chairman of the Spectroscopy Committee, who is already acting as one of the collectors of infrared spectra for the Coblentz Society. The Society has endorsed this plan and furthermore has established a procedure whereby oil chemists can obtain a packet of the reproduced spectra of fatty acids and their derivatives without the requirement of subscribing to all the spectra issued by the Society. However, to date, no spectra have been received for submission to the Coblentz Society. The committee again urges all members throughout the A.O.C.S. to participate in this activity. Spectra may be submitted to the chairman of the Spectroscopy Committee, and details of the plan, requirements for spectra to be submitted, etc., may be obtained from him.

Acknowledgment

The Spectroscopy Committee is aware that, particularly in the collaborative testing program, it is indebted to several individuals for assistance in making spectral measurement and computations and in offering suggestions. The services of these individuals is again gratefully acknowledged. The chairman, in particular, wishes to acknowledge the considerable assistance of Miss Elizabeth R. McCall in compiling, recomputing, and arranging the collaborative data and of E. Fred Schultz Jr. for the statistical analysis included in this report.

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Comparison of Fatty Acid Esters of Sucrose and of Polyoxyethylene in Built Detergent Compositions[1]

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The addition of sucrose monotallowate to an aqueous solution of alkanolamine alkylaryl sulfonate lowers the total active-agent content required for the formation of liquid crystals. In contrast, the addition of polyoxyethylene esters of fatty acids to the alkylaryl sulfonate solution increased the total amount of active agent required for the formation of liquid crystals. The deaggregating effect of the ethylene oxide-derived nonionics was reflected in reduced foam and detergency for combinations of these nonionics and alkylaryl sulfonate. Foam and detergency remained at a high level with combinations of sucrose monotallowate and alkylaryl sulfonate. Higher hydrophile-lipophile balance (HLB) values were obtained with the sugar esters than with the polyoxyethylene nonionics. The results were examined in terms of Winsor's theory of intermicellar equilibria.

AN EXTENSIVE body of literature has been developed concerning the influence of cryoscopic forces on the properties of detergent solutions. The term "cryoscopic forces" as used here refers to the forces of cohesion and repulsion between amphipathic molecules that determine the degree of packing of these molecules in surface films and micelles.

Solutions of sodium lauryl sulfate give expanded monolayers. The addition of lauryl alcohol results in a condensed monolayer at the water-air interface, as evidenced by the tremendous increase in surface viscosity (1). The lauryl alcohol addition enhances foam stability (2) and detergency. Similar effects are observed upon the addition of fatty alkanolamides to solutions of sodium dodecylbenzene sulfonate (3).

Ross (4) presented evidence to the effect that amphipathic additives that stabilize foam lower the critical micelle concentration (CMC) of the detergent while antifoaming agents increase the CMC. Otherwise expressed, the foam stabilizer favors the aggregation of molecules in micelles or surface films while the antifoam has a deaggregating effect.

Concentrated detergent solutions containing a water-insoluble amphipathic component are frequently anisotropic or liquid crystalline. It is believed that this behavior results from the formation of large lamellar micelles (5).

There are several reasons for expecting improved detergency from combinations of surfactants and amphipathic molecules that promote close packing. These combinations give lower surface tensions, thus promoting both emulsification and displacement of oily soils. Solubilization is greatly enhanced. Lawrence (5) has recently proposed a cryoscopic theory of detergency.

Combinations of ethylene oxide-derived nonionics and anionic agents, particularly alkylaryl sulfonates, are used in a variety of applications ranging from liquid household detergents to insecticidal emulsions. The purpose of this investigation has been to determine whether there are differences, and the consequence of such differences, in the cryoscopic forces acting between these combinations and between mixtures of alkylaryl sulfonates and the sucrose-derived nonionics (6).

Experimental Methods

Materials. Ultrawet 60L is a 60% active alkanolamine salt of dodecylbenzene sulfonate in water, supplied by The Atlantic Refining Company. Oronite D60 is 60% sodium dodecylbenzene sulfonate, 40% sodium sulfate, supplied by the Oronite Chemical Company. PEG400-, PEG600-, and PEG1000-monostearate were obtained from the Kessler Chemical Company. The product name indicates the approximate average molecular weight of polyoxyethylene esterified with one mole of commercial stearic acid. Sterox CD, an ethoxylated tall oil, was obtained from the Monsanto Chemical Company. Span 60, sorbitan monostearate, and Arlacel 85, sorbitan sesquioleate, were supplied by the Atlas Powder Company.

The sucrose monoesters were prepared by the alcoholysis of 0.37 mole of methyl ester of the fatty acid with 1.1 mole of sucrose in 1,275 ml. of dimethylformamide in the presence of 7.5 g. of potassium carbonate plus 2.5 g. of activated alumina. The reaction was conducted with dry materials by refluxing for 6 hrs. at 95°C. and about 95 mm. Hg pressure. At the completion of the reaction the solution was filtered and partitioned between n-butanol and 10% saline solution. The butanol layer was washed three times with additional saline solution, distilled under vacuum to two-thirds its original volume, and filtered to remove salt. The solution was then distilled to dryness. The sugar esters were further purified by recrystallization from methyl ethyl ketone.

Saponification values found were 95.5 and 97.9 for sucrose monostearate and sucrose monotallowate, respectively. Theoretical values are 92.0 for the stearate and 93.5 for the tallowate.

The methyl tallowate was obtained from the Jasonols Chemical Corporation. The methyl stearate (m.p. 36–38°C.) was from Matheson, Coleman, and Bell.

TABLE I

Formation of Anisotropic Solutions with Equal Weights of 60% Alkanolamine Alkylaryl Sulfonate and Additive

Isotropic	Anisotropic
n-Hexanol Mineral oil Polyethylene glycol- tall oil condensate	n-Dodecanol Lauric diethanolamide Sucrose monotallowate

Note: At room temperature anisotropic crystals of PEG400 monostearate separated. Upon slight warming, the nonionic dissolved to an isotropic solution.

Anisotropy. The presence of liquid crystals was determined by examining appropriate mixtures in a polarizing microscope with the aid of a first-order red-retarding plate.

Foam. The method of Ross and Miles (7) was used to determine foam heights after 1 min. and after 5 min.

Detergency. Soil removal was determined by washing F.D.S. Artificially Soiled Cotton Cloth in the Launderometer at 55°C. All tests comprised a 15-min. wash of two 2 x 3-in. swatches of soiled cloth in 100 ml. of built detergent solution contained in a one-liter jar. This was followed by a two-min. rinse with 150 ml. of water. New York City tap water was used throughout. Reflectance measurements were made with a Hunter Multipurpose Reflectometer. Each result is the average value obtained with six swatches.

Test Solutions. The solutions used in the foam and detergency tests contained 0.030% of tetrasodium pyrophosphate, 0.096% of sodium tripolyphosphate, 0.015% of sodium silicate ($Na_2O : SiO_2 = 1 : 3.25$), 0.003% of CMC-CT low viscosity, 0.081% of sodium sulfate, and 0.0 to 0.075% of surfactant. Unless otherwise stated, all test solutions contained 0.075% of surfactant for a total built detergent concentration of 0.30%.

Anisotropy

An approximate indication of the tendency of additives to promote the formation of liquid crystalline solutions was obtained by mixing the additive with an equal weight of a 60% aqueous solution of alkanolamine alkylaryl sulfonate. The results of observations under the polarizing microscope are recorded in Table I.
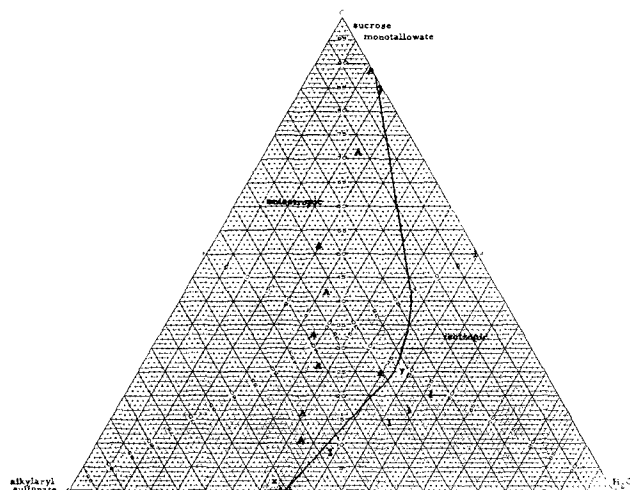

Fig. 1. Phase diagram for the system sucrose monotallowate-alkylaryl sulfonate-water.
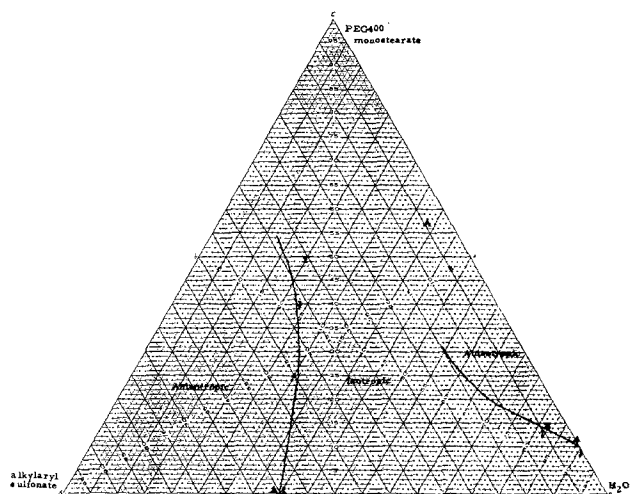
FIG. 2. Phase diagram for the system PEG400 monostearate-alkylaryl sulfonate-water.

Anisotropy was observed with lauric diethanolamide and lauryl alcohol, both of which are foam stabilizers. Mixtures containing n-hexanol and white mineral oil were inactive. These latter materials have some anti-foaming action.

Combinations containing ethylene oxide-derivatives of tall oil and stearic acid with the 60% alkanolamine salt of alkylaryl sulfonate were optically inactive. However the mixture of sucrose monotallowate and the alkylaryl sulfonate solution was found to be anisotropic.

Phase diagrams provide more conclusive evidence. Figure 1 is a triangular diagram for the system sucrose monotallowate-alkylaryl sulfonate-water. Starting from point x and proceeding to point y corresponding to the addition of sucrose monotallowate to the alkylaryl sulfonate solution, increasing amounts of water must be added for the solution to become isotropic. A similar effect is observed if a start is made with a solution of sucrose monotallowate in water and the alkylaryl sulfonate solution is added. This may be interpreted to mean that the tendency for close packing is enhanced by the use of combinations of alkylaryl sulfonate and sucrose monotallowate.

Figure 2 is a phase diagram for the ternary system PEG400 monostearate-alkylaryl sulfonate-water. Here the reverse effect is observed. The addition of PEG400 monostearate to an anisotropic solution of alkylaryl sulfonate leads to an isotropic solution. The addition of 60% of alkylaryl sulfonate to an anisotropic solu-
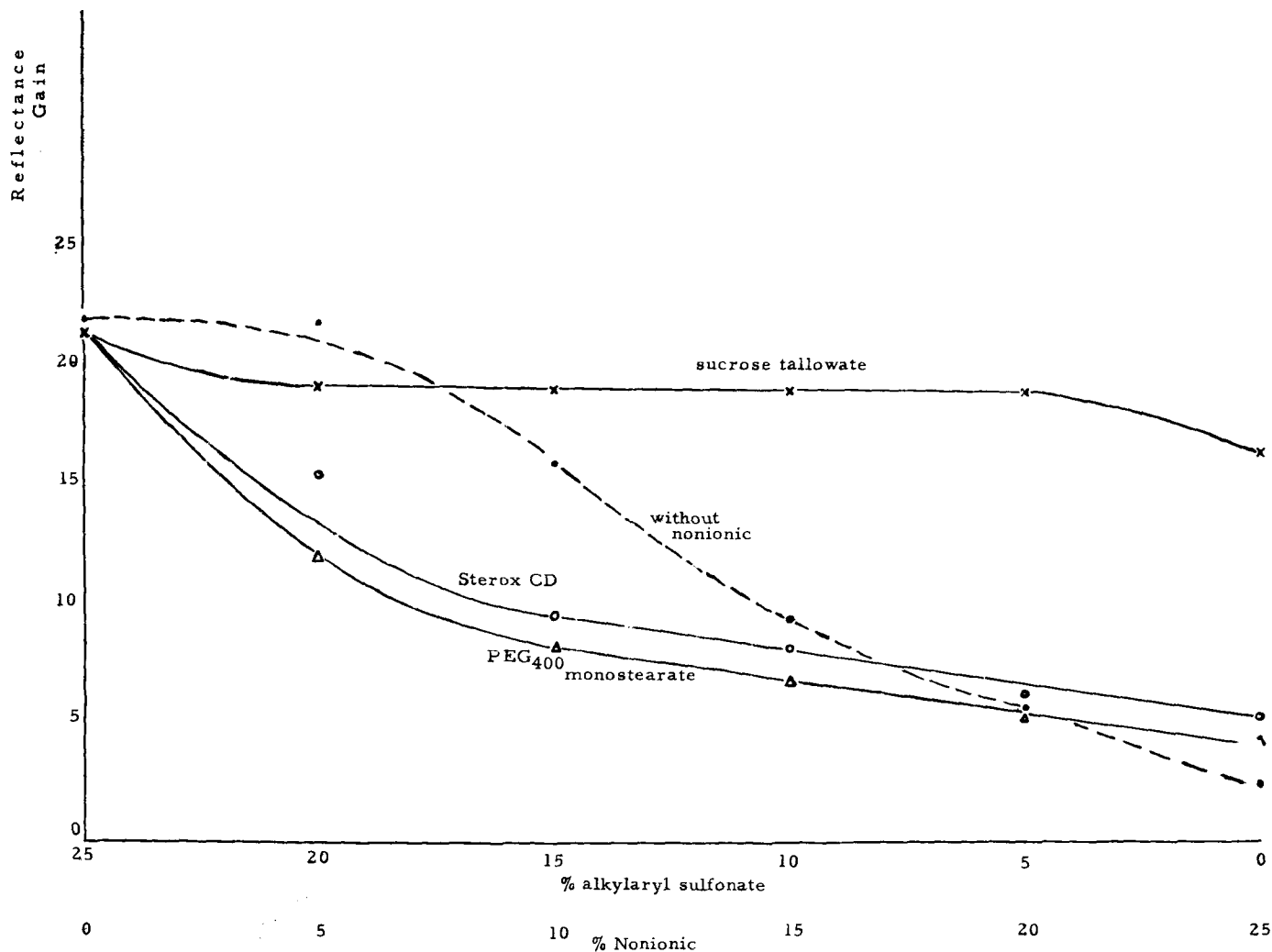

FIG. 3. Soil removal by built detergent compositions. Solutions contain 0.225% builder; ———— plus 0.075% total active agent; — — — — 0.075 to 0.00% alkylaryl sulfonate.
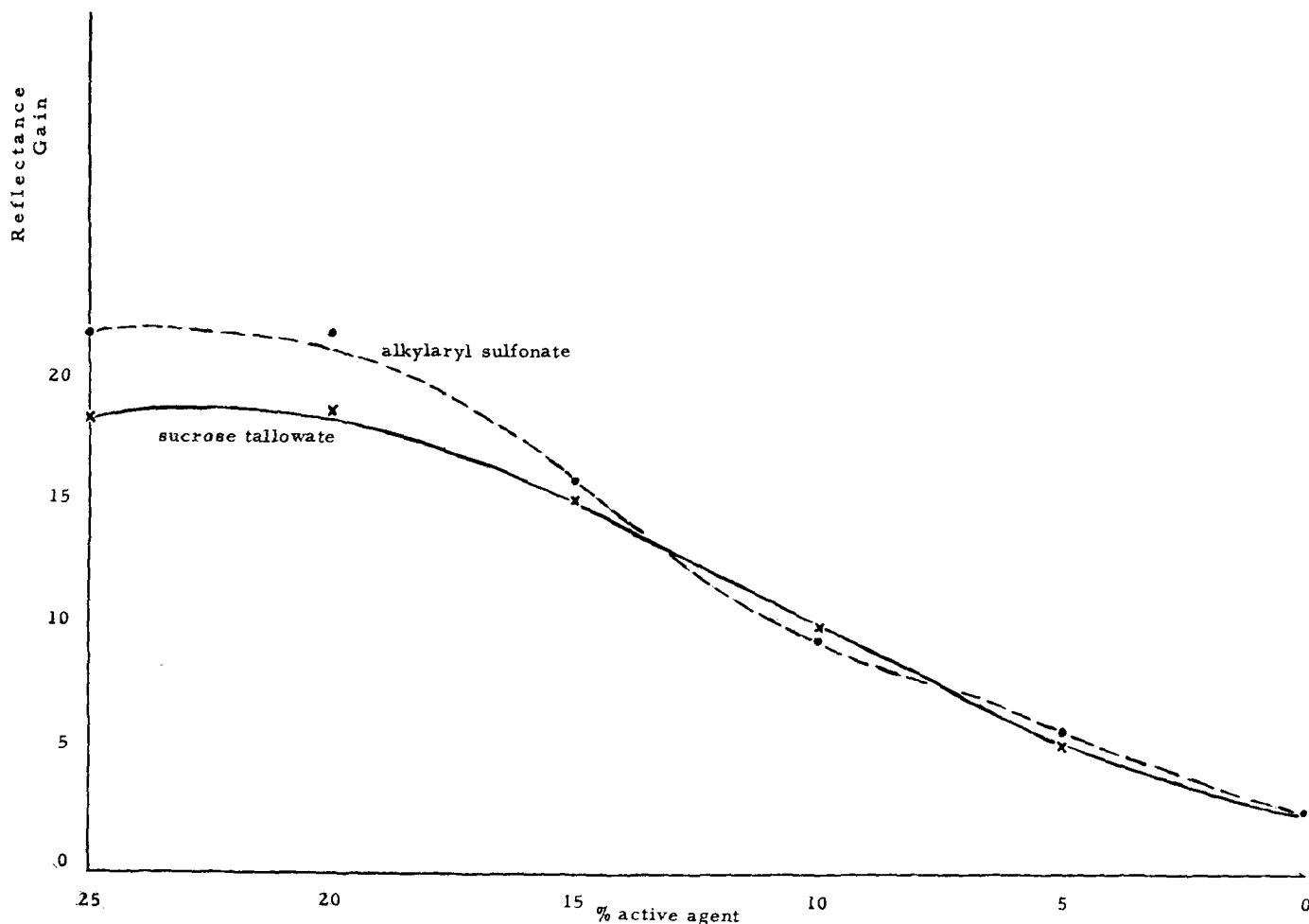
FIG. 4. Soil removal by built detergent compositions. Solutions contain 0.225% builder; ——— plus 0.075 to 0.00% sucrose monotallowate; — — — 0.075 to 0.00% alkylaryl sulfonate.

tion of PEG400 monostearate results in an isotropic solution. In both instances it is necessary to remove water to obtain an anisotropic solution.

These results suggest that PEG400 monostearate tends to expand the packing of alkylaryl sulfonate molecular aggregates. This should be evidenced by reduced detergency and foam. In contrast, sucrose monotallowate would appear to cause closer packing of the molecular aggregates.

Detergency

A heavy-duty detergent containing 25% of alkylaryl sulfonate was used to wash artificially soiled cotton. The effect of partial and complete replacement of the alkylaryl sulfonate by a nonionic surfactant is shown in Figure 3. The dashed line shows the reflectance gain when the quantity of alkylaryl sulfonate was reduced without replacement by a nonionic.

The results clearly show that the ethoxylated compounds which were examined have a depressing effect on detergency. In contrast, detergency remains fairly constant upon partial replacement of the alkylaryl sulfonate by sucrose monotallowate. Reflectance gains obtained with decreasing quantities of active agent (alkylaryl sulfonate or sucrose monotallowate) are compared in Figure 4.

Foam

Foam heights obtained with built detergents are shown in Figure 5. The solid lines refer to partial or complete replacement of the alkylaryl sulfonate by nonionic, with the total active agent constant at 25%. The dashed lines show the effect on foam height of decreasing the content of alkylaryl sulfonate without a corresponding addition of a nonionic.

It is evident from these results that the ethylene oxide-derived nonionic depresses the foam of the alkylaryl sulfonate composition. This is not the case when the sucrose ester is used for the substitution.

Krafft and Cloud Points

The Krafft temperatures of sucrose monoesters have not been reported previously. The Krafft temperature of both sucrose monostearate and sucrose monotallowate was found to be 49–50°C. by slowly warming 0.3% solutions until the disappearance of turbidity. This value could not be checked by cooling to the reappearance of turbidity because the solutions remain supersaturated for many hours.

Confirmation of the Krafft temperature for sucrose monostearate at 1.0% concentration was obtained by viscosity-temperature measurements. A sharp increase in viscosity occurred in the range 49–50°C. because of the increased concentration of sucrose monostearate

in solution. The method could not be used for sucrose monotallowate. This material gives viscous solutions at 1.0% concentration, even at room temperature. As the temperature is increased, the solution becomes more viscous and gelatinous. Viscosity measurements with these gelatinous solutions were not reproducible.

Above the Krafft temperature, solutions of sucrose monostearate and sucrose monotallowate become less viscous with a rise in temperature. The solutions are clear at the boil. If these sucrose esters have a cloud point, it is in excess of 100°C. In contrast it is necessary to condense stearic acid with about 20 moles of ethylene oxide to obtain a cloud point in excess of 100°C.

HLB Values

Hydrophile-lipophile balance (HLB) is a measure of the relative affinity of a surfactant for oil and water. A high HLB value implies a high affinity for water.

HLB values of 11.4 and 11.2 have been reported for sucrose monotallowate and sucrose monostearate, respectively (8). HLB values of 29 were obtained for sucrose monotallowate and 23 for sucrose monostearate. In all instances the method due to Griffin (9) was employed. In view of these differences our procedure is given in some detail.

In one series Span 60 was heated with a medium-viscosity mineral oil to 80°C. The sugar ester in water was heated to the same temperature and then added slowly to the oil phase with hand stirring. The emulsions were cooled under running tap water while hand stirring was continued. The emulsions were stored at room temperature in closed jars. All of the emulsions contained 10% of oil, 1% of emulsifier, and 89% of water. The HLB value of the sugar ester was calculated from that ratio of sucrose ester and Span 60 that gave the most stable emulsion. An HLB value of 4.7 for Span 60 and a required HLB value of 12 for the preparation of a mineral oil-in-water emulsion were used in calculating the values for the sugar esters.

These HLB values were rechecked by emulsifying stearyl alcohol (required HLB value = 14), using Arlacel 85 (HLB = 1.8) as the lipophilic emulsifier. The prepared emulsions were aged at 43°C.

Similar HLB value determinations were made for a series of polyoxyethylene derivatives of stearic acid. Results were as follows: PEG400 monostearate, 13; PEG600 monostearate, 14; PEG1000 monostearate, 18.

Various approximate methods of calculation were examined to check these experimental results. Davies (11) reported that HLB values can be consistently calculated by group numbers. Pertinent values by Davies for hydrophilic groups are: ester, 2.4; hydroxyl, 1.9; ether, 1.3; and ethoxy, 0.33. For the hydrophilic methyl or methylene group the value is −0.475. The relation is

HLB = Σ hydrophilic group numbers

+ n (CH$_2$ group number) + 7,

where n is the number of CH$_2$ and CH$_3$ groups.

The HLB value for sucrose monostearate calculated from group numbers is 18.5. One would expect a somewhat higher value since an ether group was used in the calculation, but a hemi-acetal is actually present. The latter is a stronger dipole and should have a larger group number.

Surprisingly the Davies method fails completely when applied to the polyoxyethylene derivatives of stearic acid. Comparison is made in Table II with an

TABLE II
Calculated HLB Values

	HLB Values	
	Davies	Griffin
PEG400 monostearate	7	13
PEG600 monostearate	8	15
PEG1000 monostearate	11	17

approximate method of calculation due to Griffin (11)

HLB = 20 (1−S/A)

where S is the saponification number of the ester and A is the acid number of the acid. In both methods of calculation an equal weight of stearic and palmitic acid in the hydrophobe has been assumed. Experimental values are in reasonable agreement with the approximate values of Griffin.

Since experimental HLB values obtained with the polyoxyethylene esters are in accord with estimated values, the results obtained with the sugar esters by the same methods should also be reasonably accurate. Further, the higher cloud-point of the sugar esters as compared with PEG1000 monostearate suggests a higher HLB value. The cloud point of PEG1000 monostearate is 95°C.

Significance of HLB Values

The reason for stressing HLB values is that these values can provide information concerning the forces involved in the formation of lamellar micelles containing mixtures of surfactants.

According to the theory of intermicellar equilibria developed by Winsor (12), the transition from a normal spherical micelle to a lamellar micelle requires a decrease in the interaction between water and the amphipathic molecules present in the micelle. Increased surfactant concentration is known to favor the formation of lamellar micelles. This is explained on the basis of a reduced activity of water. The introduction of a fatty acid or a fatty alcohol into a micelle containing ionic surfactant molecules will promote the formation of lamellar micelles because these small polar groups interact less strongly with water than do the ionic groups.

In general, it can be expected that amphipathic molecules with low HLB values will enter micelles composed of ionic surfactant molecules to promote the formation of lamellar micelles and anisotropic solutions. Since the polar groups of amphipathic molecules with high HLB values would interact strongly with water, the failure of the ethoxylated compounds to promote formation of anisotropic solutions is understandable.

However it is necessary to explain the action of the sugar esters, with their high HLB values. Hydroxyl groups present in the sugar esters are known to interact more strongly with water than ether linkages. This is confirmed both by the absence of a cloud point and by the high experimental HLB values.

Two explanations appear possible for the reduced interaction of the micellar surface with water molecules. Ion-dipole interaction between the sulfonate ion and an hydroxyl group is much stronger than between the ion and an ether group. Satisfaction of
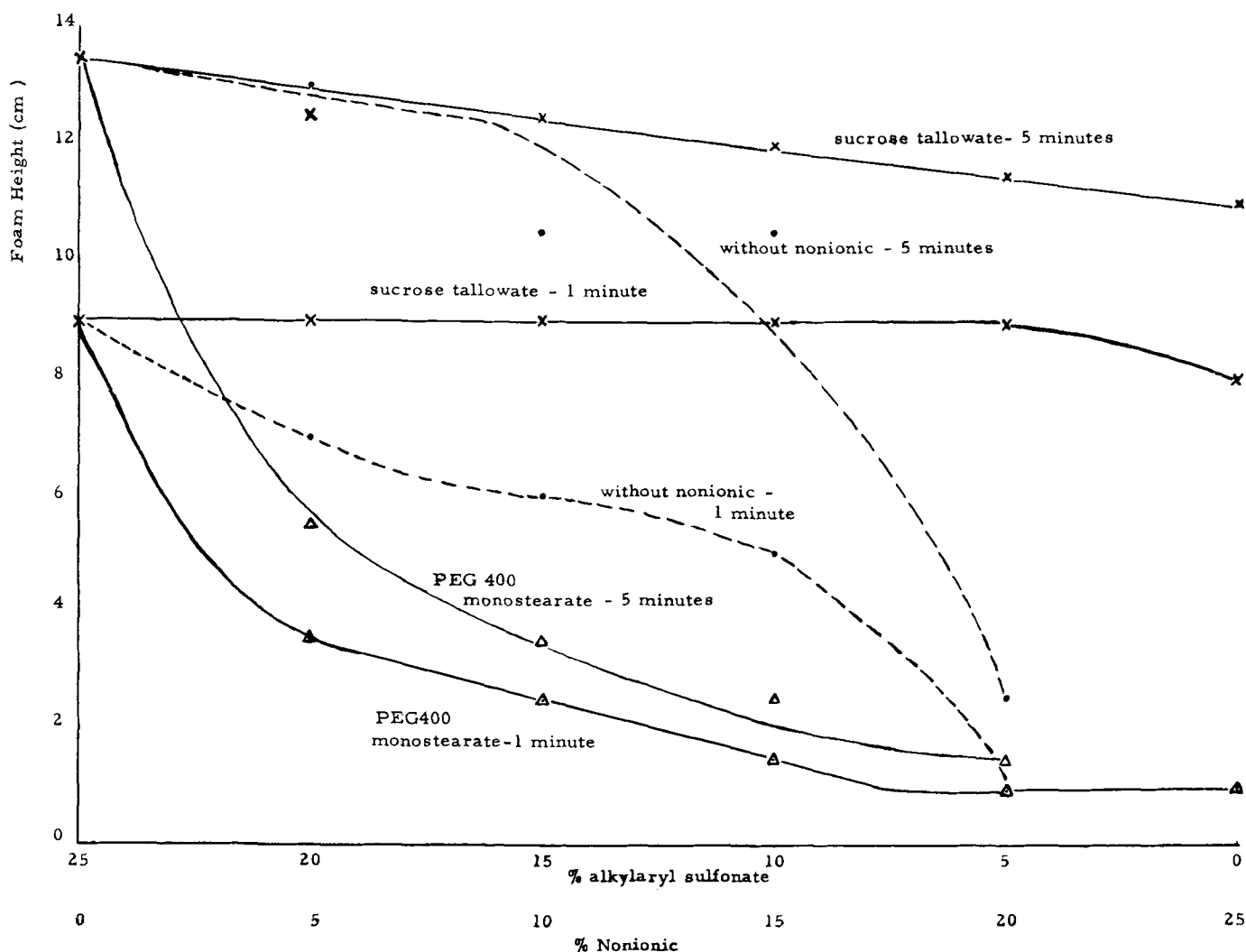
FIG. 5. Ross and Miles foam heights after one minute and five minutes at 45°C. with built detergent compositions. Solutions contain 0.225% builder; ——————— plus 0.075% total active agent; — — — — 0.075 to 0.00% alkylaryl sulfonate.

electronic forces by such interaction will reduce the force of interaction between the ion-dipole and water molecules. An alternative explanation is to ascribe reduced interaction with water to a screening of the sulfonate ion by the bulky sucrose group.

Conclusions

The sugar esters of long-chain fatty acids promote the aggregation of alkylaryl sulfonate molecules, as evidenced by the formation of anisotropic solutions at greater dilutions. Water-soluble polyoxyethylene derivatives of these fatty acids have the opposite effect.

The deaggregation effect of the ethylene oxide derivatives on alkylaryl sulfonate molecules is accompanied by reduced foam and detergency. These properties remain high in the presence of the sucrose esters.

HLB values observed for the sucrose esters are much higher than those obtainable by condensing ethylene oxide with the same hydrophobe. The fact that the sugar esters promote formation of liquid crystals, and presumably lamellar micelles, when combined

with alkylaryl sulfonate can be explained on the basis of ion-dipole interaction or steric factors.

Acknowledgment

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