Effect of Water-Soluble and Water-Insoluble Long-Chain Polar Additives on Micellar Solutions of Sodium Dodecylbenzene Sulfonate

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Additions of long-chain polar compounds to aqueous solutions of sodium dodecylbenzene sulfonate resulted in the separation of a liquid-crystalline phase. This was first observed after the addition of 0.2 to 0.25 mole of water-insoluble polar compound per mole of anionic surfactant. It was found necessary to add 0.6 to 2 moles of water-soluble long-chain polar compound per mole of anionic surfactant before a separate liquid-crystalline phase could be observed. At concentrations below that required for liquid-crystal formation, additions of PEG 400 monostearate to aqueous solutions of sodium dodecylbenzene sulfonate resulted in a steady decrease in the Krafft temperature, a viscosity minimum, and a surface-tension minimum. With sucrose monotallowate, similar results were obtained, except that a minimum was not obtained in the viscosity-concentration curve.

IMPORTANT CONTRIBUTIONS have been made by Lawrence (1, 2) and Winsor (3-6) concerning the effect of additions of water-insoluble long-chain polar compounds on the gross properties of aqueous solutions of ionic surfactants. Mixtures of water-soluble long-chain polar compounds and ionic surfactants have considerable commercial importance. Nonetheless there is a dearth of reported studies concerning the properties of solutions of such mixtures. Osipow and Snell (7) showed that sucrose esters of long-chain fatty acids promote the aggregation of dodecylbenzene sulfonate molecules, as evidenced by the formation of liquid crystals at greater water dilutions. Water-soluble polyoxyethylene derivatives had the opposite effect, and this was accompanied by reduced foam and diminished detergent action.

Experimental Methods

a. *Materials.* Ultrawet K is an 85 to 90% sodium dodecylbenzene sulfonate, containing 10 to 15% of sodium sulfate, supplied by The Atlantic Refining Company. PEG400 monostearate, PEG600 monostearate, and PEG600 distearate were obtained from the Kessler Chemical Co. The product name indicates the approximate average molecular weight of polyoxyethylene esterified with one or two moles of commercial stearic acid. Span 60, sorbitan monostearate, was supplied by the Atlas Powder Company. Myverol 18-00, glyceryl monostearate, was obtained from Distillation Products Industries. Archer-Daniels-Midland supplied the n-octadecanol, Aldol 65.

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 1275 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 six hr. 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 Corp. The methyl stearate (m.p. 36–38°C.) was from Matheson, Coleman, & Bell.

b. *Appearance of Liquid Crystals.* A concentrated solution of sodium dodecylbenzene sulfonate was prepared by dissolving 200 g. of Ultrawet K in distilled water and diluting to one liter. This solution was divided into 10-g. portions in which varying amounts of the nonionic agents were dissolved. These solutions were stored in stoppered test tubes at either 43°C. or 70°C. for three days, with periodic observations after shorter aging periods. Solutions containing n-octadecanol, glyceryl monostearate, sorbitan monostearate, and sucrose monostearate were aged at 70°C., to avoid crystallization of these high-melting additives. Solutions containing PEG400 monostearate, PEG600 monostearate, PEG600 distearate, and sucrose monotallowate were aged at 43°C. When a second phase formed after aging, it was recovered and examined in a polarizing microscope for anisotropy. Additional test series were then prepared to obtain more precise information as to the minimum concentration of additive required for the first appearance of liquid crystals.

c. *Disappearance of Foam.* The solutions used in (b) were shaken by hand and observed for foaming.

d. *Surface Tension.* The Du Nouy interfacial tensimeter was used to measure surface tension at 26–28°C.

e. *Viscosity.* Cannon-Fenske viscosity pipettes were used to measure the viscosity of the solutions at 100°F.

f. *Krafft Temperature.* The test solutions were alternately cooled and warmed until the first appearance or disappearance of turbidity. The sequence was repeated as many times as was necessary to obtain reproducible results.

Results

a. The appearance of solutions of sodium dodecylbenzene sulfonate and the water-insoluble nonionic compounds—n-octadecanol, glyceryl monostearate, and sorbitan monostearate—agreed with previous descriptions of similar combinations (1, 2). The solutions were clear at low concentrations of additive. With further additions, a second phase formed which was anisotropic. As the concentration of additive was increased the proportion of anisotropic phase increased until practically the entire volume of the composition was composed of this phase. The proportion of anisotropic phase to the total volume then decreased with still further additions of the nonionic material.

With the more water-soluble nonionic compounds, an anisotropic second phase also formed. However, considerably higher concentrations of these additives were required. In some instances up to about 50% of the total volume of the test mixture consisted of the anistropic phase. Presumably, if the concentration of the water-soluble additives had been increased sufficiently, results would have been entirely analogous to those obtained with the insoluble nonionic additives. The molar ratio of additive to sodium dodecylbenzene sulfonate required for the first appearance of an anisotropic phase is shown in Table I.

TABLE I

Proportion of nonionic polar additive required for the first appearance of liquid crystals and for the disappearance of foam in a 20% aqueous solution of commercial sodium dodecylbenzene sulfonate

	Molar Ratio Additive to Sodium Dodecylbenzene Sulfonate	
	For first appearance of liquid crystals	For the disappearance of foam
n-Octadecanol	0.25	0.45
Glyceryl monostearate	0.23	0.49
Sorbitan monostearate	0.20	0.53
PEG600 distearate	0.61	0.25
Sucrose monostearate	0.61	0.47
Sucrose monotallowate	0.93	0.15
PEG400 monostearate	1.5	0.57
PEG600 monostearate	2.0	0.53

For the water-insoluble additives, 0.2 to 0.25 mole of additive per mole of anionic surfactant was required, in agreement with Lawrence (1, 2). Liquid crystals did not form with the water-soluble nonionics until 0.6 to 2.0 mole of nonionic was added per mole of sodium dodecylbenzene sulfonate.

b. It was observed that the solutions no longer foamed after the addition of from 0.15 to 0.57 mole of nonionic per mole of anionic surfactant, as shown in Table 1. Viscosity measurements were made only with PEG400 monostearate, PEG600 monostearate and sucrose tallowate. With these three additives cessation of foaming action coincided with a viscosity of approximately 200 centistokes. This suggests that the point of non-foaming may be a secondary effect that is related to the viscosity of the solution.

c. Fig. 1 and 2 show the effect on the Krafft temperature, surface tension, and the viscosity of additions of PEG400 monostearate and sucrose monotallowate to 20% (weight/volume) solutions of the commercial sodium dodecylbenzene sulfonate. Data on the effect of additions of octanol to Teepol, a secondary alkyl sulfate, are shown in Fig. 3 for comparison (2).

Both PEG400 monostearate and sucrose monotallowate lowered the Krafft temperature uniformly. With both additives, the surface tension fell to a minimum value and then increased with further additions of the nonionic. The surface tension minimum occurred at about 0.06 mole of PEG400 monostearate per mole of anionic surfactant, while only 0.007 mole of sucrose monotallowate per mole of anionic surfactant was required.

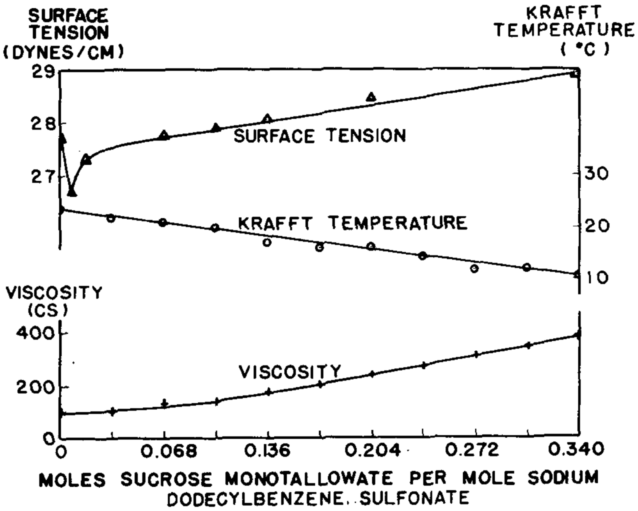

FIG. 1. Effect on the Krafft temperature, viscosity, and surface tension of additions of sucrose monotallowate to 20% aqueous solutions of commercial dodecylbenzene sulfonate.

In comparing these surface tension curves with the corresponding curve for the water-insoluble nonionic shown in Fig. 3, it should be noted that for the additions of the water-soluble nonionics, liquid crystal formation occurred at concentrations of nonionics considerably in excess of those shown in the curves. The corresponding surface tension curve in Fig. 3 shows a steady decrease in surface tension beyond the point of liquid-crystal formation, followed by an increase in surface tension and then a decrease, with further additions of octanol. Liquid-crystal formation occurred at about 0.2 mole of octanol per mole of anionic surfactant.

The viscosity curve for the addition of PEG400 monostearate to sodium dodecylbenzene sulfonate passed through a minimum at 0.15 mole of additive per mole of anionic surfactant. A similar minimum was found with additions of PEG600 monostearate to this anionic surfactant. This system was not ex-

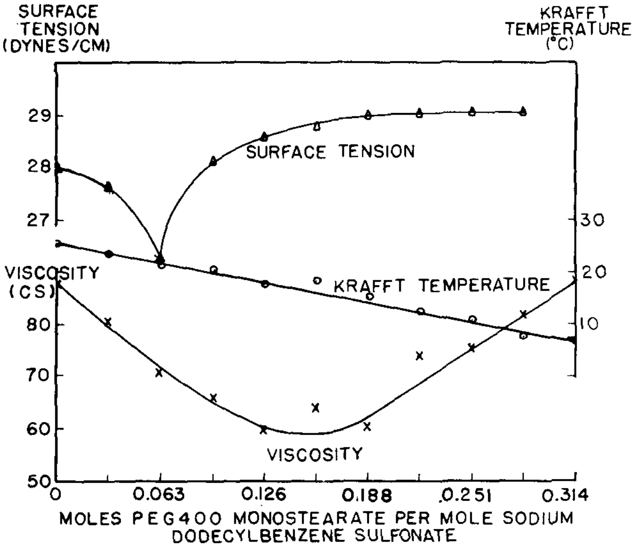

FIG. 2. Effect on the Krafft temperature, viscosity and surface tension of additions of PEG400 monostearate to 20% aqueous solutions of commercial dodecylbenzene sulfonate.

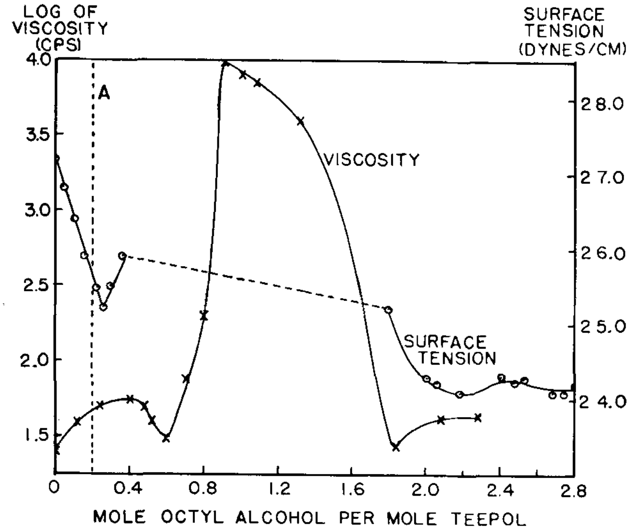

FIG. 3. Effect of n-octanol upon the viscosity and surface tension of 36% Teepol at 25° C. (2)—estimated values. A is the concentration corresponding to the first appearance of liquid crystals.

amined experimentally in sufficient detail to justify inclusion here. With sucrose monotallowate there was no viscosity minimum possibly due to the inherently high viscosity of aqueous solutions of sucrose monotallowate alone. The viscosity curve for octanol shows a secondary maximum at the point where liquid crystals appear, followed by a minimum, and then a large increase in viscosity to a maximum, with further additions.

Discussion

It has been shown that water-soluble nonionic surfactants, similar to their water-insoluble counterparts, form liquid crystals in aqueous solutions of sodium dodecylbenzene sulfonate. However, with essentially the same hydrophobic group, considerably higher molar concentrations of the soluble additives were required for the first appearance of liquid crystals.

The data show that the additions of nonionic polar compounds to solutions of sodium dodecylbenzene sulfonate result in substantial alterations in the properties of these solutions. The changes observed provide background information that may be helpful in the formulation of liquid detergents. Speculations of a more fundamental nature have not been presented, because of the complexities of these systems. There is insufficient knowledge of the micellar properties in concentrated solutions of even the most simple systems. When such information becomes available, these data may provide greater insight into the effect of nonionic polar compounds on micellar properties in concentrated solutions.

Acknowledgment

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Passive Cutaneous Anaphylaxis in the Detection of Seed Antigens of *Ricinus Communis* (Castorbean)

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The phenomenon of passive cutaneous anaphylaxis in guinea pigs was shown to be applicable in the laboratory determination of residual antigenicity in fractionated and chemically treated castor-seed proteins. Six protein fractions obtained by paper-strip electrophoresis of castor-seed protein were shown to be antigenic.

Castor-seed meal which had been cooked 20 minutes at 100°C. in $Ca(OH)_2$ solution at pH 12.4 was shown to retain some of its original antigenicity, while meal cooked for 32 minutes under the same conditions of pH and temperature would not elicit the P.C.A. reaction in guinea pigs sensitized with rabbit antiserum to castor-seed protein.

WHEN BLOOD from an allergic human is transfused into a non-allergic human the recipient frequently becomes temporarily allergic to the antigen responsible for hypersensitivity in the donor (1). If blood serum from the allergic indi-

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