Nonbleach Process for the Purification of Palm C16–18 Methyl Ester Sulfonates

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ABSTRACT: There has long been interest in methyl ester sulfonates (MES) derived from natural or renewable sources, such as palm oil, with considerable effort focused on process development. A major drawback with current process technology is the formation of dark brown impurities that create aesthetic and odor issues in the final product. These issues are usually addressed by bleaching rather than by chemical purification. This paper reports on a simple yet highly effective nonbleach, two-step process for purifying palm C16–18 potassium methyl ester sulfonates. The first step comprises addition of water to the impure surfactant mixture. Preferably, the temperature of the system is maintained above the Krafft point of the surfactant, thereby completely solubilizing the surfactant and associated impurities. Once completely dissolved, the surfactant mixture is allowed to cool, and the potassium-neutralized methyl ester sulfonate precipitates out selectively. In the second step, the purified surfactant is recovered by gravity- or pressure-filtration or by centrifugation, followed by drying. The process significantly improves C16–18 MES analytical purity and color without raising safety or environmental concerns. It also allows for the purification of products derived from lower-grade methyl esters, resolves odor issues, and does not require use of substantial amounts of solvent such as methanol.

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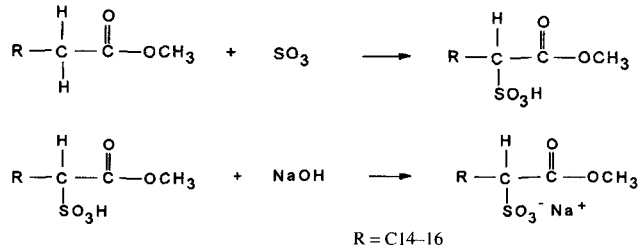
KEY WORDS: Alkali metal methyl ester sulfonate, bleach, centrifugation, color, filtration, Krafft point, methanol, methyl ester sulfonate, purification, solubilization.

Aggressive palm oil development programs in Malaysia and Indonesia are likely to make C16–18 methyl ester sulfonates (MES) increasingly affordable (1,2). In principle, manufacturing MES from palm oil is straightforward (Scheme 1). Transesterification of the oil with methanol results in methyl esters that can be purified by distillation; sulfonation of them produces α-sulfonic acid methyl esters that can then be neutralized with a suitable base to yield the desired MES surfactants (3,4). In practice, MES processing is complex, mainly because the sulfonation step requires a stoichiometric excess of SO_3. The excess SO_3 is necessary because the desired sulfonation reaction proceeds *via* one or more intermediates that



SCHEME 1

require two moles of SO_3 per starting methyl ester (5,6). Thus, molar excesses of 15–30% SO_3 and temperatures as high as 195°F (~90°C) are employed in industry to ensure good reaction rates and yields. The harshness of these conditions results in some degree of charring, and unpurified MES is typically dark in color. Moreover, the dark-colored impurities tend to be substantially water-soluble, and there is no convenient method for separating them from the desired surfactant. Harsh reaction conditions also promote the formation of α-sulfo fatty acid salts, di-salts, that originate from hydrolysis of MES precursors during the manufacturing process. Di-salts do not form micelles easily and exhibit poor detergency (7).

Considerable effort has been expended over the past thirty years on processing techniques for making MES of improved color and chemical purity (8). Controlled use of bleach technology has proved effective for producing lighter color MES (9,10), while solvent technology, in combination with bleach, has helped improve final product MES-to-di-salt ratios. Lion Corporation (Tokyo, Japan) has developed a commercial process that utilizes a combined bleaching and reesterification step in which hydrogen peroxide provides the desired color benefits, and where methanol is used to esterify di-salt (11,12). The result is MES of excellent color and of low di-salt content (13). Lion's process represents a long-sought manufacturing breakthrough, but it is not without issues. The process uses bleach in an environment where many of the molecular species, including colored impurities, have yet to be identified. Bleach inherently adds complexity to the system and can have damaging effects. One concern is the potential for formation of α,β-unsaturated–γ-sultones by reaction of

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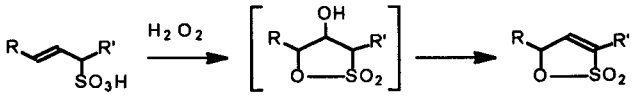

SCHEME 2

unsaturated impurities with hydrogen peroxide (Scheme 2) (14,15). α,β-Unsaturated–γ-sultones have previously been invoked as potential skin sensitizers (15). Plant safety represents another potential issue because of the large quantities of bleach and methanol that must be handled, and the need to continually flash off methanol for reuse (16).

Bleach processes raise issues, and this has led to consideration of alternative methods of color improvement. One of the more recently developed processes replaces bleach with an adsorbent treatment in substantially anhydrous methanol (17). Crude MES with dark-colored impurities is solubilized in methanol, and the dark-colored impurities are then separated with activated carbon; MES of improved color is then recovered. Unfortunately, this method of color improvement requires continual recycling or replacement of the adsorbent and solvent, and does not free MES surfactant from many of the co-produced impurities.

This paper reports on another alternative for obtaining MES of good color and chemical purity, based on physical property differences between the sodium and potassium salts of MES and associated by-products. A process that advantageously relies upon solubility differences between potassium-neutralized MES and other impurities has been discovered: an impure mixture, containing dark-colored impurities and C16–18 potassium methyl ester sulfonates (KMES), is formed in water to substantially solubilize the color bodies, and these are then separated from the surfactant by filtration or centrifugation at a temperature below the surfactant Krafft point.

EXPERIMENTAL PROCEDURES

Reagents. Commercially available palm stearin C16–18 methyl esters were obtained from the Procter and Gamble Company (Cincinnati, OH). The methyl esters comprise 65% C16 and 33% C18 chainlengths. The glycerin content is less than 0.25% and is removed prior to sulfonation by distillation. Iodine values (IV) (18) of most methyl ester starting materials are around 0.3; "low-grade" methyl esters, as described in this text, have IV ~1.9. Potassium hydroxide, methanol, and other chemical reagents are used as obtained without further purification. Unless otherwise specified, all purification procedures are performed with laboratory quantities of KMES (50–200 g C16–18 KMES).

General procedure for making KMES. A block diagram of the KMES manufacturing process is illustrated in Figure 1. Methyl ester sulfonation is carried out at 105°F (~40°C) in a Chemithon (Seattle, WA) annular falling-film reactor at a 5% by volume SO_3-to-air mixture with a 20–25% molar excess of SO_3 per methyl ester starting material (19,20). The sulfonated esters are digested at 175–195°F (~80–90°C) for 35–40 min to obtain high sulfonation yields (90–95%) and limit fatty acid di-salt precursors (21). The digested acid mix is reacted with 10–15% methanol by weight of the acid mix to further ensure high reaction yields (11,17). The α-sulfonic acid methyl esters are then neutralized with KOH, affording lighter surfactant compositions that are of lower viscosity than those generated by NaOH neutralization. As a result, KMES is easier to handle and isolate.

Purification by "hot" and "cold" processes. Deionized water is added to dried neutralized C16–18 KMES samples to form 5–20% surfactant mixtures at ambient temperature (~70°C, 21°C). In the cold process, the mixture is agitated for 10–15 min at ~70°F (21°C), leaving KMES mostly undissolved. In the hot process, the mixture is heated to ~130°F (54°C) and agitated for 10–15 min, and then cooled back to 70°F. Heating solubilizes surfactant and impurities into a single, coffee-colored translucent solution. Upon cooling, the solution becomes hazy, then opaque, and eventually separates into a two-phase heterogeneous mixture, comprising a white precipitate and a dark brown liquor.

Purification of C16–18 KMES via *the hot process by filtration.* Impure, dried C16–18 KMES is dissolved in distilled water to from a 10% solids mixture and heated to ~130°F (54°C) to completely solubilize the surfactant composition. The mixture is then allowed to cool to about 70°F (21°C) and eventually separates into two phases. The separation procedure is completed by gravimetric filtration on a Whatman #40 ashless filter paper (Maidstone, England). The water-soluble distillates (dark-colored liquids) are collected and evaporated to dryness. The water-insoluble (precipitated) fractions remain on the filter paper and are recovered. The collected precipitates are then redissolved in distilled water, and the purification process is repeated. Each purification procedure yields a product of visibly improved (i.e., lighter) color. Repeating the procedure affords a white final product, which is then dried at 70°F at reduced pressure.

Purification of C16–18 KMES via *the hot process by centrifugation.* Samples of impure C16–18 KMES powder are mixed in water, heated, and cooled as described above and purified with a Dupont (Wilmington, DE) Sorvall Model SS-3 automatic centrifuge at 11,000 rpm for 15 min at ~70°F (21°C). Centrifugation causes the composition to separate into two distinct layers: a lighter paste layer and a darker liquor layer. Separation is completed by recovering the paste layer. KMES compositions derived from high-IV methyl ester feedstocks (IV = 1.9) are purified by running the centrifugation procedure on the collected paste layer a second time.

Pilot-plant trials. The laboratory procedures for C16–18 KMES purification may be scaled up as illustrated next. Four lbs (1.8 kg) of dried palm C16–18 KMES are mixed into 36 lbs (16.3 kg) distilled water and heated to ~135°C (52°C). The mixture is agitated to completely solubilize the KMES and then cooled to room temperature and agitated for an additional 6 h. The agitation is stopped, and the mixture is allowed to settle overnight. The two-phase mixture is then

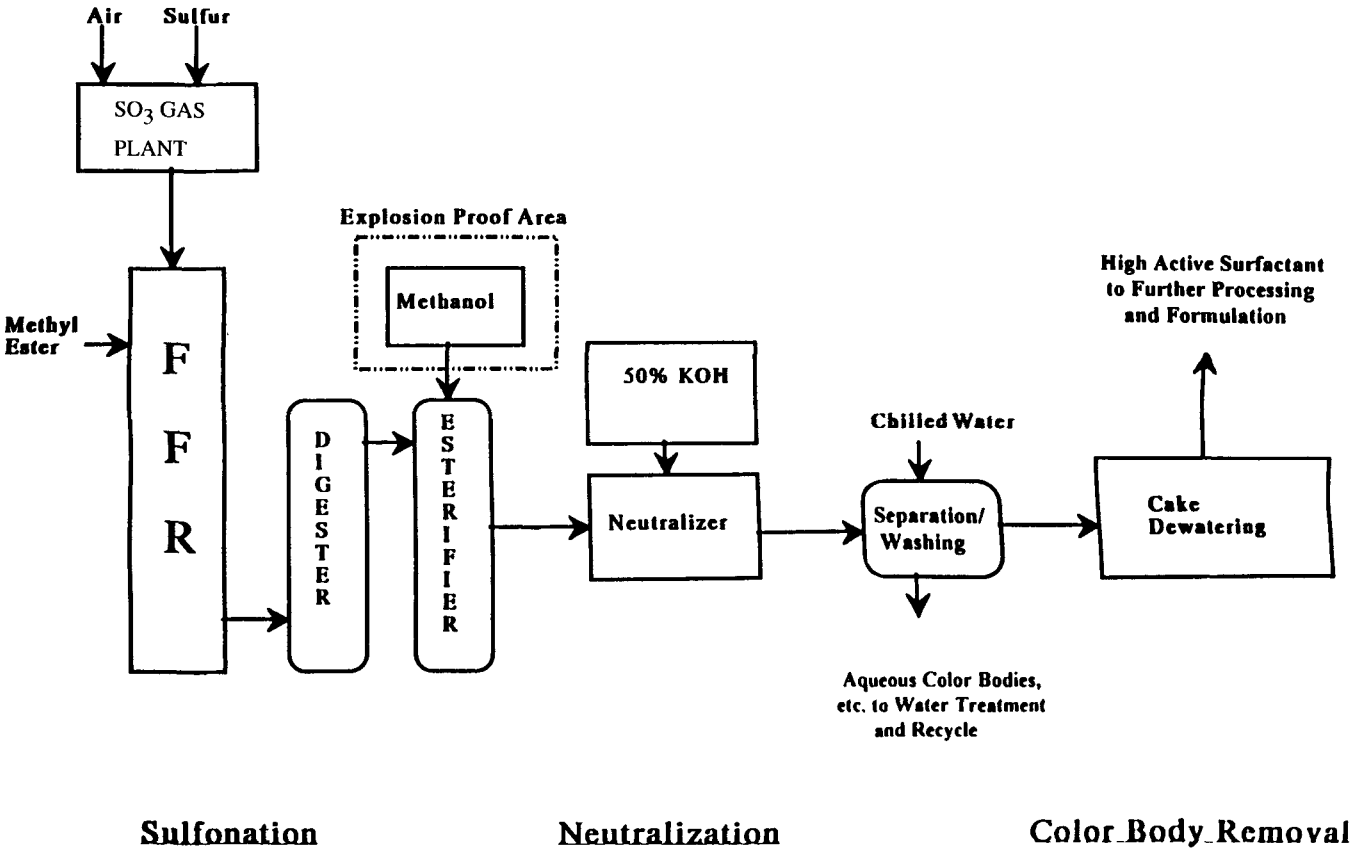

FIG. 1. Palm C16–18 postassium methyl ester sulfonates (KMES) process block diagram. FFR, falling-film reactor.

pumped through a Sperry type 41, size-10 plate and frame at a rate of 2–3 L/min. The press is fitted with nine filter cells, which measure 22 × 22 × 2.5 cm each. The filtering media consists of three separate layers of materials: (i) Whatman #54 filter paper, 25 cm in diameter with a porosity of 20–25 microns; (ii) a heavy-gauge (#70) fast filter paper with a porosity of 20 microns as a backup to the Whatman #54 filter paper; (iii) a canvas backing layer to protect the filter paper from tearing or bursting. After the heterogeneous mixture is pumped through the filtration apparatus, the filter cake is washed with ~9–10 gallons (34–38 L) distilled water and then dried and analyzed for purity and color.

Color analysis. Color of the dried solids is quantitated with a Hunter (Reston, VA) colorimeter. The Hunter colorimeter provides "L," "a," and "b" values that correspond to degree of brightness, redness, and yellowness exhibited by the product (22). Higher L values (up to 100) indicate improved product brightness, while near zero "a" and "b" values point to good (e.g., white) color. The color of KMES is also monitored as 0.1% solution in water with a Klett-Summerson (New York, NY) photoelectric colorimeter at 400–500 nm (23). Klett color values below 50 suggest satisfactory solution color.

Chemical characterization of purified KMES. All C16–18 KMES samples are analyzed for chemical purity before and after purification. Analyses of MES, unreacted methyl ester, fatty acid di-salts, and fatty acid soaps are performed by using slight modifications to established methods (24–26). The poor C16–18 KMES water solubility at room temperature is overcome by predissolving the surfactant in 6% butanol in water solutions; butanol does not interfere with the analytical methods. Potassium sulfate and potassium methyl sulfate levels are determined by capillary zone electrophoresis (27). No dimethyl sulfate was detected by either gas chromatography (GC) or high-performance liquid chromatography methods. All analyses are reported on a percent solids basis, neglecting residual amounts of water that may be present in dried KMES powders either before or after purification.

RESULTS

In the first step of the purification process, a mixture of dark-colored impurities and KMES is formed in water so as to substantially solubilize the color bodies. In the second step, the dark soluble color bodies are separated from the surfactant at a temperature below the C16–18 KMES Krafft point. The purification procedure may be run either cold or hot. The hot process comprises heating the impure mixture in step 1 above the KMES Krafft point to form a homogeneous solution, followed by cooling to precipitate the purified surfactant, whereas the cold process involves keeping the impure surfactant mixture below the C16–18 KMES Krafft point throughout. By analogy to purification of common organic com-

TABLE 1
Purification of Palm C16–18 KMES with "Hot" and "Cold" Processes[a]

	Unpurified	Cold process purified (72°F)	Hot process purified (130°F)
KMES (%)	80.6	93.5	95.5
K_2 Di-salt (%)	6.1	3.8	3.0
$K(CH_3)SO_4$ (%)	12.6	0.7	0.8
K_2SO_4	1.6	0.5	1.5
		Hunter color of dried solids	
L	73.9	74.1	84.1
a	1.8	1.8	0.8
b	11.1	11.5	9.2
		Klett color of dried solids as a 0.1% solution in water	
	230	210	30

[a]Surfactant recovery achieved by centrifugation; methyl ester feedstock iodine value = 0.3; KMES, potassium methyl ester sulfonates.

pounds, the hot process may be viewed as consisting of one or more recrystallization steps; the cold process involves washing the impure surfactant with copious amounts of cold water. Running the process hot is most advantageous because it results in product of improved purity and color (Table 1).

Due to low solubility in water at ambient temperatures, the identity of C16–18 KMES was first ascertained by high-temperature nuclear magnetic resonance (NMR) methods. The five sets of resonances observed in the proton spectrum at 130°F (~54°C) and the measured 1.0:1.0 alkyl methyl-to-methyl ester proton ratio unequivocally establish the purified product as high-quality MES (Figure 2). Standard wet chemical methods support the NMR analysis and are used to further quantitate the degree of purification achievable. In a typical run, purification of 50 g of crude 80% active C16–18 KMES (40 g KMES on an active basis) by three consecutive recrystallizations resulted in isolation of ~38 g of a 95% pure product (~36 g on an active basis, 90% recovery yield). The purified KMES shows large reductions in the level of di-salt, methyl sulfate, sulfate, and soap impurities (Table 2). Analysis of the dried water-soluble fraction reveal that high levels of potassium methyl sulfate and α-sulfo-fatty acid di-potassium salt are removed by the purification process (Table 2).

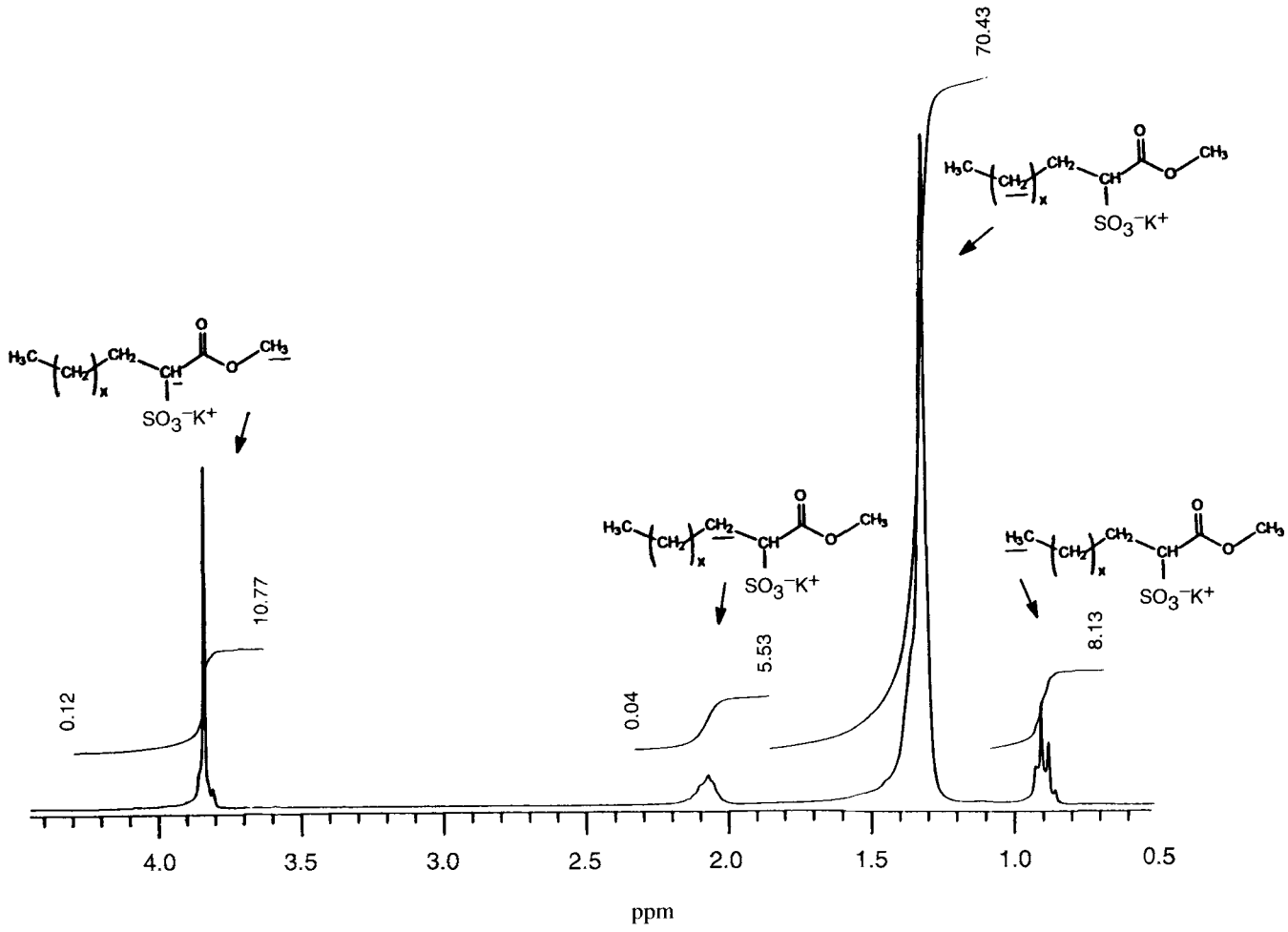

FIG. 2. Proton nuclear magnetic resonance spectrum of purified C16–18 KMES in D_2O at 130°F (54°C). The RC-*H*(SO_3-K^+)CO_2CH_3 proton appears as a multiplet at nearly the same resonance frequency as the ester CH_3 protons (at δ ~ 3.85 ppm). The multiplet is partially masked by the methyl ester proton resonance so that integration of the alkyl methyl protons at δ ~ 0.90 ppm relative to the signal at δ ~ 3.85 ppm yields a 3:4 ratio. Abbreviation as in Figure 1.

TABLE 2
Laboratory Purification of Palm C16–18 KMES[a]

	Unpurified basis (brown)	Purified KMES (white)	Dried aqueous phase (brown)
KMES (%)	87.3	97.9	10.1
K_2 di-salt (%)	1.7	0.7	23.1
K_2SO_4 (%)	2.5	0.6	10.4
$K(CH_3)SO_4$ (%)	8.0	0.6	41.6
K fatty acid soap (%)	1.0	0.4	1.4
	Hunter color of dried solids		
L	71.3	91.6	33.9
a	2.4	0.4	2.9
b	14.1	6.6	8.5
	Klett color of dried solids as a 0.1% solution in water		
	119	14	900

[a]Hot process; surfactant recovery achieved by filtration; methyl ester feedstock iodine value = 0.3; see Table 1 for abbreviation.

TABLE 4
Purification of Palm C16–18 KMES Derived from High-IV Methyl Esters[a]

	Unpurified basis	Purified (130°F) 2X Centrifugation
KMES (%)	86.0	95.3
K_2 Di-salt (%)	2.0	1.6
$K(CH_3)SO_4$ (%)	6.6	2.1
K_2SO_4 (%)	1.9	0.5
	Hunter color of dried solids	
L	63.9	73.6
a	2.3	1.4
b	11.1	9.4
	Klett color as a 0.1% solution in water	
	450	98

[a]Hot process; methyl ester feedstock iodine value = 1.9; see Table 1 for abbreviation.

Purification of pilot-plant quantities of surfactant may be achieved after a single filtration and washing step or by centrifugation (Table 3). The choice of separation method is a matter of convenience and does not alter final product specifications significantly. KMES compositions prepared from higher-IV (lower grade) methyl esters are darker in color as first isolated, but the process still affords significant color and chemical purity improvements (Table 4).

DISCUSSION

Below the KMES Krafft point, micelles cannot form, and surfactant solubility is determined by monomer solubility. As temperature is raised, monomer solubility gradually increases. Once monomer solubility reaches the surfactant's critical micelle concentration (i.e., at the Krafft point), surfactant solubility is dominated by micelle solubility, which is high, and thus a sudden and substantial increase in surfactant solubility takes place (Fig. 3) (28). The high Krafft point for C16–18 KMES (~125°F or 52°C) relative to C16–18 NaMES (~60°F or 15°C) (7) means that KMES is virtually insoluble at a range of temperatures where NaMES is very soluble (29), and accounts for the fact that only KMES can be purified by the new process.

The Krafft point for C16–18 α-sulfo-fatty acid di-salt is higher than C16–18 KMES because of increased Coulombic repulsions in the micelles, but monomer solubility is also enhanced because of the increased hydrophilic character provided by the di-anionic charge (7,30). Thus, despite a higher Krafft point, di-salt is much more soluble in water than KMES below ~125°F (~52°C). Our process exploits the dif-

TABLE 3
Pilot Plant Purification of Palm C16–18 KMES by Filtration and Batch Centrifugation[a]

Purification method	Unpurified	Filtration	Centrifugation
KMES (%)	80.6	95.0	95.5
K_2 Di-salt (%)	6.1	3.0	3.0
$K(CH_3)SO_4$ (%)	12.6	0.3	1.5
K_2SO_4 (%)	1.6	0.1	0.8
	Hunter color of dried solids		
L	73.9	85.6	84.1
a	1.8	0.7	0.8
b	11.1	8.2	9.2
	Klett color of dried solids as a 0.1% solution in water		
	106	23	30

[a]Hot process; methyl ester feedstock iodine value = 0.3; see Table 1 for abbreviation.

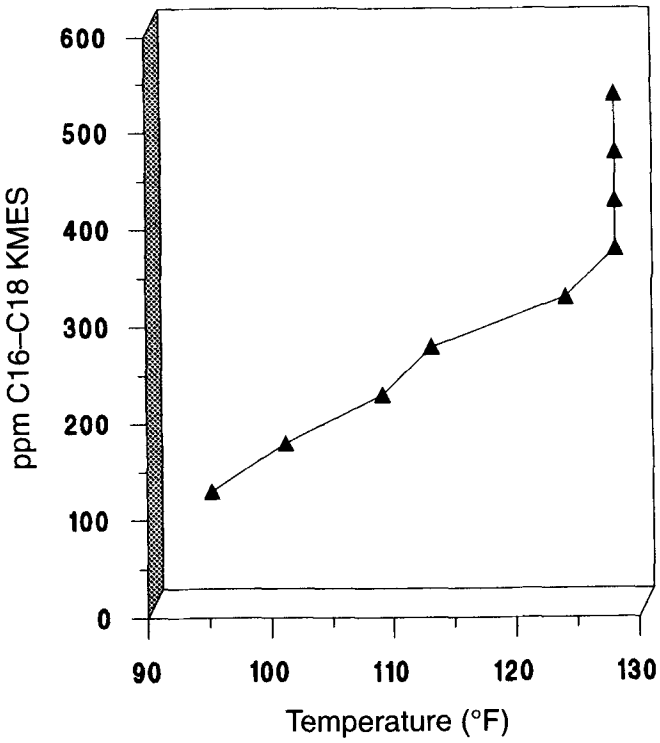

FIG. 3. Estimation of palm C16–18 KMES solubility and Krafft point. Abbreviation as in Figure 1.

ference between KMES and di-salt solubilities below the KMES Krafft point and provides a simple yet effective means for purifying MES. Recovery yields are high due to low KMES monomer solubility, and the process virtually eliminates water-miscible components, such as methanol, as well as water-soluble process by-products, including K_2SO_4 and $K(CH_3)SO_4$. Chemical purification can be achieved by keeping the crude neutralized mixture of KMES and associated impurities below the KMES Krafft point throughout (cold process), or by heating the mixture above the KMES Krafft point followed by cooling (hot process). In industrial settings, the heat of reaction due to methyl ester sulfonic acid neutralization is usually sufficient to keep the mixture in a single homogeneous phase above the KMES Krafft point, and temperature must ultimately be lowered for purification purposes. Hot and cold processes each result in enhancement of KMES analytical purity, but only the hot process provides color improvement. Methyl ester sulfonation and neutralization generate color bodies, which can become adsorbed on, or occluded in, the surfactant crystalline structure. Heating impure compositions allows for dissociation of the adsorbed or occluded species and facilitates their removal. Best results are anticipated when the separation is achieved by slowly cooling the surfactant mixture to a temperature just below the KMES Krafft point. Such an approach is not always practical, and some dark impurities can remain entrained in the surfactant paste even after purification. Improvements can be realized by centrifuging the product prior to recovery, or by washing the C16–18 KMES paste after filtration.

The process is more versatile than other color improvement methods in that it is applicable to compositions derived from lower-grade (i.e., higher-IV) methyl esters. Methyl ester grade is of critical importance because unsaturation is known to lead to final products of darker color that are more difficult to purify (31). Palm stearin KMES compositions made from higher-IV methyl esters are also very dark, but the process can still deliver noticeable color improvements (Table 4). Additionally, the higher degree of unsaturation does not impact final KMES analytical purity. Consequently, an economic advantage may be imparted by use of cheaper (i.e., lower-grade) methyl esters, which is particularly important in geographies where higher-grade fatty acid esters are unavailable from local suppliers.

The development of this new purification method as a bleach-free process provides several additional benefits. The most obvious is simplicity, which alleviates safety concerns and reduces capital equipment needs. A second advantage lies in significant reduction of volatile reagents. Efficient bleach processes require high concentrations of methanol to reduce di-salt levels in the final product (11,12). By contrast, the new process can be run without methanol for reesterification purposes. MES yields will certainly be somewhat lower, but the efficacy of the separation process ensures a final product with low di-salt content. Whatever levels of methanol are used in the process will conveniently be removed during surfactant recovery; other processes require a separate alcohol removal step (11,17). By eliminating color bodies and bleach, the new process also provides for better surfactant odor. Finally, lack of bleach precludes the formation of unsaturated sultones (15). From a practical standpoint, the process may seem flawed because it produces a raw material that is only sparingly soluble in water over a broad range of temperatures of interest. Indeed, one of the key benefits of C16–18 NaMES is good low-temperature detergency (32). Low-temperature solubility may be restored to C16–18 KMES *via* counter-ion exchange, preferably with sodium carbonate or sulfate present in most detergent matrices. Standard co-surfactants are also effective in promoting enhanced water solubility, presumably *via* formation of mixed micelle systems (Fig. 4), and our preliminary testing indicates KMES detergency is fully equivalent to that of NaMES, in agreement with earlier predictions (29).

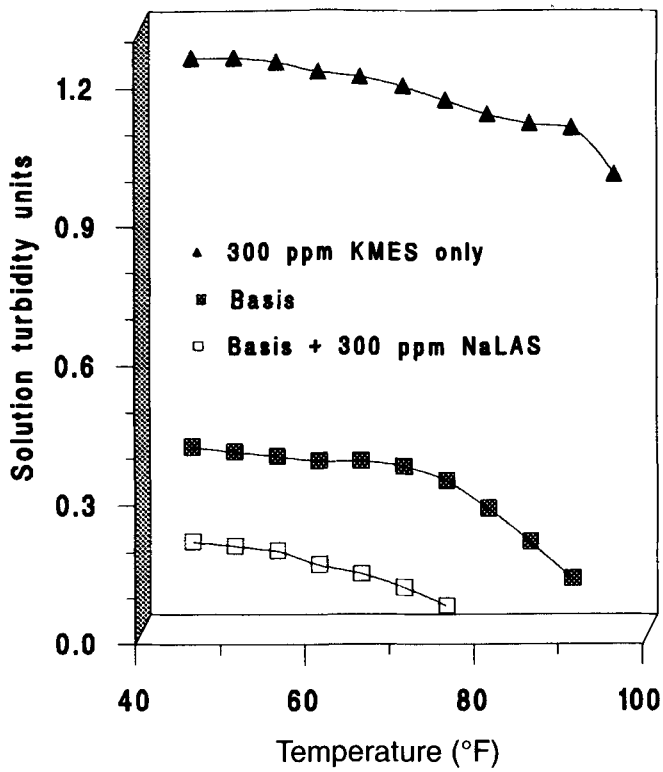

FIG. 4. Relative solubility of formulations that contain 300 ppm KMES + 100 ppm sodium carbonate + 100 ppm sodium silicate. Basis: 300 ppm KMES + 100 ppm sodium carbonate + 100 ppm sodium silicate; NaLAS: C11.8 linear alkyl benzene sulfonate, sodium salt. See Figure 3 for abbreviation.

One of the larger obstacles for successful MES development has been the need for a process that produces high-purity surfactant and addresses color and odor issues without raising costs or safety concerns. While prior MES manufacturing improvements have concentrated on whitening by bleaching, the new process delivers color and chemical purity improvements by manipulation of differential solubilities. The simplicity of the approach virtually eliminates process issues and likely provides improved manufacturing economics as well.

ACKNOWLEDGMENT

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