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SURFACE TENSION, FOAMING AND DETERGENCY PROPERTIES OF MIXED ALPHA-SULPHONATED METHYL ESTERS DERIVED FROM PALM STEARIN WITH SOME COMMERCIAL SURFACTANTS

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The effects of sodium alpha-sulphonated methyl esters derived from palm stearin salt (α-SMEPS) and commercial surfactants (CS) in mixed micelle systems were studied as a function of their weight ratios. Changes in the surface tension were observed as the different weight ratios of the mixed surfactants. Only the α-SMEPS:AE-3EO system reduced the surface tension of α-SMEPS solution. Incorporation of a commercial surfactant into a solution of α-SMEPS also changed its foaming properties (foaming power and foam stability) and washing performance. No synergy was observed in dish washing performance. However, synergy effect on cloth washing was exhibited by α-SMEPS:AE-3EO, α-SMEPS:SLES-2EO and α-SMEPS: ALS systems.

Keywords:

α-SMEPS, surface tension, foaming profile, detergency properties.

INTRODUCTION

Studies on the surface activity and physical properties of mixed surfactants (anionic: nonionic and anionic:anionic) have been widely carried out, especially in formulating commercial products. Frequently, a mixture of surfactants is superior to a single or pure surfactant because of synergistic interaction between the surfactants (Tsujii, 1998; Somasundaran and Ramanchandran, 1988). This synergism affects the surfactant properties, such as foaming (Holland, 1992; Rubingh, 1979), wetting, emulsification (Holland, 1984; Zahariah *et al.*, 1999), detergency and the flotation separation of minerals (Stirton *et al.*, 1962).

Sodium salts of alpha-sulphonated methyl esters (α-SME) surfactants have been quite intensively studied because of their good detergency and biodegradability (Zahariah *et al.*, 1999). The surface properties of α-SME with the different chain lengths of their alkyl groups determine the critical micelle concentration (CMC), interfacial tension and surface tension of the surfactant solution (Stirton *et al.*, 1962). Other parameters, include the Krafft temperature which, increases with the carbon chain length of the hydrophobic tails (Stein and Baumann, 1975).

The α-SMEPS exhibited comparable detergency performance as pure α-SME surfactants of palmitate and stearate hydrophobic chain lengths (unpublished data). They are cheaper to produce than a pure surfactant. In previous studies (Lim, 1999a,b; Lim and Salmiah, 1999; Lim and Ho, 1999), α-SMEPS: nonionic mixtures have been found to have better detergency and physical properties.

This paper reports on some of the physicochemical properties - surface tension, foaming

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ability and detergency - of different weight ratios of mixed α-SMEPS and commercial surfactants (SLES-2EO, ALS, AE-9EO, AE-3EO and APG-12/4) in aqueous solutions.

MATERIALS AND METHODS

Material

The α-SME from palm stearin, 94.4% active ingredient, supplied by Chemithon Corporation (USA) was used as received. CS, SLES-2EO (TEXAPON N70), ALS (TEXAPON ALS), AE-3EO (DEHYDOL LS3), AE-9EO (DEHYDOL 100) and APG-12/4 (GLUCOPON 600 CSUP) supplied by Henkel were also used as received. Deionized water of 18.0 mΩ cm^{-1} was used in all the experiments.

Tallow and soyabean oil were of Japanese Pharmacopoeia grade. Monoolein from TCI, oil red (Sudan III) CI26100 from Sigma Chemicals and chloroform of 99.5% purity from Surechem were used as received. Calcium chloride (dihydrate, >97% purity) and magnesium chloride (hexahydrate, >99% purity) were purchased from Merck.

Three types of soiled cloth, AS-9 (cotton stained with groundnut oil and pigments), 60-MU (washed and bleached plain weave wool fabric soiled with make-up) and 70-MU (spun silk, plain weave 70 g m^{-2}, degummed and washed, soiled with make-up), from Westlairds, UK, were used in the test for detergency.

Methods

Surface tension measurements. Measurements were taken with a KRUSS K-10 surface tensiometer using the Du Nouy ring technique at 30.0±0.1°C. This instrument was able to measure the surface tension of a solution to a precision of ±0.1 mN m^{-1}. The temperature was held constant by circulating thermostated water through a water-jacketed vessel, and the instrument calibrated against deionized water of 18.0 ΩS cm^{-1}. Each sample solution of 1.0 g dm^{-3} was transferred to the vessel well before measurement to allow the temperature to equilibrate. Sets of measurements were taken until no significant change occurred.

Foam stability. This measurement involved 'pumping' a perforated disc 10 times through 200 ml of 1.0 g dm^{-3} surfactant solution in a 500 ml measuring cylinder to generate foam. The foam height was measured over time to determine its stability.

Detergency Evaluation

Dish washing. Six pieces of clean glass plates of known weight were soaked for 1-2 s in a soil bath containing 20 g of a 1:1 mixture of tallow and soyabean oil, 0.25 g monoolein and 60 ml chloroform with 0.1 g oil red dissolved. The glass plates were dried for 24 hr, washed and then immersed in a 1 g dm^{-3} surfactant solution containing 59.0 ppm calcium chloride dihydrate and 27.2 ppm magnesium chloride. Subsequently, the plates were washed for 3 min at 30.0±0.1°C and a stirrer speed of 250±10 rpm using Leenert's Improved Detergency Tester, and rinsed with water containing 59.0 ppm calcium chloride dihydrate and 27.2 ppm magnesium chloride for 1 min at 30.0±0.5°C stirred at 250±10 rpm. After rinsing, the plates were air dried for 24 hr and the soil was dissolved in 100 ml chloroform for evaluation in a Lovibond Colour Tintometer Model PFX 990. The soil removed by washing was calculated by the formula:

$$\% \text{ Soil removal} = [OR_0 - OR_1]/[OR_0] \times 100\%$$

where OR_0 = redness colour of the soil bath before washing, and OR_1 = redness colour of the soil bath after washing (both in comparative units).

Cloth washing. Before washing, the reflectance (whiteness) of the soiled swatches was measured using a Macbeth Colour-Eye 3000. A 250 ml of a surfactant solution of 1 g dm^{-3} were poured into each stainless steel container of the Terg-o-Tometer at the desired washing temperature. Four pieces of soiled swatches were placed in each container of detergent solution and stirred for 10 min at 120 rpm. The liquor was then discarded, and the swatches squeezed and returned to the containers. A rinse solution of 250 ml water was poured into each container, stirred for 3 min and discarded. This rinsing was repeated twice. The swatches were dried by spinning for 1 min and ironed. The reflectance of these washed swatches was measured. The percentage of soil removal was calculated by:

$$\% \text{ Soil removal} = [AW - BW]/[OC - BW] \times 100\%$$

where AW = reflectance of the swatches after washing, BW = reflectance of the swatches before washing and OC = reflectance of the original cloth before soiling (both in comparative units).

RESULTS AND DISCUSSION

Surface Tension Measurements

Figure 1 shows the change in the surface tension of individual surfactants (α-SMEPS, SLES-2EO, ALS, AE-9EO, AE-3EO and APG-12/4) and their mixtures at different weight ratios at 30±0.1°C. The surface tension of α-SMEPS was higher than that of CS. Incorporating CS reduced the surface tension of the α-SMEPS surfactant solution. Most of the surfactant mixtures reduced the surface tension above the 40:60 weight ratio of α-SMEPS:CS, except for the α-SMEPS:ALS mixture. A greater reduction in surface tension was observed for the α-SMEPS: AE-3EO system. No synergy in surface tension was noted for all the α-SMEPS:CS systems.

All the commercial surfactants consisted of similar hydrocarbon chains but different hydrophilic groups - sulphate, ethoxylate sulphate, ethoxylate alcohol and polyglycoside. Thus, the changes in surface tension could be attributed to changes in the size and hydrophilicity of the hydrophilic groups in the different surfactants and α-SMEPS. As mentioned previously, a change in the surface tension was noted. The nonionic surfactants (AE-9EO, AE-3EO and APG-12/4) had lower surface tension than the anionic surfactants (SLES-2EO, ALS, α-SMEPS). The surface tension decreased from α-SMEPS > ALS > SLES-2EO > AE-9EO > APG-12/4 > AE-3EO.

The interaction between molecules on the air/water interface can be determined by the change in surface tension. At 1 g dm^{-3} surfactant concentration, the surface of the solution was fully occupied by the surfactant with the hydrophilic group immersed in the bulk solution and the hydrophobic portion in air. As a foreign surfactant (SLES-2EO, ALS, AE-9EO, AE-3EO and APG-12/4) is added to the monolayer, the surfactant system becomes disturbed. Competition between the surfactant molecules at the interface changes the interface of the solution, decreasing or increasing the surface tension. The results indicated that the α-SMEPS:CS (ALS, SLES-2EO and AE-9EO) systems had a stronger interaction than the α-SMEPS:CS (APG-12/4 and AE-3EO) systems.

Foam Properties

The foam properties (stability and foaming power) of the pure surfactants (α-SMEPS, SLES-2EO, ALS, AE-3EO, AE-9EO and APG-12/4) and their mixtures in dilute solutions are illustrated in *Figures 2* and *3*, respectively. Among the individual surfactants, APG-12/4 and SLES-2EO produced comparable foaming power as α-SMEPS, followed by EA-9EO and, lastly,

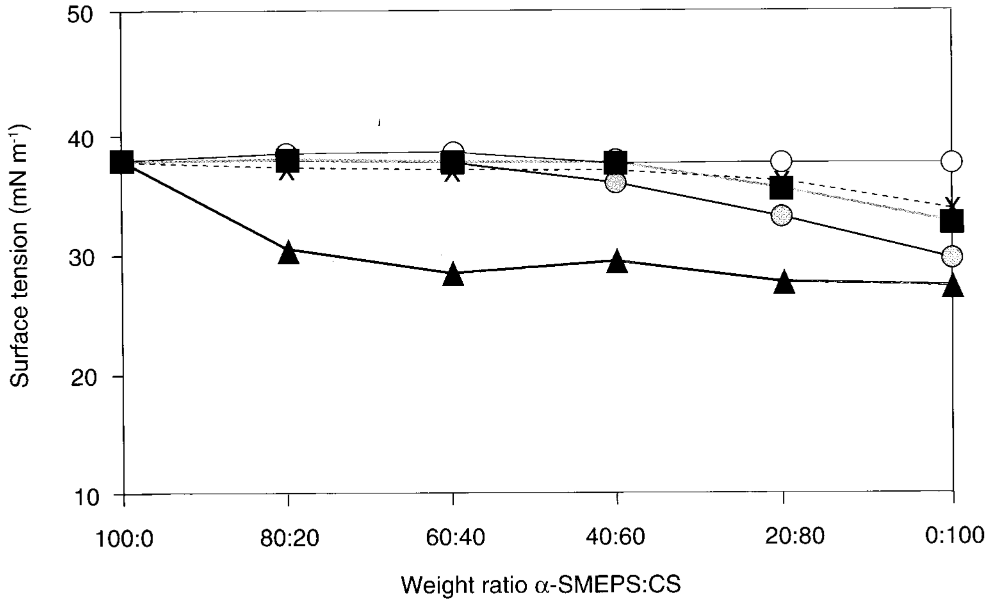

Figure 1. Surface tension versus weight ratio of α-SMEPS:CS at 30.0±0.1°C. α-SMEPS:ALS (○), α-SMEPS:SLES-2EO (x), α-SMEPS:AE-3EO (▲), α-SMEPS:AE-9EO (■), and α-SMEPS:APG-12/4 (◎).

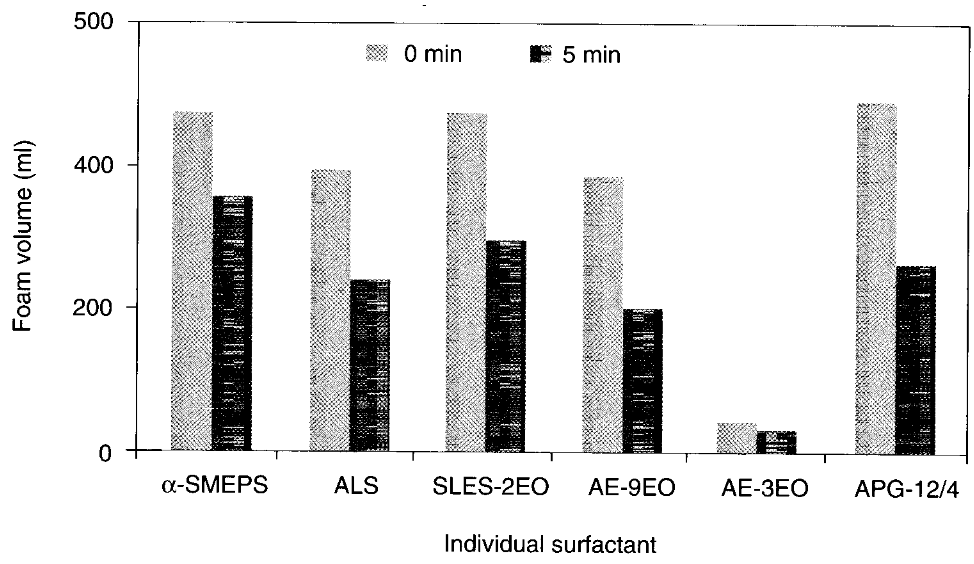

Figure 2. Foam volume of individual surfactants at 30.0±0.1°C.

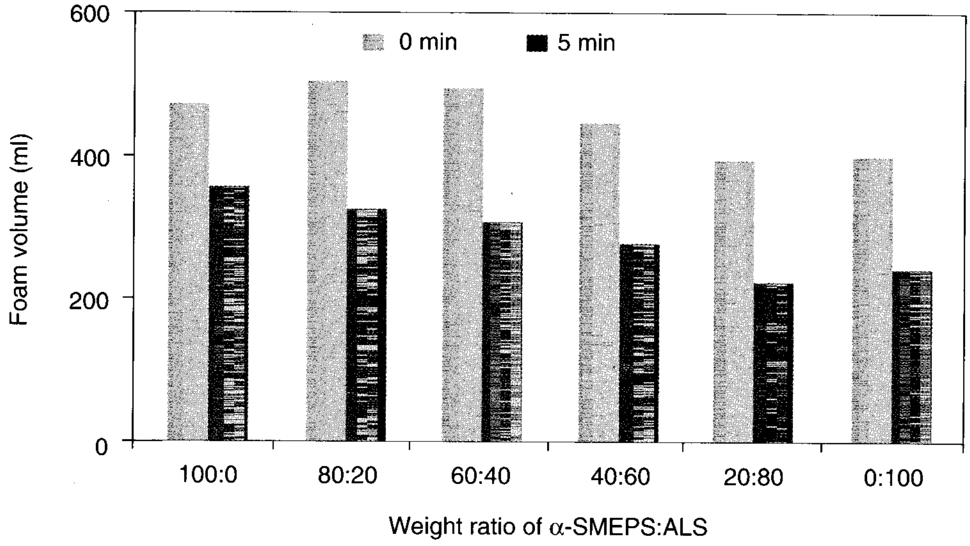

Figure 3a. Foam volume at different weight ratios of α-SMEPS:ALS at 30.0±0.1°C.

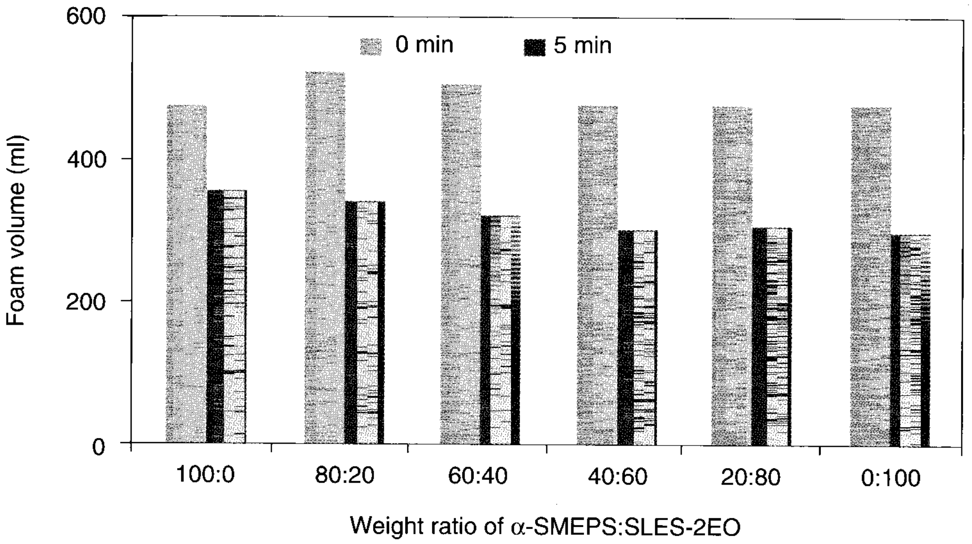

Figure 3b. Foam volume at different weight ratios of α-SMEPS:SLES-2EO at 30.0±0.1°C.

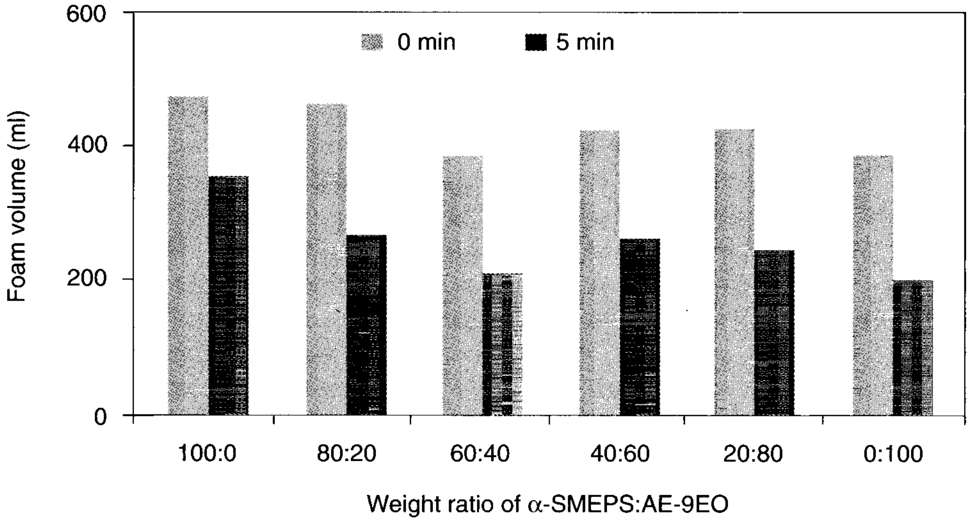

Figure 3c. Foam volume at different weight ratios of α-SMEPS:AE-9EO at 30.0±0.1°C.

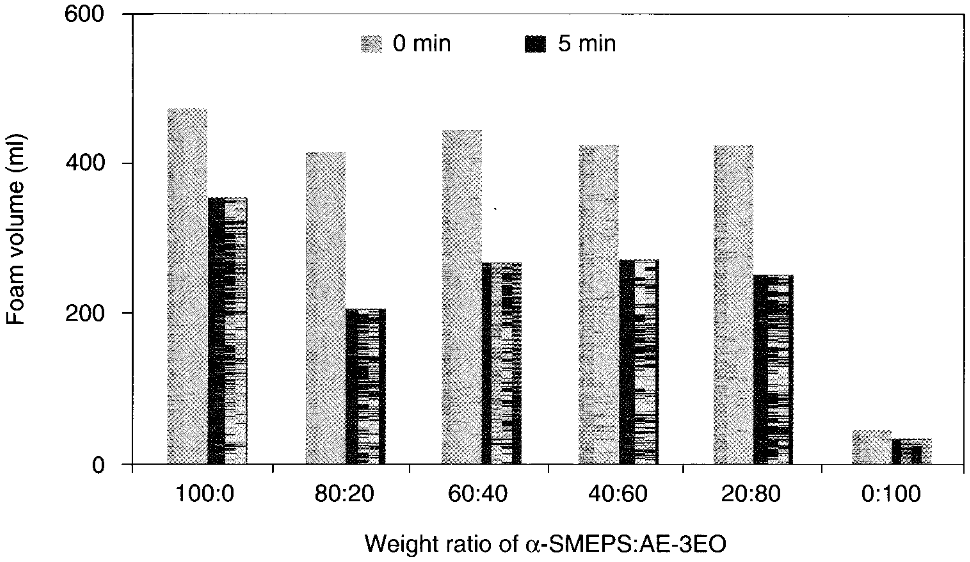

Figure 3d. Foam volume at different weight ratios of α-SMEPS:AE-3EO at 30.0±0.1°C.

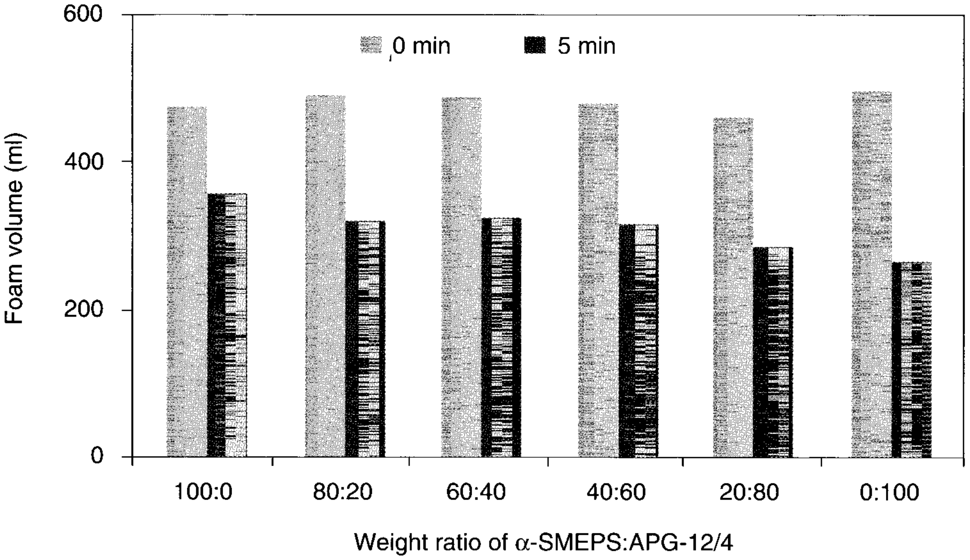

Figure 3e. Foam volume at different weight ratios of α-SMEPS:APG-12/4 at 30.0±0.1°C.

AE-3EO. However, the foam produced by α-SMEPS was the most stable, followed by SLES-2EO > APG-12/4 > ALS > AE-9EO > AE-3EO. As more surfactant (SLES-2EO, APG-12/4, ALS, AE-9EO and AE-3EO) was incorporated into the α-SMEPS solution, stability of the foam decreased. An increase in foaming power was observed at 80:20 and 60:40 weight ratios of α-SMEPS:CS (SLES-2EO and ALS). All the foam volume decreased with time.

A stable foam is formed when a surfactant is adsorbed onto the air/water interface with the molecules arranged parallel in a lamella structure (Anil and Wasan, 1988). The stability is affected by extraneous factors, like temperature, *etc*. The high foaming ability of α-SMEPS may have been due to the high critical packing parameter (CPP) for its molecules at the interface (Jönsson *et al*., 1998; Rosen, 1986). Incorporating a foreign component, *e.g*. a commercial surfactant, disturbs this molecular arrangement, lowering the CPP and increasing hole formation in the foam. This decreases the life of the foam. Interaction between the hydrophilic groups of surfactants in the bilayer arrangement of the foam may also affect their foaming stability besides their interaction on the interface.

Detergency Performance

The removal of soil stains from glass and cloth was tested at 30±0.1°C. The detergency of α-SMEPS, SLES-2EO, APG-12/4, ALS, AE-9EO, AE-3EO and their mixtures was evaluated and compared (*Figures 4* to *8*). No synergy in dish washing performance was observed in all the α-SMEPS:CS systems (*Figures 4* and *5*). The dish washing performance of the individual surfactants increased from AE-3EO < ALS < APG-12/4 < AE-9EO < α-SMEPS < SLES-2EO. The performance of α-SMEPS decreased when CS was added to the solution, except in the α-SMEPS:SLES-2EO system. A comparable detergency was obtained by incorporating 20 w/w % SLES-2EO instead. Almost all the systems achieved > 80% soil removal. Only > 60 w/w % AE-3EO in the α-SMEPS: AE-3EO system exhibited < 80% detergency.

The detergency on different cloths was also assessed using a mixture of α-SMEPS with CS. *Figure 6* shows no significant change in the detergency (between 20%-30% soil removed) on AS-9 cloth. However, the α-SMEPS:AE-3EO, α-SMEPS: SLES-2EO and α-SMEPS:ALS systems exhibited synergistic detergency with 60-MU (*Figure 7*). An increase in detergency by 70-MU was also observed in the α-SMEPS:SLES-2EO and α-SMEPS:ALS systems (*Figure 8*).

CONCLUSION

Better performance and multi-functionality were obtained by mixing α-SMEPS with CS (SLES-2EO, ALS, APG-12/4, AE-9EO, AE-3EO).

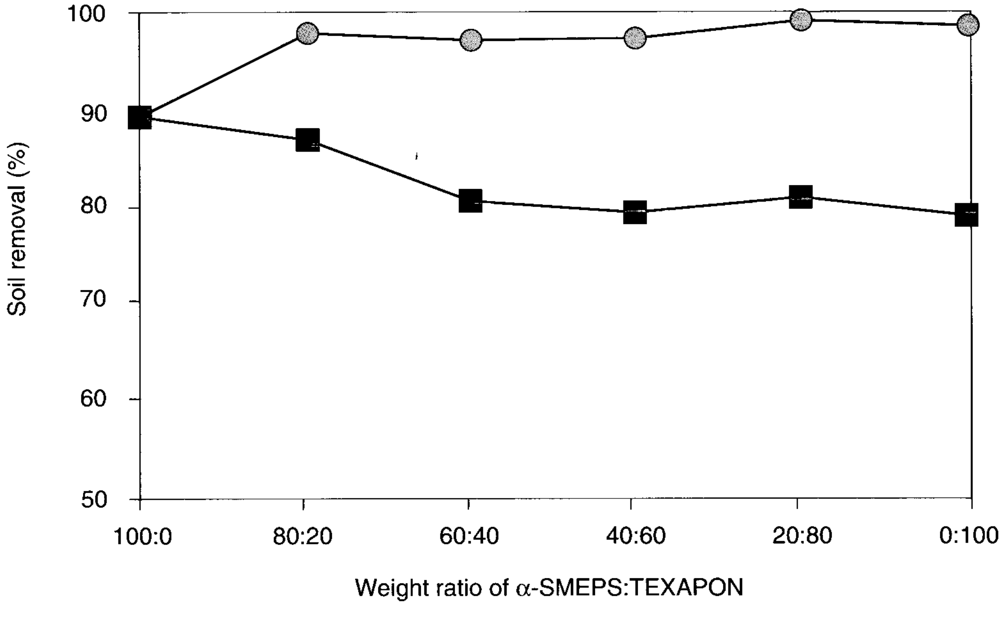

Figure 4. Percentage soil removal from dishes washed at 30.0±0.1°C by different weight ratios of α-SMEPS:SLES-2EO (●) and α-SMEPS:ALS (■).

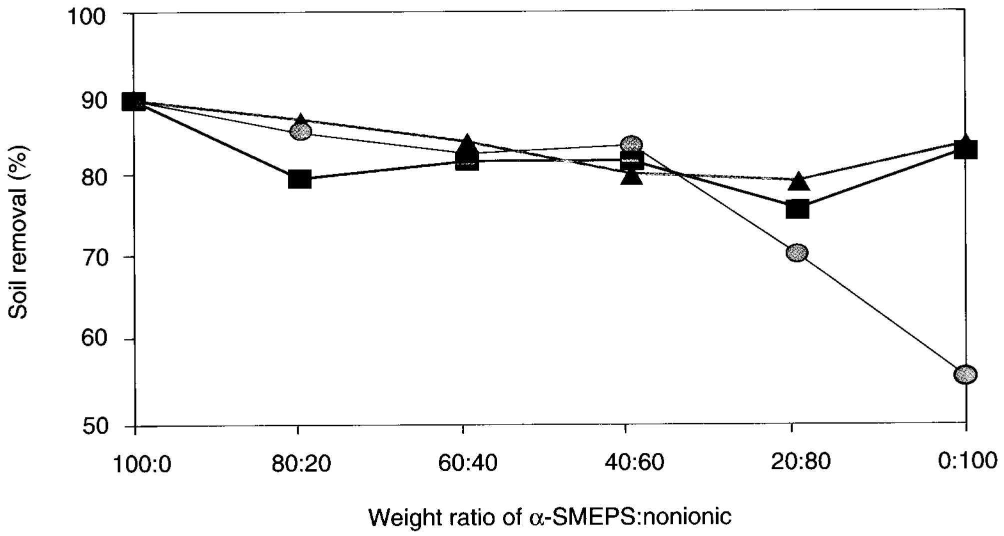

Figure 5. Percentage soil removal from dishes washed at 30.0±0.1°C by different weight ratios of α-SMEPS:AE-9EO (■), α-SMEPS:AE-3EO (●), and α-SMEPS:APG-12/4 (▲).

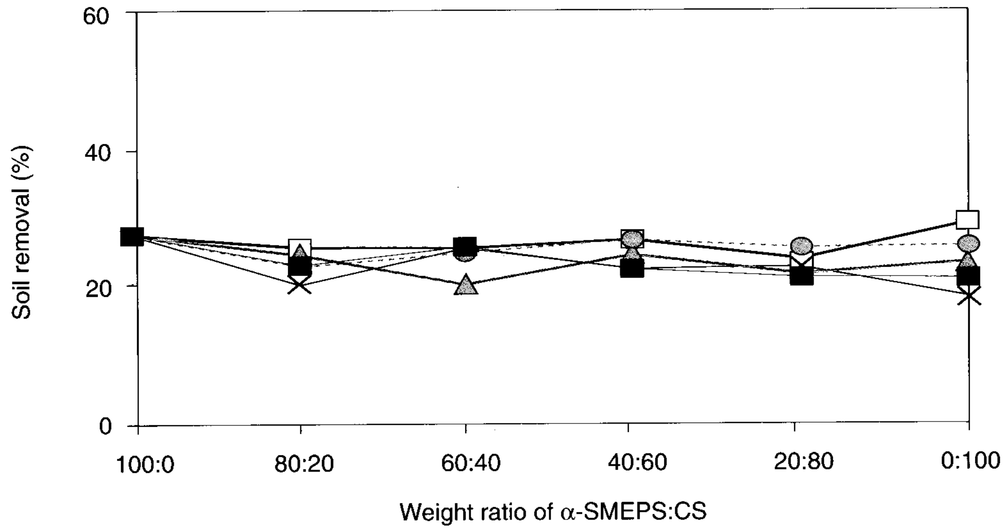

Figure 6. Percentage soil removal on AS-9 at 30.0±0.1°C by different weight ratios of α-SMEPS:SLES-2EO (●), α-SMEPS:ALS (■), α-SMEPS:AE-9EO (□), α-SMEPS:AE-3EO (x), and α-SMEPS:APG-12/4 (▲).

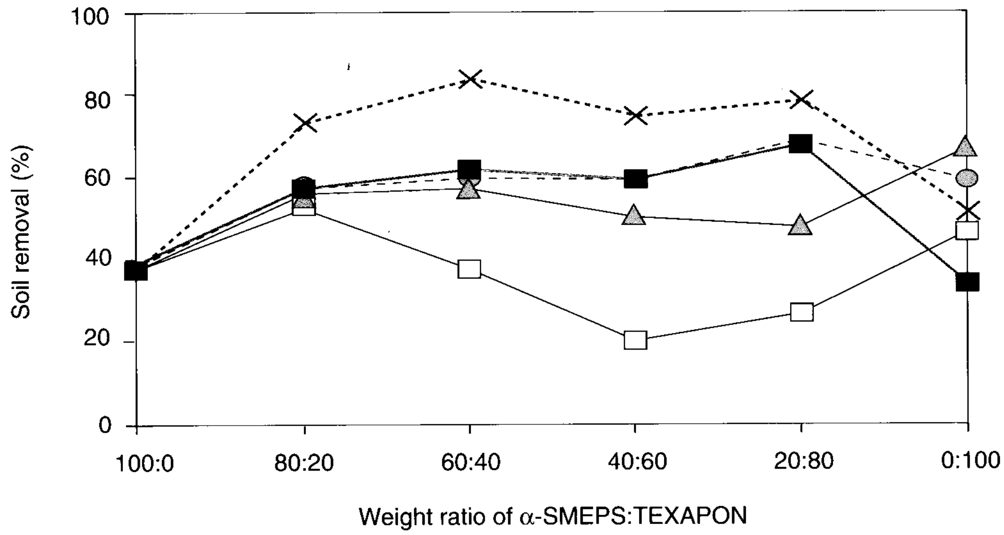

Figure 7. Percentage soil removal on 60-MU at 30.0±0.1°C by different weight ratios of α-SMEPS:SLES-2EO (●), α-SMEPS:ALS (■), α-SMEPS:AE-9EO (□), α-SMEPS:AE-3EO (x), and α-SMEPS:APG-12/4 (▲).

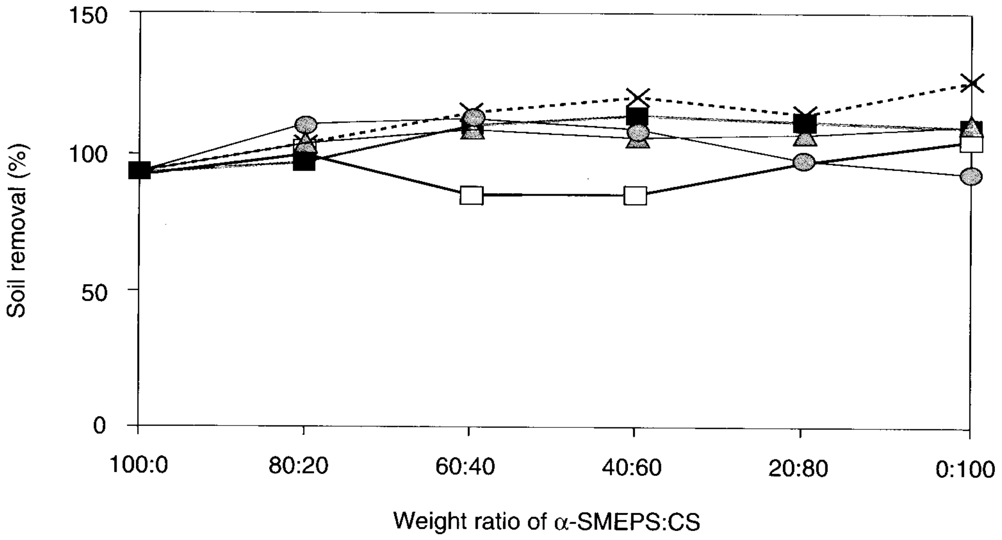

Figure 8. Percentage soil removal on 70-MU at 30.0±0.1°C by different weight ratios of α-SMEPS:SLES-2EO (●), α-SMEPS:ALS (■), α-SMEPS:AE-9EO (□), α-SMEPS:AE-3EO (x), and α-SMEPS:APG-12/4 (▲).

The low surface tension achieved by incorporating a small amount of AE-3EO into α-SMEPS solutions enabled the active ingredient to be dissolved easily compared to other α-SMEPS:SC systems. The dish washing performance was enhanced by incorporating a small amount of SLES-2EO in α-SMEPS solution. Synergistic effects on selected cloth washings were obtained using the α-SMEPS:AE-3EO, α-SMEPS:SLES-2EO and α-SMEPS:ALS systems.

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