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PHYSICO-CHEMICAL PROPERTIES OF BINARY SYSTEMS OF ALPHA-SULPHONATED METHYL ESTER DERIVED FROM PALM STEARIN AND NONIONIC SURFACTANTS

LIM, W H*; SALMIAH AHMAD*
and ZAHARIAH ISMAIL*

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The effects of mixing sodium alpha-sulphonated methyl ester derived from palm stearin salt (α-SMEPS) with nonylphenol ethoxylate alcohol (NONIPOL) and polyoxyethylene (20) sorbitan monoester (TWEEN) in mixed micelles systems were studied as a function of their weight ratios. Changes in the critical micelle concentration (CMC) and surface tension were observed at different weight ratios of the mixed surfactants. Incorporating the nonionic surfactants into a-SMEPS solution changed the surface properties of the system by lowering the Krafft temperature and decreasing the foaming stability. The effects of these mixed anionic-nonionic surfactants were due to interaction between the different hydrophobic and hydrophilic portions of the surfactants.

INTRODUCTION

Numerous studies on the surface activity and physical properties of mixed anionic-nonionic surfactants solution have been carried out, especially in formulating commercial products. A surfactant mixture is frequently used to give superior performance over a single or pure surfactant because of synergistic interaction between its surfactants (Tsujii, 1998; Scamehorn, 1986; Somasundaran and Ramanchandran, 1988). This synergism will affect some of the surfactant properties, such as foaming (Holland, 1992; Rubingh, 1979), wetting, emulsification (Holland, 1984; Ismail *et al.*, 1999), detergency (Maurer *et al.*, 1977) and flotation separation of minerals (Stirton *et al.*, 1962).

Sodium salts of alpha-sulphonated methyl ester (α-SME) surfactants are gaining popularity because of their good detergency and biodegradability (Ismail, 1994; Ismail *et al.*, 1999; Maurer, 1977). The properties of a-SME very much depend on the chain length of the alkyl

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* Malaysian Palm Oil Board,
P.O. Box 10620,
50720 Kuala Lumpur, Malaysia.

groups of the methyl ester – the CMC, interfacial tension and surface tension decreasing as the chain length of the alkyl group increases (Stirton et al., 1962). On the other hand, the Krafft temperature of a-SME increases with the carbon chain length of its hydrophobic tail (Stein and Baumann, 1975).

Nonionic surfactants, like polyoxyethylene sorbitan fatty esters are widely used in the pharmaceutical, cosmetic, food and agrochemical industries, and their physical properties and synthesis pathways have been extensively studied. The applications of polyoxyethylene alkylphenols have been reviewed frequently (Benson, 1966; Mayhew and Woodward, 1960). The properties of nonylphenol ethoxylate alcohols are very much dependent on the hydrophilic-lipophilic balance (HLB) of the chemicals (Benson, 1966). These surfactants are widely used as emulsifiers, especially in household products.

This paper reports on some of the surface properties at different weight ratios of mixed a-SMEPS with nonylphenol ethoxylate alcohol (NONIPOL 95, NONIPOL 120 and NONIPOL 400) and polyoxyethylene (20) sorbitan monoesters (TWEEN 20, TWEEN 60 and TWEEN SO) in aqueous solutions.

MATERIALS AND METHODS

Chemicals

The a-SME from palm stearin, 94.4% active ingredient, supplied by Chemithon Corporation (USA) was used as received. Three nonylphenol alcohols with different ethoxylated lengths – NONIPOL 95, NONIPOL 120 and NONIPOL 400 – from Sanyo Chemical were used as received. Three polyoxyethylene (20) sorbitan monoesters with different hydrophobic chain lengths – laurate (TWEEN 20), stearate (TWEEN 60) and oleate (TWEEN 80) – from ICI Chemicals were also used as received. Deionised water of 18.0 Ωs cm^{-1} was used for all the experiments.

Surface Tension Measurements

Measurements were performed with a KRUSS K-10 surface tensiometer using the Du Nouy ring technique. This instrument was able to measure the surface tension of a solution to ±0.1 mN m^{-1}. The temperature was held constant at 25.0 ± 0.1°C by circulating thermostated water through a water-jacketed vessel, and the instrument calibrated against deionised water of 18.0 Ωs cm^{-1}. Each sample solution was transferred to the thermostated water-jacketed vessel before measurement. Sets of measurements were taken until no significant change occurred.

Krafft Temperature

The Krafft temperature was determined as the temperature at which the turbidity of the surfactant solution disappeared during slow heating. The temperature of a 1.0 g dm^{-3} solution of each mixture (a-SMEPS:NONIPOL and a-SMEPS:TWEEN) was first decreased to 1°C and held for 24 hr, and then slowly increased until the cloudy solution became clear.

Foam Stability

This measurement involved 'pumping' a perforated disc at a constant rate through 200 ml of the surfactant solution (1.0 g dm^{-3}) in a 500 ml measuring cylinder to generate foam. The foam height was monitored every 5 min for 30 min to determine the foaming ability.

RESULTS AND DISCUSSION

Surface Tension Measurements

The surface tension of each mixed surfactant solution was measured and the break point (the point of formation of CMC) determined from the surface tension curve. *Figure 1* shows the surface tension of the individual surfactants (a-SMEPS, NONIPOL 95, NONIPOL 120, NONIPOL 400, TWEEN 20, TWEEN 60 and TWEEN 80) at different concentrations. The surface properties of the mixed surfactants (a-SMEPS:NONIPOL and a-SMEPS:TWEEN) are shown in *Figures 2a* and *2b* respectively.

All the mixed surfactants (a-SMEPS: NONIPOL 95, a-SMEPS: NONIPOL 120, a-SMEPS:NONIPOL 400, a-SMEPS:TWEEN 20, a-SMEPS:TWEEN 60 and a-SMEPS: TWEEN 80) exhibited negative synergism – deviating below the ideal curve – with a mini-

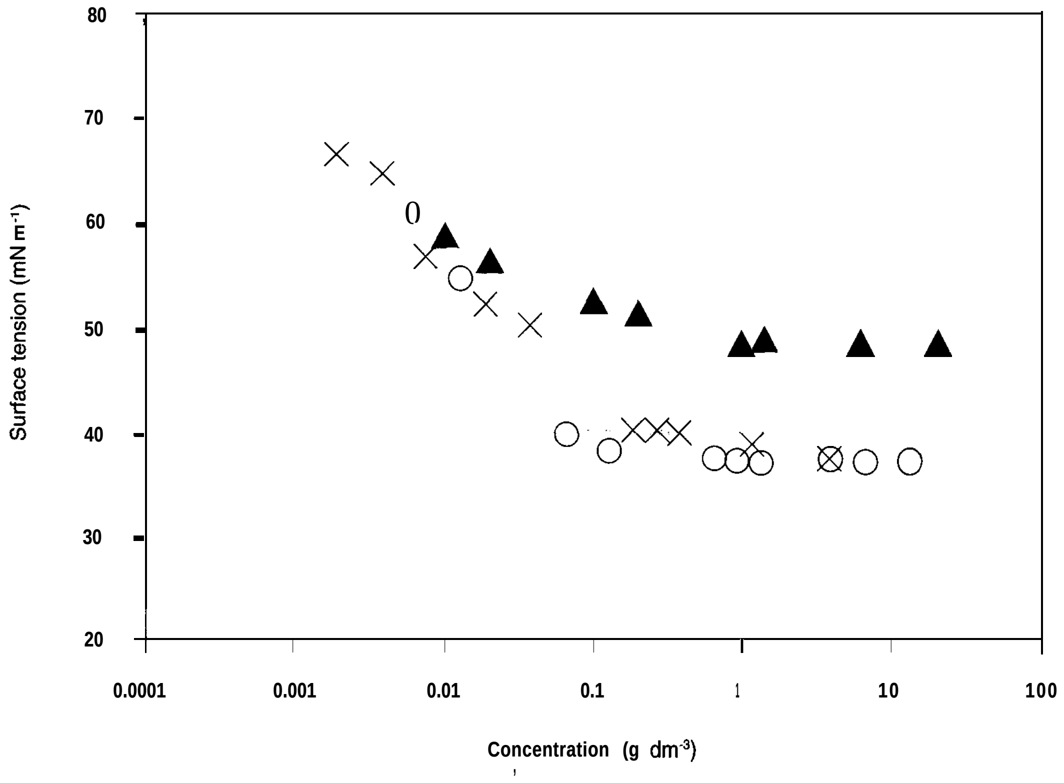

Figure 1. Surface tension versus concentration of (×) a-SMEPS, (▲) NONIPOL 400, and (○) TWEEN 20 at 25.0±0.1°C.

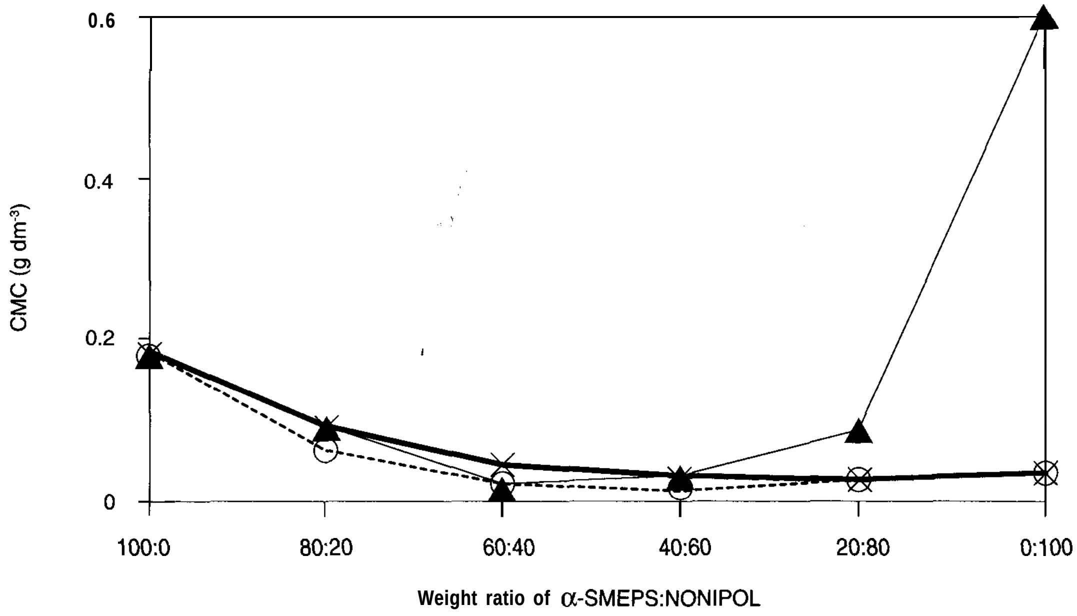

Figure 2a. CMC at different weight ratios of a-SMEPS:NONIPOL: (○) α-SMEPS:NONIPOL 95, (×) α-SMEPS:NONIPOL 120, and (▲) a-SMEPS:NONIPOL 400 at 25.0±0.1°C.

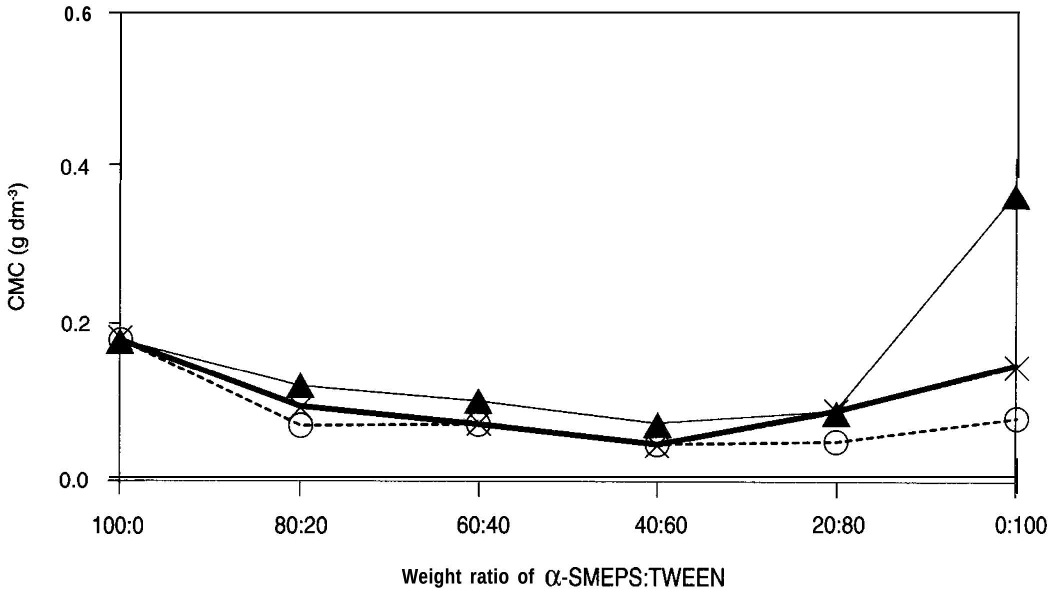

Figure 2b. CMC at different weight ratios of a-SMEPS:TWEEN: (0) a-SMEPS:TWEEN 20, (X) a-SMEPS:TWEEN 60, and (▲) a-SMEPS:TWEEN 80 at 25.0±0.1°C.

mum CMC value. This indicated that the interaction between the anionic-nonionic surfactant pair was greater than the interactions between the individual surfactants (a-SMEPS, NONIPOL 95, NONIPOL 120, NONIPOL 400, TWEEN 20, TWEEN 60 and TWEEN 80).

The strongest interaction among the mixed surfactants of the a-SMEPS:NONIPOL system occurred at 40:60 (a-SMEPS:NONIPOL - 95 and 120) and 60:40 (a-SMEPS:NONIPOL 400) weight ratios. However, mixtures of the α-SMEPS:TWEEN (20, 60 and 80) systems showed a strong molecular interaction at 40:60 weight ratio.

Krafft Temperature

The Krafft temperatures of a-SMEPS, NONIPOL 95, NONIPOL 120 and NONIPOL 400, and their mixtures are shown in *Table 1*. The solubility temperature decreased as the amount of NONIPOL in the mixed surfactants solution increased. The Krafft temperature of the mixtures decreased below 0°C as the weight ratio of a-SMEPS: NONIPOL decreased below 40:60. *Table 1* also shows the Krafft temperatures of a-SMEPS, TWEEN 20, TWEEN 60, TWEEN 80, and their mixtures. The α-SMEPS:TWEEN series also showed a decrease

TABLE 1. KRAFFT TEMPERATURE OF DIFFERENT WEIGHT RATIOS OF MIXED a-SMEPS:NONIPOL AND a-SMEPS:TWEEN SURFACTANTS

Weight ratio (Anionic:Nonionic)	a-SMEPS: *X					
	NONIPOL 95	NONIPOL 120	NONIPOL 400	TWEEN 20	TWEEN 60	TWEEN 80
100:0	19.9	19.9	19.9	19.9	19.9	19.9
80:20	16.0	16.0	14.5	17.3	17.9	18.0
60:40	15.0	13.4	< 0	12.7	13.1	13.0
40:60	< 0	< 0	< 0	7.8	8.0	6.0
20:80	< 0	< 0	< 0	< 0	< 0	< 0
0:100	< 0	< 0	< 0	< 0	< 0	< 0

Note: *X = NONIPOL (95, 120, 400) or TWEEN (20, 60, 80).

in temperature with increases in TWEEN surfactants in the mixtures. The Krafft temperature of the mixtures fell below 0°C as the weight ratio of a-SMEPS:TWEEN decreased below 20:80.

Thus, NONIPOL and TWEEN surfactants in an a-SMEPS solution suppressed its Krafft temperature. In comparison, a decrease in the Krafft temperature was observed as the ethoxylate unit in the hydrophilic portion increased in the mixed surfactant (a-SMEPS:NONIPOL) solution. However, no significant differences of Krafft temperature were observed between the mixed a-SMEPS:TWEEN surfactants.

Foam Properties

The foam stability profiles of the individual surfactants (a-SMEPS, NONIPOL 95, NONIPOL 120, NONIPOL 400, TWEEN 20, TWEEN 60 and TWEEN 80) are illustrated in *Figure 3.* Among them, a-SMEPS generated the largest foam volume, followed by NONIPOL 120, NONIPOL 95, NONIPOL 400, TWEEN 20, TWEEN 80 and, lastly, TWEEN 60. The foam volumes of all the individual surfactant solutions decreased with time.

Figures 4a to *4c* show the foaming profiles of mixed a-SMEPS:NONIPOL (95,120 and 400) surfactant solutions. The foam volumes decreased with time for each solution but did not show a consistent trend in mixing. As the amount of NONIPOL increased in the a-SMEPS solutions, the foam volumes of the surfactant mixtures decreased. A similar trend was also observed in the a-SMEPS:TWEEN system (*Figures 5a* to *5c*). The foam volume decreased with increases in the TWEEN content.

A stable foam is formed when the surfactant is adsorbed on the air/water interface, the molecules arranging themselves parallel in a lamella structure (Anil and Wasan, 1988). The foaming ability of a-SMEPS may be due to the high critical packing parameter (CPP) produced by the self-orientation of the surfactant molecules to form a stable and less steric interaction between the hydrophilic and hydrophobic portions in the lamellar layer of the foam. Among the NONIPOL (95, 120 and 400) surfactants, NONIPOL 120 produced more stable foam. The TWEEN (20, 60 and 80) surfactants produced the least. The volume of foam produce by TWEEN decreased from TWEEN 20 to TWEEN 80 and then to TWEEN 60. This was probably

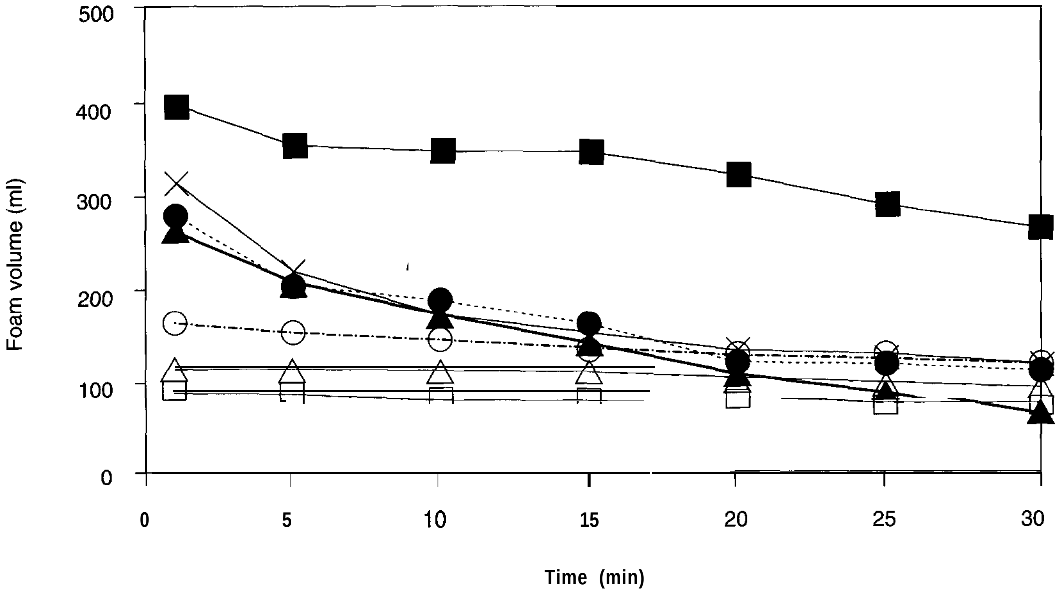

Figure 3. Foam volumes of individual surfactants (■) a-SMEPS, (●) NONIPOL 95, (X) NONIPOL 120, (▲) NONIPOL 400, (○) TWEEN 20, (□) TWEEN 60, (△) TWEEN 80.

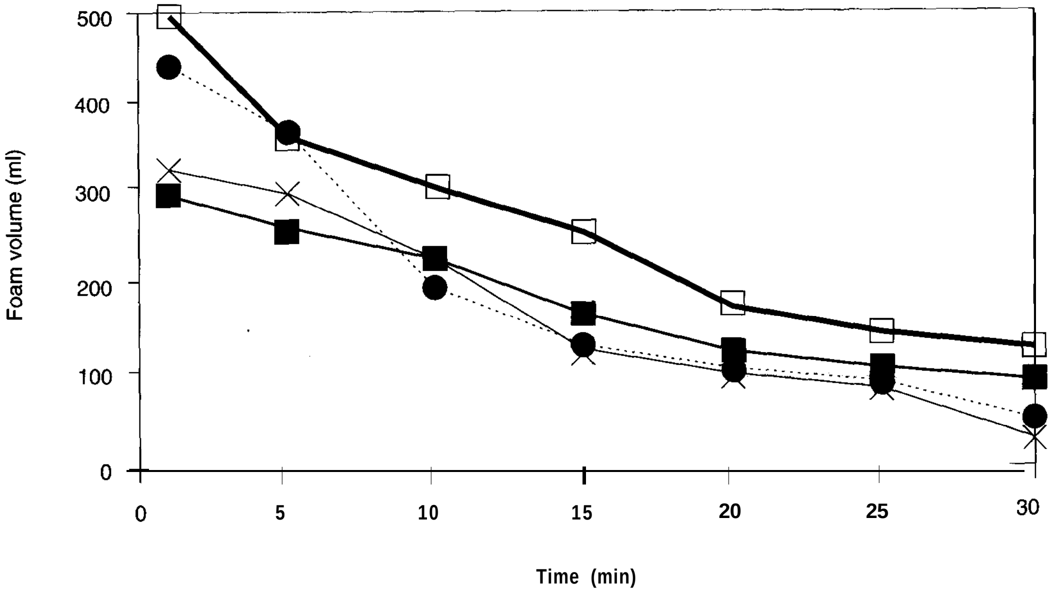

Figure 4a. Foam volumes at different weight ratios **of** *α-SMEPS:NONIPOL 95 at (■) 20:80, (X) 40:60, (●) 60:40, (□) 80:20.*

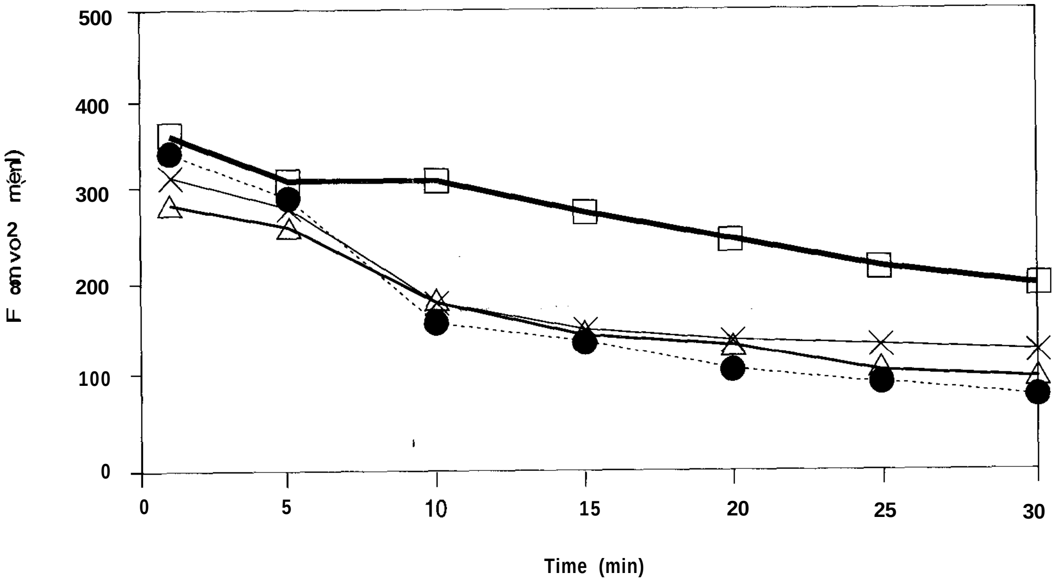

Figure 4b. Foam volumes at different weight ratios **of** *α-SMEPS:NONIPOL 120 at (X) 20:80, (△) 40:60, (●) 60:40, (□) 80:20.*

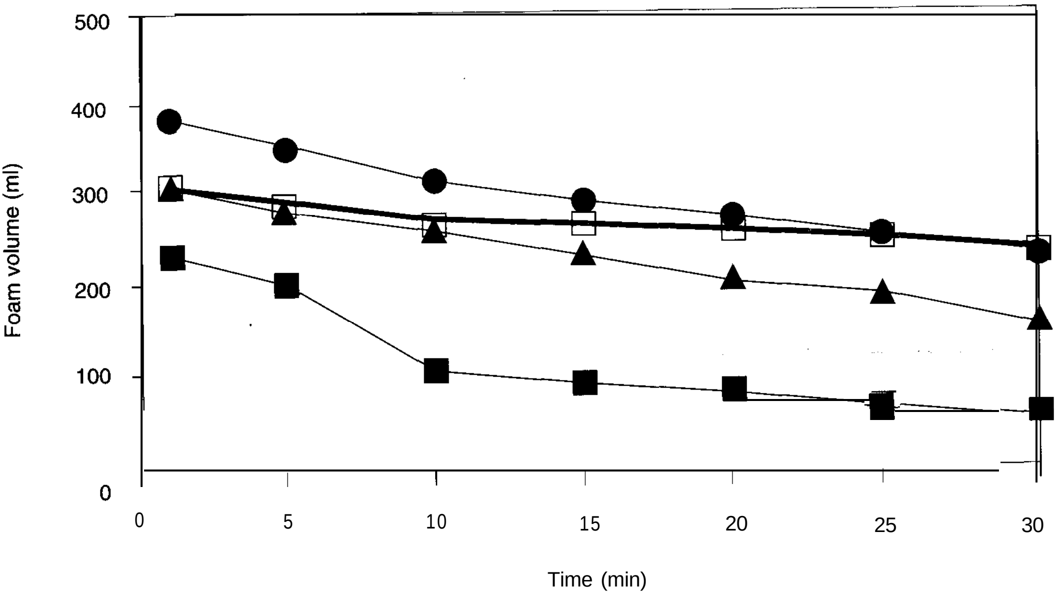

Figure 4c. Foam volumes at different weight ratios of a-SMEPS:NONIPOL 400 at (■) 20:80, (▲) 40:60, (●) 60:40, (□), 80:20.

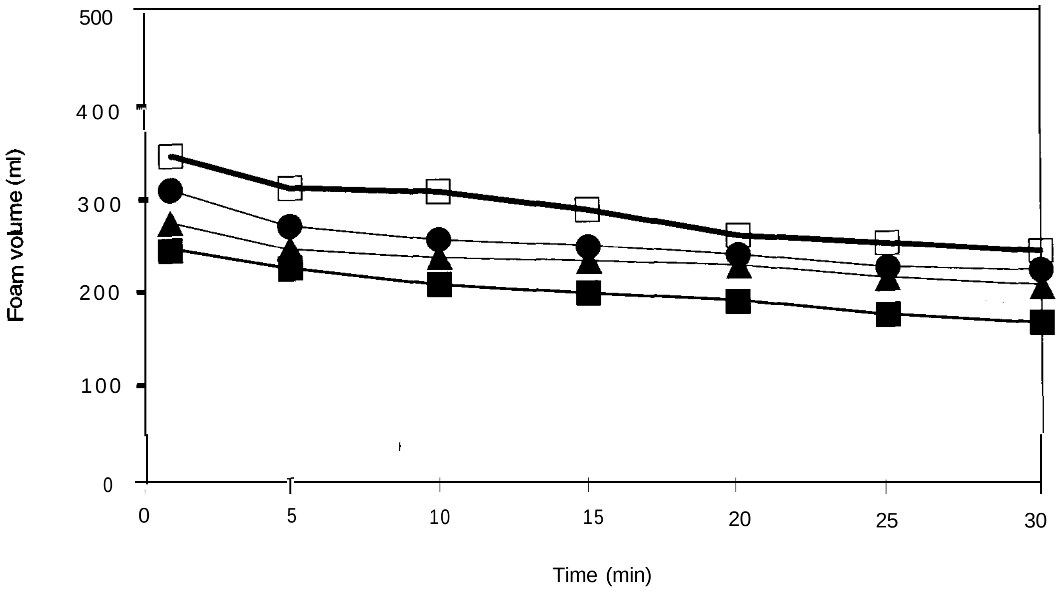

Figure 5a. Foam volumes at different weight ratios of a-SMEPS:TWEEN 20 at (■) 20:80, (▲) 40:60, (●) 60:40, (□) 80:20.

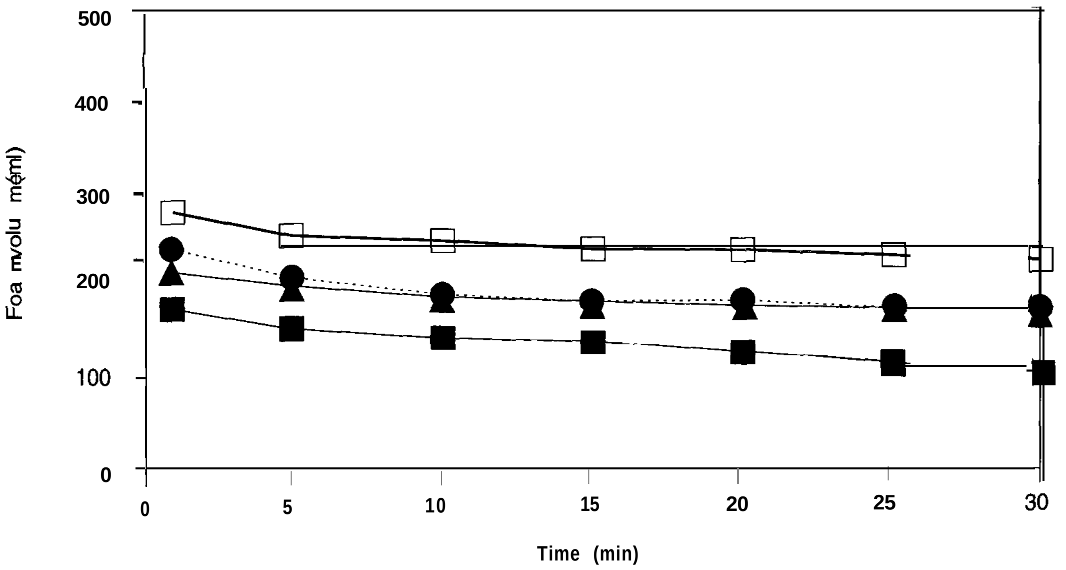

Figure 5b. Foam volumes at different weight ratios of a-SMEPS:TWEEN 60 at (■) 20:80, (▲) 40:60, (●) 60:40, (□) 80:20.

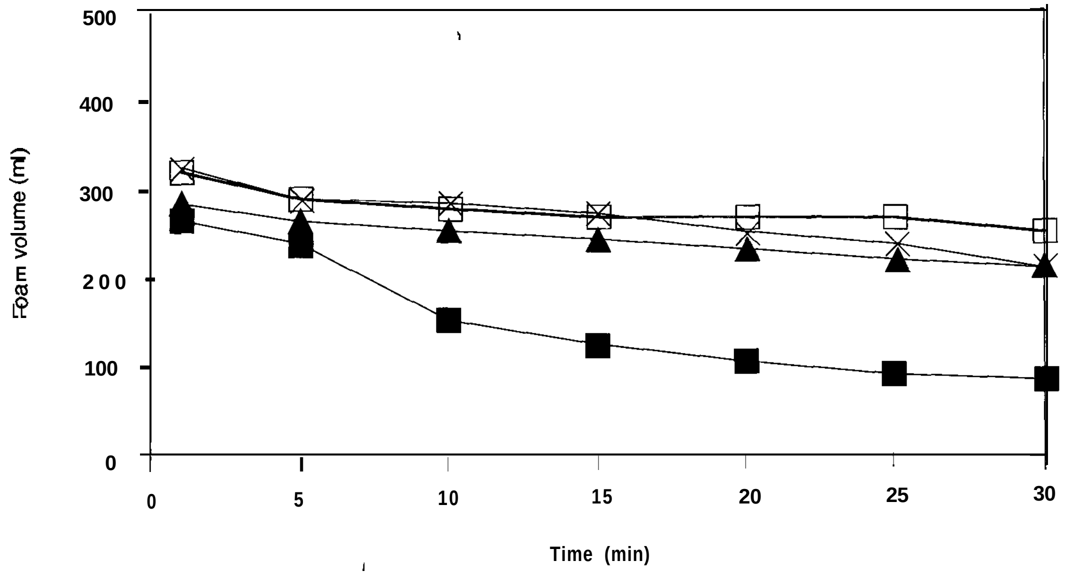

Figure 5c. Foam volumes at different weight ratios of α-SMEPS:TWEEN 80 at (■) 20:80, (▲) 40:60, (X) 60:40, (□) 80:20.

due to the increase in hydrophobicity in the hydrocarbon chain of the surfactant.

Incorporation of a nonionic surfactant (TWEEN or NONIPOL) disrupted the lamellar layer of the foam and increased the steric interaction between the anionic-nonionic surfactants. As a result of this disruption, an 'ease of hole' formed as the nonionic surfactant (NONIPOL and TWEEN) was incorporated into the solution (Jönsson *et al.*, 1998; Rosen, 1989). This shortened the life of the foam.

CONCLUSION

Better performance and multi-functionality can be obtained by mixing a-SMEPS with the nonionic surfactants, NONIPOL and TWEEN. Incorporating NONIPOL or TWEEN surfactants into a-SMEPS solution can increase the surfactant aggregation and decrease its Krafft temperature. The a-SMEPS:NONIPOL 400 mixture of 60:40 weight ratio gave the best result in decreasing the Krafft temperature. However, the TWEEN surfactants had little effect. The foaming ability of a-SMEPS can be reduced by the presence of nonionic surfactants, NONIPOL and TWEEN.

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