

# Some Characteristics of Sugar Ester Nonionic Microemulsions in View of Possible Food Applications

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This study explores some characteristics of microemulsions composed of sucrose monostearate (SMS), medium-chain triglycerides (MCT), or *R*-(+)-limonene, alcohols, and water. The systems are homogeneous, soft, and waxy solids at room temperature but liquefy and structure into homogeneous microemulsions when heated to >40 °C. The amount of solubilized water is enhanced as a function of the alcohol/oil ratio and is inversely proportional to the alcohol chain length. Over 60 wt % water can be solubilized in systems consisting of propanol/MCT/SMS at a weight ratio of 3:1:4 (initial weight ratio). These microemulsions are unique and differ from nonionic ethoxylated-based microemulsions in that their viscosity is very low and is reduced with increasing amounts of solubilized water. The electrical conductivity increases only slightly as a function of the water content and does not show typical bicontinuous or percolated behavior. The water in the core of the microemulsion strongly binds to the headgroups of the surfactant. Only at >15 wt % solubilization of water was free or bulk water detected in the core of the microemulsions. Such unique behavior of the core water might have a possible application in systems requiring monitoring of enzymatic (lipase) reactions carried out in the microemulsions as microreactors.

**Keywords:** *Sucrose esters; W/O microemulsions; water solubilization; nonionic surfactants; phase diagrams; solid–liquid transitions; bound and free water; viscosity*

## INTRODUCTION

Nonionic microemulsions have been extensively investigated. Phase diagrams, solubilization capabilities, curvatures, interfacial compositions in the presence of cosurfactants/cosolvents, and microstructures have been elucidated (Bansal et al., 1980; Strey and Jonstromer, 1992; Kunieda and Yamagata, 1993; Paul and Moulik, 1997; Garti et al., 1996).

In most nonionic microemulsions the nonionic surfactants are ethoxylated alcohols, acids, oils, etc. However, only a limited amount of work was conducted with polyol types of nonionic surfactants, such as ethers (sucrose glycosides) or esters (sucrose esters) (Thevenin et al., 1996, 1999; Garti et al., 2000a,b). Although few scientific reports on the use of sucrose esters for the preparation of microemulsions are available, several patent applications have been filed (Nishinohara et al., 1975; Schreiber et al., 1996), emphasizing again the advantages of sucrose esters, particularly their large emulsifying capacity and their stability to stress.

Due to the fact that sucrose esters do not lose solubility with temperature, attempts have been made to prepare temperature-insensitive microemulsions based on sucrose monoalkanoate and cosurfactant (Pes et al., 1993; Baran and Wade, 1995; Kunieda and Solans, 1996). Others have made similar temperature-insensitive microemulsions based on sucrose monolaurate mixed with ethoxylated alcohols; the oil phase was heptane (Kunieda et al., 1993).

Keipert and Schulz (1994) have used isopropylmyristate (IPM) with propylene glycol and a mixture of two types of sucrose laurates (HLB 5 and 16) and have solubilized pilocarpine in the formed microemulsions. The system was discussed as a potential drug carrier for ocular administration with modified availability. No phase diagrams were reported.

The cosmetic industry is well aware of the possibilities arising from the use of sucrose esters for the preparation of nonionic water/oil (W/O) microemulsions. The food industry is not yet utilizing microemulsions, and no commercial applications of nonionic microemulsions are known. Technologists may have numerous reasons for not using these formulations: (1) Sucrose esters are not able to form microemulsions in which considerable amounts of water are solubilized unless considerable amounts of cosurfactant (alcohols) are used (Thevenin et al., 1996). (2) Sucrose esters are scarce or inadequately available, and consequently their relative cost is high. (3) Sucrose esters have been neither well characterized nor sufficiently purified because most commercial sucrose esters are complex mixtures of mono- and polyesters of mixed fatty acids. (4) Sucrose esters are not approved for use in foods in many countries. Only recently have some hydrophilic sucrose esters become available in more purified and well-characterized forms and approved for some food applications in Europe and the United States. The more hydrophobic esters are still not permitted in some countries for use as food emulsifiers.

In our previous studies (Garti et al., 1996) we aimed at developing a microemulsion-based fire-resistant hydraulic fluid. We investigated the influence of cosurfac-

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tants (straight-chain alcohols) on the water solubilization capacity of certain nonionic water-in-oil microemulsions. We demonstrated the validity of the empirical solubilization equation known as "the BSO equation" and the concept of chain length compatibility (Kahlweit et al., 1991; Garti et al., 1998) that can predict, within some limits, conditions for maximum water solubilization. This equation was examined because polyol sucrose esters are temperature insensitive and water binding to hydroxyl groups is similar to that of ethoxylated groups. Our present interest is in the food area and, therefore, attempts have been made to study phase diagrams, solubilization, and microstructuring of microemulsions made with sucrose esters with the aim to improve the solubilization of active matter.

In the present study we extended the studies to food-permitted solvents (*R*-limonene) and vegetable oils (rather than hydrocarbons) and concentrated on only one hydrophilic emulsifier, sucrose monostearate, microemulsions of which are solid at room temperature and liquefy only upon heating. We explored the role of the cosurfactants, their nature, and the ratios of oil to cosurfactant required for maximum solubilization of water. The advantages that these microemulsions can offer are immobilization of active matter for sustaining release and protection of media for sensitive or active matter that must be stored "on the shelf" for prolonged periods of time.

## EXPERIMENTAL PROCEDURES

**Materials.** The sucrose ester used in this study was a commercial sucrose monoester of stearic acid (SMS), which is mixture of mostly monoester with di- and polyesters of stearic and palmitic acids (S-1570, HLB 15 and minimum 70 wt % monoester). The surfactant was of food grade and was obtained from Mitsubishi-Kagaku Food Corp. (Tokyo, Japan). The molecular weight (MW) of this surfactant was calculated on the basis of averaging the internal composition of the commercial product. The MW is 519 based on 70% monoester plus 30% di- and polyesters. Other surfactants in use such as distilled glycerol monostearate (GMO), distilled diglycerol monostearate (DGMO), and diglycerol of mono- and distearate (DGMDO) were courtesy of Danisco (Brabrand, Denmark) and were used for preparation of reference microemulsions.

The oil phase consisted, in most cases, of caprylic/capric triglycerides, also known as medium-chain triglycerides (MCT, Miglyol 818), and was obtained from Huls AG, Germany. Miglyol 818 is composed of caproic acid ( $C_{6:0}$ ) maximum 2 wt %, caprylic acid ( $C_{8:0}$ ) 40–60 wt %, capric acid ( $C_{10:0}$ ) 25–40 wt %, and lauric acid ( $C_{12:0}$ ) maximum 3 wt %, as per the producer's claim. Miglyol 818 does not contain any significant amounts of mono- and diglycerides. For comparison, *R*(+)-limonene (98%, GC grade) and soybean oil were also used in some microemulsions. The *R*(+)-limonene was purchased from Fluka Chemie AG (Buchs, Switzerland), and soybean oil (pharmaceutical grade) was obtained from Nutriswiss Morgia AG, Lyss, Switzerland. Oleic acid (99%, GC grade) was also obtained from Fluka Chemie AG.

Medium-chain alcohols, 1-propanol, 1-butanol, and 1-pentanol, were obtained from Merck Chemicals (Darmstadt, Germany). All compounds were chemically pure and used without further purification.

Double-distilled water was used. Sodium chloride of analytical grade was purchased from J. T. Baker Inc. (Phillipsburg, NJ), and 0.05 wt % was added in some microemulsions for measuring electrical conductivity trends.

**Determination of Phase Diagrams.** The behavior of a four-component system is described on pseudoternary phase diagrams in which the weight ratio of two components was fixed. Usually, the oil/alcohol weight ratio was held constant at 1:1. The construction of the phase diagram was conducted

in a thermostatic bath ( $50 \pm 0.2$  °C). Ten weighted samples composed of mixtures of surfactant, alcohol (cosurfactant), and oil were prepared in culture tubes sealed with viton-lined screw caps at predetermined weight ratios of (alcohol + oil) to surfactant. These mixtures were titrated with water. These aqueous mixtures are samples along water dilution lines drawn to the water apex from the opposite side of the triangle. In all of the samples tested, evaporative loss was negligible. Nearly all samples were equilibrated during a time interval of up to 24 h. The tubes were then inspected visually. Appearance of turbidity was considered as an indication for phase separation. The phase behavior of such samples was determined only after sharp interfaces had become visible. The completion of this process was hastened by centrifuging the samples. Every sample that remained transparent and homogeneous after vigorous vortexing was considered as belonging to a monophasic area in the phase diagram (Garti et al., 1996, 1998, 2000b; Waysbort et al., 1997).

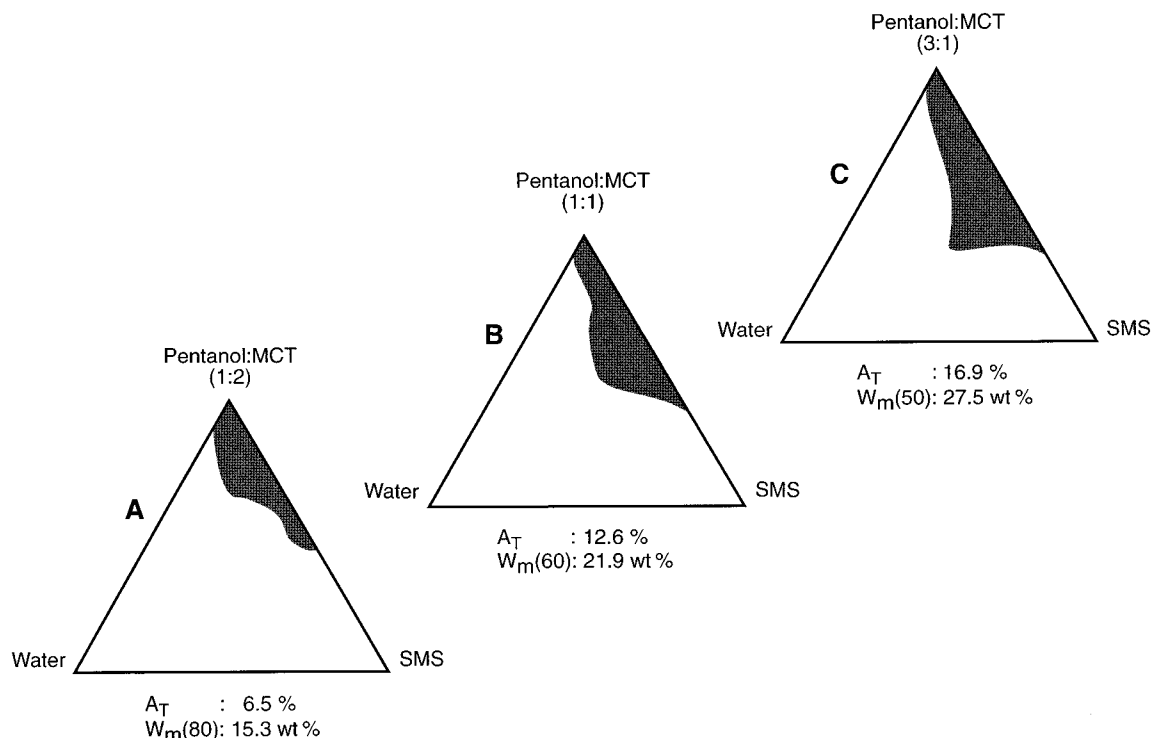
**Solubilization Parameters.** The goal of our work was to incorporate a large amount of water into the microemulsion. Thus, the water solubilization was estimated as the monophasic areas of the relevant phase diagrams. It is well documented that the water solubilization capacity of different amphiphilic systems should be strictly compared at optimal solubilization capacity (Shinoda and Friberg, 1986; Paul and Moulik, 1997). Because the maximum solubilization of water appears sometimes on different water dilution lines (a line in the phase diagram beginning with a mixture of alcohol, oil, and surfactant at a fixed ratio, which is diluted with water), it is common to list the maximum solubilization of water ( $W_m$ ) on the dilution line in which maximum solubilization was obtained. The problem of comparing  $W_m$  values that lie on different dilution lines was discussed in our previous paper (Garti et al., 1996). In our sucrose ester based systems  $W_m$  values lie, within experimental error, on virtually the same specific dilution line (Garti et al., 2000a,b), and therefore we feel that the comparison between the  $W_m$  values is a proper way of estimating the maximum solubilization. A comparison of systems with different surfactant/alcohol ratios that lead possibly to different interface compositions was done.

Li et al. (1989) have employed as a solubilization parameter the total monophasic area. It is the sum of the five cross-sectional areas in the tetrahedral phase diagram, each with a different oil/surfactant ratio. We will call this area  $A_T$ . The relative error in determining the  $A_T$  and (wt %)  $W_m$  was estimated to be  $\pm 0.5\%$  for all systems studied. In our comparative studies we used both the  $A_T$  and (wt %)  $W_m$  values.

**Viscosity Measurements.** Viscosity was measured on a Carry-Med viscometer, model CLS2 100, TA Instruments GmbH (Alzenau, Germany). A "double cylinder" geometry was used. The temperature was controlled and kept constant at  $50 \pm 0.2$  °C using a model 9100 thermostat from Polyscience (Division of Preston Industries, Inc., Niles, IL). Sample preparation included preshearing for 2 min and equilibration for 30 s at 50 °C. The flow step included a continuous ramp at 50 °C and shear stress (0 Pa and end value at 9 Pa). Ramp duration was 5 min. The set gap was 500  $\mu$ m. The sample volume was 4 mL.

**Electrical Conductivity Measurements.** Electrical conductivity of the isotropic phases (at 50 °C) was measured with a conductivity meter, a model CDM 83 Radiometer (Copenhagen, Denmark). For electrical conductivity measurements all microemulsions were made using a 0.05 wt % aqueous solution of NaCl. The electrode was dipped in the microemulsion sample until an equilibrium was reached and the reading became stable (20 min).

**Calorimetric Measurements.** A Perkin-Elmer model Pyris-RS (Perkin-Elmer Europe B.V., Rotkreuz, Switzerland) thermal analysis system was used. The DSC measurements were carried out as follows: microemulsion samples (5–15 mg) were weighed, using a Mettler M3 microbalance, in standard 50  $\mu$ L aluminum pans and immediately sealed. The instrument was calibrated using indium as reference material. An empty pan was used as the reference. All DSC measurements were performed in the endothermic scanning mode (i.e., the con-



**Figure 1.** Phase diagrams of SMS/water/pentanol+MCT-based microemulsions at 50 °C and various pentanol/MCT initial weight ratios: (A) 1:2; (B) 1:1; (C) 3:1. The black and white areas represent the one- and two-phase regions, respectively. No attempt was made to further identify the liquid crystals or any other phase within the two-phase area. Each apex represents 100 wt % of the relevant component.

trolled heating of previously frozen samples), thus circumventing possible complications from supercooling when measurements are performed in cooling (exothermic) mode. The samples were rapidly cooled by liquid nitrogen at a predetermined rate from ambient to  $-60$  °C and then heated at a constant scanning rate (usually 5 °C/min) back to ambient temperatures. The same results were obtained when the samples were kept at the minimum temperature for 1 h. The calorimeter measured and recorded the heat flow rate (in W/g) of the sample as a function of temperature, whereas the sample underwent the cooling and heating procedure mentioned above. The instrument also determined the total heat transferred in the observed thermal processes. The enthalpy changes associated with thermal transitions,  $\Delta H_{\text{melt}}$ , were evaluated by integrating the area of each pertinent DSC peak. DSC temperatures reported here were reproducible to  $\pm 0.5$  °C and have absolute values calibrated to  $\pm 1$  °C.

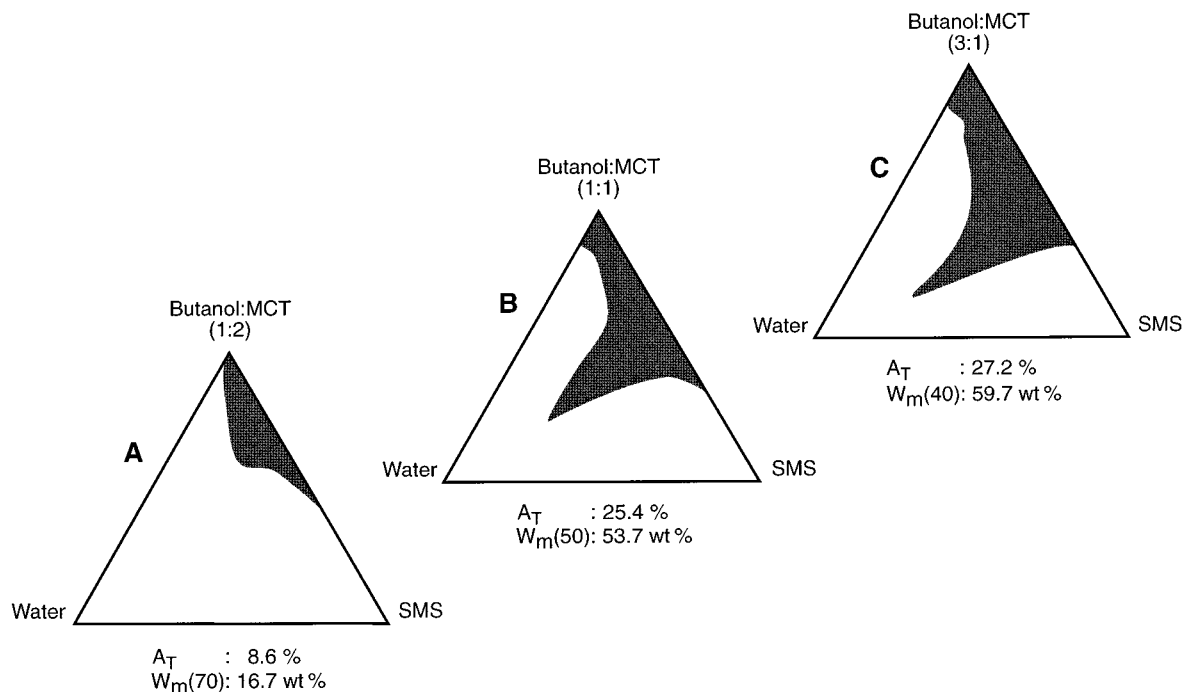
## RESULTS AND DISCUSSION

**Phase Diagrams.** Binary mixtures of sucrose monostearate (SMS) and MCT revealed that the oil is a poor solvent for this amphiphilic compound and that there is practically no miscibility between the two compounds. Sucrose monostearate appears to be too hydrophilic for dissolution into MCT. However, the addition of cosolvents ( $C_3$ – $C_5$  alcohols) to the MCT turned the oil phase into a better solvent for the sucrose monostearate and allowed significant dissolution of the emulsifier (up to 60 wt %). The maximal solubility of the sucrose monostearate in the alcohol/oil mixture is between 50 and 60 wt % (depending on the nature of the alcohol). The solubilities are very similar for all alcohols investigated in this study (initial alcohol/oil weight ratios were varied from 1:2 to 3:1). Moreover, the emulsifier solubility increases only slightly with increasing alcohol/MCT ratio.

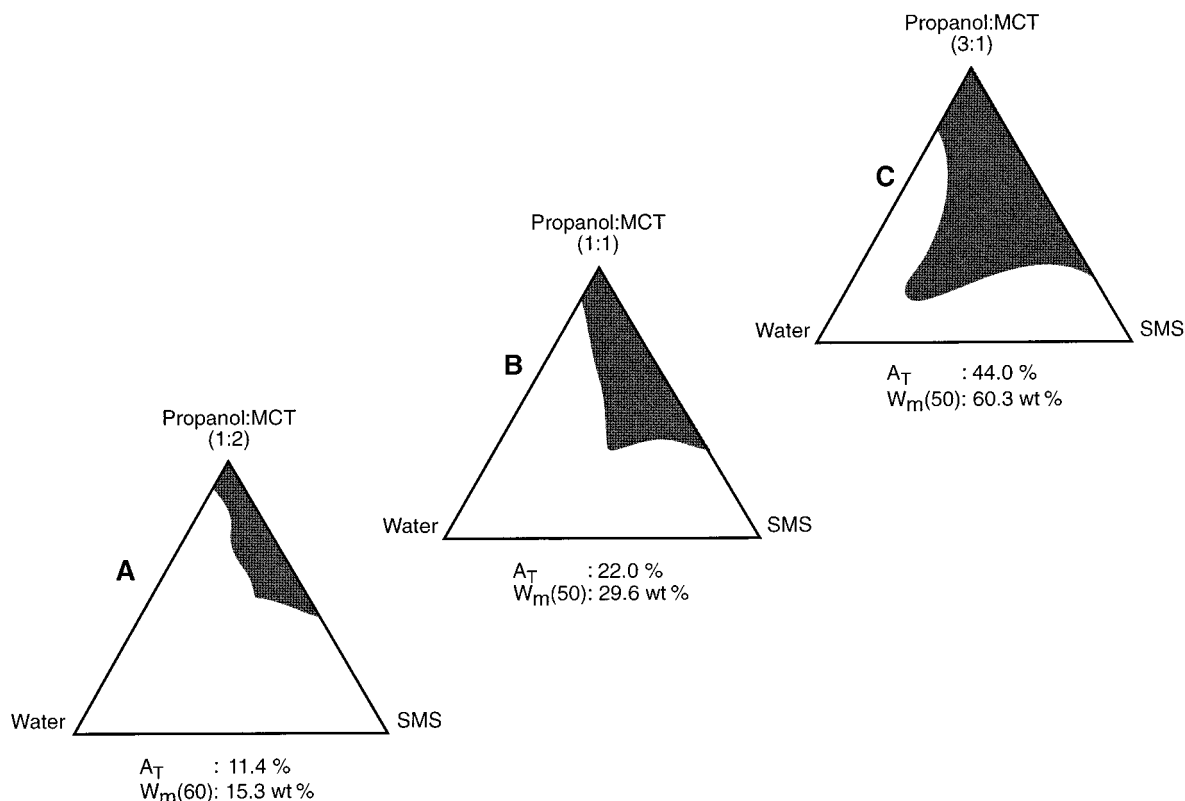
The phase diagrams and the isotropic areas in which water was solubilized at three different initial pentanol/

MCT weight ratios are shown in Figure 1. Whereas the water solubilization capacity of the micellar system at an initial pentanol/MCT weight ratio of 1:2 is below 16 wt % ( $W_m = 15.3$  wt %),  $W_m$  increases to 27.5 wt % at an initial pentanol/MCT weight ratio of 3:1. It should be stressed that the binodal line determining the boundary of the microemulsion single-phase region is not a straight line but bends toward the water corner at increasing sucrose ester contents. This means that the water solubilization capacity, i.e., the maximal amount of water solubilized per gram of sucrose monostearate, increases overproportionally with the addition of surfactant. A consequence of this finding is that microemulsions having a composition in the vicinity of the binodal will phase separate upon dilution with the oil phase. The practical aspect of this behavior is that these microemulsions are not easily dilutable with oil. Another conclusion that can be drawn from the inspection of the phase diagrams is that when W/O microemulsions are formulated at sucrose monostearate concentrations  $< 20$  wt %, maximal water solubilization capacity is slightly increased when the alcohol/oil ratio is decreased from 3:1 to 1:2. This is the opposite of what is observed for higher emulsifier concentrations ( $> 20$  wt %). These findings suggest that the composition of the droplet interface depends on both the initial pentanol/MCT weight ratio and the sucrose ester content in the system.

Figures 2 and 3 show the isotropic areas of solubilized water and the phase behavior of systems in the presence of 1-butanol and 1-propanol, respectively, at different initial alcohol/MCT weight ratios. In these cases the oil phase is more hydrophilic than in the presence of pentanol at comparable initial alcohol/MCT weight ratios. As a consequence, smaller amounts of alcohol (lower alcohol/oil proportion) are needed to significantly



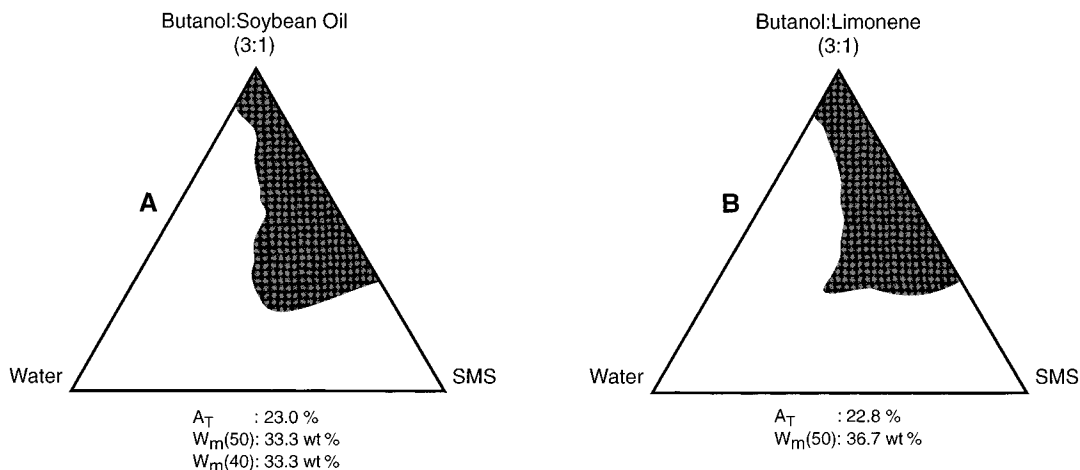
**Figure 2.** Phase diagrams of SMS/water/butanol+MCT-based microemulsions at 50 °C and various butanol/MCT initial weight ratios: (A) 1:2; (B) 1:1; (C) 3:1. The black and white areas represent the one- and two-phase regions, respectively. No attempt was made to further identify the liquid crystals or any other phase within the two-phase area. Each apex represents 100 wt % of the relevant component.



**Figure 3.** Phase diagrams of SMS/water/propanol+MCT-based microemulsions at 50 °C and various propanol/MCT initial weight ratios: (A) 1:2; (B) 1:1; (C) 3:1. The black and white areas represent the one- and two-phase regions, respectively. No attempt was made to further identify the liquid crystals or any other phase within the two-phase area. Each apex represents 100 wt % of the relevant component.

increase the  $W_m$  value. With a butanol/MCT ratio of 1:1 the  $W_m$  value is 53.7 wt % and still slightly increases when the ratio is even higher. A similar behavior is observed for the *n*-propanol system. However, the solubilization capacity of this system is maximal only at the

highest alcohol/MCT ratio. Notice also that for the more hydrophilic alcohols the binodals bent more to the water corner. Again, this means that all alcohol-based microemulsions are not dilutable with the lipidic phase without risk of phase separation.



**Figure 4.** Phase diagrams of the SMS/water/butanol+oil system (weight ratio of butanol/oil is 3:1) compositions. The oil phase is (A) soybean oil or (B) *R*-(+)-limonene. The black and white areas represent the one- and two-phase regions, respectively. No attempt was made to further identify the liquid crystals or any other phase within the two-phase area. Each apex represents 100 wt % of the relevant component.

The use of ethanol was avoided to prevent high mutual miscibility of surfactant–oil–alcohol at the expense of micellization and microstructure formation. All microemulsions were prepared and inspected at 50 °C. When allowed to cool to room temperature, they solidified into a homogeneous waxy solid. Upon reheating, the system remelted and the water remained solubilized.

In conclusion, if one compares the three alcohols on the basis of the constant initial alcohol/MCT weight ratio of 1:1, butanol is the optimal alcohol as cosolvent for maximum solubilization into the sucrose monostearate/water/MCT system. The butanol solubilizes 53 wt % water in comparison to 22 and 30 wt % of solubilized water for pentanol and propanol, respectively. Pentanol seems to be too lipophilic and propanol slightly too hydrophilic. At lower initial alcohol/MCT weight ratios, i.e., 1:2, however, the maximum solubilization is only ~15 wt % for all of the alcohols. Obviously, more alcohol is needed to get differentiation between the three alcohols in terms of maximal water solubilization. The solubilization effect of butanol was demonstrated also in our previous work (Garti et al., 2000a,b).

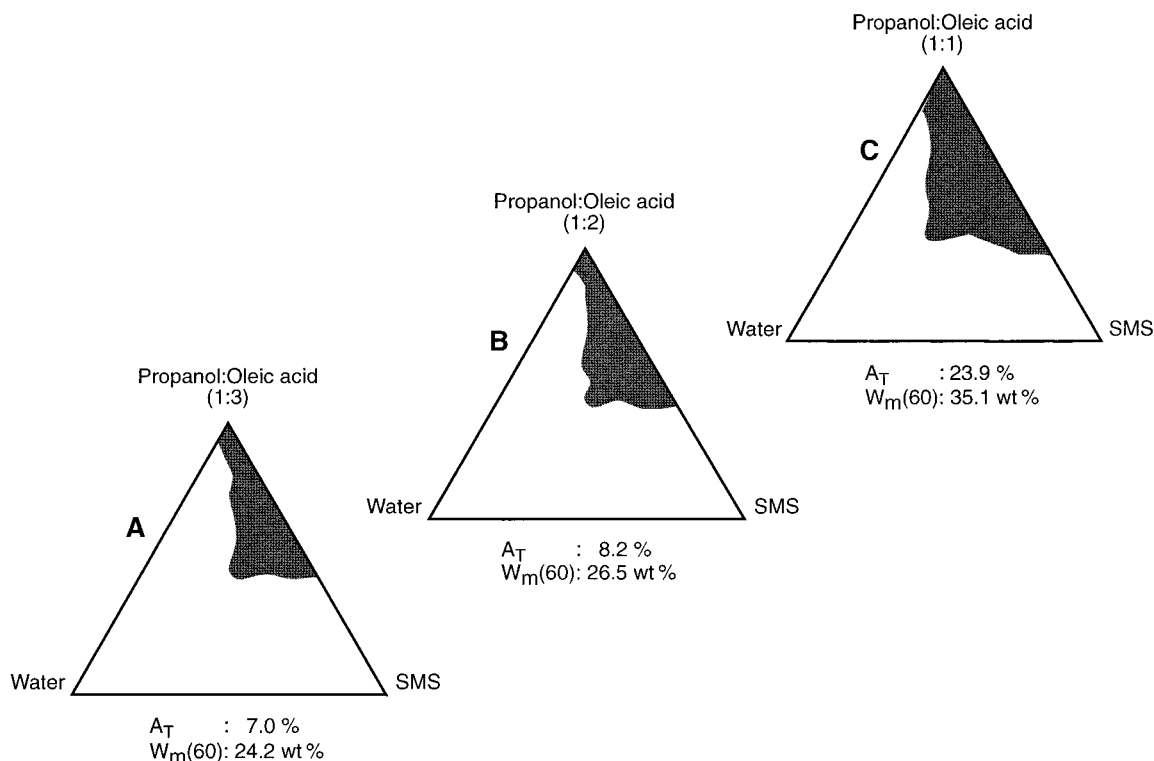
#### Effect of Oil Phase on Water Solubilization.

**Soybean Oil.** The fatty acids in the MCT are relatively short and the oil, therefore, is more hydrophilic than vegetable oils, which have longer fatty acid chains. We examined the solubilization of water into sucrose ester formulations containing soybean oil in the presence of butanol (butanol/soybean oil = 3:1) and compared the phase behavior with the MCT system. The ratio 3:1 instead of 1:1 was used because soybean oil at ratio of 1:1 does not solubilize any amount of water. This phenomenon is known and is related to the high molecular volume of the triglyceride, which prevents packing into small swollen micelles. The  $A_T$  values of MCT and soybean oil are indeed quite similar. However, the  $W_m$  values are very different (59 wt % for MCT and 33 wt % for soybean oil). At low initial surfactant concentrations the differences in  $W_m$  are very small because only a very small amount of water is solubilized in both cases. However, when the initial surfactant concentration is increased and more water is solubilized, the oil molecular volume plays a more significant role, and therefore the differences are expressed in terms of  $W_m$  rather than in terms of  $A_T$ . Figure 4A shows that

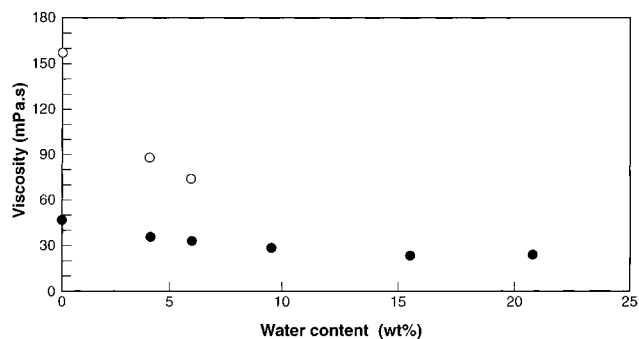
the system is capable of solubilizing up to 33 wt % of water in the presence of ~35 wt % of surfactant. This is a significant amount of water solubilization, however, still substantially lower than the solubilization in the MCT containing system (59 wt % water with ~25 wt % sucrose ester).

***R*-(+)-Limonene.** The triglyceride oils were replaced by *R*-(+)-limonene, which is derived from citrus peels. The solvent is composed of isoprene (hydrocarbon) dimers and, therefore, is even more lipophilic than the MCT and soybean oil. The measured phase diagram is shown in Figure 4B. The solubilization behavior is very similar to that found for the soybean oil. Obviously, the relatively large difference in the molecular weight of the two oils is not significantly influencing the maximum water solubilization capacity of the system. Surprisingly, less water can be solubilized under optimal conditions ( $W_m = 36.7$  wt % at ~30 wt % surfactant) in comparison to the MCT system. We assume that this is related to the reduced miscibility of the alcohol/surfactant mixture in this solvent.

**Oleic Acid.** Our commercial interest is in lipase-based specific reactions in microemulsions. The vegetable oil is attacked by the enzymes and must, therefore, be replaced by a liquid fatty acid such as oleic acid. The oleic acid will increase the hydrophilicity of the oil and is not susceptible to hydrolysis. The systems were composed of initial propanol/oleic acid weight ratios of 1:3, 1:2, and 1:1 (for comparison, see system B in Figure 3 in which the oil was MCT and system C in Figure 5 for oleic acid). The solubilization capacity of the alcohol-rich composition is quite remarkable because >35 wt % water can be solubilized on the 60% dilution line (propanol/oleic acid, 1:1). It should be noted that oleic acid microemulsions that have been coemulsified with butanol showed lower solubilization capacity than those composed of propanol as the cosolvent (not shown). The improved solubilization in the oleic acid microemulsions can be again explained in terms of molecular volume and packing parameters and in terms of improved miscibility in the alcohol/surfactant mixture. Structural data will probably clarify the differences. Small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) techniques are currently being applied to these oleic acid microemulsions coemulsified with butanol or propanol.



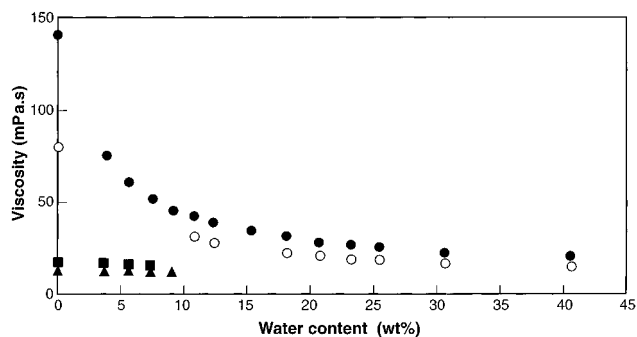
**Figure 5.** Phase diagrams of the SMS/water/propanol+oleic acid composition system at 50 °C. The propanol/oleic acid initial weight ratios are (A) 1:3, (B) 1:2, and (C) 1:1. The black and white areas represent the one- and two-phase regions, respectively. No attempt was made to further identify the liquid crystals or any other phase within the two-phase area. Each apex represents 100 wt % of the relevant component.



**Figure 6.** Viscosity as a function of water content of the microemulsions made of SMS/water/pentanol+MCT at 50 °C. Initial weight ratios of pentanol/MCT/SMS: 1:1:2 at (●) 50% dilution line; 1:1:3 at (○) 60% dilution line.

**Viscosity Measurements.** *Sucrose Ester Microemulsions.* All binary, ternary, or quaternary single-phase mixtures under investigation behave like Newtonian fluids at 50 °C. The measured viscosities of the binary mixtures of MCT and alcohols (pentanol and butanol) at the initial alcohol/oil weight ratios of 3, 1, 0.5, 0.3, and 0.2 were for butanol-based system 2.7, 3.8, 5.0, 6.0, and 7.4 mPa·s, respectively, and for pentanol-based system <1.0, 3.9, 4.9, 5.8, and 7.0 mPa·s, respectively. The viscosity increases only slightly when the alcohol/oil ratios are decreased. The pentanol/oil mixtures were slightly less viscous than the butanol/oil compositions.

The viscosity of two quaternary pentanol-based microemulsions (oil/sucrose ester ratios of 1:1 and 3:2) at an alcohol/MCT ratio of 1:1 was measured as a function of the solubilized water content at 50 °C (Figure 6). It was quite surprising to find that the viscosity in both systems was reduced as the water content increased. Ternary mixtures (oil/alcohol and oil/alcohol/sucrose

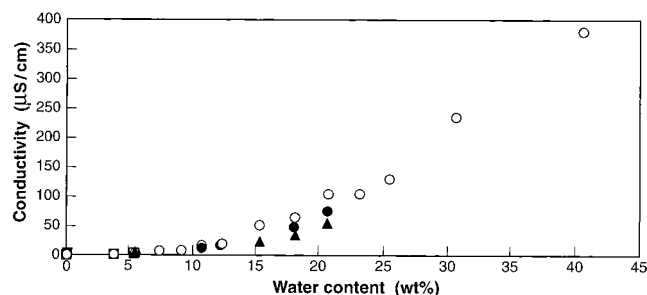


**Figure 7.** Viscosity as a function of water content of microemulsions made of (●) butanol/MCT/SMS at initial weight ratio of 1:1:2, (○) butanol/MCT/SMS at initial weight ratio of 3:1:4, (▲) butanol/MCT/GMO at initial weight ratio of 1:1:2, and (■) butanol/MCT/DGMDO at initial weight ratio of 1:1:2 at 50 °C.

ester) were more viscous than the corresponding quaternary water-containing microemulsions. Figure 6 also reveals that in the system with the higher sucrose ester content the decrease in viscosity is more significant than in the system with less surfactant.

Figure 7 shows the viscosity of two butanol-containing systems with initial alcohol/oil weight ratios of 3:1 and 1:1 as a function of the solubilized water content. The reduction in viscosity was similar to that found in the pentanol-containing systems, and viscosity decreased as water percentage increased. The differences between the two systems were not dramatic but nevertheless indicated that systems "rich" in alcohol are slightly less viscous than alcohol-poor systems when diluted on the same dilution line (the same sucrose ester/oil ratio).

Generally, swelling microemulsion droplets tend to self-interact more and more due to the increasing volume and entanglement of the aggregates. As a



**Figure 8.** Electrical conductivity (at 50 °C) as a function of water content in microemulsions (loaded with 0.05 wt % NaCl) made of (○) butanol/MCT/SMS (1:1:2) and water, (●) butanol/MCT/SMS at initial weight ratio of 3:1:4, (■) butanol/MCT/SMS at initial weight ratio of 2:1:3, (▲) pentanol/MCT/SMS at initial weight ratio of 1:1:3 on the dilution line of 60 wt %, and (□) pentanol/MCT/SMS at initial weight ratio of 1:1:2 on the dilution line of 50 wt %.

consequence, the viscosity is expected to increase in swelling microemulsion systems. Such an increase in viscosity was observed, for instance, in ethoxylated nonionic microemulsions (Garti et al., 1996; Ezrahi et al., 1998) and lecithin-based (phosphatidylcholine) systems (Silberstein, 2000). However, this is not found in our described sucrose ester-containing microemulsions.

In all of our results we indeed measured higher viscosity in the ternary mixtures than in the microemulsions. The reduction in the viscosity, when water is added, seems to be related to the fact that surfactant is moved from the bulk to the interface to cover the water in the oil droplets. More water solubilization causes fewer interdroplet interactions and reduction in the viscosity. Therefore, the viscosity of the continuous phase is decreased.

**GMO- and DGMDO-Based Microemulsions.** To find the correlation between the structure of the surfactant and the viscosity effect in the microemulsion, GMO and DGMDO-based microemulsions were prepared. Figure 7 summarizes the rheological properties of three different systems, all formulated with an initial butanol/MCT weight ratio of 1:1 and 50 wt % surfactant concentration in the water-deficient systems. GMO, due to its hydrophobicity, is not capable of solubilizing much water and, therefore, viscosity measurements were limited to up to 10 wt % water. The viscosity in these systems was also very low and was not influenced by the water content. Similar results were obtained with DGMO (not shown). No change in viscosity with increasing water content was observed in any of these reference systems. Therefore, it seems that the decrease in viscosity with the increase in water content should be correlated solely to the compositional and structural effects derived from the interfacial packing. In the presence of excess alcohol more surfactant can be packed at the interface, allowing better water solubilization and less free water.

**Microemulsion Electrical Conductivity Measurements.** The electrical conductivity of the microemulsions (Figure 8) was carried out by introducing 0.05 wt % NaCl into the water phase. The electrical conductivity of the brine solution was 1300  $\mu\text{S}/\text{cm}$ . The electrical conductivity of the microemulsions increased gradually with water content. Even after 40 wt % solubilization of water, the system conductivity did not exceed 400  $\mu\text{S}/\text{cm}$ . It seems, therefore, that the microemulsions have a microstructure that even at high water contents (> 50 wt %) does not change to be bicontinuous and does not invert.

These findings are quite surprising and will need further investigation and clarification in view of the previously reported systems in which bicontinuous phases have been detected (Thevenin et al., 1999). One must bear in mind that the cosmetic system previously studied was composed of sucrose monolaurate, sucrose dilaurate, alkyl ester (the oil phase), diethyleneglycol monoethyl ethers, and water, which is quite a unique composition and most probably dictates a bicontinuous structure, whereas our system is much simpler and seems to behave differently.

The electrical conductivity of the pentanol-containing system was slightly lower than that of the butanol-containing system at the same alcohol/oil ratios and at the same dilution lines with the same solubilization levels. This is fully expected as the cosolubility of butanol and water is higher than that of the mutual solubility of pentanol and water. As a result, more water/butanol is present in the oil phase than pentanol/water and it contributes more to the electrical conductivity than the pentanol/water mixture. It could also be assumed that the microdroplet structure of pentanol-containing systems is better re-formed and more structured and, therefore, prevents migration of water to the continuous phase.

**Water Binding.** Water–surfactant interactions may lead to the formation of various types of “bound” and “free” water. The definitions of “free” and “bound” water are usually considered to be technique-dependent and difficult to interpret in dynamic systems such as microemulsions. We have used in the past subzero temperature differential scanning calorimetry for studying the thermal behavior of these types of water. More details concerning the relevance of this technique are given elsewhere (Garti et al., 1996, 1998; Ezrahi, 1997).

The definitions of the “bound” and “free” water are not necessarily phenomenologically accurate in general and, in particular, for systems that are cooled and removed from their equilibrium state. However, qualitatively or semiquantitatively the first type of water molecules melting at subzero temperatures are those of practically “immobilized water” strongly “bound” to the interface. The other type of water melting at temperatures in the vicinity of zero degrees are those of “bulk” water, which are located far from the interfacial layer and thus have high mobility. This differentiation between free and bound water is important for enzymatic processes and for water soluble active molecules that need to be mobile in the inner aqueous phase of the microemulsions. If the activity of the enzyme or the release of the active matter has to be slowed or controlled, it is essential to provide the system with physical means to control their mobility. This can easily be achieved by changing the ratio of free to bound water. These layers of bound (interfacial) water also protect active and sensitive molecules from exposure to oxygen or other “invading” molecules.

**Mixtures in the Absence of Water.** Ternary mixtures of butanol/oil/surfactant at two compositional ratios were studied. The results of the main findings are summarized in Table 1 (0.0 et % added column). The thermogram (flash cooling the microemulsion from room temperature to  $-60$  °C and slow heating to 50 °C) of the ternary mixture of butanol/oil/surfactant (without water) at 1:1:2 initial weight ratio shows two separate endothermic events. The first peak, at  $-22.3$  °C, is a typical melting of pure MCT, and the second peak, at

**Table 1. Thermal Behavior of Microemulsions Made of Butanol/MCT/SMS/Water at Two Butanol/Oil Ratios in Water Content >37.5 wt %<sup>a</sup>**

sample	added water													
	0.0 wt %		9.1 wt %		12.3 wt %		16.7 wt %		18.0 wt %		23.1 wt %		37.5 wt %	
	<i>T</i> (°C)	$\Delta H$ (J/g)	<i>T</i> (°C)	$\Delta H$ (J/g)	<i>T</i> (°C)	$\Delta H$ (J/g)	<i>T</i> (°C)	$\Delta H$ (J/g)	<i>T</i> (°C)	$\Delta H$ (J/g)	<i>T</i> (°C)	$\Delta H$ (J/g)	<i>T</i> (°C)	$\Delta H$ (J/g)
BuOH/MCT/SMS (1:1:2) <sup>b</sup>	-22.3	0.6	-23.2	4.8	-24.0	0.1	-22.4	0.5	-24.0	0.1	-22.2	0.3	-25.0	traces
	-13.5	8.2	-14.8	6.5	-15.9	4.7	-13.5	2.3	-14.9	traces	-13.3	2.0	-15.0	1.8
	none	none	-12.0	0.9	-11.0	4.2	-11.0	traces	-10.9	3.0	none	none	none	none
	none	none	-10.3	0.6	-7.8	14.2	-8.2	2.7	none	none	-7.9	2.4	-9.6	2.5
	none	none	none	none	none	-4.8	2.9	-4.2	23.2	-3.6	26.0	-3.6	79.1	
BuOH/MCT/SMS (3:1:4) <sup>b</sup>			-25.1	4.3	-25.0	traces			-25.0	traces	-23.0	traces	none	none
			-16.0	0.9	-15.9	traces			none	none	none	none	none	none
			-11.4	2.6	-10.9	29.4			-10.6	7.4	-10.6	7.0	-10.3	4.7
									-6.7	7.5	-5.5	23.4	-4.7	75.2

<sup>a</sup> The results summarize the endothermic events ( $T = T_{\text{melt}}$ ,  $\Delta H = \Delta H_{\text{melt}}$ ) of the heating cycle of the microemulsions that have been cooled to  $-60$  °C and reheated (at 5 °C/min) to 50 °C. <sup>b</sup> Initial weight ratio.

$-13.5$  °C, is attributed to MCT/alcohol/SMS microstructure (reverse micelles) in the oil phase. When the alcohol content was increased to a ratio of 3:1:4, the two endothermic peaks disappeared, suggesting that the alcohol/MCT totally solubilized the MCT. This is a good prerequisite for significant water solubilization.

*Swollen Micelles with Water.* The endothermic events of the microemulsion composed of butanol/MCT/SMS at 1:1:2 initial weight ratio with increasing amounts of solubilized water were closely examined. The endothermic events occurring during the heating cycle reveal the existence of several additional melting events related to the freezing of water in the microemulsion. The melting points and the shape of the endothermic peaks vary with the amount of solubilized water in the oil phase (Table 1). At low water contents (9 wt % of solubilized water) one can detect the melting of the MCT and the butanol/MCT/SMS peaks (as per the ternary mixture) that are followed by two additional melting events at  $-12.0$  to  $-10.3$  °C, which are attributed to the melting of bound water. The two different peaks might suggest the existence of two different hydration layers of water in the microstructure. The one with lower melting ( $-12.0$  °C) might be of the direct hydration shell of the sugar ester hydroxyl groups, whereas the other ( $-10.3$  °C) can be of the bound (interfacial) water.

The melting points of the water in microemulsions containing increasing amounts of water are gradually moved to more elevated temperatures. At a 12.3 wt % water content, the endothermic events occur at  $-11.0$  and  $-7.8$  °C.

A significant change in the melting pattern was detected at a water content of 16.7 wt %. The melting points occurred at  $-8.2$  and  $-4.8$  °C. Microemulsion containing 18.0 wt % water melted at  $-10.9$  and  $-4.2$  °C, respectively. At higher water content (23.1 wt %) most of the water melts at  $-3.6$  °C with small amounts still melting at  $-7.9$  °C. At higher water fractions the water melts at a relatively constant temperature of  $-3.6$  °C and the low-melting water peaks ( $-12.0$  to  $-8.2$  °C) cannot be detected (see Table 1). At 37.5 wt % total water content, the endothermic events are similar to those of lower water contents. The disappearance of the low melting peaks is not phenomenological but rather attributed to the dilution effect and technical restrictions of the DSC instrument, which is unable to detect small amounts of the bound water.

The data in Table 1 suggest that at low water content the water molecules in the microemulsion are bound to

the headgroups of the surfactant at the interface and thus melt at lower temperatures than free (bulk) water. As the total solubilized water fraction increases, the sucrose ester hydroxyls seem to be gradually hydrated and saturated with bound (interfacial) water. At this stage free (bulk) water appears in the core of the microemulsion. The enthalpy change ( $\Delta H_{\text{m}}^{\text{f}}$ , free) of the free (bulk) water grows, and the enthalpy change of the bound (interfacial) water ( $\Delta H_{\text{m}}^{\text{b}}$ , bound) gradually decreases and eventually vanishes (because the proportions in the total mixture become very small).

It should be stressed that at the surfactant–water saturation point, at which the surfactant becomes fully hydrated, a significant alteration of the viscosity and electrical conductivity of the system could be detected. It is at the same water content ( $\sim 15$ – $20$  wt %) that the viscosity levels off and the electrical conductivity increases sharply.

If we compare the melting temperature, at the same water content, in the presence of higher alcohol fractions (butanol/MCT/SMS of 3:1:4 initial weight ratio), it can be seen that water binding is strengthened as a function of alcohol content (for example, see Table 1 at 23 wt % water content). Similarly, as the alcohol becomes more hydrophilic (compare propanol versus butanol) the water molecules bind more strongly to the amphiphilic headgroups at the interface.

Table 2 gives the calculated bound and free water fractions based on the change in the enthalpy of melting  $\Delta H_{\text{melt}}$ . The calculations are very approximate because (1) they do not correct for the differences in the  $\Delta H$  of melting of the two types of water, (2) they do not account for the dilution effects affecting  $\Delta H_{\text{melt}}$  and (3) error in the values of  $\Delta H_{\text{melt}}$  can occur when small peaks are calculated. Examination of the melting temperatures ( $T_{\text{melt}}$ ) of the water and the heat enthalpy ( $\Delta H_{\text{melt}}$ ) involved in this transition as a function of total added water in microemulsions composed of butanol/MCT/SMS (1:1:2 initial weight ratio) and gradually increasing water concentration reveals that the binding energy of the water molecule to the headgroups is reduced as the total water concentration is increased (Table 2). One can clearly see, from Table 2, that free water is detected only after  $\sim 16$  wt % of water is solubilized. The alcohol tends also to participate in the binding process of water. As the proportion of alcohol increases or as the alcohol becomes more hydrophilic, more water is bound to the alcohol with higher enthalpy changes and, therefore,



**Table 2. Endothermic Event ( $T_{\text{melt}}$ ) and Calculated Percentages of Free and Bound Water in Microemulsions Composed of Butanol/MCT/SMS/Water**

sample	water (wt %)	$T_{\text{melt}}$ (°C)	bound water (%)	$T_{\text{melt}}$ (°C)	free water (%)	mol of water/mol of SMS
BuOH/MCT/SMS (1:1:2) <sup>a</sup>	0.0					
	9.1	-12.0, -10.3	100	none	none	8.6
	12.3	-11.0, -7.8	100	very small	very small	12.0
	16.7	-8.2	50	-4.8	50	8.7
	18.0	-10.9	11	-4.2	89	2.1
	23.1	-7.9	8	-3.6	92	2.0
37.5	-9.6	3	-3.6	97	1.5	
BuOH/MCT/SMS (3:1:4) <sup>a</sup>	9.1	-11.4	100	none		14.4
	12.3	-10.9	100	none		20
	18.0	-10.6	50	-6.7	50	16
	23.1	-10.6	23	-5.5	67	10
	37.5	-10.3	6	-4.7	94	5.2

<sup>a</sup> Initial weight ratio.

**Table 3. Thermal Behavior of Microemulsions Made of Butanol/MCT at 1:1 Weight Ratio with Three Different Surfactants (SMS, GMO, and DGMDO)<sup>a</sup>**

sample	water (wt %)	$T_{\text{melt}}$ (°C)	$\Delta H_{\text{melt}}$ (J/g)
BuOH/MCT/SMS (1:1:2) <sup>b</sup>	9.1	-23.2	4.8
		-14.8	6.5
		-12.0	0.9
		-10.3	0.6
BuOH/MCT/GMO (1:1:2) <sup>b</sup>	9.1	-17.0	1.4
		-14.0	0.1
		-7.2	10.1
		-1.7	6.0
BuOH/MCT/DGMDO (1:1:2) <sup>b</sup>	9.1	-36.2	23.4
		-29.2	0.6
		-17.2	4.9
		-1.0	2.0

<sup>a</sup> Endothermic events ( $T_{\text{melt}}$ ,  $\Delta H_{\text{melt}}$ ) of the heating cycle of microemulsions consisting of 9.1 wt % water. Samples were cooled to -60 °C and reheated (at 5 °C/min) to 50 °C. <sup>b</sup> Initial weight ratio.

free water is detected only at higher total solubilized water contents.

Note that the  $\Delta H_{\text{melt}}$  in the butanol/MCT/SMS system reaches a plateau value at 23 wt % water.  $\Delta H_{\text{melt}}$  values are characteristic of the nature of oil, alcohol, and surfactant and the internal microemulsion composition. In another typical example when the microemulsion is composed of higher butanol ratios such as butanol/MCT/SMS (3:1:4 initial weight ratio), the sucrose ester together with the alcohol strongly bind the water so that after 23 wt % of total solubilized water no free water could be detected. The free water can be detected only at water levels of 25 wt %.

**Glycerol Esters as Emulsifiers.** The water binding phenomenon is very common in polyol or polyethylene glycol surfactants. However, water of hydration is not significant in classical hydrophobic food emulsifiers containing only one hydroxyl group (such as glycerol esters of fatty acids). Table 3 compares the thermal behavior of systems containing sugar esters (SMS) to glycerol esters (such as GMO and DGMDO) as emulsifiers at 9.1 wt % total added of water content. The endothermic events found during the heating mode in the DSC of the GMO- and DGMDO-based microemulsions reveal that free water appears in the core of the microemulsion already at 9.1 wt % water content (melts at -1.7 to -1.0 °C). This is in contrast to the SMS systems in which free water is detected only at 16 wt %

water content. For comparison, see also Table 1. One can speculate that since GMO and DGMDO are hydrophobic and have by far fewer hydroxyl groups available for binding water, they will be saturated at lower water content (9 wt %).

**Surfactant/Alcohol Binding Capacity.** Attempts were made to calculate the binding capacity of each hydroxyl group of the surfactant to the water at the interface. The calculations are difficult because several assumptions have to be made: (1) the molecular weight of the surfactant was averaged to 519 on the basis of the product composition declared by the manufacturer; (2) the solubilities of pentanol, butanol, and propanol in water are 3, 7, and 25 wt %, respectively; (3) all of the alcohol (except the water miscible fraction) is assumed to be at the interface and not in the oil.

The calculations are summarized in Table 4 and indicate as expected that the molar ratio of alcohol to SMS at the interface is not constant and depends on the nature of the alcohol and the alcohol/surfactant ratio. Taking the mentioned assumptions into account, it can be seen that a single SMS molecule can hydrate between 3 and 8 molecules of alcohol.

From these measurements (Table 4) one can also calculate the alcohol/SMS molar ratio, which means how many molecules of alcohol are accommodated per molecule of SMS at the interface. The main difficulty arises in trying to explain the high molar ratio of pentanol to SMS, which was found to be 8.3 (by our calculations). We do not have an explicit explanation for this anomaly.

It seems that at the point of maximum water solubilization, an average of 3.2–5.1 molecules of alcohol are accommodated per molecule of surfactant. These calculations are quite crude, and additional parameters have to be considered before final conclusions on the average binding capacity of SMS for alcohol or water can be drawn.

Micelles of SMS and butanol in MCT swell as water is added. At a butanol/SMS initial weight ratio of 1, the added water first gradually saturates the surfactant hydroxyl groups. This is reflected in the number of molecules of water per molecule of SMS, which increases to a maximum of 75. The different types of water (bound or free water) are detected by the SZT-DSC, the first 12 water molecules per SMS molecule are detected as bound (interfacial) water. As the amount of total added water increases to >16.7 wt %, free (bulk) water is detected and the number of molecules of water per molecule of SMS gradually decreases due to the core

**Table 4. Surfactant/Alcohol Binding Capacity, on the Maximum Solubilization Dilution Line, Calculated from the Thermal Behavior of the Microemulsions<sup>a</sup>**

alcohol/MCT ratio <sup>b</sup>	alcohol	dilution line [(ROH + MCT)/SMS] (wt)	composition at $W_m$ (wt %)		composition at $W_m$ (mol/100 g)	alcohol/SMS (molar ratio) at the interface
3	PrOH	50:50	H <sub>2</sub> O	60.32	3.35	4.7
			SMS	19.84	0.04	
			PrOH	11.16	0.19	
3	BuOH	40:60	H <sub>2</sub> O	59.68	3.32	3.0
			SMS	24.19	0.05	
			BuOH	11.25	0.15	
3	PeOH	50:50	H <sub>2</sub> O	27.54	1.53	4.3
			SMS	36.23	0.07	
			PeOH	26.35	0.30	
1	PrOH	50:50	H <sub>2</sub> O	29.58	1.64	3.1
			SMS	35.21	0.07	
			PrOH	13.21	0.22	
1	BuOH	50:50	H <sub>2</sub> O	53.70	2.98	3.7
			SMS	23.15	0.04	
			BuOH	10.77	0.15	
1	PeOH	60:40	H <sub>2</sub> O	21.88	1.22	4.3
			SMS	31.24	0.06	
			PeOH	22.73	0.26	
0.5	PrOH	60:40	H <sub>2</sub> O	15.25	0.85	3.2
			SMS	33.90	0.07	
			PrOH	12.71	0.21	
0.5	BuOH	70:30	H <sub>2</sub> O	16.67	0.93	4.8
			SMS	25.00	0.05	
			BuOH	18.08	0.24	
0.5	PeOH	80:20	H <sub>2</sub> O	15.25	0.85	8.3
			SMS	16.95	0.03	
			PeOH	21.92	0.25	

<sup>a</sup> Systems were prepared with three different alcohols (propanol, butanol, and pentanol) at three initial weight ratios (alcohol/oil ratios of 3, 1, and 0.5) with increasing amounts of solubilized water. The results summarize calculations of the alcohol/SMS molar ratio and the water molecules bound to each SMS molecule and to each hydroxyl group. <sup>b</sup> Initial weight ratio.

**Table 5. Water to Surfactant and Water to Surfactant plus Alcohol Molar Ratios Calculated for Three Initial Weight Ratios of Alcohol to MCT at Maximum Water Solubilization ( $W_m$ )**

alcohol/MCT ratio <sup>a</sup>	$\omega_0$					
	PrOH		BuOH		PeOH	
	SMS	SMS/Alc	SMS	SMS/Alc	SMS	SMS/Alc
3	83.7	14.6	66.4	16.6	21.9	4.1
1	23.4	5.7	74.5	15.7	20.3	3.3
0.5	12.1	3.0	18.6	3.2	28.3	3.0

<sup>a</sup> Initial weight ratio.

water growth at the expense of the bound water. When the micelles are more rich in alcohol (butanol/SMS initial weight ratio of 3), the number of molecules of water per molecule of SMS is larger and reaches a maximum value of 20 and slowly drops to 5.2.

The saturation point occurs at lower water content (12.3 versus 16.7 wt % water, respectively), and the total amount of solubilized water increases and as does the number of molecules of water per molecule of SMS (5.2 versus 1.5, respectively).

In Table 5 the maximal amounts of water  $W_m$  solubilized into the different microemulsion systems are given. It can be seen that the  $W_m$  values increase with increasing alcohol/MCT ratio. The slope of the increase is, however, different for the three alcohol systems: in the pentanol system the  $W_m$  value increases from 15.3 to 27.5; in the butanol or propanol system the  $W_m$  value increases from 15–16 to 53–60. Note that this observa-

tion does not take into account the amount of SMS in the system, which is bigger when the alcohol/MCT ratio increases.

To get a more realistic view on the water solubilization capacity of the microemulsion droplets in the different alcohol systems, we calculated the  $\omega_0$  value, which is the molar ratio of solubilized water to sucrose ester in the microemulsion at the  $W_m$  point. Table 5 summarizes the calculated  $\omega_0$  value as a function of the three investigated alcohol/MCT ratios. From Table 4 it becomes clear that in the pentanol system the calculated  $\omega_0$  values are almost independent of the alcohol/MCT ratio. This is the case both when only the sucrose ester is assumed to be at the interface (Table 5) and when the alcohol is also assumed to be located at the interface acting as a cosurfactant. This means that the increase of the total amount of water in the system when the alcohol/MCT ratio is augmented is due to a simultaneous increase in the interfacial SMS solubility. The water solubilization capacity of the microemulsion droplets is not increased significantly. However, in both the butanol and propanol systems, the  $\omega_0$  values considerably augment with increasing alcohol/MCT ratio. This indicates that the water solubilization capacity of the microemulsion droplets is dramatically improved. Taking the BSO concept, developed by Leung and Shah (1987a,b), into account, this finding could reflect a difference in the mechanism that determines the maximal amount of water solubilizable into the system: (1) one mechanism is governed by the natural curvature

of the emulsifier film (assumed to be effective in the pentanol system) and (2) one mechanism in which the attractive droplet interaction potential sets the limits for solubilization (assumed to be effective in the propanol or butanol system). More experimental evidence is needed to verify this hypothesis.

## CONCLUSIONS

This study examined the unusual behavior of sucrose monostearate (SMS) as a nonionic emulsifier, in the presence of alcohols as cosolvents and coemulsifiers, in relation to its ability to form reverse microemulsions. The enhanced miscibility of the emulsifier in the oil plus alcohol phase as the alcohol becomes more hydrophilic, and as its fraction in the mixture increases, allows improved water solubilization. As much as 60 wt % water can be solubilized in propanol/MCT/SMS (3:1:4 initial weight ratio) mixtures. The solubilization decreases as a more hydrophobic phase, for example, soybean oil or *R*-(+)-limonene, or a more hydrophilic oil, for example, oleic acid, is used and when its fraction in the system composition increases. The "maximum solubilization dilution line" depends on the hydrophilicity/hydrophobicity balance of the oil+alcohol/surfactant. Solubilized water binds strongly to the hydroxyl groups of the surfactant and is immobilized. Only at relatively high water levels (15–25 wt %) does the water behave as free water.

The viscosity of the microemulsions decreases with increasing water or alcohol content. This phenomenon is explained in terms of a decrease in the hydrophobic interaction of the surfactant tails as the alcohol accommodates more of the surfactant at the interface, which allows for extra amounts of solubilized water.

The four component systems are homogeneous waxy solids at room temperature and, therefore can immobilize, protect, inactivate, or slow the activities of solubilized water-soluble matter during storage or when coated on certain food surfaces. The solid system will liquefy and convert or restore spontaneously into microemulsions upon heating. The activity of the solubilized matter can be thereafter regenerated. The microemulsions once formed are heat-resistant, meaning that no change in the phase diagram boundaries will occur upon further heating. The heat resistance boundaries were not examined.

The solidified microemulsions are capable of solubilizing and immobilizing water-soluble or oil-soluble entrapped matter. For example, we could demonstrate that a controlled latency in the enzymatic hydrolysis of aroma compounds was obtained upon cooling of the microemulsions and that the reaction was restarted as the temperature reached a stage in which mobility was restored and the microemulsion was reformed (Fanun, 2000; Silberstein, 2000). The oleic acid system is very promising when microemulsions are considered as reservoirs for solubilization of in situ generated aromas and as microreactors for chemical and enzymatic reactions to be carried at the water–oil core of the microemulsions. An "on–off" process can be designed when using these types of microemulsions. The solid/liquid transition is an important feature in the use of such microemulsions as microreactors.

The microstructures of these microemulsions will be further discussed in a future paper.

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