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Food-Grade Microemulsions Based on Nonionic Emulsifiers: Media To Enhance Lycopene Solubilization

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Water-dilutable food-grade microemulsions consisting of ethoxylated sorbitan esters, and in some cases blended with other emulsifiers, water, (*R*)-(+)-limonene, ethanol, and propylene glycol, have been prepared. These microemulsions are of growing interest to the food industry as vehicles for delivering and enhancing solubilization of natural food supplements with nutritional and health benefits. Lycopene, an active natural lipophilic antioxidant from tomato, has solubilized in water-in-oil, bicontinuous, and oil-in-water types of microemulsions up to 10 times the oil [(*R*)-(+)-limonene] dissolution capacity. The effects of aqueous-phase dilution, nature of surfactant (hydrophilic−lypophilic balance), and mixed surfactant on solubilization capacity and solubilization efficiency were studied. Structural aspects studied by self-diffusion NMR were correlated to the solubilization capacity, and transformational structural changes were identified.

KEYWORDS: Ethoxylated sorbitan esters; food microemulsion; lycopene; nonionic surfactants; (*R*)-(+)-limonene; SD-NMR; solubilization capacity

INTRODUCTION

The growing interest in microemulsions as vehicles for food formulations arises mainly from the advantages of their physicochemical properties (*1*). The capability of a microemulsion to solubilize large amounts of lipophilic and hydrophilic food additives, to enhance reaction efficacy, and to allow selective extraction has attracted the attention of scientists and technologists (*1*, *2*).

In our previous studies we examined phase behavior of food-grade microemulsions based on nonionic surfactants (*3*−*5*) and the effect of cosurfactant and other components on the water solubilization capacity of water-in-oil (W/O) microemulsions based on sugar esters. Recently, food-grade oil-in-water (O/W) microemulsions have been prepared using certain nonionic surfactants, polyols, and short-chain alcohols (*5*). Addition of short-chain alcohols (such as ethanol) and polyols (glycerol or propylene glycol, PG) induced the formation of both W/O and O/W microemulsions (*5*). The phase behavior of a system based on (*R*)-(+)-limonene, ethanol, water/PG (1:1), and polyoxyethylene(20) sorbitan monostearate (Tween 60) was characterized by a single continuous microemulsion region starting from a pseudobinary solution (micellar system containing surfactant and oil phase) and proceeding to the microemulsion water/PG (1:1) corner (*5*). This means that all the structural changes occurring in the isotropic phase develop continuously (no phase separation takes place).

In the food industry, food supplements have become more prominent in recent years, due to the increased production of prepared, processed, and convenience foods. They play a vital role in today's beneficial and nutritious food supply by improving the nutritional value of certain foods, as well as their taste, texture, consistency, and/or color. The possibility of enhancing the solubility of hydrophobic vitamins, flavors, and other nutrients in O/W microemulsions is of great interest, as doing so can provide a well-controlled way to incorporate active ingredients and may protect the solubilized components from undesired degradation reactions (*1*). Food supplements with nutritional and health benefits are often termed "nutraceuticals". Lycopene is an important member in this category.

The study of lycopene solubilization properties of O/W microemulsions is motivated by human health concerns (*6*). Lycopene is an essential carotenoid that provides the characteristic red color of tomatoes. It is a lipophilic compound (**Figure 1a**) that is insoluble in water and in most food-grade oils. For example, the lycopene solubility in one of the most efficient edible essential oils, (*R*)-(+)-limonene (**Figure 1b**), is 700 ppm. Several recent studies have indicated the important role of lycopene in reducing risk factors of chronic diseases such as cancer, coronary heart disease, and aging (*6*−*8*). In turn, this has led to the idea of studying the effect of lycopene uptake on human health.

The bioavailability of lycopene is affected by several factors: (1) The food matrix containing the lycopene and, as a

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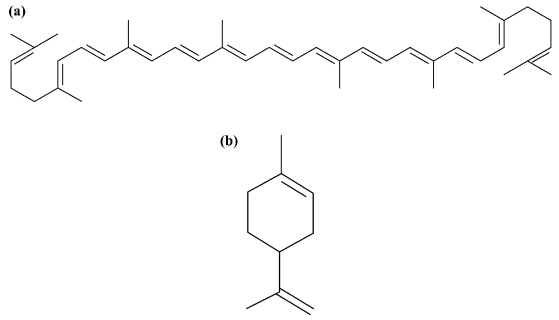

Figure 1. Molecular structures of (a) lycopene and (b) (*R*)-(+)-limonene.

result, the intracellular location of the lycopene and the intactness of the cellular matrix. Tomatoes converted into tomato paste enhance the bioavailability of lycopene, as the processing includes both mechanical particle size reduction and heat treatment (*9*). (2) The amount and type of dietary fat present in the intestine. The presence of fat affects the formation of the micelles which incorporate the free lycopene. (3) Interactions between carotenoids that may reduce absorption of either one of the carotenoids (*9*). The reduced absorption is due to competitive absorption between the carotenoids. On the other hand, simultaneous ingestion of various carotenoids may induce antioxidant activity in the intestinal tract and thus result in increased absorption of the carotenoids (*9*). (4) The molecular configuration (cis/trans) of the lycopene molecules. The bioavailability of the cis isomer is higher than that of the trans isomer. This may result from the greater solubility of cis isomers in mixed micelles and the lower tendency of cis isomers to aggregate (*10*, *11*). (5) The decrease in particle size (*12*).

Care must be taken in the application of lycopene as a food additive, since this highly conjugated carotenoid becomes unstable when exposed to light or oxygen.

The enhanced solubilization of lycopene in O/W microemulsions is also believed to enhance its bioavailability and to maximize its absorption in human tissues. This is because the particle size is in the range of several nanometers.

The objectives of the present study are to explore the ability of these unique food-grade microemulsions to solubilize lycopene (an important natural pigment) and to investigate the influence of solubilized lycopene on the microemulsion microstructure.

Phase diagrams were constructed, lycopene was solubilized, and self-diffusion (SD-NMR) spectroscopy was employed to determine the microstructure.

MATERIALS AND METHODS

Materials. Ethoxylated sorbitan esters in use were Tween 60 [polyoxyethylene(20) sorbitan monostearate], Tween 80 [polyoxyethylene(20) sorbitan monooleate], Tween 40 [polyoxyethylene(20) sorbitan monomyristate], and Tween 20 [polyoxyethylene(20) sorbitan monolaurate]. All Tweens were commercial grade and purchased from Sigma Chemical Co. (St. Louis, MO). Triglycerol monooleate (3G1O) was obtained from Solvay (Hannover, Germany). Sucrose monooleate (O-1570) was obtained from Mitsubishi-Kasei Food (Mie, Japan). Ethoxylated monodiglycerides was obtained from PPG (Gurnee, IL). (*R*)-(+)-Limonene (98%) was supplied by Sigma Chemical Co. Ethanol (EtOH) was obtained from Frutarom (Haifa, Israel). Propylene glycol, PG (1,2-propanediol) was purchased from BDH (Poole, England). Lycopene (oleoresin with 7% lycopene) was obtained from Lycored (Beer-Sheva, Israel). All components were used without further purification. The water was double distilled.

Phase Diagrams. The five-component systems were described on pseudoternary phase diagrams. They were constructed (at 25 °C) as recently reported (*5*).

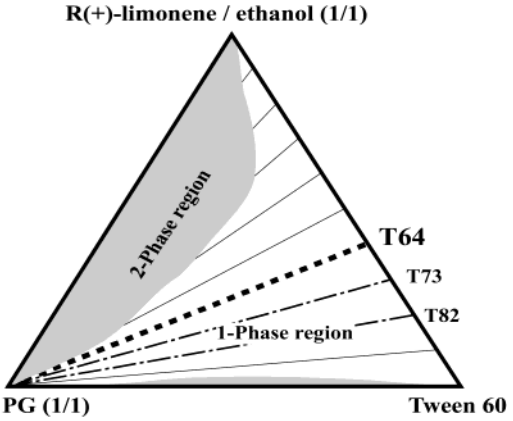

Figure 2. Pseudoternary phase diagram (25 °C) of water/PG/(*R*)-(+)-limonene/ethanol/Tween 60 system with constant weight ratios of water/PG (1:1) and (*R*)-(+)-limonene/ethanol (1:1). Solubilization of lycopene was studied along dilution line T64.

Solubilization Measurements. Lycopene and (*R*)-(+)-limonene were heated for 5 min to 140 °C in the presence of N_2. Water, PG, ethanol, and the surfactant were added dropwise to obtain a single-phase microemulsion with the desired composition. The samples were cooled and stored at 25 °C. Samples that remained transparent for at least 10 days were considered to be microemulsions.

Self-Diffusion Measurements. NMR measurements were performed at 25 °C on a Bruker DRX-400 spectrometer with a BGU II gradient amplifier unit and a 5-mm BBI probe equipped with a *z*-gradient coil, providing a *z*-gradient strength (g) of up to 55 G cm^{-1}. The SD coefficients were determined using pulsed field gradient stimulated spin−echo (BPFG-SSE). In this work we used bipolar gradient pulses as described by Wu et al. (*13*) to reduce the eddy-current effects.

Experiments were carry out by varying the gradient strength, g, and keeping all other timing parameters constant. The self-diffusion coefficient (D) is given by eq 1,

$$I = \frac{I_0}{2} e^{-R(t)-(\gamma G\delta)^2 D(\Delta-(\delta/3))} \quad (1)$$

where I is the measured signal intensity, I_0 is the signal intensity for $g = 0$, γ is the gyromagnetic ratio for the ^{1}H nucleus, δ is the gradient pulse length, Δ is the time between the two gradients in the pulse sequence (and hence defines the diffusion time), and $R(t)$ is a constant that takes into account nuclear relaxation. Since in our experiments $R(t)$ is constant, we do not consider it further. Typically, we use $\Delta =$ 100 ms, $\delta = 8$ ms, and vary g from 1.7 to 32.3 G cm^{-1} in 32 steps.

RESULTS AND DISCUSSION

A microemulsion is not an inert vehicle. Adding new components such as lycopene to the system may affect its phase behavior. It is of vital importance to examine both the influence of the solubilized material on the microstructure and the stability of the microemulsion (*14*).

A. Effect of Dilution. First we studied the influence of microemulsion composition on the solubilization of lycopene in a five-component system consisting of (*R*)-(+)-limonene, ethanol, water/PG (1:1), Tween 60 (**Figure 2**).

Solubilization capacity (SC) was defined as the amount (ppm) of lycopene solubilized in the microemulsion, and solubilization efficiency (α) was defined as the amount (ppm) of lycopene solubilized in the microemulsion per amount of (*R*)-(+)-limonene in the microemulsion (normalized against oil).

Solubilization Capacity. Figure 3 shows the SC of lycopene along water dilution line T64 (at this line the constant ratio of (*R*)-(+)-limonene/ethanol/Tween 60 is 1:1:3). Four different regions can be identified along this dilution line. At 0−20 wt

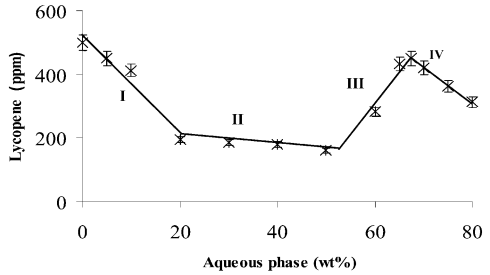

Figure 3. Solubilization capacity (SC) curve of lycopene along dilution line T64 at 25 °C. The four regions along the curve are (I) W/O microstructure, (II) bicontinuous microstructure, (III) O/W microstructure, and (IV) diluted O/W microstructure. It should be noted that the line presented in this figure is only a guideline for the eyes.

% aqueous phase (region I), the solubilization capacity of lycopene decreases dramatically from 500 to 190 ppm (reduction of 62%). This dramatic decrease in the solubilization capacity can be related to the increasing interactions between the surfactant and water molecules. Yaghmur et al. (*15*) have indicated that surfactant/alcohol/PG can strongly bind water in the inner phase. In systems containing up to 25 wt % aqueous phase, most of the water is bound to the polyol or to the alcohol. The water can also strongly bind to the hydroxyl groups of the surfactant at the interface. When water is introduced to the core, the micelle swells, and more surfactant and cosurfactant are participating at the interface, replacing the lycopene and therefore decreasing its solubilization. We have concluded that in region I the reverse micelles swell gradually and become more hydrophobic, causing less free volume to be available to the solubilized lipophilic lycopene and a reduction in its solubilization capacity.

At 20−50 wt % aqueous phase (region II), the solubilization capacity remains almost unchanged (decreased only by additional 7%). This fairly small decrease in the solubilization capacity could be associated with the fact that the system transforms gradually into a bicontinuous phase, and the interfacial area remains almost unchanged when the aqueous-phase concentration increases.

Surprisingly, in region III (50−67 wt % aqueous phase), the SC increases from 160 to 450 ppm (an increase of 180%).

In region IV, the solubilization capacity decreases to 312 ppm (a decrease of 30%).

To explain the changes in solubilization capacity of lycopene, we characterized the microstructure of microemulsions along the dilution line T64, using the SD-NMR technique.

To evaluate the self-diffusion data in terms of microstructure, the calculation of the relative diffusion coefficient, D/D_0, of the two solvents is needed (*16*). Relative diffusion coefficients were obtained by dividing water (D^W) and oil (D^O) diffusion coefficients in the microemulsion by the diffusion coefficient of water in the pure water phase (D_0^W) and oil in the net phase (D_0^O). It is well documented (*16*) that if the D/D_0 values of water and oil differ by more than 1 order of magnitude, discrete particles of the slowly diffusing solvent are implied, whereas if the D/D_0 values of water and oil are of the same order of magnitude, a bicontinuous structure is suggested.

Figure 4 shows the relative diffusion coefficients of water and (*R*)-(+)-limonene in empty microemulsions (**Figure 4a**) and in microemulsions solubilizing lycopene (**Figure 4b**) as a function of the aqueous-phase concentration (w/w). One can clearly see that the general diffusion coefficient behaviors of microemulsion ingredients [(*R*)-(+)-limonene and water] with or without lycopene are not very different. The total amount of

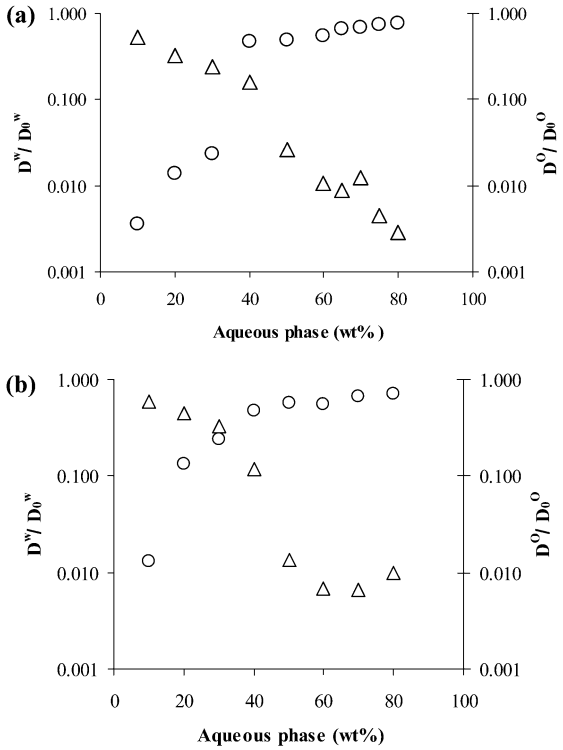

Figure 4. Relative diffusion coefficients of water (○) and (*R*)-(+)-limonene (△) in microemulsions with (a) and without (b) lycopene, as calculated from SD-NMR results at 25 °C. D_0^W was measured in a solution containing water/PG (1:1) to be 55.5×10^{-11} m^2 s^{-1}. D_0^O, the pure diffusion coefficient of (*R*)-(+)-limonene, was determined to be 38.3×10^{-11} m^2 s^{-1}.

lycopene does not cause dramatic changes in the diffusion patterns of the ingredients.

It can also be seen that at the two extremes of aqueous-phase concentrations (up to 20 wt % and above 70−80 wt % aqueous phase), the D^W/D_0^W values are easily interpreted, while the in-between regions are somewhat more difficult to explain since gradual changes take place. Regions II and III are difficult to distinguish. However, the structural changes in the presence of lycopene (**Figure 4b**) are more pronounced than those in the absence of lycopene (**Figure 4a**).

As **Figure 4b** indicates, microemulsions containing up to 20 wt % aqueous phase, and solubilizing lycopene, have a discrete W/O microstructure, since the relative diffusion coefficients of water and (*R*)-(+)-limonene differ by more than 1 order of magnitude.

Microemulsions solubilizing lycopene and containing 20−50 wt % aqueous phase have a bicontinuous microstructure, as the diffusion coefficients of water and (*R*)-(+)-limonene are of the same order of magnitude.

Increasing the aqueous-phase concentration to above 50 wt % induces the formation of discrete O/W microstructure, as the relative diffusion coefficients of water and (*R*)-(+)-limonene differ by more than 1 order of magnitude.

From the solubilization capacity and SD-NMR results, it is clear that lycopene SC is structure-dependent.

The four different regions in the solubilization capacity curve (**Figure 3**) are an indication of the microstructure transition along the dilution line. The first region indicates the formation of W/O (L_2) microstructure. The second region indicates the transition from L_2 microstructure to a bicontinuous microemulsion. In the third region a transition from a bicontinuous

Table 1. Lycopene Solubility at 25 °C

medium	lycopene (ppm)
vegetable oil	200
(*R*)-(+)-limonene	700
Tween 60	800
ethanol	20
water	<10
propylene glycol (PG)	<10
(*R*)-(+)-limonene/Tween 60 (4:6)	2500

microemulsion to an O/W (L_1) microstructure occurs. In the fourth region a discrete L_1 microstructure was found.

While the general behavior of the diffusion coefficients is the same for microemulsions with or without lycopene, the transition point from one microstructure to another is different. **Figure 4** indicates that solubilization of lycopene influences the transition from L_2 to bicontinuous microstructure and further to L_1 microstructure. In empty microemulsions, the formation of bicontinuous microstructure occurs when the microemulsion contains 40−60 wt % aqueous phase (**Figure 4a**), whereas in a microemulsion containing lycopene, bicontinuous microstructure starts at low aqueous-phase content (20 wt %) and continues up to an aqueous-phase content of 20−50 wt % (**Figure 4b**). It seems that the more water is solubilized in the swollen reverse micelles, the less free interfacial volume there is for the lycopene. It seems that lycopene disturbs both the flexibility of the micelle and the spontaneous curvature. As a result, the interface changes into a flatter curvature (bicontinuous) at an early stage of water concentration, more so in the presence of lycopene than in empty micelles.

Solubilization Efficiency (α). To compare the solubility of lycopene in (*R*)-(+)-limonene to its solubilization in a microemulsion, one must calculate the amount of lycopene per amount of (*R*)-(+)-limonene in the microemulsion. **Table 1** shows the solubility of lycopene in the microemulsion components. Note that the solubilization of lycopene in a reverse micelle system is 4 times (2500 ppm) higher than the solubility of lycopene in (*R*)-(+)-limonene (700 ppm). This enhanced solubilization is remarkable. Yet swollen micelles have no practical value without the capability of being diluted by water, since many of the final food applications will be in a water continuous phase. Moreover, such mixtures cannot be diluted with any type of oil phase (including (*R*)-(+)-limonene) and, therefore, are not practical for oil continuous phase applications, either. It is essential, therefore, to construct micellar concentrates that are capable of dilution in both oil and water phases. The microemulsions described in this paper are unique in those properties.

Figure 5 and **Table 1** show the solubilization efficiency (α) as a function of the aqueous-phase content. The solubilization efficiency of lycopene in microemulsion is higher than the solubility of lycopene in (*R*)-(+)-limonene.

The solubilization efficiency curve (as seen in **Figure 5**) can also be divided into four regions, similar to the solubilization capacity curve in **Figure 3**. The four regions overlap the microstructure changes (**Figure 4b**).

In the first region (0−20 wt % aqueous phase), the solubilization efficiency decreases by 50% (from 2500 to 1220 ppm). The decrease in solubilization efficiency can be attributed to the decrease in the interfacial area as the micelles swell.

In the second region (20−50 wt % aqueous phase), the solubilization efficiency remains almost unchanged (increased by 20%). Systems containing 20−50 wt % aqueous phase seem to have a bicontinuous microstructure (as indicated in **Figure 4**). The interfacial area in a bicontinuous microemulsion does not change as a result of the increase in the aqueous-phase content.

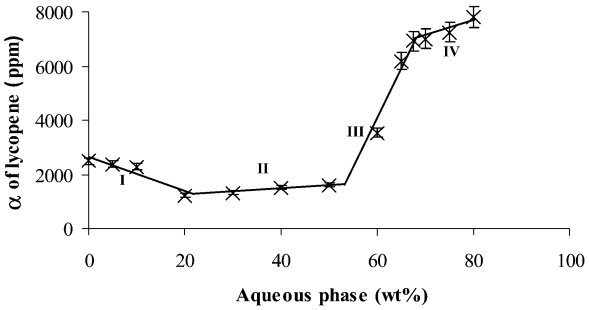

Figure 5. Solubilization efficiency (α) curve along dilution line T64 at 25 °C. The four regions along the curve are (I) W/O microstructure, (II) bicontinuous microstructure, (III) O/W microstructure, and (IV) diluted O/W microstructure. It should be noted that the line presented in this figure is only a guideline for the eyes.

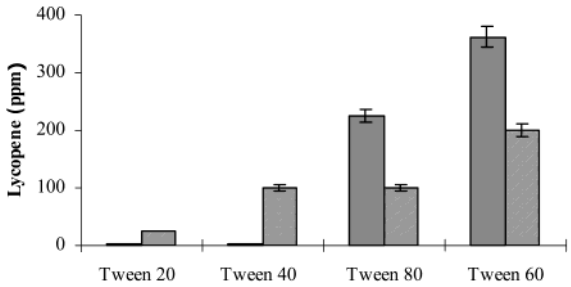

Figure 6. Solubilization capacity (SC) of lycopene in microemulsions stabilized by different surfactants at 25 °C. Composition A (solid bars): (*R*)-(+)-limonene/ethanol/Tween 60 (1:1:3) and 75% aqueous phase. Composition B (hatched bars): (*R*)-(+)-limonene/ethanol/Tween 60 (1:1:8) and 75% aqueous phase.

In the third region, the solubilization efficiency dramatically increases by 340%. This dramatic increase suggests that lycopene prefers the O/W interface.

In the fourth region (67−80 wt % aqueous phase), the solubilization efficiency is almost unchanged (increased by 11%). The unchanged solubilization efficiency indicates that no further microstructure changes occur.

B. Effect of HLB. The hydrophilic−lipophilic balance (HLB) of the surfactant influences, as expected, the amount of solubilized oil in the aqueous surfactant phase (*5*).

The HLB effects were measured in two different compositions, the first containing (*R*)-(+)-limonene/ethanol/Tween 60 (1:1:3) and 75 wt % aqueous phase (composition A), and the second composition containing (*R*)-(+)-limonene/ethanol/Tween 60 (1:1:8) and 75 wt % aqueous phase (composition B).

As indicated in **Figure 6**, Tween 60, being the most hydrophobic surfactant (HLB 14.9), solubilized the maximum amount of lycopene in the two compositions. Replacing Tween 60 with Tween 80 decreases the solubilization capacity of lycopene in both compositions by 30 and 50%, respectively. Using a more hydrophilic surfactant, such as Tween 40, decreases the solubilization capacity even further. In composition A no solubilization of lycopene occurs, while in composition B the solubilization capacity decreases by 50% in comparison to the solubilization of lycopene in a system containing Tween 60. Replacing Tween 60 with Tween 20 (the most hydrophilic surfactant among the Tweens, HLB 16.7) prevents the formation of microemulsion (in composition A) even without the presence of lycopene. The use of Tween 20 in composition B decreases

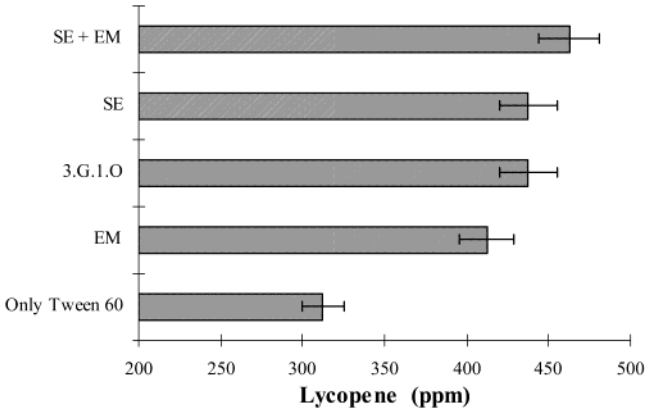

Figure 7. Solubilization capacity (SC) of lycopene in microemulsions stabilized by mixed surfactant at 25 °C. Composition of the microemulsion: (*R*)-(+)-limonene/ethanol/Tween 60 (1:1:3) and 80% aqueous phase. EM, ethoxylated monodiglyceride; 3G1O, triglycerol monooleate; SE, sucrose ester O-1570.

the solubilization capacity of lycopene by 88%. The solubilization capacity of lycopene increases as the surfactant becomes more hydrophobic.

These results are in good agreement with our previous results (*5*), which showed increased solubilization capacity of (*R*)-(+)-limonene as the surfactant becomes more hydrophobic. It seems that lycopene, like (*R*)-(+)-limonene, penetrates into the surfactant hydrophobic region. Lycopene, like (*R*)-(+)-limonene, is sensitive to the hydrocarbon chain length and thus favors surfactants with long hydrocarbon chain length. Since an optimal interaction of the solubilized oil with the hydrophobic part of the surfactant is very important in the formation of microemulsions (*5*, *17*, *18*), it seems that an optimal interaction of lycopene with the hydrophobic part of the surfactant would be just as important.

C. Effect of Mixed Surfactants. Ten percent of Tween 60 was replaced by three different surfactants: ethoxylated monodiglyceride, sucrose ester (O-1570), and triglycerol monooleate (3G1O). The first two are hydrophilic surfactants with HLB 14 and 15, respectively. The last is a hydrophobic surfactant with HLB 6. The solubilization capacity of lycopene in microemulsions stabilized by each of the above surfactants is lower by 20−60% in comparison to the solubilization capacity in microemulsions stabilized by Tween 60 alone.

However, it can be seen from **Figure 7** that microemulsions stabilized by mixed surfactants enhance the solubilization capacity of lycopene by 32−48% in comparison to microemulsions stabilized by Tween 60 alone.

Microemulsions stabilized by a mixture of Tween 60 and ethoxylated monodiglyceride were capable of solubilizing 32% more lycopene than those made of Tween 60 alone.

Microemulsions stabilized by a mixture of Tween 60 and 3G1O or a mixture of Tween 60 and O-1570 have solubilization capacity higher by 39% in comparison to microemulsions stabilized by Tween 60 only.

Microemulsions stabilized by a mixture of three surfactants, Tween 60, sucrose ester, and ethoxylated monodiglyceride, increased the solubilization capacity of lycopene by 48% in comparison to microemulsions stabilized by Tween 60 only.

It seems therefore, as expected, that the mixture (blend) of surfactants enhances the surfactants partitioning at the interface, thus increasing the stability of the amphiphilic film (better curvature and improved flexibility) and lycopene solubilization. Therefore, the increased surfactant partitioning at the interface in the surfactant mixtures is synergistic.

Synergism phenomena in surfactant mixtures were attributed to Coulombic, ion−dipole, or hydrogen-bonding interactions (*19*). Therefore, nonionic surfactant mixtures are expected to have a minimum intermolecular interaction and weak synergistic effects. Nevertheless, Huibers and Shah (*19*) demonstrated a strong synergism in nonionic surfactant mixture, similar to the findings in our study. When the microemulsions were loaded with lycopene, the synergistic effect was found to be more pronounced than in empty microemulsions, suggesting that improved solubilization of any solute should be examined (and probably also obtained) in microemulsions based on mixtures of surfactants.

Conclusions. We have demonstrated the use of food-grade microemulsions as vehicles for solubilizing lycopene, a nutraceutical with health benefits.

Lycopene was solubilized up to 10 times its dissolution capacity in the microemulsions, in comparison to the lycopene solubility in (*R*)-(+)-limonene or any other edible oil.

The lycopene solubilization along any dilution line is microstructure-dependent. Solubilized lycopene influenced both the microstructure and the composition in which transformation from W/O to bicontinuous and from bicontinuous to O/W microstructure occurred.

The HLB of surfactant homologues (Tweens) also influenced quite significantly the solubilization capacity of lycopene. As the surfactant becomes more hydrophobic, the solubilization capacity increases. The microemulsion lycopene solubilization capacity is maximal at an optimal interaction of the lycopene with the hydrophobic part of the surfactant.

The use of mixed surfactants increases the solubilization capacity, indicating a synergistic effect. The synergism phenomenon may be a result of better interface organization (orientation) of the mixed surfactants around the oil droplet that allows better interfacial solubilization (enhanced partitioning of the surfactant at the interface). The enhanced lycopene solubilization can also be due to improved lycopene−surfactant interactions. In any case, the mixed surfactants cause enhanced solubilization.

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