Improved Oil Solubilization in Oil/Water Food Grade Microemulsions in the Presence of Polyols and Ethanol

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Microemulsions based on five-component mixtures for food applications and improved oil solubilization have been studied. The compositions included water, oil phase [such as $R(+)$-limonene and medium-chain triglycerides (MCT)], short-chain alcohols (such as ethanol), polyols (propylene glycol and glycerol), and several surfactants and their corresponding mixtures (nonionic, such as ethoxylated sorbitan esters, polyglycerol esters, sugar ester, and anionic, such as phosphatidylcholine). The phase behavior of these systems is discussed with respect to the influence of polyols and short-chain alcohols on the degree of solubilization of oils in the aqueous phase. The alcohol and polyols modify the interfacial spontaneous curvature and the flexibility of the surfactant film, enhancing the oil solubilization capacity of the microemulsions. The solubilization of $R(+)$-limonene was dramatically improved in the presence of the alcohol and polyols, whereas the improvement of solubilization for triglycerides containing MCT was less pronounced. In some systems high oil solubilization was achieved, and some of them can be easily diluted to infinity both with the aqueous phase and with the oil phase. Viscosity measurements along selected dilution lines [characterized by a single continuous microemulsion region starting from a pseudo binary solution (surfactant/oil phase) to the microemulsion (water/polyol corner)] indicate that at a certain composition the system inverts from a W/O to an O/W microemulsion.

Keywords: *Food grade surfactants; phase behavior; oil-in-water microemulsions; polyols; R(+)-limonene; solubilization*

INTRODUCTION

The growing interest in microemulsions as vehicles for food formulations arises mainly from the advantages of their physicochemical properties, such as spontaneous formation, clear appearance, low viscosity, thermodynamic stability, and high solubilization capacity (*1–3*). The capability of a microemulsion to solubilize large amounts of lipophilic and hydrophilic food additives, to enhance reaction efficacy, and to allow selective extraction (*1, 4*) has attracted the attention of technologists.

The possibility of enhancing the solubility of hydrophobic vitamins, flavors, and other nutrients in oil-in-water microemulsions is of great interest, as it can provide a well-controlled and stable medium for the incorporation of these ingredients and may protect the solubilized components from undesired degradative reactions (*1, 5*).

The complexity of food systems and the need for all of the components to be approved as being of food grade limit the choice of components, leading to difficulties in

formulations. Furthermore, in many applications the amount of surfactant and/or cosurfactant used must be kept low (*1*).

Very little work has focused on researching the formation, phase behavior, and microstructure of both water-in-oil (W/O) and oil-in-water (O/W) microemulsions from completely food grade materials. Most O/W microemulsions that have been reported in the literature are based on nonfood grade surfactants (*6–9*). It is well-known that edible oils are difficult to solubilize in O/W microemulsions. In some of these studies nonfood grade surfactants and cosurfactants were used to incorporate edible oils within water (*6, 10–12*).

Microemulsions containing water, lecithin, butanol, and long-chain triglycerides (*6, 13*) have been discussed. The butanol makes the microemulsion unacceptable for food applications. If the medium-chain alcohol is removed from the formulation, the phase diagrams exhibit liquid mesophase formulations and small areas of oil solubilization within the water surfactant phase. Moreover, certain of the systems cannot be diluted with water. This phenomenon makes the microemulsions unpractical for most food applications.

Surfactant molecules are known to self-assemble in highly polar organic solvents such as propylene glycol, glycerol, and formamide (*14, 15*). These solvents are similar to water, because they form hydrogen bonds, have relatively high dielectric constants, and are immiscible in apolar (hydrocarbon) solvents (*15, 16*). Critical micelle concentrations are higher in polar

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nonaqueous solvents than in water (*17, 18*). When these solvents are used as water substitutes, their resulting penetration into the surfactant interface can "break" or minimize the liquid crystal phase regions (*19, 20*).

It is known that in water/polyoxyethylene-type nonionic surfactant (C_iE_j)/hydrocarbon systems, the structure of the microemulsions inverts from oil-in-water (O/W) to water-in-oil (W/O) with increasing temperature at low surfactant concentration (*21*). It was observed, in some investigations, that the structural transition of microemulsions from O/W to W/O occurs when mixtures of water and glycerol or propylene glycol and glycerol are used instead of pure water (*16, 22*).

On the basis of the findings existing in the literature on the role of alcohols and polyols in oil solubilization in microemulsions, we designed the present study. The main aim was to formulate O/W microemulsions with food grade nonionic surfactants with significantly improved oil solubilization and to form aqueous phase dilutable systems.

Food O/W microemulsions are difficult to formulate mostly because of the fact that with the available food grade emulsifiers the areas of solubilized oil phases are restricted to the water corner of the phase diagram, which permits solubilization of only minor amounts of oil.

In an attempt to better understand the requirements for improved solubilization of the oil phase and consequently food oil-soluble supplements and nutraceuticals in food products, we first examined some of the nonfood grade formulations and consequently replaced the potential solubilizers by blends of food grade components.

The oil phase commonly in use in food applications and mainly in emulsion formulations is oil of unsaturated long-chain fatty acid triglycerides (LCT) such as soy, corn, cotton, or sunflower oil. In some applications medium-chain triglycerides (MCT) are used mainly because they are fully saturated and stable to oxidation. In a few applications palm or coconut oils are used. However, the triglycerides, because of their high molecular volume fraction and because of the limited solubility of the food grade emulsifiers in them, are difficult to solubilize in water/surfactant phases. Moreover, recently it has become a trend with food formulators to explore the use of liquid fractions of nonsaponifiable natural products. Some of these "solvent-like" fractions are termed essential oils and contain terpenes along with triglycerides and other lipid components. It was, therefore, decided to start our study with a unique and interesting solvent (essential oil, lipophilic perfume constituent) that is present in several natural products. The monoterpene hydrocarbon $R(+)$-limonene, the major constituent of citrus essential oils, is often used in foods, cosmetics, and coating materials. $R(+)$-Limonene is essentially insoluble in water and requires addition of a surfactant to be solubilized or emulsified in water (*23*). R(+)-Limonene is used in the preparation of cloudy macroemulsions for beverages. Citrus essential oils are also in use in some "green" cleaning formulations and known to have powerful detergency abilities (solubilization) (*23, 24*). R(+)-Limonene was used, therefore, in some of the presently studied formulations.

This paper, which is the first contribution of a more extensive study of food grade O/W microemulsion structure and reactivity relationships, reports on the phase diagrams of systems containing nonionic surfactants, polyols, and alcohols in five-component systems. Rheo-

logy measurements were done to detect the inversion region from W/O to O/W as affected by the composition of the aqueous phase.

MATERIALS AND METHODS

Materials. Brij 96v [polyoxyethylene (10) oleyl alcohol ($C_{18:1}E_{10}$)] was purchased from ICI Specialty Chemicals (Essen, Germany). Ethoxylated sorbitan esters Tween 60 (ethoxylated-20 EO-sorbitan monostearate), Tween 80 (ethoxylated-20 EO-sorbitan monooleate), and Tween 20 (ethoxylated-20 EO-sorbitan monolaurate) were of commercial grade and purchased from Sigma Chemical Co. (St. Louis, MO). Polyglycerol esters triglycerol monooleate (3.G.1.O) and decaglycerol oleate (10.G.1.O) were obtained from Solvay (Hannover, Germany). Sucrose monolaurate (L-1695) and sucrose monostearate (S-1570) were obtained from Mitsubishi-Kasei Food (Mie, Japan). Soybean phosphatidylcholine (PC) (Epikuron 200) was purchased from Lucas Meyer GmbH Co. (Hamburg, Germany). It consists of phosphatidylcholine (92%) and small amount of accompanying phospholipids (2%). The distribution of the fatty acids in Epikuron 200 is reported as follows: saturated fatty acids = 13−17%, $C_{18:1}$ = 6−8%, $C_{18:2}$ = 68−72%, and $C_{18:3}$ = 7−9%.

$R(+)$-Limonene (98%) was supplied by Sigma Chemical Co. The medium-chain triglyceride (MCT) (Tegosoft CT) was obtained from Th. Goldschmit AG. (Essen, Germany). According to the manufacturer, the chain-length distribution of the fatty acids was $C_{6:0} \leq 2\%$, $C_{8:0} \leq 50-80\%$, $C_{10:0} \leq 18-28\%$, and $C_{12:0} \leq 3\%$. Soybean oil was supplied by Sigma Chemical Co. Ethanol (EtOH), 1-propanol, and 1-butanol were obtained from Frutarom (Haifa, Israel). Propylene glycol (PG) (1,2-propanediol; BDH, Poole, U.K.) and glycerol (Gly) (Frutarom) were used. These materials were used without further purification. The water used was double-distilled.

Phase Diagrams. The behavior of five-component systems is described on a pseudo-ternary phase diagram. The phase diagrams were constructed in the following way. Stock solutions of water and polyol at a constant weight ratio of 1:1 (if it is not reported otherwise) were made. The alcohol/oil weight ratio was held constant at 1:1. Mixtures of surfactant−oil phase (alcohol and oil) or mixtures of surfactant−aqueous phase (water and polyol) were prepared in culture tubes sealed with viton-lined screw caps at predetermined weight ratios of oil phase (alcohol plus oil) to surfactant or aqueous phase (polyol plus water) to surfactant and kept in a 25 ± 0.3 °C water bath. Microemulsion areas were determined in phase diagrams by titrating either the oil−surfactant phase or aqueous phase−surfactant mixtures with the aqueous phase or the oil phase, respectively. All samples were vigorously stirred. The samples were allowed to equilibrate for at least 24 h before they were examined. In all of the samples tested, evaporation loss was negligible. The different phases were determined using ocular and optical (crossed polarizers) methods. Every sample, which remained transparent and homogeneous after vigorous vortexing, was considered as belonging to a monophasic area in the phase diagram.

Solubilization Capacity. Two suitable solubilization parameters were used in this work to compare the solubilization capacities of different food grade nonionic surfactants: maximal amount of aqueous phase (water and polyol), denoted W_m (*25, 26*), and total monophasic region, denoted A_T (*26, 27*). W_m was determined from the titration of the oil phase with the aqueous phase (water and polyol mixture) as described above. These solubilization parameters were described previously (*26*). For our systems, a relative error of ±4.0% was estimated in the calculation of A_T (%) and W_m (wt %).

Rheological Behavior. Viscosity measurements were performed using a model CLS2 100 Carri-Med viscosimeter (TA Instruments GmbH, Alzenau, Germany). A double-cylinder geometry (set gap of 500 μm) was used. The samples were thermostated at 25 °C using a model 9100 thermostat from PolyScience, Division of Preston Industries, Inc. (Niles, IL). Preshearing of the samples for 1 min and equilibration
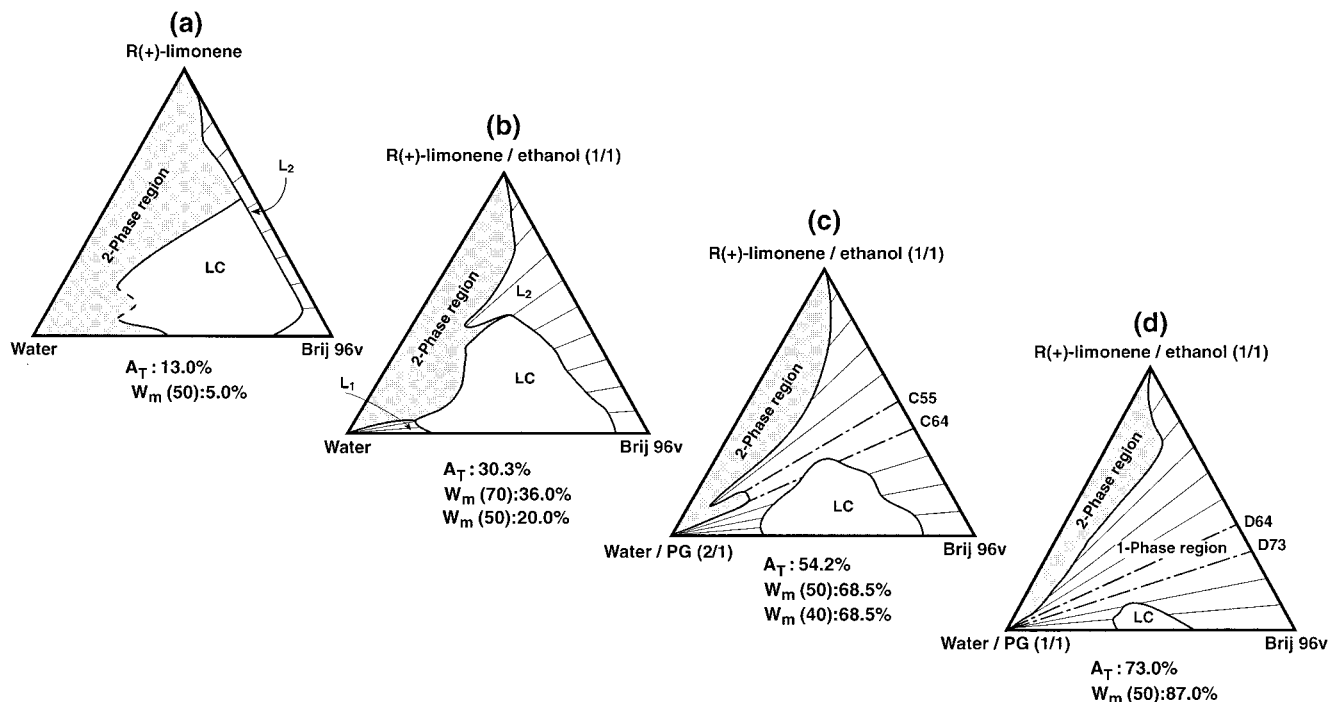
Figure 1. Phase diagrams of the system water/PG/R(+)-limonene/EtOH/Brij 96v at 25 °C. The composition of the aqueous phase was (a) water, (b) water, (c) water/PG (2:1), or (d) water/PG (1:1). The composition of the oil phase is given in the upper corner of the phase diagrams. L_1 denotes O/W microemulsion. L_2 denotes W/O microemulsion. LC denotes the liquid crystalline phase.

for 30 s at 25 °C were carried out. The flow step was made by continuous ramp at 25 °C, and the shear stress ranged from 0 to 9 Pa. Ramp duration was 3 min. All of the measurements were carried out with 4 mL of the tested sample.

RESULTS AND DISCUSSION

A. Influence of PG and Ethanol on the Phase Behavior of the $C_{18:1}E_{10}$ System. The phase diagram of a three-component system of R(+)-limonene/water/$C_{18:1}E_{10}$ (Brij 96v) is presented in Figure 1a. One can clearly see that W/O microemulsions (L_2) are formed along with large liquid crystalline (LC) areas [A_T = 13.0%; W_m(50) = 5.0%]. Phase separation occurs in both the oil and water corners of the phase diagram.

The phase behavior and the microstructure of microemulsions (systems with low interfacial tensions) were found to be dependent on two interfacial parameters, namely, the spontaneous film curvature (the curvature that the amphiphilic film would like to attain) and the elasticity of the amphiphilic film (*22, 25, 28–30*). H_0 is the spontaneous film curvature describing the microstructure of the microemulsion, and κ and $\bar{\kappa}$ describe the elastic properties of the surfactant film and are often referred to as bending moduli (these properties describe how difficult it is to deform the amphiphilic film). For $H_0 > 0$, the surfactant film is convex toward water (O/W droplet microemulsion). For H_0 close to 0, bicontinuous microemulsions or lamellar liquid crystalline phases are formed. If the surfactant film is convex toward oil (W/O droplet microemulsion), H_0 is regarded to be negative. H_0 can be affected by the nature of the surfactant and the composition of the polar and apolar phases (*7, 31*). In this work, polyols and short-chain alcohols are used as "tuning parameters" to change H_0 and to increase the flexibility of the surfactant film. They may affect the spontaneous curvature of the interface in two ways: They change the polarity of the polar and apolar phases, and they penetrate into the interface, increasing

the flexibility of the interface and destabilizing the LC phase.

The change of the phase behavior in the presence of ethanol is shown in Figure 1b. The ethanol was used at a 1:1 weight ratio to the R(+)-limonene. The liquid crystalline phase area decreased as ethanol was added. The change in the solubilization parameters was dramatic [A_T = 30.3%; W_m(70) = 36.0%], and the decrease in the LC area was also very significant. This seems to imply that a considerable part of ethanol penetrated into the interfacial film effectively. The solubilization process was found to be limited either by the radius of the spontaneous curvature of the interface, R^0 (curvature effect), or by the critical radius of the droplets, R^c (effect of attractive interaction among the droplets) (*25*). The solubilization capacity in Figure 1b is limited by R^0; the addition of ethanol increased the solubilization capacity by increasing the fluidity of the interface, which increased R^0 and decreased R^c. A large isotropic L_2 area was formed along with some LC phase area and a small O/W microemulsion area (L_1 phase). Because ethanol is soluble in all three components, the oil phase, the water phase, and the surfactant, the phase behavior indicates that some quantities of oil (possibly together with alcohol) were solubilized in the water (possibly with alcohol) surfactant phase. From the decrease in the LC area it was concluded that the improvement of the solubilization of the oil in the surfactant aqueous phase is also related to the factors affecting the spontaneous curvature of the interface and the elasticity of the amphiphilic film.

PG is one of the least hydrophilic simple polyols that are soluble in water but practically nonsoluble in the oil phase. The PG was dissolved in the aqueous phase at a water/PG weight ratio of 2:1 (Figure 1c). The isotropic monophasic area in the phase diagram is now more extended and controls most of the phase diagram area [A_T = 54.2%; W_m(50) = 68.5%]. The LC phase

diminished drastically, and the area of the two-phase region shrank significantly. Although the L_1 phase was dramatically increased, one can clearly see that there are no "diluting channels" in the microemulsion compositions with the aqueous phase at any of the dilution lines (dilution lines C55 and C64 do not "reach" the water corner of the phase diagram). Increasing the PG content (by changing the water/PG ratio to 1:1) caused a further decrease in the polarity of water, resulting in a larger isotropic phase dominating most of the phase diagram area [$A_T = 73.0\%$; $W_m(50) = 87.0\%$] (Figure 1d). Moreover, now the microemulsion can be diluted (see D64 or D73 lines). Another important observation (not shown) was that all of the systems represented in parts c and d of Figure 1 are temperature-resistant over a large temperature range (20–70 °C). There is no change in the monophasic area. The observed temperature independence of these systems can be a consequence of the nonionic surfactant solubility in the mixture of PG and water. At all temperatures the surfactant is more soluble in the aqueous phase (PG/water mixture) than it is in oil. These results are in agreement with previous publications explaining that PG and alkylpolyglycol ether (C_iE_j) surfactant interact differently with increasing temperature than do water and C_iE_j (*16*), resulting in no tendency for enhanced hydrophobicity of the C_iE_j surfactant with temperature. This effect is important in food systems that should remain stable under fluctuating temperatures.

Our results show that the addition of a food grade short-chain alcohol (ethanol) to the oil phase and of a polyol (such as PG) to the aqueous phase increased the microemulsion area significantly. The change in phase behavior caused by the addition of ethanol and PG can be interpreted in terms of film properties; that is, the flexibility of the surfactant film is increased because the LC phase is destabilized in favor of a microemulsion phase that even connects the aqueous with the oil phase. In addition, the increase in interfacial fluidity for the formation of isotropic microemulsions from organized structure (LC) is clearly an important factor.

Polyols such as PG and short-chain alcohols are known to have a "salting-in" effect and to act as cosurfactants (*16, 19*). Therefore, it is assumed that a considerable part of PG is incorporated into the surfactant layer and thus will increase the interfacial fluidity, and the other part of PG will decrease the polarity of the water because PG is mainly soluble in water. The addition of PG will decrease the bending moduli. The addition of both PG and ethanol does not change only the polarity of the aqueous or oil phase and/or the rigidity of the surfactant film but they do affect H_0 (the spontaneous film curvature). This suggests the formation of "asymmetric" surfactant films (the system will adopt the Gaussian curvature "phase topology" for which the lowest bending energy is needed to bend the film toward the water or oil phase), and the transition from LC to droplet microemulsions is preferred (*13*). Gradzielski (*32*) found that the addition of short-chain alcohols to nonionic O/W microemulsions lowered the bending moduli significantly (a reduction in $2\kappa + \bar{\kappa}$ was observed, which was proportional to the concentration of added alcohol). The significant reduction in the bending moduli explains why for high surfactant concentrations isotropic phases are formed instead of LC phases (*32*).

It seems that PG acts as a coupling agent between the O/W and W/O microemulsion region as demonstrated in Figure 1. The coupling agent relates oil-soluble and water-soluble compounds and connects the O/W and W/O regions to one monophasic region (*8*). This means that all of the structural changes occurring in the isotropic phase develop continuously (no phase transition takes place). Further work is needed to elucidate the nature of the LC phase appearing at high $C_{18:1}E_{10}$.

It is now easily seen that there are several compositions and more than one dilution line that "cross" the entire phase diagram. This means that the microemulsion can be diluted with the aqueous phase (see, for example, dilution lines D64 and D73 in Figure 1d). Compared with Figure 1a, Figure 1d has ~5.6 times more total monophasic area [denoted A_T (%)] (13.0 versus 73.0%), and the increase in W_m was significant [$W_m(50) = 5.0\%$ versus $W_m(50) = 87.0\%$]. However, the main drawback of these systems is the surfactant, which is not of food grade.

B. Effect of PG on the Phase Behavior of Ethoxylated Sorbitan Ester Systems. The phase diagrams presented in Figure 2 are based on replacing the Brij 96v by the food grade ethoxylated sorbitan esters (Tweens). The oil/ethanol weight ratio (1:1) remained unchanged, and the water/PG weight ratio was also kept constant. Tween 20 being the most hydrophilic surfactant (HLB = 16.7) solubilized the minimum oil [$R(+)$-limonene], whereas Tween 60 (HLB = 14.9) being the most hydrophobic surfactant solubilized the maximum oil in the aqueous surfactant phase [$A_T = 64.0\%$; $W_m(50) = 67.0\%$]. This different phase behavior is most probably due to the interaction between the oil and the apolar parts of the interface. This observation could be a consequence of the ability of $R(+)$-limonene to penetrate, that is, mix, significantly into the surfactant hydrophobic region. This is also reflected by the fact that the interaction between the interface and the oil decreased as the hydrocarbon chain length of the surfactant decreased. Solubilization of $R(+)$-limonene is sensitive to the hydrocarbon chain length of the studied surfactants, and it is favored with surfactants having a long hydrocarbon chain length. An optimal interaction of the solubilized oil with the hydrophobic part of the surfactant is very important in the formation of microemulsions (*25, 33–35*).

Table 1 shows the phase behavior of the system water/PG/$R(+)$-limonene/ethanol/Tween 60 as a function of the ethanol concentration at different $R(+)$-limonene/ethanol ratios and at a constant water/PG ratio (1:1). The two-phase region shrank considerably with increasing ethanol concentration in the oil phase [$R(+)$-limonene/ethanol]. One possible explanation for the increase in the isotropic phase area is an increased incorporation of ethanol into the surfactant film, which would lead to a decrease in the bending moduli of this film. The increased penetration of the surfactant film and the decrease of the polarity of water would affect H_0, and in the water-rich region the spontaneous curvature (H_0) of the surfactant film seems to have positive values favoring the formation of O/W droplet microemulsion. The same trend of behavior was also found in this system as a function of the PG concentration at different water/PG ratios and a constant $R(+)$-limonene/ethanol ratio (1:1) (see Table 1). With increasing concentration of PG in the aqueous phase, the isotropic phase region
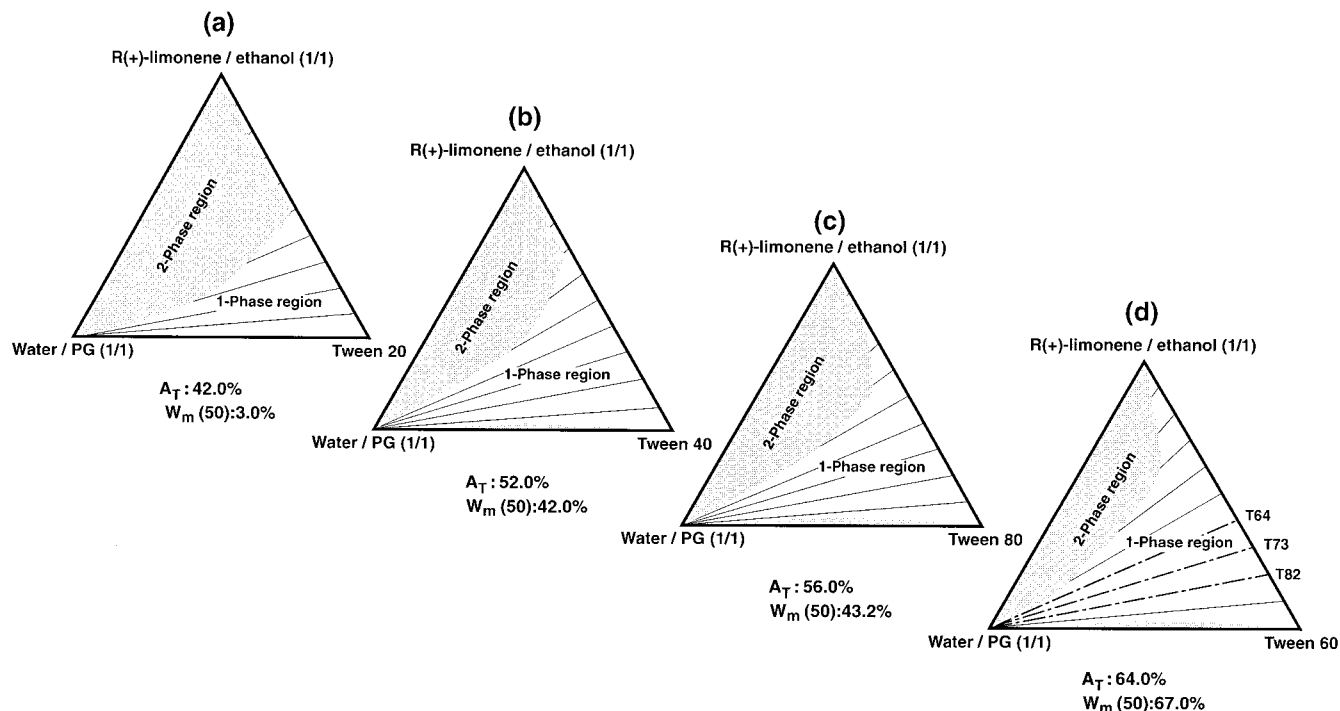
Figure 2. Phase diagrams of the system water/PG/R(+)-limonene/EtOH/ethoxylated sorbitan monoester at 25 °C with constant weight ratio of water/PG (1:1) and constant weight ratio of R(+)-limonene/EtOH (1:1). Ethoxylated sorbitan monoesters used in these phase diagrams were (a) Tween 20, (b) Tween 40, (c) Tween 80, and (d) Tween 60.

Table 1. A_T (Total Monophasic Region) Values for Some of the Phase Diagrams Described in This Study

system	aqueous phase	oil phase	surfactant (s)	A_T (%)
a1	water/PG (3:2)	R(+)-limonene/EtOH (1:1)	Tween 60	60.0
a2	water/PG (3:1)	R(+)-limonene/EtOH (1:1)	Tween 60	57.5
a3	water/PG (4:1)	R(+)-limonene/EtOH (1:1)	Tween 60	52.0
b1	water/PG (1:1)	R(+)-limonene/EtOH (3:2)	Tween 60	58.0
b2	water/PG (1:1)	R(+)-limonene/EtOH (3:1)	Tween 60	37.0
b3	water/PG (1:1)	R(+)-limonene/EtOH (4:1)	Tween 60	28.0
c1	water/PG (1:1)	R(+)-limonene/EtOH (1:1)	L1695	47.0
c2	water/PG (1:1)	R(+)-limonene/EtOH (1:1)	triglyceride monooleate	62.0
d1	water/Gly (3:1)	R(+)-limonene/EtOH (1:1)	Tween 60	49.0
d2	water/Gly (4:1)	R(+)-limonene/EtOH (1:1)	Tween 60	45.0
e1	water/PG (1:1)	MCT/EtOH (1:1)	Tween 80	43.3
e2	water/PG (1:1)	MCT/EtOH (1:3)	Tween 80	49.7

increased, but these results suggest that PG and ethanol have different impacts on the system. Ethanol seems to be more effective in decreasing the rigidity of the surfactant film.

The effect of temperature on these phase diagrams was investigated in the temperature range of 20–70 °C. The systems were found to be temperature-insensitive similarly to the phase diagrams formed with ethoxylated alcohols in the presence of polyols/alcohols (Figure 1c,d).

One can clearly see that the goal of formulating isotropic water dilution lines was easily achieved in the Tween-based system. The LC phase was not detected, and the two-phase region was drastically reduced. The differences in the behavior of the ethoxylated fatty alcohols in comparison to the ethoxylated sorbitan fatty acid esters are mainly seen in the LC formation. The bulky heads with high packing molecular volume fractions of the sorbitan esters are probably restricting the formation of highly ordered packed layers of lyotropic LC noncurved (or moderately curved) interfaces.

C. Influence of Short-Chain Alcohols. Attempts to replace the ethanol with other short-chain alcohols with improved ability to serve as cosurfactants, participating in the composition of the curved interface, were

very meaningful in the design of future systems. Replacing ethanol by propanol (Figure 3a) or butanol (Figure 3b) shrunk the two-phase area to its minimum. The more hydrophobic alcohols (pentanol and hexanol) were less efficient. The solubilization process in these systems is limited by R^0, so the addition of long-chain alcohols such as pentanol or hexanol decreased the solubilization capacity (*25*). This is of no surprise because a similar behavior was detected in our previous study on the four-component systems composed of ethoxylated alcohols/water/hydrocarbon and medium-chain alcohols (*26*). A detailed description of the role of the alcohol in W/O interfaces can be found in our previous work (*26*). The main drawback of these systems is the nonfood grade alcohols.

It must be also stressed that when butanol (A_T = 79.0%) (see Figure 3b) or ethanol (A_T = 64.0%) (see Figure 2d) is used in the compositions, the effective dilution lines are quite rich in surfactant with >50% of the oil content (see lines 64, 73, and 82), whereas when pentanol (A_T = 66.0%) or hexanol (A_T = 62.5%) is present, the dilution lines consist of <50% surfactant (dilution lines 46 and 55 for hexanol and pentanol, respectively). Note that surfactant-rich compositions are not recommended in most food applications.
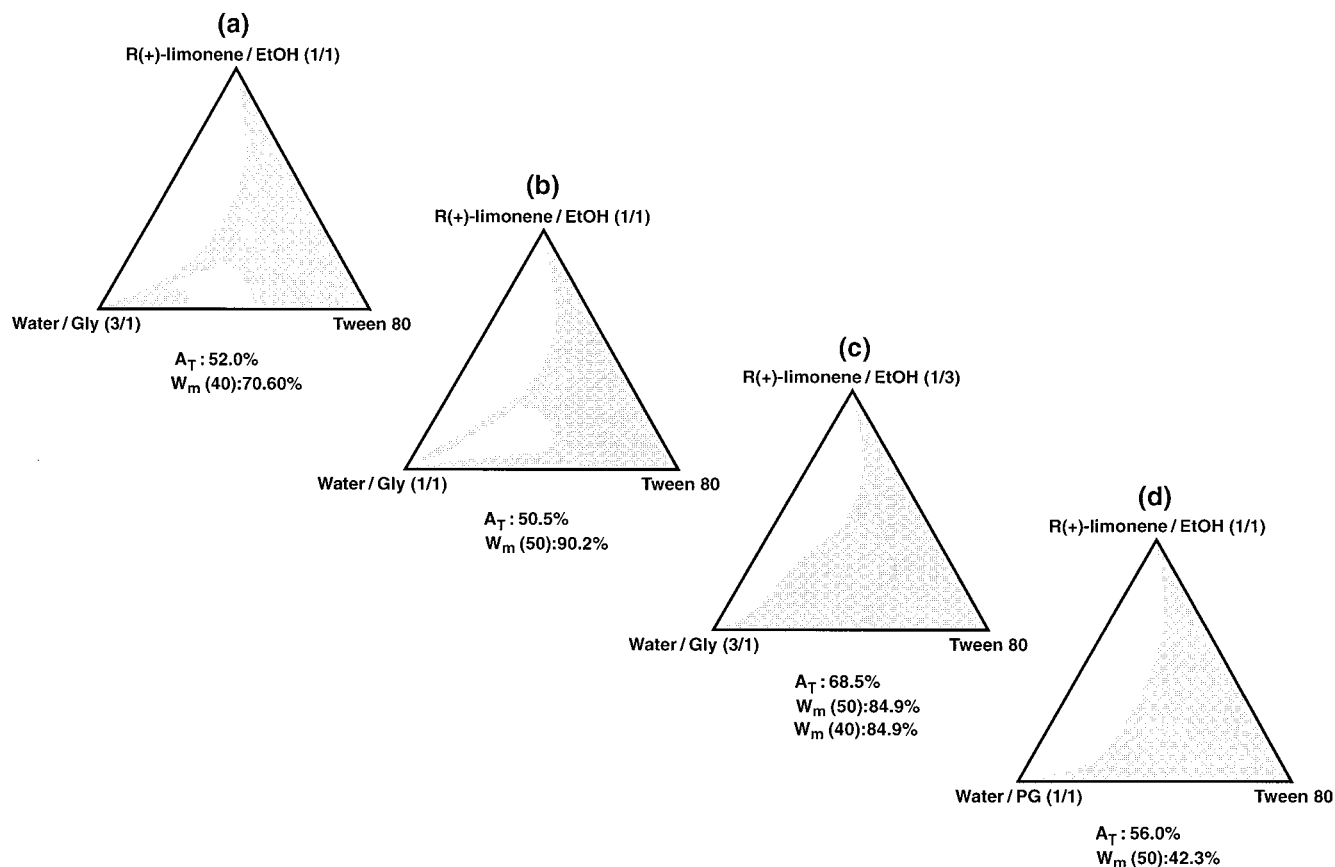
O/W Food Grade Microemulsions

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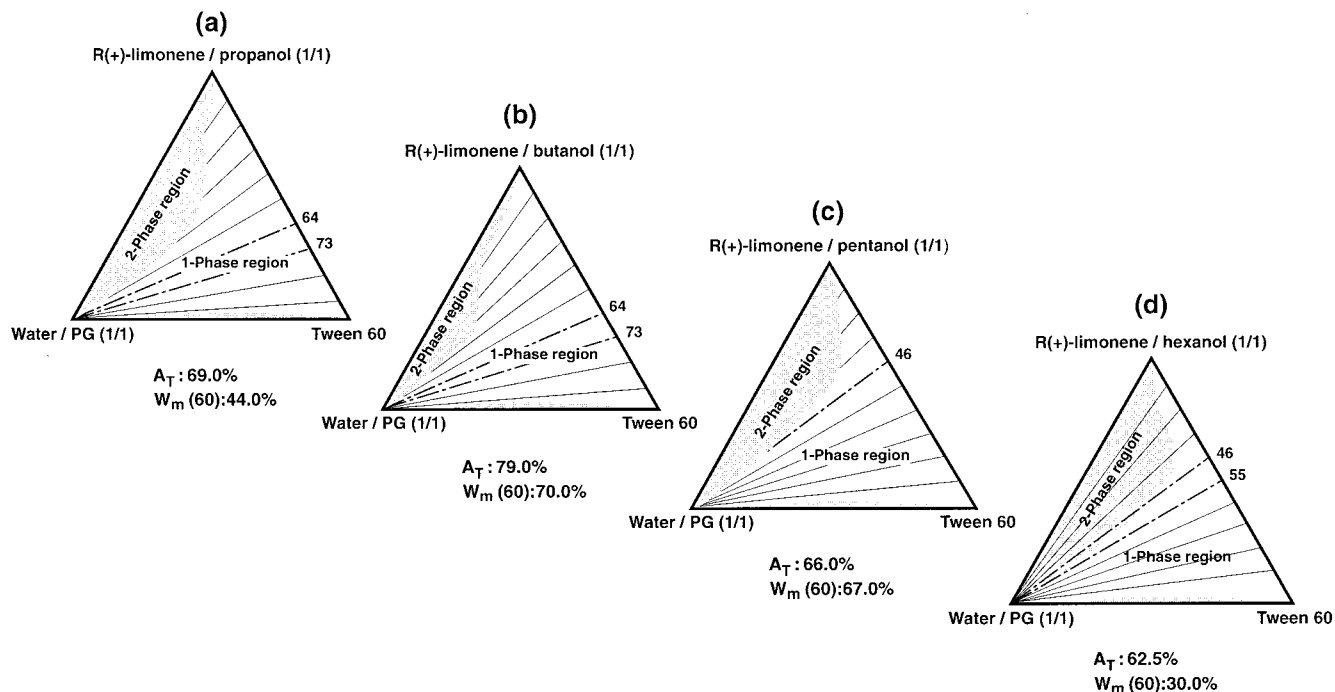
Figure 3. Phase diagrams of the system water/PG/R(+)-limonene/short-chain alcohol/Tween 60 at 25 °C with constant weight ratio of water/PG (1:1) and constant weight ratio of R(+)-limonene/short-chain alcohol (1:1). Short-chain alcohols used were (a) propanol, (b) butanol, (c) pentanol, and (d) hexanol.
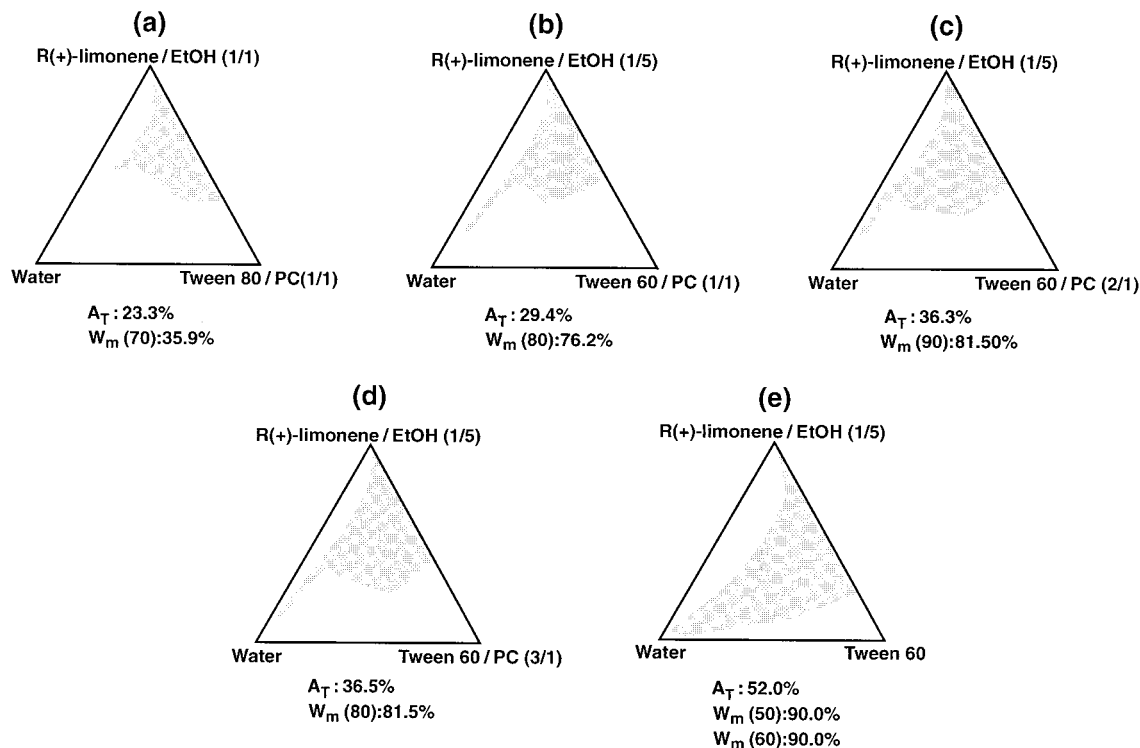
Figure 4. Phase behavior of the system water/R(+)-limonene/EtOH/Tween 60 (or Tween 80)/PC at 25 °C with different weight ratios of Tween 60 (or Tween 80)/PC: (a) Tween 80/PC (1:1); (b) Tween 60/PC (1:1); (c) Tween 60/PC (2:1); (d) Tween 60/PC (3:1); (e) Tween 60. The composition of the oil is given in the upper corner of these phase diagrams. Gray areas represent one-phase regions.

D. Phase Behavior of Food Grade Anionic—Nonionic Mixed Surfactant Systems. Tweens are food grade surfactants with a negative image. In many countries there is constant pressure to remove them from major food formulations. Lecithins are considered to be generally recognized as safe (GRAS) compounds with health benefits. The aim of many formulators will be to explore mixtures of Tweens and lecithins in foods and to find ways to minimize the use of Tween by replacing all or part of it with lecithins or lecithin fractions. The solubilization of R(+)-limonene in mixed Tween/PC surfactant solutions has been examined (see Figure 4). It can be clearly seen that at low ratios (1:1 ratio Figure 4a) of Tween 80/PC (high PC content) the isotropic areas are very limited and only W/O microemulsions are formed [A_T = 23.3%; W_m(70) = 35.9%].

(a)
R(+)-limonene / EtOH (1/1)
Water / Gly (3/1)   Tween 80
A_T: 52.0%
W_m (40):70.60%

(b)
R(+)-limonene / EtOH (1/1)
Water / Gly (1/1)   Tween 80
A_T: 50.5%
W_m (50):90.2%

(c)
R(+)-limonene / EtOH (1/3)
Water / Gly (3/1)   Tween 80
A_T: 68.5%
W_m (50):84.9%
W_m (40):84.9%

(d)
R(+)-limonene / EtOH (1/1)
Water / PG (1/1)   Tween 80
A_T: 56.0%
W_m (50):42.3%

Figure 5. Effect of polyols (Gly and PG) and ethanol (EtOH) on the behavior of the isotropic regions of the system water/polyol/ R(+)-limonene/EtOH/Tween 80 at 25 °C for different ratios of water/polyol: (a) water/Gly (3:1); (b) water/Gly (1:1), (c) water/Gly (3:1); (d) water/PG (1:1). The composition of the oil phase in these phase diagrams is given in the upper corner. Gray areas represent one-phase regions.

Phase separation occurs before inversion to O/W microemulsion takes place. If the R(+)-limonene is enriched with ethanol [Tween 60/PC ratio of 1:1 and R(+)-limonene/ethanol ratio of 1:5, Figure 4b] or as the Tween 60/PC ratio increases from a ratio of 1:1 (Figure 4b) to 2:1 (Figure 4c) and to a ratio of 3:1 (Figure 4d), one-phase channels are formed. The best results are as expected with pure Tween 60 (A_T = 52.0%) (see Figure 4e). PC is known to be a "balanced surfactant". It is quite lipophilic, and its spontaneous curvature is close to 0 (*31*). It was reported that in order to form a W/O microemulsion based on PC, short-chain alcohols (such as propanol and butanol) (*6, 13, 31*) must be added. The negative effect on the O/W microemulsion is clearly seen (Figure 4d,e). To compensate for its flattening effect, one must use excess amounts of alcohol and Tween. It was concluded that using short-chain alcohols decreases the spontaneous curvature of the PC interface to negative values [the microstructure changed from bicontinuous ($H_0 \approx 0.0$) to a W/O microemulsion ($H_0 < 0.0$)] (*7, 31*). On the basis of these facts we investigated the possibility of increasing the spontaneous curvature of a PC-based microemulsion to a positive curvature (>0) that is needed for the formation of O/W microemulsions. It was found, as seen from the phase diagrams (see Figure 4b–e), that using high alcohol and high Tween 60 levels increased the spontaneous curvature and phase inversion to O/W is achieved along with limited possibility for water dilution. An increased amount of ethanol and Tween 60 seems to increase the dissolution of PC and the fluidity of the PC film due to the considerable

amount of ethanol and Tween 60 that incorporated into the film.

The increase of isotropic areas by the dilution of the surfactant (PC) with another more hydrophilic surfactant is only possible if a further dilution of the oil phase with alcohol and a further dilution of the water are done in parallel.

E. Effect of Gly on the Phase Behavior of the Ethoxylated Sorbitan Ester Systems. Glycerol is known as a good cosolvent but has no surface activity. It is known that Gly has a "salting-out" effect, and it is not incorporated in the surfactant film (*16, 19*). The Gly effect on the phase behavior of the Tween 80 systems was examined (see Figure 5a–c). Mixtures of water and Gly were used as the aqueous phase and were compared to the phase behavior of the Tween 80 system prepared with water/PG.

Microemulsions based on Gly show behavior similar to that of those made of PG. As the water/Gly weight ratio decreases from 3:1 (Figure 5a) to 1:1 (Figure 5b) and as the alcohol content increases from an R(+)-limonene/ethanol weight ratio of 1:1 to 1:3 (Figure 5c), larger isotropic areas are formed with broader dilution channels. In Figure 5a we can practically see the formation of a bicontinuous channel prior to the inversion and the formation of the O/W microemulsion (A_T = 52.0%). In Figure 5b there are two separate channels, which will have to be further explained, and in Figure 5c (excess of alcohol and Gly) the two channels coincide into one large isotropic area without clear distinction between the W/O and O/W inversions (A_T = 68.5%).

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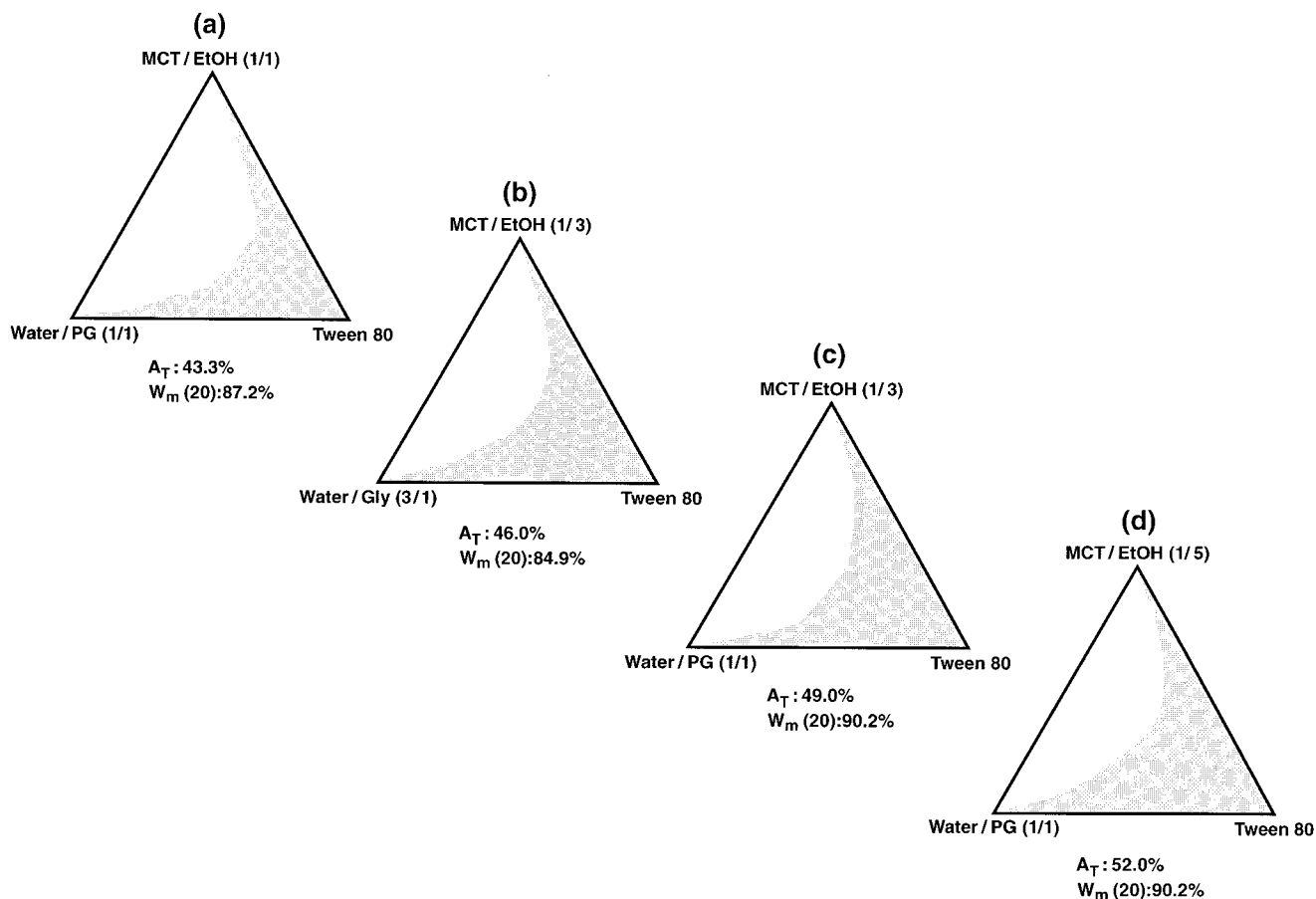
Figure 6. Effect of polyols (Gly and PG) and ethanol (EtOH) on the behavior of the isotropic regions of the system water/polyol/ MCT/EtOH/Tween 80 at 25 °C for different weight ratios of water/polyol: (a) water/PG (1:1); (b) water/Gly (3:1), (c) water/PG (1:1); (d) water/PG (1:1). The composition of the oil phase in these phase diagrams is given in the upper corner. Gray areas shown represent one-phase regions.
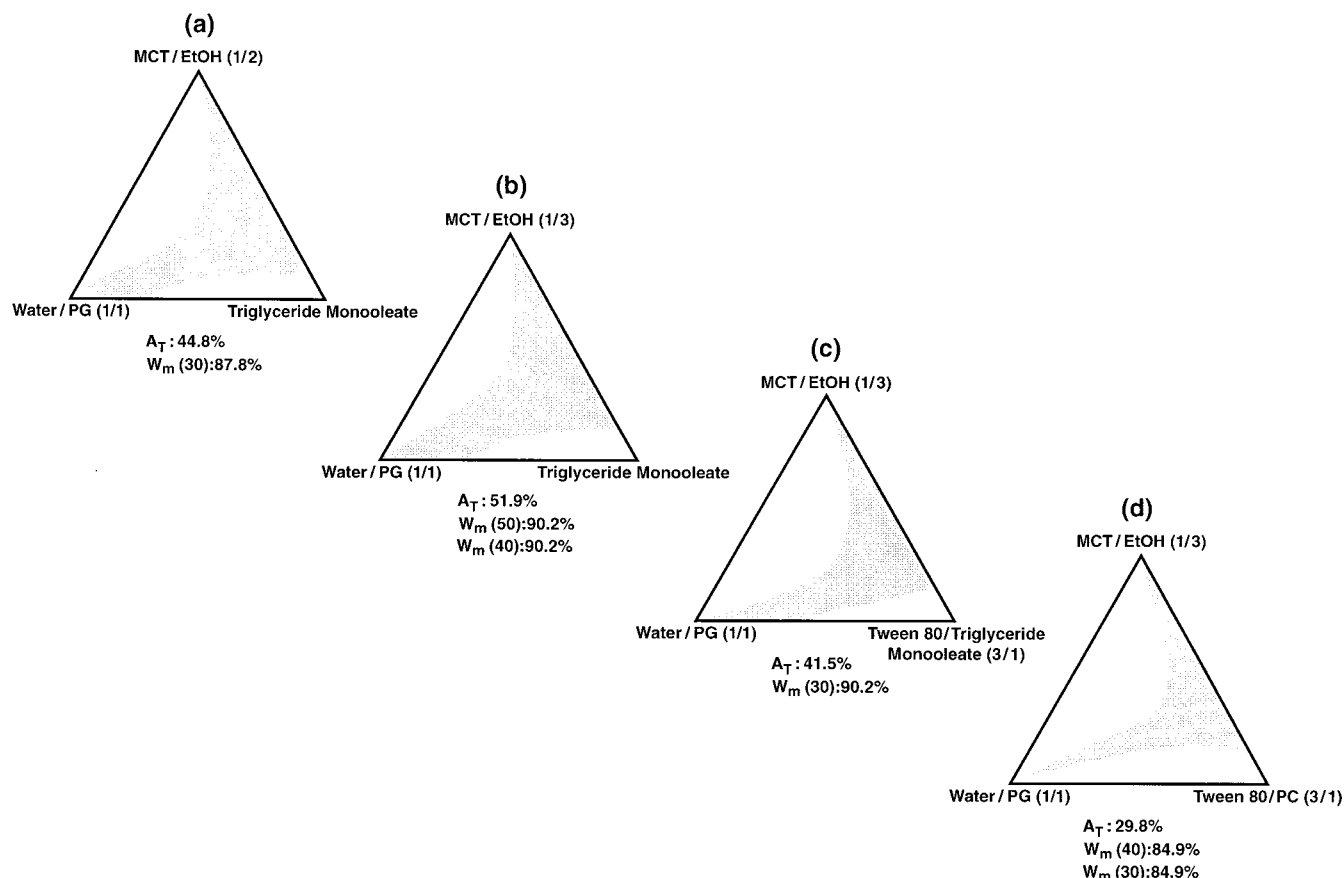
Close examination of the systems made with the PG versus those made with Gly reveals that the PG is a slightly better cosolvent than the Gly at otherwise similar compositions. The two-channel areas coincide into one isotropic area, and dilution line 82 permits a total dilution of the system with the aqueous phase, which is not possible in the glycerol system (see Figure 5b versus Figure 5d). It is also possible that the PG is partially propagating into the interface while Gly remains mostly in the water phase. The phase behavior of the system water/Gly/R(+)-limonene/ethanol/Tween 60 as a function of the concentration of glycerol in the aqueous phase at two different water/Gly weight ratios and a constant R(+)-limonene/ethanol weight ratio (1:1) was studied (see Table 1). The change in A_T in these two systems was not pronounced. This indicates that the same trend of behavior as in systems with PG is found in these Gly-containing systems.

F. Effect of the Nature of the Oil in Tween 80-Based Systems. The R(+)-limonene can impart some off-flavor if oxidation upon storage occurs. MCT is an "oxidation-free" oil and, therefore, it is considered to be a "safe oil" and is widely used in food formulations. Most attempts to use MCT in classical Tween-based microemulsions were difficult. In a typical Tween 80/MCT/water system only W/O miocroemulsions with a limited isotropic area could be formulated. Addition of ethanol did not improve much the solubilization of the MCT in the water–surfactant mixture. The different phase behaviors of R(+)-limonene and MCT are most probably due to the difference in the molecular volume of these two oils (*10, 25*). The molecular volumes of R(+)-limonene and MCT are 162 and 530 cm³ mol⁻¹, respectively. The isotropic phase in R(+)-limonene was formed at lower ethanol concentration compared with that for MCT. It seems that R(+)-limonene has a higher degree of interaction with the hydrophobic part of the surfactant film than MCT. For this reason, Tween 80 is less effective in solubilizing MCT compared with R(+)-limonene. Only upon mixing the water with the polyols and the oil with ethanol were O/W microemulsions formed, and the channels were extended to the water corner of the phase diagram (Figure 6). Similarly to the R(+)-limonene, in MCT systems Gly formed two channels (Figure 6b) while the PG formed one larger channel (Figure 6c) at comparable concentrations. As can be clearly seen from the water/PG system, with increasing alcohol content (lower MCT/ethanol ratio) the channels are more pronounced and extend to the water corner at more dilution lines (see Figure 6a,c,d). Moreover, all investigated combinations of Tween with PC failed to increase the isotropic areas (data not shown). However, diluting the MCT with ethanol at a 3:1 ratio and diluting the water with Gly at a 3:1 ratio dramatically improved the size of the isotropic areas, and surfactant-poor (or oil-rich) dilutable microemulsions could be formed (data not shown).

G. Phase Behavior of Other Hydrophilic Food Grade Surfactants (Polyglycerol Esters). As was clearly indicated from the above formulation, it was essential to explore more hydrophilic surfactants to replace the ethoxylated sorbitan esters (Tweens). As

(a)

MCT / EtOH (1/2)

Water / PG (1/1)   Triglyceride Monooleate

A_T : 44.8%
W_m (30):87.8%

(b)

MCT / EtOH (1/3)

Water / PG (1/1)   Triglyceride Monooleate

A_T : 51.9%
W_m (50):90.2%
W_m (40):90.2%

(c)

MCT / EtOH (1/3)

Water / PG (1/1)   Tween 80 / Triglyceride
                          Monooleate (3 / 1)

A_T : 41.5%
W_m (30):90.2%

(d)

MCT / EtOH (1/3)

Water / PG (1/1)   Tween 80 / PC (3 / 1)

A_T : 29.8%
W_m (40):84.9%
W_m (30):84.9%

Figure 7. Effect of different food grade nonionic surfactants (or different mixtures of nonionic surfactants or nonionic−anionic surfactants) on the behavior of the isotropic regions in the system water/PG/MCT/EtOH/food grade nonionic surfactant at 25 °C with constant weight ratio of water/PG (1:1): (a) triglyceride monooleate (3.G.1.O); (b) triglyceride monooleate (3.G.1.O); (c) Tween 80/triglyceride monooleate (3.G.1.O) (3:1); (d) Tween 80/PC (3:1). The composition of the oil phase in these phase diagrams is given in the upper corner. Gray areas represent one-phase regions.

previously shown, PC is not an optimal candidate because of its poor performance and its high cost. Polyglycerol esters are nonethoxylated hydrophilic emulsifiers and possible candidates for the formation of O/W microemulsions.

Polyglycerol Esters and MCT. Triglycerol monooleate (3.G.1.O) was found to be a good choice for MCT/ethanol mixtures (1:2 wt ratios) (see Figure 7). From Figure 7a one can see that large isotropic areas of O/W micro-emulsions can be formed with good dilution properties (A_T = 44.8%).

Polyglycerol Esters and R(+)-Limonene. Surprisingly, triglycerol monooleate (3.G.1.O) was an inadequate emulsifier for R(+)-limonene solubilization in the aqueous phase [A_T = 30.6%; W_m(50) = 54.6%] (see Figure 8a). Phase separation occurred prior to inversion. Similarly, blends of hydrophilic sugar esters with triglycerol monooleate did not improve the isotropic area (Figure 8b) but indicated that probably for the oil phase a more hydrophilic polyglycerol ester must be used. A decaglycerol ester such as decaglycerol oleate (10.G.1.O) was found to be practically similar to the 3.G.1.O and improved only slightly the isotropic area (see Figure 8e).

Sucrose Monolaurate and R(+)-Limonene. The phase behavior of the system water/PG/R(+)-limonene/ethanol/ sucrose monolaurate (L-1695) at a constant R(+)-limonene/ethanol weight ratio (1:1) and a constant water/PG weight ratio (1:1) was studied (see Table 1). The two-phase region shrank considerably in this system, and an isotropic large monophasic area was formed.

H. Rheological Behavior. Viscosity is a useful tool to elucidate the structural changes of the corresponding systems. Figure 9 shows the variation of viscosity along dilution lines D64 (Figure 1d) and T64 (Figure 2d). These lines, containing a 1:1:3 R(+)-limonene/ethanol/ surfactant weight ratio, are characterized by a single continuous microemulsion region starting from a pseudo binary solution (surfactant/oil phase) and ending up with an O/W microemulsion in the water/PG (1:1) corner. The investigated samples along these dilution lines exhibit a Newtonian flow behavior (viscosity being independent of the shear rate). For these systems, when the aqueous phase concentration was increased gradually by following the dilution lines D64 and T64, the viscosity increased. For T64 at ϕ_w = 0.45−0.5 a maximum was reached, and at higher ϕ_w values the viscosity was dramatically reduced. The same behavior was found for D64 but the maximum viscosity was now at ϕ_w = 0.55−0.60; also at all weight fractions, the viscosity along T64 was higher. At ϕ_w < 0.45 in T64 and < 0.55 in D64 the increase in the viscosity with the increase of the aqueous phase content may be due to an increase in the dispersed globule sizes, and also it may be due to the formation of clusters of globules that are sufficiently close to each other, which increases the interaction between them. When the weight fraction of the aqueous phase is low, it is well-known that the interaction between the globules is low and the microemulsion consists of isolated dispersed globules (hard spheres) in the continuous oil medium (*36, 37*). The sudden decrease in the viscosity beyond a certain amount of the aqueous

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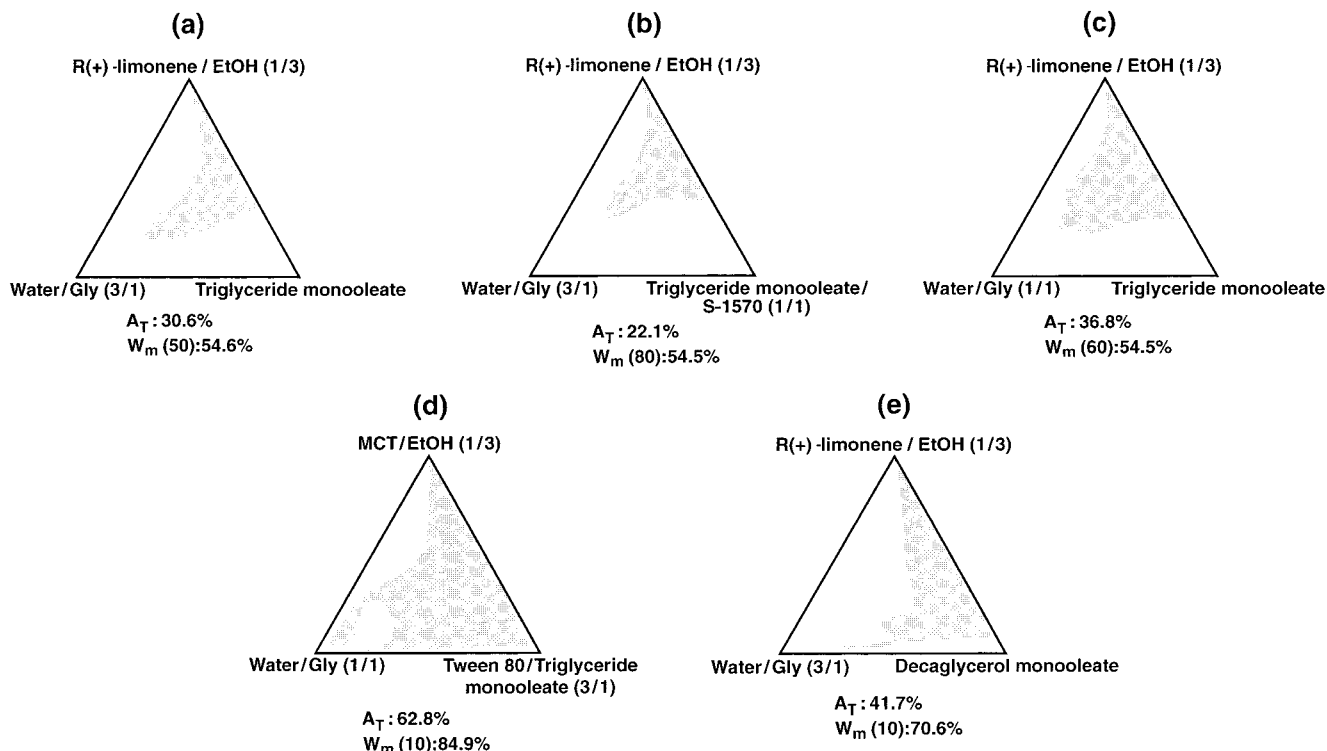
Figure 8. Effect of different food grade nonionic surfactants (or different mixtures of nonionic surfactants) on the behavior of the isotropic regions in the system water/Gly/MCT/EtOH/food grade nonionic surfactant (or mixed nonionic surfactants) at 25 °C with different weight ratios of water/Gly and a constant weight ratio of $R(+)$-limonene (or MCT)/EtOH (1:3): (a) triglyceride monooleate (3.G.1.O); (b) triglyceride monooleate (3.G.1.O)/S-1570 (1:1); (c) triglyceride monooleate (3.G.1.O); (d) Tween 80/triglyceride monooleate (3.G.1.O) (3:1); (e) decaglycerol monooleate. Gray areas represent one-phase regions.
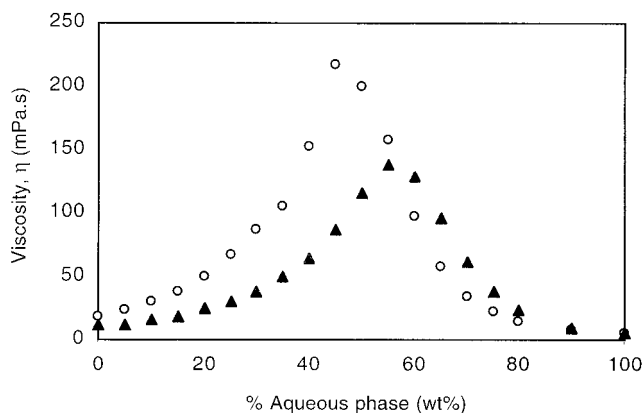
Figure 9. Variation of the viscosity (η) of the five-component microemulsion systems along dilution lines D64 (▲) (see Figure 1d) and T64 (○) (see Figure 2d) at 25 °C.

phase in the system is related most likely to structural changes. A transition from a W/O microemulsion to an O/W microemulsion most likely occurred, and this transition was sharp because the aqueous phase is the continuous phase and the viscosity should gradually decrease due to the dilution of the O/W microemulsion droplets. The viscosity of the solution, which contains just PG and water at a weight ratio of 1:1, is 5.9 mPa·s.

CONCLUSIONS

The effects of polyols (PG and Gly) and a short-chain alcohol (ethanol) on the phase behavior of nonionic and nonionic/PC surfactant mixtures and food grade oils have been elucidated in this work. Attempts were made to find mixtures of ingredients (1) that will impart a

positive interfacial curvature of the surfactant film in order to form O/W microemulsions, (2) that inhibit liquid crystal formation, and (3) that maximize mutual dissolution of the ingredients.

The main conclusion of this work is that the formulation of food grade O/W microemulsions is difficult to formulate from a three-component systems based on water, oil, and single surfactant. However, it is possible to formulate these microemulsions by using a suitable nonionic surfactant and by the addition of polyols and short-chain alcohols. The increase in the oil solubilization capacity followed by the addition of polyols and short-chain alcohols is clearly reflected in the phase behavior of the systems.

The isotropic microemulsion region formed in systems containing ethoxylated fatty alcohols or ethoxylated sorbitan fatty esters, ethanol, $R(+)$-limonene, PG, and water was found to be quite temperature-insensitive.

The phase behavior of the system of $R(+)$-limonene, ethanol, water/PG (1:1) and polyoxyethylene sorbitan monostearate (Tween 60) containing a 1:1:3 $R(+)$-limonene/ethanol/surfactant weight ratio is characterized by a single continuous microemulsion region starting from a pseudo binary solution (surfactant/oil phase) to the microemulsion water/PG (1:1) corner. Along this dilution line the viscosity measurements indicate that at a certain composition the system inverts from W/O to O/W microemulsion.

Optimal composition of the polar and apolar phases leads to formation of a large isotropic area with a high content of solubilized oil.

Investigation of the solubilization of $R(+)$-limonene in systems containing PC/Tween 80 mixed surfactant solutions instead of Tween 80 resulted in more restricted isotropic regions. There was a significant nega-

tive synergistic effect (a significant reduction in the tendency of solubilization) as a result of the addition of a too lipophilic surfactant. The viscosity measurements demonstrate a continuous inversion of the microemulsion from W/O to O/W.

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