

Model Microemulsions Containing Vegetable Oils

2. Ionic Surfactant Systems

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The phase behavior and the structure of ionic microemulsions, stabilized by sodium oleate and different alcohol cosurfactants, containing fatty acid esters or triglycerides as lipophilic components, have been investigated. Microemulsions containing triglycerides display a smaller stability region than microemulsions containing hydrocarbons or fatty acid esters. From structural investigations, using the NMR FT pulsed gradient spin echo method for measuring self-diffusion coefficients, differences in the microstructure are revealed as well. Adding an ester (or a hydrocarbon) to a microemulsion containing sodium oleate/pentanol will at certain compositions lead to a gradual transition from a bicontinuous to an oilcontinuous system, while this behavior cannot be detected when adding a triglyceride. Instead, a phase-separation occurs, and it is suggested that the larger molecular size of the triglyceride is responsible for the difference.

Microemulsions, isotropic lowviscous solutions of water, oil and at least one surfactant, (1) have been carefully investigated during the last twenty years due to their large actual and potential technological interest (2). While an extensive amount of data have been collected for model microemulsion systems containing low molecular weight aliphatic or aromatic hydrocarbons, studies of vegetable oil-based systems are more scarce. Only water monoglyceride/triglyceride microemulsions have been carefully studied (3-7), while a few other investigations have been performed with other surfactant systems (8,9) e.g., in connection with the use of vegetable oils as diesel fuels (10,11). However, a fundamentally oriented study directed towards the clarification of any possible differences between microemulsions containing triglycerides and those containing hydrocarbons has, to our knowledge, not been performed. In this and our preceding paper (12), such a study is described.

In the first part of this study (12), the phase behavior of microemulsions stabilized by nonionic surfactants has been mapped, and differences between a methyl ester and a triglyceride pointed out. In this second part of our investigation, the phase behavior and structure of ionic microemulsions containing fatty acid esters or triglycerides are described. Structural studies, performed with multi-component selfdiffusion measurements using the FT-NMR pulsed gradient spin echo technique (13), have been aimed at detecting differences in the microstructure between these and other microemulsion systems and at a possible correlation to the phase behavior of the systems.

MATERIALS AND METHODS

Chemicals. The triglycerides and alkyl esters employed

in this study have been analyzed and described previously (12): isooctyleate (denoted IOO); methyl ester (denoted ME) containing mainly methyl oleate; MCT triglyceride (denoted MCT), a C8-C10 triglyceride; peanut oil (denoted PNO), a C16-C18 triglyceride. Sodium oleate (Riedel-de-Haen, techn), butanol (KEBO, >99.5%), and pentanol (Fluka, >99%) and decanol (Fluka, >99%) were used as received. A comparison with corresponding ternary phase diagrams from the literature revealed no differences (14). Water was twice distilled.

Phase diagrams. Determinations of phase diagrams were carried out by titration and polarization microscopy as described previously (12).

NMR-measurements. Structural investigations of the microemulsions were performed with the FT-NMR pulsed gradient spin echo method (13). The measurements were performed on a Jeol FX-100, operating at 100 MHz for ¹H at the ambient temperature 25±0.5°C (15, 16). The gradient was calibrated with a sample containing HDO in D₂O (17). Some difficulties in the data-treatment occur due to overlapping resonances and exchange of hydroxyls protons. The ester or triglyceride self-diffusion coefficients can be directly obtained from the α-carboxylic methylene. The alcohol selfdiffusion can then be obtained from a biexponential fit to peaks from the α-hydroxylic protons of the alcohol and any of the oils, where the accuracy is improved since the self-diffusion of the latter components are independently known. The relative accuracy of the measurements is not less than 10%.

RESULTS

The quaternary phase diagrams for the systems water/sodium oleate/alkanol/MCT are shown in Figure 1. All diagrams are determined for a fixed weight ratio oleate/alkanol = 1/2 for 1-butanol, 1-pentanol and 1-decanol. The trends found are those expected for varying the chain length of the alcohol cosurfactant (14,15). The butanol system yields an extensive solution phase extending from the water corner over a wide concentration regime (Fig. 1a). At equal amounts of water and MCT more than 35 wt% surfactant mixture is needed to create a single homogenous microemulsion phase L. (This rather high amount of surfactant needed is of course considerably decreased when adding electrolyte). Thus, slightly more surfactant must be used than with an alkane or aromatic hydrocarbon as oil component, where less than 30 wt% surfactant/cosurfactant mixture is needed to create a homogenous solution (18). Using pentanol as alcohol cosurfactant results in the formation of two solution phases, L₁ and L₂ using the Ekwall nomenclature (19). The L₁-phase is a thin salient stretching from the water corner while the L₂-phase is a larger microemulsion phase; it shows a slightly smaller demand of surfactant/cosurfactant in order to create a microemulsion containing equal

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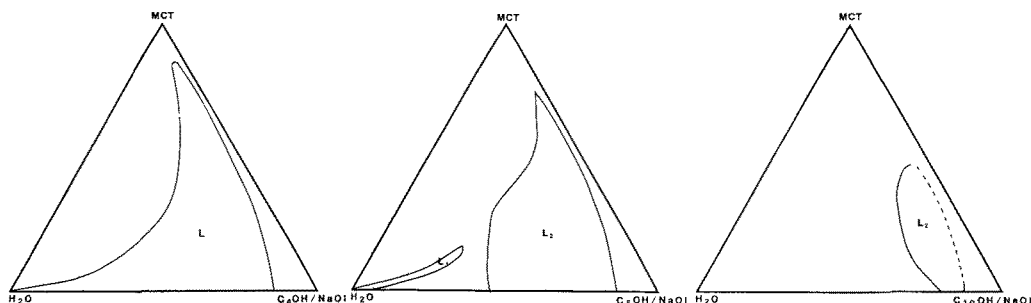


Fig. 1. Quaternary (pseudo-ternary) phase diagrams for the systems: a) water/sodium oleate:butanol/MCT, b) water/sodium oleate:pentanol/MCT, c) water/sodium oleate:decanol/MCT, at 25°C and the fixed weight ratio sodium oleate:alkanol 1:2. L (with or without index) denotes solution phases. Only the regions of the solution phases have been marked out in the phase diagram.

amounts of water and MCT, around 30 wt% (Fig. 1b). Again this is some 5 wt% more than what is needed to create a homogenous microemulsion with an ordinary hydrocarbon component (20). Finally, the decanol system yields only a small L_2 -phase at this ratio surfactant/alcohol.

While the trend due to the variation of the alcohol cosurfactant for a triglyceride microemulsion is similar to the one encountered for normal hydrocarbons, there are more unexpected effects when varying the oil for a fixed cosurfactant. In Figure 2, four different phase diagrams are shown for microemulsions stabilized by sodium oleate/1-pentanol (at a weight ratio $1/2$) for two alkyl esters, ME (Fig. 2a) and IOO (Fig. 2b), and two triglycerides, MCT (Fig. 2c) and PNO (Fig. 2d). ME and IOO yield similar phase diagrams; the main difference is that the L_2 -phase is slightly larger in the IOO-system. (This difference might just as well be coincidental; at a slightly different weight ratio surfactant/cosurfactant, this effect is not noticeable.) MCT gives a somewhat smaller L_2 -phase, in particular in the oil-rich region; the miscibility gap water/oil is more extensive. Finally, for PNO the effect is dramatic. The L_2 -phase has shrunk to a very small region in the surfactant-rich corner. At equal amounts of water and oil, close to 60 wt% surfactant is needed to create a homogenous microemulsion solution. In addition, no L_1 -phase is found at this ratio surfactant/co-surfactant.

It should be noted that these effects are significant regardless of how the comparison is done. Recalculating the phase diagram to volume percent or mole percent still results in large and noticeable differences. For mole fractions the effects are even more drastic. Take, e.g., a composition in the ternary, oil-free system corresponding to 50 wt% water and 50 wt% surfactant. (This corresponds to a composition of 86.5 mole% water, 1.7 mole% oleate and 11.8 mole% pentanol.) By adding oil to such a sample, it is possible to solubilize 50 wt% ME, 47 wt% IOO, 35 wt% MCT or 7 wt% PNO. This corresponds to the 5 mole% ME, 3.6 mole% IOO, 2.1 mole% MCT or 0.25 mole% PNO. Of course, the matter of comparing the extension of one-phase regions in different systems could be ambiguous not only because of different ways of calculating the concentration, but also because of the choice of, in this case, a fixed composition of the surfactant mixture. However, the effects are simi-

lar when choosing different compositions of the surfactant mixture (1/1 or 1/3) in our systems. There is a significant decrease in the extension of the L_2 -phase using MCT as an oil component instead of a fatty acid ester (or an ordinary hydrocarbon), and this effect becomes dramatic with PNO.

A characterization of the structure of different microemulsion systems was performed using the FT-NMR PGSE method (12). Results from diffusion measurements in two systems — water/sodium, oleate: pentanol/ME or MCT — are shown in Figures 3 and 4, respectively. Oil was added to samples with the fixed weight ratio 0.50/0.17/0.33 of water/oleate/pentanol. The self-diffusion coefficients of all components, except sodium oleate, were measured at varying amounts of ME or MCT. In the ME-system, the decrease in self-diffusion for water is quite marked, while in the MCT-system, no changes occur up to the phase boundary (at 45 wt% MCT). Measurements were performed also for the corresponding samples with added PNO; up to the phase boundary (i.e., for 7 wt% PNO) the water self-diffusion coefficient remains constant.

DISCUSSION

The main point of this investigation has been to characterize and explain any difference in behavior of microemulsions containing esters or triglycerides compared to the hydrocarbon-containing systems normally chosen as model systems. One point is clear: triglycerides, in particular large triglycerides such as PNO, are considerably more difficult to solubilize into microemulsions than hydrocarbons or alkyl esters.

The differences clearly detectable in this work were found, although less marked, also in the corresponding microemulsions stabilized by nonionic surfactants (12). When comparing ternary systems containing water/nonyl phenol ethoxylate/ME or MCT, there are two marked differences: the amount of surfactant needed for obtaining an isotropic single-phase microemulsion is slightly higher with MCT than with ME at optimum conditions for the systems, and no free-lying microemulsion region, a surfactant phase, is found with MCT. Our other observations also suggest that the effect is even more marked with PNO — higher amounts of surfactant are needed.

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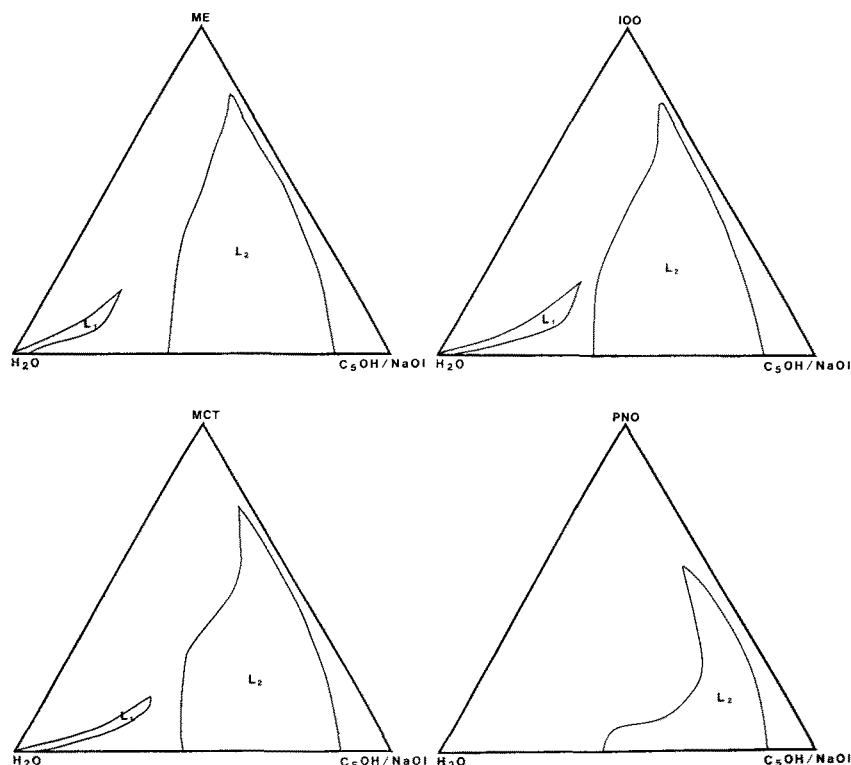


Fig. 2. Quaternary (pseudo-ternary) phase diagrams for the systems: a) water/sodium oleate:pentanol/ME, b) water/sodium oleate:pentanol/IOO, c) water/sodium oleate:pentanol/MCT, d) water/sodium oleate:pentanol/PNO. Notations and other conditions as in Figure 1.

The knowledge of phase equilibria and microstructure in microemulsion systems stabilized by an ionic surfactant and an alcohol cosurfactant mixture is extensive (21,22). The main outlook of the phase diagram is determined by the co-surfactant, as is the structure of the system (at no added electrolyte). For medium-chain alcohol cosurfactants, such as butanol and pentanol, extensive microemulsion regions are anticipated (21, 22). A continuous transition between different preferred structures occurs with butanol. In the water-rich region a normal micellar solution exists, which at higher amounts of cosurfactants and/or hydrocarbons gradually is transformed to a bicontinuous structure. Finally, at higher hydrocarbon contents the system is gradually transformed to an inverse micellar region with distinct water droplets in a lipophilic continuum. For pentanol, the transition between micellar aggregates and a bicontinuous phase is normally interrupted by a liquid crystalline, lamellar phase. In addition, regardless of which cosurfactant is used, the surfactant-rich and water-poor region has a very low degree of structure: the surfactant exists in the form of hydrated ion-pairs or in smaller aggregates (19,23). The most interesting composition regime is for many systems intermediate water contents where it is possible to follow the transition between the different preferred structures.

The measured self-diffusion coefficients (Figs. 3 – 4) reveal a significant difference in behavior between methyl oleate [or even more so with a hydrocarbon such

as toluene or dodecane, where extensive literature data are available (15, 24)] and a triglyceride. The transition between a bicontinuous and oilcontinuous structure known to occur for microemulsions containing water/potassium oleate/ pentanol/hydrocarbon (15, 24) occurs also to some extent with methyl oleate. However, the water self-diffusion decreases almost an order of magnitude when adding 40 wt% toluene or dodecane to a sample with similar composition. With methyl oleate the self-diffusion is reduced with a factor of three. With MCT the picture is completely different: the system remains bicontinuous up to the phase-separation.

A possible reason for the detected differences is the varying molecular size of the lipophilic molecules. We suggest that the reasons for the difficulty in solubilizing larger molecules can be explained in the following way. It is known that penetration of hydrocarbons into the palisade layer of surfactant/co-surfactant can play a decisive role for the phase diagram and structure in certain cases. Such effects are very marked in the system water/hydrocarbon/didodecyldimethylammonium bromide, where Ninham and co-workers have suggested that only small hydrocarbon molecules, e.g. hexane, can penetrate into the surfactant layer, something which facilitates the transition from a bicontinuous to an oilcontinuous system with increasing water contents; this transition does not occur with, e.g., tetradecane (25). In these systems, the effects are very sharp; but also for more complex ionic microemulsions containing an alcohol cosurfactant, similar effects can

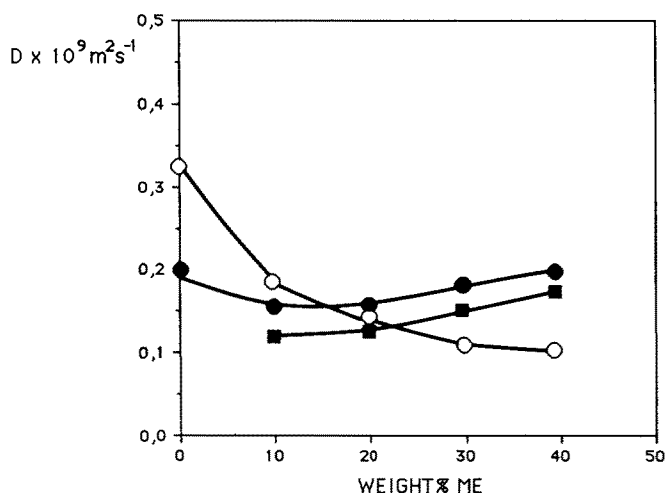


Fig. 3. Self-diffusion coefficients for the different components in the quaternary system water/sodium oleate:pentanol/ME, at 25°C, a fixed weight ratio water:oleate:pentanol 50:17:33 and varying amounts of added ME (in wt%) — (O) water, (●) pentanol, and (■) ME.

occur. There is a variation in structure when going from hexane to hexadecane in microemulsions also containing water/sodium dodecyl sulphate/pentanol, and this difference is suggested to be due to the difference of penetration into the palisade layer (26). Larger hydrocarbon molecules fail to penetrate which leads to a larger concentration of alcohol in the palisade layer, in particular in inverse micellar systems (26). It seems reasonable to suggest that these effects are even more marked with larger and bulkier molecules such as PNO. The failure to penetrate into the alkyl chains of the surfactant and cosurfactant in the palisade layer makes inverse micellar systems less energetically favored. The molecular size of the oil component forces the system to remain bicontinuous and finally, above a certain oil concentration, it becomes unstable and phase-separate. The region of the solution phase that disappears is (in particular for the PNO system) the region where the gradual transition to reverse micelles occurs. The remaining region of the solution phase is, to a large extent, concentration domains where ion-pairs or similar, small aggregates are anticipated to occur (23).

While our explanation is intuitively reasonable, a more consistent theoretical explanation is presently not accessible. The *a priori* modelling of microemulsions containing medium-chained alcohols is still not conclusive, and continuum models normally employed for these systems do not include any size effects for the molecules in the lipophilic region. On the other hand, in similar systems of more well-defined structure, the mixing of components between the palisade layer and the continuous phase gives a very important free-energy contribution of entropic origin to reverse micellar systems. This was found by Jönsson and Wennerström who, using a minimum number of parameters, succeeded in a semi-quantitative calculation of the phase diagram for the system water/octanol/potassium decanoate (27). However, such an *ansatz* is not possible for the present systems where no suitable model of the

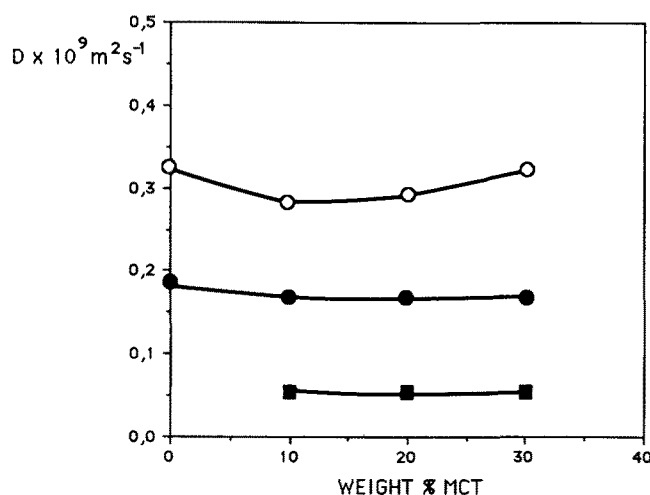


Fig. 4. Self-diffusion coefficients for the different components in the quaternary system water/sodium oleate:pentanol/MCT, at 25°C, a fixed weight ratio water:oleate:pentanol 50:17:33 and varying amounts of added MCT (in wt%) — (O) water, (●) pentanol, (■) MCT.

bicontinuous structure exists, and where the exact composition of the palisade layer and the extent of the penetration of the oil cannot be predicted.

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