Increasing the Stability of Vegetable Oil Solutions with the Aid of Monoglycerides and a Cosurfactant[1]

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ABSTRACT

The conditions for an enhanced mutual miscibility of water and Canola oil, with the aid of one or two surface active components, were investigated at 25 C. First, the ability of short chain alcohols to increase the mutual solubility was charted. Such systems frequently are denoted detergentless microemulsions. Second, normal microemulsion systems were formed by using surface active monoglycerides of foodstuff grade. Third, the synergism was monitored when both the surfactant and the cosurfactant (the alcohols) were mixed either with water or oil. Finally, the combined effect was determined when all four components were mixed together into a microemulsion system.

It is shown that the extension of the ternary solution phase is dependent primarily on the surfactant used. Some improvement of the mutual solubility of water and oil, however, also was produced by the alcohols. The solubilization capacity of water in the quaternary systems is easily understood when the solution phase is compared with the microemulsion phases of the ternary systems included. Although no dramatic composition dependency was found, an enhanced solubility of water was observed for the oil rich microemulsions of roughly equal weight fractions of the surfactant components.

INTRODUCTION

Vegetable oils have gained considerable attention recently due to the renewability of the resource and the applicability of these oils in a number of new ways such as engine fuels (1), lubrication oils and carrier liquids (2). It is of special interest to investigate how the limited stability of vegetable oil solutions can be improved by the use of suitable additives.

The goal set is easier to reach if the vegetable oil is chosen as one component of a microemulsion system, the other components being water and one or two surfactant components. Such systems are known to dissolve (solubilize) components which otherwise would be insoluble in the solvent. A great deal is known about the behavior of microemulsion systems both from the theoretical (3-8) and experimental points of view (9-10). Based on this general knowledge it should be possible to foresee which properties of the surfactant component(s) are to be changed in order to achieve the effect wanted.

The microemulsions may be divided into two main groups, detergentless microemulsions and normal microemulsions. The former group is characterized by the absence of any "real" surfactant component. The enhanced solubility of, for example, nonpolar components (typically an oil) is attained by using a short chain alcohol which creates a mixed solvent system with water. The mixed solvent then has an improved ability to dissolve oil in comparison with pure water. One important feature of detergentless microemulsions is the frequent presence of three-phase triangles in these systems. The alcohol rich microemulsion is hence simultaneously in equilibrium with both a water-continuous and an oil-continuous solution. In order to achieve this ability the surface tension at the interfaces has to be very low (9-13). Moreover, the alcohol-rich microemulsion represents the transition composition between the oil and water phases. In a series of papers, the solution behavior of such systems as a function of temperature and salinity has been correlated with the presence of critical phenomena in the binary systems included (6-8) and the special features of typical surfactant systems (9,10).

The increased solubility of water and oil insoluble substances in normal microemulsions is obtained as a result of the association behavior of the surfactant component(s). Due to this special behavior, the phase equilibria found in such systems usually are complex, including liquid crystalline and crystalline phases (17-19). The solubilization power of microemulsions may be organized conveniently with the use of the Hydrophilic-Lipophilic Balance (HLB) value of the surfactant (20). Typically the surfactant action is fortified by the introduction of a cosurfactant (e.g. an alcohol), although the reverse also may be true (24). The microemulsions reported consequently include both three- and four-component systems (19,21-22).

In the present article, we describe the solubility areas found for ternary and quaternary microemulsions, stabilized by five alcohols and/or three monoglycerides of foodstuff grade, respectively.

EXPERIMENTAL

Chemicals

The isopropanol (99,5%), the tertiary butanol (99%) and the 1-hexanol (98-99%) all were supplied by EGA-Chemie, Steinheim, W. Germany. The sorbitol (98-100,5%) of food grade was supplied by Sokerikemia Oy, Kotka, Finland/Xyrofin Ltd., Switzerland. The ethoxyethanol/Oxitol (100%) and the butoxyethanol/Butyl Oxitol (100%) were supplied by Suomen Plastkem Oy, Vantaa, Finland. The Dimodan PV is a distilled monoglyceride made from edible, refined, hydrogenated soybean oil. The monoester content was min 90%, and the fatty acid composition was 10-15% palmitic acid and 85-90% stearic acid. The iodine value was max two and the saponification value 150-160. Dimodan LS is a distilled monoglyceride made from edible, refined sunflower oil. The monoester content was min 90%. The iodine value was ca. 105 and the saponification value was 150-165. The Cetodan 90-40 is an acetic acid ester of monoglycerides made from edible, refined lard. The main fatty acids were palmitic, stearic and oleic. The degree of acetylation was 0.9, the iodine value was ca. 35 and the saponification value ca. 375. The monoglyceride content was in all cases ca. 1%. The samples were supplied by Grindsted Products, Brabrand, Denmark.

The Canola (rapeseed) oil (*Brassica campestris*) has a fatty acid composition of 3-5% palmitic acid, 1% stearic acid, 58% oleic acid, 22% linolenic acid, 11% linoleic acid, 1-5% eicosenoic acid and 0.9% erucic acid. The iodine value was 120 and the saponification value about 1%. The oil was supplied by Öljynpuristamo Oy, Helsinki, Finland. The water used was distilled.

Phase Diagrams

In the ternary systems the boundary limits for the thermodynamically stable solution phase were determined by titration with one component to solutions with different weight

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ratios of the two others. The approximately 30 solutions so obtained were titrated until the lines representing the resulting samples intersected. The samples were stored in screw cap vials with Mininert valves (Supelco Inc., Bellefonte, Pennsylvania) for multiple syringe injection. After each addition, samples were weighed and stirred. The samples, including sorbitol, Dimodan PV or Dimodan LS were first heated in an ultrasonic bath (Ultra Sonic Finland Ltd., Lahti, Finland) before cooling to 25. Finally all the samples were allowed to equilibrate for at least three hr before the phase equilibria were observed visually at 25 C. The visual inspection method for phase boundary estimations should be satisfactory in this study because only solution phases were considered (the equilibrium is established rapidly) (23). Some of the boundary solutions in the systems where liquid crystalline phases separated were checked between crossed nicols. Due to extensive foaming the phase boundaries in multi-phase areas of systems including Cetodan 90-40 were difficult to estimate with great precision.

In the quaternary systems the liquid phase boundaries were determined first by mixing ca. 40 samples per system, evenly distributed within the Cetodan 90-40-Canola oil-alcohol base triangle. Then water was added to solutions until phase separation occurred.

RESULTS

Detergentless Microemulsions

As discussed above, the alcohol-rich microemulsion of a three phase triangle represents the limit between oil-continuous and water-continuous solutions. When discussing the mixed solvent properties of alcohol-water or alcohol-oil solutions it seems straightforward to use the microemulsion as a reference point. Consequently, the saturation compositions of the mixed solvent with the solute liquid, i.e. the phase border of the microemulsion, are plotted only to pass this transition point (Fig. 1).

The solubility areas formed with the aid of isopropanol (IPA) and tertiary butanol (TBA) are presented in Figure 2. As expected, IPA displays a complete miscibility with water but is too polar to mix fully with the oil. Also, the microemulsion area is very narrow in the IPA system. TBA is much more effective in dissolving both oil and water, resulting in a continuous and relatively broad solution range. Due to its increasingly hydrophobic character, the transition composition is shifted to a higher oil concentration. The solubility limits are quantified in the left-hand diagrams. In the top diagram the mass of oil solubilized by the mixed alcohol-water solvent is plotted against the amount of alcohol, both given per kilogram of water. The contribution of the alcohol is accentuated in the lowest diagram where the mass of oil introduced per mole of alcohol is plotted against the amount of alcohol per kilogram of water. IPA initially is able to introduce only about 1.3 g of oil into the mixed water-rich solvent, whereas TBA "carries" about eight g of oil. The solvent action of tertiary butanol is further fortified prior to the transition point shown as a peak in the diagram.

The alcohol-oil mixed solvent action on water was investigated using hexanol (Fig. 3). As expected, we found only a slight miscibility of water in the hexanol-oil solutions, and almost no solubility of hexanol in water. Expressing the solubilization capacity in a fashion corresponding to the above, we note that hexanol can bind about four g of water per mole of hexanol added, while TBA is nearly twice as effective (6-7 g of water per mole of TBA). In both cases the hydration complex formed remains up to the transition point.

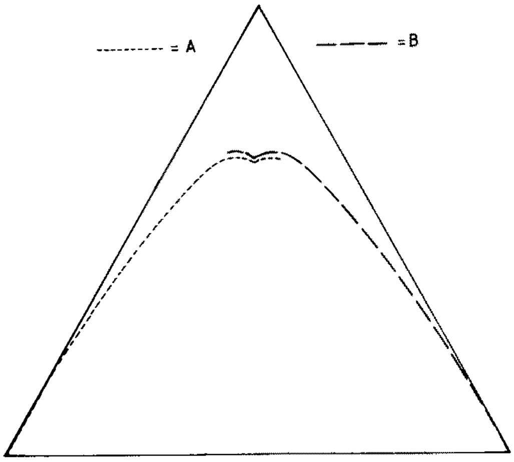

FIG. 1. The solubilization capacity of the microemulsions is quantified starting from the water corner (A) or from the oil corner (B) to overlap the phase inversion composition.

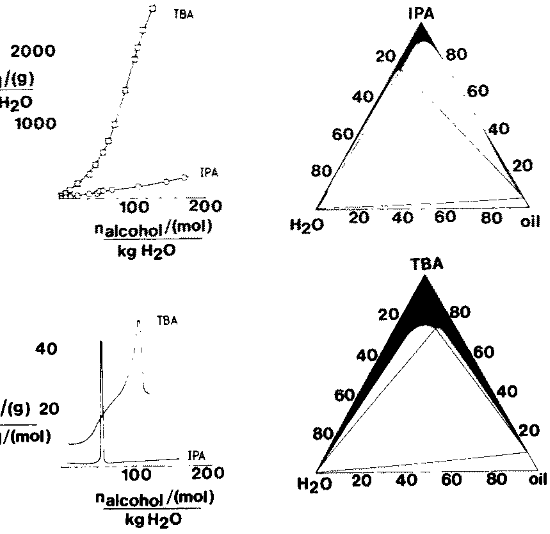

FIG. 2. The isotropic microemulsion areas (black) of the water-Canola oil-isopropanol and water-Canola oil-tertiary butanol systems at 298 K. The relative amount of each component is given in weight per cent along each axis. Each corner represents the pure (100%) component. The diagrams to the left quantify the solubilization capacity of oil dissolvable in water-alcohol mixtures (above) and the increment of oil dissolved per mole of alcohol (below).

Alcoxyethanols are known for their good solvent properties, which motivated the inclusion of them in the experimental program (Fig. 4). It was found that both ethoxy- and butoxyethanol form narrower solution regions than TBA. Initially ethoxyethanol (EE) is about as effective at dissolving oil into the aqueous solutions as IPA (1-2 g oil/mole EE), while butoxyethanol (BE) dissolves more than twice that amount (4-5 g oil/mole BE). Both alcoxyethanols reach a region of enhanced solubilization capacity prior to the phase transition point, the region of EE being wider. The hydration of EE in oil is low (2-3 g water/mole EE), but the advantage of the double functionality is revealed clearly by the high capacity of the BE-oil solutions to "carry" water (11-13 g water/mole BE). Moreover, the solubility of water further increases when the inversion point is approached.

Sorbitol was chosen as one of the alcohol components in order to obtain information about the role of steric contributions on the solubility. Although sorbitol is almost com-

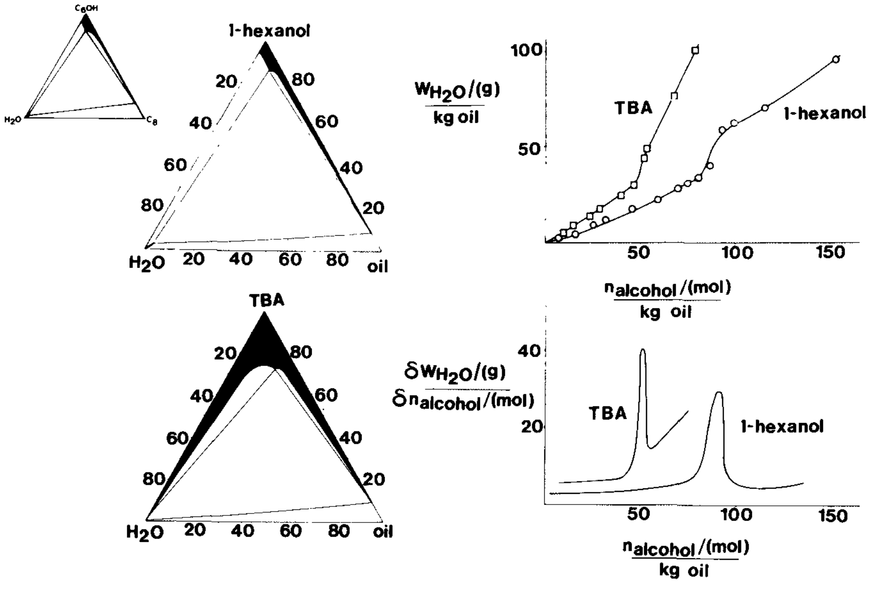

FIG. 3. The isotropic microemulsion area (black) of the water-Canola oil-hexanol, water-Canola oil-tertiary butanol and water-octane-hexanol (insertion with permission of I. Vikholm) systems at 298 K. The diagrams to the right quantify the solubilization capacity of water dissolvable in alcohol-oil mixtures (above) and the increment of water dissolved per mole of alcohol (below).

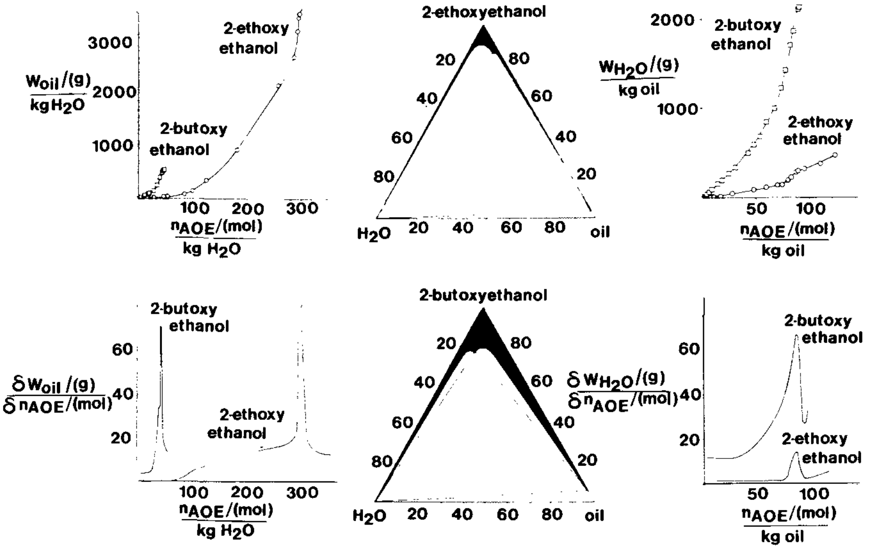

FIG. 4. The isotropic microemulsion area (black) of water-Canola oil-ethoxyethanol and water-Canola oil-butoxyethanol systems at 298 K. The diagrams correspond to those in Figs. 2 and 3.

pletely soluble in water, only a negligible amount (max 2 weight %) of oil could be dissolved in these solutions; sorbitol could not improve the solubility of water in the hexanol-oil solutions, either. When different sorbitol-water mixtures were added to four mixtures of hexanol and oil, almost no shifts on the phase extension, compared with the ternary hexanol system (Fig. 3), could be observed. A considerably better result was obtained when 90, 50 and 20% by weight mixtures of hexanol in oil were titrated with 75/25 and 25/75 % by weight mixtures of TBA/water, respectively (Fig. 5). The solution phase grew almost threefold with the aid of TBA. However, this is expected solely as a result of the larger solution stability produced by TBA (Figs. 2 and 3).

Normal Microemulsions

The phase equilibria of systems including real surfactant components are in general characterized by a large complexity. Because our interest is focused on the solution phases, only the composition ranges for microemulsions are given for these systems. First the cosurfactant action of IPA and TBA on Cetodan 90-40-water mixtures was studied (Fig. 6). There is an almost nonexistent ability of IPA and TBA to introduce Cetodan 90-40 into the aqueous IPA and TBA solutions (ca. one g Cetodan 90-40/mole alcohol), respectively. At about 18 mole IPA or about five mole TBA per kg water there is, however, a sudden increase in the Cetodan solubility. The ability to solubilize water into the

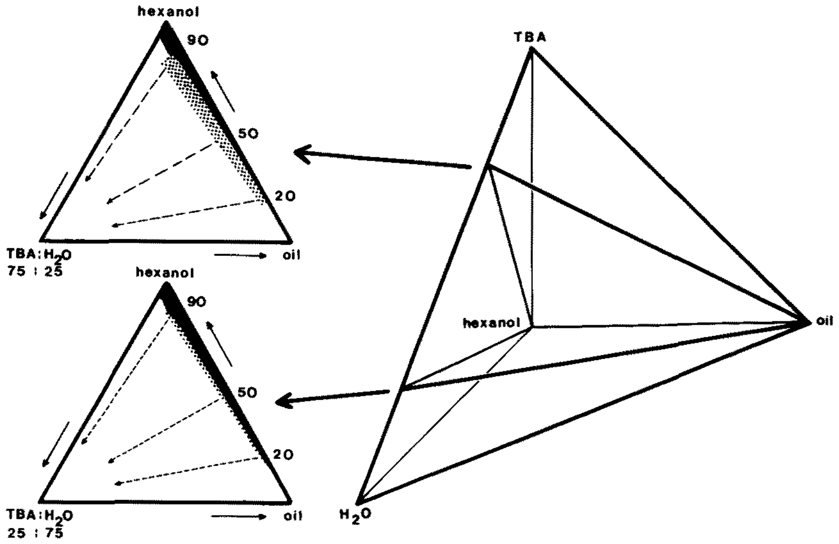

FIG. 5. The isotropic microemulsion area (shaded) obtained when 20, 50 and 90 weight % mixtures of hexanol in oil are titrated with 25 and 75 weight % mixtures of water in tertiary butanol at 298 K. (The black areas describe the system hexanol-Canola oil-water.)

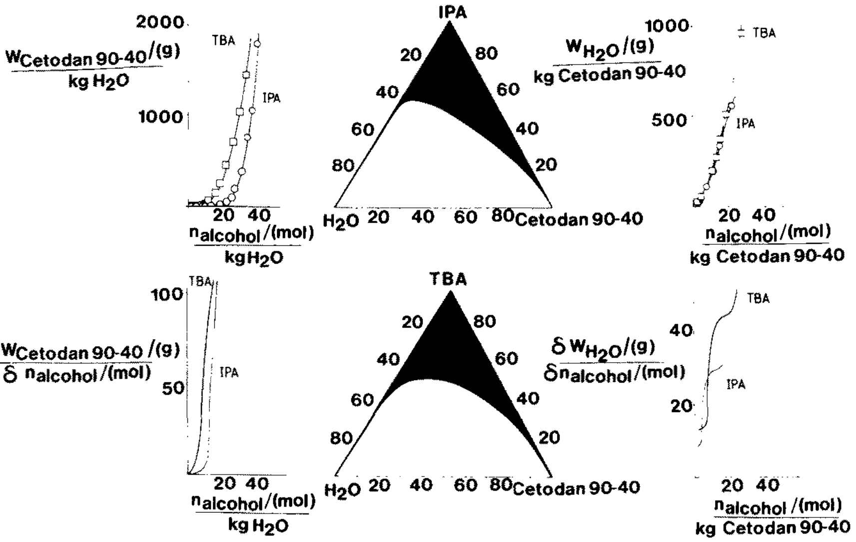

FIG. 6. The isotropic microemulsion areas (black) of the water-Cetodan 90-40-isopropanol and water-Cetodan 90-40-tertiary butanol systems at 298 K. Diagrams correspond to those in Figs. 2 and 3.

Cetodan-oil solutions (nine g and 13-14 g of water/mole of IPA and TBA, respectively) is good over the entire composition range. Note that the solubilization capacity is increased in two steps as the cosurfactant concentration is increased.

The next step was to investigate the influence of the alcohols on the miscibility of the oil with three monoglycerides of decreasing polarity. The solution phase areas of Dimodan PV (a good W/O emulsifier) are narrow and extend only to low Dimodan PV fractions (Fig. 7). The top right-hand diagram shows that a plateau value of Dimodan PV dissolvable in the oil is reached at comparatively high alcohol concentrations. TBA is about twice as effective as IPA at dissolving Dimodan PV. The plateau appears, of course, as a zero derivative, and the lower diagram is thence of less informative value.

Dimodan LS should, on the basis of its increased hydrophobicity, have a larger oil solubility. As expected, the solution phase area is very broad, covering the major part of the phase diagram (Fig. 8). The consequence is that the fraction of Dimodan LS brought into solution per mole of alcohol is up to twice as large as those found in the previous system.

The hydrophobicity is further increased when shifting to Cetodan 90-40 and a total miscibility of the components is achieved in the case of TBA (Fig. 10). When IPA is used as a cosurfactant, the solubility gap found at the IPA-Canola oil axis is rapidly closed for the ternary solutions (Fig. 9).

The final goal is to see how the solution properties found above are developed when four of the components are mixed together. In Figure 9 all the separate three-

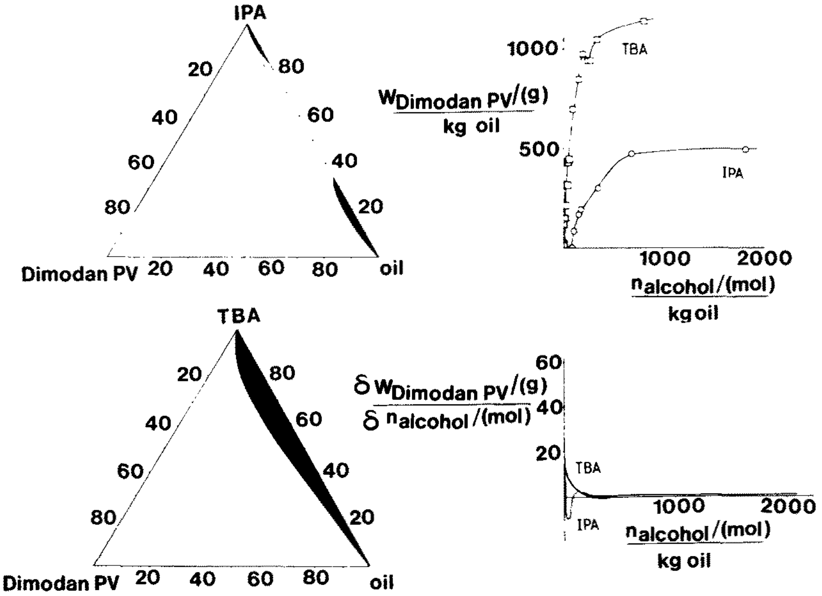

FIG. 7. The isotropic microemulsion areas (black) of the Dimodan PV-Canola oil-isopropanol and Dimodan PV-Canola oil-tertiary butanol systems at 298 K. The diagrams correspond to those in Figs. 2 and 3.

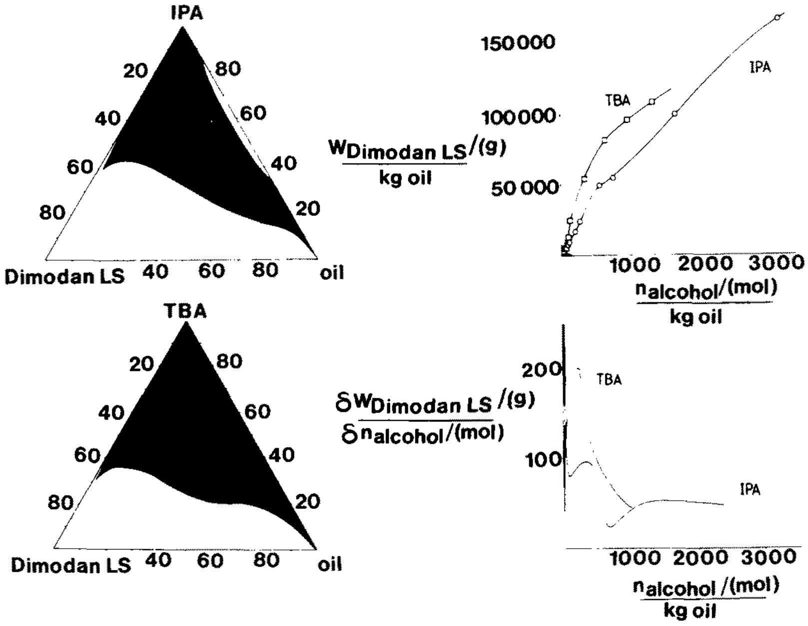

FIG. 8. The isotropic microemulsion areas (black) of the Dimodan LS-Canola oil-isopropanol and Dimodan LS-Canola oil-tertiary butanol systems at 298 K. The diagrams correspond to those in Figs. 2 and 3.

component systems considered are illustrated in the lower lefthand corner. Note the small water solubility found for the Cetodan 90-40 oil mixtures (max 1.2 weight %). If we fold the sides up we obtain the quaternary Canola oil-Cetodan 90-40-IPA-water system shown in the lefthand uppermost corner. This tetrahedron is then sliced in cuts defined by constant weight ratios of oil to Cetodan 90-40 (the top righthand figure). For the solutions thus defined we determined the maximum amount of water soluble in the microemulsion. The solubilization capacity is given as a function of the decreasing IPA weight fraction for each cut at the bottom righthand diagram. The front cut represents the ternary system oil-water-IPA, the farthest cut the ternary system Cetodan 90-40-water-IPA and the front edge the solubility of water in the Cetodan 90-40-oil mixtures. The bottom of the prism represents the ternary system oil-Cetodan 90-40-IPA, the miscibility gap shown in the front. Note the enhanced solubility of water developed for the quaternary solutions (oil:Cetodan cuts of 2:8 to 6:4) in the concentration range W(IPA)=0.3-0.6.

The exchange of IPA for TBA makes Cetodan 90-40, oil and TBA fully miscible in each other and improves the miscibility of oil and water in the oil-water-TBA system. The surface representing the solubilization capacity of water

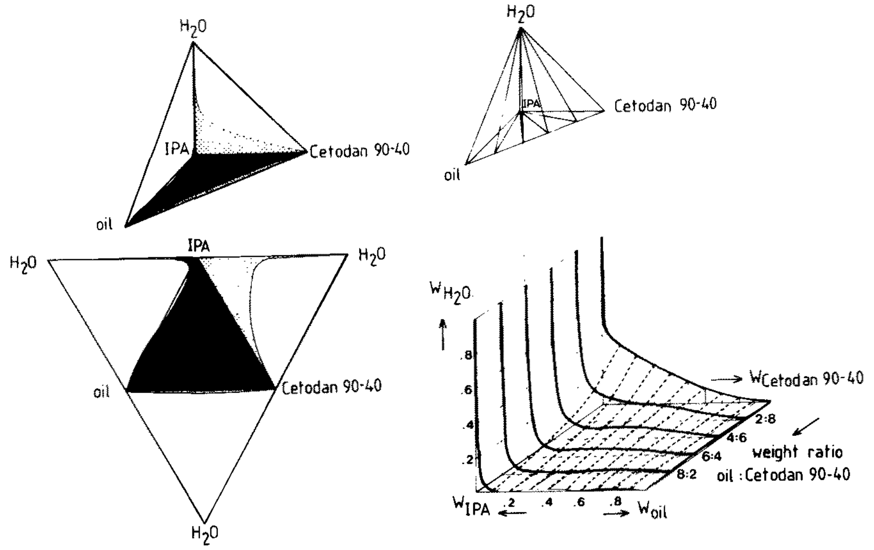

FIG. 9. The isotropic microemulsion areas (darkened) at 298 K in ternary systems including water, Canola oil, Cetodan 90-40 and isopropanol, respectively. To the left the systems are displayed in one plane (below) and folded to a tetrahedron (above). To the right the maximum solubility of water in microemulsions, defined by constant weight ratios of Canola oil:Cetodan 90-40, is given as a function of the weight fraction of alcohol (below). The different pseudo-ternary systems are illustrated by planes through the tetrahedron (above).

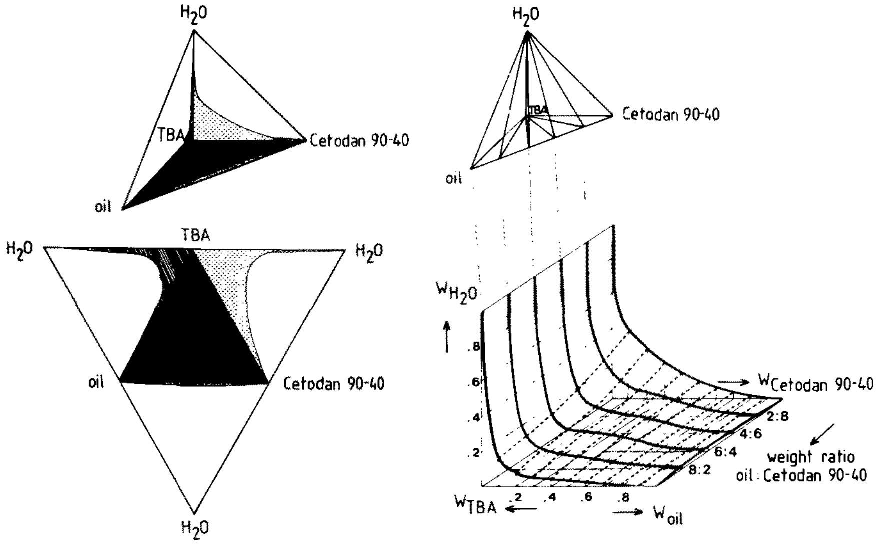

FIG. 10. The isotropic microemulsion area (darkened) at 298 K in ternary and quaternary systems including water, Canola oil, Cetodan 90-40 and tertiary butanol, respectively. The extension of the quaternary solution is quantified as in Fig. 9.

is thence at a higher level for all compositions. The hump reflecting the increased water solubility is somewhat more pronounced but appears in the same concentration range.

DISCUSSION

The results show that the most advantageous conditions for a wide detergentless microemulsion range were obtained using tertiary butanol. The characterizing feature for this system is the appearance of a three-phase triangle. Moreover, the TBA-rich microemulsion, in equilibrium with the saturated water and oil phases, has a composition of about equal fractions of the latter components. It is known from previous investigations of similar systems that the composition of the microemulsion rotates clockwise with the temperature and the hydrophobicity of the surfactant component (5-10). At low temperatures the microemulsion gets richer in water. The microemulsion finally merges with the saturated aqueous solution. At this point the three-phase triangle, of course, disappears. At high temperatures the microemulsion merges with the saturated oil phase. In both cases the enrichment of the microemulsion with either water or oil causes the solubility area to shrink.

Using the additivity principle (20) we may estimate the theoretical Hydrophilic-Lipophilic-Balance (HLB) values of 7.5, 7.0 and 6.0 isopropanol, tertiary butanol and hexanol, respectively. The figures are all in line with the rotation of the microemulsion from the water- to the oil-rich side with the increasing hydrophobicity. Also, the HLB values of nearby seven are accordant with the presence of the three-phase triangle. The exchange of Canola oil for a less polar oil, n-octane (insertion in Fig. 3), has on the other hand a negligible effect on the phase behavior of the hexanol system.

Applying the additivity principle we obtain the HLB values of 8.3 and 7.8 for ethoxy- and butoxyethanol, respectively. This would imply a microemulsion rich in water. Surprisingly, the more polar EE is richer in oil than BE. The latter system resembles the TBA system although the microemulsion in the former (EE-) system is somewhat richer in water. The slight deviations from the sequence predicted indicate that the introduction of the polar functionality within the chain makes the contributions of specific interactions significant to the solubility behavior of detergentless microemulsions. These conclusions are supported by the experience obtained with sorbitol as cosurfactant. No significant synergism was observed either when the water solubility character of hexanol was improved by adding TBA to the mixture.

The unique ability of cosurfactants to improve the solubilization capacity of surfactants is clearly revealed when comparing the detergentless and real microemulsion systems. Although the surfactant did not produce any important miscibility of oil and water, the introduction of an alcohol created the conditions for a mutual miscibility of all four components.

The surfactant systems were investigated by mixing the components first in water and then in oil. Because a large amount of alcohol is required to bring the hydrophobic surfactant into aqueous solution (Fig. 6, lefthand diagrams), it is obvious that the interaction between water and alcohol determines the microemulsion behavior. The discrete steps found for the "hydration capacities" (Fig. 6, righthand diagrams) in the presence of both alcohols indicate that some structural rearrangements occur as a function of the surfactant content. Thus the interaction between the surfactant components also influences the solution stability.

When the monoglycerides and the alcohols were mixed in oil the solution behavior was determined by the hydrophobicity of the surfactant. In the experiments the HLB value of the monoglycerides varied from 4.3 (Dimodan PV), over about 3 (Dimodan LS) to 1.8 (Cetodan 90-40). The exchange of the surfactant produced the effects that were expected. The Dimodan PV system had only small microemulsion regions which is typical for good W/O-emulsion systems (Fig. 7). Cetodan 90-40, with its very low HLB value, on the other hand, was fully miscible with both the alcohol and Canola oil (Figs. 9 and 10).

The miscibility of water in the quaternary solutions may be considered a continuation of the solubilization capacities found in the ternary systems. In general, the nature of the monoglyceride is of prime importance for the solution stability. It is also evident that the balanced solubility of the alcohol in water and in oil influences the solution behavior. The hump of improved water solubility found at the oil-rich side of the "quaternary cuts" indicates, however, that the nature of oil also influences the water solubility in the microemulsions. No such divergence in the solubility of oil can be observed in the aqueous quaternary microemulsions (vertical back side of the diagrams).

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REFERENCES

1. Strayer, R.C., J.A. Blake and W.K. Craig, JAOCS 60:1587 (1983).
2. Industry News, JAOCS 59:926A (1982).
3. Mitchell, D.J., and B.W. Ninham, J. Chem. Soc. Faraday Trans. II 77:601 (1981).
4. Ruckenstein, E., J. Dispersion Sci. Technol. 2:1 (1981).
5. Barton, A.F.M., "Handbook of Solubility Parameters and Other Cohesion Parameters," CRC Press Inc., Boca Raton, Florida, 1983.
6. Herrman, C.-U., G. Klar and M. Kahlweit, J. Colloid Interface Sci. 82:6 (1981).
7. Kahlweit, M., Ibid. 90:197 (1982).
8. Kahlweit, M., E. Lessner and R. Strey, J. Phys. Chem. 87:5032 (1983) and 88:1937 (1984).
9. Robbins, M.L., in Micellization, Solubilization and Microemulsions (Mittal, K.L., ed.) Vol. 2, p. 713, Plenum Press, New York, 1977.
10. Rosenholm, J.B., Kemia-Kemi 10:611 (1981).
11. Taber, J.J., Pure and Appl. Chem. 52:1323 (1980).
12. Drecher, K.D., and S.C. Jones in Solution Chemistry of Surfactants (Mittal, K.L., ed.) Vol. 2, p. 627, Plenum Press, New York, 1979.
13. Morgan, K.D., R.S. Schechter and W.H. Wade, Ibid., Vol. 2, p. 749.
14. Shinoda, K., J. Colloid Interface Sci. 24:4 (1967).
15. Kunieda, H., Bull. Chem. Soc. Jpn. 56:625 (1982).
16. Kunieda, H., and S. Friberg, Ibid. 54:1010 (1980).
17. Winsor, P.A., "Solvent Properties of Amphiphilic Compounds," Butterworths Sci. Publ., London, 1954.
18. Ekwall, P., in Advances in Liquid Crystals, (Brown, G.H., ed.) Vol. 1, p. 1, Academic Press, New York, 1975.
19. Shinoda, K., and S. Friberg, Adv. Colloid Interface Sci. 4:281 (1975).
20. Becher, P., in Surfactants in Solution (Mittal, K.L., and B. Lindman, eds.) Vol. 3, p. 1925, Plenum Press, New York, 1984.
21. Danielsson, I., M.-R. Hakala and M. Jorpes-Friman in Solution Chemistry of Surfactants (Mittal, K.L., ed.) Vol. 2, p. 659, Plenum Press, New York, 1979.
22. Herrmann, C.-U., U. Wurz and M. Kahlweit, Ibid., p. 879.
23. Friberg, S., and J.-H. Fang, JAOCS 61:801 (1984).
24. Desnoyers, J.E., D. Hetu and G. Perron, J. Solution Chem. 12:427 (1983).

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