Model Microemulsions Containing Vegetable Oils Part 1: Nonionic Surfactant Systems

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Nonionic microemulsions containing triglycerides and fatty acid esters as lipophilic components have been studied. The phase inversion temperature (PIT) of the systems was determined by a conductometric method. Partial phase diagrams were constructed in the phase inversion temperature range. Water solubilization capacity of the nonionic surfactant systems studied was dependent on surfactant and oil types in analogy to ordinary hydrocarbon systems. The PIT:s increased with increased molecular weight for both esters and triglycerides.

Microemulsions, apart from being fundamentally interesting, also have a significant technological potential. These low-viscous, isotropic systems containing oil and water and stabilized by surfactants are thermodynamically stable (1). They have proven useful as model systems for enhanced oil recovery (2), for replacing solvents with water in cleaning processes (3–4), for preparing microsized particles (3–6) and for providing a vehicle for transporting reactive components into a porous matrix (7).

Microemulsion systems containing low molecular weight aliphatic or aromatic hydrocarbons have been extensively studied and there exists a large amount of data on their compositions, properties and structure. There is, however, a growing interest in systems where the hydrocarbon oil is replaced by an oil derived from natural sources, e.g., triglycerides or fatty acid esters. Microemulsions containing vegetable oils or fatty acid esters could be used, for example, in cosmetics, lubricants, food products, ect., where there is a demand for environmentally more acceptable formulations.

A few systems based on triglycerides have been reported in the literature. The phase behavior of a system containing a triglyceride, a monoglyceride and water has been extensively studied by Larsson *et al.* (8–11). Diesel fuel alternatives containing alcohols and triglycerides have been reported by Schwab and Pryde (12–13) and by Vesala *et al.* (14). However, a direct and fundamentally oriented study directed towards the clarification of any possible differences between vegetable oil microemulsions and ordinary hydrocarbon-based microemulsions has, to our knowledge, not been performed.

This and the following study have been directed toward studying the behavior of systems containing a vegetable oil or a fatty acid ester, an anionic or nonionic surfactant and water. The model systems were chosen in order to highlight the differences and similarities compared to more familiar hydrocarbon formulations. Differences in phase behavior and structure have been studied by different methods and correlated to the composition of the oils and surfactants. It should be emphasized that the purpose has not been to choose the components in order to optimize a possible functionality of a formulation, but to facilitate a comparison with our present knowledge of more well-characterized microemulsion systems.

MATERIALS AND METHODS

The nonionic surfactants in the study are commercially available products and used as received. Table 1 gives a summary of the characteristics of these products.

The oils were chosen in order to give a range of molecular structures from simple esters to long-chain fatty acid triglycerides. The characteristics of the oils are presented in Table 2.

PIT measurements. The phase inversion temperature (PIT) was measured by determining the conductivity of an emulsion as a function of temperature. In nonionic systems there is a dramatic decrease in conductivity as the emulsions change from water continuous to oil continuous. The temperature range where this happens is taken as the PIT range.

For the PIT measurements a Philips conductivity meter PW 9527 was used.

The PIT measurements were conducted in systems consisting of 5% (w/w) surfactant, 47.5% oil and 47.5% of KCl-solution (0.1%; conductivity approx. 1400 μS/cm). Emulsions were prepared by pouring the mixture of surfactant and oil into the water while stirring vigorously. The temperature of the water was adjusted before the addition of oil/surfactant to the vicinity of the desired starting temperature.

The reported PIT:s are averaged from two runs where the PIT is determined from both heating and cooling cycles.

In order to have reproducible and reversible phase inversions, the rate of heating or cooling must be kept low, preferably below 1K/minute.

Due to experimental difficulties, the temperature range is limited to the interval 0–80°C. Above 80°C the reliability of the conductivity electrode decreases and the water evaporation becomes appreciable.

Phase diagrams. Partial phase diagrams were constructed by titrating oil/surfactant mixtures with water until turbidity. All titrations were conducted with careful temperature control. Liquid crystalline phases were identified with a Reichert polarizing microscope. The extension of liquid crystalline phases was confirmed with NMR as described (15).

RESULTS AND DISCUSSIONS

PIT measurements. Results from the PIT measurements in systems containing MCT and different surfactants are shown in Figures 1a (ethoxylated fatty alcohols) and 1b (ethoxylated nonylphenols). Corresponding data for dodecane systems (16) are shown for comparison. There is a similar increase in PIT with increased surfactant HLB in both systems. For a fixed

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TABLE 1

Surfactants Used in the Experiments

Surfactant	Manufacturer	Hydrophobe	Number of EO units	HLB	PIT (MCT) °C
Dehydol LS 2	Henkel	Lauryl alcohol	2	6.0	19
Brij 30	ICI	Lauryl alcohol	4	9.7	54
Brij 35	ICI	Lauryl alcohol	23	16.9	⩾80
Brij 92	ICI	Oleyl alcohol	2	4.9	13
Brij 98	ICI	Oleyl alcohol	20	15.3	⩾80
Lutensol A03	BASF	Oxo alcohol	3	8.0	30
Lutensol A010	BASF	Oxo alcohol	10	13.5	⩾80
Antarox C0430	GAF	Nonylphenol	4	8.8	30
Berol 02	Berol	Nonylphenol	6	10.9	50
Berol 09	Berol	Nonylphenol	10	13.3	⩾80

TABLE 2

Oils Used in the Experiments

ME:	Methylester of mixed fatty acids, predominantly C18:1 (58%) and C18:2 (22%), manufactured by Oleofina.
IOO:	2-Ethylhexanol ester of mixed fatty acids, predominantly C18:1, manufactured by Unichema.
PNO:	Peanut oil, triglyceride of mixed fatty acids, predominantly C18:1 (42%) and C18:2 (37%), manufactured by Karlshamns AB, Sweden.
MCT:	Medium-chain triglyceride, containing C8 (48%) and C10 (45%) fatty acids, manufactured by Dynamit-Nobel.

surfactant, the PIT:s for MCT systems are 10–30°C higher.

The PIT has also been measured for a fixed surfactant system with various oil components. Berol 02 (hexaethyleneglycol nonylphenol ether) gives PIT:s of 75°C (PNO), 50°C (MCT), 51°C (IOO) and 25°C (ME).

Phase diagrams. Partial phase diagrams for ethoxylated nonylphenols and the four oils are shown in Figures 2–4. (PNO, MCT, ME, IOO). The phase diagrams of the Berol 02 systems are characterized by the presence of an L_2-phase and a lamellar liquid crystalline phase (D). With ME as a lipophilic component the phase behavior is similar to that of systems containing ordinary hydrocarbons. The L_2-phase is stable at reasonably low surfactant concentrations. This is however not the case with the other oils, it is particularly difficult to solubilize water in the PNO systems. Only at temperatures above the melting point of the D-phase (>60°C) is it possible to solubilize larger amounts of water in that system (Fig. 2).

Berol 09, a more hydrophilic surfactant, gives the possibility to form a micellar solution phase (L_1). With ME as the oil component, the system behaves again like an ordinary hydrocarbon system. The L_1-phase is transformed into a surfactant phase (Fig. 3) at higher temperatures. At 50–55°C a minimum amount of surfactant (20% w/w) stabilizes a microemulsion containing equal parts of oil and water. When ME is replaced by MCT, the extent of the L_1-phase decreases, and the free-lying surfactant phase disappears (Fig. 4). An increase in water solubilization is observed above 60°C where the liquid crystalline phase (not shown in Fig. 4) starts to melt, but the system is optimal around

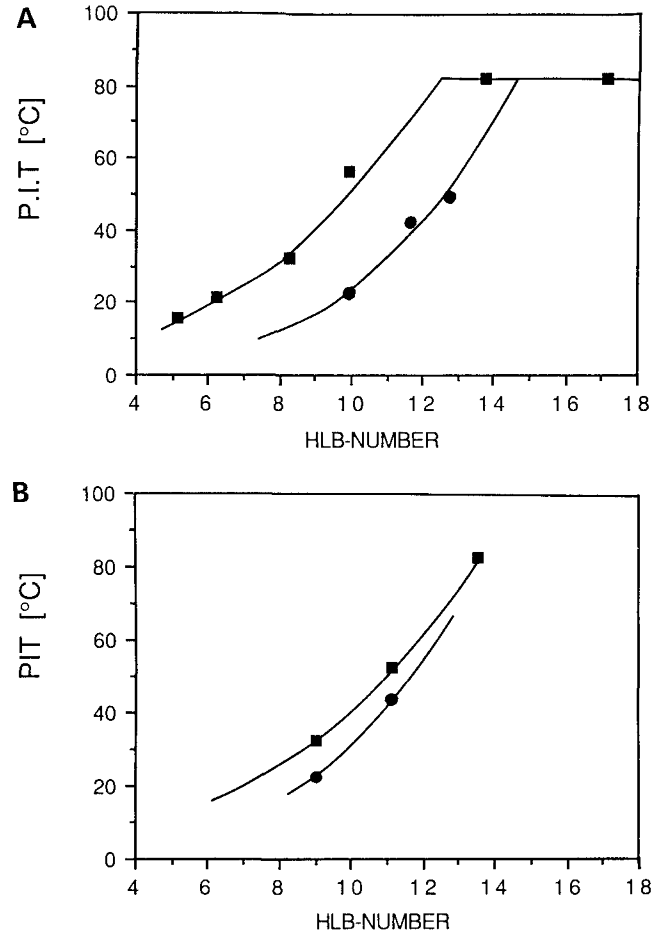

FIG. 1. PIT for surfactant/oil/water systems as function of surfactant HLB number: a) ethoxylated fatty alcohol surfactants; b) ethoxylated nonylphenol surfactants (■ MCT oil ● dodecane).

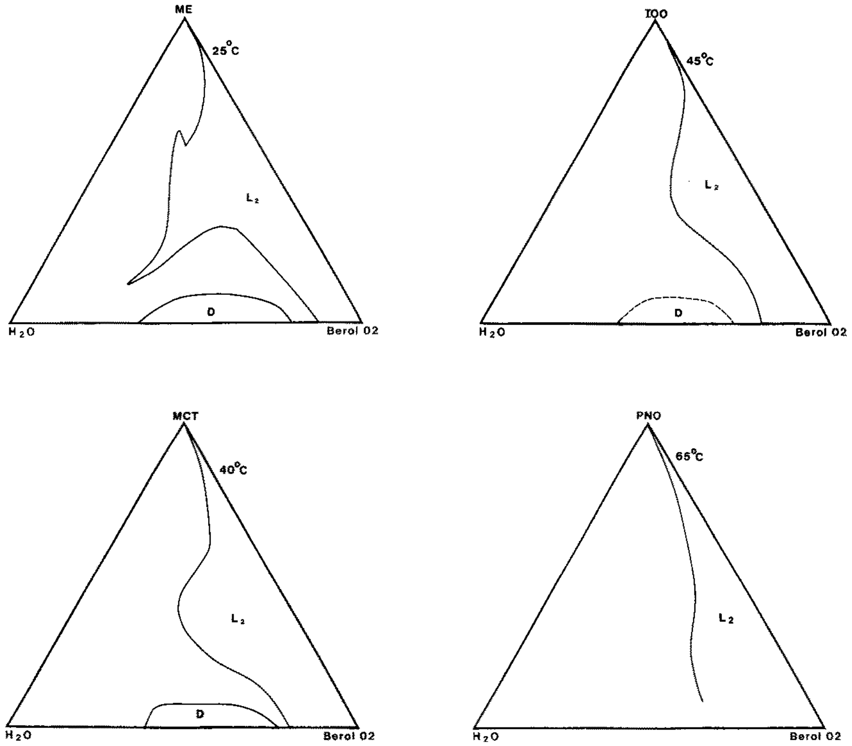

FIG. 2. Phase diagram for Berol 02 (hexaethyleneglycol nonylphenol ether) /oil/water at a fixed temperature close to the measured PIT. L_2 denotes solution phase, D lamellar liquid crystalline phase. a) Methylester (ME) b) Iso-octyl oleate (IOO) c) MCT oil (MCT) d) Peanut oil (PNO).

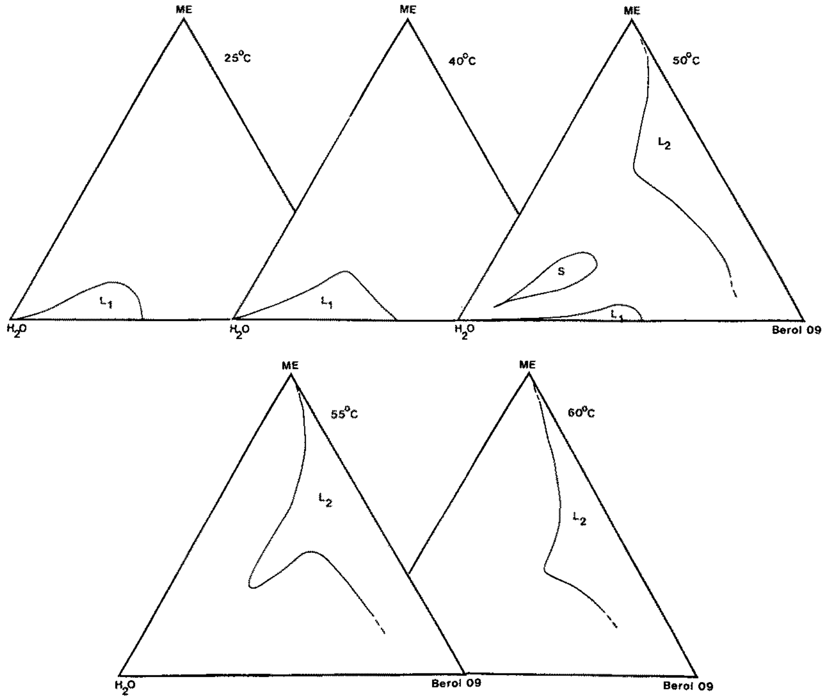

FIG. 3. Phase diagrams for Berol 09 (decaethylene glycol nonylphenol ether) /Methyl ester/water systems: a) 25°C b) 40°C c) 50°C d) 55°C e) 60°C (Notations as in Figure 2 except L_1 denotes micellar solution phase and S surfactant phase).

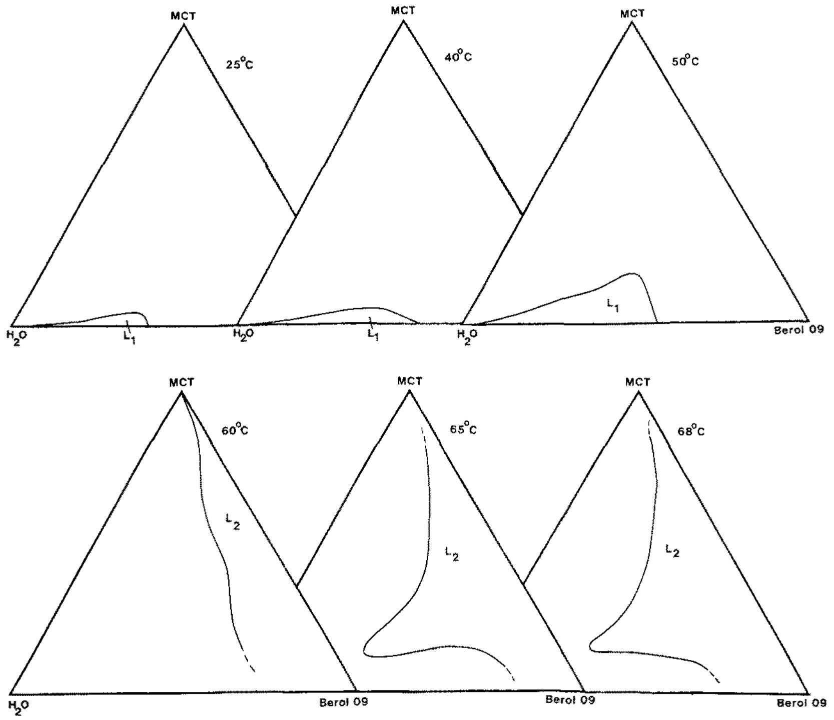

FIG. 4. Phase diagrams for Berol 09/MCT oil/water: a) 25°C b) 40°C c) 50°C d) 60°C e) 65°C f) 68°C (Notations as in Figure 3).

70°C and no significant growth of the L_2-phase can be seen at higher temperatures.

DISCUSSION

PIT measurements. The PIT concept was introduced by Shinoda (16,17) as a method to characterize and explain the phase behavior of ternary nonionic surfactant/oil/water systems. The PIT phenomenon arises from the temperature dependent hydrophilicity of the ethoxylated surfactants which in turn determines the solubility of the surfactant in the oil and water phases. The solubility of the surfactant is balanced at the PIT which leads to low interfacial tensions and conditions favorable for microemulsion formation. The measurement of PIT by the conductivity method or by some other means, serves as an aid in determining at which temperature to construct a phase diagram. It can also be used for optimization of properties in nonionic systems and for selecting surfactants or oils for a specific purpose.

The conductivity method for measuring PIT:s has some limitations. The addition of electrolyte to obtain a conducting emulsion can influence the PIT:s. The effect, however, is small for the amounts used in this study.

We encountered large problems when studying emulsions that contain solid surfactants, e.g., ethoxylated stearyl alcohols. The liquid crystals formed in other systems—ethoxylated oleyl alcohols—can also influence the measurements. In such systems large deviations from the normal behavior can be expected. The measured PIT:s do in some instances differ from PIT:s estimated from the phase behavior studies. This should probably be attributed to the formation of liquid crystals and other multiphase equilibria. There might also be hysteretic effects in some systems in spite of slow heating/cooling rates.

The method can be used to estimate the PIT of a system for solubilization optimization purposes but it must always be accompanied by a study of the phase diagram.

It should also be remembered that technical oils and surfactants are composed of several species which can lead to complex multi-phase equilibria. The sharp PIT:s often observed in systems of pure components are drawn into PIT intervals covering several degrees.

In spite of these difficulties, consistent trends in the results are observed for nonylphenol and medium-chain alcohol ethoxylates. The PIT:s show the expected increase with increasing hydrophilicity, and the slopes do not appreciably differ from those of a hydrocarbon system. There are some differences between the oils studied. In general the triglycerides have higher PIT:s than the esters and the PIT:s increase with increased molecular weight in each group.

Phase diagrams. The examination of the phase diagrams shows that systems containing simple fatty acid esters, such as the methyl ester, behave generally as normal hydrocarbon oils. However, the amount of surfactant needed to produce a L_2-phase is higher for the ester (20%) than for a hydrocarbon such as hexane (10–15%).

The solubilization optimum is shifted toward higher temperatures in a system containing triglycerides. With

PNO there is also seen a decrease in the extent of the L_2-phase.

An important feature in the phase diagrams in Figure 3 and 4 is the disappearance of the surfactant phase for MCT oil. It shows that the solubilization pattern for triglycerides is qualitatively different from that of hydrocarbons and not only an effect of shifting the optimum solubilization temperature.

Among the factors determining the solubilization capacity of a given system are the molecular size of the solute, its polarity expressed as interfacial tensions, dipole moment or polarizability and the structure of the resulting microemulsion. In this study the differences in the phase behavior of different oils are marked. The most evident difference between the oils is, of course, the molecular size, the differences in polarity being too small to explain the observed behavior. However, this first part of the investigation only illustrates these differences. A mechanistic explanation is offered in the second part which deals with anionic surfactant systems.

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REFERENCES

1. Danielsson, I., and B. Lindman, *Colloids Surf. 3*:391 (1981).
2. Shah, D.O., and R.S. Shechter (Eds.), "Improved Oil Recovery by Surfactant and Polymer Flooding," Academic Press, New York, 1977.
3. Stenius, P., in "Colloides et Interfaces," (A.M. Cazabat and M. Veyssie, Eds.), p. 373, Les Ulis 1984.
4. Gillberg, G., in "Emulsions," (K.J. Lissant, Ed.), Vol. III, Marcel Dekker, New York, 1984.
5. Boutonnet, M., J. Kizling, P. Stenius and G. Marie, *Colloids Surf. 5*:209 (1982).
6. Candau, F., Y.S. Leong, G. Poyet and S.J. Candaug, *J. Colloid Interface Sci. 101*:167 (1984).
7. Sjöblom, J., H. Söderlund and T. Wärnheim., in "Chemical Reactions in Organic and Inorganic Constrained Systems," (R. Setton, Ed.), Nato Asi 165, Reidel Dordrecht 1986.
8. Larsson, K., *J. Colloid Interface Science 72*:152, (1979).
9. Lindström, M., H. Ljusberg-Wahren, K. Larsson and B. Borgström, *Lipids 16(10)*:749 (1981).
10. Gulik-Krzywicki, T., and K. Larsson, *Chem Phys Lipids 35*:127 (1984).
11. Pilman, E., K. Larsson and E. Tornberg, *J. Dispersion Sci. Technol. 1(3)*:267 (1980).
12. Schwab, A.W., H.C. Nielsen, D.D. Brooks and E.H. Pryde, *J. Dispersion Sci. Technol. 4(1)*:1 (1983).
13. Schwab, A.W., and E.H. Pryde, *J. Disp. Sci. Technol. 6(5)*:563 (1985).
14. Vesala, A.-M., J.B. Rosenholm and S. Laiho, *J. Am. Oil Chem. Soc. 62(9)*:1379, (1985).
15. Khan, A., K. Fontell, G. Lindblom and B. Lindman, *J. Phys. Chem. 86*:4266 (1982).
16. Shinoda, K., and S. Friberg, "Emulsions and Solubilization," Wiley, New York, 1986.
17. Shinoda, K., and B. Lindman, *Langmuir 3(2)*:135 (1987).

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