

# Phase studies of ethoxylated surfactants-oil-water-undecylenic acid

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Two non-ionic surfactants (Simulsol OL 50 and Simulsol 98) separately or as 1:1 mixtures, together with corn oil-undecylenic acid and water formed various phases. Phase equilibrium studies were made. In all phase equilibrium diagrams investigated, both at 20 and 37 °C, lamellar and hexagonal liquid crystalline and oily isotropic phases were found, besides the emulsion system. Emulsions were composed of mixed lamellar and hexagonal liquid crystalline phases which formed at low concentrations of surfactant and oil and correspondingly high water concentrations.

Non-ionic surfactants present interesting problems in their temperature-dependent interaction with water and oily materials. The present study describes a phase study of systems containing non-ionic surfactants, an antifungal agent, undecylenic acid as active ingredient, corn oil as the oil phase and water, at 20 and 37 °C. The systems, consisting of different amounts of ethoxylated castor oil and ethoxylated oleyl alcohol and the 1:1 mixtures, oil, active ingredient and water, produced complex dispersions containing a number of liquid and liquid crystal phases which can be identified on ternary phase diagrams. The data show that non-ionic surfactants show similarities with ionic agents in phase and dispersion behaviour.

## MATERIALS AND METHODS

### Materials

Ethoxylated castor oil (Simulsol OL 50) and ethoxylated oleyl alcohol (Simulsol 98) Seppic, France; corn oil, Adayar Ltd. Turkey T.S. 888; undecylenic acid, Sigma Chem. Co. England; distilled water prepared by distillation in a glass still.

### Methods

*Constitution of phase diagrams.* Emulsion systems were prepared by using Simulsol OL 50 and Simulsol 98 separately or in 1:1 mixtures in water and undecylenic acid at a constant 5% in corn oil were placed, 20 g of each, in 5 ml sealed vials. Later, the two dissolved systems were mixed, stirred by hand for 10 min and then hand-homogenized, four times. The systems were then allowed to reach equilibrium at 20 and 37 °C.

All containers were stored at these temperatures for periods of up to two months to ensure that equilibration had been reached, although observation indicated that 12 h was probably adequate.

\* Correspondence

Phases present were observed by the naked eye and under a polarizing microscope. The samples prepared with Simulsol OL 50 alone were centrifuged using a laboratory centrifuge and an ultracentrifuge to separate the different phases. The 1:1 mixtures of the two surfactants gave waxy or nearly waxy samples.

All the liquid crystal phases were birefringent and according to their positions in the ternary phase diagram varied in consistency from jelly-like to waxy and solid gels. Characterizations of the liquid crystal types was by the microscope method of Rosevear (1954, 1968) and Lachampt & Vila (1969). Oily isotropic phases were fluid like an oil and could be distinguished from the liquid crystalline phases under the microscope.

The results obtained are plotted in Figs 1, 2 which describe the phases and dispersions observed in the various composition regions and are not intended to rigorously represent the systems according to phase rule principles.

## RESULTS AND DISCUSSION

The phase diagrams are useful in considering the changes in the phase and dispersion characteristics of the systems by variations in the proportions of the components and change of the surfactant.

According to Winsor (1954, 1968) all three main types of surfactants (anionic, cationic and non-ionic) form liquid crystalline phases in aqueous systems. In our investigation, liquid crystalline phases were observed with both non-ionic surfactants. Although several phase diagrams of systems water-oil and non-ionic surfactant have been published (Salisbury 1954; Burt 1965; Lachampt & Vila 1967; Groves et al 1974) no results have been given on the relation between the surfactant phase and lamellar liquid crystalline phase in such systems. The effect of surface active agents in the regions observed at phase

equilibrium diagrams, depends on their chain length (Mulley 1964). Liquid crystalline areas form very extensively with long-chain surface active agents. Since the surfactants used in this investigation (ethoxylated castor oil and ethoxylated oleyl alcohol) have long chains, liquid crystals were observed widely in these systems.

The phase diagrams of Simulsol OL 50 and Simulsol 98 and their 1:1 mixtures with corn oil, undecylenic acid and water showed an oily isotropic liquid phase, emulsion plus lamellar liquid crystalline phase, emulsion plus hexagonal liquid crystalline phase, a lamellar liquid crystalline phase and an hexagonal liquid crystalline phase which are some of the typical areas described by Mulley (1961).

The phase diagrams are drawn at 20 and 37 °C. When Simulsol OL 50 was used alone as an emulsifier in systems equilibrated at these temperatures, at 20 °C an oily isotropic phase, an oily isotropic plus lamellar liquid crystalline phase, a lamellar liquid crystalline phase and an emulsion

plus lamellar liquid crystalline phase were identified. At 37 °C the number of the regions remained the same but the oily isotropic phase increased in area whereas the lamellar liquid crystalline phase alone and together with emulsion decreased (Fig. 1a and b). When Simulsol 98 was used as an emulsifier at 20 and 37 °C, nine and ten regions were obtained respectively (Fig. 1c and d). The main observation was a decrease in the solid parts of the systems with an increase in temperature. At 20 °C there was a lamellar liquid crystalline phase region between the solid and oily isotropic phase regions, whereas at 37 °C, this phase was replaced by a lamellar phase plus isotropic phase region. An angular texture to the hexagonal phase was observed, with the polarizing microscope, in undecylenic acid-corn oil-water-Simulsol 98 (5-5:30:60) mixture, however, polarization crosses in the lamellar phase were observed with the same mixture but in different proportions (e.g. 5-25:20:60) at 20 °C.

When 1:1 mixtures were used, eight and nine

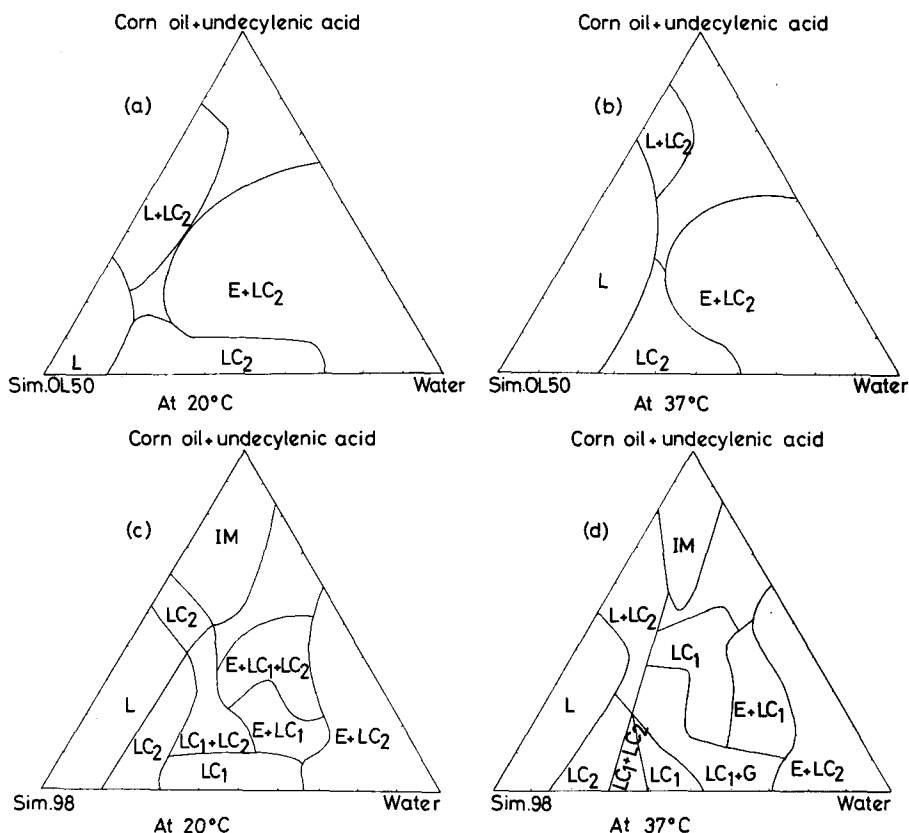


FIG. 1. Phase equilibrium diagrams for (a and b) Simulsol OL 50-water-corn oil- undecylenic acid at 20 and 37 °C, respectively and (c and d) Simulsol 98-water-corn oil- undecylenic acid at 20 and 37 °C, respectively. L = oily isotropic liquid phase,  $LC_1$  = hexagonal liquid crystalline phase,  $LC_2$  = lamellar liquid crystalline phase, E = emulsion, IM = insoluble material, G = Gel.

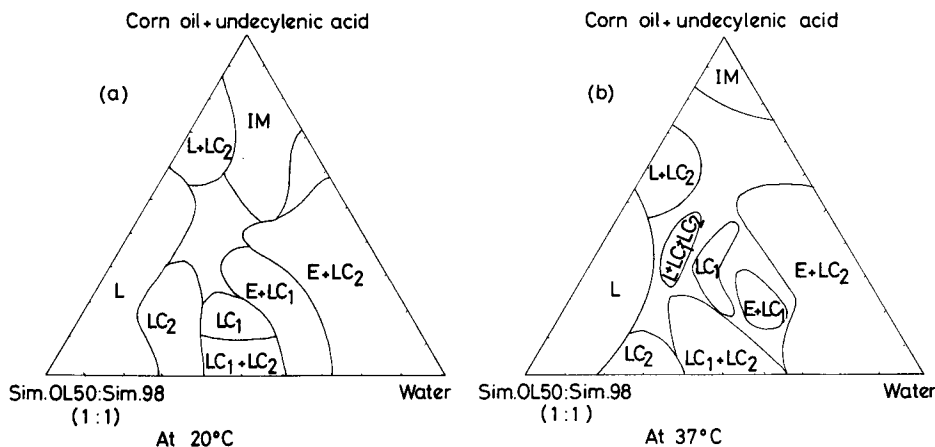


FIG. 2. Phase equilibrium diagrams for (a and b) Simulsol OL 50 and Simulsol 98 (1:1)-water-corn oil-undecylenic acid at 20 and 37 °C, respectively. L = oily isotropic liquid phase,  $LC_1$  = hexagonal liquid crystalline phase,  $LC_2$  = lamellar liquid crystalline phase, E = emulsion, IM = insoluble material.

regions were obtained at 20 and 37 °C, respectively (Fig. 2a, b). As the temperature was increased from 20 to 37 °C, there was a decrease in the insoluble material phase. Oily isotropic liquid phase was increased and a new phase consisting of oily isotropic liquid phase plus hexagonal and lamellar liquid crystalline phase was formed. The region consisting of lamellar plus hexagonal liquid crystalline phases was increased and the hexagonal liquid crystalline phase was decreased. There was no significant change in the emulsion and lamellar liquid crystalline phase regions.

Although only lamellar phase liquid crystals were observed with Simulsol OL 50; both kinds of mesomorphic phases were observed with Simulsol 98 and the 1:1 mixtures. Increase in temperature changed some regions in the equilibrium phase diagrams. The decrease observed in the region of insoluble material as the temperature increased from 20 to 37 °C, could have resulted from undecylenic acid and Simulsol 98 melting. In all the phase diagrams studied, as the temperature increased, the oily isotropic phase increased. This was in line with the decrease in the liquid crystalline phases. All of these changes could be due to the decrease in hydrophilic character of the surface active agents as explained by Marland & Mulley (1971). Non-ionic surfactants containing a polyoxyethylene chain differ from other surfactants in the sensitivity that their association structural organisation has to temperature. This feature was noted by Shinoda (1963) with regard to their micellar association and solubility. A corresponding sensitivity may also be observed in the strong dependence of the liquid crystalline regions on temperature found in phase diagrams of the

system: water-surfactant and hydrocarbon (Friberg et al 1969).

Stable emulsion regions were found mixed with liquid crystals in all of the six phase diagrams.

These kinds of emulsions were named three-phase emulsions by Friberg (1979). It was shown that emulsion stability was greatly enhanced in the presence of liquid crystals in emulsions (Friberg 1971; Ali & Mulley 1978).

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