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Gel dispersed liquid crystals

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Abstract: Microemulsion based gels (MBG) can be used as carrier materials for dispersed thermotropic liquid crystals (LC). The viscosity of the carrier material can be specifically changed by varying the gelatin content. The LC droplet sizes and their distribution in the MBG system are influenced by both the ratio between AOT surfactant and alcohol co-surfactant and the length of the carbon chain of the co-surfactant. LC droplets without or with only a small amount of alcohol co-surfactant have the same droplet size and show a radial structure.

Key words: Gel dispersed LC – microemulsion based gel – surfactant-cosurfactant – viscosity

Introduction

Low molecular weight nematic, cholesteric and smectic liquid crystals (LC) dispersed in polymeric carrier materials (polymer dispersed liquid crystals, PDLC) have been widely investigated in recent years [1–4]. The LC structure in the PDLC are discussed in literature [1, 2], including the possibility of a preferred orientation of the LC molecules in separate LC droplets, i.e., an orientation [5] without an electric field which is induced by the structure of the carrier material (biopolymer) only [5–8]. These thermotropic LC are water insoluble. In organic solvents, for instance in hydrocarbons, they are soluble. Solved in organic solvents these substances lose their specific LC-properties.

Thermo-electrooptical effects may influence the diameter and the shape of the LC droplets [9]. The change of the droplets shape is expected to depend on temperature and/or electric fields, but also on the specific carrier materials properties, i.e., for example, the viscosity. That means, reducing the viscosity of the carrier material makes a LC-droplet deformation in electrical field easier. An analogous effect, change of droplet shape, is observed by stretching PDLC [10]. In one of our last works thermotropic liquid crystals were investigated, which were embedded in a high water gel on the basis of an aqueous polyvinyl alcohol-borax solution [11]. This high water gel-liquid crystal (HWG-LC) system contained nearly 80 wt% water and more LC wt% than polymer. The HWG-LC showed electrooptical behavior depending on an electric field when constrained between transparent electrodes.

The aim of the present work is to investigate the possibility of using a microemulsion-based gel (MBG) as carrier material for dispersed thermotropic LC. This is of interest, especially regarding the transparency, the viscosity, and electrical properties of the carrier material, because these physico-chemical properties have an important influence on the macroscopic and electrooptical properties of the embedded separate LC-phase [7–9].

Solubilization of macromolecules in microemulsion is of considerable current interest [12–14]. These macromolecules can form networks in both the water-rich and oil-rich phase. These microemulsion-based gels (MBG) are optically transparent and some of them have found application in pharmaceuticals, cosmetics, the food and photo industries.

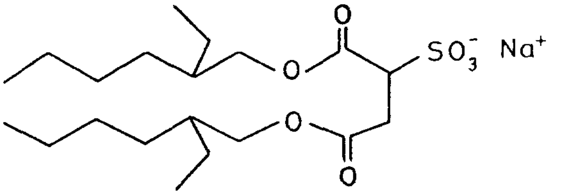


Fig. 1. Structure of Na(AOT)

The rheology of an oil-in-water MBG can be influenced by both the content of the network forming polymer and the content of the organic solvent. In comparison to the so far known carrier materials , this seems to be an advantage.

It is, however, an unsolved question if LC-molecules can be principally involved in systems of high amounts of organic components. In the present work it will be shown that the embedding of LC-molecules with anisotropic properties in MBG is possible. We chose gelatin as the gel-forming component [15] and AOT (sodium salt of bis(2-ethylhexyl) sulphosuccinate, Fig. 1) as a microemulsion forming surfactant. Both components are often used to prepare MBG [16, 17].

Experimental and methods

The following procedure was adopted to produce MBGs with and without [16, 17] embedding thermotropic liquid crystals as a separate phase. In a first step, a dispersion of lime processed gelatin in water (5–28 wt%) was prepared and heated up to approximately 55 °C. To this dispersion were added an optical clear surfactant solution of AOT in heptane (0.5 M) and a co-surfactant solution of butanol or dodecanol in heptane (both 0.15 M or 0.5 M). The mixture was vigorously shaken. After this procedure an optically transparent microemulsion is produced (by cooling slowly this micro-emulsion, a MBG, is formed at room temperature). In a last step the nematic LC K15 (substituted cyanobiphenyl, Firma Merck) 8 vol% was added to the microemulsion at 40 °C. The mixture was stirred and cooled slowly at room temperature. The resulting mixture is turbid. This visual effect leads to no knowledge about the present system. If it is really a LC containing MBG has to be shown by investigating the optical properties. A polarization microscope Axioskop (Firma Carl Zeiss) was used to solve this question. The viscosity-shear rate relationship of the carrier material was characterized by means of a Rheotest 2 rheometer (MLW Medingen) equipped with a cone-plate geometry system.

Results and discussion

The main question is to prove the existence of a separate LC-phase in the system prepared.

Using the polarization microscope the micrographs shown in Figs. 2a–d were obtained. The figures show the existence of separate droplets. These droplets are formed by optical anisotropic material. The pattern observed show the characteristic LC radial structure [2]. Therefore, using the procedure described above, the LC was embedded in the MBG as a separate phase. The hydrophobic LC obviously does not solve in the hydrophobic phase (heptane) of MBG. For better understanding it should be mentioned that even small contents of oil in LC would lead to loss of anisotropy. The MBG-LC system contains more wt.% LC than the network-forming gelatin.

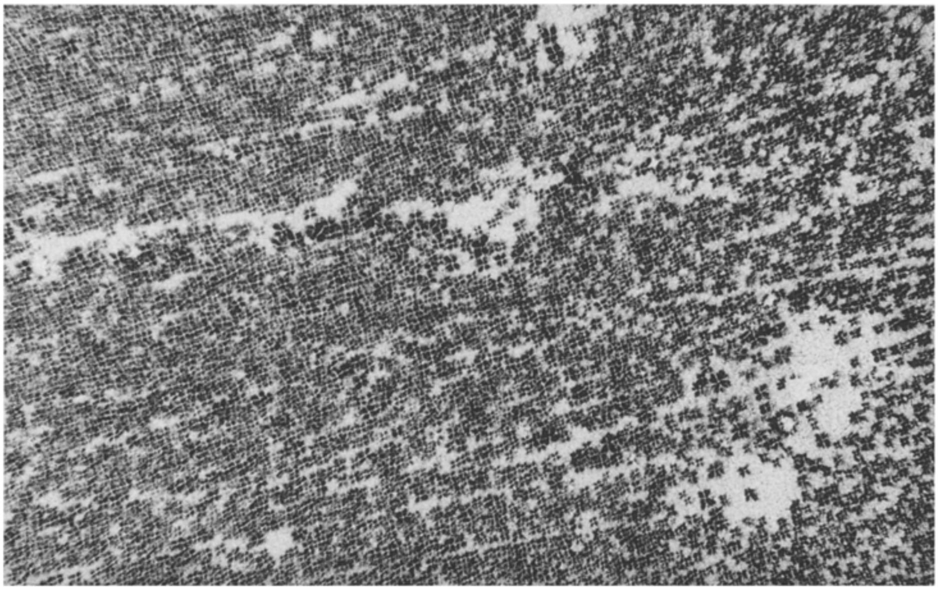
The LC bulk exists in the form of very sharp droplets. This is comparable to the case of embedded LC in a high water gel (HWG) system on the basis of an aqueous polyvinyl alcohol-borax solution [11]. In contrast to the HWG-LC system, the LC droplets in the MBG without or containing only very small amounts of cosurfactant have the same droplet size and show a radial structure.

The formation of stable droplets in the system and their characteristic configuration obviously produces an ordered shell-like AOT surfactant cover. This means that the AOT molecules have a function analogous to the polyvinyl alcohol molecules in the HWG system.

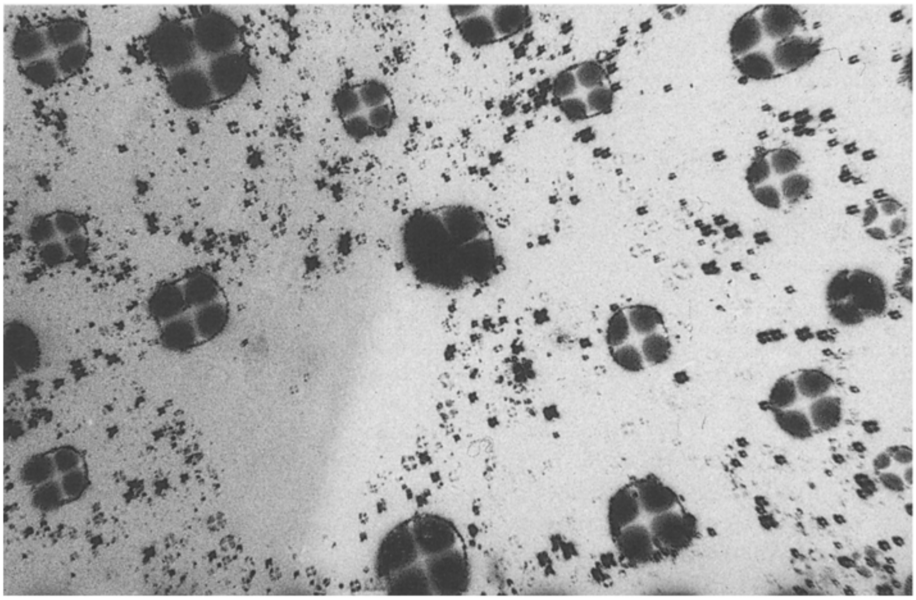
By adding the co-surfactant butanol or dodecanol to the MBG system it is possible to influence droplet size and their distribution. Two effects can be observed:

In presence of the co-surfactant the droplet size and their distribution increases. On the other hand, this effect depends on the nature of the co-surfactant, too. Figure 2a shows a MBG-LC system with a concentration ratio AOT/butanol of 2:1. The droplet sizes (25–30 μm) and their distribution is nearly constant, and comparable to a system without co-surfactant. By overwhelming co-surfactant concentration, for example, a ratio AOT/butanol of 1:2, the systems are characteristically changed (see Fig 2b). Contrary to the former case, there are different droplet sizes (25–350 μm) and the distribution of the droplets is not constant. Of course, the hydrophobic and hydrophilic behavior of the MBG is influenced by adding the co-surfactant. Usually, similar effects are explained by taking into account geometrically ideas about the interaction between surfactant and co-surfactant [18, 19]. Nevertheless, the background of these effects can be explained alternatively.

Figure 3 shows a scheme of the two principle kinds of the interaction between AOT surfactant and alcoholic co-surfactant. Hydrophobic interaction between the carbon chains (Fig. 3a) or hydrophilic interaction between the head groups are possible, involving solvation shells (Fig. 3b).



2a



2b

Fig. 2. (*continued*)

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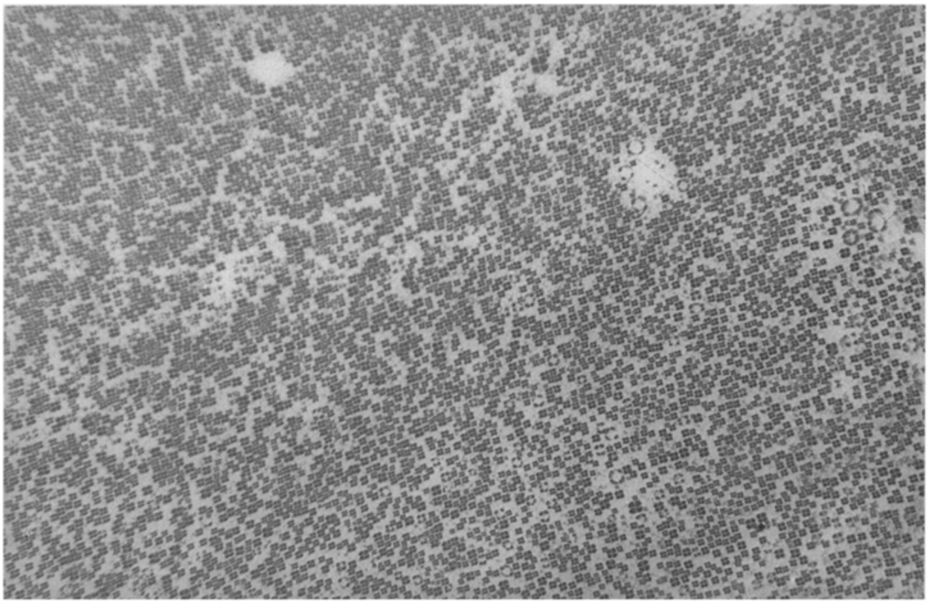
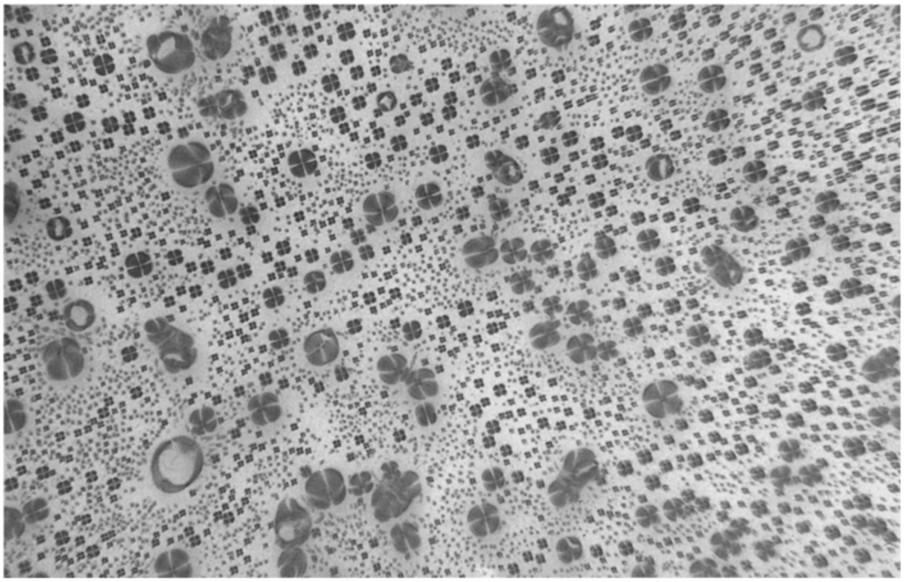


2c



2d

Fig. 2. Dispersion of thermotropic LC droplets in a microemulsion base gel (MBG) between cross polarizer of an optical microscope. a) 0.5 M AOT: 0.5 M butanol = 2 : 1, magnification 50 x b) 0.5 M AOT: 0.5 M butanol = 1 : 2, mag. 50 x c) 0.5 M AOT: 0.15 M dodecanol = 2 : 1, mag. 50 x d) 0.5 M AOT: 0.5 M dodecanol = 2:1, mag. 12.5 x

The hydrophobic interaction is believed to be favored. In this case, the co-surfactant competes with oil (heptan) contained in the system . The resulting MBG gets more hydrophilic by means of an apparent impoverishment of AOT. The hydrophobic effect increases with increasing carbon atoms in the carbon hydrogen chain of the co-surfactant [20]. Therefore, it should be expect that the MBG system becomes not only more hydrophilic by adding the alcoholic co-surfactant,

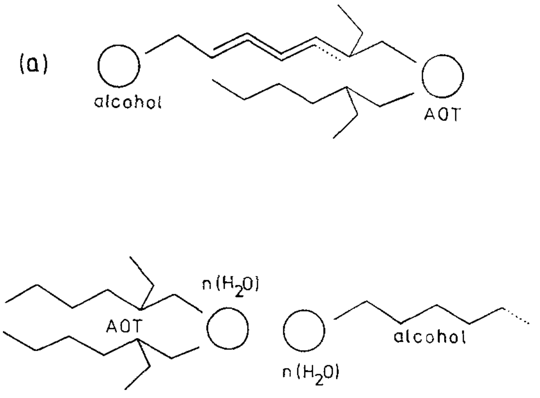


Fig. 3. Schematic model of the interaction between AOT surfactant and alcohol co-surfactant: a) hydrophobic b) hydrophilic

but this effect also depends on the specific nature of the co-surfactant. The hydrophility of an AOT-dodecanol system is higher (Figs. 2c and 2d) in comparison to an AOT-butanol system. The change of the hydrophilic-hydrophobic balance in the MBG-LC system is the reason for the change of size and distribution of embedded LC droplets. With increasing hydrophilic behavior the droplet size increases, too.

The influence of the shear rate on viscosity of samples with different gelatin contents was investigated in order to characterize the stability and the rheological properties of the MBG carrier material (Fig. 4). The flow behavior of the gels is obviously not Newtonian. The apparent viscosity increases when the gelatin content increases from 2.75 to 6.25 wt%. That means the network is more stable in MBG containing higher gelatin content. In the system the gelatin chains are interacting and forming networks with attendant hydration of the chains. Therefore, the viscosity of the MBG can be directly changed by the ratio of the single components in composition. These results are expected.

Nevertheless, this is very important, especially for application of these gels as carrier materials for dispersed thermotropic liquid crystals. The change of the LC droplet shape, which depends on temperature and/or electric fields [9], can be assumed to depend on the rheological behavior too, i.e., on the stability of the gel-network. Furthermore, the conductivity of the system can be altered by means of the gelatin content in the

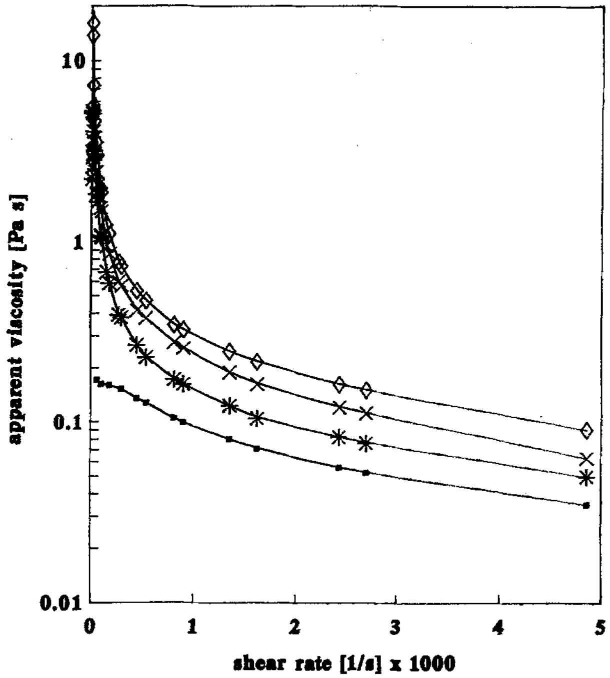


Fig. 4. Viscosity-shear rate relationship in dependence on the gelatin content in MBG 2.75, 3.25, 5.0, and 6.25 wt% gelatin

MBG. A critical amount of gelatin is required to form an electrical conducting network [17]. Our recent investigations show that the resistance of the carrier materials of polymer dispersed LC layers can be changed by adding electrolyte. As a result, the threshold voltage of PDLC between transparent electrodes may be influenced [8].

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