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J. G. Dominguez

J. L. Parra

J. Heuser

*et. al.* For a complete list of authors, see [https://scholarsmine.mst.edu/chem\\_facwork/3600](https://scholarsmine.mst.edu/chem_facwork/3600)

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## Gelled emulsions with a high water content

C. Solans<sup>1)</sup>, J. G. Dominguez<sup>1)</sup>, J. L. Parra<sup>1)</sup>, J. Heuser<sup>2)</sup>, and S. E. Friberg<sup>3)</sup>

<sup>1)</sup> Instituto de Tecnología Química y Textil (C.S.I.C.), Barcelona, Spain

<sup>2)</sup> Department of Physiology, Washington University, St. Louis, U.S.A., and

<sup>3)</sup> Chemistry Department, University of Missouri-Rolla, Rolla, U.S.A.

*Abstract:* The structure of a gel containing 99% water, 0.5% of a nonionic surfactant and 0.5% of a hydrocarbon was investigated by analysis of its equilibrium phases and their state of dispersion by liquid helium freeze fracture electron microscopy.

The gel consisted of aqueous droplets of micron size separated by a thin membrane of a lamellar liquid crystal and a W/O microemulsion with droplets varying between 200 and 1000 Å in diameter.

*Key words:* Emulsions, gelled, high water content, nonionic surfactant, equilibrium phases, electron microscopy, microemulsion W/O.

### Introduction

Gels formed by surfactants and water are used in pharmaceutical and cosmetic technology and their applied aspects have been described [1]. The knowledge about their structure is less thorough. Barry [2, 3] discussed the "self-bodying" action of long chain alcohols and suggested that a liquid crystal could form a three dimensional network providing body to a formulation. The fact that liquid crystals serve as stabilizers for emulsion systems was known earlier [4] and a specific stabilizing mechanism has been discussed [5, 6]. Electron microscopy of samples freeze-fractured at the temperature of liquid nitrogen have left some information [5] about dispersions of lamellar liquid crystals, but freeze damage from that method cannot be ruled out.

After these pioneering investigations, different aspects of the phenomenon have been investigated extensively. Liquid crystals in emulsions have been applied by Sagitani [7] in his phase emulsification method and in lecithin emulsion by Rydhag [8]. Müller has investigated liquid crystals in pharmaceutical formulations [9] and Frank et al. applied such systems to slow release formulations [10]. Groves

has recently investigated several of these aspects [11, 13].

Gels applied in cosmetics [1] usually contain surfactants at concentration levels of several percent and the gel properties are obtained from a dispersion of a liquid crystalline phase, as discussed by Barry [2, 3]. However, recent results from the Institute for Chemical Technology and Textiles in Spain [14, 16] demonstrated a gel system with surfactant concentration of only 0.5% by weight.

It appears obvious that this gel system owes its features to different phenomena than those found in the traditional gel systems [1-3]. We found an investigation into the structure of this gel well justified, against the fact that its extremely low surfactant content gives it an advantage over other systems.

This report relates the gel structure to the phase diagram of its three components; water, hexadecane and a nonionic surfactant at equilibrium. Three phases (an aqueous solution, a hydrocarbon solution and a lamellar liquid crystal) were found to be present in the gel. In addition, a detailed picture of the distribution of the three phases was obtained from electron microscopy freeze-fracturing using liquid helium temperatures [16-18].

## Experimental

### Materials

The surfactant was a commercial ethoxylated dodecyl alcohol supplied by Tensia Surfac S. A., Barcelona, Spain. The characteristics of this surfactant were as follows: molecular weight: 350.4; ethylene oxide content (Mols EO/mo): 3.6; hydrophobic chain: 75.4% C<sub>12</sub>; 1.2% C<sub>13</sub>; 20.3% C<sub>14</sub>; 3.1% C<sub>16</sub>; polyglycols: 0.68%. The hydrocarbon was decane from Aldrich Chemical Co. (> 99%) and the water was twice distilled.

### Gel preparation

The water content of all gels was 99% by weight. They were prepared at 50°C by weighing the components into test tubes followed by agitation by hand until the gel was formed. Glass balls were added to facilitate the mixing and formation of the gel. After their preparation, the samples were kept at room temperature.

### Small angle X-ray diffraction

X-ray diffraction was carried out in a Kiessig small angle camera from Richard Seifert. Ni filtered Cu radiation was used and the reflections determined by a Tennelec position-sensitive detection system (Model PSD-1100).

### Ultracentrifugation

A Beckman ultracentrifuge (Model L3-40) was used.

### Optical microscopy

An Olympus-BH polarizing microscope, attached to an automatic exposure camera was used for photomicrography. A Bayley Instruments Thermoelectric stage (Model TS-2) with automatic temperature control was used in the optical analysis.

### Electron microscopy

A new quick-freezing method was used [17-19] in the freeze-fracture analysis. The samples were quick-frozen by slamming them against an ultrapure block of copper which had been pre-cooled to 4 K (-269°C) by a spray of liquid helium. The design and operation of the apparatus used for freezing have been described in detail elsewhere [17-19]. All the frozen samples were stored in liquid nitrogen until transfer into a Balzers' 301 freeze-fracture machine (Balzers Corp., Nashua, NH). Standard platinum/carbon shadowed replicas were made and examined by a JEM 100B or 100C transmission electron microscope at 80 kV.

## Results

The formation of the gels with 99% water took place at 50°C for compositions with hydrocarbon/surfactant ratios between 3/7 and 6/4. Hydrocarbon/surfactant ratios outside this range gave no gels. At

temperatures below 35°C, no gels were formed in this system for any hydrocarbon/surfactant ratios.

The phase equilibria of a system with commercial nonionic surfactant is complex because of the multitude of isomers in the surfactant. Hence, in Fig. 1, only the extent of the liquid crystalline region and the isotropic hydrocarbon solution have been represented at 50°C (the temperature at which the gel was formed) and at 28°C, (a temperature at which the gel could not be formed). The extent of the liquid crystalline region with no decane present was similar at 50°C and 28°C. With addition of decane, the liquid crystalline region was displaced towards higher surfactant contents at 50°C and the amount of decane solubilized in the liquid crystalline phase was 25%. Optical microscopy, as well as X-ray diffraction, showed the liquid crystalline region to be lamellar at both temperatures.

The phase behavior of the region with low surfactant content (not shown in Fig. 1) indicated that 28°C was a temperature close to the HLB-temperature and that 50°C, therefore, was above the HLB-temperature [20, 21]. The phase equilibria of compositions with 99% water showed that those able to form gelled emulsions separated in three phases: two isotropic liquid phases and one lamellar liquid crystalline phase. However, of the compositions which separated in those three phases, only those with a hydrocarbon/surfactant ratio in the range 0.43-1.5 formed gels.

After ultracentrifugation of the gels, three layers were obtained: an aqueous phase (96% of the total volume), an oil phase, and a liquid crystalline phase. When the latter phase was examined under the microscope, a typical lamellar liquid crystalline pattern with

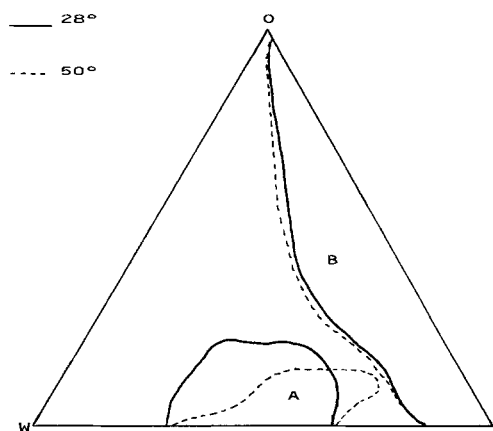


Fig. 1. Partial phase diagram for the system water (W) ethoxylated dodecyl alcohol (3.6 EO) (S) and decane (O). (A) Liquid crystal region; (B) isotropic liquid solution

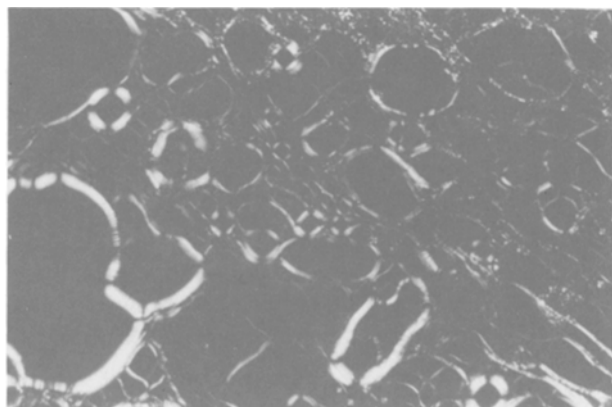


Fig. 2. The optical pattern, typical of a liquid crystalline phase of the lamellar type ( $\times 300$ )

dispersed droplets (Fig. 2) was observed. X-ray diffraction of the liquid crystal obtained from the gel confirmed that it was of the lamellar type with an interlayer spacing of  $59.7 \text{ \AA}$ , similar to the interlayer spacing of the liquid crystal obtained from the liquid crystalline phase in equilibrium with the aqueous phase. Such an interlayer spacing corresponded to a water content of 46%, as can be observed in the plot of interlayer spacing versus weight fraction of solvent (Fig. 3).

Optical microscopy of the gels showed the existence of close-packed spherical droplets with an average diameter of  $2 \text{ \mu m}$ .

The electron microscopy photos gave a detailed picture of the emulsion (Figs. 4 A, B). At a magnification of  $\times 52\,000$  a pattern of close-packed micron-size droplets are shown separated by an extremely thin

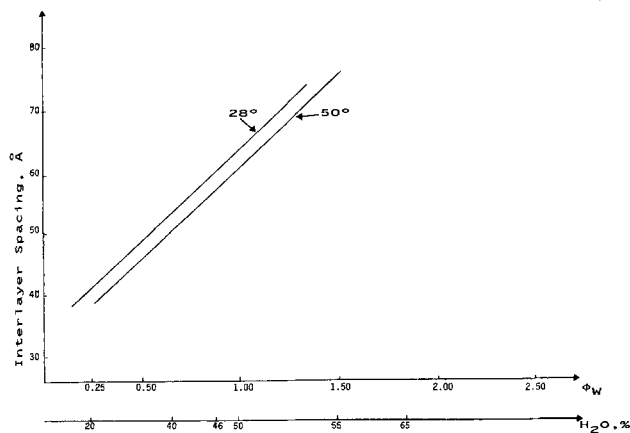


Fig. 3. Interlayer spacing in lamellar liquid crystals of water and ethoxylated dodecyl alcohol (3.6 EO).  $\phi_w$  = solvent weight ratio

membrane. The small space between the close-packed droplets is filled with smaller droplets varying in size from a diameter of 200 to  $1000 \text{ \AA}$ .

## Discussion

The results clarified both the phase being present in the gel and the detailed structure of the gel. The phase diagrams, Fig. 1, are typical of a system at temperatures far above the cloudpoint; even above the HLB-temperature [20, 21]. The multi-phase area close to the water corner could not be analyzed for the number of phases, because the commercial surfactant did not behave as one chemical component but ultracentrifugation of the gel produces both a liquid crystalline phase and an oil phase in addition to the aqueous phase. This

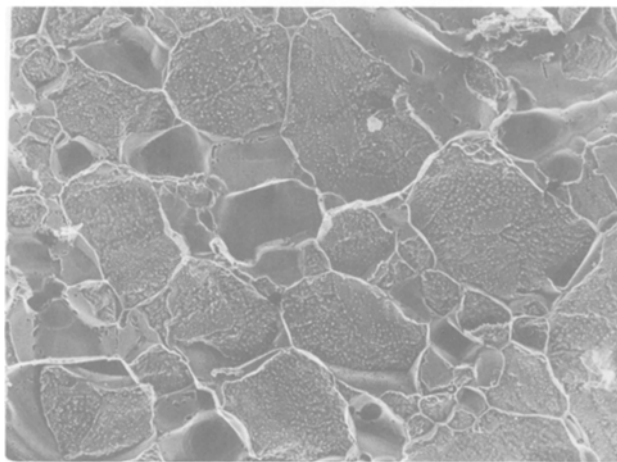
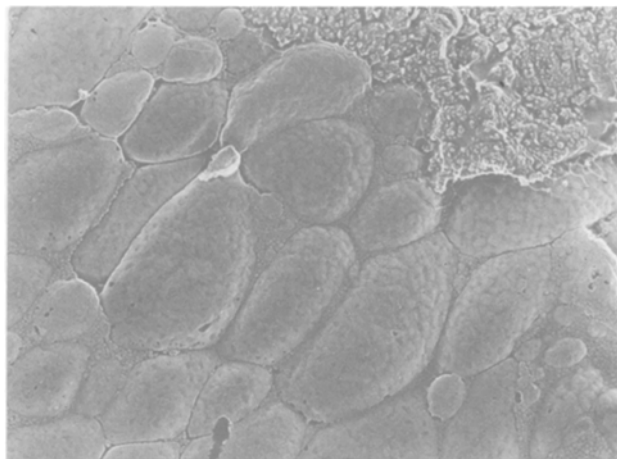


Fig. 4. Electron micrograph of the gel emulsion. Magnification:  $\times 52\,000$

result was confirmed by the microscopy photographs, showing the typical optical pattern of a lamellar liquid crystalline phase.

The question of the specific structure giving the gel properties was answered by the results from the electron microscopy. The gel is essentially a water-in-liquid crystal-in oil (W/LC/O) emulsion with extremely high ratio of oil to water.

Its stability depends on two factors. The first one is the efficient spreading of the liquid crystalline phase around the water droplets. The spreading of this liquid crystalline phase between the oil and the aqueous phase was so efficient that the photos as in Fig. 4 are similar to corresponding electron microscopy photos of the bimolecular layer in biomembranes.

Biomolecular layers in biomembranes consist of two amphiphile layers back-to-back; the present membrane in all probability consists of three layers because it separates an aqueous compartment from the continuous phase of the oil. The essential feature of the emulsions is the pronounced spreading power of the lamellar liquid crystal.

In this respect this emulsion is different from earlier ones with liquid crystals [2–12]. These have shown thick liquid crystalline layers with inhomogeneous spreading around the emulsion droplets and also macroscopic droplets of liquid crystal in the continuous phase. The present liquid crystalline layers at the oil/water interface are similar to black liquid films [22] in air or between two compartments in solution.

The fact that the layers spread so efficiently between the water droplets and the oil phase depends on the relation between the surface tensions. As a zeroth order approximation, the surface free energy may be considered the driving force, as in Young's equation. A comparison between separate liquid crystal and water droplets in the oil (I) and the present organization (II) gives the condition for spreading of the liquid crystal

$$4\pi r_W^2 \gamma_{O/W} + 4\pi r_{LC}^2 \gamma_{LC/O} \quad (I)$$

$$> 4\pi r_{W+LC}^2 \gamma_{W/LC} + 4\pi r_{(W+LC)}^2 \gamma_{LC/O}. \quad (II)$$

Assuming that the ratio between liquid crystal and water droplets in I is  $R$ , the different  $r$ 's may be related

$$r_{CL} = r_W \cdot R$$

$$r_{W+LC}^3 = r_W^3 + r_{LC}^3 = r_W^3(1 + R^3)$$

$$\gamma_{O/W} > \gamma_{W/LC} + \gamma_{LC/O} [(1 + R^3)^{2/3} - R^2].$$

The present case of small  $R$  value gives the spreading condition

$$\gamma_{O/W} > \gamma_{W/LC} + \gamma_{LC/O}.$$

The interfacial tension between a liquid crystal and oil is extremely low, as has recently been demonstrated by Ghosh and Miller [23].

The mere fact that the liquid crystals spreads so efficiently in the present case demonstrates a low interfacial tension also between the aqueous phase and the liquid crystalline phase. Unfortunately, no data on the interfacial tension between a liquid crystal and an aqueous solution are available.

The oil is present as a  $W/O$  microemulsion with droplet sizes down to radii of 100 Å filling the voids between the large emulsion droplets.

The gel properties arise from the energy dissipated on the resistance from the  $W/O$  microemulsion to flow in the small voids between the high water droplets when the shape of the large droplets is distorted. High oil/surfactant ratios are detrimental to the properties of the gel, which now becomes fluid because the thick  $W/O$  microemulsion layers between the large droplets offer too little resistance to flow. Too high surfactant ratios, on the other hand, make the gel unstable. The disruption of the structure is probably due to the fact that insufficient  $W/O$  microemulsion is present to reduce the stress at high energy corners during shear of the water droplets.

In this emulsion, the liquid crystalline phase appeared to play a decisive role. This by no means implies that the liquid crystalline phase is necessary for gel formation; gels of this kind have been observed in other emulsion systems without the presence of a liquid crystal.

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Authors' address

Dr. S.E. Friberg  
Clarkson University  
Department of Chemistry  
Potsdam, NY 13676, U.S.A.