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Hironobu Kunieda

Stig Friberg
Missouri University of Science and Technology, stic30kan@gmail.com

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Foams from a Three-Phase Emulsion*

HIRONOBU KUNIEDA** and STIG E. FRIBERG

Chemistry Department, University of Missouri-Rolla, Rolla, MO 65401 (U.S.A.)

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ABSTRACT

Foam stability was related to phase behavior in a foamed three-phase region consisting of an aqueous solution (L_1), an alcohol solution (L_2) and lamellar liquid-crystalline (LC) phases in the $C_8H_{17}SO_3Na/C_8H_{17}OH/H_2O$ system. The state of the system before foaming was $LC/L_2 + LC/L_1$ or $L_1 + L_2/LC$ type emulsions up to a high octanol/water ratio of 77/23. In $L_2 + LC/L_1$ emulsion, the LC droplets exist separately from the alcohol droplets in an aqueous continuous medium. The viscosity of the system was enhanced with an increase in the content of dispersed phases, i.e., alcohol and/or liquid crystal phases contributing to the stabilizing of the foam. With higher than optimal liquid-crystalline phases present the high viscosity prevented foaming. Higher than optimal alcohol amounts led to phase inversion and instability. The drainage rate of the alcohol phase was considerably faster than of the other phases. As a result, the three-phase foam was stabilized by the liquid-crystalline phase for the water continuous part of the system in spite of the presence of a foam-destabilizing compound, octanol.

INTRODUCTION

Traditionally, the stability of foams has been related to the colloidal stability of thin films [1–5] and the combination of surface free energy and the potential over the thin film has proven extremely satisfactory [6] to clarify the stability of isolated films under controlled conditions.

However, there are foams for which the foaming body has a more complex structure and where that structure has a decisive influence on the stability of foams. One example is the case of organic solutions close to their critical point. Such systems have been analyzed by Ross and Nishioka [7, 8], who could demonstrate the relation between critical points and foamability.

For systems in which the foamed vehicle consists of several phases an old interesting observation [9] deserves notice. An emulsion was found to give stable or unstable foams depending on its preparation and at the time no expla-

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*Dedicated to the memory of Professor G.D. Parfitt.

**Permanent address: Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai. Hodogaya, Yokohama, Japan.

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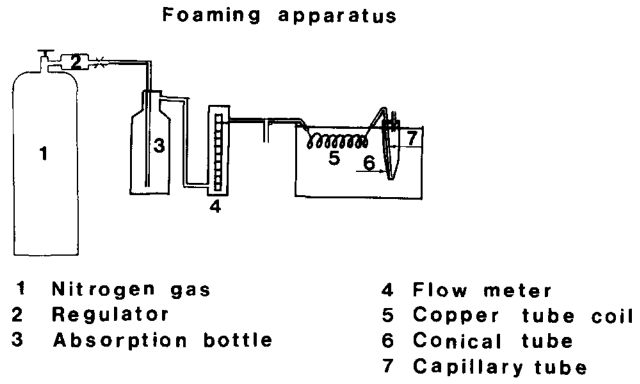


Fig. 1. The foaming apparatus.

nation could be offered. Ross and Nishioka [10] gave a rational explanation in the form of spreading coefficients based on their studies of foaming in critical systems [7, 8]. Water/oil (W/O) or oil/water (O/W) ratio decided the stability of the foam.

Foaming from multiphase systems is of great importance in the field of extended oil recovery using carbon dioxide because of the common collapse of aqueous foams when contacted with oil. This fact combined with an earlier experience with the stabilization of hydrocarbon foams with liquid crystals [11, 12] made an investigation into the behavior of a W/O system in combination with a lamellar liquid-crystalline phase both essential and appealing.

In this investigation water, octylsulfonate and octanol were used in order to benefit maximally from earlier investigations into surfactant association structures [13].

EXPERIMENTAL

Procedures

Phase diagram. Various amounts of water, alcohol and surfactant were sealed in ampoules and kept well shaken in a thermostat. Phase equilibria were determined by observing respective phases identifying liquid crystals by their pattern in a microscope with polarized light.

Foam stability. The apparatus for determining foam stability is shown in Fig. 1. Nitrogen gas was passed through a regulator into an absorption bottle containing volatile components of the foam. The foaming gas was passed through a flow meter, a copper tube coil to achieve correct temperature, 25 °C, and ultimately through a capillary into the solution being foamed. A conical tube with a total volume of 50 ml was chosen as the foam container. One milliliter of each preparation was foamed to a volume of around 50 ml or until no liquid

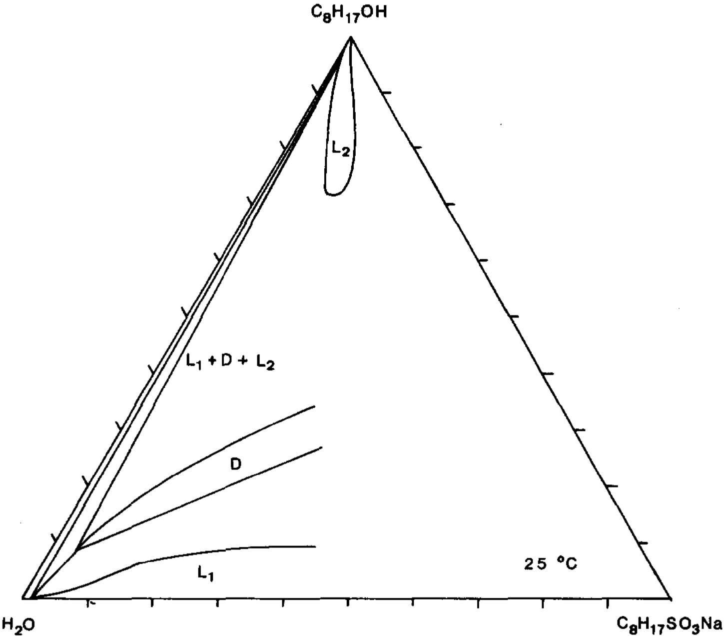


Fig. 2. Partial phase diagram of a $C_8H_{17}SO_3Na/C_8H_{17}OH/H_2O$ system at 25 °C.

remained. The foam volume and the foam drainage was measured as a function of time.

Determination of emulsion type. In order to determine the emulsion type, we used the so-called Becke line effect. This method depends on the fact that when rays pass through a prismatic or lenticular object they are bent inwardly or centripetally if the object (droplet) is of higher refractive index than the continuous phase and outwardly or centrifugally if the refractive index of the droplet is lower than that of the continuous medium. In order to exploit the Becke line effect, one may focus sharply on the droplet and then rack the microscope tube upwards while observing the fringe of light around the object. If the fringe appears to contract as the tube is racked up, it is concluded the droplet is of higher refractive index than the continuous medium (O/W emulsion). If the fringe appears to expand on this maneuver the droplet is of lower refractive index (W/O emulsion).

RESULTS AND DISCUSSION

Phase behavior and emulsion type in a three-phase region

It is well known that an isotropic normal micellar solution or reversed micellar solution, and a lamellar liquid-crystalline phase are formed in an ionic surfactant/middle- or long-chain alcohol/water system, depending on the

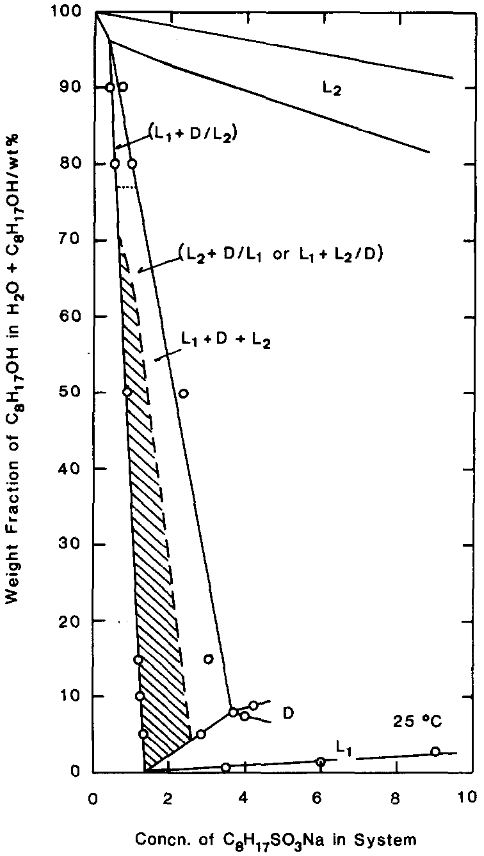


Fig. 3. Partial phase diagram of a $C_8H_{17}SO_3Na/C_8H_{17}OH/H_2O$ system in a dilute region at 25 °C. The stable foam is produced in a shaded area in a three-phase region. L_2 + LC/L_1, L_1 + L_2/LC and L_1 + LC/L_2 means L_1, LC, and L_2 continuous emulsions, respectively.

composition [13]. The lamellar liquid-crystalline phase (LC or D) coexists with aqueous (L_1) and alcohol (L_2) phases in a three-phase triangle in the three-component system at constant temperature and pressure. The partial phase diagrams of a $C_8H_{17}SO_3Na/C_8H_{17}OH/H_2O$ system were determined at 25 °C and are shown in Figs 2 and 3. There is a very narrow three-phase triangle in which the ratio of LC phase in systems is changed with a small increase in a surfactant concentration. In order to know the correlation between the foam stability and bulk property in a three-phase region, the type of emulsion in a bulk system was first investigated.

In the alcohol-rich region, an L_2 continuous emulsion was obtained. This emulsion was very unstable and a concentrated W/O emulsion immediately sedimented to the bottom of the container. Although a non-aqueous foam is possible in this area, the foam was extremely unstable; similar to that in a pure

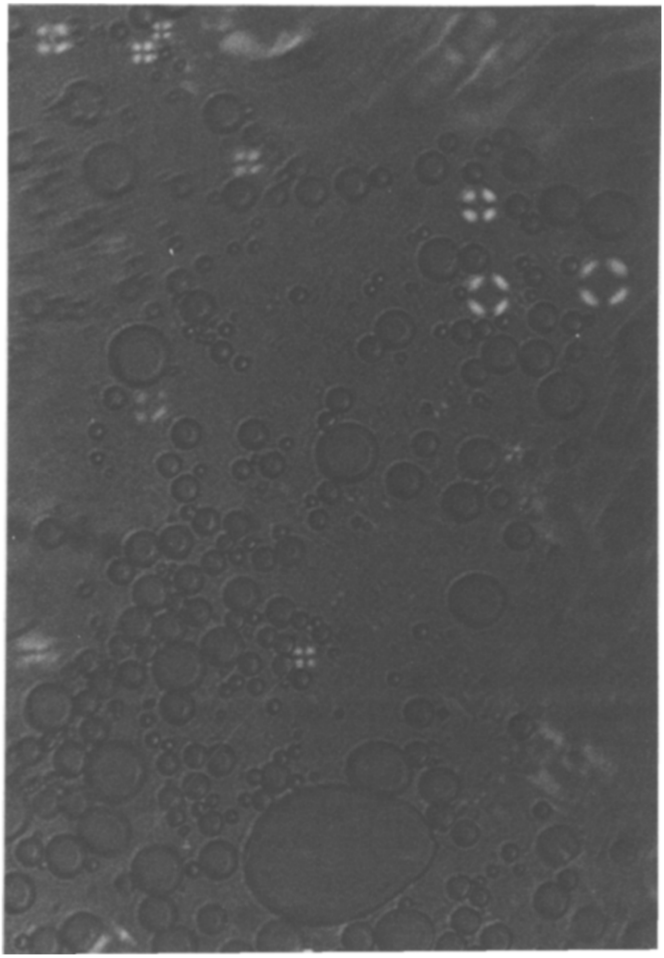
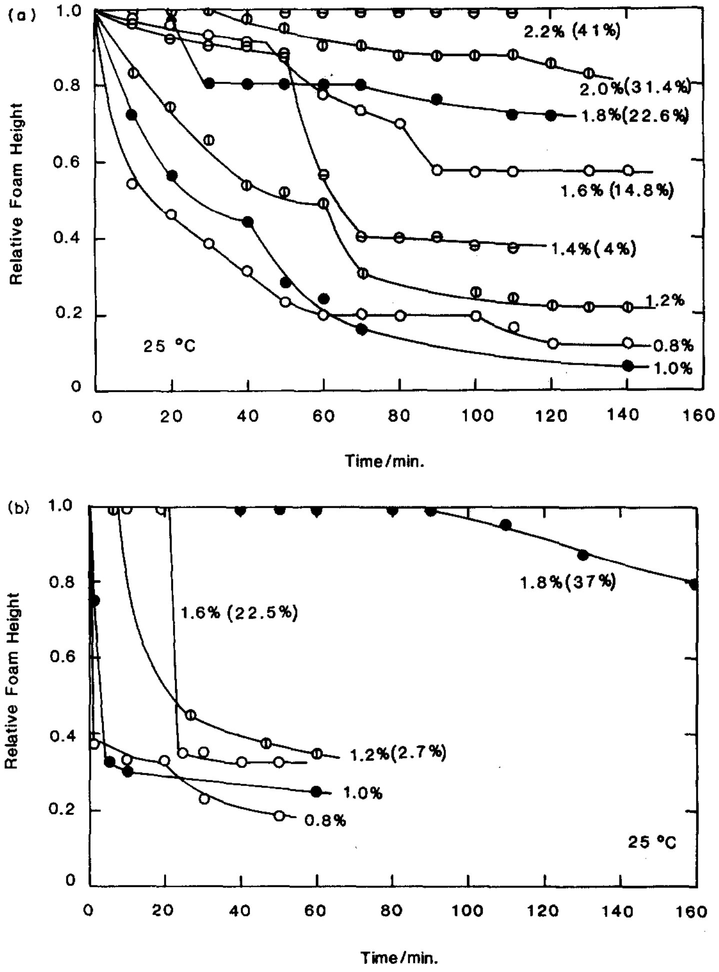


Fig. 4. The microphotograph of L_2 + LC/L_1 type emulsion under polarized light. A liquid-crystalline particle (shining particle) exists separately from an alcohol droplet. The concentration of $C_8H_{17}SO_3Na$ is 2 wt% in system. The octanol/water ratio is 25/75.

organic liquid. This type of emulsion was formed above an alcohol/water ratio of 77/23, where a phase inversion in the emulsions occurred. This volume ratio is almost the same value as that of close-packed spheres as expected for a hydrophilic surfactant preferentially stabilizing a water-continuous emulsion.

Below this ratio, $(L_2 + LC)/L_1$, i.e. L_1 emulsions or $(L_1 + L_2)/LC$ type emulsion, a paste was found depending on the phase volume ratio of LC and L phases. The boundary between these two kinds was very difficult to observe and no distinction was made, Fig. 3. The microphotograph of $(L_2 + LC)/L_1$ type emulsion under polarized light is shown in Fig. 4. As is shown in this figure, a liquid-crystalline droplet coexists with an alcohol droplet in the aqueous



solution. Although LC phase is not a normal liquid phase, the fact that separate L_2 and LC droplets exist means that the relation between interfacial tensions between respective phase is as follows:

$$\gamma_{L_1\text{-}L_2} < \gamma_{L_1\text{-}LC} + \gamma_{L_2\text{-}LC} \tag{1}$$

where $\gamma_{i\text{-}j}$ means the interfacial tension between i and j phases. This relation is the same as that in the three isotropic coexisting phases and, hence, the liquid-crystalline phase does not spread on the alcohol droplet.

When the phase volume ratio of the LC phase is very high inside of the three-phase region, the viscosity of the system becomes too high to produce a foam. That region is the non-shaded area in $(L_2 + LC)/L_1$ and $(L_1 + L_2)/LC$ regions in Fig. 3. As a result, as far as the emulsions are concerned, there are three areas inside of a three-phase triangle. One area is a $(L_1 + LC)/L_2$ emulsion,

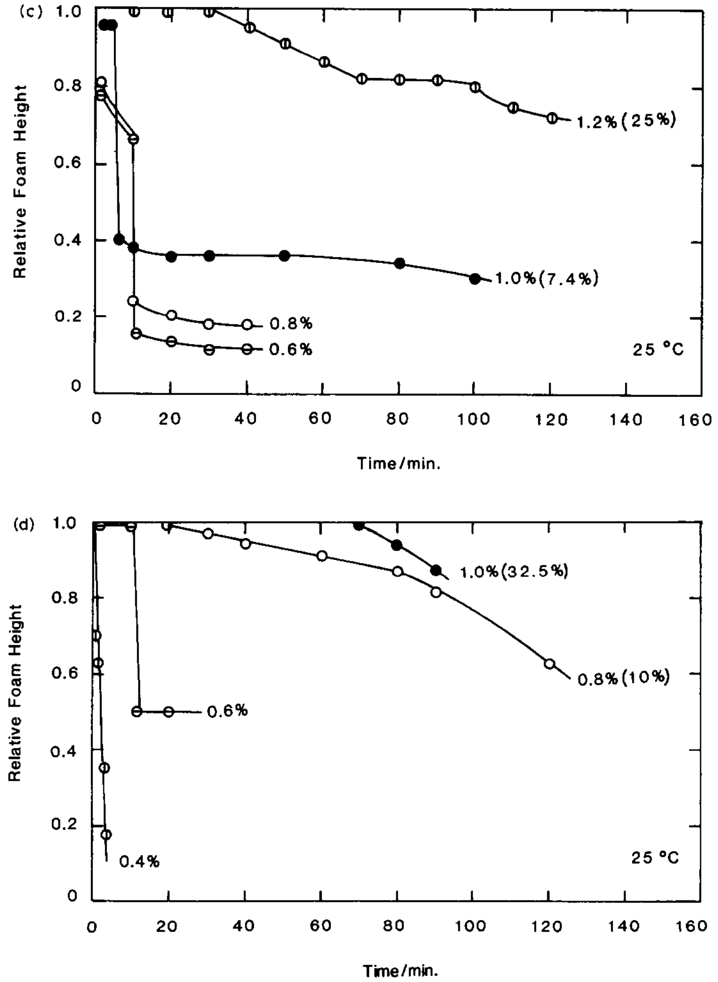


Fig. 5. Relative foam height as a function of time. Numerical numbers in the figure indicate the concentration of $C_8H_{17}SO_3Na$ in system. The numbers in parentheses indicate the weight percentages of LC phase in LC + L_1. Water/octanol ratio: (a) 90/10; (b) 75/25; (c) 50/50; (d) 37.5/62.5.

which is very unstable. The second is the (L_1 + L_2)/LC emulsion which may be located at higher surfactant concentration and the third is (L_2 + LC)/L_1 emulsion. There is practically no foam formation in the (L_1 + LC)/L_2 emulsion area because the emulsion is very unstable and the cream separated from the alcohol phase very quickly. In (L_2 + LC)/L_1 and (L_1 + L_2)/LC regions, when the system contains a large amount of LC or L_2 phases, it is very difficult to produce a foam due to the high viscosity. Therefore, the foam stability was measured in the shaded area in Fig. 3. The type of emulsion in this area was mainly (L_2 + LC)/L_1.

Foam stability in a three-phase region, (L_2 + LC)/L_1 emulsion

In the shaded area of Fig. 3, a (L_2 + LC)/L_1 type emulsion, i.e., water-continuous emulsion was produced. In order to understand the correlation between the foam stability and bulk properties in a three-phase region, the relative foam height was determined with change in the alcohol/water ratio and surfactant concentration as a function of time. The results are shown in Fig. 5. The water-/octanol ratios are (a) 90/10, (b) 75/25, (c) 50/50 and (d) 37.5/62.5, respectively. The numerical numbers in the figures indicate the concentration of surfactant in system. The numerical numbers within parentheses indicate the weight percent of LC phase in L_1 + LC. In the two-phase region of L_1 and L_2 phases, foam is very unstable compared to a foam in the three-phase region, but it is still more stable than the foam in $C_8H_{17}SO_3Na$ aqueous solution without alcohol, the life-time of which was less than one minute.

Since the stability of foam increases with increasing LC phase content, the presence of it has a stabilizing effect on the foam. The microphotograph of the foam in the L_2 + LC/L_1 region is shown in Fig. 6. Although the LC phase coexists with an alcohol phase and is not adsorbed at the L_2/water interface (Fig. 4), it is adsorbed at an air/water interface, i.e., at the surface of foam as is shown in Fig. 6. One aspect of the stabilizing action of the liquid crystal appears to be the action of an adsorbed thick and viscous film at the air/water surface.

The L_2 phase remains as a droplet inside of a film of foam. As described before, the viscosity of system increases with increasing LC and/or L_2 droplets. This effect contributes to increasing foam stability, because the most stable foam is achieved along the border of the "too-viscous region", the concentrated region of the shaded area.

Another factor concerning foam stability in a system with multiple phases in the condensed part of the foam is the partition of different phases between foam and drainage liquid. Hence, the relation between the foaming time and the phase volume ratio in the drainage phase has been measured and is shown in Fig. 7. For a system of 1.6 wt% of $C_8H_{17}SO_3Na$ and 98.4% of octanol—water [water/octanol ratio = 75/25 (w/w)], the volume fraction of the alcohol phase increased with increasing foaming time. This means that an alcohol phase is drained from the foam film, much faster than either the aqueous or the LC phase. Therefore, if a film contains a large amount of alcohol phase, the thinning of the film is rapid due to the fast drainage of the alcohol; e.g. the film reaches critical thickness faster. From the results in Fig. 5, even a stable foam collapsed after a while if the water/octanol ratio is low, i.e., containing a lot of alcohol phase.

CONCLUSION

The results demonstrate some features of the stability of foams from the investigated three-phase system water/oil/liquid crystal.

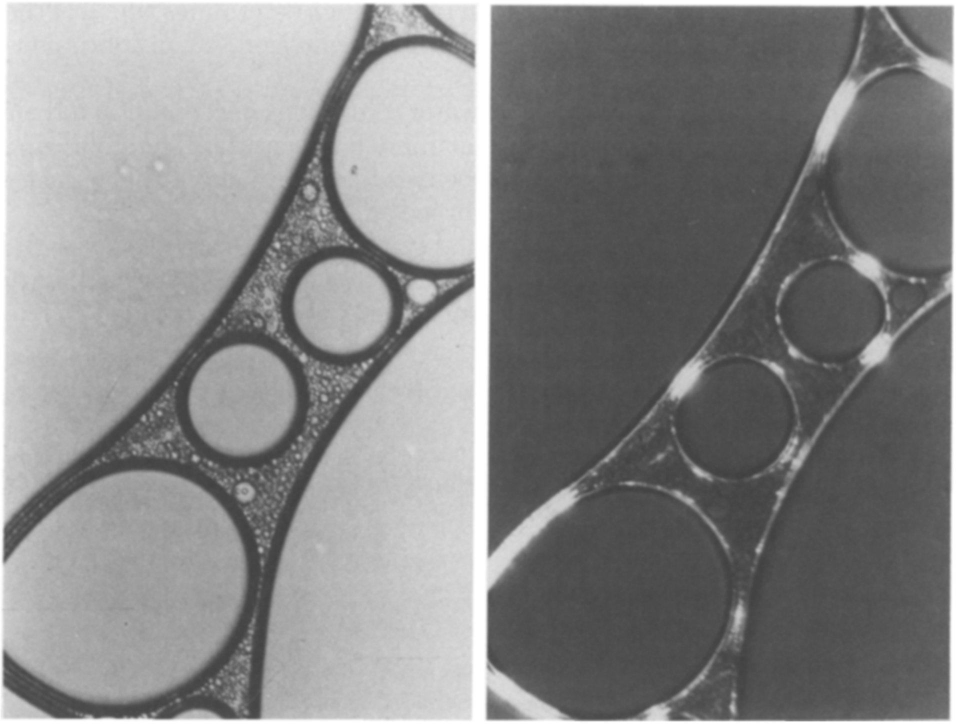


Fig. 6. The microphotographs of foam. (a) Under normal light; (b) under polarized light. The concentration of $C_8H_{17}SO_3Na$ is 1.6 wt% in system. $H_2O/C_8H_{17}OH$ ratio is 75/25 (w/w).

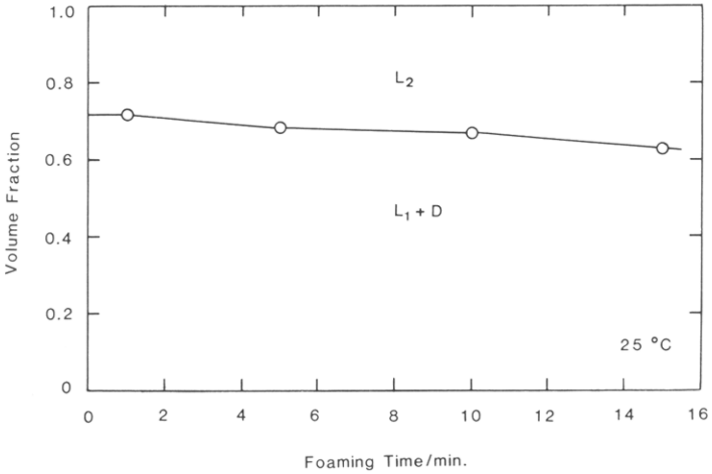


Fig. 7. The phase volume ratio in drainage as a function of a foaming time. The concentration of $C_8H_{17}SO_3Na$ is 1.6 wt% in system. $H_2O/C_8H_{17}OH$ ratio is 75/25% (w/w).

The decisive element was the water/oil ratio, which determines which of the two phases is the continuous phase in the original emulsion. An oil continuous system lead to unstable foams.

Foams from the emulsions, which are water continuous were stable and their stability was enhanced with increased amount of liquid crystal. The stabilizing action of the liquid crystal appeared to be two-fold: it enhanced the viscosity and, hence, retarded drainage and it adsorbed at the water/air interface.

For very high ratios of liquid crystal the system became continuous in this phase. The viscosity was now increased to such a level that the necessary spreading of the continuous phase to form a foam bubble was impeded and no foam can be formed.

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