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Amphiphilic association structures and some aspects of foam stability

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AMPHIPHILIC ASSOCIATION STRUCTURES AND SOME ASPECTS OF FOAM STABILITY

By

JIA-HWA FANG, 1957 -

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DOCTOR OF PHILOSOPHY IN CHEMISTRY

1986

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P. Neogi

Samir B. Hanna

To My Parents

PUBLICATION THESIS OPTION

This dissertation consists of four manuscripts. The first two sections have been prepared by following the UMR dissertation specifications. They supply background information for this investigation. The last two articles are being prepared for publication. The first article will be submitted for publication in The Journal of Dispersion Science and Technology. The second article will be submitted for publication in Journal of the American Oil Chemical Society.

ABSTRACT

This investigation was performed in order to study two interesting and important problems in foams.

Foam separation was studied in the model system of water - sodium octylsulfonate - decanol. The efficiency of foam separation as a function of surfactant concentration and decanol content were measured. The results were related to the association structures of amphiphiles in aqueous systems.

Foam polymerization was conducted in the amphiphilic system containing water, polymerizable surfactant and oleyl alcohol. Liquid foams were produced in one three - phase region. The location and optical pattern of liquid crystals on the foam surface were observed by photomicroscope with polarized light. Solid foams were obtained when the liquid foams polymerized.

The investigation was successful. The effect of amphiphile association structure on foam separation was established. The polymerized foam obtained in this study showed a novel development in solid foams.

ACKNOWLEDGMENTS

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INTRODUCTION

The present investigation covers two subjects, foam separation and foam polymerization, in aqueous surfactant systems.

Foam separation is a general name for separation techniques using foam as the separation medium (1-4). These separation processes are widely applied in practice. Examples are separation and collection of minerals from solutions (5-7), separation and recovery of surfactants (8-14), protein recovery by a continuous foam separation method (15), the removal of powdered active carbon from water (16), and the removal of heavy metals from waste water (17).

In the above applications, surfactants are usually present in the system to serve as surface active materials, carry the separated substances, and stabilize generated foam. Therefore, the behavior of surfactants in solution is an important factor for foam separation. The association structures of surfactants in aqueous systems have been extensively studied (18). One of the subjects of the present investigation is to establish the function of surfactant association structures and phase equilibria in foam separation.

The other subject is foam polymerization. In this study a polymerized, solid foam was obtained from an aqueous surfactant system at room temperature. This is a new and important development for making solid foams. Conventional solid foams are prepared from polymerized materials, such as polyurethane, polystyrene, polyvinyl chloride, etc. (19,20). The preparation process is quite complex. Polymers are fused or processed to expandable beads and additives are necessary for modifying the foaming conditions. However, in this investigation, the preparation of solid foam was simple and direct. Foaming from an aqueous system and polymerizing at room temperature are the most striking differences between and advantages of the present solid foams compared to conventional plastic foams.

This dissertation consists of four related parts. The first two sections are the literature review. Section I reviews surfactants and their association structures. Section II contains a general introduction to soap bubbles, foams, foam stability, and the effect of amphiphile association structures on foam stability.

For the second half of this dissertation, two articles concerning the present investigation, foam separation and foam polymerization were prepared for publication. Article I is a study of foam stability and foam separation in an aqueous surfactant solution with or without cosurfactant. The results are presented and discussed. The conclusion gives the relationships for the amphiphile association structures, foam surface structures, foam stability and foam separation.

Article II deals with the new preparation methods for solid foams. The experimental part describes the synthesis of a polymerizable surfactant. Association structures for this polymerizable surfactant combined with water and oleyl alcohol were determined. Foam stability in this three component system was studied. A stable liquid foam was polymerized to a solid foam. The results are a presentation of the phase diagram, foam stability, foam polymerization, and a microscopic study of the polymerized foam. The results are correlated and discussed. The conclusion is that the whole process of making polymerized foam is now feasible.

REFERENCES

1. Grieves, R. B., Kelman, S., Obermann, W. R., and Wood, R. K., Can. J. Chem. Eng. 41, 252 (1963).
2. Pinfold, T. A., Separ. Sci. 5, 349 (1970).
3. Talmon, Y., and Rubin, E., Separ. Sci. 11, 509 (1976).
4. Leonard, R. A., and Blacyki, J. D., Ind. Eng. Chem. Process Des. Dev. 17, 358 (1978).
5. Somasundaran, P., and Moudgil, B. M., J. Colloid Interface Sci. 47, 290 (1974).
6. Shakir, K., and Aziz, M., Transition Met. Chem. 4, 244 (1979).
7. Kelebek, S., and Smith, G. W., Int. J. Mineral Processing 14, 275 (1985).
8. Grieves, R. B., and Bhattacharyya, D., Nature 204, 441 (1964).
9. Grieves, R. B., Crandall, C. J., and Wood, R. K., Int. J. Air Wat. Poll. 8, 501 (1964).
10. Newson, I. H., J. Appl. Chem. 16, 43 (1966).
11. Zwierzkowski, W., and Medrzycka, K. B., Separ. Sci. 11, 581 (1976).
12. Zajic, J. E., Berk, D., and Behie, L. A., Can. J. Chem. Eng. 57, 321 (1979).
13. Charewicz, W. A., and Strzelbicki, J., J. Chem. Tech. Biotechnol. 29, 149 (1979).

14. Hsu, S. N., and Maa, J. R., Ind. Eng. Chem. Process Des. Dev. 24, 38 (1985).

15. Gehle, R. D., and Schugerl, K., Appl. Microbiol. Biotechnol. 20, 133 (1984).

16. Bishop, P. L., Separ. Sci. Tech. 13, 47 (1978).

17. Huang, S.-D., and Wilson, D. J., Separ. Sci. 11, 215 (1976).

18. Ekwall, P., in "Advances in Liquid Crystals." Vol. 1 (G. H. Brown, Ed.), Academic Press, 1975, P.1.

19. Benning, C. J., "Plastic Foams : the Physics and Chemistry of Product Performance and Process Technology." Vol. 1 & 2, John Wiley & Sons, New York, 1969.

20. Woods, G., "Flexible Polyurethane Foams, Chemistry and Technology." Applied Science Publisher, London, 1982.

I. AMPHIPHILE ASSOCIATION STRUCTURES

A. SURFACTANTS

Surfactants are amphiphilic substances also called surface active reagents, colloidal electrolytes, paraffin chain salts, and tensides (1). They are molecules which have a common form consisting of a polar portion and a nonpolar portion. The polar portion of a surfactant molecule is hydrophilic and interacts with water molecules. The hydrocarbon portion is hydrophobic and imcompatible with water molecules. The polar portion is called the head group and the nonpolar portion is the tail of the surfactant molecule. The head group may be anionic, cationic, nonionic or zwitterionic. The nonpolar tail may be linear or branched, saturated or unsaturated, and consist of hydrocarbon or fluorocarbon chains. In general, a circle (o) is used to represent the head group and a zigzag tail is used to represent the hydrocarbon chain. Figure 1 shows the schematic diagram of a surfactant molecule.

1. Anionic Surfactants

The most common types of anionic surfactant (2) are the alkali-metal soaps, which are the salts of naturally occurring fatty acids. The chain length of most useful soaps is between C_{12} and C_{18}. Above C_{20}, a soap generally becomes too insoluble to be used. Natural soaps have the disadvantage

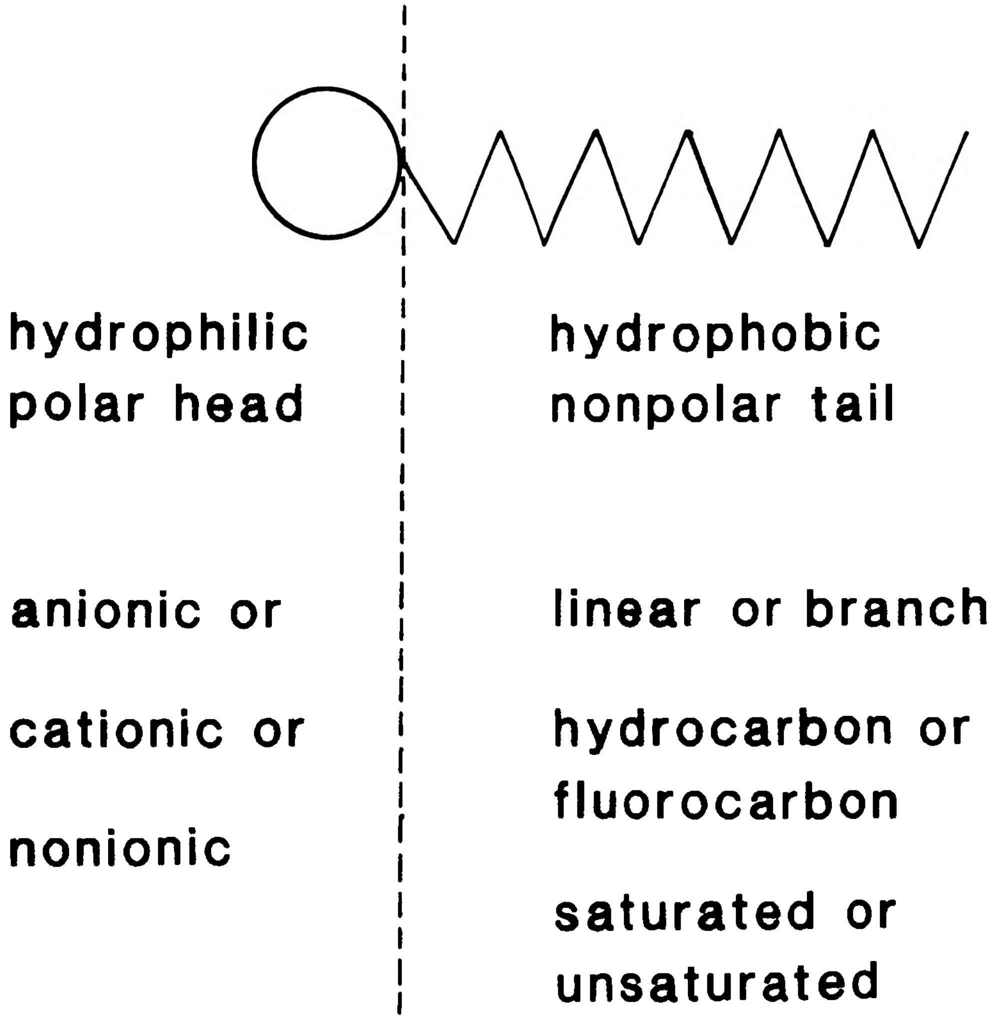

Figure 1. Schematic diagram and general structure of the surfactant molecule

of pH sensitivity. At low pH, the free acid forms reducing the amount of soluble soap.

Among synthetic surfactants, salts of organic sulfonic acids have a market similar to the natural soaps. Linear alkylbenzene sulfonates (LAS) are the major product of sulfonic acid salts. Their solubility is not affected by the presence of electrolyte or hard water or by low pH.

The third major group of anionic surfactants is the sulfuric acid ester salts, as for example, sodium dodecyl sulfate (SDS). Overall anionic surfactant has the largest market among all surfactants. It makes up about 73% of the U. S. surfactant markets (3).

2. Cationic Surfactants

Cationic surfactants include fatty quaternary ammonium salts, fatty amine salts, imidazoline derivatives, and pyridinium compounds. They have a positively charged nitrogen atom connected with at least one hydrophobic alkyl chain of 8 to 22 carbon atoms. The anions of cationic surfactants may be halogens, methylsulfate or dimethyl phosphate, but the halogens are the most common anions used (4).

Cationic surfactants are strongly adsorbed onto negatively charged surfaces, because of their positive charges. Hence, they have a high affinity for textile (cotton, cellulose fibers etc.), mineral (clay minerals, soil colloids) and biological (bacterial) surfaces. These particular properties make possible wide applications of cationic surfactants as disinfectants, antiseptics, fabric softners, antistatic agents, water-repellent agents, flotation chemicals, corrosion inhibitors, foam depressing agents, etc (1).

Cationic surfactants are important to the detergent industry due to their fabric softening and antistatic properties. Dialkyl quaternary ammonium salts with chain length 16-18, and imidazoline derivatives are the major surfactants used for this purpose. Reviews of the use of cationic surfactants in laundry detergents and of their ecological behavior are available (5,6).

3. Nonionic Surfactants

The most known and most studied series of nonionic surfactants is the polyoxyethylene glycol monoethers, $RO(CH_2CH_2O)_nH$, where R is a saturated hydrocarbon chain or an alkyl chain with a aromatic rings (7). The solubility of these compounds in water depends on the number of ethylene ether groups, the structure of the hydrocarbon chain and the temperature. Their water solubility increases with the number of ethylene ether group and decreases with the length of the hydrocarbon chain. The temperature effect on the solubility of nonionic surfactants in water is negative. They become less soluble at high temperatures. At a certain narrow temperature range, the solution becomes turbid. This is called the cloud point.

Nonionic surfactants are commonly used in the detergent industry. They are stable in hard water or salt water and they are unaffected by changes in solution pH. There are two shortcomings of nonionic surfactants which limit their use in certain fields. First, their poor foaming power and poor foam stability compared to those of the anionic surfactants. Some nonionic surfactants foam well but in limited ranges of temperature and concentration. Second, most nonionic surfactants are viscous liquids or soft pastes at room temperature. They are not easily formulated as dry, free-flowing powders (8).

4. Zwitterionic Surfactants

Zwitterionic surfactants, also called amphoteric amphiphiles (9), are surfactants containing both anionic and cationic polar groups. The naturally occurring zwitterionic surfactants are phospholipids such as lecithin, which is one of the few edible surfactants (10). Commercial lecithin is used as an emulsifying agent in the cosmetic, textile and leather industries (8). PH-sensitive zwitterionic surfactants show the properties of cationic surfactants at low pH. At high pH, they show anionic surfactant properties. PH-insensitive zwitterionic surfactants show both anionic and cationic properties at all pHs (3).

B. ASSOCIATION STRUCTURES

Most surfactants have crystalline structures and many of them show the characteristics of thermotropic liquid crystals when heat is applied. Surfactant molecules have both short range and long range ordered structures, which arise from the crystalline packing of hydrocarbon tails and the layered structure of molecules respectively (Fig.2A). When solid crystalline surfactant is heated, thermal energy causes the onset of free rotation of the hydrocarbon chains and destroys the short range order (Fig.2B). At this stage, the surfactant molecules exist as a liquid crystalline phase with long range organization only. With additional energy, the long range order disappears, and the molecules can move randomly within the system (Fig.2C). On the other hand, when water is added to surfactant molecules (Fig.3), the crystalline molecules will form (lyotropic) liquid crystals, micelles and monolayer structures with increasing amounts of water. An example is given by Figure 4 which shows the variation in behavior of a cationic surfactant (dodecyl trimethyl ammonium chloride) as a function of temperature and water content (11). Below $90^{\circ}C$, the surfactant is in the solid state. Above $90^{\circ}C$, the lamellar liquid crystal phase is formed. With addition of water at $40^{\circ}C$, the lamellar liquid crystal phase appears at 6% water content, an isotropic viscous phase exists at 10% - 18%, hexagonal liquid crystal phase appears at 20% - 43%, another isotropic viscous phase is present at 46% - 53%, and finally

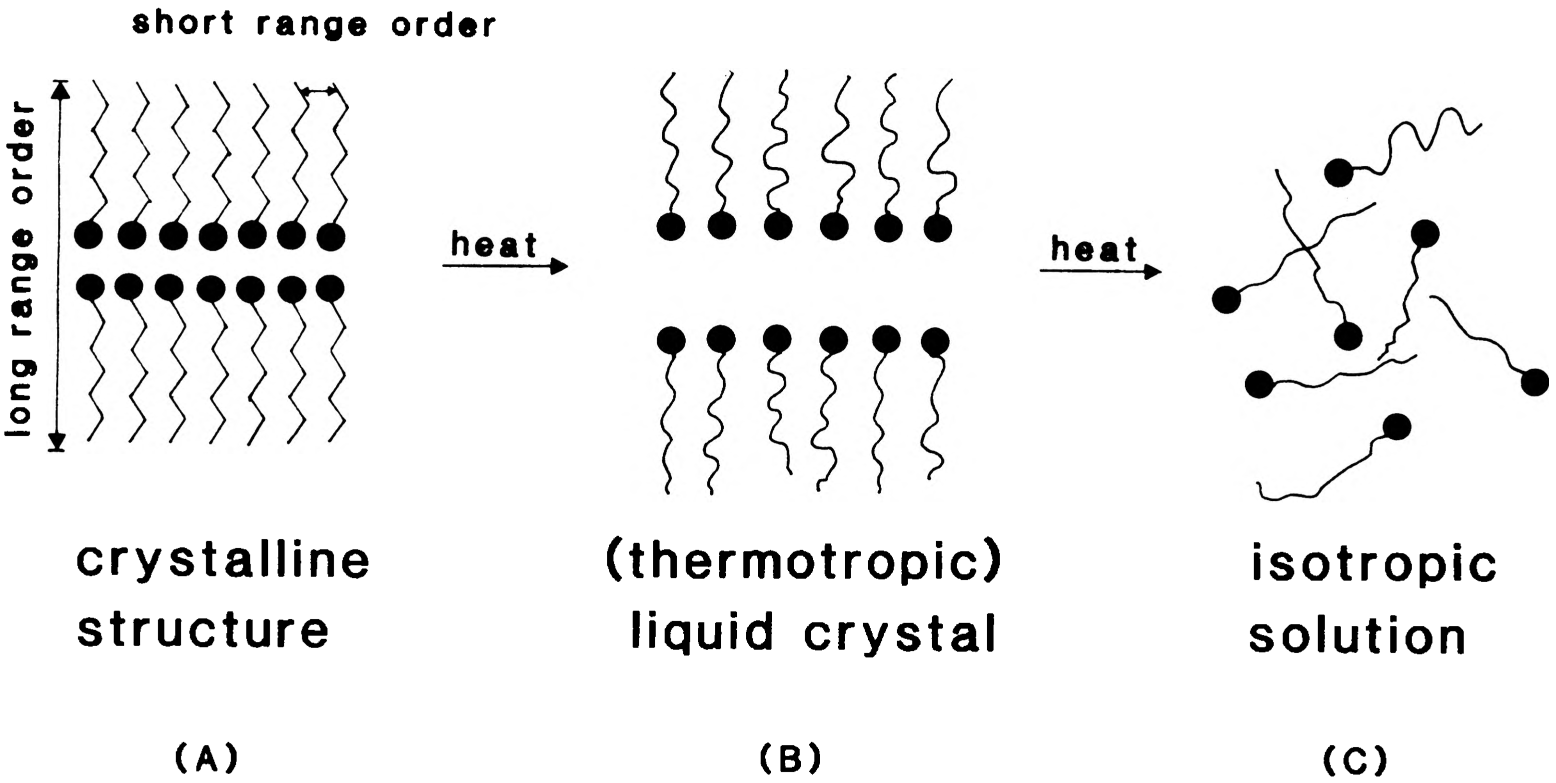

Figure 2. Structural forms for thermotropic liquid crystal forming surfactants as a function of temperature

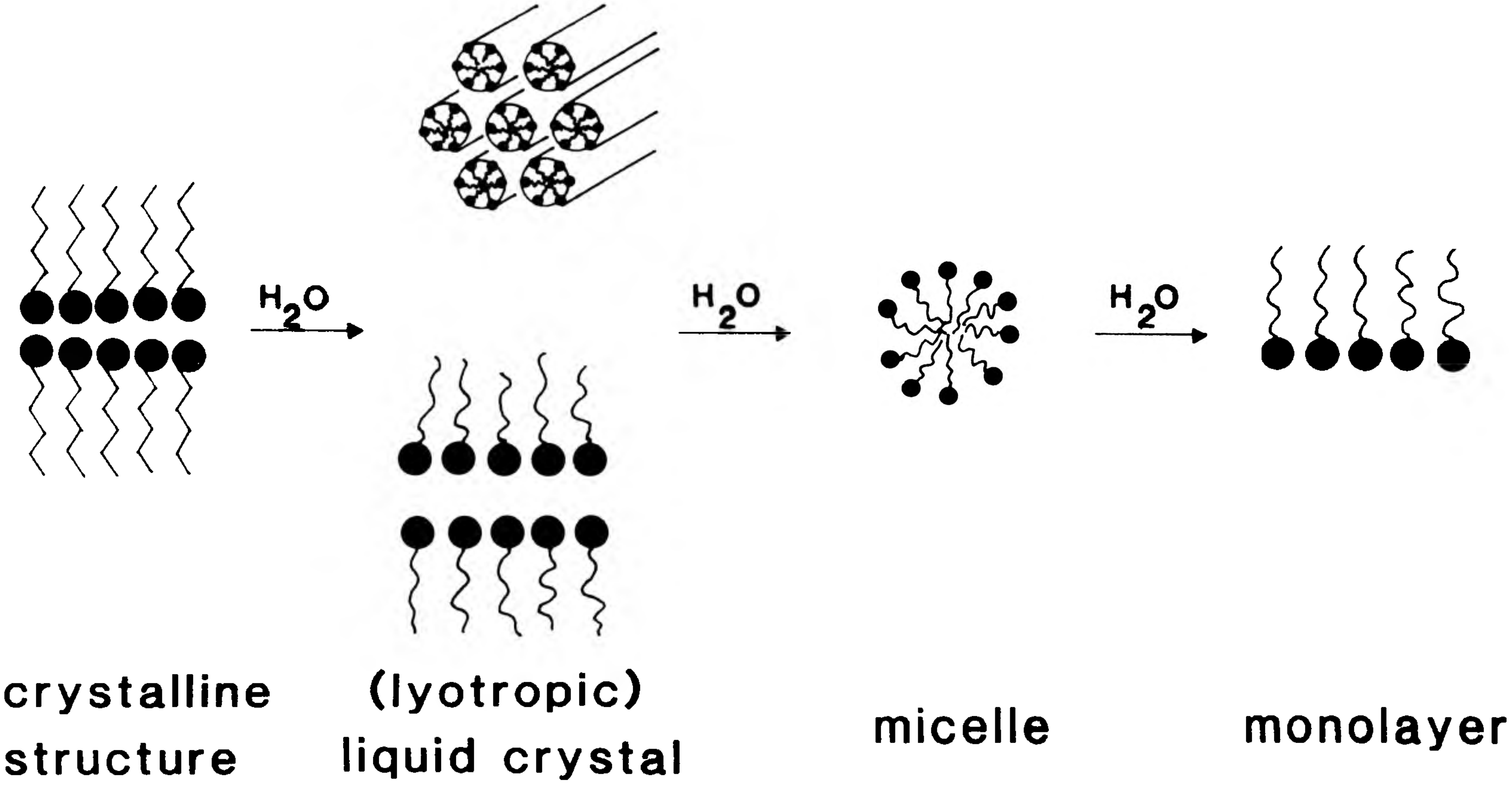

Figure 3. Structural forms for lyotropic liquid crystal forming surfactants as a function solvent content

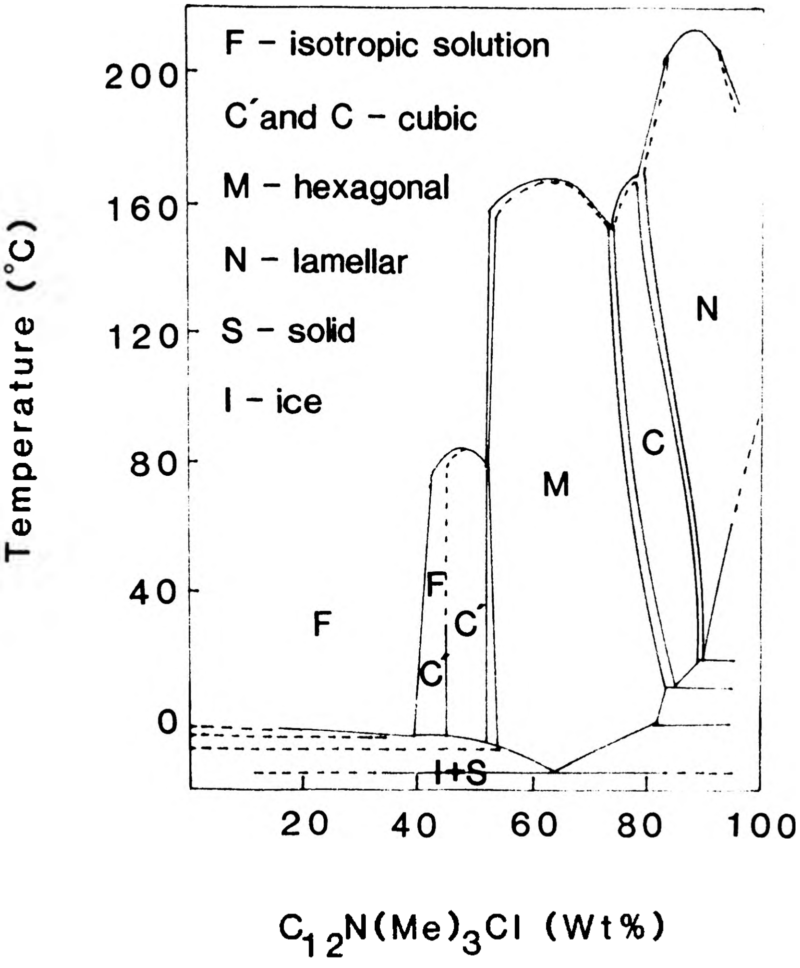

Figure 4. Phase diagram for dodecyltrimethylammonium chloride and water (11)

the completely isotropic solution phase appears at 58% to 100% water content (Fig.4).

1. Lyotropic Liquid Crystals

As shown in Figure 3, lyotropic liquid crystal is obtained by the addition of a solvent (water). Depending on the geometric arrangement, lyotropic liquid crystals are divided into lamellar, hexagonal, nematic and cubic structures (12-14).

a. Lamellar Liquid Crystals

Figure 5 shows that the lamellar structure consists of an amphiphile bilayer and a water layer. The thickness of each repeating layer is determined by small angle x-ray diffraction. Bragg spacing ratios of 1 : 1/2 : 1/3 : 1/4 are characteristic of a lamellar structure. The optical patterns of lyotropic liquid crystals have been extensively studied by Rosevear (15,16). Lamellar phases show three typical patterns, Maltese crosses (Fig.6), an oily streak pattern (Fig.7) and striated patterns (Fig.8).

b. Hexagonal Liquid Crystals

There are two types of hexagonal phases, normal and inverse, as shown in Figure 9. The surfactant molecules aggregate as cylinders which are in a two-dimensional hexagonal arrangement. When the head group of the surfactant

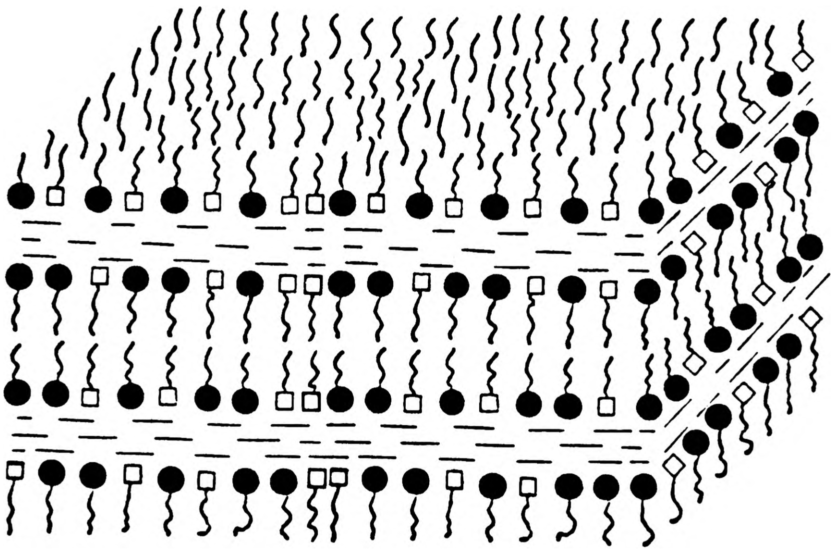

Figure 5. Schematic diagram of lamellar liquid crystal phase

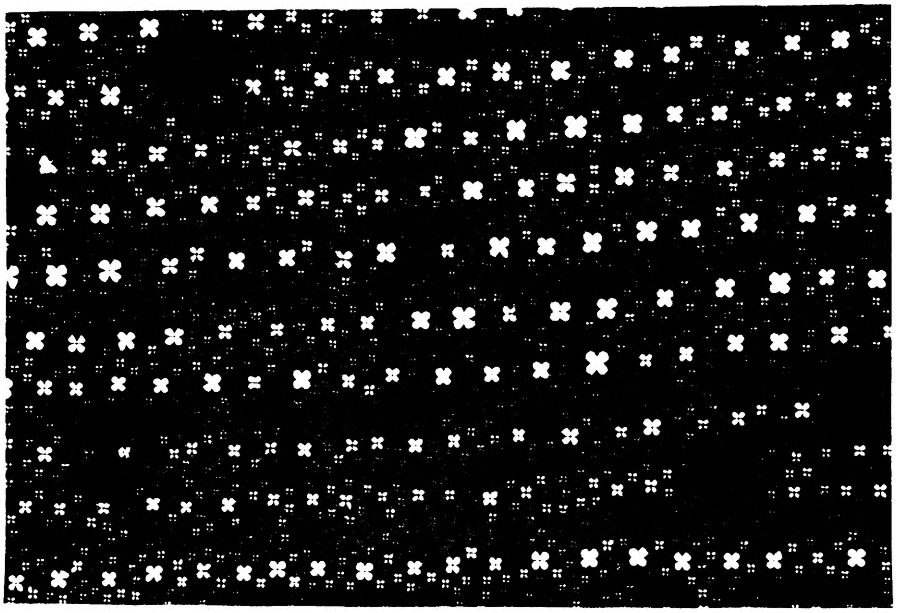

Figure 6. Maltese cross optical pattern of a lamellar liquid crystal

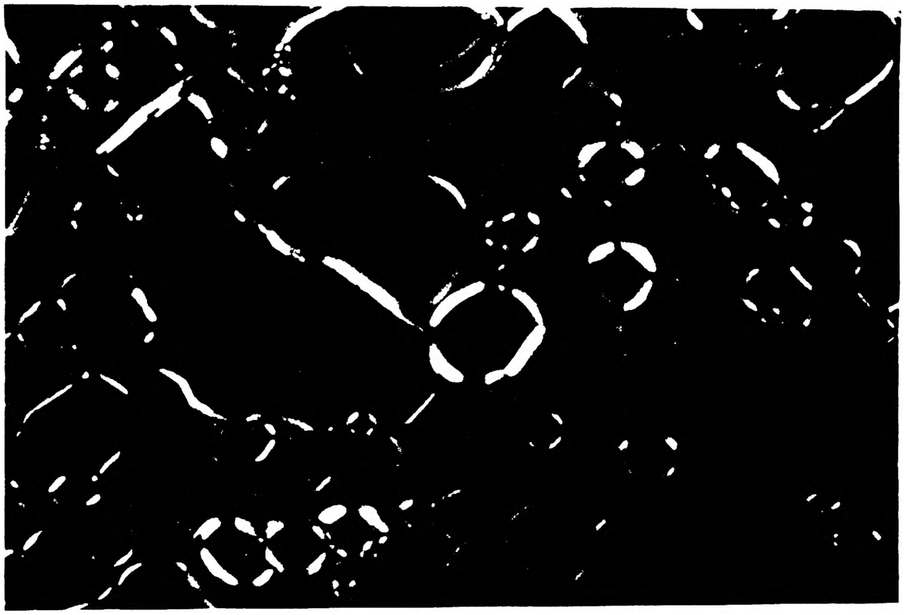

Figure 7. Oily streak optical pattern of a lamellar liquid crystal

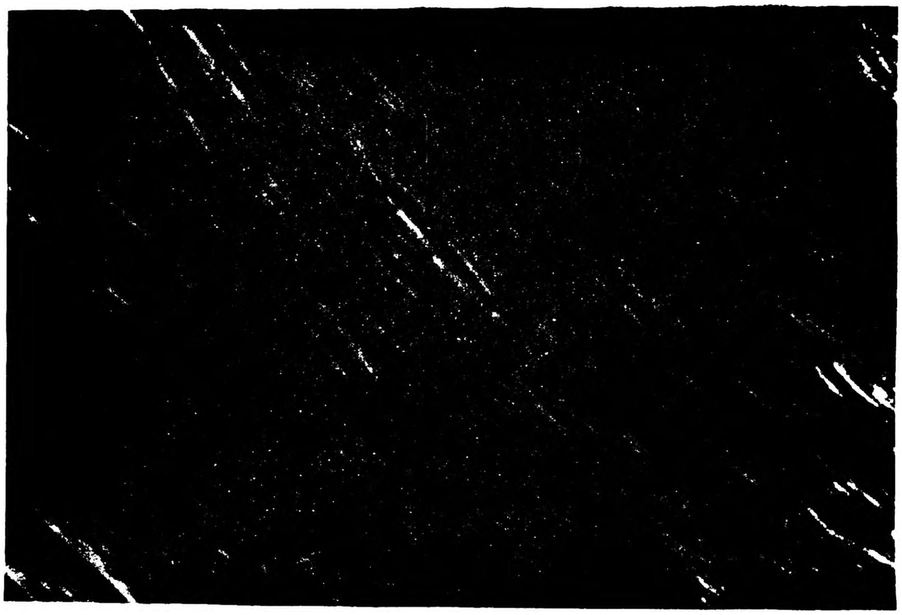

Figure 8. Striated optical pattern of a lamellar liquid crystal

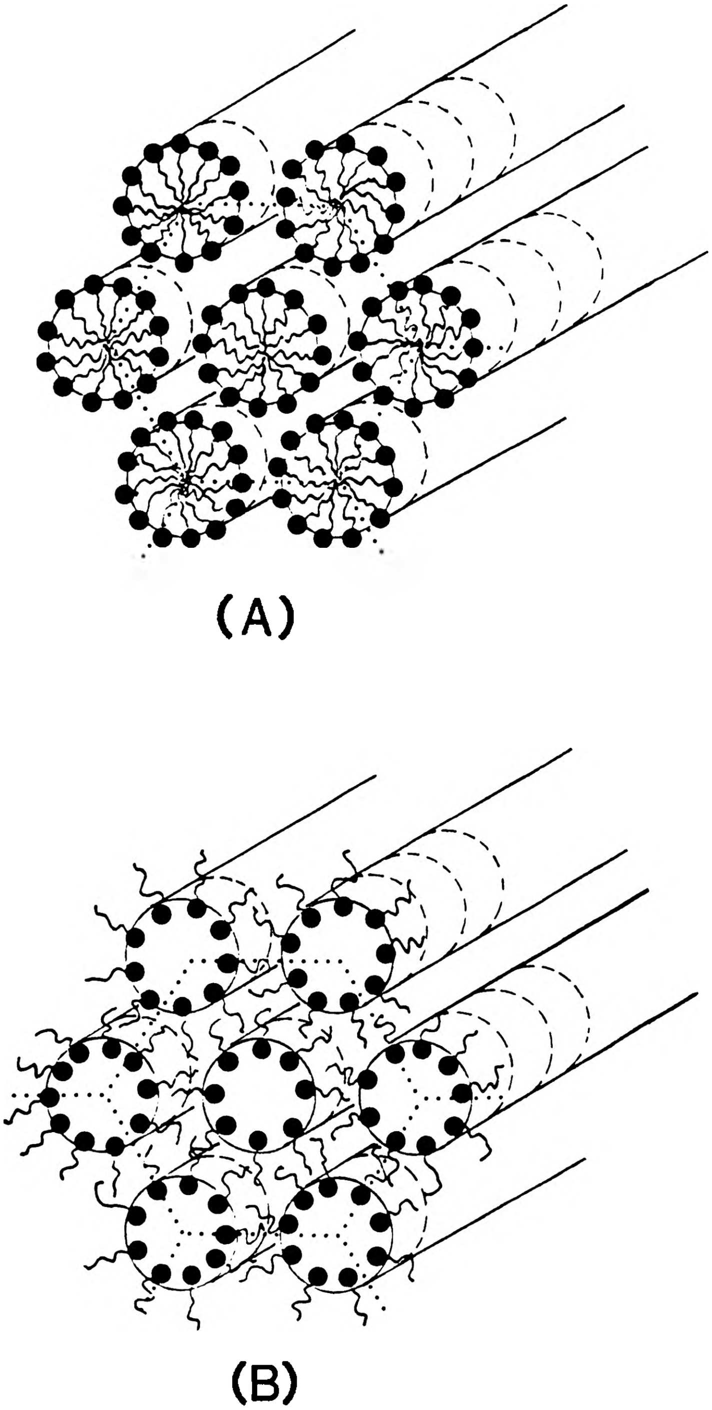

Figure 9. Schematic diagram of (A) normal and (B) inverse hexagonal liquid crystals

molecules is located on the surface of the cylinder, the phase is called normal hexagonal. When the head group faces the cylinder core and the hydrocarbon tails make up the cylinder surface, the structure is called inverse hexagonal. Except for different interlayer spacing, both normal and inverse types have the same Bragg spacing ratios and optical patterns. The Bragg spacing ratio for hexagonal phase is $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7}$. Figure 10 shows the characteristic angular geometric optical pattern which is observed under the microscope with crossed polarizers.

c. Cubic Liquid Crystals

The cubic phases have been observed in some systems at locations between lamellar and hexagonal phases (11,12,17,18), and between hexagonal liquid crystal and clear solution phases (11,12). The special characteristics of cubic phases are their extremely high viscosity and optical isotropicity. Hence, cubic phases are also called "viscous isotropic" phase structures. Cubic phases can be distinguished from isotropic phases by small angle x-ray diffraction (11,12,17,18).

d. Nematic Liquid Crystals

Nematic liquid crystals are a new and less common lyotropic mesophase. A nematic phase can be easily aligned by a magnetic field and has been suggested for use as an ordering

Figure 10. Optical pattern of a hexagonal liquid crystal

solvent which will orient small solute molecules for NMR studies (19). However, progress in investigating nematic liquid crystal has not been rapid.

2. Micelles

a. Normal Micelles

The crystalline structure of a surfactant molecule will be changed to the liquid crystal, micellar, and monolayer structures by the addition of water as illustrated in Figure 3. If a small amount of surfactant is added to a huge amount of water, the surfactant molecules are dissociated by water and adsorbed monomolecularly on the water surface due to their surface active properties. With increasing amounts of surfactant, the surface becomes saturated and all additional surfactant molecules form spherical normal micelles in solution (Fig.11A). Normal micelles exist in polar environments, with the polar part of the surfactant molecules exposed to the polar solvent and the hydrocarbon tails forming the micellar core.

b. Inverse Micelles

When surfactant molecules are placed in a nonpolar environment, the hydrocarbon tail interacts with the solvent and the polar head groups will avoid contact with nonpolar solvent. The presence of some water is necessary to solvate

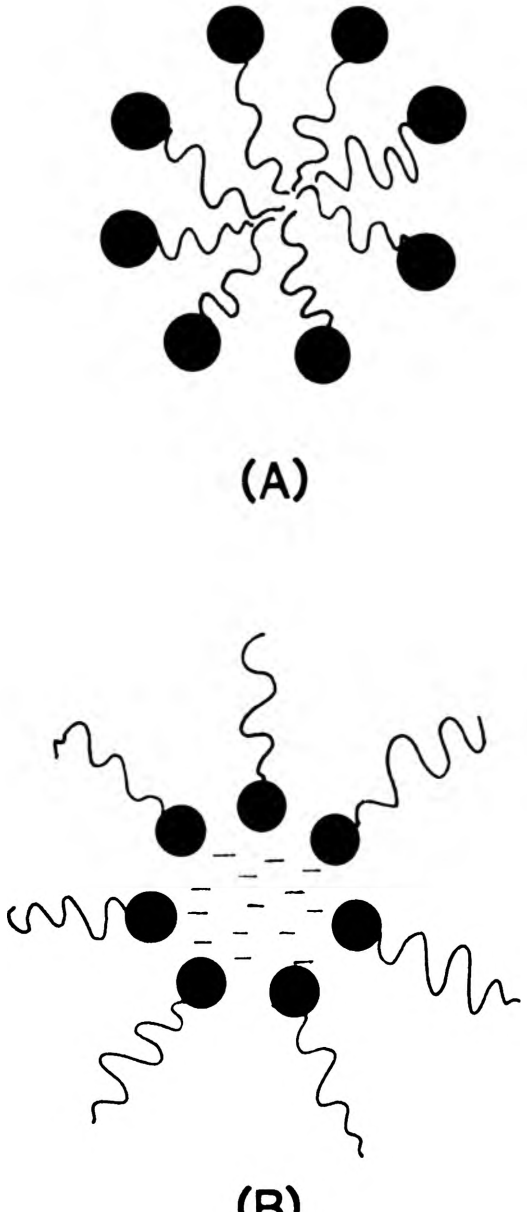

Figure 11. Schematic diagram of (A) normal and (B) inverse micelles

these head groups. An inverse micelle structure is formed (Fig.11B).

c. Multicomponent Systems

When a third component is added to the binary water - surfactant micellar system (Fig.12A), its location depends on its polarity. For example, hydrocarbon is insoluble in water but has about 5 wt% solubility in an aqueous micellar solution. The hydrocarbon is solubilized into the hydrocarbon tail core in normal micelles (Fig.12B). Solubilized materials of medium polarity, such as alcohols, will be incorporated between surfactant molecules with their polar end facing the water phase (Fig.12C). However, the maximum solubility is still low.

The most useful system combines water, surfactant, alcohol, and hydrocarbon. This combination gives a much enhanced mutual solubility of both water and hydrocarbon (Fig.13). Alcohol is called cosurfactant in this system and the clear solutions obtained by these combinations are called microemulsions (20-22). Depending on the continuous phase, water in oil (W/O) and oil in water (O/W) microemulsion are possible. The structures of the micelles in W/O and O/W microemulsions are shown in Figure 13. It has been demonstrated that the W/O microemulsion region is a direct continuation of the inverse micellar solution region in a three component system of water, surfactant and cosurfactant

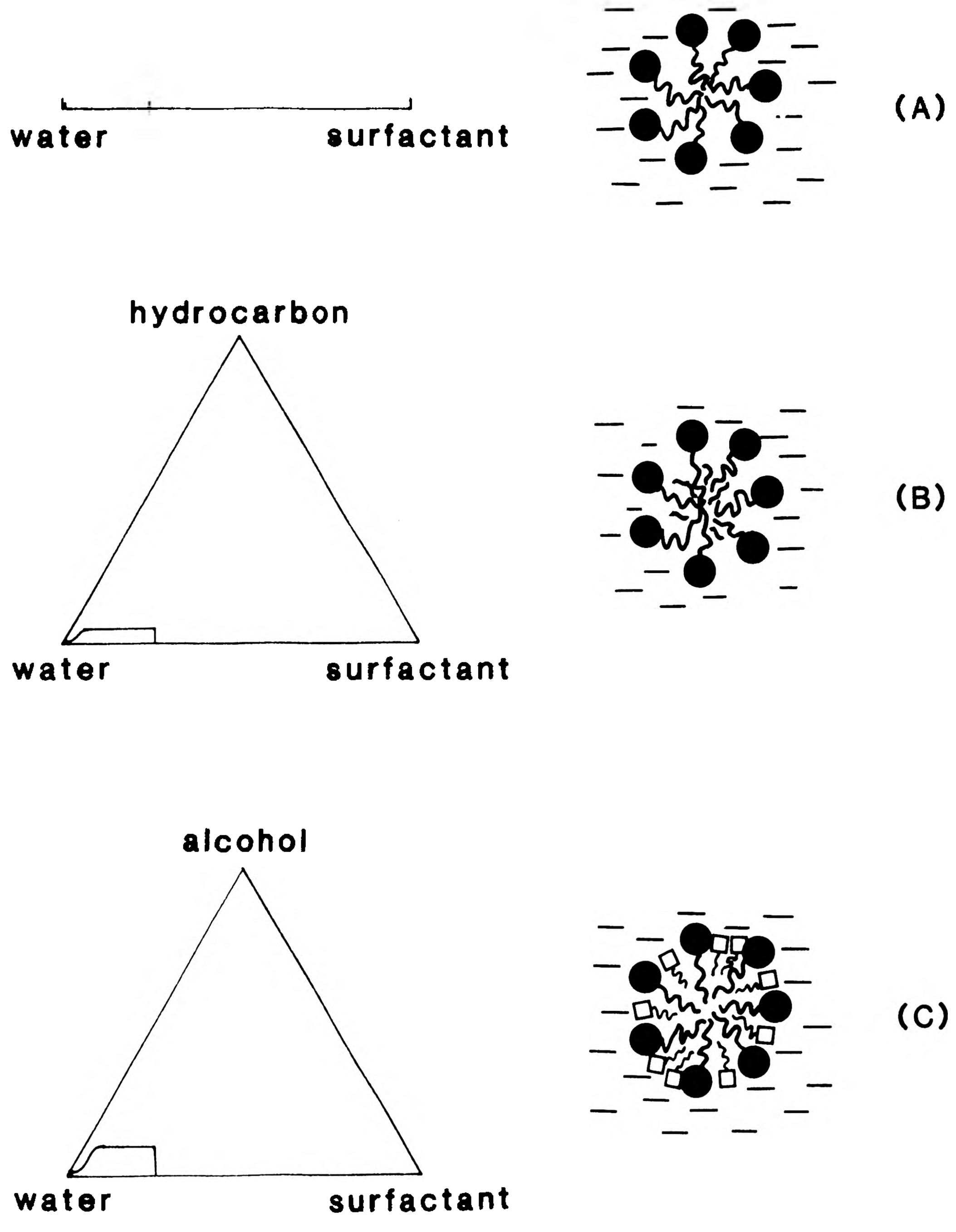

Figure 12. Illustration of normal micelle structures in (A) water-surfactant (B) water-surfactant-hydrocarbon (C) water-surfactant-alcohol systems

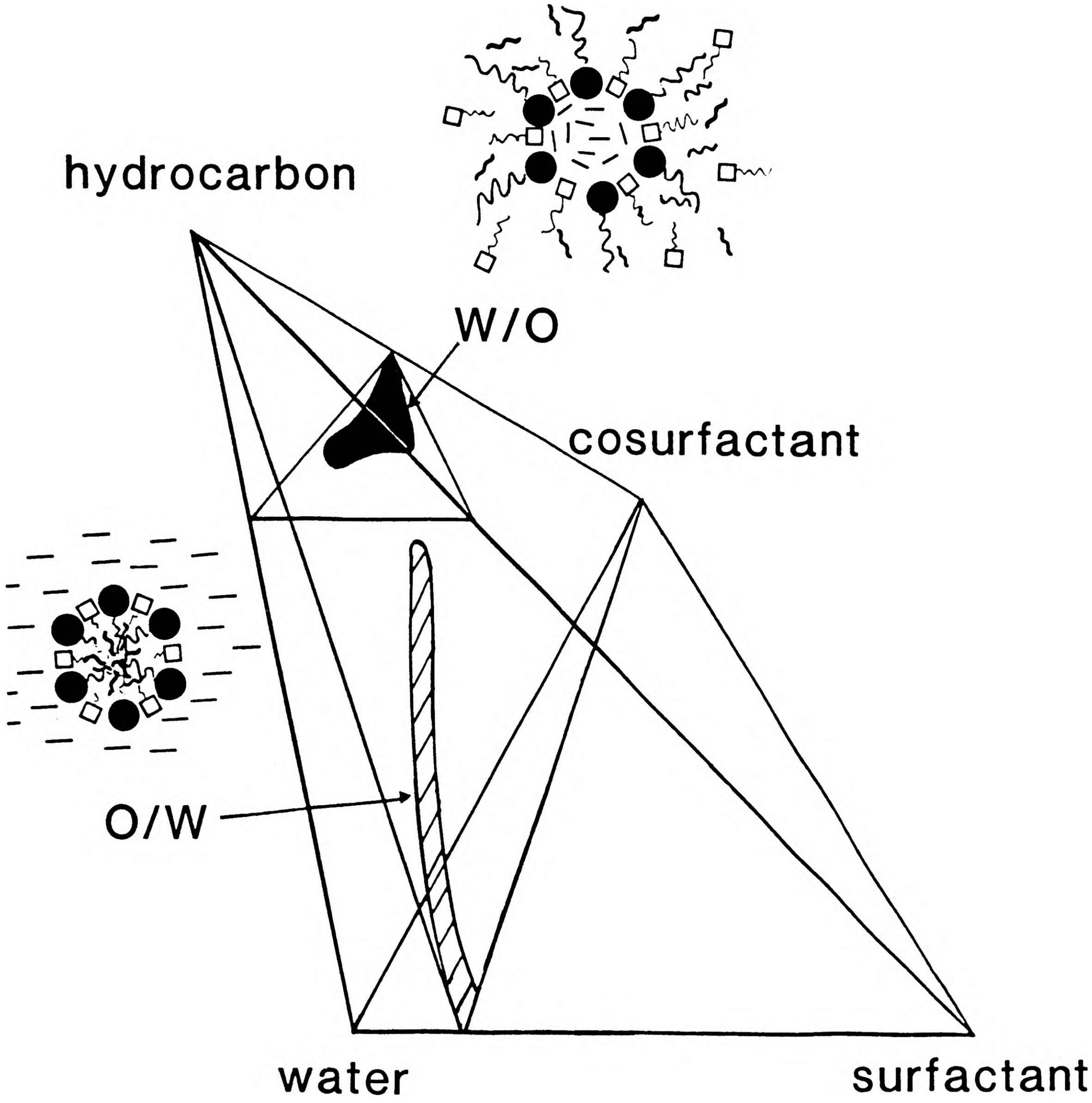

Figure 13. Phase diagram showing W/O and O/W microemulsions (21)

(22). The complete phase diagram for this system is shown in Figure 14.

d. Applications

The properties of amphiphile association structures provide numerous studies for science and applications for industry. Microemulsions have been applied to tertiary oil recovery, lubrication and corrosion inhibition, artificial photosynthesis and drug delivery etc (23). Liquid crystals are important in the stability of foam and emulsion (24,25).

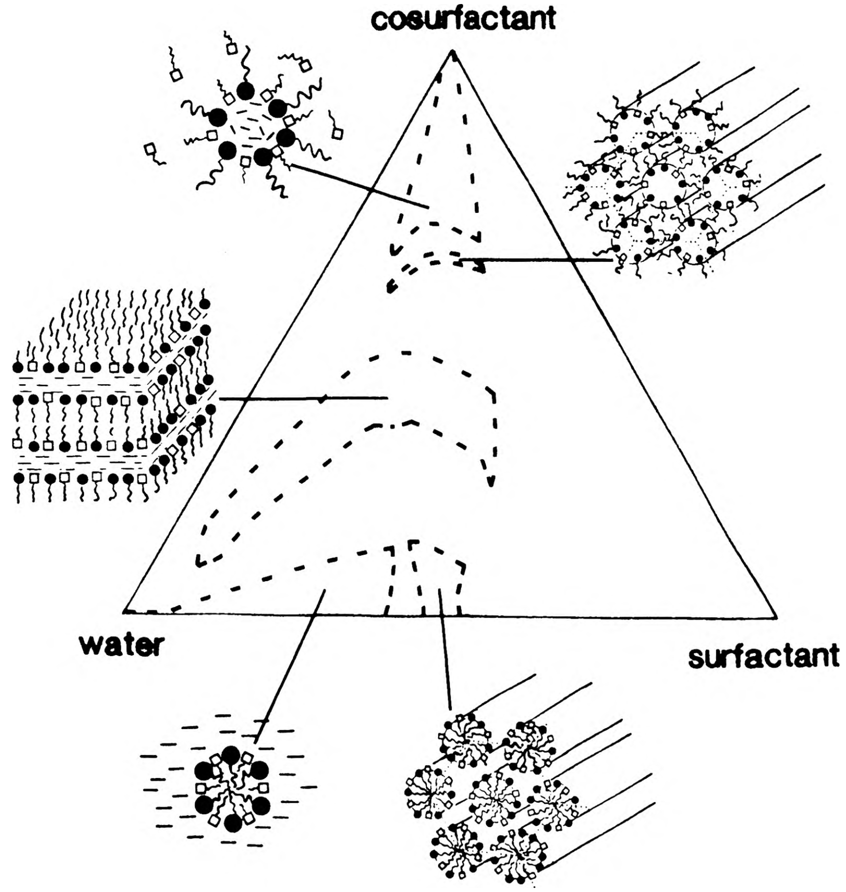

Figure 14. Typical ternary phase diagram of a water-surfactant-cosurfactant system (14)

II. FOAMS

A. SOAP BUBBLES

The beauty of soap bubbles has not only attracted children but has also attracted scientists to the study of the formation, structure, and stability etc., of soap films and bubbles for over two centuries (26).

Natural soaps are alkaline salts of animal or vegetable fatty acids. They are composed of a long hydrocarbon chain as the nonpolar part and a terminal carboxylate ion as the polar part. Synthetic soaps have similar structure to natural soaps but the polar part can be anionic, cationic, or nonionic, such as sulfate, quaternary ammoniums and polyether esters respectively. Due to their dual nature, soap molecules play an important role in the formation, structure and stability of foam.

1. Structures

A typical structure of a soap bubble is shown in Figure 15. The bubble is spherical in shape. Soap molecules are adsorbed monomolecularly at the gas/liquid interfaces between the inside gas and the surrounding solution, and between the surrounding solution and the atmosphere. As a result of hydrophobic interactions, the hydrocarbon chain of the soap molecules is out of the interface and is exposed to the gas phase. The anionic polar groups of the soap molecules are at

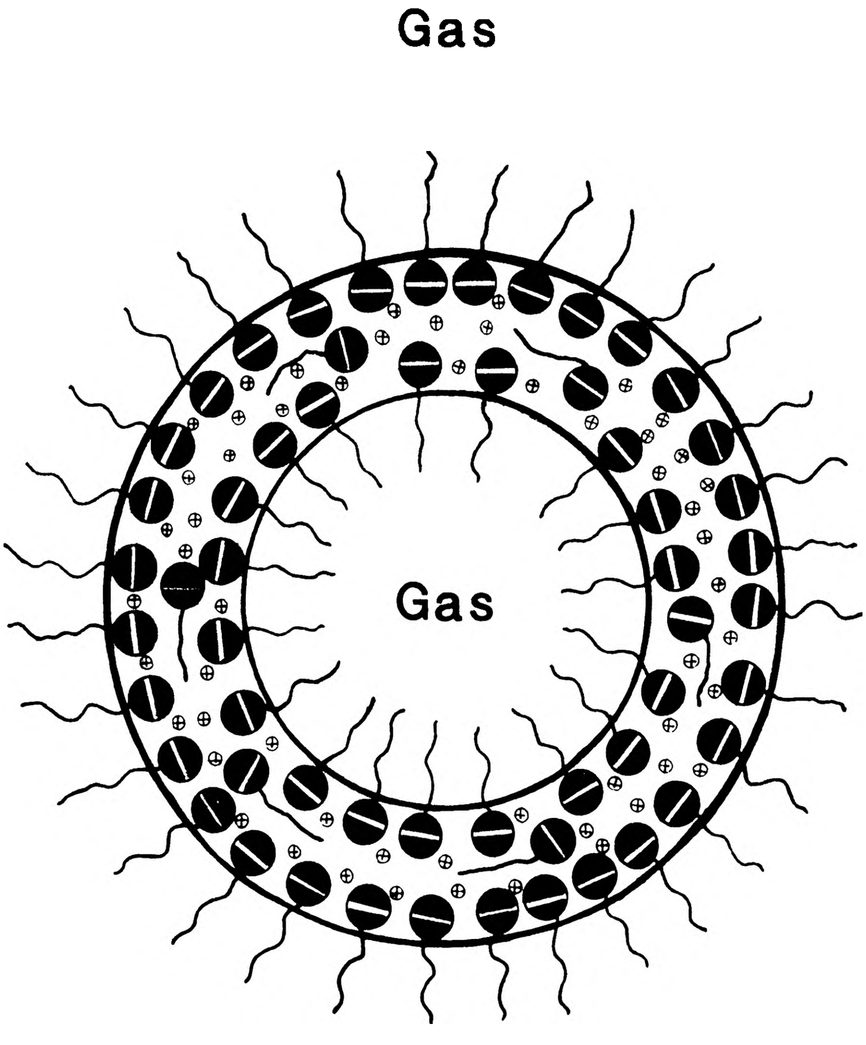

Figure 15. Schematic Structure of an individual soap soap bubble

the surface of the liquid, and the counterions are distributed around the polar groups.

When the soap bubbles with different radius (r_1 and r_2) approach each other and flocculate (Fig.16A), each bubble is still largely covered by spherical soap film shell. The two bubbles are separated by a curved internal surface of soap film with radii of curvature (r') satisfying the following equation (27):

$$r' = r_1 r_2 / (r_1 - r_2)$$

The curved interface is due to the pressure difference between neighboring bubbles of different sizes. In the case of $r_1 = r_2$, the pressure difference is zero, and, from above equation, $r' = \infty$, the two flocculating bubbles are separated by a straight plane (Fig.16B). When a very small bubble is in contact with a much bigger bubble (i.e. $r_2 << r_1$), then, $r' \approx r_2$, and there is almost no deformation of the very small bubble (Fig.16C).

The main feature of these flocculated bubbles is that the angles of intersection of the tangent planes to the three soap film surfaces are 120^o. This relationship is also valid for all bubble clusters with three or more bubbles.

Foam is a bubble cluster containing a large number of different sized bubbles. The structure of foam consists of polyhedral cells with different faces (Fig.17). These faces

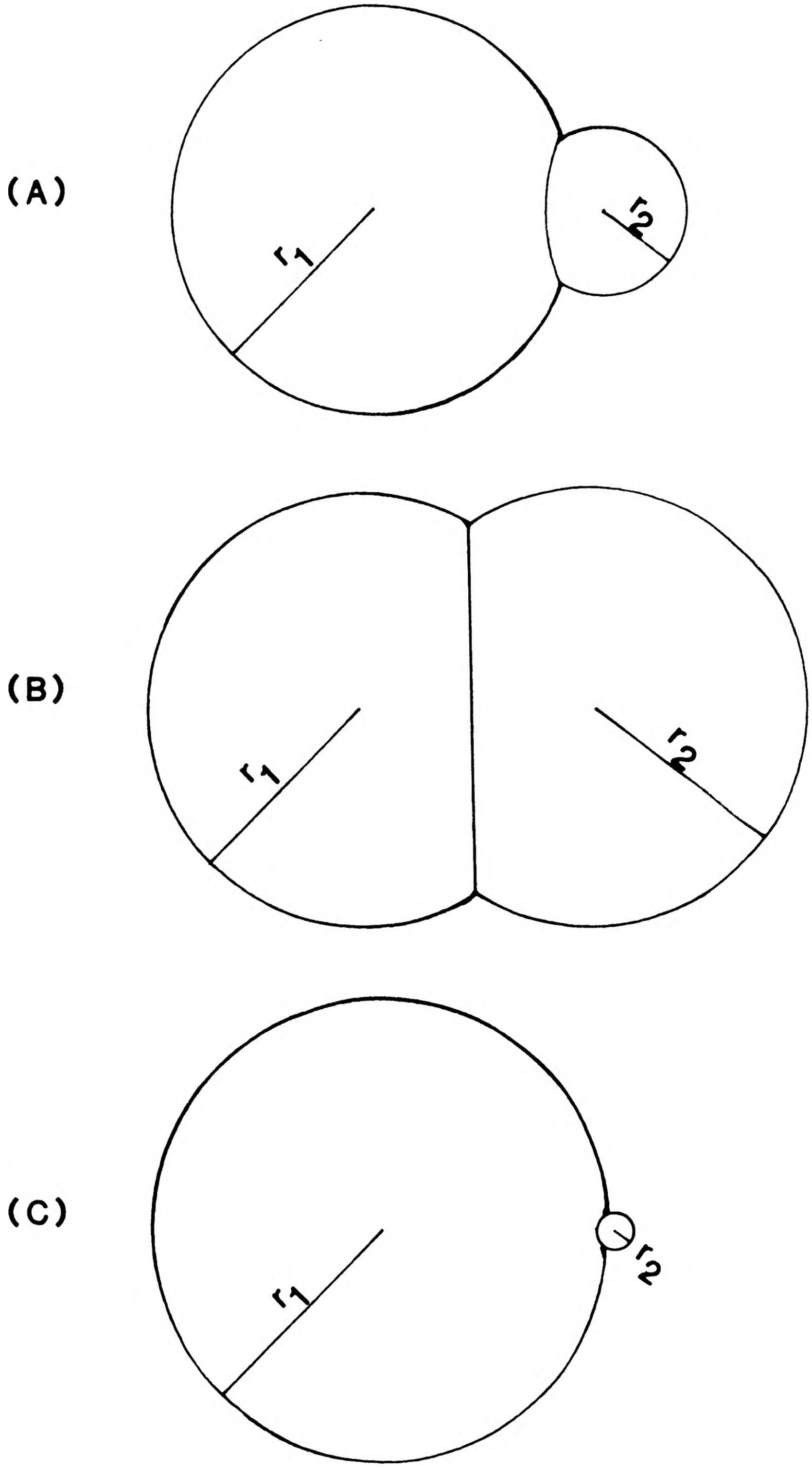

Figure 16. The flocculation structure of two bubbles in contact (A) $r_1>r_2$ (B) $r_1=r_2$ (C) $r_1>>r_2$

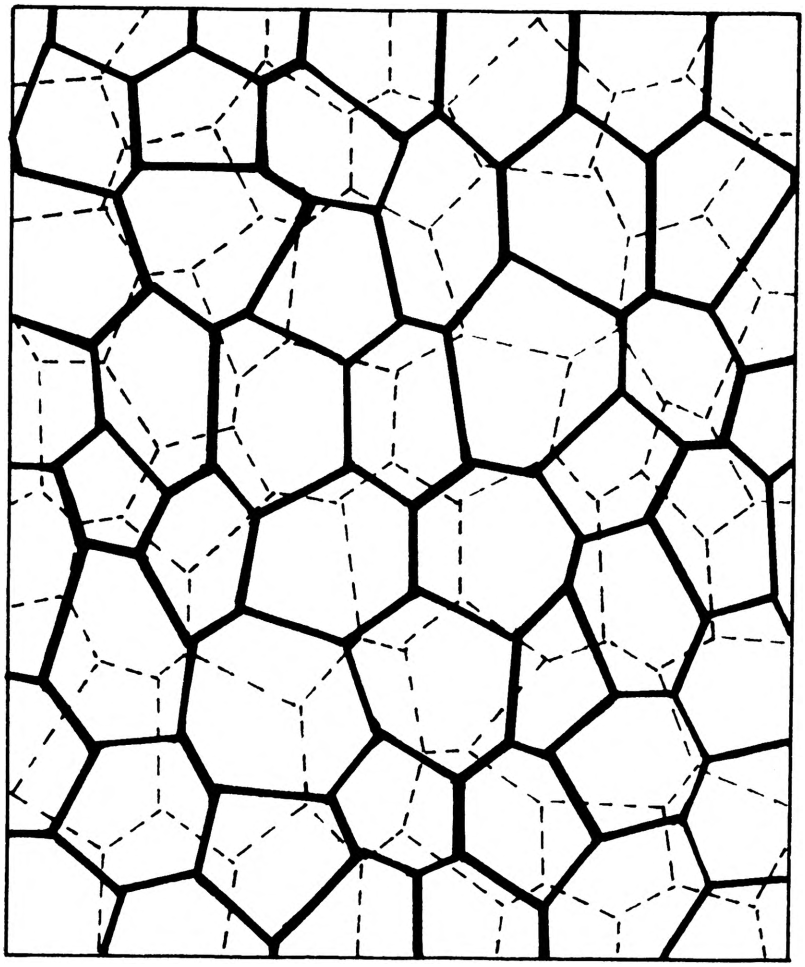

Figure 17. Polyhedral cells in foam

may be either curved or planar as a result of the pressure difference across them. According to Plateau rules (28), the geometric configuration of foam requires three films meeting at an edge (i.e. Plateau border) along lines at 120° (Fig.18) and four soap films meeting at a corner with adjacent lines intersecting at $109^{\circ}28'16''$. When foam is treated as an agglomeration of polyhedral cells, the following relationship is valid (28):

$$4c + 2S = 3E + 2n$$

where c is the number of corners, S is the number of sides, E is the number of Plateau borders and n is the number of bubbles.

2. Colloidal Forces

Three major forces present in soap films have been investigated in order to explain some of the properties of foam. These are the van der Waals interaction between molecules and ions, electric double layer repulsions, and the Laplace pressure, shown in Figure 19.

a. Van Der Waals Interactions

The van der Waals potential energy between two isolated molecules may be estimated by the London potential (29)

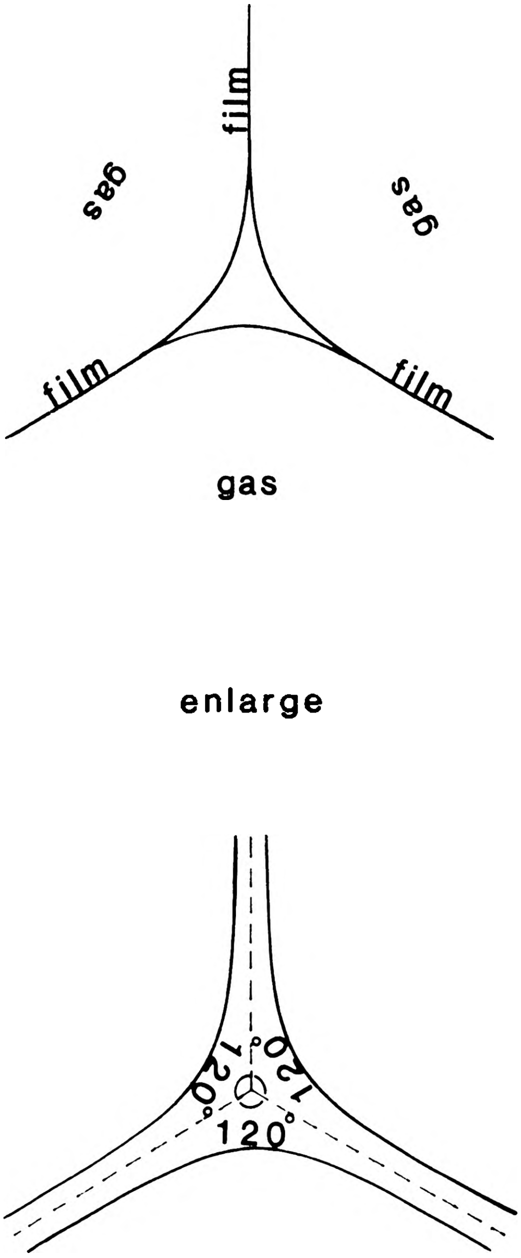

Figure 18. The Plateau border at the junction of three soap films

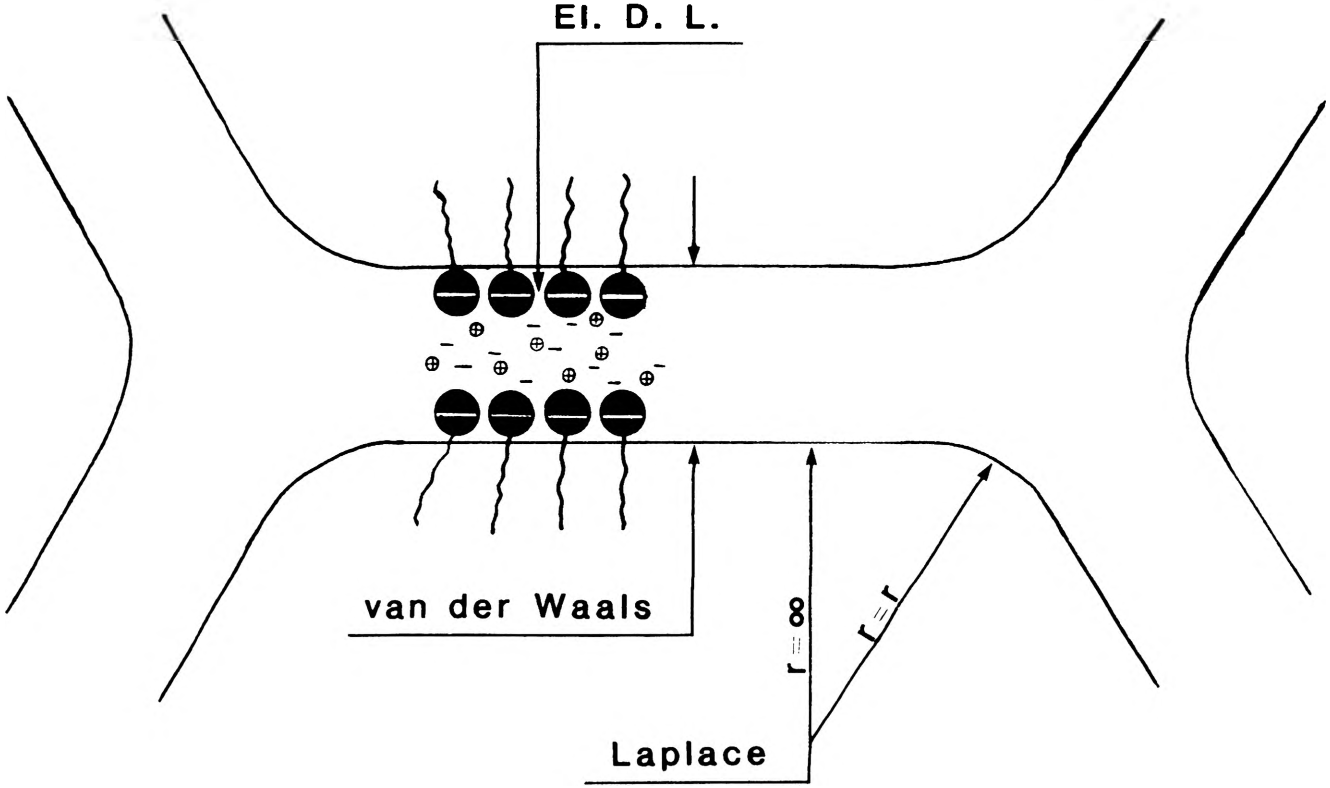

Figure 19. The three main colloidal forces over thin liquid films in a foam (1) the van der Waals attraction (2) the Lapace Suction Pressure (3) the electric double layer repulsion (24)

$$E_L = - \beta / \ell^6$$

where β is constant $\approx 10^{58}$ erg•cm^6

ℓ is the distance between two molecules

For a soap film of thickness, d, the total van der Waals interaction energy (V_a) between all the molecules is calculated by integration of the London potential over the thin film

$$V_a = - A_H / 12\Pi d^2$$

where A is a constant. The negative sign indicates that the forces are attractive. The van der Waals pressure is given by

$$P_{vdw} = A_H / (6\Pi d^3)$$

The Hamaker constant contains the constants for all three different interaction between two media,

i.e. $A_H = (A_{H\ell\ell}{}^{1/2} - A_{Hgg}{}^{1/2})^2 = A_{H\ell\ell} + A_{Hgg} - 2A_{Hg\ell}$

The Hamaker interaction constant for gas with gas A_{Hgg} and gas with liquid $A_{Hg\ell}$ are relatively small compared to the constant for liquid with liquid $A_{H\ell\ell}$. Therefore, the attractive pressure can be expressed as

$$P_{vdw} = A_{H\ell\ell} / (6\Pi d^3)$$

b. Laplace Suction Pressure

The Laplace suction pressure arises from the difference in radius of curvature between the lamellae and the Plateau border (Fig.19).

This pressure difference is expressed as

$$\Delta P = \gamma \left(1/r_1 + 1/r_2 \right)$$

where γ is the surface tension, r_1 and r_2 are the two principal radii of curvature. From the geometry of border

$$r_1 \rightarrow \infty \quad \text{and} \quad r_2 = r$$

the Laplace suction pressure can be calculated as

$$\Delta P = \gamma / r$$

where r is the radius of curvature for a plane perpendicular to the border and the plane of the thin film.

c. Electric Double Layer Repulsion

As shown in Fig.19, the electric double layer in a foam lamella is established due to the charged surface consisting of soap molecules and their counterions. When the two surfaces approach, the counterions begin overlapping and repulsive forces arise.

The simplest treatment of this phenomenon is based on the model by Gouy (30) and Chapman (31). The repulsion force can be expressed as

$$P_{EDL} = 64\ n\ k\ T\ \Phi^2\ e^{-Hd}$$

where n = the number ions per unit volume

k = Boltzmann constant

T = temperature

$\Phi = \tanh(\ ze\Psi/4kT\ )$

$H = (\ 8\Pi e^2 z^2 n\ /\ \varepsilon kT\ )^{1/2}$

= inverse of the Debye-Hückel length

d = distance between two interfaces

z = valency of the symmetrical electrolyte

e = charge of an electron

ε = dielectric constant for solvent

Ψ = electric surface potential

3. Draining and Thinning

Liquids surrounded by the bubble surface will drain out of the film by convection, evaporation, gravitation, and suction. These draining processes have both static and dynamic mechanisms (26). Static draining processes such as evaporation cause no position change of the film surface, while dynamic processes produce the movement of the film surface. Convection is an example of dynamic draining. If the film does not rupture, the thinning process will continue until an equilibrium thickness in the range 50 Å to 300 Å is reached. This thickness is far less than the wavelength of visible light, and the film appears black due to the destructive interference of reflected light. Soap films around 300 Å, and 50 Å are known as the common black film and Newton black film respectively.

Figure 20 shows that the draining of a polyhedral foam by gravitational force will take place from both the lamellae and the intersections of three films (i.e. the Plateau borders).

Based on Bikerman (28), the drainage from lamellae is modelled as from a slit, and the flow rate of liquid, $(dv/dt)_L$, cm^3/sec, is estimated as

$$(dv/dt)_L = g\rho\omega d^3 \;/\; 12\eta$$

where g is gravitational acceleration (cm/sec^2), ρ is density (g/cm^3), ω and d are the width (cm) and the thickness (cm) of lamellae, η is the viscosity of liquid (g/cm-sec).

The drainage from the Plateau border is considered as a cylindrical flow of radius r (cm), and the flow rate, $(dv/dt)_P$, cm^3/sec is calculated as

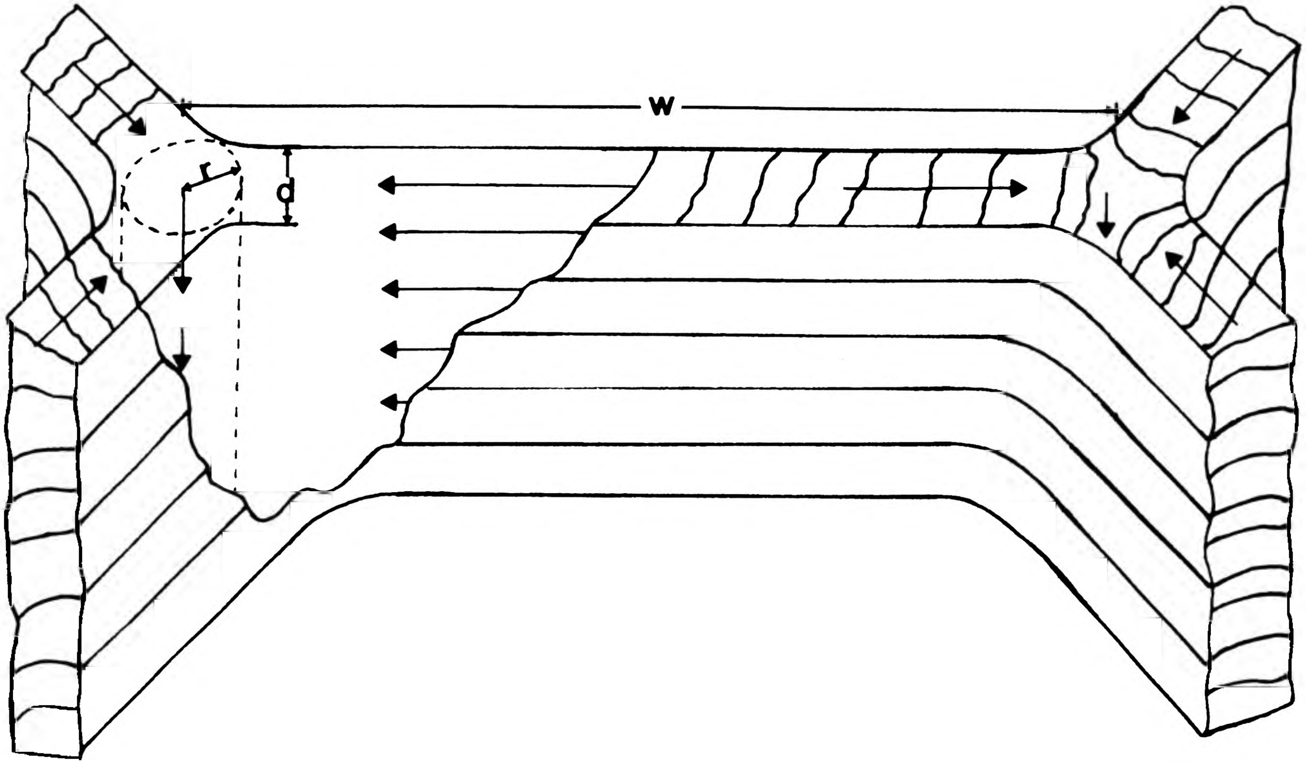

Figure 20. Schematic diagram of the drainage flow from foam lamellae and the Plateau border

$$(dv/dt)_P = \Pi g \rho r^4 / 8\eta$$

From the above two equations, the ratio (f) of drainage rate between lamellae and Plateau border is expressed as

$$f = (dv/dt)_L / (dv/dt)_P = 2wd^3 / 3\Pi r^4$$

This ratio provides a comparison of drainage rate between lamellae and Plateau border. When $(dv/dt)_L > (dv/dt)_P$, $f > 1$, or vice versa.

Usually, the volume of drainage comes mostly from the Plateau borders. An example is a foam of thickness 1000 A, width of lamellae 0.1 cm and having a radius in the Plateau border of 1 μm. These reasonable dimensions give a ratio of drainage, f, equal to 2.2×10^{-5}. This shows that the flow rate of liquid from the Plateau border is greater than that from the lamellae.

The draining of soap films depends on the chemical composition of the film, the surface rigidity, viscosity, and environmental conditions such as temperature, pressure, and humidity. These features will be discussed in the following sections.

4. Rupture

Drainage causes soap film to become thinner and thinner, which gives larger and larger van der Waals attractions. If the thinning process is not stopped by other factors, rupture occurs at a certain film thickness. The critical thickness (h_{cr}) at which film rupture occurs is given by Scheludko et. al. (32,33)

$$h_{cr} = (0.97\ (K_B T)^{1/10}\ A_{VW}^{2/5})\ /\ (\eta^{1/5}\ \gamma^{3/10}\ V^{1/5})$$

$$\approx (0.044\ A_{VW}^{2/5})\ /\ (\eta^{1/5}\ \gamma^{3/10}\ V^{1/5})$$

(at room temperature, $K_B T = 4.1 \times 10^{-14}$ erg / molecule)

A soap film is not completely flat. Thermal energy produces perturbations in the film. Figure 21 illustrates the wave perturbation patterns which deform the plane film into areas that are thinner and thicker (24). This deformation leads to larger van der Waals attraction in the thinner areas, which destabilizes the film.

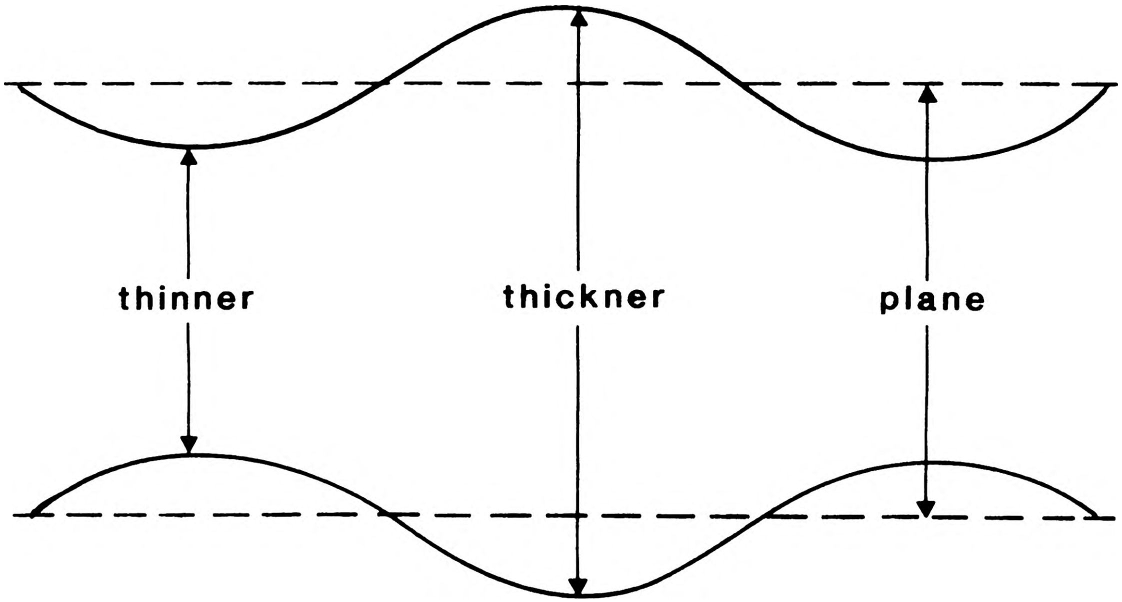

Figure 21. Perturbation of a thin film produces thinner and thicker films

B. FOAM STABILITY

The formation of gas bubbles produces a large surface area and increases the free energy of the system. Therefore, foam is not thermodynamically stable. The breakdown of foam (i.e. the reverse process) is thermodynamically spontaneous. Although inherently unstable, foam can be treated as a metastable state for a considerable time by controlling stability factors such as environmental conditions, chemical composition, and surface structures etc.

1. Environmental Conditions

The stability and life time of bubbles are affected by the evaporation of liquid from the surface, the humidity of the surroundings, air currents, shocks, vibrations and foreign gases. However, these factors can be eliminated by controlling the environment of the bubble. Foam can be produced in a closed system with saturated humidity and free from shocks, temperature and pressure changes. With the controlled environment, bubbles can exist for a long period. An example is reported for a bubble of diameter 32 cm in a controlled conditions which lasted for 108 days (27).

2. Chemical Compositions

Stable foam can be produced in the open air by improving its chemical composition. As an example, by adding 50% glycerol to a soap solution, the life time of bubbles can be increased from 15 seconds to more than an hour (27).

Many recipes for long lasting bubbles without special precautions have been summarized in books by Boys (26) and by Bikerman (28). In fact, the improvement of chemical composition is related to the improvement of surface properties such as structure, elasticity and viscosity of foam. These surface properties are the important factors for determining foam stability.

3. Surface Elasticity

The surface elasticity describes the resistance of a film to deformation. It is defined by Gibbs (34) as

$$E = 2\,A\,(\,d\gamma/dA\,)$$

where E is the surface elasticity, A is the surface area of the film, γ is the surface tension, and $(d\gamma/dA)$ is the variation of surface tension with surface area.

For pure liquids, the surface elasticity is zero because the surface tension of pure liquids does not change with a change in surface area. This is the reason why pure liquids will not foam. With soap solutions, the change of surface area (stretching or contraction) will change the density of soap molecules in the surface and the surface tension (35).

The Gibbs surface elasticity is used for a system in thermodynamic equilibrium where the surface tension of the stretched film is an equilibrium value. For non-equilibrium conditions, the resistance of a surface film to deformation is described by the Marangoni effect (28).

4. Viscosity

The stability of a soap bubble is affected by both bulk and surface viscosities (36). Bubbles generated from a highly viscous solution will have viscous walls which hold neighboring molecules somewhat, slow down the drainage rate, and help to give stable foam. However, there is no quantitative relationship between bulk viscosity and foam stability. Viscous films do not guarantee a particularly stable foam.

Surface viscosity is related to the molecular packing on the bubble film. High surface viscosity implies an ordered and rigid film. The stability of this ordered and rigid film is due to the reduced thinning rate and especially the increased resistance to pertubations such as shock and thermal fluctuations. A number of papers have been reported which correlate foam stability and the surface viscosity of foam (36-38).

5. Colloidal Forces

As the foam thins, the decreasing thickness and the consequent increasing van der Waals attractions promote further thinning. However, the electric double layer repulsion also increases with decreasing thickness. The increased repulsion counteracts the increased attraction and stops further thinning. The balance of van der Waals attraction and electric double layer repulsion determines the equilibrium thickness of films during drainage. If a balance is not possible, film rupture will take place.

C. AMPHIPHILE ASSOCIATION STRUCTURES AND FOAM STABILITY

Amphiphilic association structures including micelles, lyotropic liquid crystals and inverse micelles were introduced in Section I. The importance of these association structures, especially lamellar liquid crystal, for the stability of foams, has been emphasized by Friberg and his collaborators (39-44). Figure 22 shows the typical phase region and phase equilibrium diagram of a three component systems of water, water soluble surfactant, and alcohol. It contains a normal micellar solution region (L_1), lamellar liquid crystal region (D), and inverse micellar solution region (L_2). Phase equilibria among these one-phase regions are indicated by tie lines. When a hydrocarbon is added to the above base system, oil in water (O/W) and water in oil (W/O) microemulsion regions are produced as in Figure 23 (45). For an oil soluble surfactant, cosurfactant (alcohol) is not neccessary to produce the solubility region. An example of a phase diagram for water - oil soluble surfactant - hydrocarbon system is given in Figure 24. Inverse micellar solution region (L_2) and lamellar liquid crystal region (D) are shown. Foaming properties and foam stability of one-phase or multi-phase regions in the above systems are discussed in the following sections.

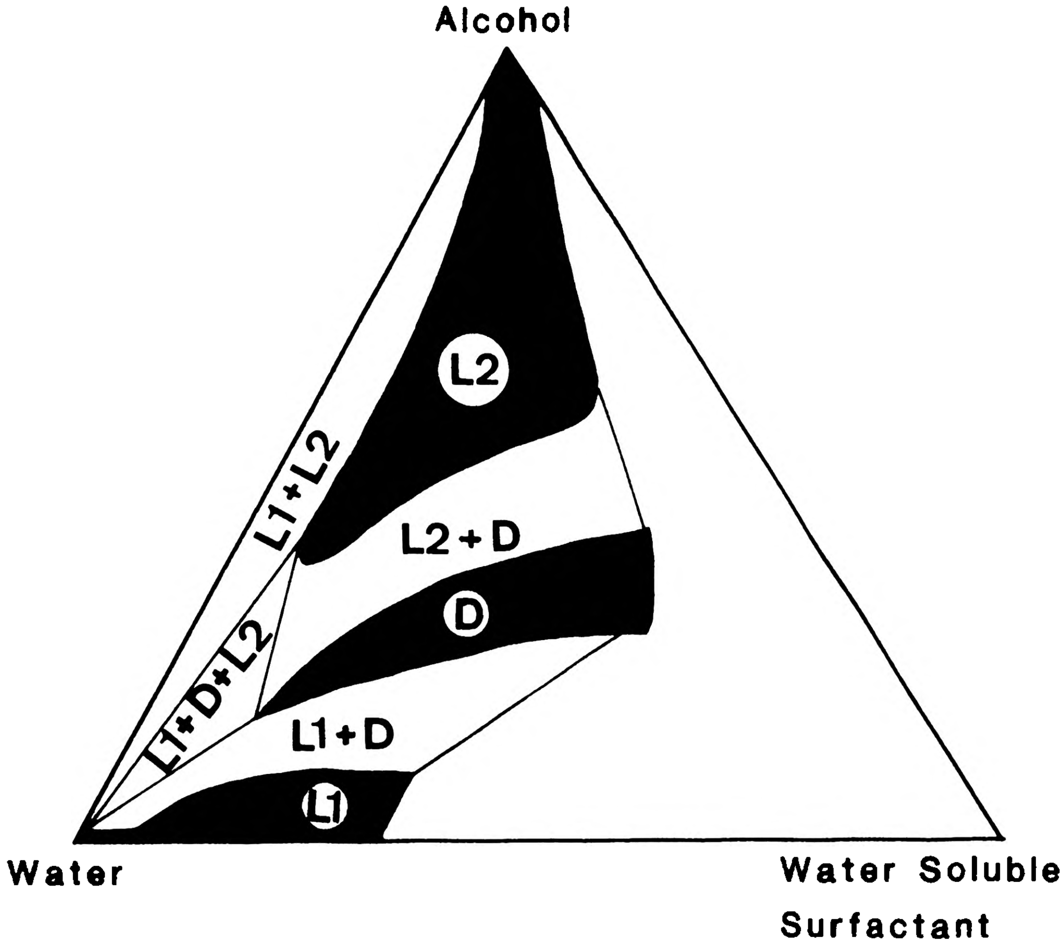

Figure 22. Typical phase regions on a phase equilibrium diagram for the ternary system water / water-soluble surfactant / alcohol (24)

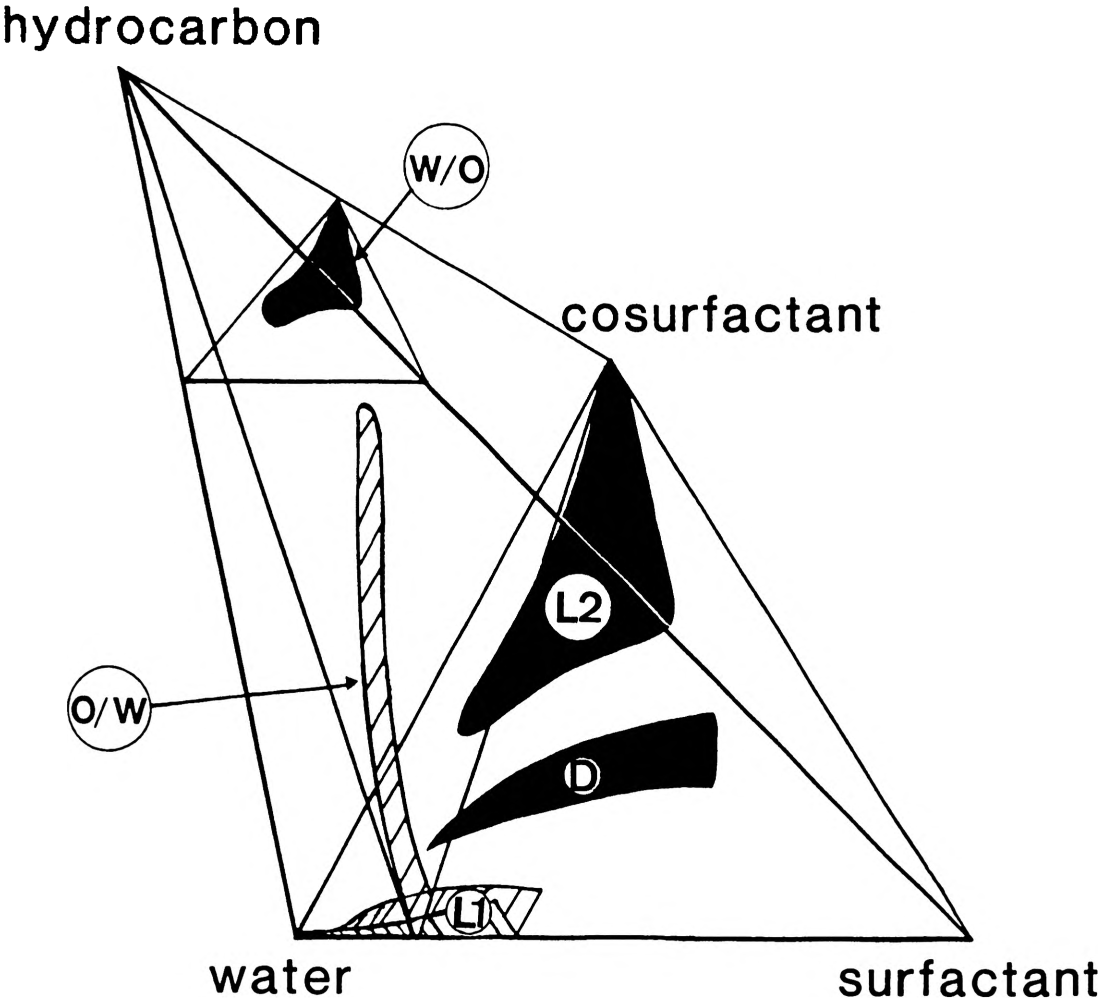

Figure 23. Three dimensional phase diagram of a four component system of water / water-soluble surfactant / alcohol / hydrocarbon
L_2 - inverse micellar, L_1 - normal micellar
D - lamellar liquid crystal
W/O - water in oil microemulsion and
O/W - oil in water microemulsion (45)

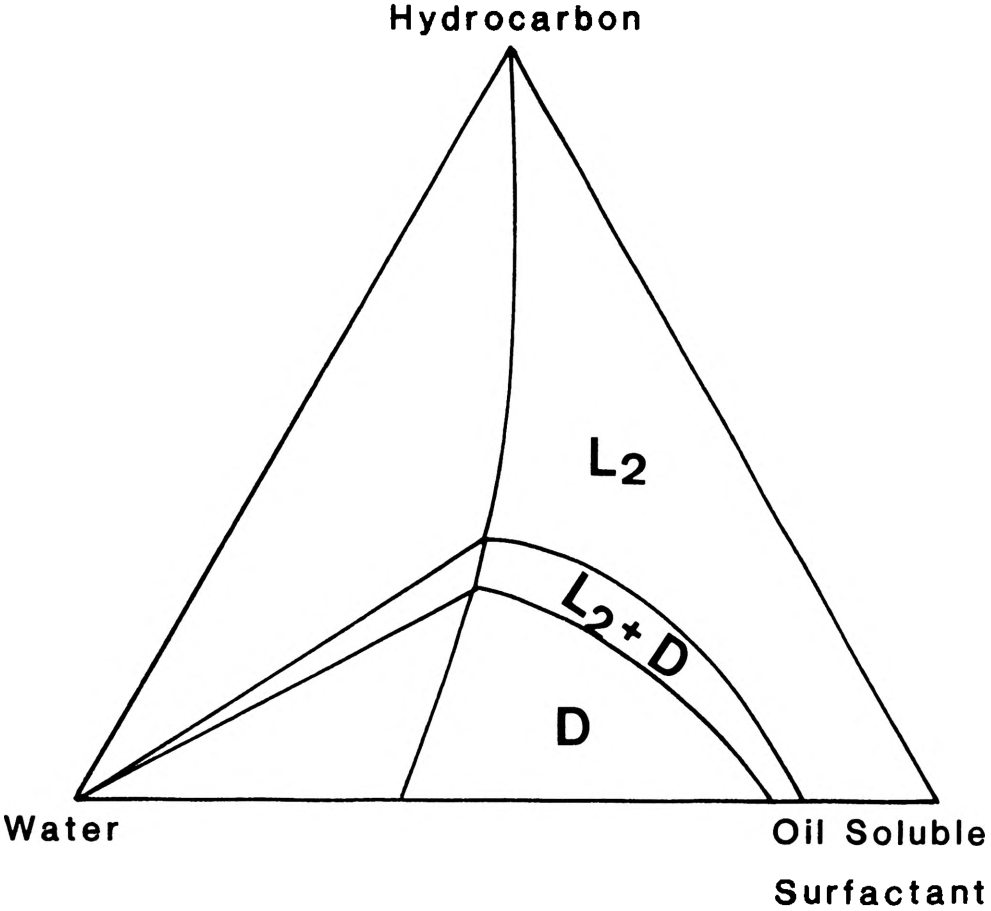

Figure 24. In a water, oil-soluble surfactant, and hydrocarbon system; stable foams are found in the L_2 + D area (24)

1. Water-Soluble Surfactant System

For the water / water-soluble surfactant / alcohol system (39,43,44), the aqueous micellar solution (L_1) will produce foam. The most stable foam is found at low surfactant concentration (i.e. less than 10 wt%) in two phase mixtures of liquid crystal and aqueous micellar solution (L_1 + D). The pure liquid crystal (D) is too viscous to foam.The inverse micellar solutions (L_2) in which alcohol is the continuous phase give extremely unstable foam as the result of the foam breaking effect of alcohols with medium chain length (46,47). Therefore, sample solutions in the phase equilibria region containing inverse micellar solution such as L_1 + L_2, L_2 + D, give especially unstable foam. However, alcohol also acts a foam stabilizer as reported (37) by increasing the surface viscosity and surface elasticity of foam. In water - surfactant systems, whether alcohol functions as a foam breaker or as a foam stabilizer depends on the amount of alcohol in the association system. Figure 25 shows a method for distinguishing. When the ratio of alcohol to surfactant is less than at B (Fig.25), the alcohol is serving as a foam stabilizer, because the alcohol is incorporated with surfactant to enhance the surface properties of the foam. When the alcohol to surfactant ratio is larger than at A (Fig.25), the excess alcohol exists as free alcohol and serves as a foam-breaker (43).

Microemulsions (Fig.22) usually give unstable foam.

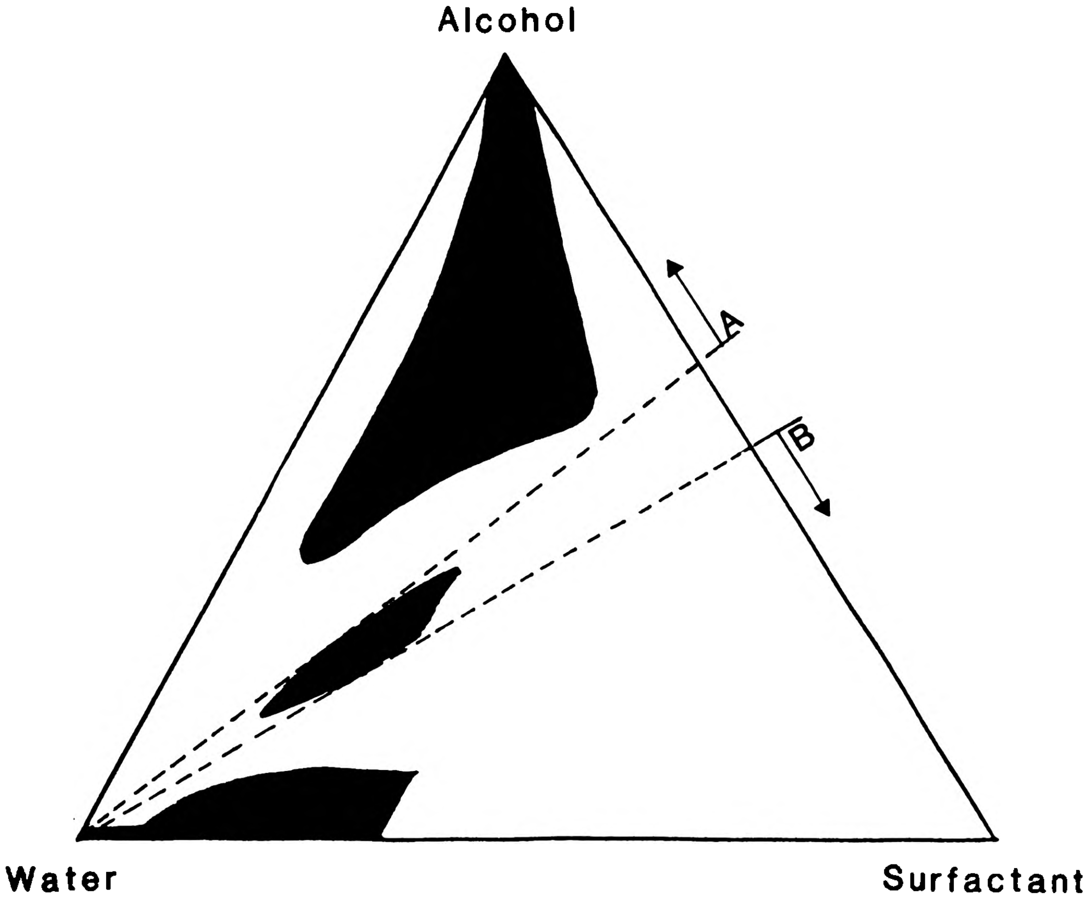

Figure 25. Alcohol / surfactant ratios at which alcohols can act as foam breakers lie above line A; as foam stabilizers below line B (43)

Bubbles generated from the water in oil (W/O) microemulsions break immediately as they reach the surface of the solution (45). The reason for this extremely low foam stability in W/O microemulsions is the low surface elasticity. This explanation is based on the observation of the independence of surface tension on composition in the inverse micellar solution region (48).

2. Oil-Soluble Surfactant System

In contrast to water-soluble surfactant systems, stable foams in oil-soluble surfactant systems (24,39,49) are reported in the region where lamellar liquid crystal is in equilibrium with the inverse micellar solution (L_2 + D) (Fig.24). The hydrocarbon solution (L_2) has no foaming ability. Foam is not stable for any other regions containing aqueous phase because of the insolubility of surfactant in water.

The large difference in surfactant tension between water and hydrocarbon, leads to the difference in solubility behavior of surfactant in these two solvents. Water has a high surface tension. The solubilized surfactant will adsorb on the surface of water and reduce the surface tension (Fig.26A). Hydrocarbon, on the other hand, has a low surface tension. Surfactant molecules are dispersed in the hydrocarbon without preferential adsorption and do not reduce surface tension (Fig.26B). Hence, aqueous foam and hydrocarbon foam have different foam stability behavior.

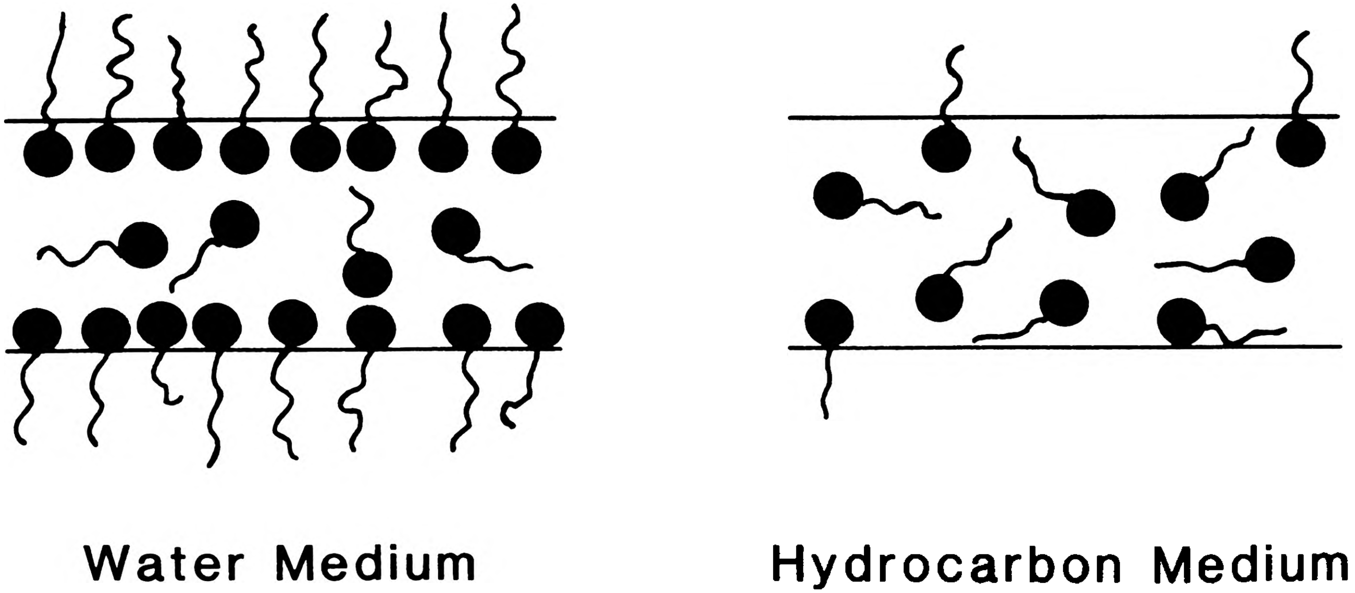

Figure 26. Surfactants adsorb strongly at the water-air interface but not at the hydrocarbon air interface (49)

D. THE FUNCTION OF LIQUID CRYSTAL IN FOAM STABILITY

As described in the last section, liquid crystal in the composition is important for foam stability. Stable foam is found when either aqueous micellar solution or a hydrocarbon micellar solution is in equilibrium with lamellar liquid crystal. These two equilibria, however, will not exist in the same system.

The function of the lamellar liquid crystal as an enhancer of foam stability is related to the geometric structure, high viscosity, and low surface tension of the lamellar phase (24,49). Liquid crystals are preferentially adsorbed on the surface of bubbles compared to liquids (43,44). Hence, the foam surface is surrounded by a multilayer liquid crystal structure. This multilayer structure (Fig.5, Section I) increases the foam surface elasticity and viscosity, so that it resists perturbation, slowing the drainage from the foam. The multilayer structure also provides preferential exposure of the methyl groups of amphiphile molecules. Because the methyl group has a lower surface tension (γ = 23 dynes/cm) than the methylene group (γ = 28-30 dynes/cm) (50), lamellar liquid crystals have a lower surface tension than micellar solutions with similar compositions. This lower surface tension allows to be easily adsorbed onto the foam surface and provide higher foam stability (49).

REFERENCES

1. Haupt, D. E., JOACS., 60, 1914 (1983).
2. Linfield, W. M., Ed., "Anionic Surfactants." Marcel Dekker, New York, 1976.
3. Rosen, M. J., "Surfactants and Interfacial Phenomena." Wiley-Interscience Publication, New York, 1978.
4. Jungermann, E., "Cationic Surfactants." Marcel Dekker, New York, 1970.
5. Puchta, R., JAOCS 61, 367 (1984).
6. Huber, L. H., JAOCS 61, 377 (1984).
7. Schick, M. J., Ed., "Nonionic Surfactants." Marcel Dekker, New York, 1967.
8. Shwartz, A. M., and Perry, J. W., "Surface Active Agents, Their Chemistry and Technology." Interscience Publishers Inc., New York, 1977.
9. Bluestein, B. R., "Amphoteric Surfactants." Marcel Dekker, New York, 1982.
10. Szuhaj, B. F., and List, G. R., Eds., "Lecithins." American Oil Chemists Society, Washington, D. C., 1984.
11. Balmbra, R. R., Clunie, J. S., and Goodman, J. F., Nature 222, 1159 (1969).
12. Ekwall, P., in "Advances in Liquid Crystals." (G. H. Brown, Ed.), Academic Press, New York, 1975, pp.1-142.

13. Friberg, S., Naturwissenschaften 64, 612 (1977).

14. Tiddy, G. J. T., Phys. Rep. 57, 1 (1980).

15. Rosevear, F. B., J. Am. Oil Chem. Soc. 31, 628 (1954).

16. Rosevear, F. B., J. Soc. Cosmetic Chemists 19, 581 (1968).

17. Lawson, K. D., Mabis, A. J., and Flautt, T. J., J. Phys. Chem. 72, 2058 (1968).

18. Lawson, K. D., and Flautt, T. J., J. Phys. Chem. 72, 2066 (1968).

19. Flautt, T. J., and Lawson, K. D., J. Am. Chem. Soc. 89, 5489 (1967).

20. Friberg, S., Chemical Technology 6, 124 (1976).

21. Friberg, S., in "Microemulsions, Theory and Practice." (L. M., Prince, Ed.), Academic Press, New York, 1977, p.133.

22. Sjoblom, E., and Friberg, S., J. Colloid Interface Sci. 67, 16, (1968).

23. Langevin, D., in "Reverse Micelles." (P. L. Luisi, and B. E. Straub, Eds.), Plenum Press, New York, 1984, p.287.

24. Friberg, S., in "Advances in Liquid Crystals." Vol.3, (G. H. Brown, Ed.), Academic Press, New York, 1978, p.149.

25. Friberg, S., Jansson, P. O., and Cederberg, E., J. Colloid Interface Sci. 55, 614 (1976).

26. Boy, C. V., "Soap Bubbles and the Forces Which Mould Them." Willian Heinemann, London, 1965, and "Soap Bubbles their colors and the forces which mould them." Dover, New York, 1959.
27. Isenberg, C., "The Science of Soap Films and Soap Bubbles." Tieto Ltd., England, 1978.
28. Bikerman, J. J., "Foams." Springer-Verlag, Berlin, 1973.
29. London, F., Z. Phys., 63, 245 (1930).
30. Gouy, G., J. Phys., 9, 457 (1910).
31. Chapman, D. L., Phil. Mag. 25, 475 (1913).
32. Sheludko, A., Proc. Koninkl. Ned. Akad. Wetensehap. 365, 76 (1962).
33. Radoev, B. P., Scheludko A. D., and Manev, E. D., J. Colloid Interface Sci. 95, 254 (1983).
34. Gibbs, J. W., "Collected Works." Vol. 1, Yale University Press, New Haven, 1948, p.300.
35. Osipow, L. I., "Surface Chemistry, Theory and Industrial Applications." Reinhold Pub. Corp., New York, 1962.
36. Miles. G. D., Shedlovsky, L., and Ross, J., J. Phys. Chem., 49, 93 (1945).
37. Brown, A. G., Thuman, W. C., and McBain, J. W., J. Colloid Sci. 8, 491 (1953) and J. Colloid Sci. 8, 508 (1953).
38. Kanner, B., and Glass, J. E., Industrial and Engineering Chemistry, 61, 31 (1969).

39. Friberg, S., and Ahmad, S. I., J. Colloid Interface Sci. 35, 175 (1971).

40. Ahmad, S. I., and Friberg. S., Acta Polytech. Scand. Ch. 102, 1 (1971).

41. Jederstrom, G., Rydhag, L., and Friberg, S., J. Pharm. Sci. 62, 1979 (1973).

42. Friberg, S., Linden, S. E., and Saito, H., Nature, 251, 494 (1974).

43. Friberg, S., and Saito, H., Pramana 1, 537 (1975).

44. Friberg, S., and Saito, H., in "Foams." (R. J. Akers. Ed.), Academic Press, New York, 1976, p.33.

45. Torres, R., Podzimek, M., and Friberg, S. E., Colloid & Polymer Sci. 258, 855 (1980).

46. Ross, S., and McBain, J. W., Ind. Eng. Chem. 36, 570 (1944).

47. Ross, S., Chem. Ind. 64, 757 (1949).

48. Tamamushi, B. I., Progr. Colloid & Polymer Sci. 65, 180 (1978).

49. Friberg, S. E., Blute, I., Kunieda, H., and Stenius, P., in press.

50. Zisman, W., in "Contact Angle Wittability and Adhesion." (R. F. Gould, Ed.), ACS Advances in Chem. Sci. 43, 1, 1964.

ARTICLE I

AMPHIPHILE ASSOCIATION STRUCTURES AND FOAM SEPARATION

by

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ABSTRACT

Foam separation was studied in aqueous sodium octylsulfonate solutions with or without decanol. The study was concentrated at low surfactant concentrations below or near the critical micellization concentration of sodium octylsulfonate in water. The pure water -surfactant solutions gave unstable foams, and no foam separation was observed. With the addition of extremely small amounts of decanol, the generated foam became stable and transferable. Increasing the decanol content, beyond its solubility in the aqueous surfactant solution, produces more stable and more transferable foams. The result are explained by the association structures and phase equilibria in surfactant systems.

INTRODUCTION

Foam separation is a method with a long history and wide application. It is used to separate materials whose bulk concentrations are too low to be conveniently separated by other methods. Many of materials, including metals, dyes, organic anions, fatty acids, detergents, proteins, enzymes, and miscellaneous inorganic anions and organic substance have been reported in the literature as separated and recovered by foam separation. Those materials can be divided to two types (1) materials which are naturally surface active such as protein, dyes and surfactants. (2) materials which are not naturally surface active, but in association with surface active species become separable.

Foam separation techniques consist of several subdivisions, which are shown in Figure 1. These techniques are first subdivided into foam fractionation and (froth) flotation. Foam fractionation deals with the removal of surface active materials from solutions which contain no solid phase, while flotation deals with separation of suspended solid particles from solutions. Flotation (3-10) is further divided and explained in Table I. The difference between foam fractionation and froth flotation is illustrated in Figure 2. More detailed discussions of various foam separation techniques can be found in comprehensive reviews which have been presented by Rubin and Gaden (1) in 1962, by

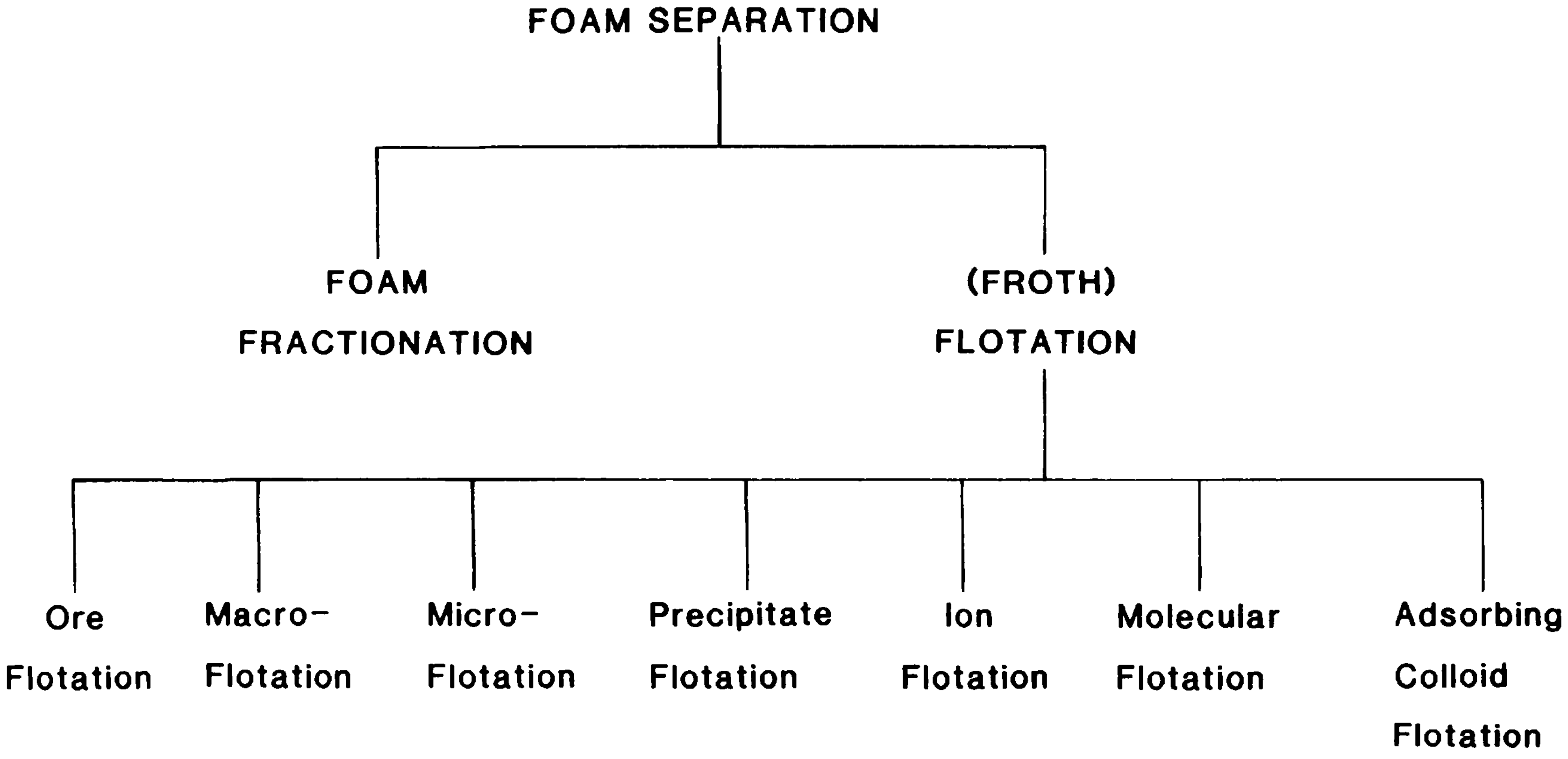
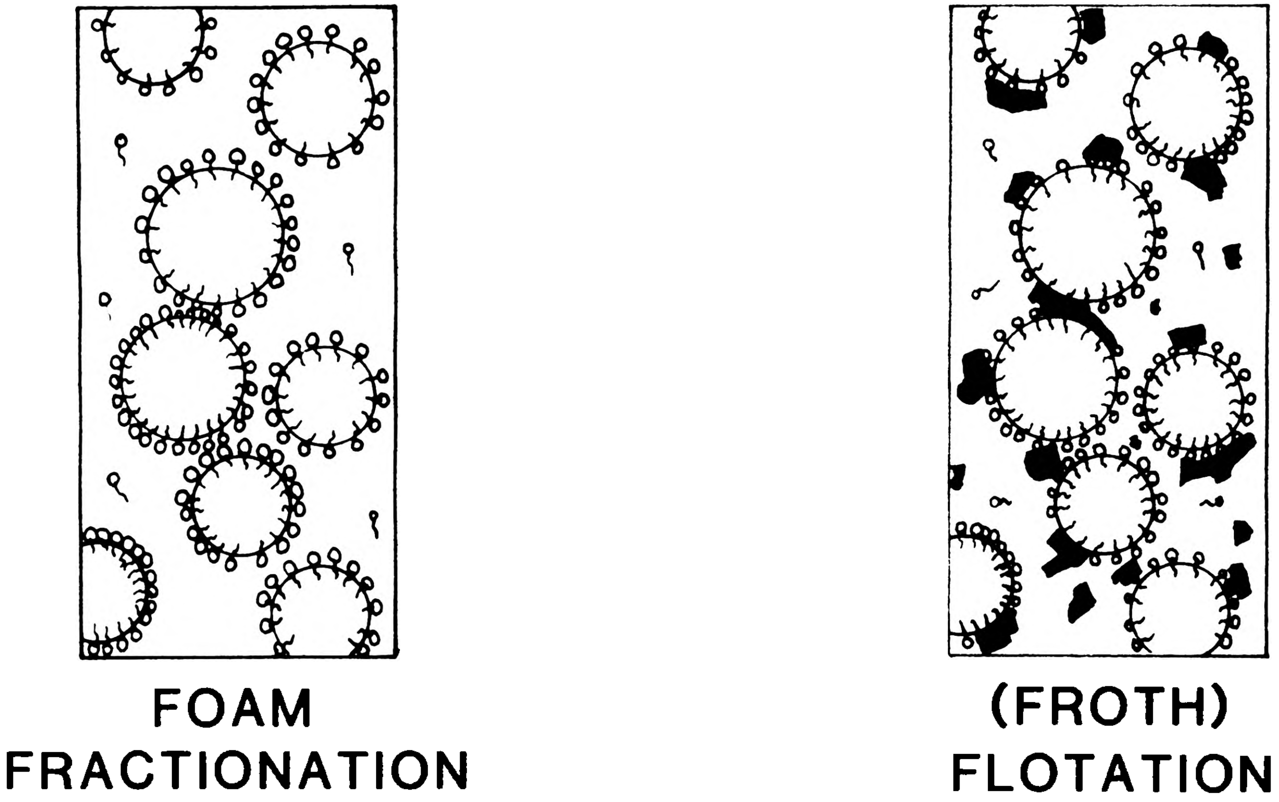


Figure 1. Classification of the various foam separation techniques

TABLE I

Classification of Froth Flotation Types with Examples

Flotation Type	Subject of Separation	Example	Ref.
ore	mineral	coal	3
macro	particles of macroscopic size	rayon, silk, casien and nylon textile fiber	4
micro	particles of microscopic size	bacillus subtilis	5,6
precipitate	surface inactive insoluble precipitate	ferrocyanide of Co,Cr,Cu,Fe,Mg, Mn,Ni,U	7
ion	surface inactive ion	orthophosphate	8
		1-chloromethyl naphthalene	9
molecule	surface inactive molecule	phenol	10
adsorbing colloid	hydrophobic colloid size	cholinesterase dextrin diastaste lipase metaprotein	1



FOAM FRACTIONATION

(FROTH) FLOTATION

Figure 2. Illustration of foam fractionation versus froth flatation

Lemlich (2) in 1972, by Somasundaran (11,12) in 1972 and 1975, by Grieves (13) in 1982 and by Clark and Wilson (14) in 1983. The present introduction will concentrate on the fundamentals of foam fractionation, which will also be applied to foam separation in general.

BASIC PRINCIPLES

Foam separation is based on the selective adsorption on a bubble surface of surface active materials which prefer to adsorb at the gas-liquid interface. These materials are removed with the rising bubbles. The preferential adsorption of surface active materials at a liquid-gas interface are due to the greater interactions between water molecules than those between water and surface active materials. The interfacial tension is reduced by the adsorption of surface active materials, and the bubble is stabilized by the properties of the surface film (15,16). The large surface area of the foam is used as a separation medium in foam separation techniques.

FOAM SEPARATION OF SURFACTANTS

In contrast to other surface active materials such as proteins and long chain alcohols, surfactants form various association structures such as micelles and liquid crystals in aqueous solution. In most foam separation studies, the surfactant forms only a monoloyer structure at the liquid gas interface.

The theoretical model to describe the adsorption of surfactants at the liquid-gas interface is given by the Gibbs equation (17):

$$\Sigma\Gamma_i = -(1/RT)\Sigma(d\gamma/d\ell n a_i)$$

For solutions containing only one surface active material:

$$\Gamma_i = -(1/RT)(d\gamma/d\ell n a_i)$$

For dilute conditions:

$$\Gamma_i = -(1/\beta RT)(d\gamma/d\ell n C_i)$$

where Γ_i = the surface excess, the concentration of adsorbed component i at the surface (mole/cm^2).

R = the gas constant.

T = the absolute temperature (^{o}K).

γ = the surface tension of the solution.

a_i = the activity of the surfactant species i.

C_i = the concentration of the surfactant species i at dilute condition.

$\beta = 1$ for nonionic surfactants or solutions containing uni-univalent ionic surfactants with excess electrolyte.

β = 2 for solutions containing uni-univalent ionic surfactants without any execss electrolyte present.

The typical variation of surface excess (Γ) with the concentration (C) is demonstrated in Figure 3. At very low concentrations, the surface excess increases linearly with increasing surfactant content. At high surfactant concentrations, the surface is saturated and the surface excess curve bends and tends to level off. This concentration is the critical micellization concentration, at which excess surfactant forms micelles. However, it should be noted that the CMC is not the lowest surfactant concentration at which association structures form. In this study, the multilayer structure was observed when decanol was added to solutions with surfactant concentrations below the CMC.

The extent of removal of the surfactant by foam separation is related to the distribution coefficient, Γ_i/C_i (3). Figure 4 shows the variation of the distribution coefficient as a function of surfactant concentration in the bulk solution. Below the critical micellization concentration, most surfactants are adsorbed at the interface, giving a constant and high distribution coefficient. Above the CMC, the surface is saturated, and the

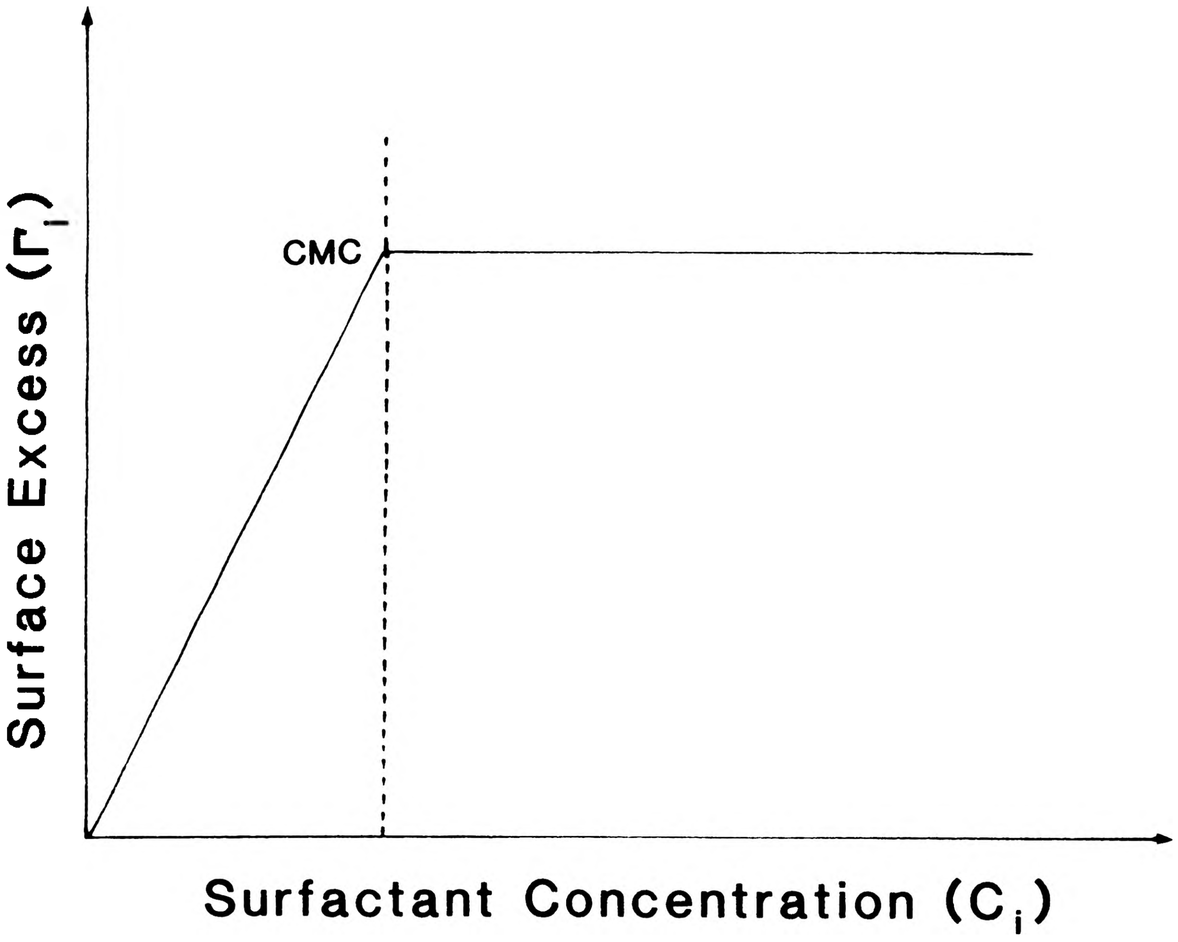


Figure 3. The variation of surface excess with surfactant concentration

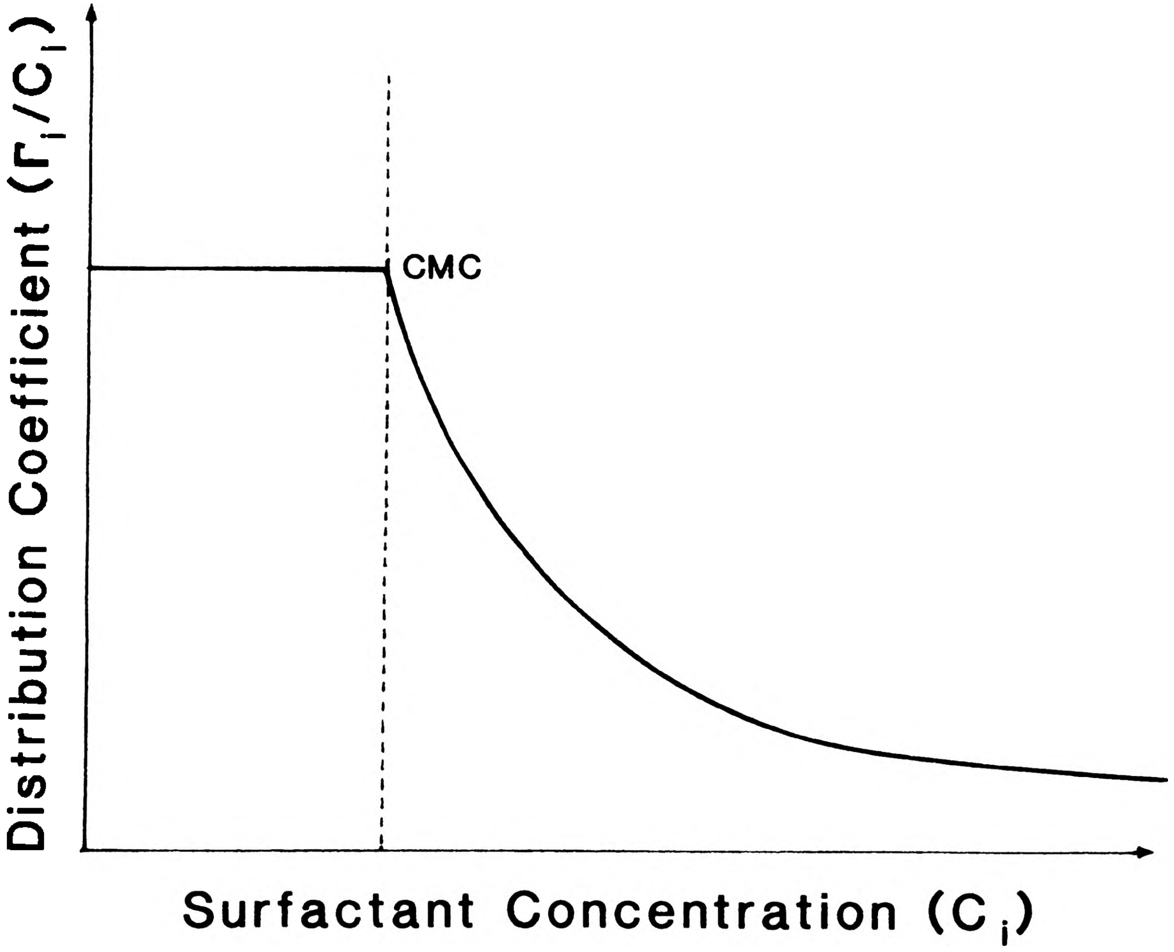


Figure 4. The variation of distribution coefficient with surfactant concentration

distribution coefficient decreases with increasing surfactant concentration. This characteristic phenomena, higher distribution coefficient at low surfactant concentration makes possible foam separation techniques for separating the surface active materials at very low concentration. The above description can be expressed by the Langmuir adsorption isotherm:

$$\Gamma_i/C_i = K_1/(K_2C_i+1)$$

where K_1 and K_2 are constants for the system under study. At very low concentrations, K_2C_i is negligible in comparision with 1. Hence, the distribution coefficient is a constant, K_1. When the concentration is increased, the distribution coefficient decreased.

The distribution of surfactant between the liquid-gas interface and the bulk solution is affected by the following factors:

1. The Nature of Surfactants

As stated earlier, incompatibility between water and surfactants leads to the adsorption of surfactant molecules at the liquid-gas interface. If the size of the polar group or the number of double or triple bonds in the surfactant increases, this incompatibility will be reduced. Hence, the adsorption of surfactant at the liquid-gas interface decreases, and the foam separation capacity of the surfactant is correspondingly reduced. On the other hand, if the hydrocarbon chain length of the surfactant increases, the incompatibility between water and surfactant is enhanced, allowing an increase in adsorption in the liquid-gas interface and foam separation. An example of the variation of surface adsorption with chain length of an alkyl ammonium acetate was given by Somasundaran (18) and is shown in Figure 5.

2. Solution Properties

Solution properties such as ionic strength and temperature will also change the distribution coefficient of the surfactants. In general, an increase of ionic strength will increase the distribution coefficient. On the other hand, an increase in temperature will decrease the distribution coefficient.

The distribution coefficient is not the only factor that determines the extent of foam separation. Other factors such as the pH of the solution, the bubble size, height of foam, height of the bulk solution, gas flow rate, and impurities present have been reported in foam separation studies.

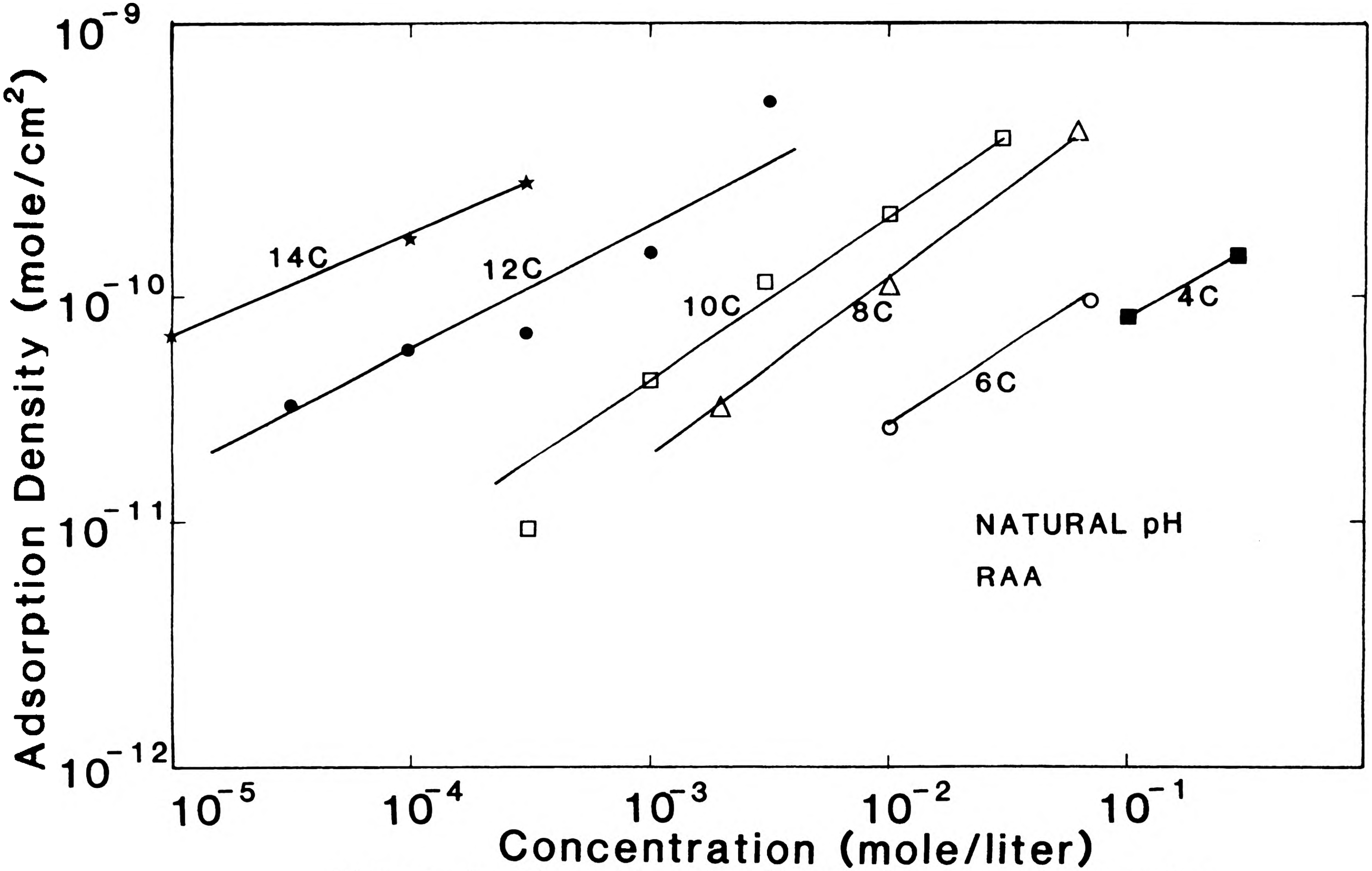


Figure 5. Adsorption densities of various hydrocarbon chain length alkyl ammonium acetates at the liquid / gas interface (18)

DEVICES FOR FOAM SEPARATION

A foam separation process may be performed in a batch mode or a continuous mode.

In a batch mode experiment, a solution with a given initial volume and concentration is placed in a foam column. The bubbles are dispersed through the solution by the foaming gas. The foam is allowed to rise and move from the system and the original solution is continuously depleted (Fig.6) (19).

In a continuous apparatus, a feed solution is continuously added to the column. The foam and drain liquid are continuously removed and the volume of the bulk solution remains constant during the experiment. The feed solution may be added directly to the liquid pool in the column or to the top of the foam column. The continuous system can also be modified for reflux. One of four types of continuous foam separation: simple mode, stripper mode, enricher mode and combined mode, may be used (Fig.7) (19).

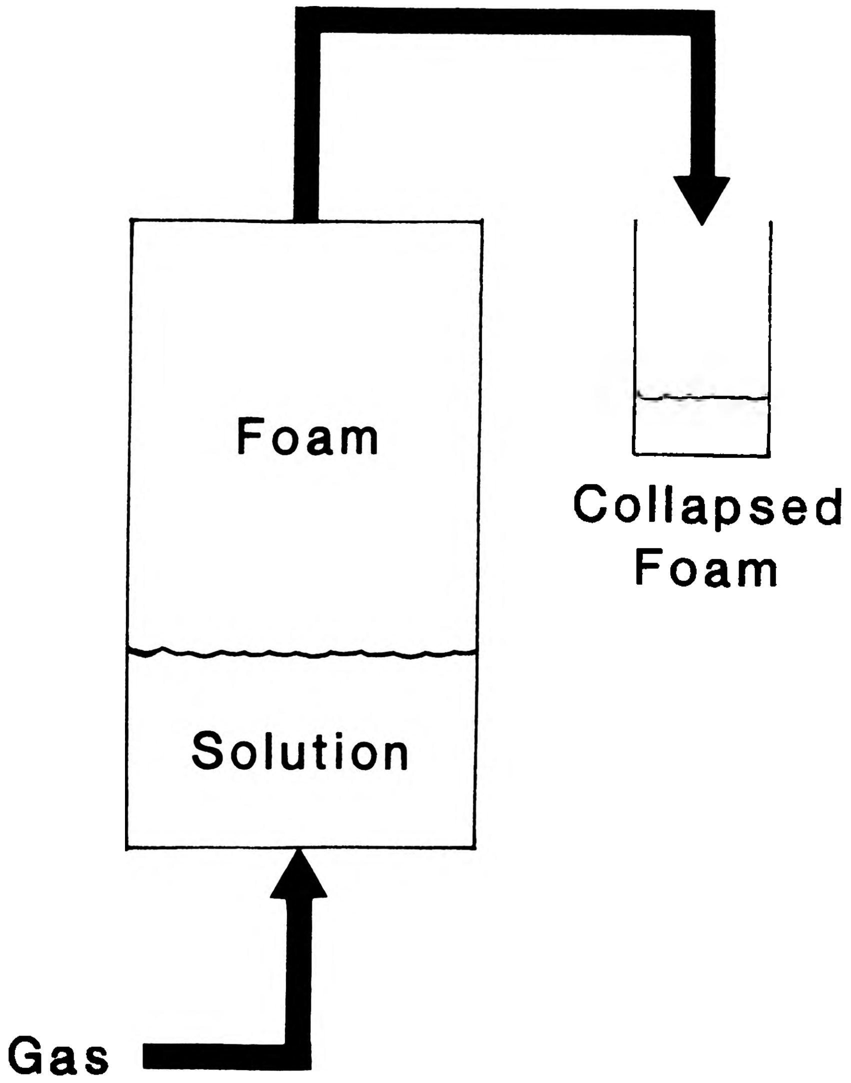


Figure 6. Foam separation in batch mode (19)

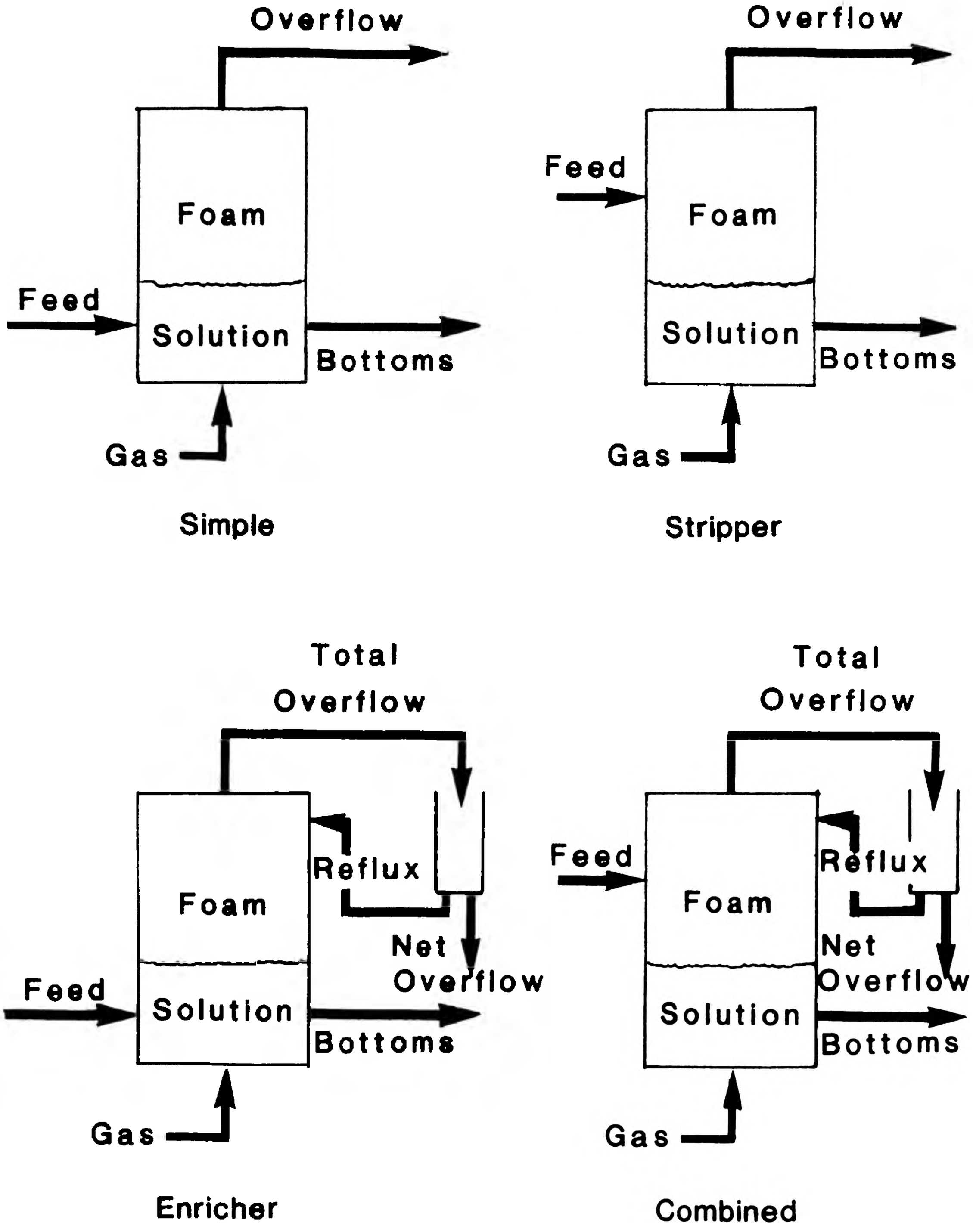


Figure 7. Four modes for continuous foam separation (19)

EXPERIMENTAL

MATERIALS

Sodium octylsulfonate (Aldrich, 98%), decanol (Aldrich, 99%), benzene (Aldrich, GOLD LABEL 99+%), benzyl alcohol (Fisher, reagent grade), butan-1-ol (Fisher, 99 mol%), hexane (Fisher, HPLC grade), sulfuric acid (Fisher, 95% min), aniline (Fisher, 99 mol%) and distilled water. All chemicals were used as supplied.

SURFACE TENSION MEASUREMENT

The critical micellization concentration (CMC) of an aqueous solution of sodium octylsulfonate was determined at 25°C by means of surface tension measurement. The solutions were prepared by weighing sodium octylsulfonate into a known amount of distilled water and mixing well. The value of the CMC is determined from the plot of surface tension of the solutions versus the logarithm of the surfactant concentration. The sharp break in the curve is taken as an indication of micelle formation and corresponds to the CMC.

The surface tension of sodium octylsulfonate solution combined with decanol at surfactant concentrations below the CMC was also studied by surface tension measurements.

The CENCO-du Noüy interfacial tensiometer was used to measure the surface tension. The tensiometer was set at a fixed height (16.8cm). Sample solutions (3.6 gram each) were poured into a special glass dish with a diameter of 3.4 cm (Fig.8A) and the measurements were done in a semiclosed system with a special care to avoid contamination and air currents (Fig.8B). The platinum ring (1.24cm diameter) was cleaned between measurements with a Bensen burner flame and rinsed with distilled water followed by absolute ethanol.

A calibration curve was drawn with liquids of known surface tension. The scale readings and the surface tension of liquids for calibration are listed as follows:

Liquid	Surface tension (dynes/cm)	Scale reading
Benzene	28.85	107.0
Benzyl alcohol	39.00	135.0
Aniline	42.58	143.5
Sulfuric acid	51.50	180.0
Butan-1-ol	24.60	96.0
Hexane	18.40	82.0

The scale readings of sample solution were converted to surface tension from the calibration curve (Fig.9). This method of calibration has the advantage of avoiding the Harkins and Jordan correction factors. The final surface tension of each solution was the average of at least three measurements.

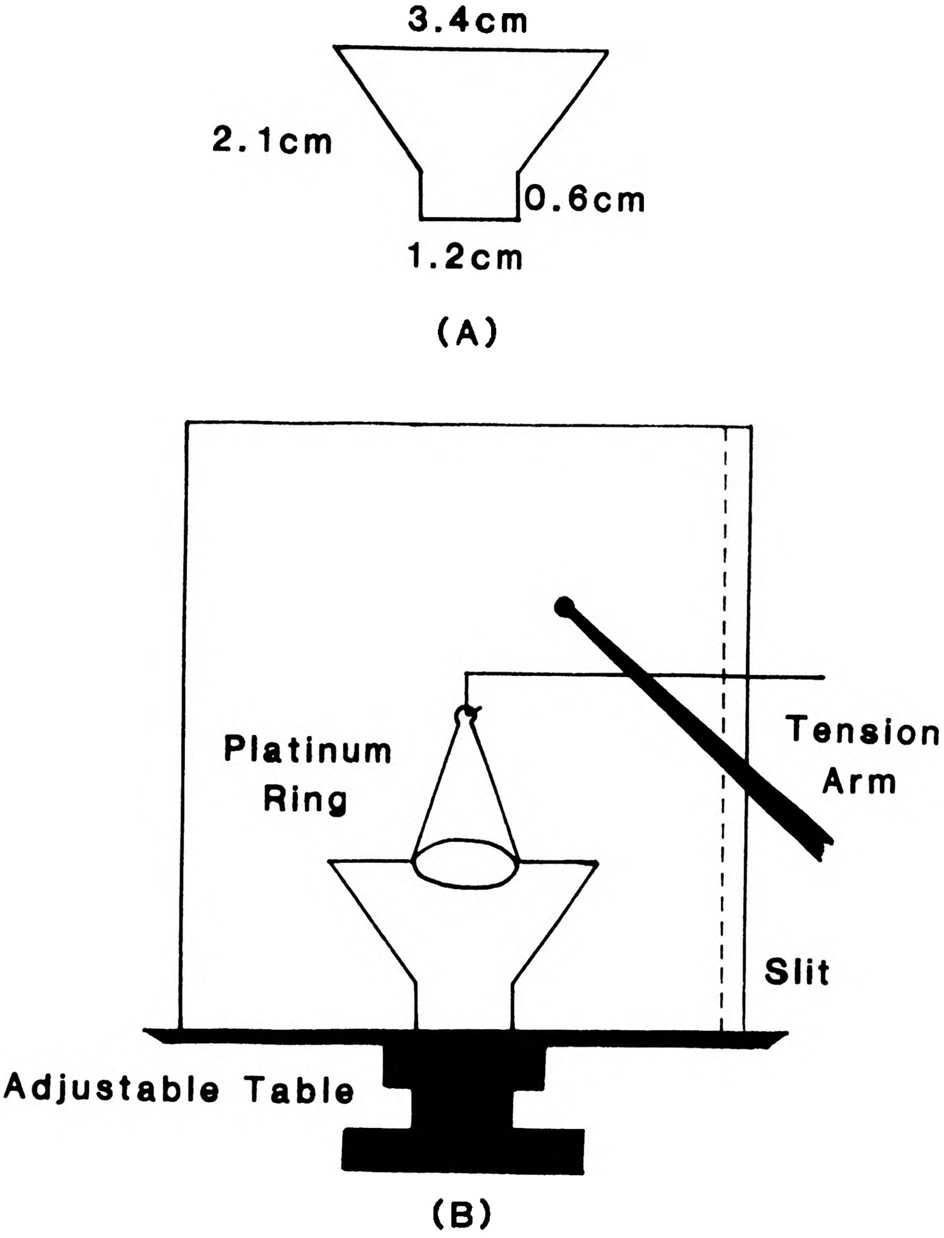


Figure 8. Schematic diagrams of the (A) glass container and (B) du Noüy interfacial tensiometer for surface tension measurement

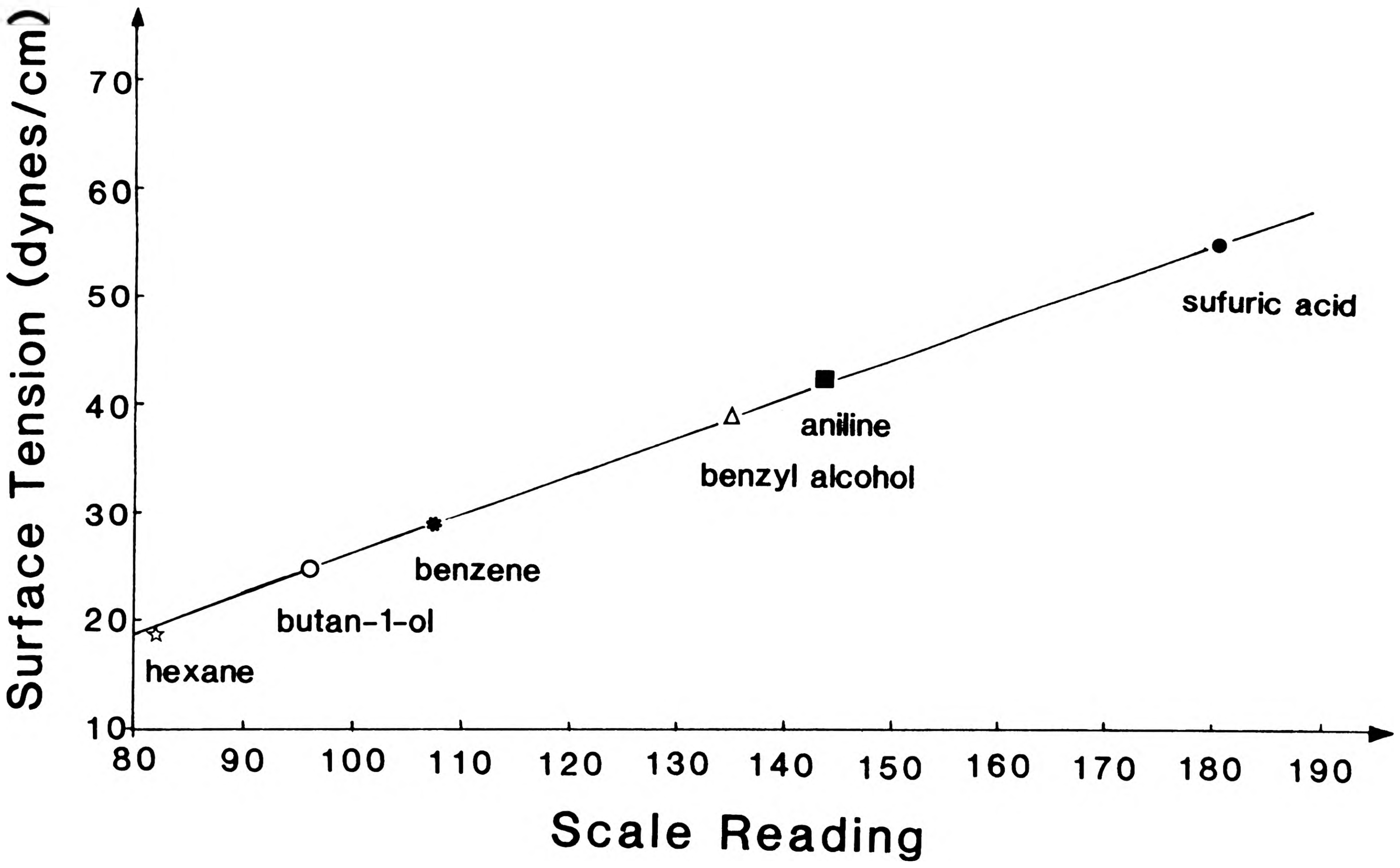


Figure 9. Calibration curve for surface tension measurement

PHASE EQUILIBRIUM DETERMINATION

The ternary phase diagram of water/sodium octylsulfonate/decanol system at 25°C was determined based on the same system investigated by P. Ekwall et. al (20) at 20°C. The phase boundaries were checked carefully. Phase equilibrium lines were determined by the following procedures:

Several series of mixtures of known compositions in weight percent were prepared. The decanol content (1% - 10%) in each series was constant and the amount of surfactant increased gradually in the range of 0.5% - 6%. Sample solutions were mixed well, centrifuged at a speed of 7000 rpm for one hour and stored in a thermostated water bath at 25°C for 48 hours.

The phase types of mixtures were detected visually. Phase changes involving liquid crystals were observed by using crossed polarizers as well as the polarizing microscope.

FOAM SEPARATION

Foam separation was investigated using the same system. Binary aqueous solutions with surfactant concentrations below and above the CMC, and ternary solutions with decanol consentration less than or equal to 6 wt% were prepared in a a glass test tube. The compositions and the equilibrium phases present in these ternary solutions are listed in Table II.

TABLE II

Compositions and Equilibrium Phases of Solutions Chosen for Foam Separation Studies in Two- and Three-phase Regions

Composition*	Equilibrium Phase**
S/W/D	
2/96/2	L_1 + D
6/92/2	L_1 + D
4/94/2	L_1 + D
1/97/2	L_1 + D + L_2
3/93/4	L_1 + D
2/94/4	L_1 + D + L_2
7/89/4	L_1 + D
11/85/4	L_1 + D
8/86/6	L_1 + D
12/82/6	L_1 + D
16/78/6	L_1 + D
1/93/6	L_1 + D + L_2

* S/W/D - Sodium octylsulfonate/Water/Decanol

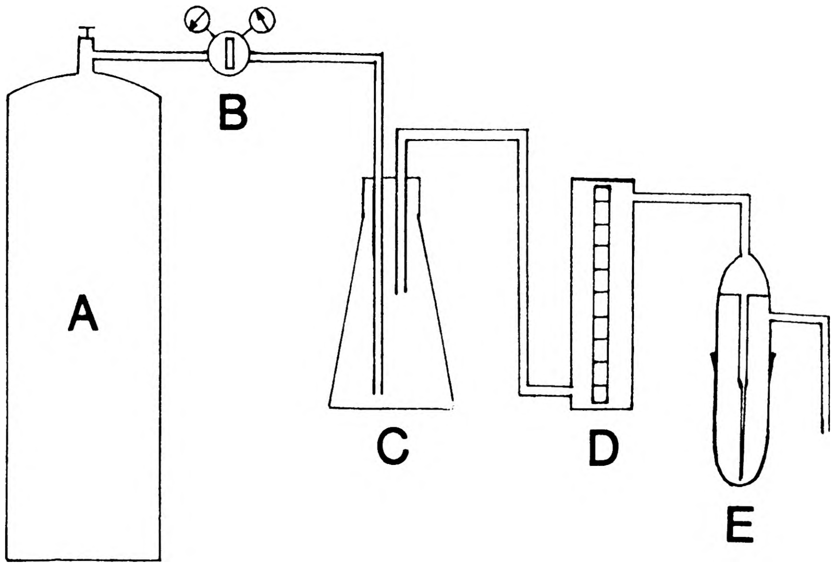
** L_1 - normal micellar solution

D - lamellar liquid crystal

L_2 - alcohol solution

The apparatus used for foam separation experiments is shown in Figure 10. Nitrogen gas (A) was used as the foaming gas. The flow rate of nitrogen gas was controlled at 6.5 ml/min by a regulator (B) and a flow meter (D). A humidifier bottle (C) filled with distilled water was used to saturate the foaming gas with moisture in order to avoid the evaporation of water from either foam or bulk phases by the dry nitrogen gas. A specially designed foam separation column (E) was built for foam generation. The apparatus is illustrated in Figure 11. It consists of a gas inlet tube which narrows to a fine capillary and a solution reservoir. A larger diameter tube surrounds the capillary to about one half of its length. This larger tube ends in a ground glass joint, which serves as the connection to the solution reservoir. This reservoir is a tube of diameter 1.53 cm and height 8.78 cm. When the ground glass joint is sealed, the capillary tip extends to about 1 mm from the bottom of the solution reservoir. A side tube is connected to the larger diameter glass tube for collecting the foams.

A sample solution of constant weight (3.6g) was placed in the solution reservior of the foam separation column. Foams were generated by introducing the nitrogen gas through the fine capillary and bubbling the sample solution. The generated foams moved upward in the column and were collected through the side tube.



A - nitrogen gas cylinder

B - pressure regulator

C - humidifier bottle

D - flow meter

E - separation column

Figure 10. The foam separation apparatus

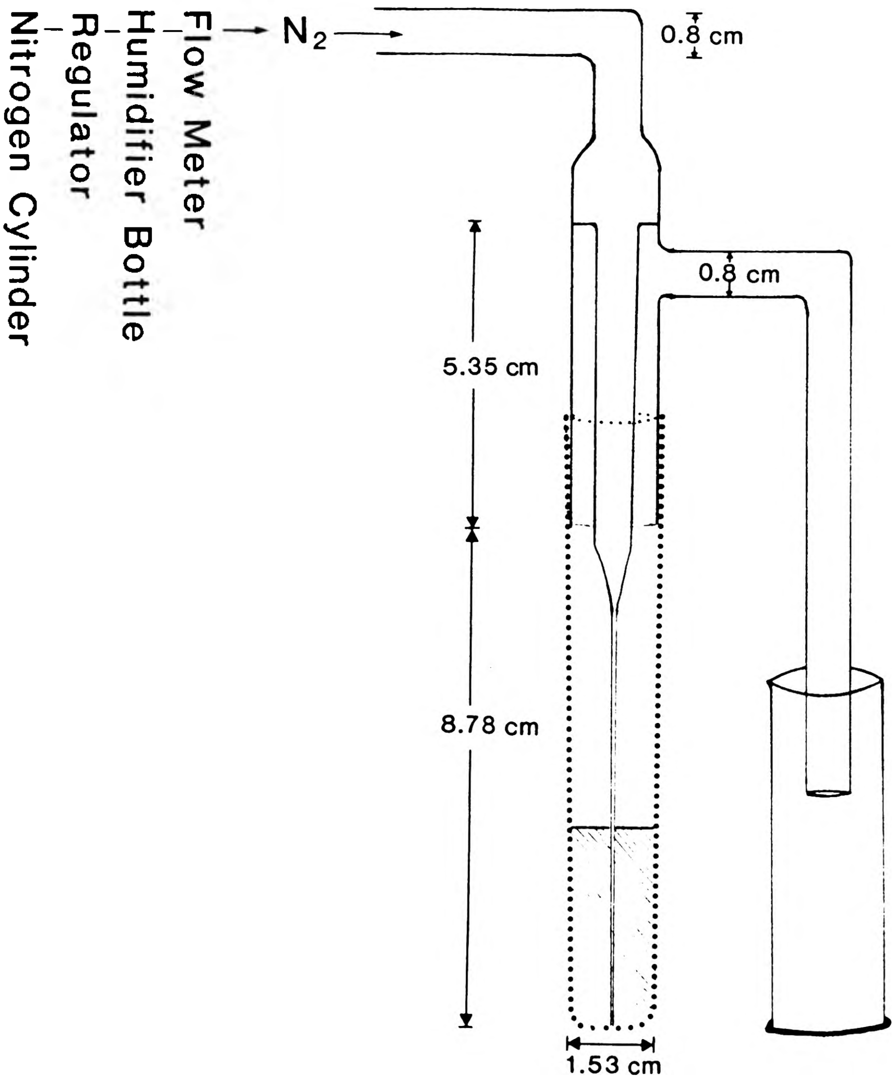


Figure 11. The foam separation column

The weight percentage of transported foam over specific periods of time (10 minutes or 30 minutes) was measured by comparing the weight of remaining solution to the weight of original solution. Surface tension of the remaining solution in the foaming tube after foam separation was determined and compared to that of the original solution.

LIQUID CRYSTAL TO LIQUID VOLUME RATIO

The volume ratios of liquid crystal to liquid for the original solution before foam separation and for the remaining solution after foam separation were measured and compared. The solutions were centrifuged at 7000 rpm for one hour. The liquid crystal portion was distinguished from the isotropic liquid partion under crossed polarizers. The heights of liquid crystal and liquid in the tube were measured.

RESULTS

PHASE DIAGRAM

Figure 12. shows the phase regions for the normal micellar solution (L_1), lamellar liquid crystal (D), inverse micellar solution (L_2), hexagonal liquid crystal (E) and three tie lines in the water/sodium octylsulfonate/ decanol system.

At low surfactant concentration, a two-liquid phase region exists where the normal micellar solution (bottom layer) was in equilibrium with the decanol solution (top layer). With increasing concentration of surfactant, the equilibrium lines moved to the right and a three-phase region was encountered, in which a liquid crystalline phase appeared between two isotropic liquids (i.e. normal micellar solution and inverse micellar solution). With more surfactant, the amount of liquid crystal phase increased and the phase equilibrium changed from three phases to two phases (liquid crystal and normal micellar solution).

CRITICAL MICELLIZATION CONCENTRATION (CMC)

The surface tension versus the logarithm of the surfactant concentration is plotted in Figure 13. The CMC was found at a concentration of 0.12 M, which corresponds to 2.6 wt% surfactant. Sodium octylsulfonate has a larger CMC value than longer chain ionic surfactants in water. This high CMC is

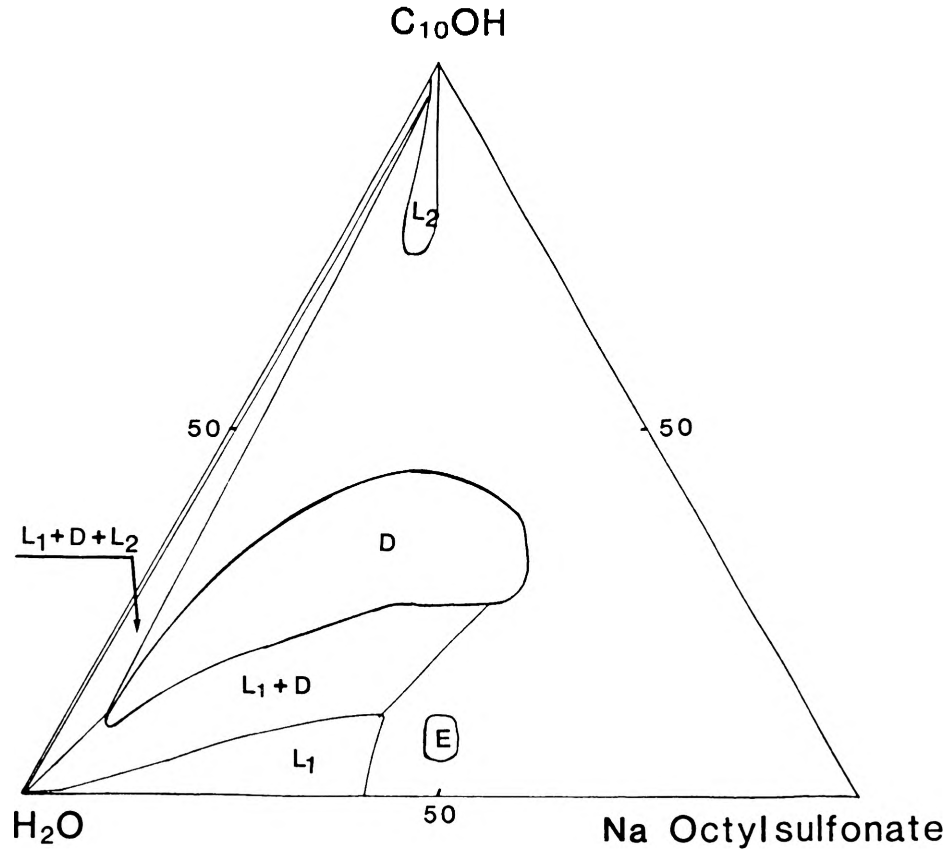


Figure 12. Phase regions and phase equilibrium diagram of the water / sodium octylsulfonate / decanol system

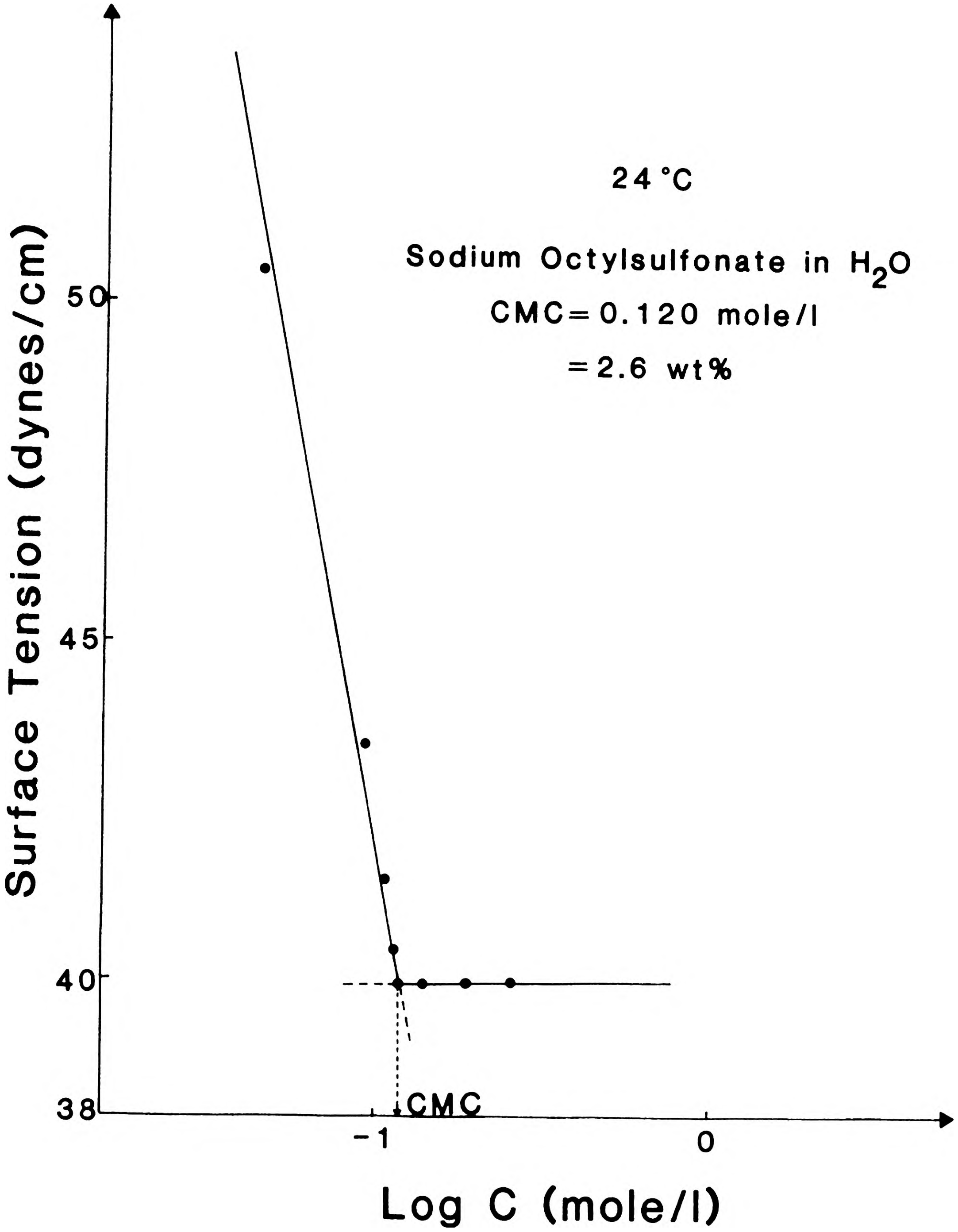


Figure 13. Surface tension versus logarithm concentration of sodium octyl sulfonate

favorable for foam separation studies at surfactant concentration near and especially below the CMC.

FOAM SEPARATIONS

The foam separation results showed that foams are extremely unstable in mixtures of sodium octylsulfonate and water at concentrations both above and below the CMC. The product foams collapsed within a few seconds, hence, no foam separations were observed with these binary combinations.

When an extremely small amount of decanol, (e.g. 2.5×10^{-3} wt%), was added to the aqueous surfactant solutions, the product foams were stable and transportable.

Figure 14 shows the effect of decanol content on the foam separation for 1 wt% and 2 wt% surfactant solutions over a period of 10 minutes. For a 1 wt% surfactant solution, the foam separation increases with increasing amount of decanol and goes to equilibrium. For a 2 wt% surfactant solution, there is a maximum point of foam separation at 0.005 wt% of decanol, above which the foam separation decreases gently to equilibrium. It is clear that the 1 wt% surfactant solution requires more decanol than the 2 wt% surfactant solution to give a stable foam. It is also interesting that for a concentration of decanol above 0.01 wt% the same amount of foam was transported for both 1 wt% and 2 wt% surfactant solutions.

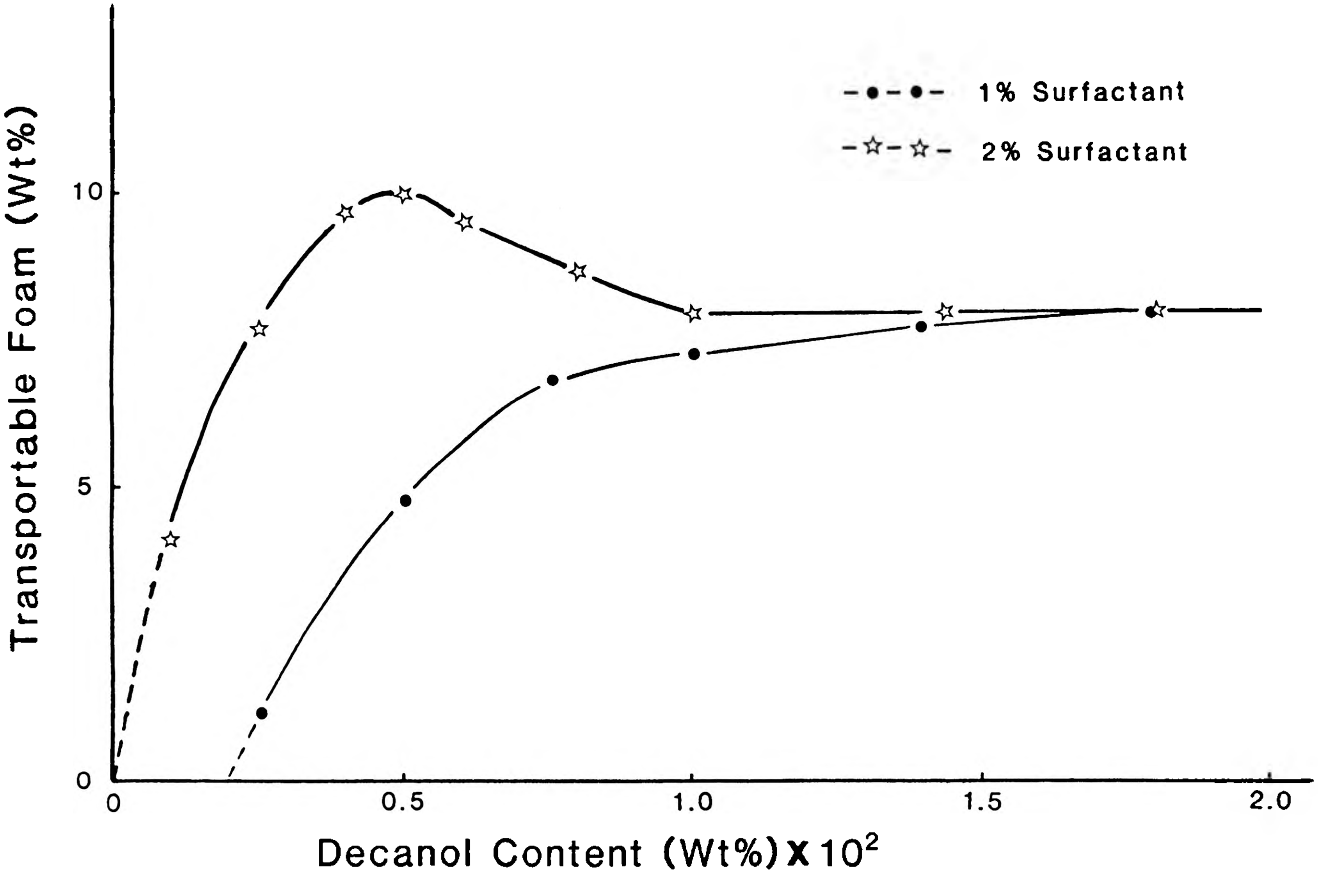


Figure 14. The effect of decanol content on the foam separation for 1 wt% and 2 wt% surfactant solutions at 10 minutes separation time

Foam separation in the two phase (L_1 + D) and the three phase (L_1 + D + L_2) regions with constant 2 wt%, 4 wt% or 6 wt% decanol content were measured and compared. Figure 15 shows the data indicating the weight percent of transported foam over 30 minutes for solutions at those compositions. The solutions which were close to the lamellar liquid crystal region gave more transported foam (i.e. higher decanol content). Maximum foam separation was found in the solutions located near the transition point from three phase (L_1 + D + L_2) to two phase (L_1 + D). Foam separations in the two phase region (L_1 + D) were better than those in the three phase (L_1 + D + L_2) region. The data points were plotted as a function of weight percent ratio of surfactant to water (Fig.16). The foam separation of solutions in the two phase region decreased with increasing surfactant to water ratio. The same tendency was obtained for separation a time of 10 minutes (Fig.17).

SURFACE TENSION MEASUREMENTS

The surface tensions of 1 wt% and 2 wt% surfactant solutions as a function of decanol content are presented in Figure 18. The value of surface tension decreased rapidly when decanol was introduced into the solution, and remained constant above 1×10^{-2} wt%. Figure 19 gives the surface tensions of 1 wt% surfactant solutions before and after foam separation over 10 minutes separation time periods. This shows that the solution remaining after foam separation has higher surface tension than that of the original solution.

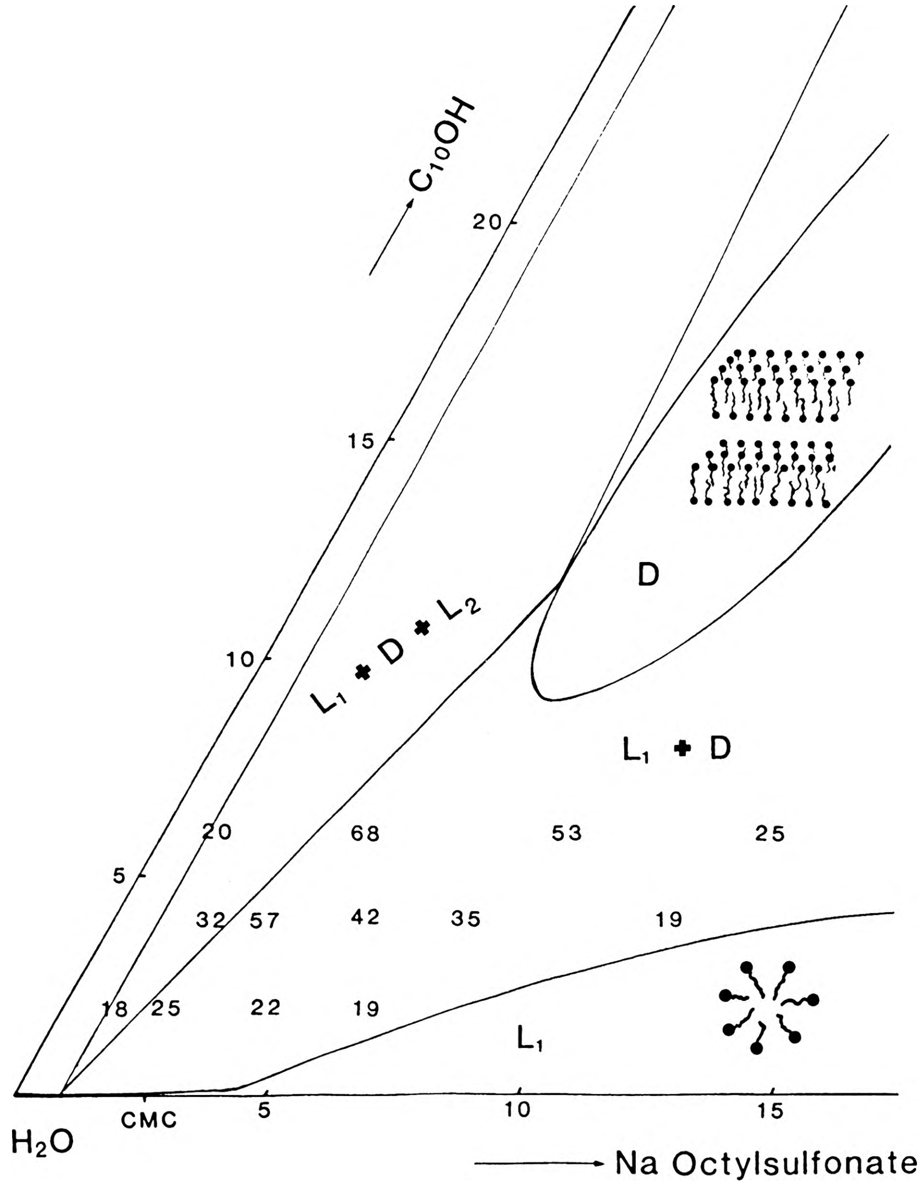


Figure 15. Weight percent of transported foam at 30 minutes separation time for different compositions

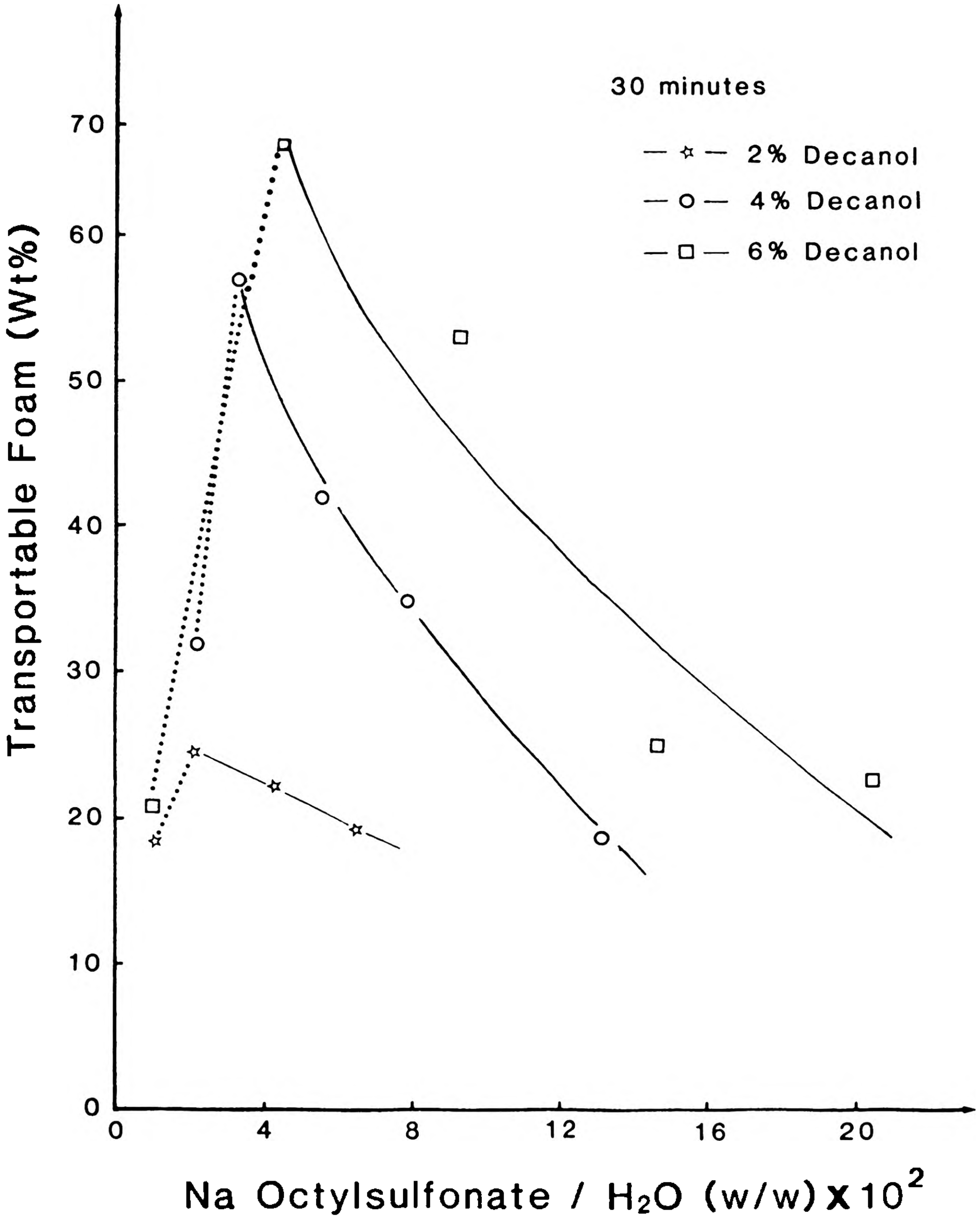


Figure 16. Weight percent of transported foam versus surfactant to water ratio at 30 minutes separation time

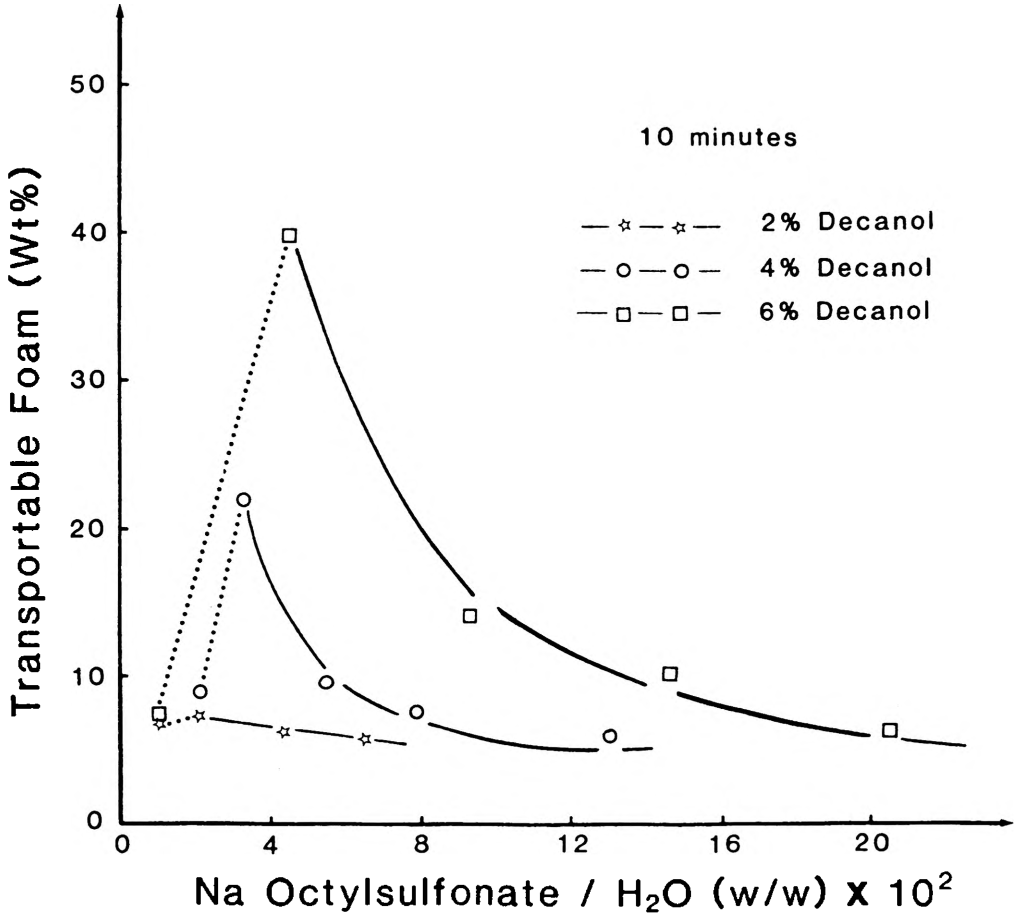


Figure 17. Weight percent of transported foam versus surfactant to water ratio at 10 minutes separation time

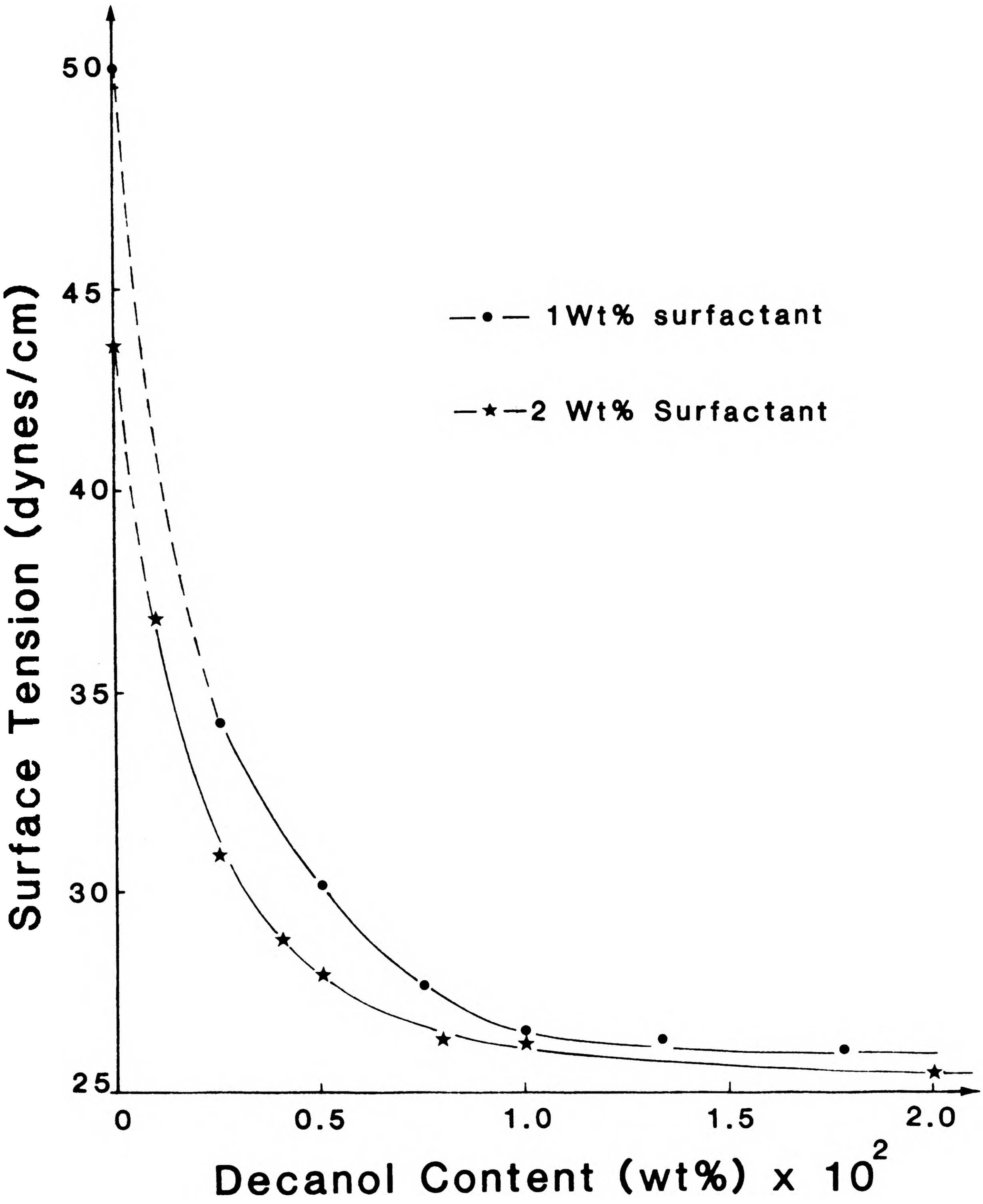


Figure 18. The effect of decanol content on the surface tensions of 1 wt% and 2 wt% sodium octyl sulfonate solution

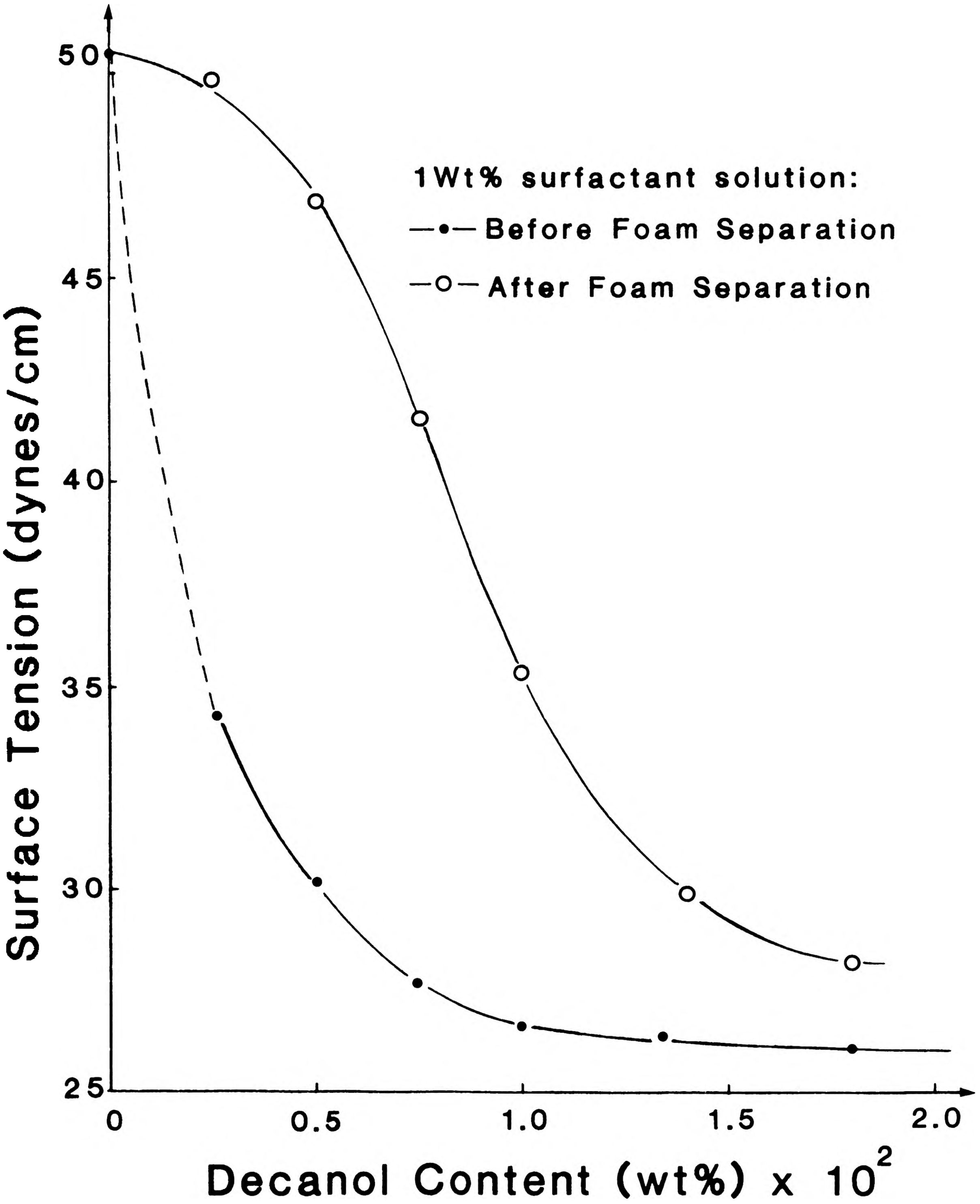


Figure 19. Surface tension versus original decanol content for solutions before and after foam separation

LIQUID CRYSTAL / LIQUID VOLUME RATIOS

The liquid crystal to liquid volume ratios for solutions of varying surfactant to water ratio at 4 wt% decanol are shown in Figure 20. The ratio of the remaining solution after foam separation were less than those of the original solution.

A list of liquid crystal to liquid volume ratios for solutions at two separation times, 10 minutes and 30 minutes is given in Table III. The percent change in ratio from 10 to 30 minutes separation time is usually less than the percent change in the first 10 minutes.

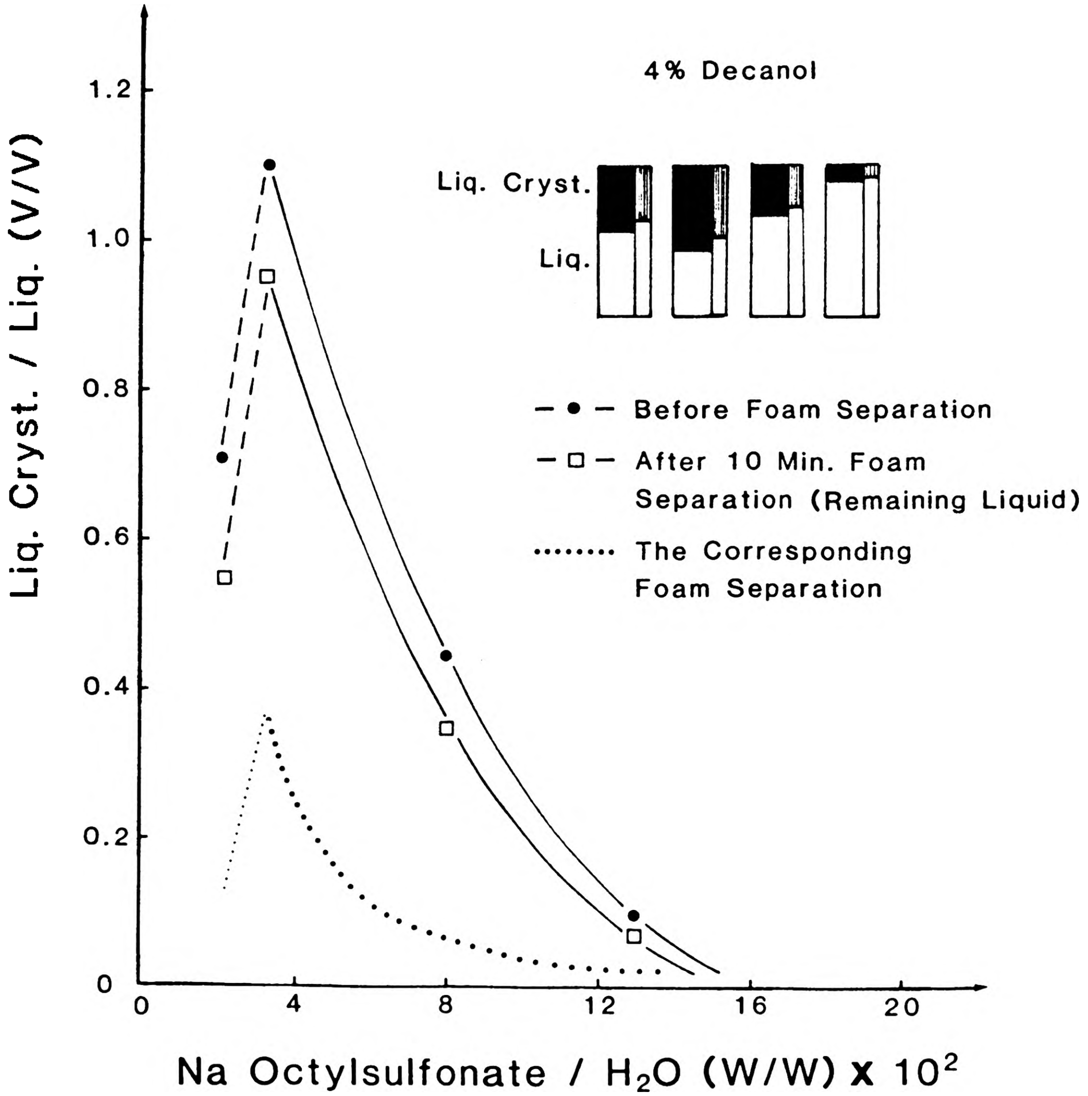


Figure 20. The liquid crystal to liquid volume ratio versus the surfactant to water ratio for solutions containing 4 wt% of decanol before and after foam separation

TABLE III

Liquid Crystal to Liquid Volume Ratios for Solutions Chosen for Foam Separation Studies in Two- and Three-phase regions

Composition[a] S/W/D	Liquid Crystal[b] liquid	Liquid Crystal[c] liquid	Liquid Crystal[d] liquid
2/96/2	0.383	0.290	0.271
6/92/2	0.132	0.111	0.094
4/94/2	0.090	0.069	0.048
1/97/2	0.0694	*	*
3/93/4	1.100	0.950	*
2/94/4	0.704	0.546	0.325
7/89/4	0.441	0.345	*
11/85/4	0.091	0.069	0.062
8/86/6	0.976	0.800	*
12/82/6	0.456	0.246	0.208
16/78/6	0.063	0.056	0.052
1/93/6	0.039	*	*

a: S/W/D - Sodium Octylsulfonate/Water/Decanol
b: solution before foam separation
c: solution after 10 minutes foam separation
d: solution after 30 minutes foam separation

DISCUSSION

EFFECT OF FOAM SURFACE STRUCTURE ON FOAM SEPARATION

The foam separation results show that the foam surface structure is an important factor on the foam stability and the efficiency of foam separation. Foam surface structure implies the packing structure of molecules on the foam film surface. For the aqueous surfactant solution below CMC, the surfactant molecules are loosely monodispersed at the gas-liquid interface (Fig.21A). Foams were not stable in this case, collapsing before reaching the top of the foam column, and no foam separation was observed. When the decanol molecules were introduced to the aqueous surfactant solution, they adsorbed at the surface strongly. The decanol molecules are incorporated between surfactant molecules, and give a much closer packed surface film (Fig.21B). With more decanol, the multilayer structure is formed (Fig.21C) instead of the compacted monolayer film. This multilayer structure gave stable foams (21-23) and enhanced foam separation.

SURFACE VISCOSITY

Surface viscosity is related to the degree of molecular packing in the surface film (i.e. the surface structure). Usually, the more close-packed the surface film, the higher the surface viscosity. In our observations, the addition of decanol to the surfactant solution gave a more close-packed

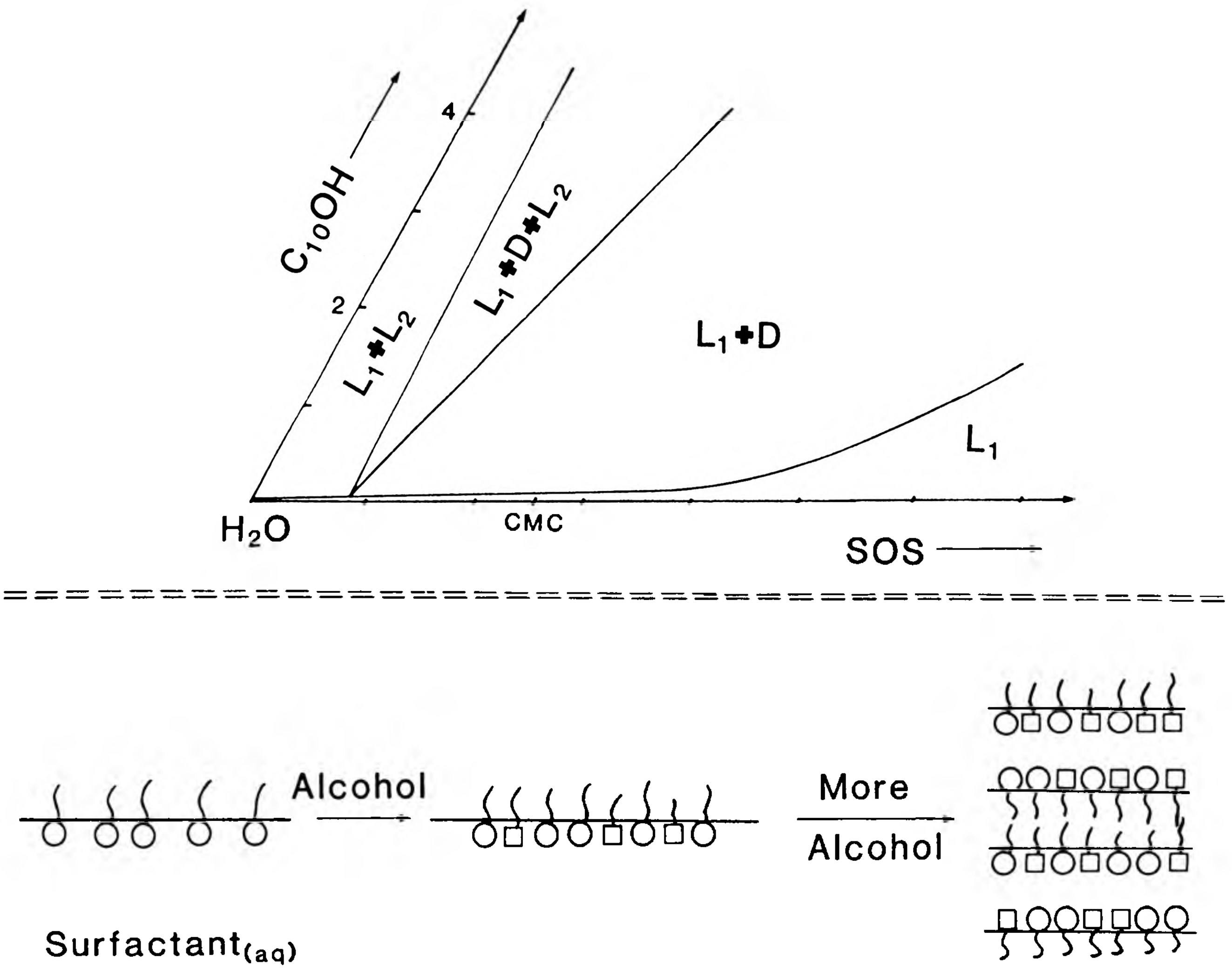


Figure 21. Three different types of surface structures for films (A) "loose" monodisperse structure (B) "compact" monolayer structure (C) "multilayer" structure

film of surfactant monolayer, causing an increase in surface viscosity. The enhanced surface viscosity inhibited the liquid drainage in the foams and the foam stability increased.

FOAM SEPARATION WITH COMPACT MONOLAYER STRUCTURE

The surface tension results (Fig.18) for 1 wt% and 2 wt% surfactant solutions show that the decanol molecules at a concentration less than 0.01 wt% are strongly adsorbed at the surface and enhance the reduction of surface tension of the original solutions. The foam film becomes more compact and viscous, which gives better foam separation. Solutions with 2 wt% surfactant have a better foam separation than with 1 wt% surfactant solution (Fig.14). The reason is that 2 wt% surfactant solution gave more compact packing of surfactant molecules on the foam surface.

When the amount of decanol is beyond the solubility limit, the additional decanol molecules produce a multilayer structure with long range order. This multilayer structure has an enormous effect on foam separation, as discussed in the following section.

FOAM SEPARATION WITH MULTILAYER STRUCTURE

The multilayer structure is a lamellar liquid crystal. The liquid crystals surrounding the foam surface stabilize the foam (21-27). During the foam separation process, the liquid crystal stays with the foam and is separated from the solution. The results show that the extent of foam separation is related to the concentration of liquid crystal in the bulk solution. The higher the concentration of liquid crystal surrounding the foam, the higher the surface viscosity, the lower the drainage rate, and the more resistant the foam. A larger amount of materials is separated from the bulk solution. The amount of foam transported from the solutions increases with decanol content in the range of 2 wt% to 6 wt%. At higher decanol level, the viscosity due to increased liquid crystal content was too high to form foam.

The maximum foam separation for solutions with a fixed amount of decanol is found at the phase transition boundaries from three phase (L_1 + D + L_2) to two phase (L_1 + D). This is also the location with the highest liquid crystal to liquid volume ratio (Table III). According to the phase diagrams when the ratio of surfactant to water is increased, in the two phase region the sample composition approaches the normal micellar solution region. The liquid crystal to liquid ratio is reduced and less foam separation should be expected.

The larger changes in liquid crystal to liquid ratio at short separation time is due to the high concentration of liquid crystal in the original bulk solution. This leads to enhance liquid crystal adsorption on the foam surface. As the foam carries liquid crystal away, the concentration of liquid crystal in the remaining bulk solution is reduced by dilution with the drainage. Foam generated thereafter has a lower liquid crystal to liquid volume ratio, and the rate of liquid crystal removal decreases with the increasing dilution.

CONCLUSION

Foams have a large surface area, hence, the molecular packing structures on the foam surface have a great influence on foam stability and foam separation. A model system of water, sodium octylsulfonate and decanol was investigated. Three types of surface structures have been proposed in order to understand the foam stability and foam separation. (1) A loosely packed surfactant monolayer. In the dilute sodium octylsulfonate solution, surfactant molecules distributed loosely at the surface gave extremely unstable foams and no foam separation. (2) A close-packed "mixed" monolayer: When a very small amount of decanol (10^{-3}-10^{-2} wt%) was present in the surfactant solution. The decanol molecules incorporated between the surfactant molecules and gave a "mixed" monolayer. This surface structure increased the foam stability and allowed foam separation, but the efficiency of foam separation was poor. (3) A multilayer structure. When decanol content in the surfactant solution was increased to 0.5 wt%, the close packed "mixed" monolayer associated to a multilayer structure which is the lamellar liquid crystal. Foam stability and foam separation were highly enhanced in the multilayer structure region. These three structures are related to the phase equilibrium in the ternary surfactant system. Therefore, the foam stability and foam separation are totally dependent on the phase equilibrium diagrams.

REFERENCES

1. Rubin, E., and Gaden, E. L., Jr., in "New Chemical Engineering Separation Techniques." (H. M. Schoen, Ed.), John Wiley & Sons - Interscience, New York, 1962, P.319.
2. Lemlich, R., Ed., "Adsorptive Bubble Separation Techniques.", Academic Press, New York, 1972.
3. Taggart, A. F., "Handbook of Mineral Dressing.", John Wiley and Sons, New York, 1964, pp. 12:55 to 12:78.
4. Preston, J. M. and Saha, S., J. Textile Inst., 40, T381 (1949).
5. Gaudin, A. M., Mular, A. L. and O'Connor, R. F., Appl. Microbiol., 8, 91 (1960).
6. Gaudin, A. M., Mular, A. L. and O'Connor, R. F., Appl. Microbiol., 8, 84 (1960).
7. Pushkarev, V. V., Egorov, Y. V., Tkachenko, E., and Zolatavin, V., Atom Energ., 16, 48 (1964).
8. Grieves, R. B., Separation Science, 1, 395 (1966).
9. Grieves, R. B., in "Adsorptive Bubble Separation Techniques." (R. Lemlich, Ed.), Academic Press, New York, 1972, Chapter 10.
10. Karger, B. L. and Roger, L. B., Anal. Chem., 33, 1165 (1961).
11. Somasundaran, P., Separ. Purif. Methods 1, 117 (1972).
12. Somasundaran, P., Separ. Sci. 10, 93 (1975).

13. Grieves, R. B., in "Treatise on Analytical Chemistry." 2nd Ed., (P. J. Elving, Ed.), John Wiley & Sons, New York, 1982, part I, Vol.5, P.371.

14. Clark, A. N., and Wilson, D. J., "Foam Flotation: theory and application." Dekker, New York, 1983.

15. Ross. S., and Nishioka, G., J. Phys. Chem., 79, 1561 (1975).

16. Ross. S., and Butler, J. N., J. Phys. Chem., 60, 1255 (1956).

17. Adamson, W., "Physical Chemistry of Surface." 3rd. Ed., John Wiley & Sons, New York, 1976.

18. Somasundaran, P., Trans. AIME, 241, 105 (1968).

19. Lemlich, R., in "Progress in Separation and Purification" Vol.1. (E. S. Perry, Ed.), John Wiley & Sons, New York, 1968, p.1.

20. Ekwall, P., in "Advance in Liquid Crystals." (G. H. Brown, Ed.), Academic Press, New York, 1975, P.1.

21. Jederstrom, G., Rydhag, L., and Friberg, S., J. Pharm. Sci. 62, 1979 (1973).

22. Friberg, S., and Saito, H., and Linden, S., Nature (London) 251, 494 (1974).

23. Saito, H., and Friberg, S., Pamara, 1, 537 (1975).

24. Friberg, S., Rydhag, L., and Jederstrom, G., J. Pharm. Sci. 60, 1883 (1971).

25. Ahmad, S. I., and Friberg, S., J. Colloid Interface Sci. 35, 175 (1971).

26. Ahmad, S. I., and Friberg, S., Acta Polytech. Scand. Chem. 102, 1 (1971).

27. Friberg, S., in "Advance in Liquid Crystals." (G. H. Brown, Ed.), Vol. 3, Academic Press, New York, 1978, pp.149-165.

ARTICLE II

POLYMERIZED FOAMS FROM ANAQUEOUS AMPHIPHILIC SYSTEM

by

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ABSTRACT

A solid foam was prepared from water - polymerizable surfactant - oleyl alcohol system. The polymerizable surfactant was the sodium salt of acryloamidoundecanoic acid and was synthesized by reacting acrylamide with undecenoic acid. The surfactant formed a micellar solution and hexagonal liquid crystal with water at room temperature. Oleyl alcohol was moderately soluble in this solubility region. A small lamellar liquid crystal region was also observed in the presence of oleyl alcohol. Stable foams were found in the three - phase region and polymerized with liquid crystal dispersions. The microscopic study showed that liquid crystals were retained and extended on the foam surface during the polymerization.

INTRODUCTION

Foam is classified as a colloidal dispersion in which gas is dispersed in liquid or in solid. Both "gas in liquid" and "gas in solid" dispersions are frequently encountered in daily life. Foam from beer is "gas in liquid", while styrofoam such as egg cartons and cold drink cups are examples of "gas in solid".

"Gas in solid" plastic foams (1-6) are the object of this study. A large variety of plastics and elastomers are produced as these cellular foams. Plastic foams have been developed since the mid. 1930's. During War World II, foamed materials were used in the military for making life rafts for troop transports and floating equipment. After War World II, the developments in and requirements for plastic foams increased very rapidly.

Plastic foams can be made from thermoplastic and thermosetting plastics or from elastomers. Reported solid foams (1-6) include polyurethane, polystyrene, polyvinyl chloride, polyolefin, epoxy, phenolic, phenol - formaldehyde, polyvinyl alcohol - formaldehyde, urea - formaldehyde, polyvinyl formaldehyde, acrylonitrile and acrylate copolymer, pyranyl, synthetic rubber and silicone (3), and polyacetylene (7) foams. Among them, polyurethane and polystyrene are the most popular plastic foams.

Polystyrene foams are excellent for insulation and packaging because of the low-cost for preparation. Polyurethane foams have become a commercial product since 1950. They can be made in different grades or densities depending on the requirements (1,3,5,6). The shortcoming of polyurethane foam is that it is not fire-resistant. When polyurethane burns, it emits toxic carbon monoxide and cyanide fumes. However, a fire retardant additive can give polyurethane foam self-extinguishing properties.

There are two general methods used for the preparation of plastic foams (1,3). One method is by direct extrusion and expansion of foamable beads and granules. Another method used is the incorporation of a "blowing agent" into a liquid resin or elastomer mixtures, followed by expansion. Blowing agents are compounds which liberate an inert gas by decomposition or by chemical reaction at room temperature or at elevated temperature. In addition to the resin material and blowing agent, a number of modifiers such as catalyst, hardener, surfactant etc. are added during the production process to control the reaction rate, enhance the original properties and reduce the manufactured price.

A typical formulation for a medium-density epoxy foam (3) is listed in Table I. The function of the surfactant is to regulate the bubble size, control the viscosity and surface tension of the bubble membranes, and stabilize the bubble during foaming.

TABLE I

The Formulation of a Medium-Density Epoxy Foam (3).

Ingradients	Parts	Function
Epoxy resin (10,000-16,000 cP at 77°F)	100.0	base resin
4,4'oxybis(benzene sulfonyl hydrazide)	2.0	foaming agent
Tween 20 (polyoxyethylene sorbitan monolaurate)	0.2	surfactant
Toluene	5.0	(1)solvent (2)aux. foaming agent
Diethylenetriamine	6.0	hardener

Depending on their structures, densities and appearances, plastic foams can be classified as closed-cell or open-cell, low density, medium density or high density, and flexible, semi-rigid or rigid foams. Closed-cell plastic foams consist of rigid noncommunicating bubbles. Each bubble cell is completely enclosed by the thin cell membrane and some pressure is maintained within the bubble during the bubble generation process. On the other hand, open-cell plastic foams are made with free expansion, each cell is interconnected with its neighbors, and air can freely pass in and out. Large quantities of fluids can be adsorbed by open-cell foams, as in, for example, a sponge. Both closed-cell and open-cell foams have their special applications. Closed-cell foams are used for making life rafts and buoys because their closed foam structure prevents water uptake. Closed-cell foam stores energy reversibly as if it were a balloon, while open-cell foams dissipate a relatively large percentage of the energy input during compression. Hence, flexible open-cell foams are usually used for vibration damping or shock absorption.

Foams with varying degrees of density are available. According to Benning (3), depending on density or gas to solid volume ratio, low-, medium- and high-density foams are classified as follows:

	density(g/cm^3)	gas/solid(V/V)
Low-density foams	< 0.1	9/1
Medium-density foams	0.1 - 0.4	9/1 - 1.5/1
High-density foams	> 0.4	< 1.5/1

Plastic foams are widely used either as a replacement for conventional materials such as wood and metals or in a completely new application because of their special properties. For example, structural foams of polystyrene, polyurethane, polypropylene or polycarbonate are light weight, very tough and shock resistant. They consist of a strong skin covering a foam core. Structural polystyrene foam has been used to replace wood in pianos designed for beginners (5). Plastic foams are not only commercially important but are also important for military applications (2) in missiles, rockets and submarines.

The extensive application of plastic foams is the result of their inherent features which combine the properties of foams and polymers. First, foamed materials have high gas contents, and the low thermal conductivity of the gas gives an excellent heat insulation. Second, any foam material will have energy-storing or dissipating capacity. When the foam breaks down on impact, it will absorb energy. For this reason foam materials are widely used for industrial packaging. In addition, the apparent low density, light weight, and valuable mechanical properties of plastic foams create numerous applications in almost every conceivable industry, such as in construction and transportation.

In this investigation, a new approach to preparing solid foams is presented. A "gas in liquid" foam was generated in an aqueous system with a polymerizable surfactant, and "gas in solid" foam was obtained when the surfactant polymerized. The major difference between this new method and conventional methods for producing solid foams is that the new method employs less raw material and lower energy in the preparation process.

EXPERIMENTAL

MATERIALS

Acrylonitrile (Aldrich, 99+%), undecanoic acid (Aldrich, 99%), carbon tetrachloride (Fisher, certified A.C.S.), distilled water, cyclohexane (Aldrich, 99+%), oleyl alcohol (Kodak, boiling pt. 205°/13mm), Sulfuric acid (Fisher, 95%min), potassium persulfate (Fisher, 99.6%) all chemical used as supplied.

SYNTHESIS A POLYMERIZABLE SURFACTANT

Polymerizable surfactant - Sodium Acryloamido-undecanoate (abbreviated as NaAAU) was prepared via a modified Ritter reaction (8) as described by Plaut (9) and Freedman, et. al. (10). in the following way:

The apparatus is shown in Figure 1. In a 500ml three-necked flask fitted with a thermometer and dropping funnel, was placed 242g of sulfuric acid. A nitrogen atmosphere was maintained an egg-shaped magnetic stirring bar was used. An ice bath was used to maintain a mixing temperature below 20°C. First 106g of acrylonitrile and then 92.14g of undecanoic acid were slowly and carefully added with stirring. After all of the reagents were well mixed, the mixture was reacted at 30°C for 3 hours and allowed to stand over-night. It was then poured into one liter of distilled water cooled by an ice bath and stirred in order to remove excess sulfuric acid. The

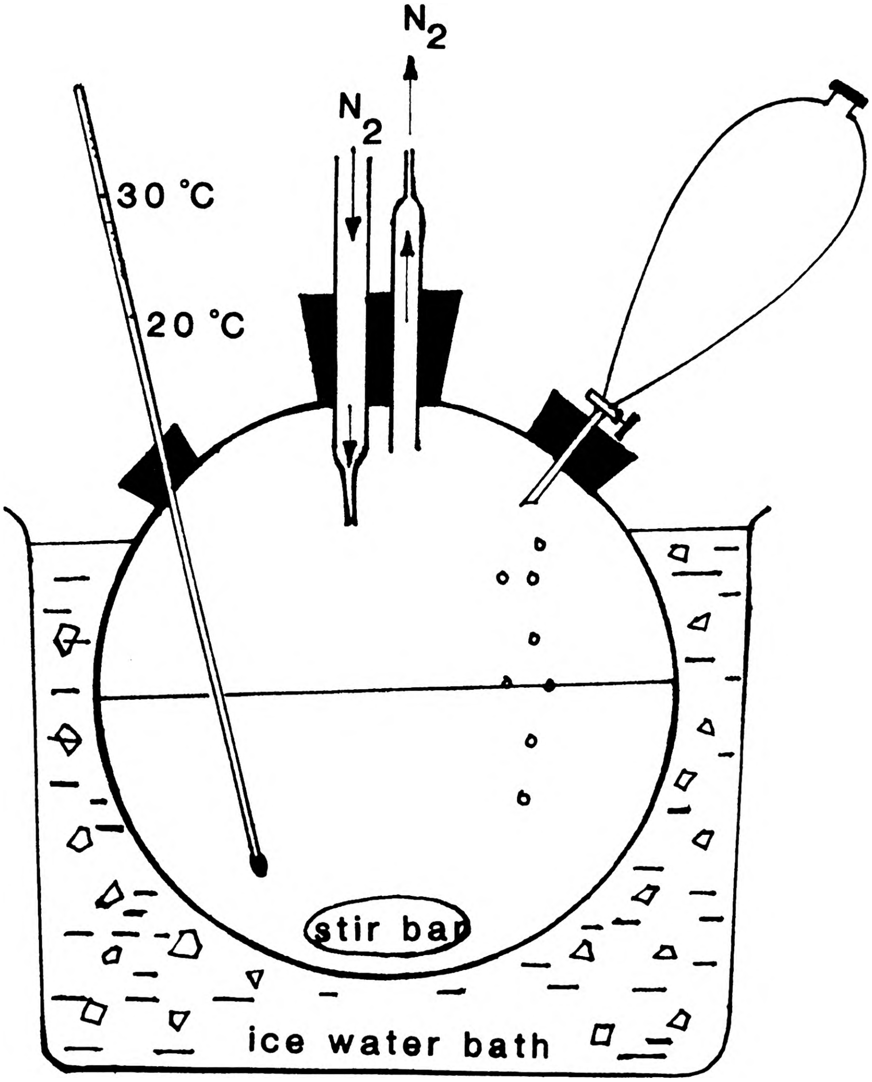


Figure 1. Apparatus for synthesis of Acryloamido-undecanoic acid

cooled distilled water was replaced every 1.5 hours 8 times until only a weak acid mixture remained as indicated by litmus paper. The mixture was then extracted with carbon tetrachloride 4-5 times to get acryloamidoundecanoic acid (AAUA). A final extraction was made with cyclohexane to remove trace amounts of carbon tetrachloride. The product was a yellow-brown, viscous material. A Perkin-Elmer 521 Infrared spectrophotometer was used to confirm the presence of vinyl double bond of the product. The absorption band of the AAUA is given in Table II.

The sodium salt of acryloamidoundecanoic acid was prepared by neutralizing the acid with saturated sodium ethoxide solution to a pH of 10. The soap was precipitated by adding acetone and centrifuged at a speed of 7000 rpm to remove the excess solvent. The soap was then dried in a vacuum oven with a nitrogen gas flow for 24 hours. Dried soap was stored in a desiccator over phosphorous pentoxide.

PHASE DIAGRAM DETERMINATION

The ternary system of water / sodium acryloamido-undecanoate / oleyl alcohol was used in this foam polymerization investigation at 25°C. For phase diagram determination, the water contained 20 ppm of hydroquinone serving as inhibitor to prevent NaAAU polymerization. The various weight ratios of water to surfactant solutions were made and then titrated with oleyl alcohol. All solutions were

TABLE II

Infrared Absorption Peaks Observed for Acryloamidoundecanoic Acid

Frequency(cm^{-1})	Group	Mode
3270	CO-NH-R	N-H stretch
3100	CH_2=CH-R	=C-H stretch (tertiary hydrogen)
2930	CH_2	C-H stretch (secondary hydrogen)
2860	CH_3	C-H stretch
1715	COOH	C=O stretch
1650	CO-NH-R	C=O stretch
1630		
1560	CO-NH-R	N-H bending
1440	COOH	
1410	CH_2=CH-R	
1320	CH_2	CH_2 bending
1240	CO-NH-R	
1040	C-OH	C-O stretch
980	CH_2=CH-R	out of plane
950	CH_2=CH-R	bending

well mixed with Vortex-Genie Vibromixer and centrifuged at a speed of 5000 rpm for 10 minutes. The liquid crystal was observed visually through crossed polarizers and the pattern of the liquid crystal determined under the polarizing microscope.

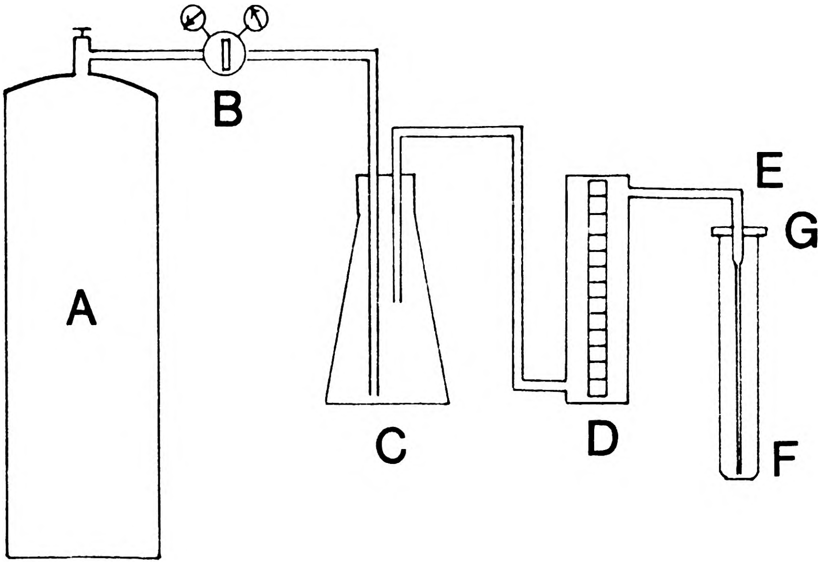
MEASUREMENT OF FOAM STABILITY

The apparatus used for measuring foam stability is shown in Figure 2. Nitrogen gas (A) was passed through a regulator (B) into a humidifier bottle (C) containing distilled water. The amount of nitrogen gas was controlled by a flow meter (D) and ultimately through a fine capillary tube (E) in the solution being foamed. A test tube (F) was selected as the foam container. After foaming, it was necessary to place a cap (G) over the test tube in order to get more reproducible results.

The following two series of different solutions were used to study the foam stability:

Series 1

Solution	NaAAU(wt%)	Oleyl alcohol(wt%)	H_2O(wt%)
a	40.0	5.0	55
b	55.5	5.5	39
c	60.0	6.0	34



A - nitrogen gas cylinder
B - pressure regulator
C - humidifier bottle
D - flow meter
E - capillary tube
F - test tube
G - cap of tube

Figure 2. Apparatus for foam stability measurement

Series 2

Solution	NaAAU(wt%)	Oleyl alcohol(wt%)	H_2O(wt%)
d	62	2	36
e	58	10	32
f	55	16	29

Nitrogen gas was introduced into 1 ml of the above solution at a flow rate of 6.5 ml/min until the foam reached a height of 4 cm, after which the height of the foam was measured versus time.

2-D POLYMERIZED FOAM

2-D polymerized foam was performed in a (75 × 25 mm) microscope glass slide within a framework of 4 (20 × 4 mm) glass chips (Fig. 3). 0.023m potassium persulfate was added as an initiator. It was foamed with a fine capillary tube through which nitrogen gas was passed. A cover glass was added, the sample observed and photographs taken under the polarizing microscope at different time intervals until complete polymerization.

3-D POLYMERIZED FOAM

3-D polymerized foam was made in a 1-cm diameter vial, with the same composition as was used for 2-D polymerized foam, after foaming the vial was placed on an undisturbed table to let the polymerization proceed. The polymerized foam

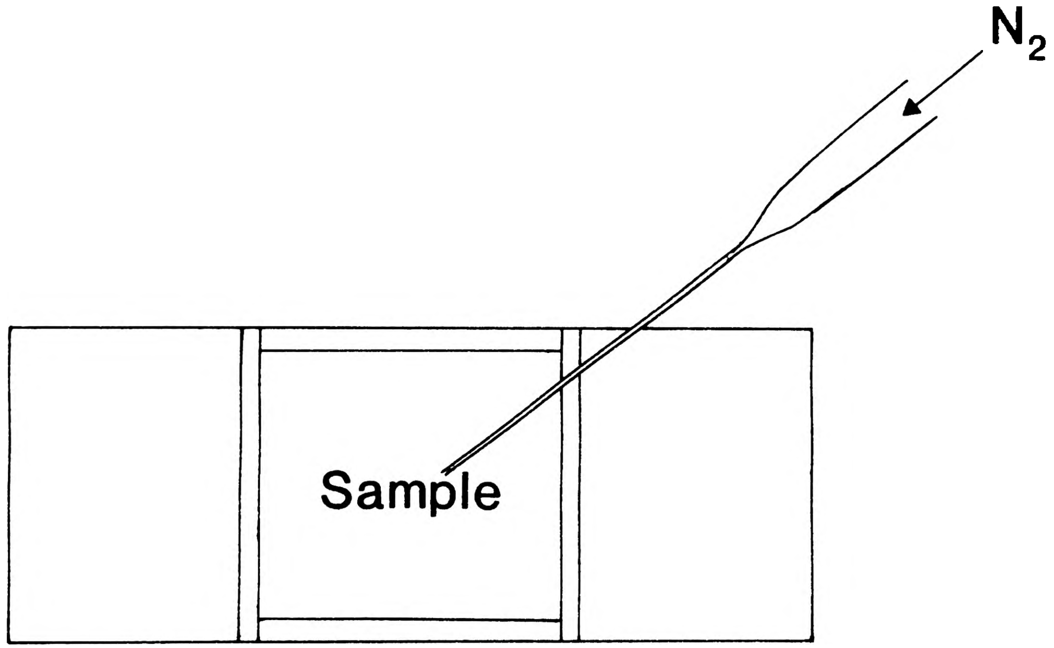


Figure 3. Generation of 2-dimensional foams

was sliced open, it was observed and microphotographs taken in polarized light. The samples were placed in a high vacuum oven at 45°C for 48 hours, observed again and photographed anew in polarized light microscope.

RESULTS

The results describe the phase diagram and the association structures for the three component system water/polymerizable surfactant (NaAAU)/oleyl alcohol.

Foam stability for solutions were studied in the two phase (alcoholic solution and normal micellar solution) and three phase (normal micellar solution, hexagonal liquid crystal and lamellar liquid crystal) regions. A stable foam was polymerized on a microscope glass slide (two-dimensional) and in glass vials (three-dimensional). The structure of the foam surface was observed in polarized light microscope.

PHASE DIAGRAM

Figure 4 shows the ternary phase diagram for water / NaAAU / oleyl alcohol at 25^{o}C. The mutual solubility of water and oleyl alcohol or oleyl alcohol and NaAAU were extremely low and can be neglected. On the water-NaAAU axis, the polymerizable soap (NaAAU) was soluble in water to a high degree and give a yellow and transparent normal micellar solution with a maximum concentration of 53 wt% of NaAAU. When more soap was added, the clear solution formed an equilibrium with a hexagonal liquid crystal. The hexagonal liquid crystal region was found between 65 wt% and 76.5 wt%. Above 76.5 wt%, additional crystalline soap could be suspended in the liquid crystal. The solubilization of oleyl alcohol in the binary

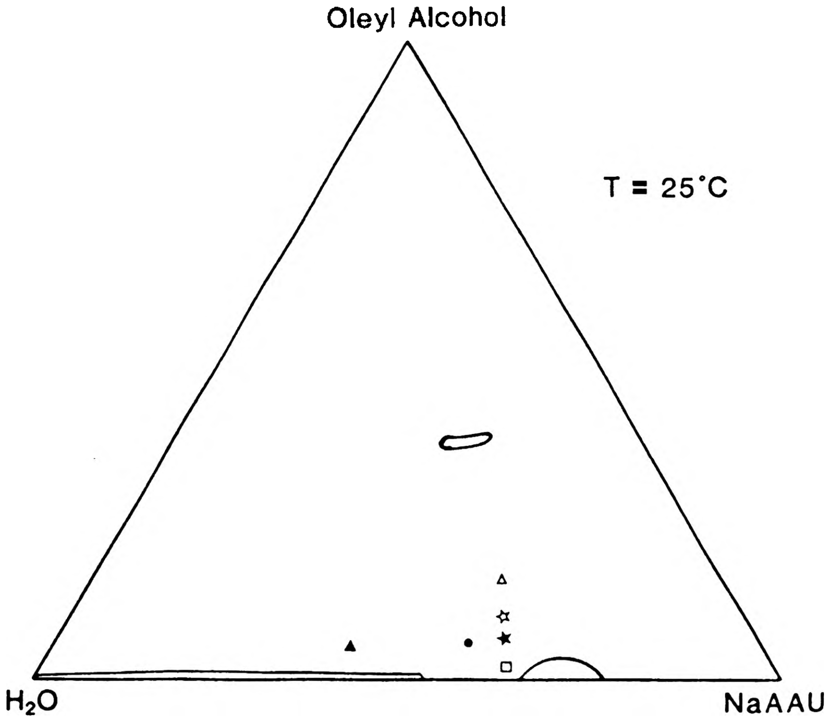


Figure 4. Ternary phase diagram for water-NaAAU-oleyl alcohol

mixtures of water and soap was very limited. A maximum of 1 wt% and 4 wt% of oleyl alcohol were found in the normal micellar solution (L_1) and hexagonal liquid crystal regions (E) respectively. In addition, a small oblong region of lamellar liquid crystal (D) was found around 37.5 wt% oleyl alcohol with the weight ratio of water/soap between 0.754 and 0.47.

FOAM STABILITY

Foam stability for two series of solutions are shown in Figure 5 and 6. The relative foam height was plotted versus time.

Series 1 contained three solutions (a, b and c) with increasing NaAAU content and slightly increasing oleyl alcohol content (Fig.5), and the foam stability was in the order of c > b > a. The foam was extremely unstable in solution a (▲), half the volume of the foam collapsing within one minute. For solution b (●), 35 % of the foam volume collapsed within 510 seconds, after which the breaking rate decreased. The half-life time for this solution was 1100 seconds. The foam made with solution c (★) was very stable until 1150 seconds. After 1150 seconds, The foam gradually collapsed and the half-life time was 2500 seconds.

Figure 6 shows the foam stability and the location in the phase diagram of the second series of solutions (d, c, e and f). Solution d (□) gave unstable foams which broke rapidly after generation. The half-life time was one minute. The other

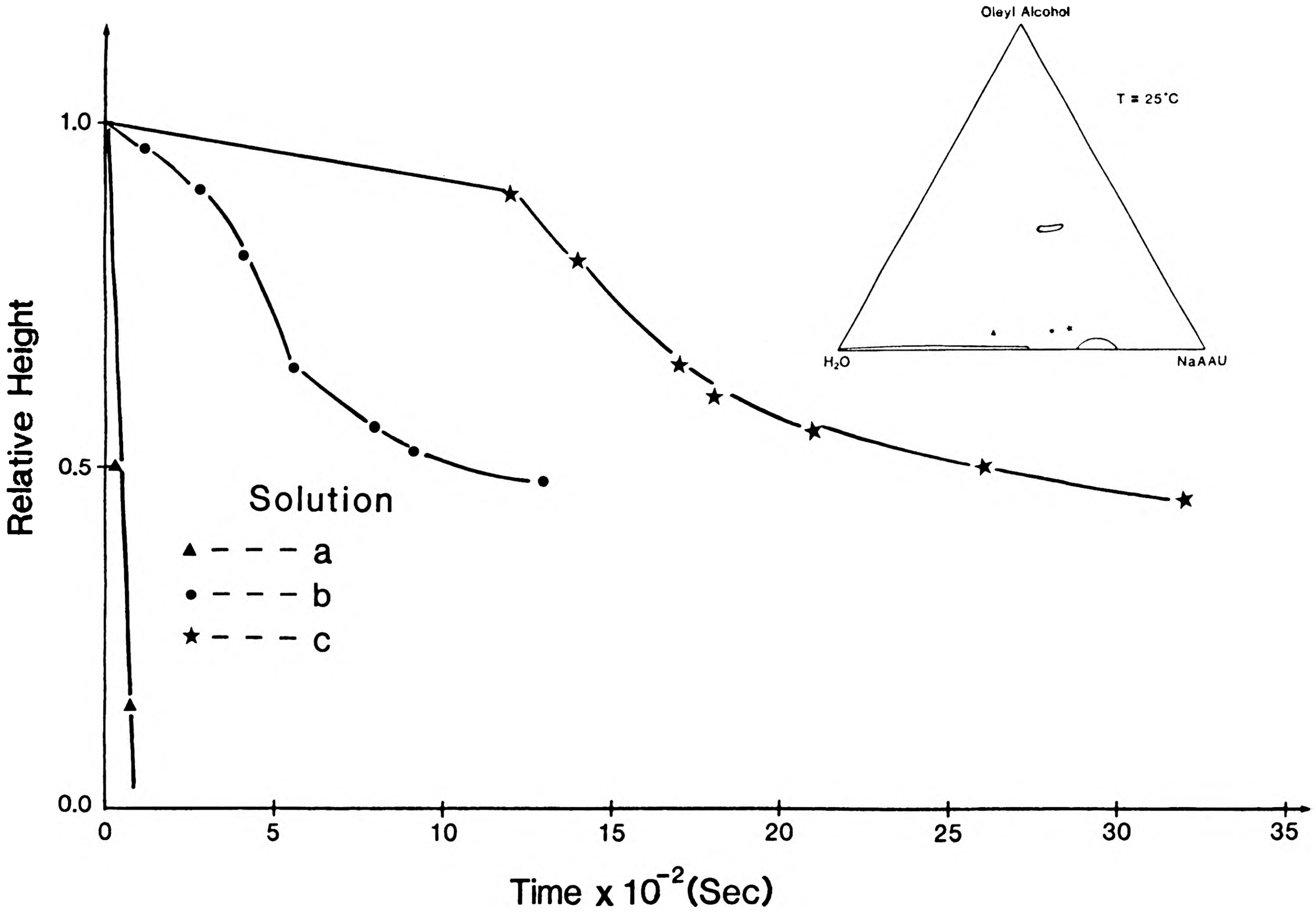


Figure 5. Foam stability with increasing surfactant content for solutions a, b, and c

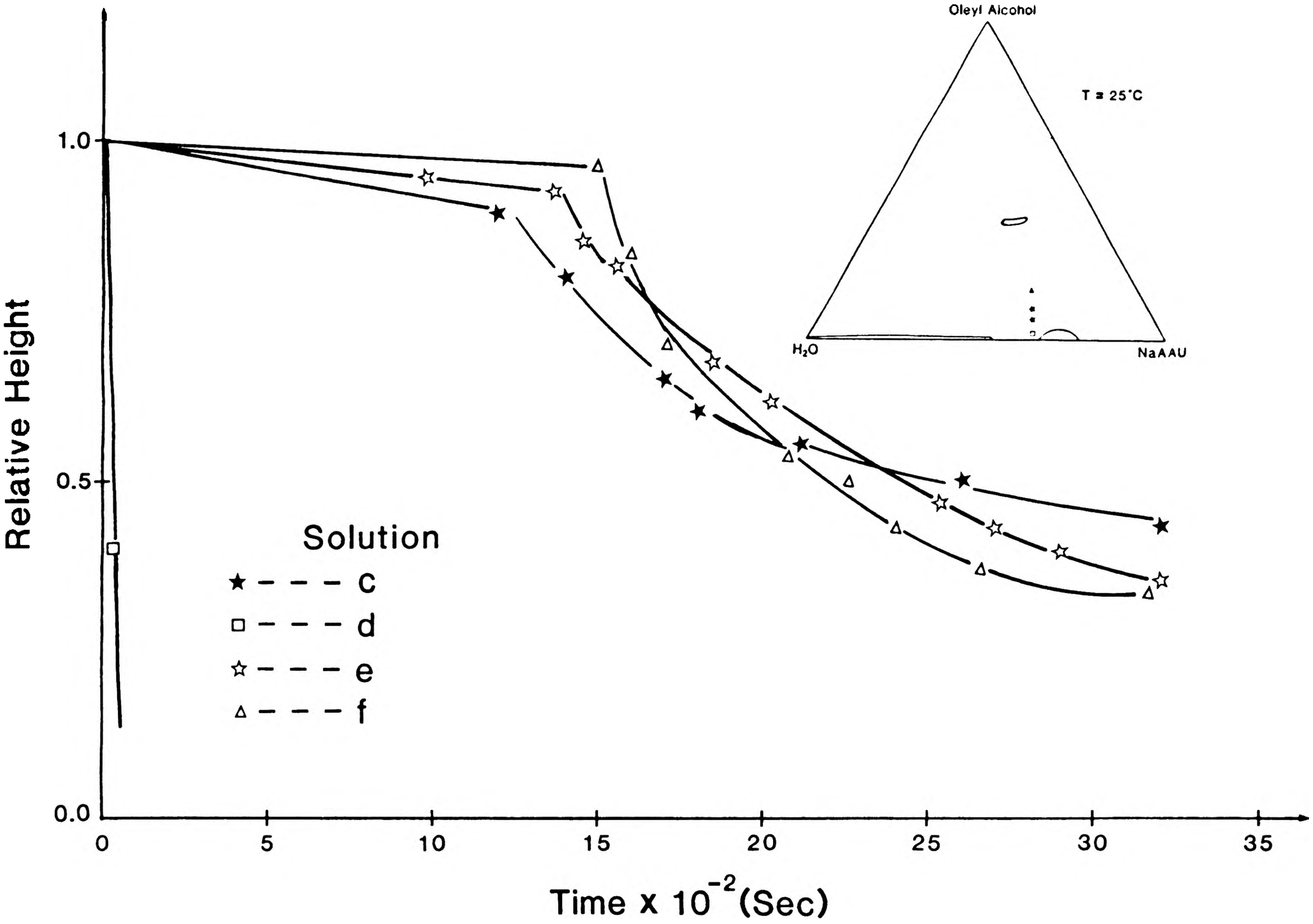


Figure 6. Foam stability with increasing oleyl alcohol content for solutions c, d, e, and f

solutions c (★), e (☆) and f (Δ) had similar foam stability; but all of them were much more stable than solution d. Foams e and f began to collapse gradually between 1350 and 1500 seconds. The half-life times for solution e and f were 2000 seconds and 2400 seconds respectively.

MICROSCOPIC STUDY OF 2-D FOAM

A mixture containing 34 wt% H_2O, 60 wt% NaAAU and 6 wt% oleyl alcohol was chosen for foam polymerization study. This composition was in the three phase region. Of the normal micellar solution, the hexagonal liquid crystal and the lamellar liquid crystal. When foam was generated, liquid crystals immediately adsorbed and arranged themselves on the foam surface. Figure 7 reveals air bubbles surrounded by liquid crystal (bright), the areas with Maltese crosses are lamellar liquid crystal, the Batonnet structures are hexagonal liquid crystal and the black background between the air bubbles is the isotropic solution. As the polymerization proceeded, the adsorbed liquid crystals gradually coagulated and extended from the foam surface (Fig. 8-11). At the Plateau border, the extended liquid crystals touched each other with a 120^0 boundary (Fig.11). When the liquid crystals were well extended, the foam was completely polymerized by placing the sample in an oven at 50^oC for 12 hours. Figure 12 shows a microscopic picture of a 2-D polymerized foam in which the bubbles were no longer symmetric circles, as compared to the

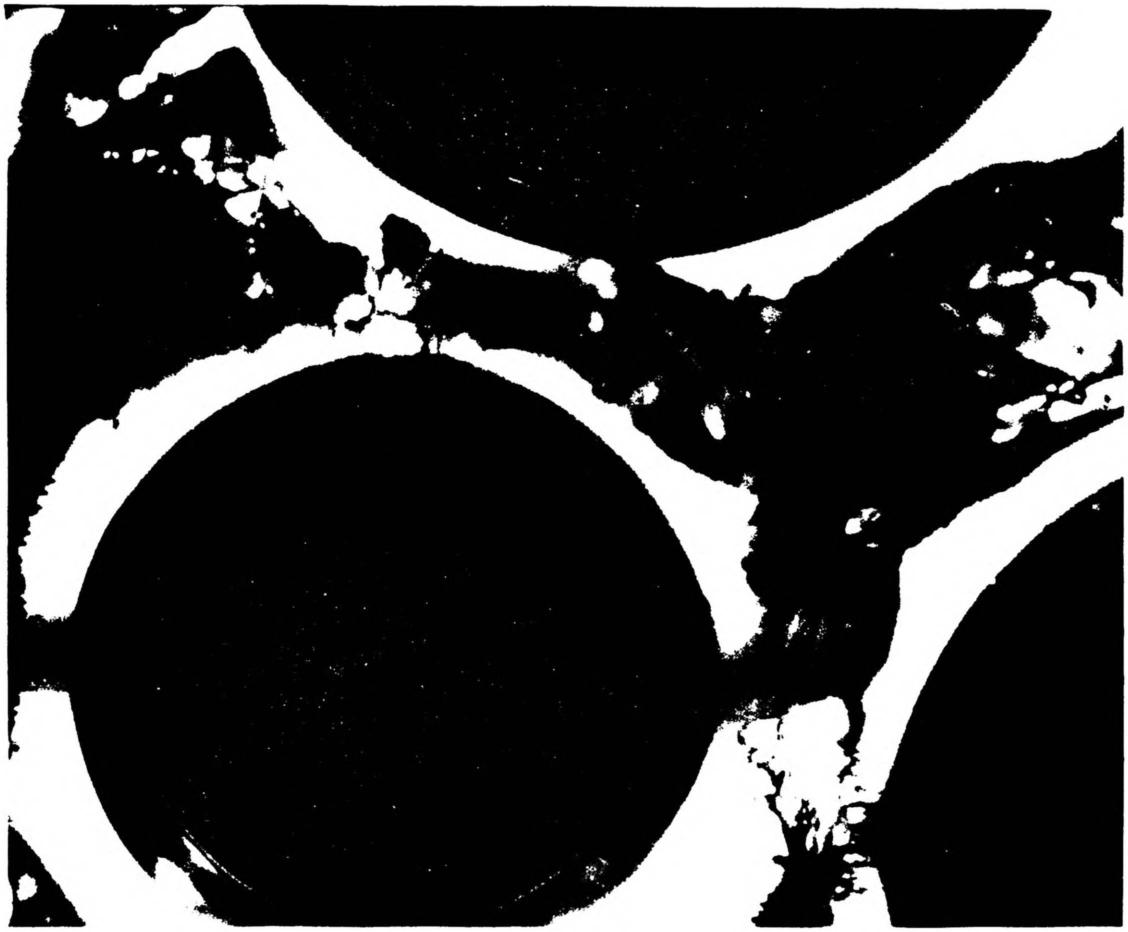


Figure 7. Photomicrograph of 2-dimensional sample used for the polymerization study containing isotropic solution and hexagonal and lamellar liquid crystals

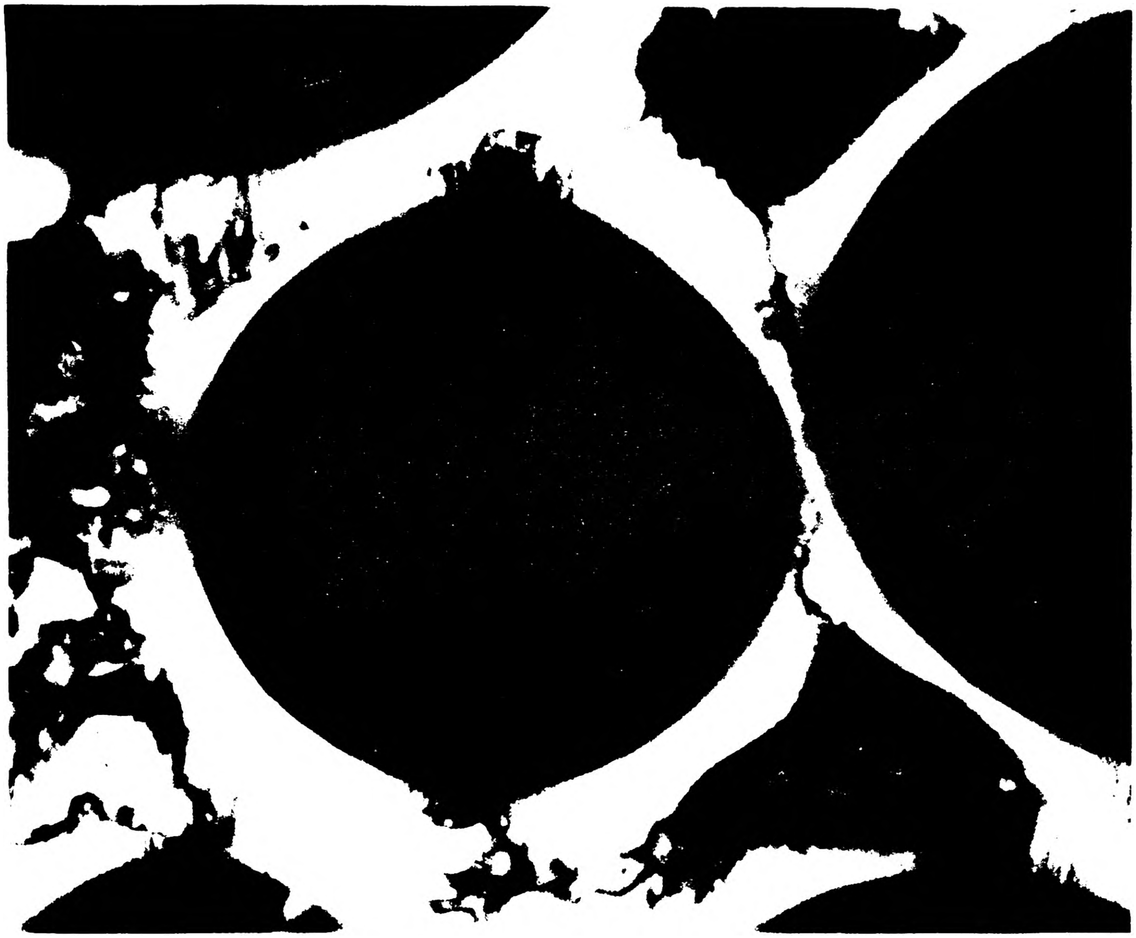


Figure 8. Optically anisotropic liquid crystals on the foam surface before polymerization

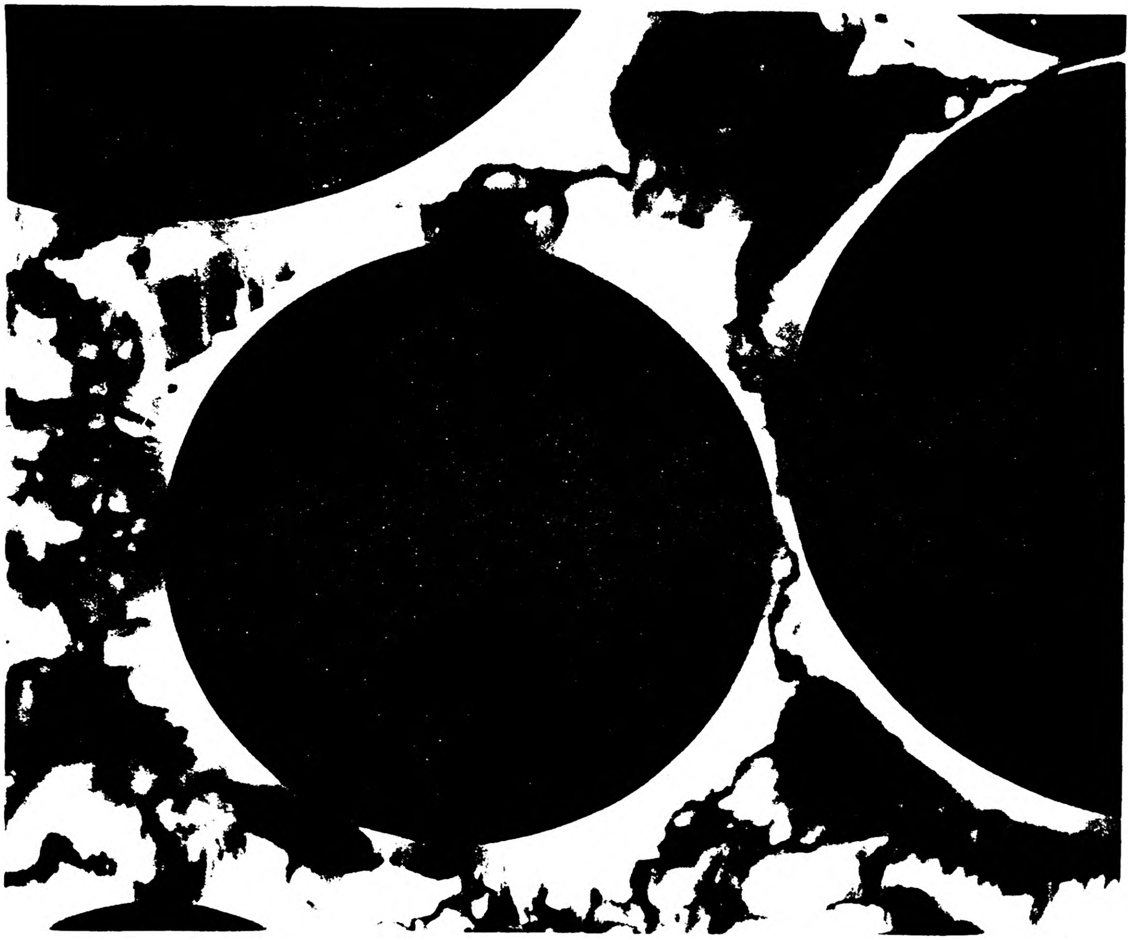


Figure 9. Optically anisotropic liquid crystals on the foam surface after partial polymerization

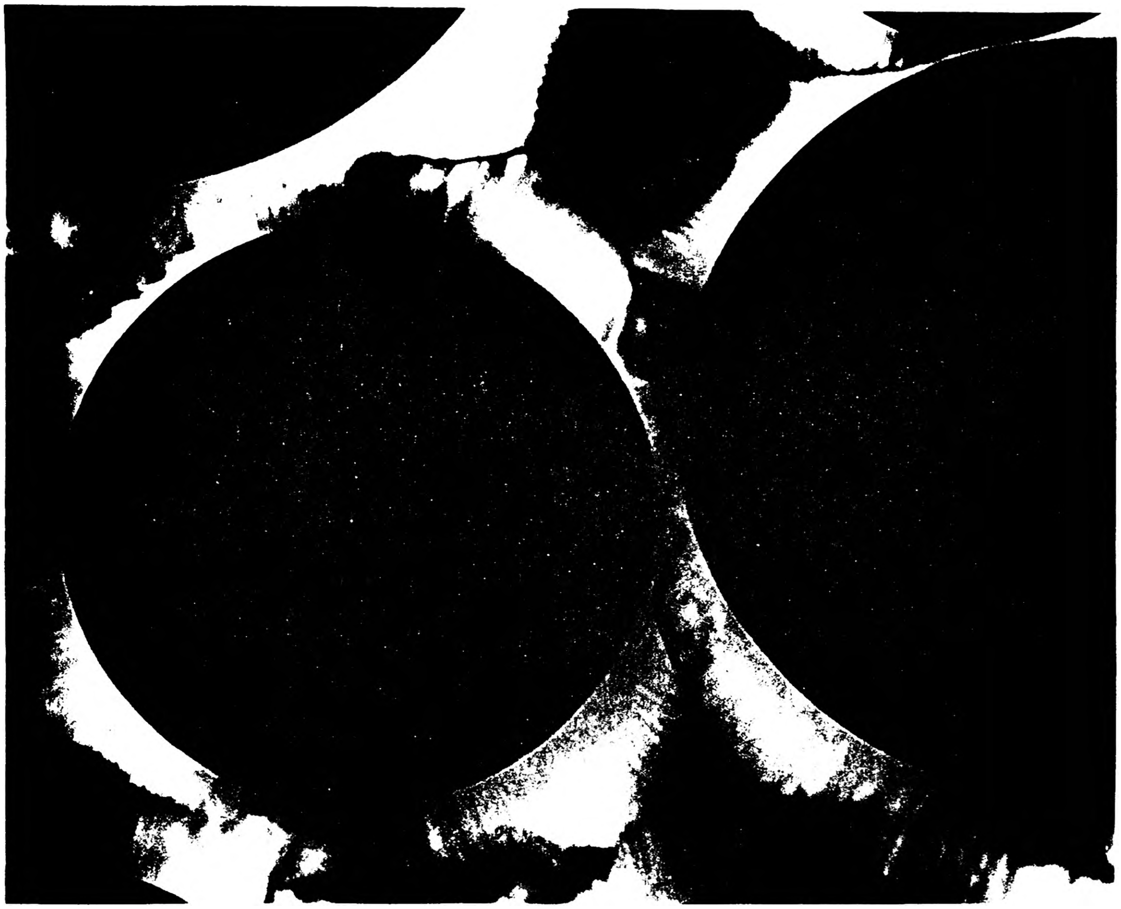


Figure 10. Optically anisotropic liquid crystals on the foam surface after further polymerization

Figure 11. Optically anisotropic liquid crystals on the foam surface after further polymerization

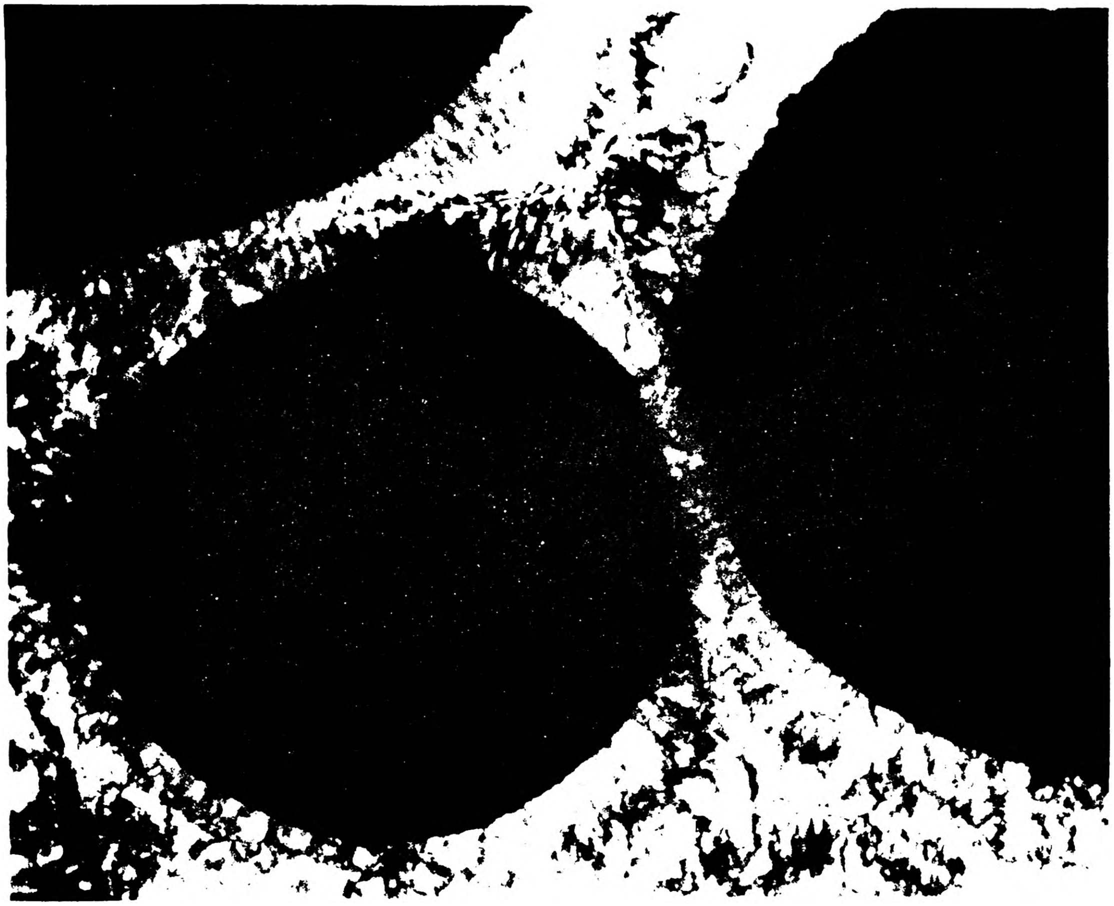


Figure 12. Optical pattern for liquid crystal at the surface of completely polymerized 2-dimensional foam

foam before complete polymerization, in which the bubbles were perfect circles.

3-D POLYMERIZED FOAM

3-D polymerized, rigid foam (Fig.13) was produced in a glass vial of 1-cm diameter. The total volume of the polymerized foam was four times the volume of the original liquid, which was 0.7 milliliter. A sliced sample from the polymerized foam was observed under the polarizing microscope. Photographs show that the polymerized foam was still coated with liquid crystal (Fig.14). The liquid crystal pattern, especially the typical lamellar liquid crystal pattern (Maltese crosses) can be seen in the picture. These liquid crystal patterns were still present after 48 hours under high vacuum at 45°C (Fig.15).

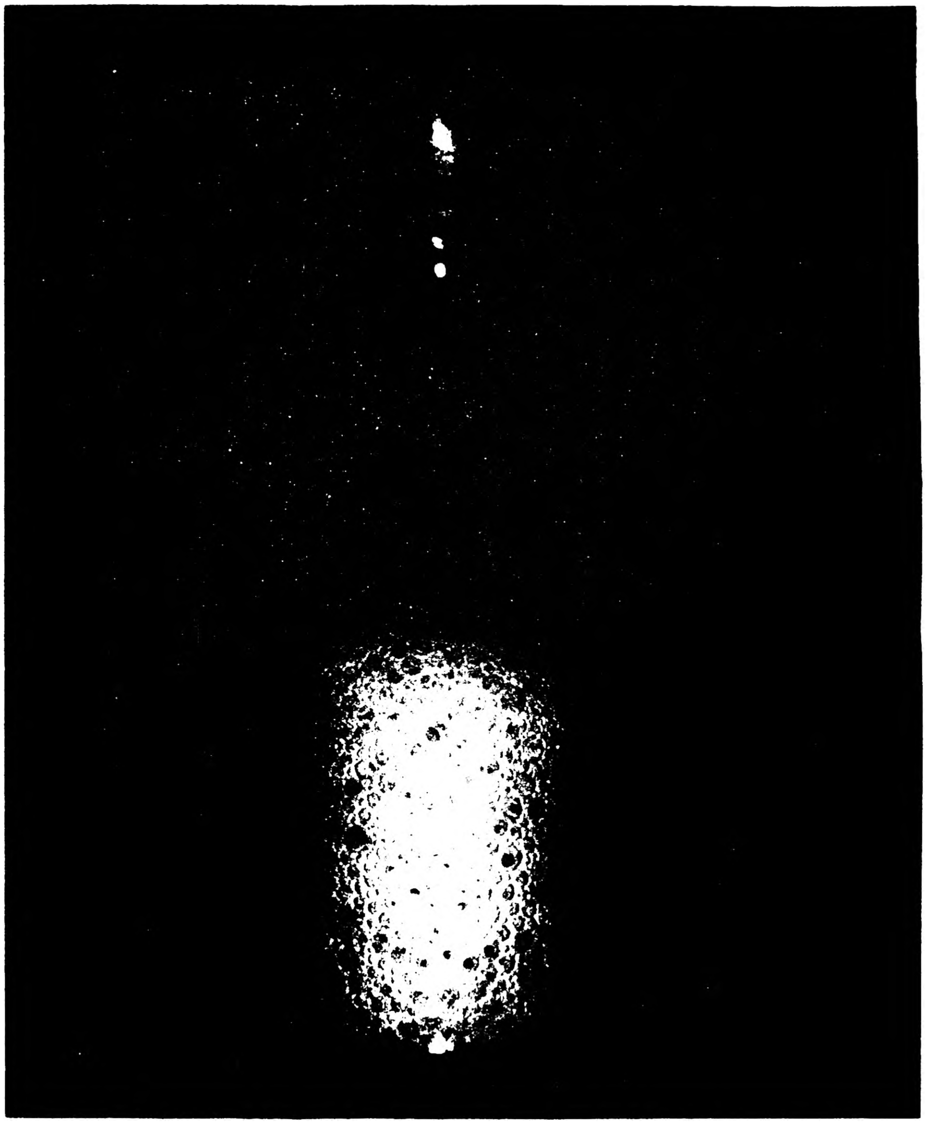


Figure 13. 3-dimensional polymerized foam in a 1-cm diameter vial

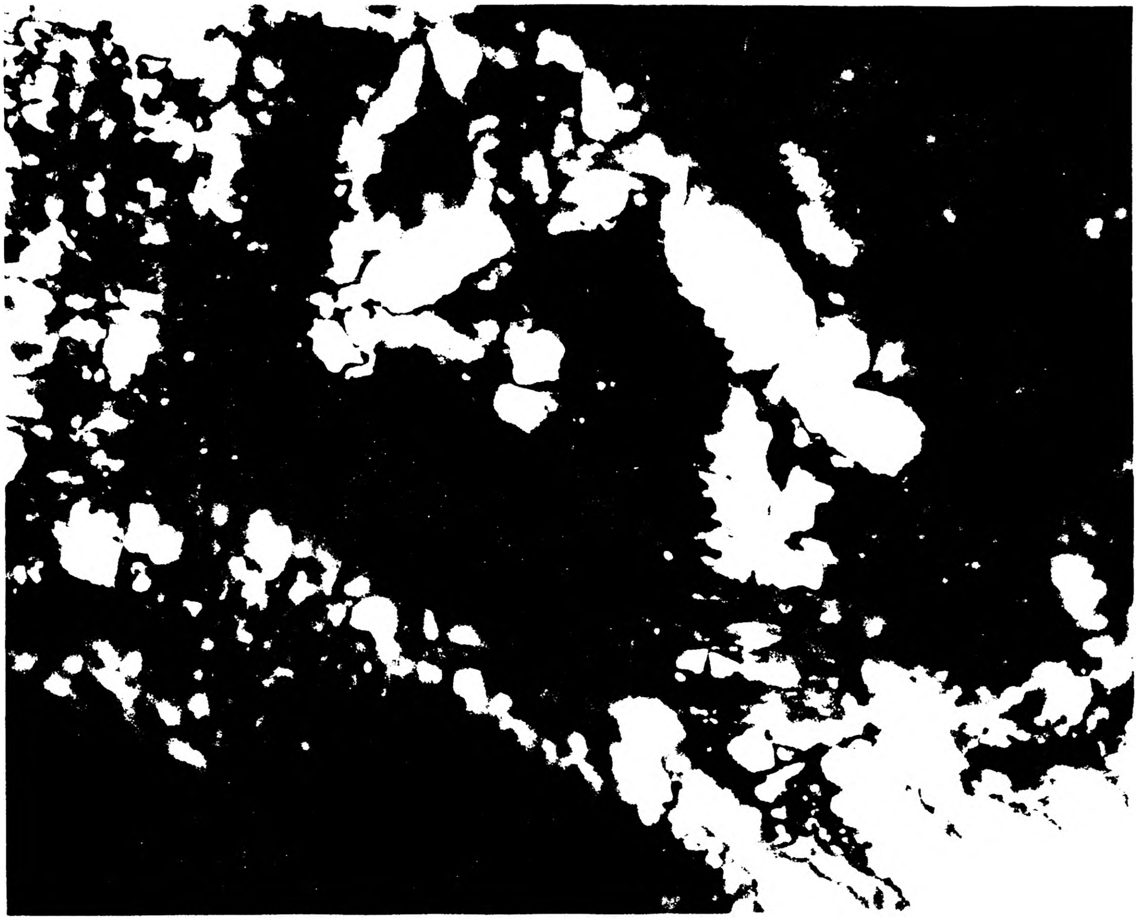


Figure 14. The optical pattern of the cut surface of the 3-dimensional polymerized foam

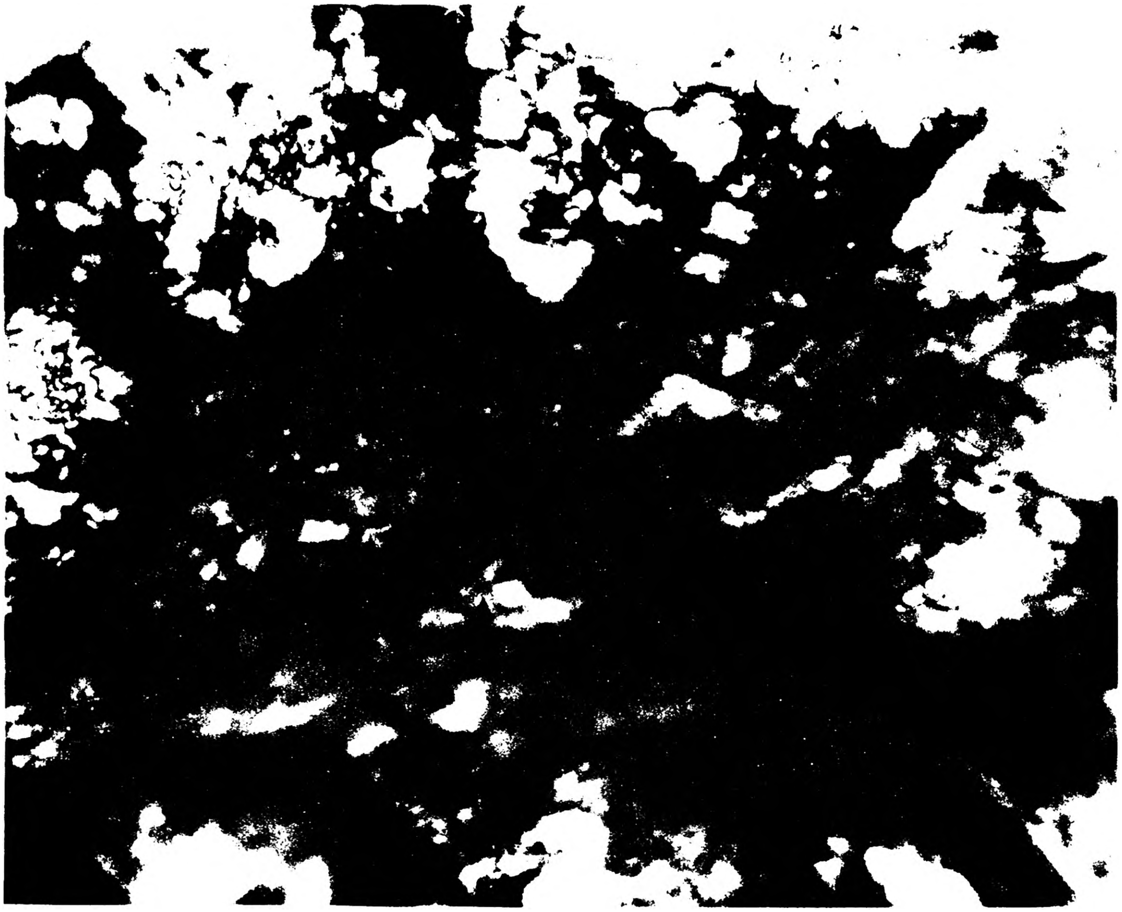


Figure 15. The optical pattern of the cut surface of the 3-dimensional polymerized foam after vacuum treatment

DISCUSSION

FOAM STABILITY

According to the above foam stability measurements, the solution a, which was a mixture of micellar and oleyl alcohol solution, gave extremely unstable foam. When liquid crystal were present in solutions b, c, e, and f, the foam stability was increased sharply (Fig.5). This indicates that the presence of liquid crystals strongly affects the foam stability. The role of the liquid crystal as foam stabilizer is localized to thin film junctions (Plateau border) in the foam. The high viscosity of the liquid crystal reduces the liquid drain through the junction. In addition, liquid crystal also serves as a surfactant reservoir to provide optimal compositions for foam stabilization (11-14).

FOAM POLYMERIZATION

Foam polymerization has to do with polymerization of the surface film. In this study, the foam surface was surrounded by liquid crystal (Fig.7). Therefore, the polymerization process took place within the liquid crystal where the polymerizable surfactant (NaAAU) formed a polymer by crosslinking, and the amphiphile molecules became connected by intermolecular bridges. This process reduced the free rotation and translation of the surfactant terminal group and gave a more ordered structure. It enhanced the stability of the liquid crystal and maintained the liquid crystal pattern on the foam surface after complete polymerization (Fig.14), and even after vacuum removal of water from the polymerized foam (Fig.15).

LIQUID CRYSTAL EXTENSION

Figures 8-11 show growth and extension of the liquid crystal from the foam surface into the liquid region until contact with each other during the process of plymerization. The reason for this extension of liquid crystal is related to the composition change in the mixtures which produced a phase change. Similar findings were reported by Finkelmann et. al. (15,16) where the liquid crystal phase area of a polymerizable amphiphile in water was extended with concentration and temperature, due to the polymerization. When the liquid crystals are completely extended so that they touch (Fig.11), the foams are fixed and present a "semi-solid" appearance in the microscope. After polymerization the foams have completely changed from a "gas in liquid" to a "gas in solid" (i.e. the polymerized foam) (Fig.12)

CONDITIONS FOR THREE-DIMENSIONAL FOAM PREPARATION

When preparing three-dimensional foams in a glass vial, the foam must be polymerized before collapse. Hence, the polymerization rate, the drainage rate and the foam stability are important factors in making this type of foam. The polymerization rate should be low enough to allow foaming and the maximum extension of the liquid crystal from the bubble surface. The drainage and foam stability are not problems in two-dimensional foams, but do affect the initial polymerization in the three-dimensional foam. After some polymerization has occurred, the viscosity of the foam surface increases and the problem of drainage becomes negligible.

CONCLUSION

A new step has been made in the field of polymerized foams. Foam was generated and polymerized in an aqueous amphiphile system containing a polymerizable surfactant (sodium acryloamidoundecanoate). The polymerizable surfactant has the same characteristic as surfactants in general associating into normal micelles and hexagonal liquid crystal in water. A phase diagram for the water/NaAAU/oleyl alcohol system has been established. Three one-phase regions, a normal micellar solution region, a lamellar liquid crystal region and a hexagonal liquid crystal region were observed. Foam stability was studied and one stable foam with a composition within the three phase was chosen for a foam polymerization study. Two dimensional foam on a microscope slide was employed to observe the adsorption and extension of liquid crystals on the foam surface during polymerization. Three dimensional polymerized, rigid foams were made in a glass vial. The liquid crystal pattern on the foam surface was maintained throughout polymerization.

REFERENCES

1. Dombrow, B. A., "Polyurethanes." Reinhold Publishing Co., New York, 1957.
2. "Cellular Plastics" N.A.C.-N.R.C., Washington, D.C., 1967.
3. Benning, C. J., "Plastic Foams: the Physics and Chemistry of Product Performance and Process Technology." Vol. 1 & 2, John Wiley & Sons, New York, 1969.
4. Whelan, A., and Brydson, J. A., Eds., "Developments with Thermosetting Plastics." John Wiley & Sons, New York, 1975.
5. Katz, S., "Plastics: Design and Materials." Studio Vista, London, 1978.
6. Woods, G., "Flexible Polyurethane Foams, Chemistry and Technology." Applied Science Publisher, London, 1982.
7. Chien, J. C. W., "Polyacetylene, Chemistry, Physics, and Material Science." Academic Press, New York, 1984.
8. Pitter, J. J., and Minieri, P. P., J. Am. Chem. Soc., 70, 4045 (1948).
9. Plaut, H., U. S. Patent 2, 701, 809 (1955).
10. Freedman, H. H., Mason, J. P., and Medalia, A. I. Org. Chem., 23, 76 (1958).

11. Friberg, S., and Saito, H., in "Liquid Crystals" (S. Chandrasekhar, Ed.), Indiana Academy of science, 1975.
12. Friberg, S., and Saito, H., in "Foams" (R. J. Akers, Ed.), Academic Press, New York, (1976), pp.31-34.
13. Friberg, S., in "Advances in Liquid Crystals" (G. H. Brown, Ed.), Vol. 3, Academic Press, New York, 1978, pp.149-165.
14. Manev, E. D., Sazdanova, S. V., Rao, A. A., and Wasan, D. T., J. Dispersion Science and Technology, 3, 435 (1982).
15. Luhmann, B., Finkelmann, H., and Rehage, G., Die Angewandte Makromolekulare Chemic 123/124, 217 (1984).
16. Finkelmann, H., Luhmann, B., and Rehage, G., Colloid & Polymer Sci. 260, 56 (1982).

SUMMARY

The effect of amphiphile association structures on foam separation was studied in the model system of water, sodium octylsulfonate and decanol. Three foam surface structures, the monolayer, the mixed monolayer, and the multilayer structures have been proposed. Foam separation was significantly increased by the presence of a multilayer structure: the lamellar liquid crystal structure. This was explained using the enhanced surface properties such as surface viscosity and surface elasiticity of foam.

A polymerized foam was obtained from the ternary system of water-NaAAU-oleyl alcohol. Two-dimensional foam on a microscope glass slide was used as a model to investigate changes in the foam surface, the Plateau border and the liquid crystal dispersion during the process of polymerization. This system was used because of its convenience for observation.

The foam is originally in the "gas in liquid" state, with most of the liquid crystals adsorbed on the surface of the foam, and the remainder dispersed in the bulk liquid between the bubbles. When polymerization begins, the vinyl double bonds of the surfactant become linked to each other, but the liquid crystal pattern still remains. The liquid crystal extends from the bubble surface into the liquid region between the bubbles. This is considered a phase change in the mixture and as a stabilization of the liquid crystal by the polymer backbone when the surfactant molecules have been polymerized.

Three-dimensional polymerized solid foam was obtained from a solution with the same optimal composition as the two-dimensional foam. It had a 4/1 volume ratio compared to the original liquid mixture. The liquid crystal pattern was still present on the surface of the foam as observed in the polarized light microscope.

This investigation has provided a novel method for the preparation of solid foam. The advantages of the method are decreased use of raw material and energy, and its simplicity, which result in a low cost solid foam.

VITA

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In September 1975, he enrolled at the Soochow University in Taipei, Taiwan, R.O.C. In June 1979, he received a Bachelor of Science degree in Chemistry from that institution. Following Graduation he was employed as a teaching assistant in the Department of Chemistry, Scoochow University, Taipei, Taiwan, R.O.C. from July 1979 to June 1981.

He has been enrolled in the graduate school in the University of Missouri-Rolla since January 1982. From January 1982 to December 1985, he was a Graduate Teaching Assistant. From January 1986 to May 1986, he held a Graduate Research Assistantship.