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## The Kendall Award Address

### Surfactant Association Structures and the Stability of Emulsions and Foams<sup>†</sup>

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Traditional surfactants in combination with water and a more hydrophobic amphiphile, such as an alcohol or a carboxylic acid, present a rich variety of colloidal association structures, both micelles and lyotropic liquid crystals. The presence of such association structures has a pronounced influence on the stability of macrodispersed systems such as emulsions and foams. A few examples of such an influence are discussed.

#### Introduction

One of the major steps to enhance the understanding of the stability of macrodispersed systems was taken with the introduction of the DLVO theory,<sup>1,2</sup> and its influence on colloid chemistry by the research it has generated is by now beyond the scope of any review article. It made possible the analysis of the colloid stability of thin films using a combination of surface rheological properties and colloidal forces merging into a picture<sup>3</sup> of outstanding simplicity and clarity.

In parallel with these efforts the knowledge of surfactant association structures has been rapidly progressing after Ekwall's pioneering contributions<sup>4</sup> to a more detailed description of structure and dynamics.<sup>5-7</sup>

These two schools of colloid chemistry have given complementary information to many problems; the foremost of which is the microemulsion structure, which was originally treated with the traditional focus on interfacial free energy,<sup>8</sup> then as a surfactant association problem,<sup>9</sup> and finally as a question of colloidal stability of particles.<sup>10</sup> The case of microemulsions is an obvious area in which the knowledge of surfactant association structures could make an impact and the implications have been well documented by now.<sup>11-13</sup>

For macrodispersed systems, on the other hand, the importance of surfactant association structures has not been as immediately evident and a review of the progress of this aspect may be justified.

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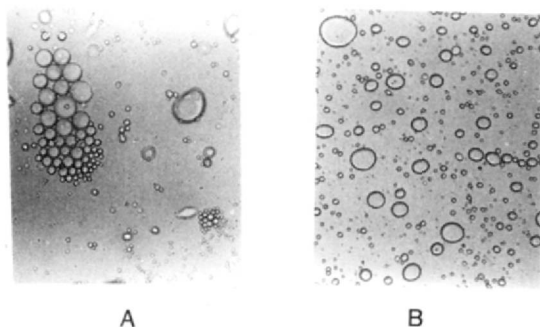
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**Figure 1.** In some emulsions the flocculation (A) is immediately followed by coalescence to give a wide range of droplet size (B).

### Emulsion Stability

It was early pointed out by Sherman<sup>14</sup> that in spite of the thorough knowledge of the factors behind emulsion stability, the sudden changes of stability with composition could not be explained. Along the same avenue, Davies<sup>15</sup> reported the change of emulsion stability when an aliphatic hydrocarbon was replaced by an aromatic one. The change to an aromatic hydrocarbon prevented the coalescence step to occur; the emulsion remained in the flocculated state as evidenced by the huge aggregates of individual droplets found (Figure 1A).

These two comments made it obvious that further factors should be involved in order to explain the aspects of the kinetic stability of emulsions.

One such factor is the formation of a lyotropic liquid crystal within the emulsion. The first such system was presented soon after these problems had been stated.<sup>16</sup> It contained water, hydrocarbon, and a commercial nonionic surfactant; approximately an octaethylene glycol nonylphenol ether. This system demonstrated both a sudden change of stability with composition and the most pronounced influence of the nature of the hydrocarbon on the stability for selected compositions.

The sudden change of stability was experienced between 3% and 4% emulsifier for a water/*p*-xylene ratio of 1:1. The phase diagram, Figure 2A showed the concentration range of emulsifier where this change of stability occurred to be accompanied by the introduction of a third phase in the system. The optical pattern and its small-angle X-ray diffraction pattern revealed this phase to be a lamellar liquid crystal.

This third phase means a new kind of emulsion and resulted in a change of the definition of an emulsion to its present IUPAC wording. "In an emulsion liquid droplets and/or liquid crystals are dispersed in a liquid".<sup>17</sup>

The presence of this third phase and its sensitivity to the nature of the hydrocarbon provide an excellent illustration to the phenomenon described by Davies.<sup>15</sup> In fact, surfactant association structures are commonly sensitive to the nature of the hydrocarbon and drastic differences between emulsions with aromatic and aliphatic hydrocarbons may be found. An illustrative example of how this sensitivity may change emulsion stability from kinetic to thermodynamic is found in a composition water plus octaethylene glycol nonylphenol ether when combined with an aromatic (Figure 2A) or an aliphatic hydrocarbon

(Figure 2B). A composition according to the point P in the diagrams gives for the system with the aliphatic hydrocarbon (Figure 2B) a common emulsion of two liquid phases with limited kinetic stability. With the aromatic hydrocarbon, on the other hand, the whole system is now changed to a single-phase liquid crystal (Figure 2A), a system with thermodynamic stability.

The presence of a liquid crystal also resulted in a new factor to be included in the total concept of emulsion stability; that of the effect of an intermediate phase between the oil and water liquid phases. The implications are several; the following ones may be worth mentioning.

Instead of only the surfactant forming a protective monolayer now the solvents are also included to large amounts into a multilayered interfacial barrier. This factor adds a dimension to bring the refuted<sup>18</sup> idea of "surfactant complexes" at the interface.<sup>19,20</sup> Instead of an assumed "complex" of amphiphilics at the interface,<sup>19,20</sup> one now has a colloidal association structure involving the solvents in addition to the emulsifier. In fact, in the system in Figure 2A<sup>16</sup> the overwhelming part of the protecting surface layers consists of the solvents; for the case in Figure 2A the third protecting phase contains approximately 79% water, 8% hydrocarbon, and only 13% of the surfactant.

It is essential to realize that 87 wt% of the protective barrier consists of the solvents. This means that the relation between the amount of added emulsifier and the amount of protective phase depends on the phase diagram. This fact is illustrated by Figure 3, which shows the percentage of protective phase vs. the percent of emulsifier for the system in Figure 2A. The comparison of the amount of the protective liquid crystalline phase (solid line) with the amount of emulsifier (dashed line) is revealing. When the emulsifier percent goes from 3% to 8%, the amount of protective liquid crystal is raised from 0% to 50%; a dramatic change which explains the efficiency of this commercial emulsifier.

The relative amount of protective phase also depends on the ratio between water and hydrocarbon since these two liquids are included in the phase. Figure 4 shows the ratio between the amount of liquid crystalline barrier and the emulsifier to reach a value of 7.5 for an emulsion with high water to oil ratio.

The protective action of the liquid crystal has several modes. Of them, two are immediately evident and trivial. It serves as a protective viscous skin around the droplets;<sup>15</sup> its three-dimensional network in the continuous phase serves to reduce the mobility of emulsion droplets.<sup>21,22</sup>

The third mode, the influence on the van der Waals attraction potential, is not as immediately evident. An estimation was made<sup>23,24</sup> by using Vold's<sup>25</sup> approach with a model according to Figure 5. A calculation was made of the change in van der Waals potential with initial approach of the full structure (Figure 5, top part) followed by a subsequent removal of pairwise water and oil layers in the model (Figure 5, lower parts).

The formula for the van der Waals potential<sup>25</sup> becomes rather unwieldy for a multilayered structure:

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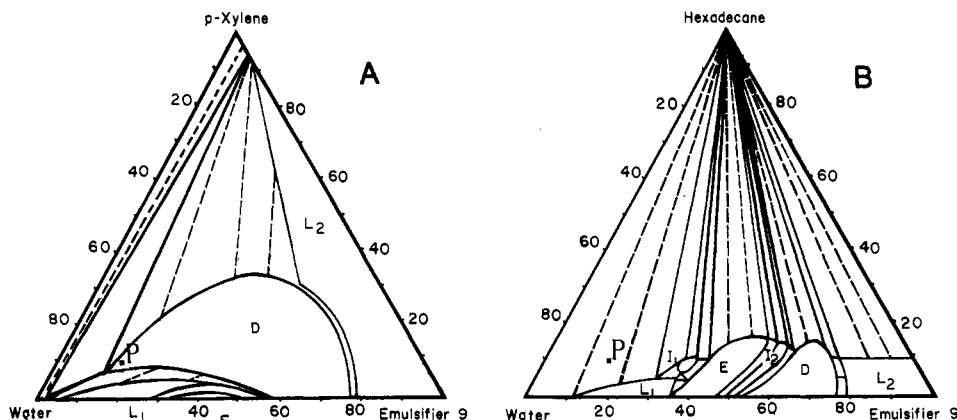
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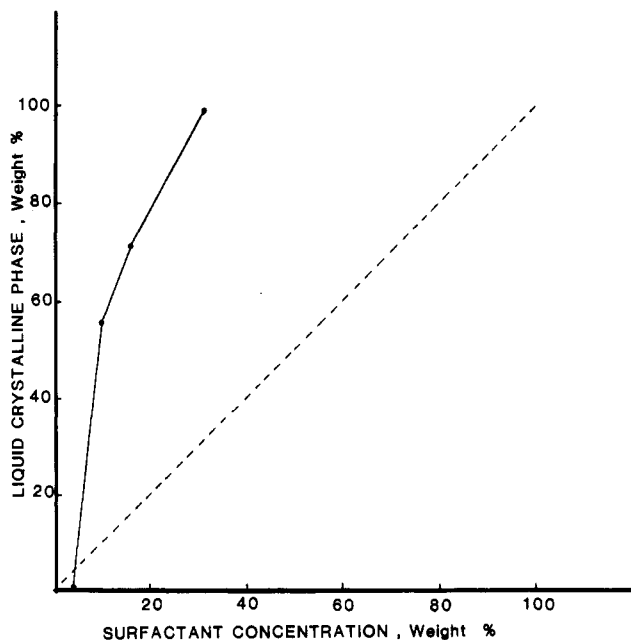


**Figure 2.** Phase equilibria in a system of water, nonionic surfactant, and hydrocarbon with an aromatic hydrocarbon (A) and with an aliphatic one (B).

$$\begin{aligned}
 V = & -\frac{1}{12} \sum_{i=1}^{2n+12n+1} a_i a_j H_{ij} = -\frac{1}{12} (A_w^{1/2} - A_o^{1/2})^2 \times \\
 & \left\{ \sum_{i=0}^{n-1} \left[ H \left( \frac{\Delta + 2i(d_w + d_o)}{2[R + (n-i)(d_w + d_o)]}, 1 \right) + \right. \right. \\
 & H \left( \frac{\Delta + 2i(d_w + d_o) + 2d_w}{2[R + (n-i)(d_w + d_o)]}, 1 \right) + \\
 & H \left( \frac{\Delta + 2i(d_w + d_o) + 2d_w}{2[R + (n-i)(d_w + d_o) - d_w]}, 1 \right) + \\
 & \left. \left. H \left( \frac{\Delta + 2n(d_w + d_o)}{2R}, 1 \right) \right] + \right. \\
 & 2 \left[ \sum_{i=1}^{n-1} \sum_{j=i-1}^n H \left( \frac{\Delta + (i+j)(d_w + d_o) - 2d_o}{2[R + (n-j)(d_w + d_o) + d_o]}, \right. \right. \\
 & \left. \left. \frac{R + (n-i)(d_w + d_o) + d_o}{R + (n-j)(d_w + d_o) + d_o} \right) + \right. \\
 & \left. \sum_{i=1}^n \sum_{j=i+1}^{n+1} \left[ H \left( \frac{\Delta + (i+j-2)(d_w + d_o)}{2[R + (n-j+1)(d_w + d_o)]}, \right. \right. \right. \\
 & \left. \left. \frac{R + (n-i+1)(d_w + d_o)}{R + (n-j+1)(d_w + d_o)} \right) - \right. \\
 & \left. H \left( \frac{\Delta + (i+j-1)(d_w + d_o) - d_o}{2[R + (n-j+1)(d_w + d_o)]}, \right. \right. \\
 & \left. \left. \frac{R + (n-i)(d_w + d_o) + d_o}{R + (n-j+1)(d_w + d_o)} \right) - \right. \\
 & \left. \left. H \left( \frac{\Delta + (i+j-2)(d_w + d_o) - d_o}{2[R + (n-j+1)(d_w + d_o) + d_o]}, \right. \right. \right. \\
 & \left. \left. \left. \frac{R + (n-i+1)(d_w + d_o)}{R + (n-j+1)(d_w + d_o) + d_o} \right) \right] \right\}
 \end{aligned}$$

where  $A_{ij}$  = Hamaker interaction constant,  $H$  = geometrical condition,<sup>25</sup>  $\Delta$  = distance between outer surfaces,  $d_w$  = thickness of water layer,  $d_o$  = thickness of oil layer,  $R$  = radius of droplet, and  $n$  = number of oil/water pair layers.

The results (Figure 6) show a strong increase of the attraction potential during the flocculation state followed by an extremely small increase during the coalescence stage. It appears reasonable to assume that this factor acts



**Figure 3.** Change on the weight percentage of liquid crystalline phase (solid line) compared to the amount of emulsifiers with a water/hydrocarbon ratio equal to 1 for the system in Figure 2A.

in a strongly protective manner against coalescence in the system.

This area of emulsions with liquid crystals is still in its infancy but several applications and investigations are reported.<sup>26-36</sup>

With the liquid crystals as the third phase stabilization of the emulsion is experienced. On the other hand, when the isotropic liquid surfactant phase is present as in the low-energy emulsification<sup>37</sup> or in the HLB temperature process for emulsifier selection<sup>38,39</sup> the emulsion becomes

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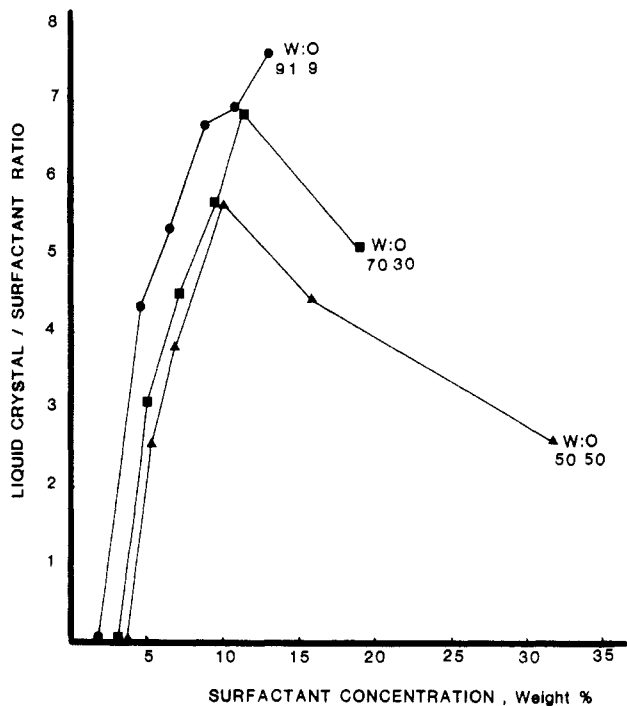


Figure 4. Ratio between the amount of liquid crystalline phase and emulsifier for different water/hydrocarbon ratios.

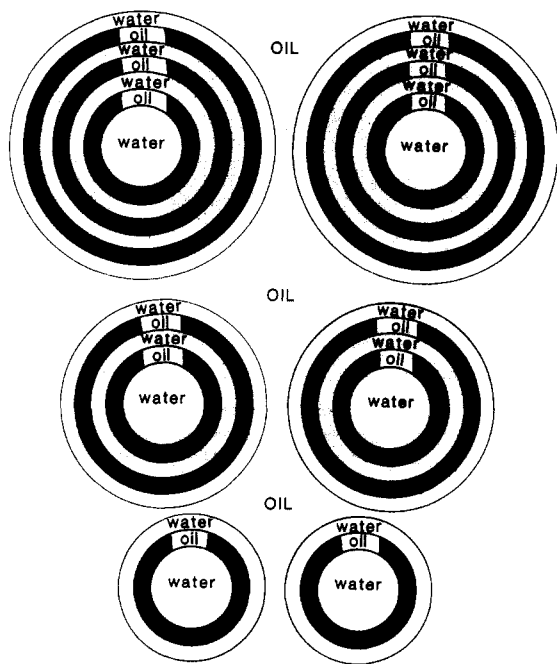


Figure 5. Model for the calculation of the change in the van der Waals potential during the coalescence process of emulsion droplets.

extremely unstable at that temperature.

This instability is due to the low interfacial tension between this phase and the oil phase as well as aqueous phase. It may, at first, appear strange to relate instability of an emulsion to low surface tension considering the fact that the main free energy excess for an emulsion compared to the state of two separate bulk solutions is the interfacial energy. However, the interfacial tension is actually instrumental in preventing extension and coalescence of the parts of two droplets which are closest when they approach each other. The van der Waals pressure is considerably higher along line P than along Q (Figure 7). In fact, for two emulsion droplets with a radius of 1  $\mu\text{m}$  and a distance between surfaces of 300  $\text{\AA}$ , this pressure ratio would be

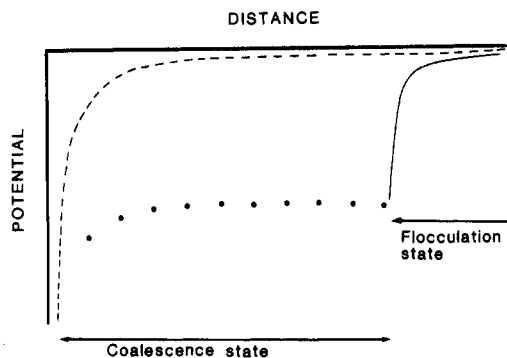


Figure 6. Energy changes during flocculation and coalescence for an emulsion covered with a model liquid crystalline phase (—) and for an uncovered one (---).

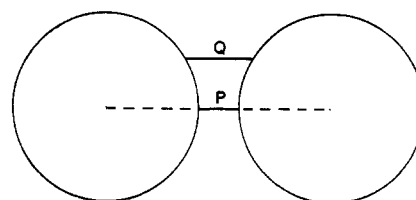


Figure 7. The van der Waals pressure between two emulsion droplets is higher along line P than along line Q.

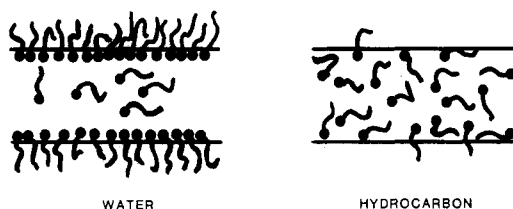


Figure 8. Surfactants adsorb strongly to a water/air interface but not to a hydrocarbon/air interface.

approximately 250 and one would expect extension and coalescence along the central line. However, common surface tensions ( $\approx 5 \text{ dyn/cm}$ ) are sufficient to prevent a significant extension along line P as shown by the following estimation.

Assuming a pressure increase along a line through the droplet centers to be  $\Delta P$  and the pressure in the nonperturbed droplet to be equal to  $P_0$  equilibrium gives

$$P_0 + \Delta P = 2\gamma / (R + \Delta R)$$

in which  $R$  is the droplet radius,  $\Delta R$  is the change of droplet radius due to  $\Delta P$ , and  $\gamma$  is the interfacial tension. (A finite value of  $\Delta R$  also causes a change in  $R$  but this is of second order and without significance.)

Assuming  $\Delta P$  emanating from van der Waals presence only and approximating to planar surfaces

$$\Delta P = \frac{A}{6\pi d^3} \left[ 1 - \frac{1}{(1 + 2/q)^3} - \frac{1}{(1 + 4/q)^3} \right]$$

in which  $A$  is the Hamaker constant,  $d$  is the distance between planar surfaces, and  $q$  is the ratio between  $d$  and radius of the emulsion droplet.

For the distance  $d$  less than 10% of the droplet radius, the two last terms contribute less than 0.02% of the van der Waals pressure and may be discarded.

Combining the two equations

$$\frac{\Delta R}{R} = - \frac{RA}{RA + 12\pi d^3 \gamma}$$

This equation relates the interfacial tension to the  $d$

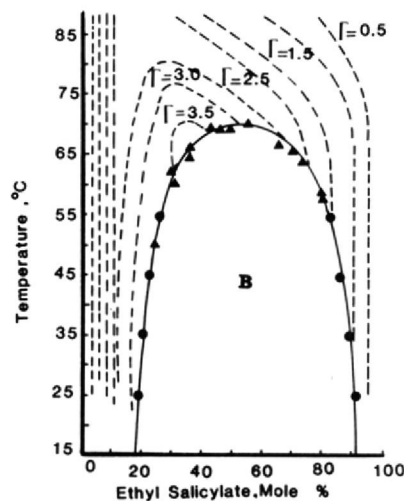
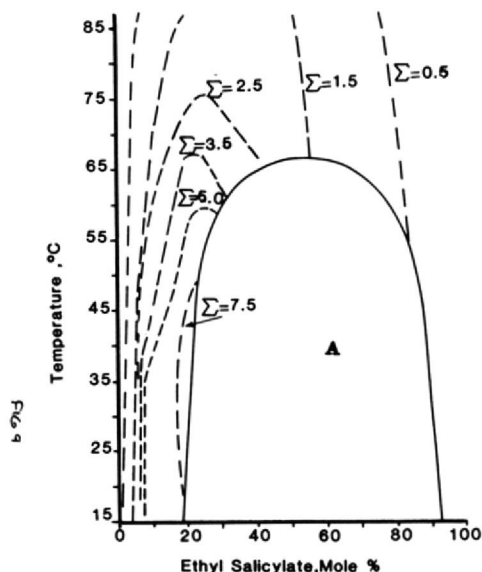


Figure 9. Foam stability ( $\Sigma$  in seconds) (A) and surface excess concentration of solute (B) of solutions of ethyl salicylate and diethylene glycol.<sup>43</sup>

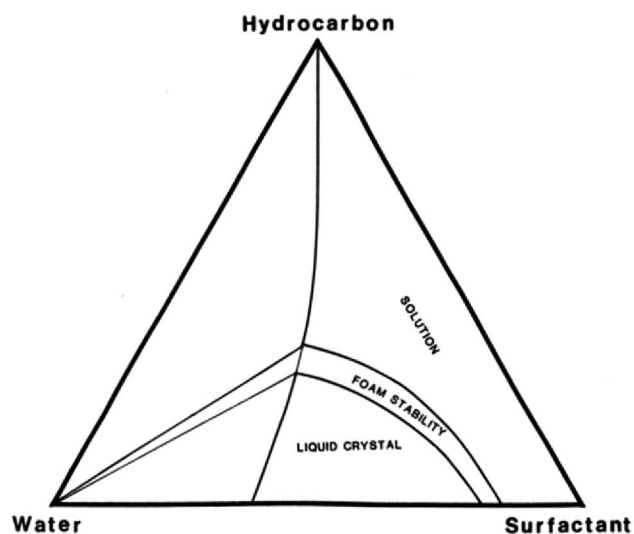


Figure 10. Two-phase region of a lamellar liquid crystal and the inverse micellar hydrocarbon surfactant solution showed excellent foam stability.

values at which an "appreciable" distortion is found. Assuming an appreciable distortion as 1% of the radius one obtains for a droplet size of 1  $\mu\text{m}$  and a Hamaker constant of  $10^{-12}$  erg

$$d = 6.4 \times 10^{-6} / \gamma^{1/3} (\text{cm})$$

An interfacial tension of 0.01 dyn/cm corresponds to a distance between outer surfaces of 16% of the droplet radius in order to cause a radius change of 1%. Interfacial tensions of this magnitude are expected in systems with a "surfactant phase" and the limited stability of these three-phase emulsions may mainly be ascribed to this factor. In an emulsion with a common value of  $\gamma$  of 5 dyn/cm, the corresponding distance is only 2% of the radius. At this distance point the hydrodynamic forces<sup>40</sup> are dominant and instead of an extension of the surface toward the second droplet a dimple occurs.

### Foams

The stability of aqueous foams has been analyzed combining surface elasticity and colloidal forces across the thin

(40) Brenner, H. *Adv. Chem. Eng.* 1966, 6, 328.

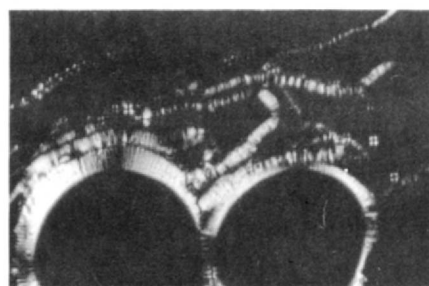


Figure 11. Lamellar liquid-crystalline phase adsorbed at the air interface.

film.<sup>3</sup> Once a rigid monomolecular film is obtained the stability is directly related to the two factors mentioned and the free energy change of a thin film due to perturbation may be written<sup>3</sup>

$$\Delta G = \text{extra area} \times \gamma + \text{extra potential energy}$$

in which  $\gamma$  is the surface tension against oil. The surface tension obviously plays a decisive role for the stability and enables stable foams to be formed also when the variation of potential does not add to the stabilization.

For a hydrocarbon foam the conditions are entirely different. An oil-soluble surfactant does not adsorb to the interface against air, because the surface tension of the hydrocarbon is at such a low level that adsorption of the surfactant would not lower it further (Figure 8). With no adsorption there is no monolayer of the surfactant and no solid surface monolayer and the hydrocarbon behaves as a pure liquid, a state well-known not to induce foam stability. This leaves only fluorinated surfactants as a choice for a stable foam from a hydrocarbon isotropic solution.

With this in mind the progress in this area of research has taken place in the direction of systems in which the film of the foam contains more than one phase. Two main facets of the problem have given noticeable results.

The first one is the approach to foamability by Ross and collaborators.<sup>41-45</sup> In this research it was found that very

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short time foam stability to give foamability was directly related to the critical point in an organic solution. A typical relation between critical point, the point of maximum surface excess of one component, and maximum life length of foam bubbles in the system ethyl salicylate/diethylene glycol is found in Figure 9A,B.<sup>43</sup>

The maximum surface excess, Figure 9B, is not found at the consolute point, approximately 45% diethylene glycol, but with considerably more of this substance, about 65%. This is expected; the point of maximum surface activity, the epicenter, coincides with the consolute point only when the two substances involved show identical surface tension in the pure state. With these two values unequal the epicenter of the surface excess contours will be displaced toward the component of higher surface tension.

The curves of identical foam stability, the isophoric contours, in general, follow the cosorption contours with the maximum even more displaced toward the compound with higher surface tension, supporting the hypothesis that Gibbs surface elasticity is the main factor for the stability of these evanescent foams.

The other avenue of this research provided foams of the excellent stability with simple rules:<sup>46-54</sup> (1) mutual solubility of the surfactant and the hydrocarbon; (2) no solubility of the surfactant in water; (3) solubility of the water in the surfactant to form a liquid crystal.

With these conditions excellent foam stability was found in the two-phase region of a lamellar liquid crystal and the inverse micellar hydrocarbon surfactant solution with solubilized water (Figure 10). Photographs of the foam showed the lamellar liquid crystal mainly to be localized to the interface to air (Figure 11).<sup>50</sup>

In this case the change from inverse micellar liquid solution to a lamellar liquid crystal obviously gave sufficient low surface tension to bring the liquid crystalline phase to the air interface.

The exact conditions for the location of one phase at an interface have been treated earlier.<sup>55</sup> One obtains

$$\gamma_{\text{air/l.cr}} < \gamma_{\text{air/liq}} + \gamma_{\text{liq/l.cr}} [Q^2 - (Q^3 + 1)^{2/3}]$$

(46) Friberg, S.; Ahmad, S. I. *J. Colloid Interface Sci.* 1971, 35, 175.

(47) Jederström, G.; Rydhag, L.; Friberg, S. *J. Pharm. Sci.* 1973, 62, 1979.

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(50) Friberg, S. E.; Wahn, C. S.; Greene, B.; Van Gilder, R. *J. Colloid Interface Sci.* 1984, 101, 593.

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(53) Roberts, K.; Axberg, C.; Österlund, R.; Saito, H. *Nature (London)* 1975, 255, 53.

(54) Bruil, H. G.; Lyklema, J. *Nature (London), Phys. Sci.* 1971, 233, 19.

in which  $Q = r_{\text{l.cr}}/r_{\text{air bubble}}$ ,  $r$  is radius.

The term within brackets is purely geometrical,  $\gamma_{\text{liq/l.cr}}$  is insignificant compared to the other terms and the condition to bring the liquid crystal to the air surface simplifies to a question of lower surface tension toward the air.

With this as a basis the problem is reduced to finding a plausible explanation of why the surface tension of a lamellar liquid crystal should be lower than the isotropic hydrocarbon solution, with which it is in equilibrium.

An assumption was made of the long-range order of the hydrocarbon chains in the lamellar liquid crystal being the cause of the low surface tension toward air. This partial order in the liquid crystal leads to a higher concentration of methyl groups at the surface compared to the case of a pure liquid. The methyl groups provide a lower surface free energy than the methylene groups as revealed by early investigations by Zisman<sup>56</sup> which gave the critical surface tensions of solids with methyl groups of the order of 23 dyn/cm while the surface tension of vehicles with only methylene groups was found about 5 dyn/cm higher.

This assumption has recently been tested by using two systems with identical water and surfactant but with different hydrocarbons.<sup>57</sup> One hydrocarbon, benzene, had an incipient surface tension of 30 dyn/cm while the other 2,2,4-trimethylpentane showed a lower value of 20 dyn/cm.

The two-phase system with liquid-crystalline phase and organic liquid (Figure 10) gave good foam stability for the entire two-phase region with benzene. On the other hand, with increasing content of the second hydrocarbon the foam stability disappeared entirely.

It is obvious that further investigations are needed to confirm this case of induced surface activity by an enhanced concentration of low-energy methyl groups at the surface of a lamellar liquid crystal, but the hypothesis has survived its first test.

## Summary

A few cases have demonstrated the decisive influence of colloidal association structures on the stability of macrodisperse systems.

An enhanced stability was found for emulsions which contained a liquid crystalline phase in addition to the aqueous and oil isotropic liquids and the long-range order of a liquid crystal was shown to induce surface activity into a system which showed none in the isotropic liquid state.

(55) Mandani, K.; Friberg, S. *Prog. Colloid Polym. Sci.* 1978, 65, 164.

(56) Zisman, W. *Adv. Chem. Sci.* 1964, No. 43, 1.

(57) Friberg, S.; Blute, I.; Kunieda, H.; Stenius, P., manuscript in preparation.