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Three-phase emulsions

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Synopsis

An emulsion is traditionally considered to consist of *TWO LIQUIDS* of which one is dispersed in the other in small droplets. To stabilize these droplets an emulsifier, a surfactant, is added that is believed to form a *MONOMOLECULAR LAYER* at the interface.

However, in many stable and commercially important emulsions the emulsifier, water and oil molecules form regular structures of *MULTIMOLECULAR LAYERS*. These layers actually are a distinct *PHASE*, that can exist independently after separation from the emulsion by centrifugation. The structure of this separate phase may be determined by X-ray diffraction, optical and electron microscopy.

This article discusses the features and the structure of these three-phase emulsions and describes the means of their identification. Finally new possibilities for the practical use of these kind of emulsions are indicated including enhanced solubility of compounds otherwise only sparingly soluble in hydrocarbon or water and slow release of active substances from the emulsion droplets.

INTRODUCTION

Emulsions have traditionally been treated as two-phase systems of one liquid dispersed in another liquid, the interface being stabilized by a monomolecular layer of surfactant molecules. The properties of such emulsions have been well described; Becher's book (1) being the classical treatment; later bibliographies (2) have added detailed knowledge of specific parts of the field. However, many properties such as sudden changes of stability and viscosity of emulsion simply could not be fully explained by the two-phase concept as pointed out by Sherman as early as 1964 (3).

This led to several studies on such multi-phase emulsions during the late 1960's, and attempts were made to examine the number of phases and their structure in practical emulsion systems (4-6). The methods to separate highly viscous phases from an emulsion had not been evaluated by that time and the problems with establishing equilibrium between the separated phases not fully realized. As a result the phase diagrams of these early investigations do probably not reflect equilibrium conditions. The problems of equilibria in soap-water systems was extensively studied by Ekwall and co-workers; their painstaking efforts to establish equilibrium between different liquid crystalline phases have been described in detail (7).

The methods by Ekwall were successfully applied to emulsions and in 1969 (8) it could

be demonstrated that the stable emulsions of water, *p*-xylene and the common commercial emulsifier, octa ethylene glycol nonyl phenol ether, actually did not consist of *two,* but of *three* phases. The third phase was a lyotropic liquid crystal.

The presence of this third phase with liquid crystalline structure stabilized the emulsion (3-5) (Figure 1); emulsions containing only two phases were considerably less stable (1, 2,) (Figure 1).

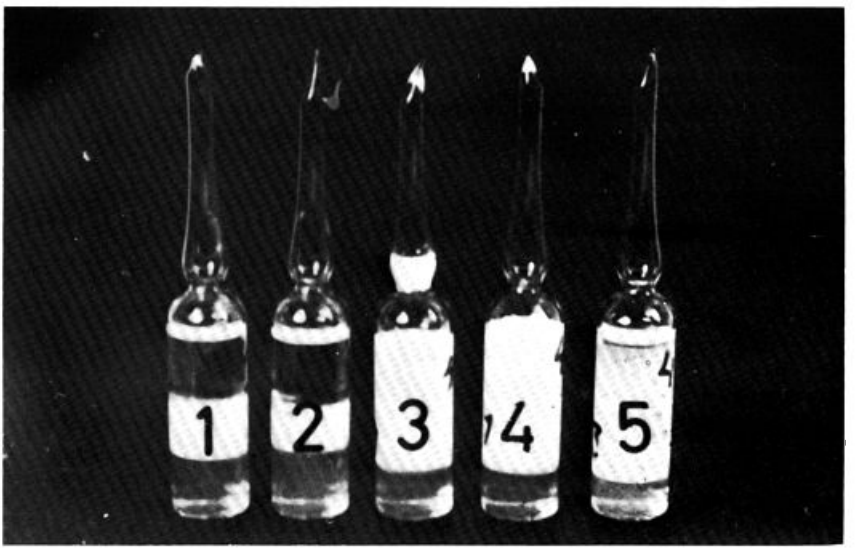

Figure 1. Water/*p*-xylene emulsions stabilized by a commercial emulsifier, octa ethylene glycol nonyl phenol ether, showed a sudden increase of stability (Em 2 → 3) when the number of phases increased from 2 to 3 (8).

This stabilization by the third phase with liquid crystalline structure has later been confirmed for other systems. The structure (9-11) and some of the fundamentals (12, 13) for the enhanced stability have been evaluated.

These contributions led to a new definition of the word emulsion by the IUPAC Commission for Colloid and Surface Chemistry in 1972. The definition now reads, "In an emulsion liquid droplets and/or liquid crystals are dispersed in a liquid." (14).

Emulsions containing a third phase of liquid crystalline character are often found in commercial cosmetics (Figure 2), which has led to a recent interest in these phenomena from the cosmetic industry. They also exist in food products in which lecithin and monoglycerides (15) are commonly used as emulsifiers. They have also been utilized in pharmaceutical preparations to obtain slow release of drugs (16).

Since an application of these multi-phase emulsions may cause considerable processing and storage problems with insufficient knowledge of their structure and properties it was considered of value to give a description of these three-phase emulsions, the separation and characteristics of the phases. This article contains a short report of the results from the original article (8) that established the relation between the number of phases and emulsion stability, an account of the detection of a liquid crystal in an emulsion, a description of the separation and structure determination of the liquid

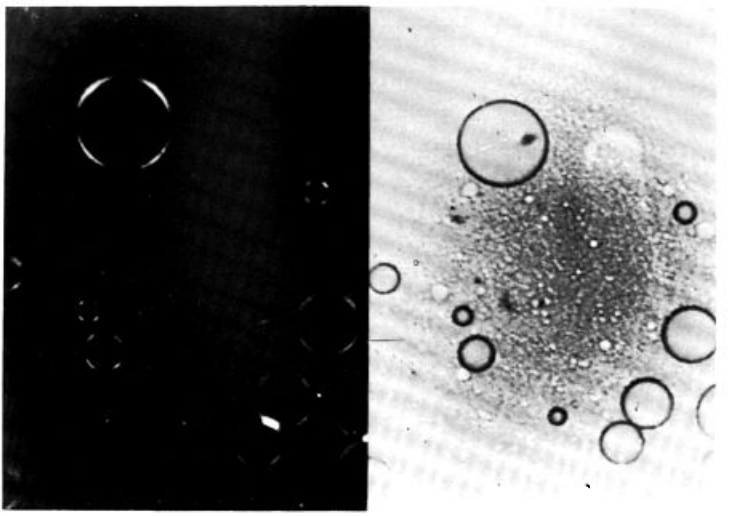

Figure 2. The presence of a liquid crystalline phase in a commercial hand lotion can be clearly observed in a microscope under polarized light (left). (Courtesy L. Rydhag, YKI, Stockholm).

crystalline phase, a few words on the factors behing the enhanced stability of such emulsions and finally some special applications of such systems.

FROM TWO TO THREE PHASES—ENHANCED EMULSION STABILITY

Separation of the phases in a stable emulsion is difficult; after the methods used by Ekwall and co-workers (7) for other systems had become generally known, a connection between emulsion stability and the number of phases could be established in 1969 (8).

The results showed that the stability increase of the oil phase emulsion between numbers 2 and 3 (Figure 3, top) was related to a change in the number of phases in the system at equilibrium (Figure 3, lower part). Emulsions 1 and 2 contained two liquid phases, an aqueous solution (A-B, Figure 3) and an oil phase (O-Q, Figure 3). When the emulsifier concentration was increased from 2.5% (Emulsion 2, Figure 3) to 4% (Emulsion 3, Figure 3), the number of phases was altered from two to three; the total composition passed the line B-Q from left to fight. The third phase had the composition marked by the point M and a lamellar liquid crystalline structure (Figure 4).

Contrary to an emulsion of two liquids that is stabilized by monolayers of the emulsifier, a three-phase emulsion of this kind is stabilized by an association structure (M) containing both oil, water and emulsifier molecules (Figure 4). The emulsifier is actually only a small fraction of the third phase. In the present example the liquid crystalline phase contained mostly water (85%) with hydrocarbon (5%) and emulsifier (10%) being minor components. The three components were accommodated into a highly viscous body; that served as stabilizer for the emulsion. It may be of interest to note that this emulsifier is a commercial one; as a matter of fact, the most used one at that time.

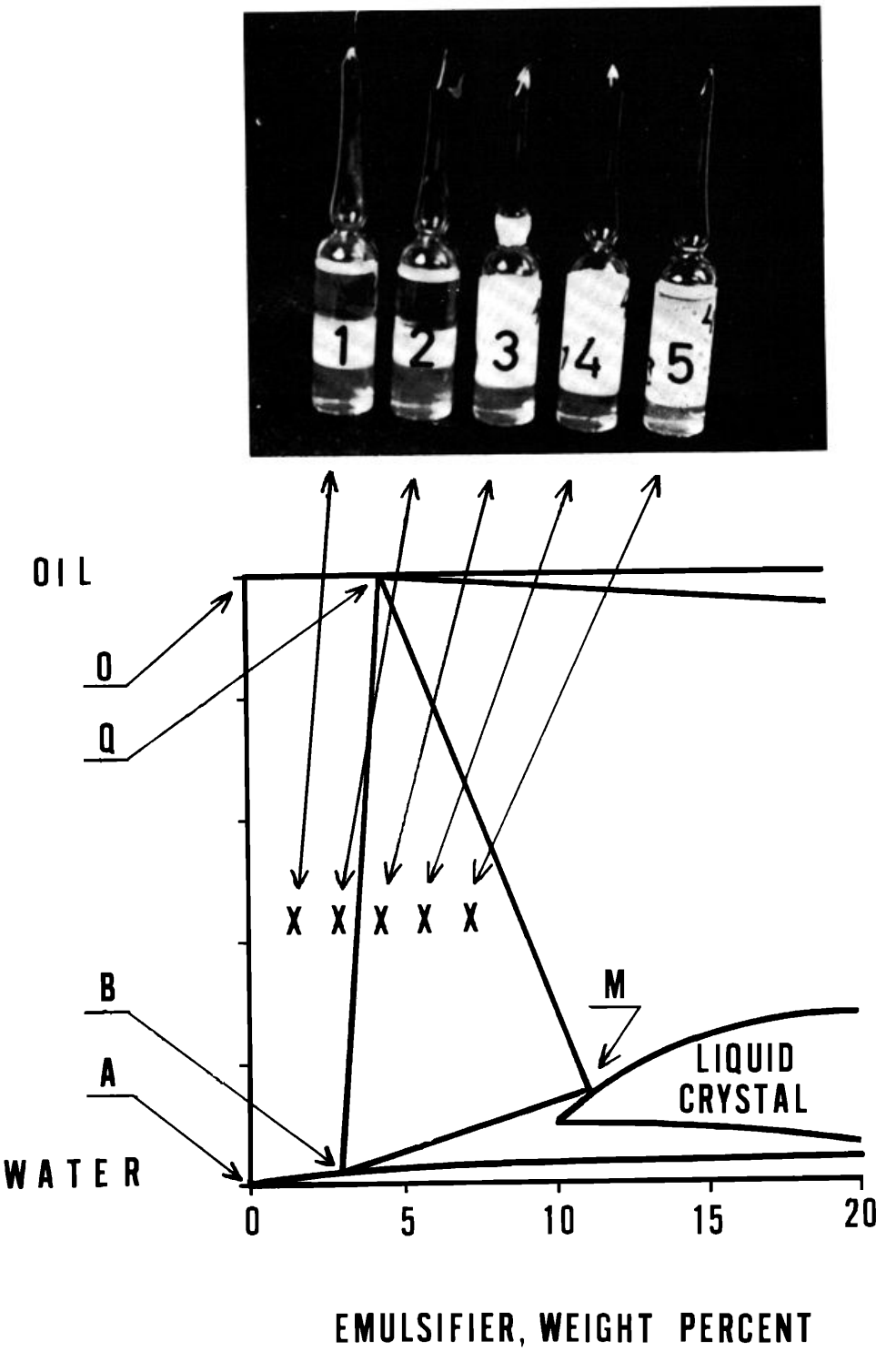

Figure 3. Emulsions to the left of line B-Q (Emulsions 1 and 2) consist of two liquids: an aqueous phase, A-B, and an oil phase, O-Q. To the right of the line B-Q the more stable emulsions 3-5 consist of three phases, the liquids B and Q plus the liquid crystalline phase M.

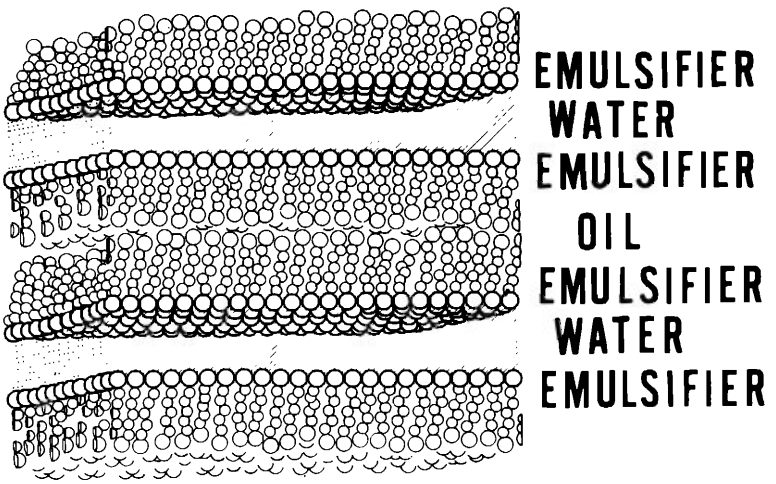

Figure 4. A lamellar liquid crystal consists of consecutive layers of.... water - emulsifier - oil - emulsifier - water....

Before discussing the identification of the liquid crystal in the emulsion a few facts related to phase diagrams must be clarified since they are sometimes misunderstood.

It is essential to realize that high amounts of emulsifier are not necessary to obtain a liquid crystalline phase; the amount of liquid crystalline phase is *not* proportional to the amount of emulsifier. In the present case, 3% emulsifier was sufficient to form the liquid crystalline phase within the system. In the combination liquid triglyceride, egg yolk lecithin and water (9), which is a common commercial base system, the liquid crystalline phase appears at extremely small concentrations of the emulsifier (~0.1% by weight). For such an emulsions with a W/O ratio 1/2, an emulsifier concentration of 2% will give a liquid crystalline phase occupying 15% of the total volume; an impressive amount of stabilizer.

The detection and identification of a liquid crystal in an emulsion is important for the cosmetic chemist; the following section deals with useful and available methods of detection and identification.

DETECTION OF THE LIQUID CRYSTAL IN AN EMULSION

Most of the liquid crystals (see next section) are optically anisotropic (10) and are directly observed in an optical microscope with polarized light. It is important to avoid optical artifacts; bad focusing of the microscope may produce reflections from the droplets, an image that may be mistaken as indicating the presence of an *optically anisotropic* material.

Mistakes of this kind are avoided by the use of a two-phase emulsion as comparison. Figure 5 (10) is a good illustration of the difference in optical pattern. The emulsion to the right (photo, upper right) contains a liquid crystalline phase; its optical pattern is clearly distinguished from that of the other emulsions, which do not contain liquid crystals. A useful further check that the radiant parts are not artifacts is to rotate the slide on the stage of the microscope in polarized light. The dark and radiant parts of the droplet layers (see Figure 2) will shift with the direction of the turntable.

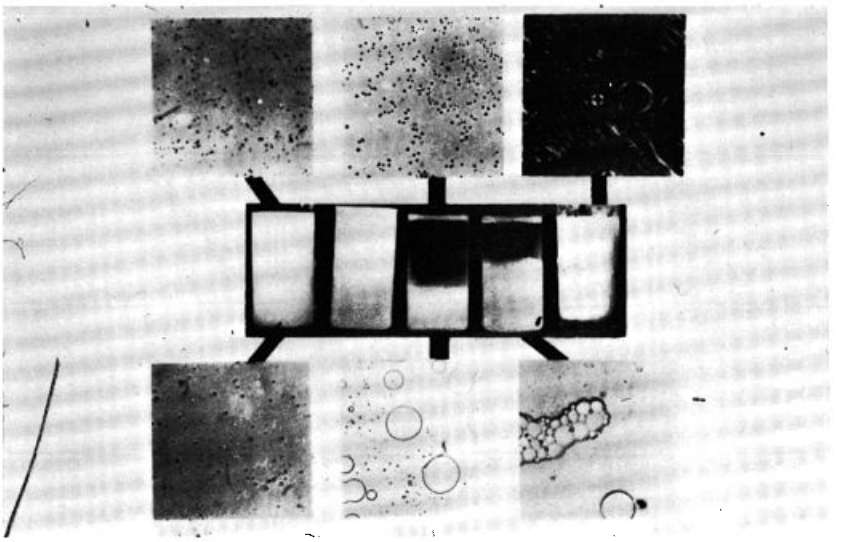

Figure 5. An emulsion with a liquid crystal (upper right) has a microscope pattern in polarized light that is clearly distinguished from the two-phase emulsions.

A more refined method to observe the liquid crystal is to use electron microscopy of carbon replicas from freeze fractured samples of the emulsion. Such photos (Figure 6) enable the direct observation of the individual layers in the liquid crystalline phase (12). The droplet in the center of the figure is flocculated with several other droplets around it; the layers of the liquid crystalline phase can be observed to follow the contours of the droplets. Electron microscopy of this kind is a time consuming, highly specialized and extremely expensive method; it is useful in order to obtain detailed information about systems of special interest but is no routine technique.

The final proof of the presence of a liquid crystalline phase is the separation and analysis of the individual phases.

SEPARATION AND STRUCTURE DETERMINATION OF A LIQUID CRYSTALLINE PHASE

The liquid crystalline phase is highly viscous and its interfacial tension towards the oil and aqueous phase is low. These properties mean that spontaneous separation is slow because the driving force is small and the kinetics of separation is hindered by viscous forces. After all, problems with the separation should also be expected; a stable emulsion may not and should not be expected to separate easily.

The separation may be achieved by ultracentrifugation. The problems encountered with a separation to *equilibrium* compositions are cumbersome when the liquid crystal contains maximal solubilization of water or oil. Emulsions may be expected to cause problems since the three-phase area oil, water and liquid crystalline phase always includes a liquid crystalline phase with high amounts of oil and/or water. Too small centrifugal force and too short centrifugation time will leave a liquid crystal with occlusions of the liquid phases. These liquid droplets have no tendency to separate since they are in equilibrium with the surrounding liquid crystalline phase with high viscosity. With some practice these droplets of the liquid phases may usually be

Figure 6. The liquid crystalline layers in an emulsion may be directly observed in an electron microscope photograph of the carbon replica from freeze-etched samples.

detected in the microscope. Too high a centrifugal field for too long a time will, on the other hand, squeeze liquid out of the liquid crystal leaving a non-equilibrium composition; this is especially the case with lamellar liquid crystals of nonionic surfactants in which large amounts of hydrocarbon are solubilized. This case cannot be observed in the microscope; instead careful analysis of changes in the relative amounts of phases will show the non-equilibrium condition. The liquid crystalline phase will spontaneously (although slowly) absorb oil and water to its equilibrium composition.

For systems in practical use, true equilibrium is not an absolute necessity. The

existence and structure of a liquid crystal may be sufficient information. Even under these conditions the results have to be handled with care because a liquid crystalline phase may be formed by sedimentation of large micelles during centrifugation. In this respect systems of water, hydrocarbon and nonionic emulsifiers are especially dangerous since they may form *microemulsions* which are isotropic liquids with large amounts of both oil and water dissolved. These microemulsions readily separate at centrifugation giving two liquid phases and one liquid crystalline phase, which are not an equilibrium with each other. The following example is illustrative: 60% water, 12% pentaoxyethylene dodecyl ether and 28% hexadecane form an isotropic liquid phase at 20°C. After centrifuging for 2 hr at 150,000 g the solution separated into one liquid crystalline phase and two liquid phases. However, these three phases are not the equilibrium state of the system. When left at 20°C the liquid crystalline phase gradually disappeared in one week. The phase boundary between the two remaining liquids disappeared after about three weeks' time and the microemulsion was reformed.

The guidelines for ultracentrifugation are to use as high centrifugal forces as possible, observe the movement of the phase boundaries as function of time and stop the centrifugation if a sudden change to slower separation rate is observed. At that point the two liquid phases are removed and the less dense one is carefully poured on top of the other. The liquid crystalline part is microscopically checked for occlusions of liquid. If such are found the centrifugation is continued of the liquid crystalline phase *only* to prevent the sedimentation of micelles to form an artifact liquid crystalline phase. The two liquids in contact with each other are checked that no liquid crystal will appear at the interface.

After the separation, the structure of the liquid crystalline phase may be determined using optical microscopy and low-angle X-ray diffractometry (17). The two common liquid crystals are the one with a lamellar structure (Figure 7, A) and the one with cylinders packed in a hexagonal array (Figure 7, C). The two structures give different patterns in the microscope in polarized light; these patterns are useful as a primary identification. The final identification is made using the low-angle X-ray diffraction patterns; the lamellar structure gives the ratio $1:1/2:1/4$ between the characteristic distances from the film; the hexagonal one $1:1/\sqrt{3}:1/\sqrt{4}$ and the cubic structure $1:1/\sqrt{3/4}:1/\sqrt{3/8}$. The latter cannot be identified by its optical pattern and only with difficulty observed in the microscope.

These structure determinations are useful for identification purposes, but have little practical utility. From the cosmetic chemist's point of view a chemical analysis of the composition of the liquid crystalline phase is more important since this information determines the usefulness of the surfactant. A low surfactant concentration in the liquid crystalline phase is beneficial. There is a wide difference between a surfactant that forms the liquid crystalline phase at 50% surfactant, such as the combination of sodium dodecyl sulfate and dodecyl alcohol, and at 5% surfactant, such as lecithin. Assuming no micellization it is easy to realize that 2% of the latter means that the emulsion will contain 20% liquid crystalline phase, a sufficient amount to ensure stability. In the first case the liquid crystal will occupy only 4% of the mixture; a considerably less amount.

Another equally important factor is the concentration of the aqueous and oil phases with which the liquid crystalline phase is in equilibrium. If the concentration of surfactant both in the oil and the water at the points connecting the three-phase area

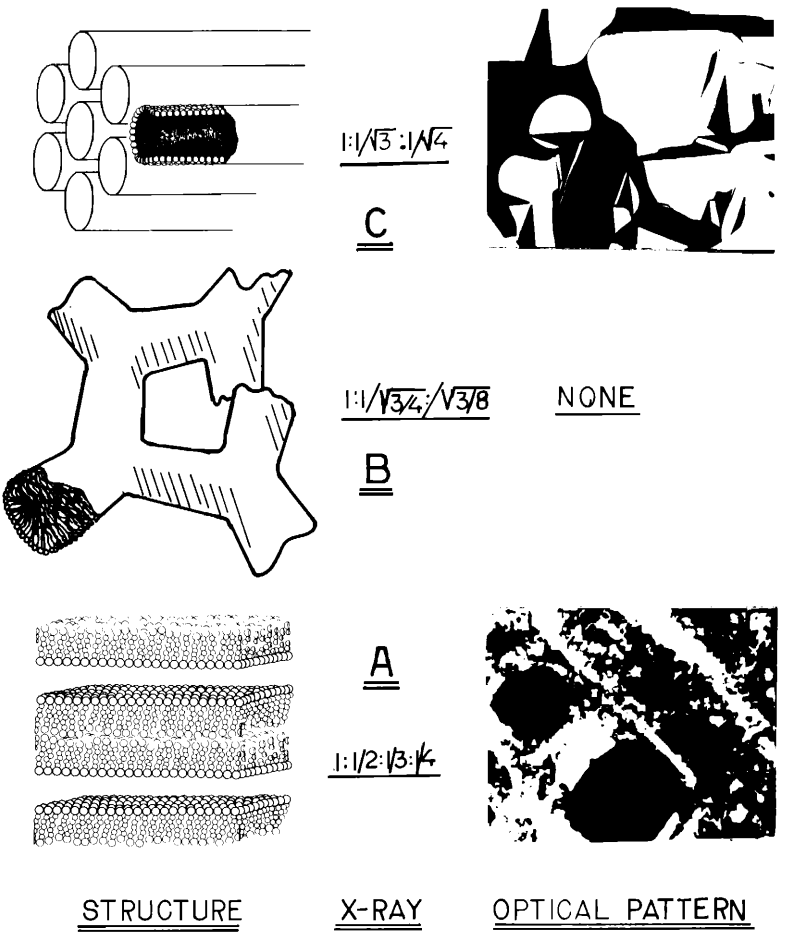

Figure 7. The low-angle X-ray reflections (middle) and the optical patterns from a microscope with polarized light (right) serve to identify the structure of the liquid crystalline phase in an emulsion.

with the liquid crystal is higher than the actual concentration in the emulsion, the liquid crystalline phase will never form and is, of course, of no use.

THE STABILIZING ACTION OF LIQUID CRYSTALS

The liquid crystals in an emulsion stabilizes it with several mechanisms.

The layers of liquid crystalline phase around the droplets act as a rheological barrier to coalescence; an extremely effective barrier considering the pronounced viscous forces encountered when the liquid crystalline phase is sheared. To this increased viscosity the change of driving force for coalescence due to the presence of the liquid crystalline phase must be added. The calculation of these changes is fairly complex (13) and outside the scope of an article of this kind, but the effect is worth observing.

In addition some liquid crystalline phases have a tendency to form a network of semi-solid phase extending through the continuous phase. This network slows the

movement of the droplets and adds to the stability in a fashion similar to the one by polymeric materials.

SPECIFIC USES OF THREE-PHASE EMULSIONS

These three-phase emulsions make it possible to obtain lotions and other cosmetic products of desired consistency with a free variation of the oil/water ratio. It is even possible to prepare creamy emulsions with no free oil present (8,9); the two-phase system water/liquid crystalline phase (B-M, Figure 3) does not contain free oil; only water and liquid crystalline phase, the latter containing solubilized oil.

The liquid crystal can also be used to dissolve higher amounts of some substances than normal liquids. Such substances, e.g., steroids which dissolve only in minute amounts in liquids, can be brought to solution in a suitable liquid crystalline phase. This means that substances with steroid structure otherwise only present as crystalline compounds can be brought into a smooth dissolved state.

Finally the liquid crystals serve to prevent fast release of a substance dissolved in the dispersed liquid phase (16). In a normal two-phase emulsion of liquids the diffusion across the interface is little hindered and the release of substance from the droplets to the continuous phase is fast. A liquid crystalline layer has a diffusion coefficient that is at least one thousand times less than the one in a liquid (18) and a layer around the droplet will effectively reduce the transport of a dissolved substance from the droplets.

SUMMARY

The properties of three-phase emulsions containing a liquid crystalline phase have been discussed, methods for their identification and analysis have been given and utilization of their specific properties in the cosmetic industry indicated.

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