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Evaporation from a complex emulsion system

BRUNO R. C. LANGLOIS and STIG E. FRIBERG, *Center for Advanced Materials Processing, Department of Chemistry, Clarkson University, Potsdam, NY 1699-5814.*

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Synopsis

The phase equilibria were analyzed in a typical skin lotion system of water, decane, triethanolamine, and isostearic acid, and the evaporation rate was determined. The system showed two isotropic solutions, one of decane/isostearic acid, and a water/triethanolamine combination. In addition, a large region of lamellar liquid crystal phase was found plus a small region of liquid crystal that consisted of close-packed cylinders. Evaporation of water and decane initially led to a transfer of triethanolamine from the aqueous solution to the decane/isostearic acid solution. With sufficient depletion of water and decane, a three-phase region was entered with the third phase, the lamellar liquid crystal.

INTRODUCTION

Cosmetic emulsions (1) are of significant interest because of their stringent stability requirements, combined with a pleasing appearance as well as appealing feel upon application. The phase changes that occur during evaporation of volatile components are important because they influence the evaporation rate *per se* (2–4). In addition, the structure remaining on the skin after evaporation has ceased is of equal importance. This structure may be an oil phase, in which case excellent occlusivity may be found (5), or a liquid crystal with its interesting structural interactions with the stratum corneum lipids (3,6).

We have earlier (7) analyzed the conditions when an emulsion is applied to a surface with a hydrophobicity similar to that of human skin. That analysis was concerned with phase changes and inversion of the emulsion as well as with its flocculation and coalescence.

In the current article we present an analysis of the phase equilibria related to the evaporation of water and decane from the system. The changes in the equilibria show a more complex behavior than expected.

EXPERIMENTAL

CHEMICALS

The decane 99.7% (Fisher Scientific), the triethanolamine 99.9%, (Fisher Scientific), the isostearic acid (Sigma), and a mixture of approximately 30% normal and methyl branched isomers and their homologs were used as obtained without further purification. The water was doubly distilled.

EMULSION PREPARATION FOR EVAPORATION

A mixture of isostearic acid/triethanolamine (65/35 weight ratio) was used as an emulsifier. The emulsions were prepared by a method previously described (7), with different W/O ratios and 10% emulsifier counted on total weight. After emulsification on a vortex mixer, the droplet size distribution was checked by microscopy and found similar for the different W/O ratios (Figure 1).

EVAPORATION STUDIES

Previously we have noted (7) that the essential factor for the evaporation is the area exposed to the atmosphere. The monitoring of the area was made possible by use of a watch glass to avoid interruption of the film during evaporation, and the atmosphere was controlled by a constant air flow to ensure identical convection. The relative humidity was ambient and varied between 24.0% and 27.0%. This small variation had no influence on our results.

The exposed area of the emulsion was slowly decreased by evaporation. To obtain the rate of evaporation per unit area, the slope of the weight loss as a function of time is divided by the exposed area. The areas measured during evaporation were divided by the largest initial area obtained for the emulsion system of different W/O ratios, giving an evaporation rate per arbitrary unit area. All the initial areas were nearly identical, since we started with similar quantities of material.

Since water and decane, which are the only volatile components of our systems at room temperature, have similar vapor pressure, it is possible to follow the evaporation rate versus the composition of each emulsion with different W/O ratios.

Finally, for some experiments, the evaporation was followed gravimetrically, while changes in phase structure that occurred during evaporation were observed under a microscope with the sample between crossed polarizers.

PHASE DIAGRAM DETERMINATION

The phases in the ternary phase diagram for the decane/water/(isostearic acid/triethanolamine, wt. ratio 65/35) were determined. The liquid crystalline phase, the isotropic phase, and the three-phase area boundaries were identified by optical microscopy.

The boundaries of the lamellar phase were also obtained by small-angle X-ray diffraction. The mixture was drawn into fine glass capillaries of 0.7-mm diameter, sealed at both ends, and placed into a brass sample holder with a 2-mm diameter opening. The X-ray radiation was K_α copper filtered by a nickel foil to give a wavelength of 0.1542 nm at 40,000 V and 18.10^{-3} A. The X-Ray equipment (Siemens Crystalloflex 4) consisted of a sensitive detector system (Tennelec PSD 100), a flow proportional

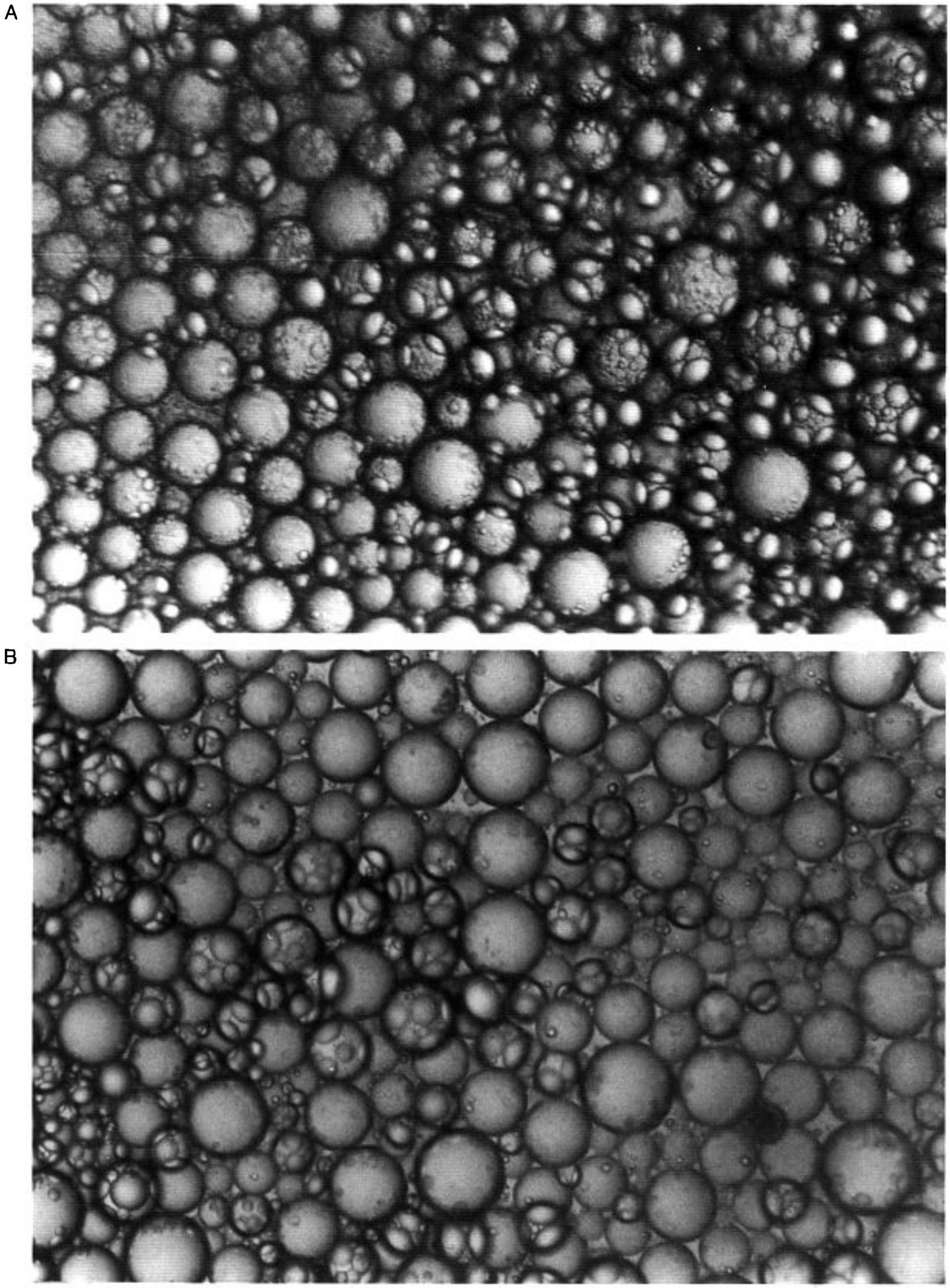

Figure 1. The drop size distribution for different emulsions was similar. a. W/O 20/80 emulsion. b. W/O 60/40 emulsion.

counter, and a Kiessig low-angle camera (Richard Seifert). The detector was flushed with a mixture of oxygen-free nitrogen and methane, at a flow rate of 15–20 ml/min^{-1}. The path length between the sample and the detector was 500 mm, corresponding to a diffraction angle 2θ lying between 5.7° and 0.7°. The exposure time for the samples was set to 600 seconds, and alignment of the instrument was checked by a lead stearate standard with an interlayer spacing of 4.82 nm. With our measuring instrument and conversion of the signal to the plotter, we obtained paired symmetric peaks on both sides of center. Interlayer spacing was determined using the Bragg equation:

$$n \cdot \lambda = 2 \cdot d \cdot \sin\theta$$

where n is the order of diffraction, λ is the wavelength, d is the interlayer spacing, and 2θ is the diffraction angle.

The diffraction angle was calculated by the following equation:

$$\tan(2\theta) = \frac{D \cdot S}{2(l + x)}$$

where D is the distance between the peaks, S is a correction factor for transferring X-rays from the detector to the plotter, l is the path length, in millimeters, between sample and detector, and x is the calculated length in millimeters from the calibration curve.

A plot of the interlayer spacing against volume ratio of water for fixed ratios of decane and emulsifier is linear for the monophasic system. A plateau appears in the plot where other phases were found to exist in equilibrium with the lamellar phase.

RESULTS

PHASE DIAGRAM

The different phases are shown in Figure 2. The emulsifier, a molar ratio 1:1 triethanolamine/isostearic acid, has a lamellar liquid crystalline structure and can accommodate up to 45% water and 22% decane. A more detailed study of the packing in such a structure is currently under investigation and will be the subject of a future publication.

An isotropic phase was observed, for decane content between 42% and 80% (weight) in the absence of water.

The boundaries of the three-phase region in the complete system are shown. It is noted that for the specific molar ratio 2:1 decane/emulsifier, a "gel-like" mixture of a lamellar phase and isotropic phase was observed. This phase contains up to 65% water. The sample in this region gave no detectable X-ray pattern and its structure is not known.

Finally, there was no significant solubility, less than half a percent, of decane and emulsifier in water, or of water and emulsifier in decane.

EMULSION EVAPORATION

The evaporation rate of the water/decane emulsions against composition fraction of the emulsifier is shown in Figure 3. All emulsions can be characterized by a fast evaporation rate and a sudden change towards a slow evaporation for a weight fraction of emulsifier between 0.11 and 0.15 counted on total weight.

Optical microscopy of the emulsion 60/40, O/W wt. ratio, between cross-polarizers

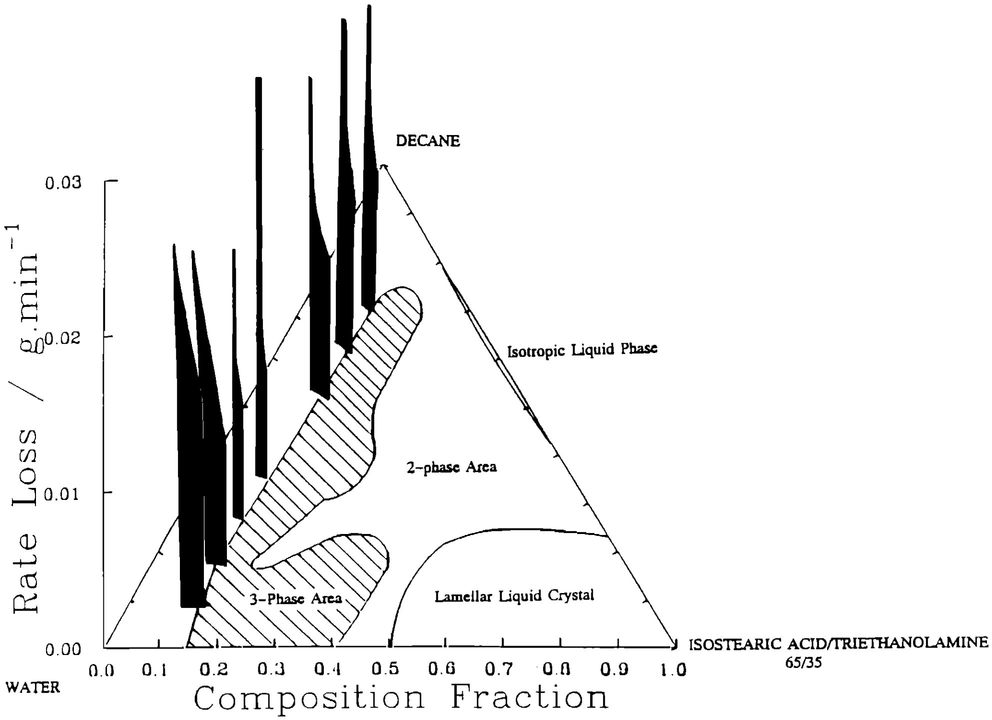

Figure 2. In the phase region in the plane investigated were three isotropic solutions: water, decane, and a decane solution of the emulsifier combination with small water solubilization and a lamellar liquid crystal. The three-phase region (Figure 4), aqueous solution, decane solution, and the lamellar liquid crystal covered a large area. The black parts illustrate the strong reduction in the evaporation rates.

showed the reduction of the evaporation rate to correspond to the appearance of the lamellar phase. With this in mind, the breaking point of the evaporation curve was determined geometrically. Its projection is marked on the ternary phase diagram. This breaking point corresponded to the composition at which a sudden change in rate was noticed. The results are shown in Figure 2, and are in good agreement with the boundary of the three-phase region determined by optical microscopy. This way a straightforward connection between the evaporation rate and the presence of a lamellar phase was established.

On the other hand, there appeared to be no correlation between the time at which the evaporation rate was suddenly reduced and the W/O ratio of the emulsion.

Finally, a change in the rate of evaporation was detected for compositions lying between 0.46 and 0.75, as shown on Figure 2. However, these changes were not as conspicuous as in the first case, but in good agreement with the compositions giving a lamellar phase as the only phase.

DISCUSSION

The results clearly demonstrated the relation between the mesomorphic structures that

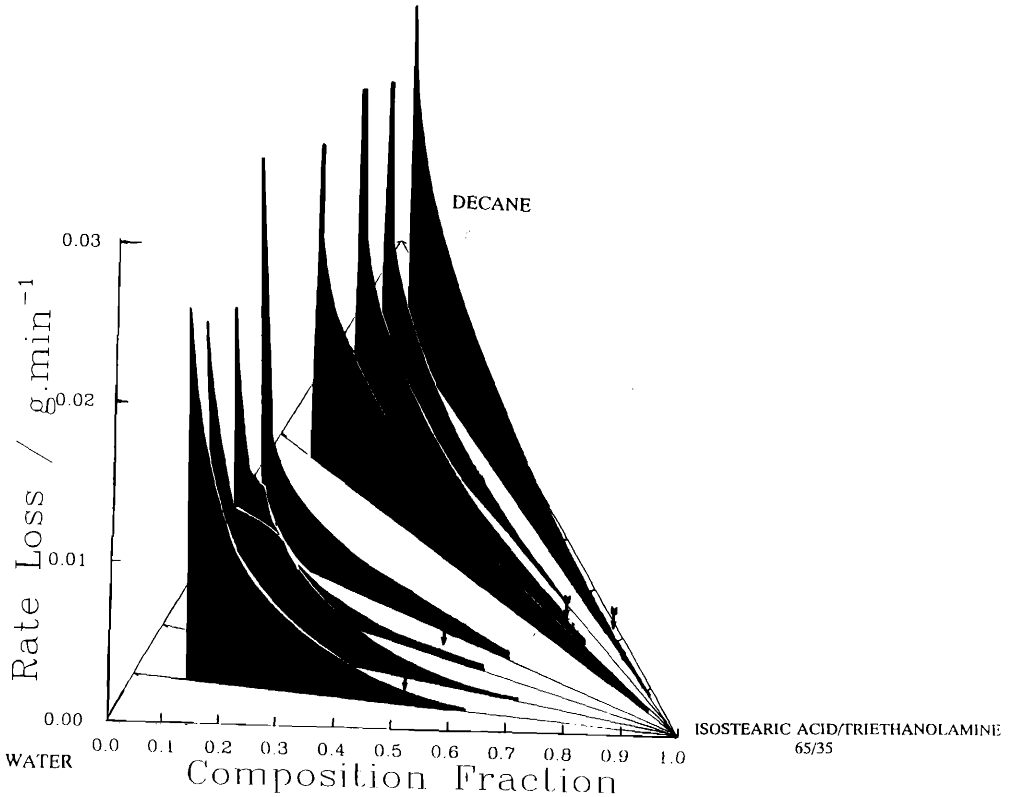

Figure 3. The evaporation rates were strongly reduced where the lamellar liquid crystal appeared in the composition (Figure 2).

occurred when composition of the system changed and the corresponding evaporation rate.

In our preceding article (7), we focused our attention on the coalescence and flocculation of oil and water droplets within the emulsion, when it was spread as a thin film. For that purpose, a very small amount of emulsifier was used (2% on total weight), and the concentration of the surfactant remained sufficiently low for a liquid crystal to enter the composition first at a late stage. Hence its effect on the evaporation rate could not be observed.

In the present article, the liquid crystalline structure of the emulsifier has a significant influence, because, with reduction of water and decane content, the composition passes through a multi-phase system containing a large amount of the lamellar phase during evaporation at an early stage. Such results have already been discussed by Lochhead (8), where a change of evaporation rate from an initial rapid rate followed by a lower rate could be related, by means of optical microscopy, to the presence of large amounts of a liquid crystalline phase. The present more complicated system merits an analysis of developments leading to the appearance of the lamellar phase.

As we look at the complete phase diagram of the system (9), the starting material consists of two isotropic liquid phases in equilibrium. One of these is water with a small amount of triethanolamine, and the other is decane with the isostearic acid and remaining triethanolamine. From these calculated values, it should noted that most of the emulsifier was in the hydrocarbon phase and that the water phase had a water fraction varying from 0.98 to 0.75, whereas the oil phase had a decane content varying from 0.92 to 0.42. Moreover, this diagram and Figure 4 show that the solubility of triethanolamine in both phases accounts for the ratio of each phase. It is interesting to note that the composition of the two phases strongly depended on the water/decane ratio of the total composition. For low water content, the triethanolamine concentration in the aqueous phase was high while isostearic acid concentration in the decane phase was low. Just the opposite was true for high water content.

The composition changes of the two liquid phases during evaporation have a decisive effect on the appearance of the lamellar liquid crystalline phase. When both water and decane evaporated, the composition of the aqueous phase remained fairly constant

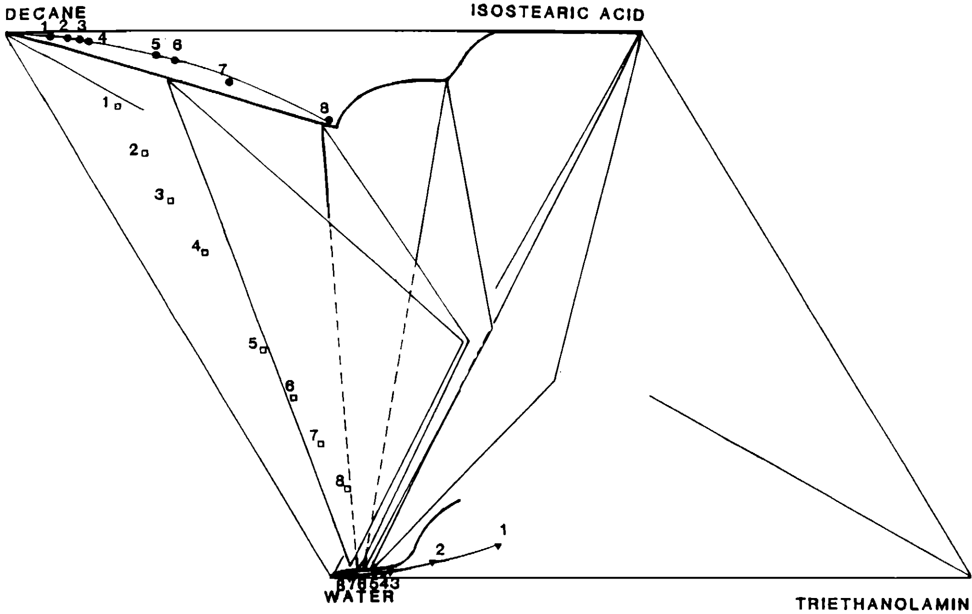

Figure 4. The composition of each phase in the emulsion varied strongly with the W/O ratio. It should be observed that the less the O/W ratio the greater the concentration of emulsifier in the oil phase and vice versa. The squares in the diagram show the total composition with 10% of the emulsifier (isostearic acid/triethanolamine, 65/35 wt. ratio) and the oil/water wt. ratio as shown below. The circles show the composition of the separated oil phase with numbers identical to those for the total compositions. Filled triangles note the composition of the aqueous phase.

Sample	O/W
1	90/10
2	80/20
3	70/30
4	60/40
5	40/60
6	30/70
7	20/80
8	10/90

(Figure 4), while the composition of the decane phase was changed towards an increase of its triethanolamine/isostearic acid content. As the water and decane were evaporated, the emulsifier concentration in the oil phase reached the weight ratio 65/35 and ceased to be soluble in the hydrocarbon phase (Figure 4). Since the total amount of triethanolamine/isostearic acid did not change, but could no longer be accommodated in the oil phase, the lamellar liquid crystal at this point entered the composition as a third phase. As shown by experimental results (Figure 5), the lamellar phase was thus formed at the surface where the evaporation takes place. The observation revealed that the lamellar phase formed covered the entire sample, appearing as a "film" at the surface. This film reduced the evaporation rate of the remaining composition. Under the conditions of our earlier investigations (7), a low concentration of emulsifier was used and the lamellar phase formed only at the edge of the sample (Figure 5B). Hence its appearance had *de facto* no noticeable effect on the evaporation rate from the remaining composition. A comparison of the two rates of evaporation (Figure 6) illustrates these observations. The change in rate was not as marked with 2% emulsifier as it was with 10%.

With this in mind, it is instructive to determine the composition of each phase when the lamellar crystalline phase enters the composition. These preliminary calculations were done for the emulsion 40/60, assuming the following conditions:

Before entering the three-phase region, the composition of the water phase was 0.98 fraction of water and the rest 0.02 fraction of triethanolamine, according to the three-phase area equilibrium in Figure 4. Weight loss of water and decane (no diffusion barrier case) is directly proportional to their ratio. The composition of the oil phase is water/isostearic acid/triethanolamine/decane (0/0.103/0.054/0.838, where the ratio between isostearic acid and triethanolamine is exactly 65/35.

The last assumption leading to this result merits an explanation as to its validity. In the case of evaporation with no diffusion barrier, the evaporation follows first order kinetics. The weight loss of the sample with time is then:

$$W_{\mathrm{loss}} = (k_{\mathrm{H_2O}} \cdot w_{\mathrm{H_2O}} + k_{\mathrm{dec}} \cdot w_{\mathrm{dec}}) \cdot t$$

where W_{loss}, $w_{\mathrm{H_2O}}$, and w_{dec} are respectively the weight loss of the sample, at the instant t, the original amount of water, and the original amount of decane, and $k_{\mathrm{H_2O}}$ and k_{dec} are first order kinetic constants.

Finally, since the water and decane have similar vapor pressure, it is assumed that $k_{\mathrm{H_2O}} \approx k_{\mathrm{dec}}$ for each emulsion.

If this is a valid assumption, then a plot of the logarithm of the concentration of the emulsifier versus time should be linear. This linear variation of the concentration versus time, during the time when the liquid crystalline phase did not enter the composition, is shown in Figure 7.

The absence of a sharp break-point in the experimental results suggests a gradual formation and thickening of a film on the sample as the liquid crystalline phase entered the composition. This slowed down the evaporation rate, from a high convection to a diffusion process.

In a solubility-diffusion process the rate of evaporation is quantified by a parameter

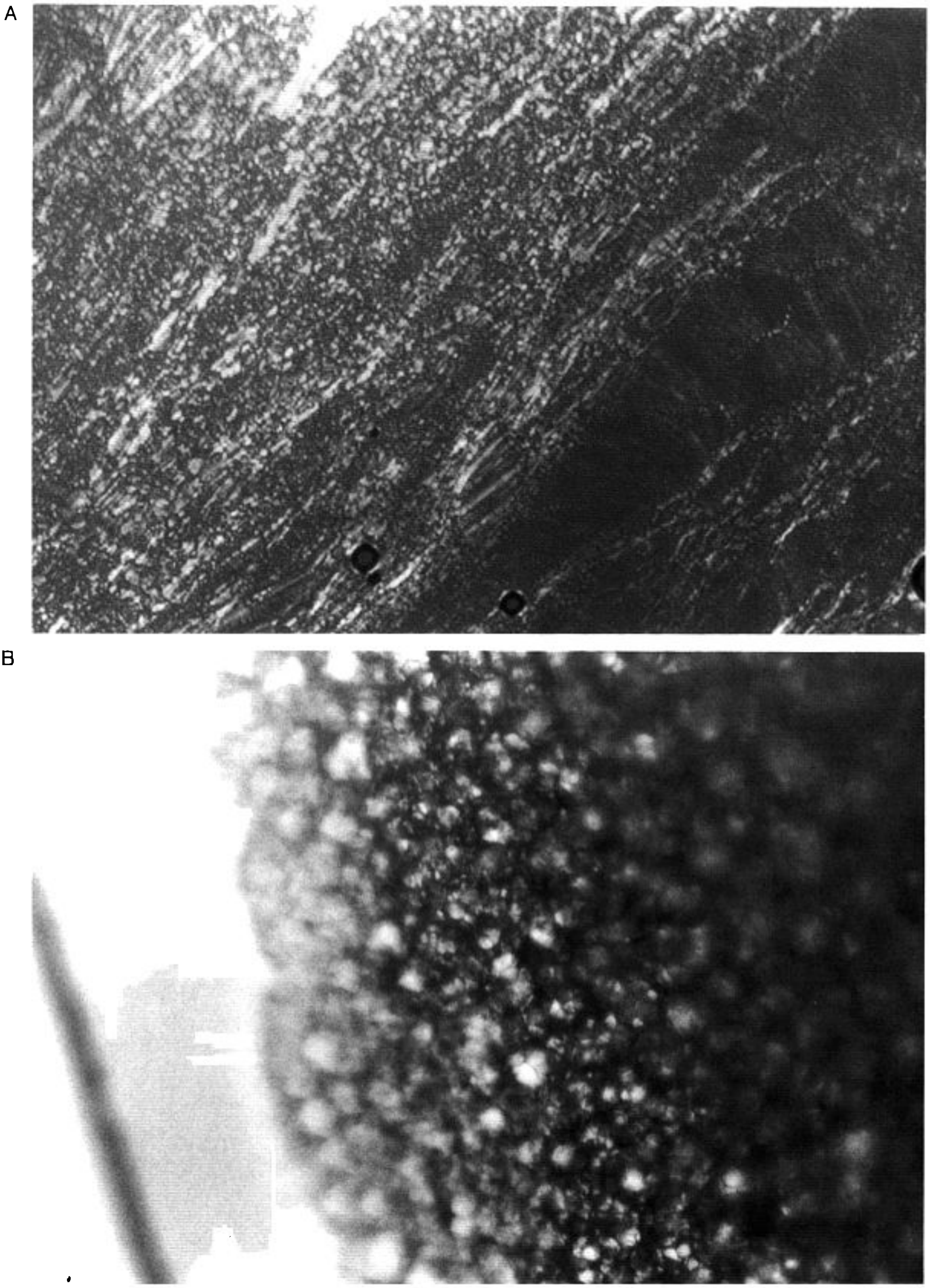

Figure 5. In the present investigation the emulsifier concentration was initially high (10% by weight of total), and a film of lamellar liquid crystal was observed in the optical microscope with the sample between crossed polarizers (A). With the emulsifier concentration initially low (2%), the liquid crystal was found peripherically only (B).

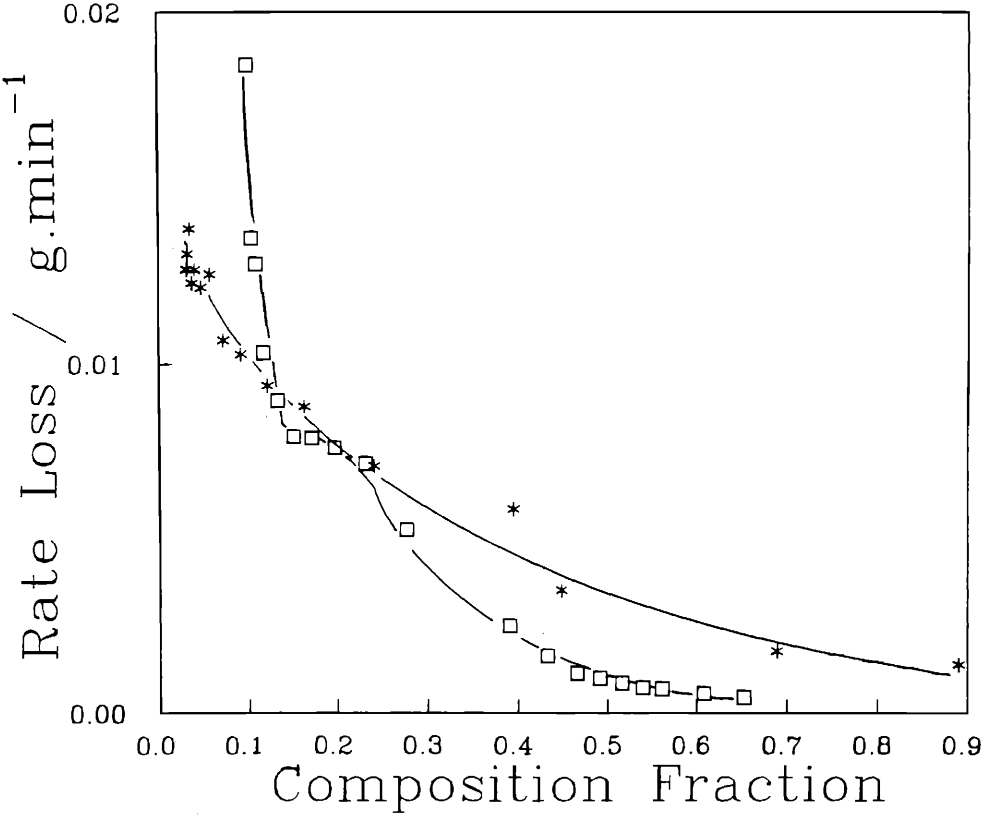

Figure 6. With a higher initial emulsifier concentration (□), the liquid crystalline film (Figure 5A) caused a strong and immediate evaporation retardation. Lower initial concentration (*) gave liquid crystal only peripherically (Figure 5B), and the retardation was modest.

called the transport resistance, *r*, where $1/r$ is dimensionally equivalent to the diffusion coefficient divided by the path length (10,11).

This equation is derived from Fick's first law, where the quantity of material diffusing through the area A, per unit of time, is given by:

$$\left(\frac{dQ}{dt}\right) = -A \cdot D \cdot \frac{\Delta C}{\Delta x}$$

where ΔC is the difference of concentration of the diffusing component, D is the diffusion coefficient, and Δx is the thickness of the section.

In this case, the thickness of the section has to be replaced by the path length, since in a lamellar phase, the components can diffuse only via a tortuous path, δ (12,13). We finally have:

$$\left(\frac{dQ}{dt}\right) = -A \cdot \left(\frac{1}{r}\right) \cdot \Delta C$$

where $1/r$ is a function of D/δ.

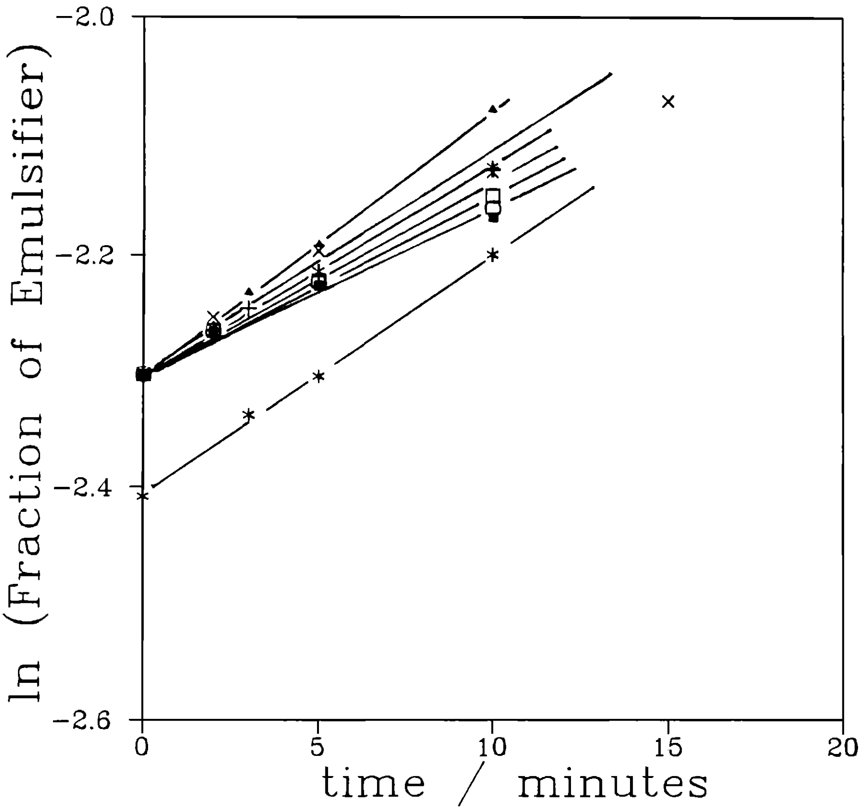

Figure 7. The increase of emulsifier concentration due to the evaporation of solvents was a logarithmic function of time.

For pure water, *r* is of the order of $2 \cdot 10^{-3}$ s · cm^{-1}, whereas with a diffusion coefficient three orders of magnitude smaller, along with a tremendous increase in the path length, one can expect slow evaporation through a lamellar film (14).

This is indeed what we observed. However, this simplistic model must be applied with caution, since the formation of the lamellar film has not been proven to be uniform, and hence the switch from an evaporation accompanied by convection to a diffusion-controlled one does not take place at the same time for all the surface exposed.

SUMMARY

The phase transition in a cosmetic emulsion system was followed during evaporation of water and the solvent. The result demonstrated the transition to more ordered structures with a reduced amount of water and organic solvents.

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