

Effect of Surfactant Migration on the Stability of Emulsions

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Synopsis—A new technique, which involves analyzing solutions from successively centrifuged emulsions, was developed and applied to determine the SURFACTANT CONCENTRATIONS in the aqueous phase of O/W emulsions. By following the surfactant MIGRATION from one phase of the freshly prepared emulsion to the other phase, the effects of the migration on the DROPLET SIZE DISTRIBUTION and EMULSION STABILITY were investigated.

It was found that, at a low mixing speed, the surfactant location had a significant influence on the stability as well as the droplet size distribution of the newly formed O/W emulsions. In general, the emulsion prepared by initially placing the surfactant in the oil phase produced a more stable emulsion than a corresponding emulsion, with an identical composition, prepared by placing the surfactant in the aqueous phase. Microphotographic examinations suggested that the initial formation of a double emulsion was probably responsible for the difference.

At a high mixing speed, this effect was not very pronounced. The data indicated that under intensive mixing, the time required from the moment of emulsification to the time when the average emulsion droplet size reached the minimum was approximately equal to, or slightly less than, the time required to reach surfactant equilibrium. Once the surfactant equilibrium was attained, further mixing of the emulsion did not improve the emulsion stability.

INTRODUCTION

Cosmetic chemists are often puzzled as to why the first batch of the emulsion manufactured in the factory differs so much in physical characteristics or stability from those of the emulsion originally developed in the laboratory. If there is no weighing error or raw material variation, it is most likely due to the difference in manufacturing conditions. A plant's equipment is rarely identical to its laboratory equipment and the difference can easily influence one of the many physical factors which can affect the formation of the emulsion (1).

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However, among many important factors such as mixing and cooling rates which are known to affect emulsions, one factor which has not been thoroughly studied is the location of the surfactant in the emulsion (2).

In manufacturing emulsions, it is generally regarded best to form the emulsifier *in situ* (3). However, except when fatty acid soaps are used as the emulsifiers, it is usually impractical to prepare emulsions by such a method. More frequently, the surfactant is either dispersed in the oil or aqueous phase prior to emulsification. Since all surfactants have some solubility in both oil and water, if the surfactant is first dispersed in the oil phase containing all oil-soluble components and then added to the aqueous phase to form an emulsion, some of the surfactant originally in the oil phase will migrate to the aqueous phase until an equilibrium is established. Conversely, migration would take place from the aqueous phase to the oil phase if the surfactant were first placed in the aqueous phase.

The main purpose of this work was to determine if the initial surfactant location and the migration of the surfactant immediately after emulsification had any significant effect on the stability and droplet size distribution of the emulsion prepared.

Theoretically, since the surfactant plays a major role in stabilizing the emulsion, any movement of the surfactant during the emulsification process can affect the adsorption of the surfactant at the interface and thus influence the quality of the emulsion formed. If the equipment or procedure used for emulsification affects surfactant migration, the formation of the emulsion may also be indirectly affected. Similarly, the migration of the surfactant after the formation of an emulsion can also alter the emulsion properties and emulsion stability. Conceivably, this may be one of the factors controlling the often troublesome changes in the rheological properties of freshly prepared cosmetic emulsions upon aging.

However, in order to quantitatively study the effect of surfactant migration on emulsion stability, one must accurately know the distribution of the surfactant in both phases of the emulsion at a given time. There is definitely a paucity of such data as the measurement of surfactant distribution in an emulsion is no simple task. This is because, first of all, the surfactant is not only dissolved in the bulk phases of the emulsion but is also present as micelles in both phases and a substantial portion of it is adsorbed at the oil/water interface of the emulsion droplets. Secondly, no method is available which allows a direct measurement of the surfactant concentration in either the continuous or dispersed phase of a stable emulsion without first breaking or creaming the emulsion.

If an emulsion is first cracked by coalescing the dispersed droplets using chemical or physical means, the surfactant present in one of the phases or in both phases can then be analyzed without too much difficulty. However, this would only provide the information on the surfactant distribution in a cracked emulsion. In order to know the distribution in the original stable emulsion,

one would have to know the migration of the portion of the surfactant desorbed from the interface when the coalescence took place. Clearly, it would be extremely difficult to experimentally or theoretically follow precisely the complex movements of the surfactant molecules after desorption.

Thus, the major difficulty in measuring the surfactant distribution in a stable emulsion is that the means of the measurement would invariably change the original distribution, making the interpretation of the results extremely difficult. To overcome this difficulty, a method was devised to allow a gradual cracking of an emulsion so as to permit an indirect measurement of the original distribution from the data obtained at different stages. This was accomplished by a successive centrifuge of the stable test emulsion, followed by a chemical analysis of the surfactant content in the separated phase at each stage, and, finally, by the extrapolation of the data to zero separation. By making such measurements on emulsions prepared with different oils at different intervals after emulsification, and also by measuring the particle size distribution of emulsion droplets by microphotography, the effect of surfactant migration on the emulsion stability was investigated.

EXPERIMENTAL

Emulsions were made both under a very high mixing speed using T-K Homomixer Model M* and also under a relatively low mixing speed using a paddle mixer. For rapid mixing emulsification, 2-kg batches of emulsions were made in 3-liter beakers using the following formulation:

	% by Wt.
Oil	32.00
Arlacel 80®†	1.40
Tween 80®‡	1.60
Carbopol 934®‡	0.10
NaOH	0.04
Deionized water	64.86
	<u>100.00</u>

In this work, only the migration of the hydrophilic surfactant, Tween 80, was followed. The hydrophobic surfactant, Arlacel 80, which has a very low water solubility, was dispersed in the oil phase before emulsification. The aqueous phase consisted of water and Carbopol 934 neutralized with sodium hydroxide. The migrating surfactant, Tween 80, was divided between the

* Manufactured by Tokushukita Kogyo Co., Ltd., Osaka, Japan.

† Arlacel 80 (Sorbitan monooleate), Tween 80 (Polyoxyethylene sorbitan monooleate), Atlas Chemical Industries, Wilmington, Del.

‡ Carbopol 934 (Carboxyl vinyl polymer), Goodrich Chemical Co., Cleveland, Ohio.

aqueous and oil phases according to the experimental requirement. The combination of Arlacel 80 and Tween 80 gave an HLB value of 10 in the formulation. Carbopol 934 was added to improve the stability of the emulsion since it would be difficult to make accurate measurements if the emulsion were unstable. The oils tested were cosmetic grade mineral oils, oleyl alcohol, isopropyl myristate, castor oil, and others commonly used for cosmetics.

To make a test emulsion, the aqueous phase was first placed in the beaker and the Homomixer was placed at the center of the beaker with the clearance between the mixer tip and the bottom of the beaker set at exactly 20 mm. The predispersed oil phase was then carefully placed on the top of the aqueous phase and the Homomixer was turned on to start emulsification. The Homomixer speed was kept constant at $11,900 \pm 100$ rpm and all operations were carefully controlled to avoid air entrapment and to assure good reproducibility.

To determine the distribution of Tween 80 in the prepared emulsion, a set of samples of emulsion were subjected to centrifuge for various lengths of time, usually in six stages starting from 1 min up to 10 min. The rpm of the centrifuge used for a given set of samples was such that a reasonable amount of the aqueous phase could be separated at each stage for analysis. In most cases the rpm ranged from 4,000 to 6,000. The separated aqueous phase was carefully withdrawn with a hypodermic needle and the Tween 80 concentration was determined by a sodium tetraphenylborate titration method described by Kasai *et al.* (4).

By plotting the Tween 80 concentrations in the separated aqueous phases at various stages of centrifugal separation, the data were extrapolated to zero separation in order to obtain the surfactant concentration in the unseparated sample of the emulsion. The experiments were repeated until a consistent result was obtained. The surfactant concentration in the aqueous phase was determined as a function of emulsification time in order to follow surfactant migration as the emulsification progressed.

The stability of the emulsions was measured by placing the samples at 37°C for several months and observing any sign of creaming or separation. Photographs of the emulsion were also taken under a microscope to measure the droplet size distribution.

For emulsification under slow mixing, several laboratory mixers with identical straight paddle-type impellers were used. The length of the paddle was 60 mm and the height was 20 mm. The batch size of the test emulsions was 400 g and emulsifications were made in 500-ml beakers at speeds ranging from 170 to 650 rpm.

The formula used for slow mixing emulsification was the same as the one used for the rapid mixing experiments except Carbopol 934 and the neutralizer were taken out and replaced with water to allow a relatively quick separation. In most cases, six emulsions with varying initial surfactant location were

made simultaneously, and the emulsions were placed in graduated cylinders for stability observation. Photographs were taken under the microscope to allow observation of change in droplet size distribution.

RESULTS AND DISCUSSION

Rapid Mixing Emulsification

Emulsions prepared under rapid mixing with the Homomixer were generally stable and had average droplet sizes ranging from 1 to 4 μ . Figure 1 shows typical curves obtained by successive centrifugation of a group of oleic acid

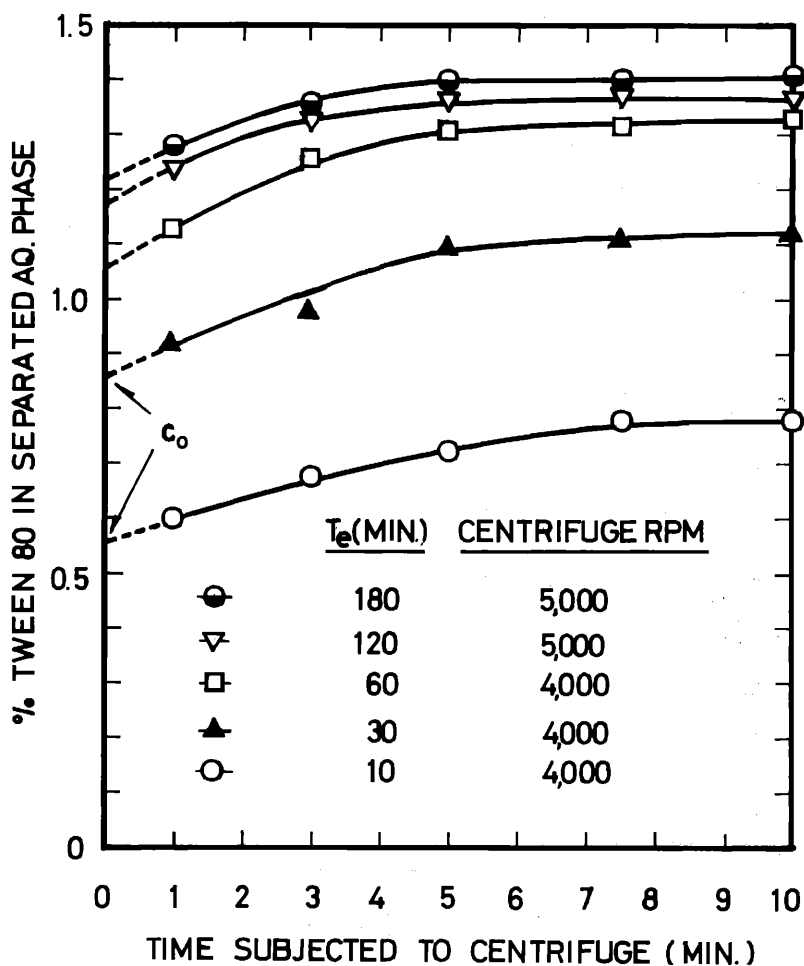


Figure 1. Extrapolation of Tween 80 concentrations in centrifuged emulsions to obtain C_0 (oleic acid system, Tween 80 initially in oil phase)

emulsions subjected to various lengths of mixing times, T_e , during emulsification. As indicated, these curves were extrapolated to zero time to obtain C_0 , the concentration of Tween 80 in the aqueous phase of the undisturbed, stable emulsion.

Two centrifuge speeds (4,000 and 5,000 rpm) were employed in this series of experiments. The emulsions made at longer mixing times (120 and 180 min) were more stable and required a higher speed to separate the aqueous phase for analysis.

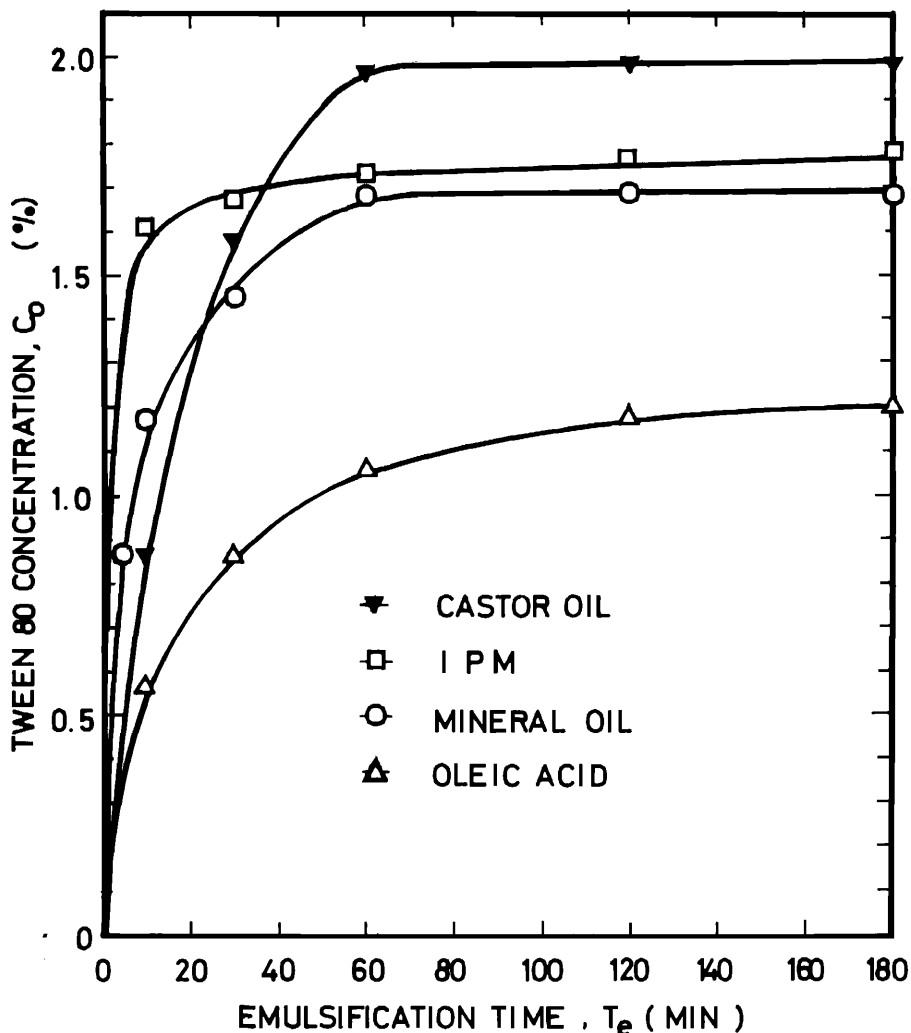


Figure 2. Effect of emulsification time on C_0 , concentration of Tween 80 in the continuous phase of stable emulsion, prepared with 4 different oils (Tween 80 initially placed in the oil phase)

The values of C_o were then plotted against T_e to study the change in surfactant concentration as the mixing time increased. An example of such a plot is shown in Fig. 2 for oleic acid, mineral oil, isopropyl myristate (IPM), and castor oil systems in which the migrating surfactant, Tween 80, was initially placed in the oil phase. Figure 3 shows the curves for the similar systems in which Tween 80 was initially placed in the aqueous phase. The flat portion of the curve indicates that no further migration is taking place, i.e., the system has apparently reached an equilibrium with respect to the surfactant movement.

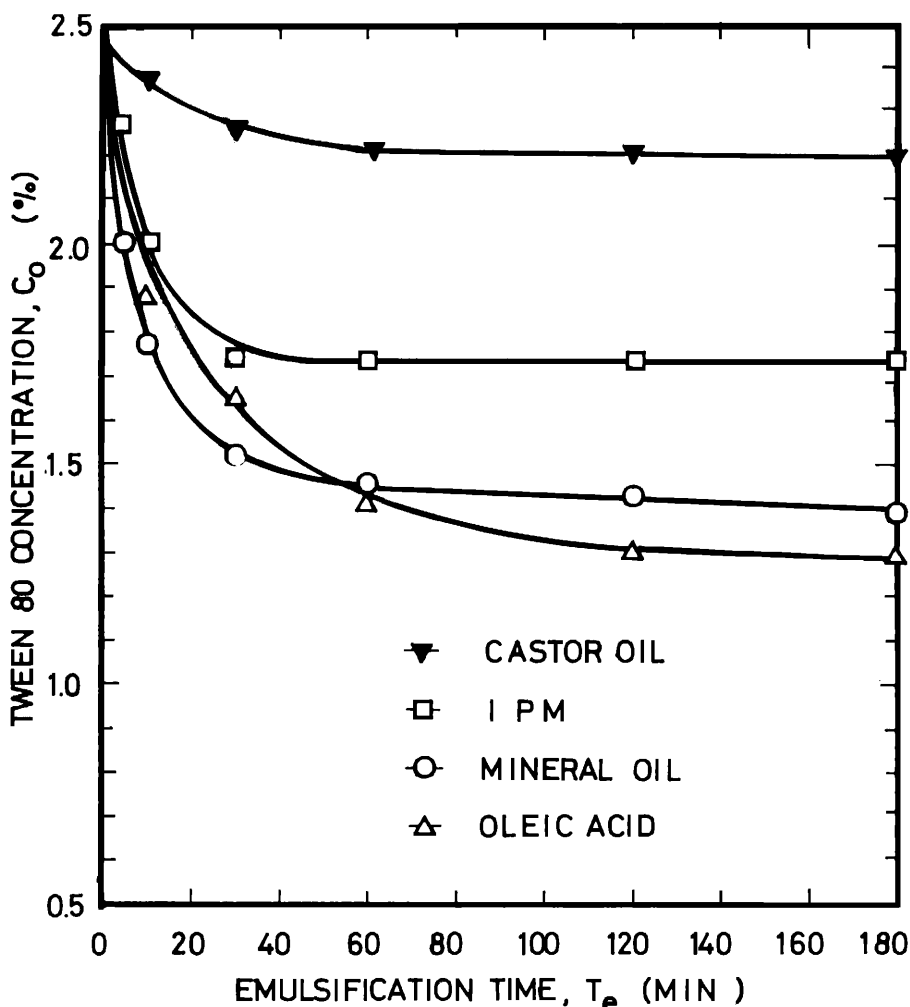


Figure 3. Effect of emulsification time on C_o , concentration of Tween 80 in the continuous phase of stable emulsion, prepared with 4 different oils (Tween 80 initially placed in the water phase)

It can be seen that different oils required different lengths of time to reach surfactant equilibrium even though the mixer speed was set constant at 11,900 rpm in all cases. For example, isopropyl myristate required less than an hour whereas oleic acid required nearly 2 hours before the apparent equilibrium was attained.

The particle size distribution of each emulsion was measured from microphotographic prints by counting and the result was expressed in terms of mean volume diameter, d_m , defined as follows:

$$d_m = \sqrt[3]{\frac{\sum nd^3}{\sum n}}$$

where n is the number of droplets and d is the droplet diameter. The results of d_m as a function of emulsification time, T_e , are presented in Figs. 4-7.

By comparing the d_m curve against the corresponding C_o curve, it is interesting to note that the time required for the emulsion droplets to reach a minimum was approximately equal to, or slightly less than, the time required to reach surfactant migration equilibrium. Apparently, under a high mixing speed, very little migration took place once the droplets were reduced to the minimum size and the adsorption at the interface was completed.

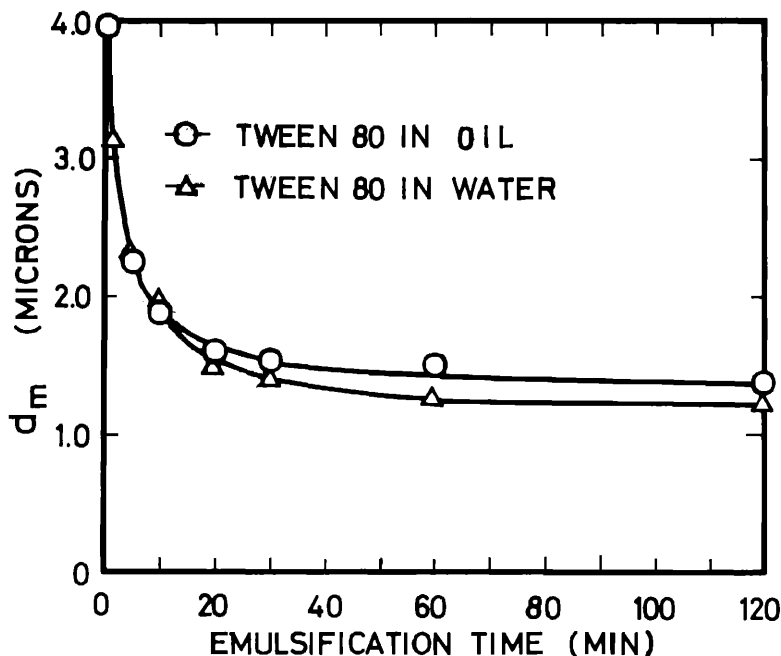


Figure 4. Change of mean volume diameter, d_m , of emulsion droplets with mixing time during emulsification (oleic acid system)

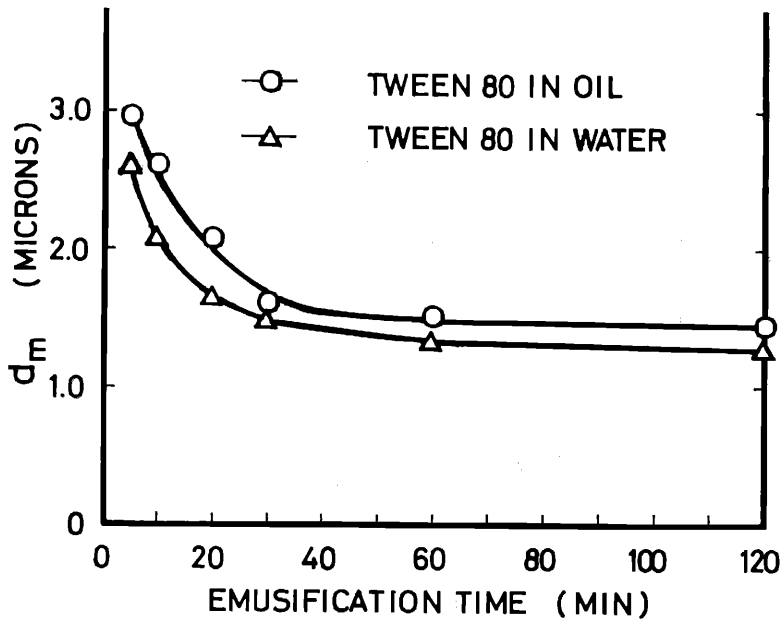


Figure 5. Change of mean volume diameter, d_m , of emulsion droplets with mixing time during emulsification (mineral oil system)

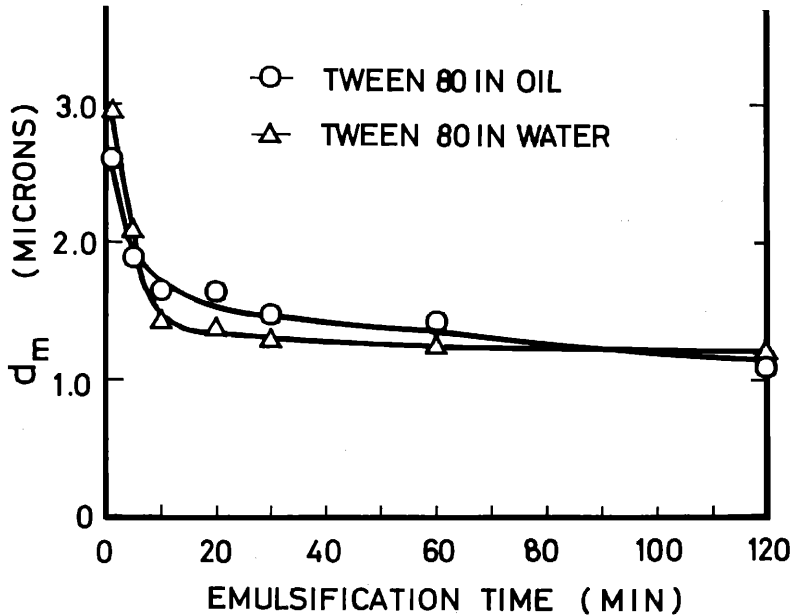


Figure 6. Change of mean volume diameter, d_m , of emulsion droplets with mixing time during emulsification (isopropyl myristate)

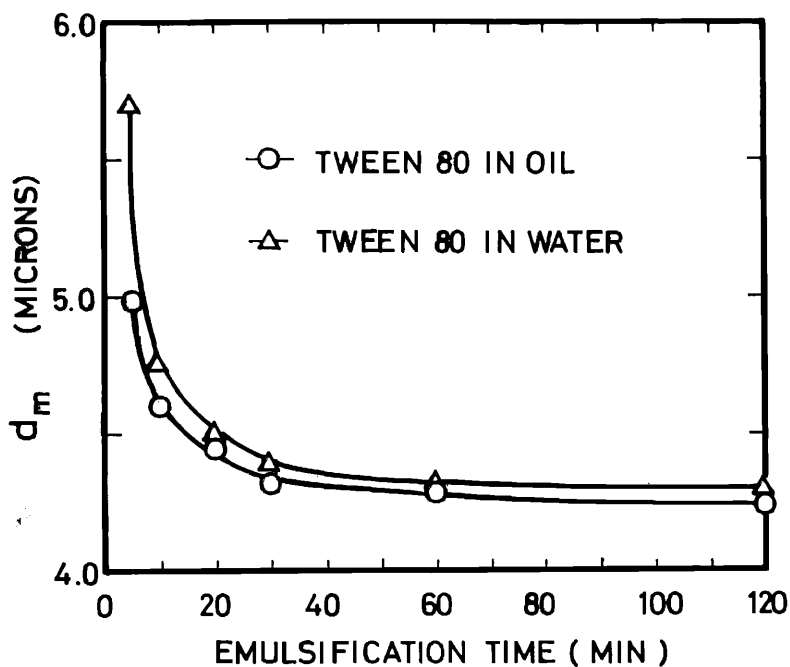


Figure 7. Change of mean volume diameter, d_m , of emulsion droplets with mixing time during emulsification (castor oil system)

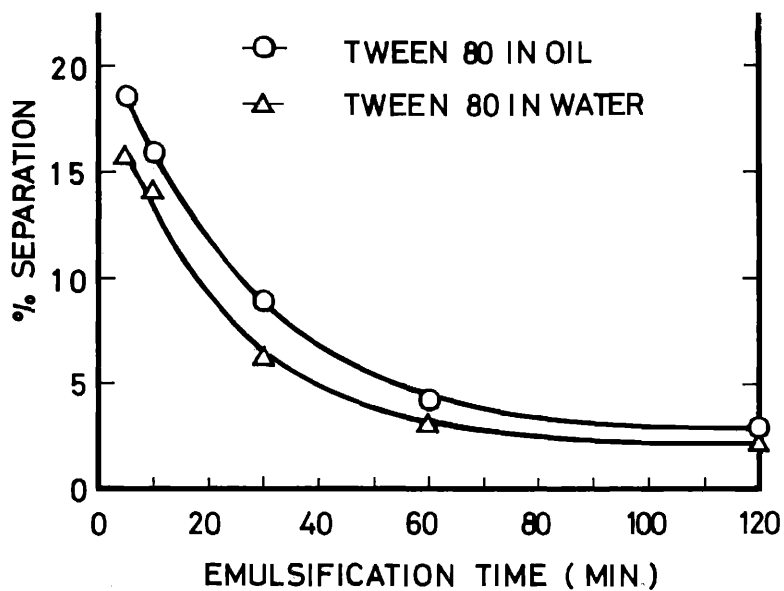


Figure 8. Effect of emulsification time on stability of mineral oil emulsion (% separation after 116 days)

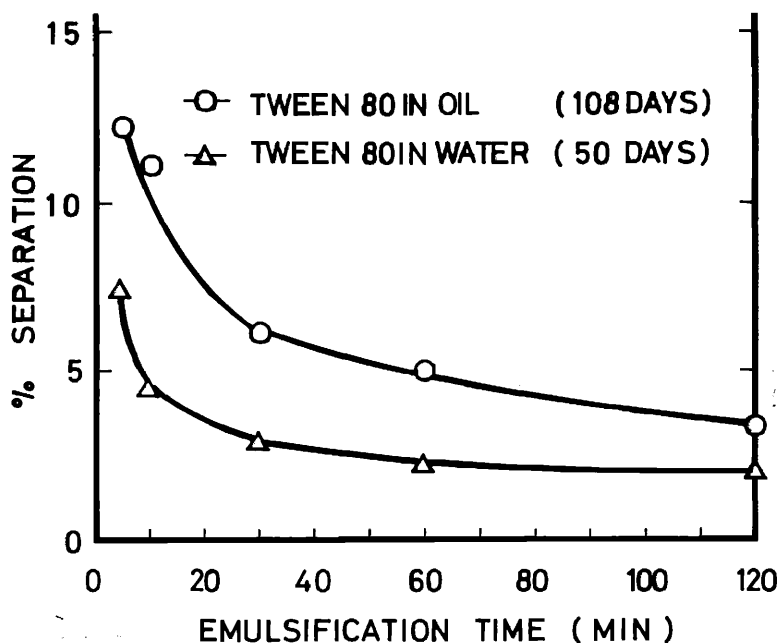


Figure 9. Effect of emulsification time on stability of isopropyl myristate emulsion (% separation after 108 and 59 days)

The stability data of the mineral oil and isopropyl myristate are shown in Figs. 8 and 9. The stability was evaluated in terms of the percentage of the separated phase after 2 to 4 months' storage at 37°C. In these systems, separation took place on the bottom of the container. By comparing these stability data against C_0 data presented before, it can be seen that for the emulsions tested, no further stability improvement was obtained after the system was mixed long enough to achieve a surfactant equilibrium. Moreover, it is to be noted that under a high-speed mixing, the initial location of the migrating surfactant did not appear to be an important factor as far as the droplet size and emulsion stability were concerned.

Slow Mixing Emulsification

The results of the stability study of the emulsion prepared under a slow mixing speed (170 rpm) using a paddle mixer were very different from the results obtained with a high speed Homomixer presented above. For example, as shown in Fig. 10, the stability of the oleyl alcohol emulsion was much greater when the surfactant was initially placed in the oil phase. A similar trend was observed in the oleic acid, octyl dodecyl triglyceride emulsions shown in Figs. 11 and 12.

To investigate this trend further, 26 oils which are commonly used in cosmetics were selected and emulsions were made with a Tween 80—Arlacel 80

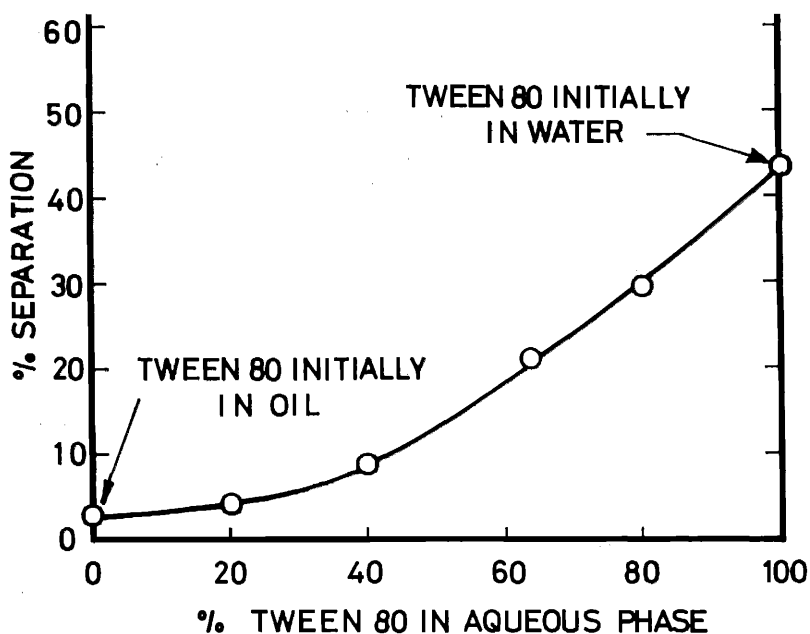


Figure 10. Effect of initial surfactant location on emulsion stability for oleyl alcohol system prepared at slow mixing speed (170 rpm, 18-hour mixing, 15-min standing)

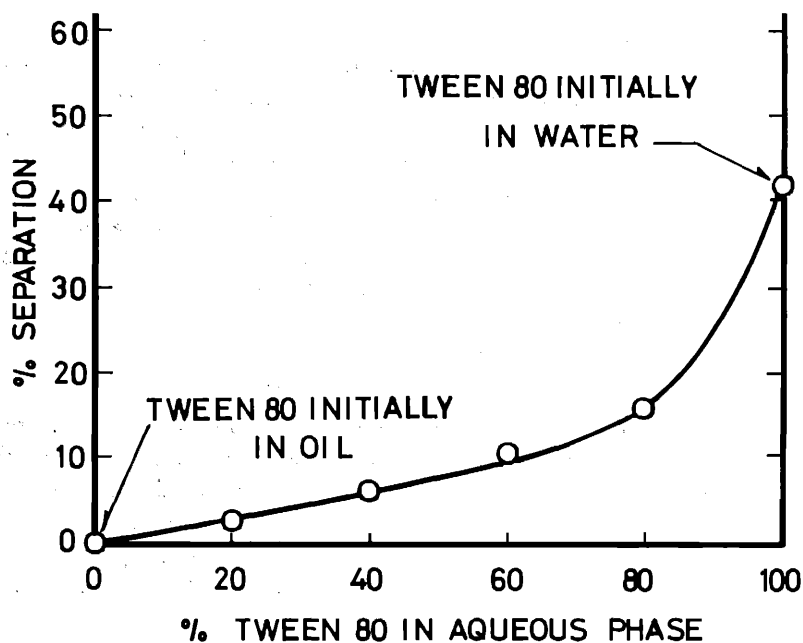


Figure 11. Effect of initial surfactant location on emulsion stability for oleic acid system prepared at slow mixing speed (170 rpm, 18-hour mixing, 15-min standing)

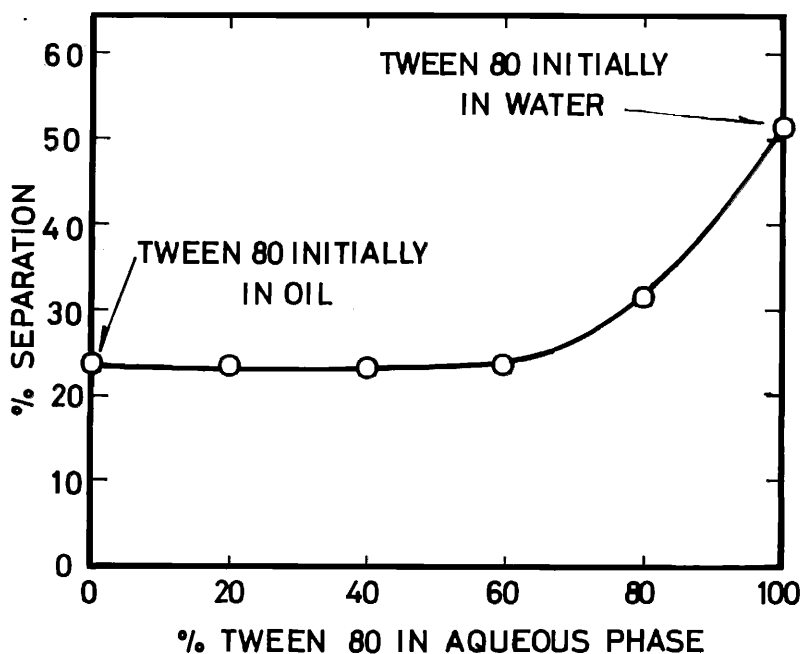


Figure 12. Effect of initial surfactant location on emulsion stability for octyldecyl triglyceride system prepared at slow mixing speed (170 rpm, 18-hour mixing, 15-min standing)

combination at HLB 10 using the same procedure with varying initial surfactant location. The results given in terms of visually observed emulsion quality are presented in Table I. Emulsion O is the emulsion which was prepared by initially placing the Tween 80 in the oil phase and Emulsion W denotes the corresponding emulsion, with the same composition, prepared with the Tween 80 initially in the aqueous phase. The better emulsion here means a finer particle size and, usually, better stability.

Clearly, under a slow mixing speed, initial placement of Tween 80 in the oil phase produced more stable emulsions in all of the above oils tested.* It is of interest to note that this difference diminishes as the mixer speed used for emulsification was increased from 170 to 650 rpm as shown in the data presented in Fig. 13.

Under very slow mixing, the rate of emulsification was also relatively low. To study the reasons for the above difference, microphotographs were taken

* The only exception to this statement was found in emulsions prepared with multiterol dispersed in mineral oil. This material is sold in the U.S.A. under the trade names of Amerchol L-101® and Ritachol®. However, since it is a complex mixture with sterols acting as low HLB surfactants, it is not too surprising that it acts differently from other oils. Moreover, it was found that raising of the total HLB by increasing the Tween 80 / Arlacel 80 ratio reduced the above difference.

Table I

Stability Difference between Emulsions Prepared with Tween 80 Initially in Oil (Emulsion O) and Corresponding Emulsions with Tween 80 in Water (Emulsion W) for Various Oils (Slow Mixing)

Emulsion O considerably better than Emulsion W	Oleyl alcohol, <i>n</i> -decyl alcohol, 2-octyl-dodecyl alcohol, oleic acid, ricinoleic acid, linoleic acid, isopropyl myristate, dioctyl phthalate, diethyl phthalate, diethyl sebacate, methyl benzoate, hexadecyl lanolate, octyldecyl triglyceride, cottonseed oil, rapeseed oil
Emulsion O slightly better than Emulsion W	2-Hexyldecyl alcohol, liquid lanolin, di-2-hexyldecyl ether, 2-hexyldecyloctyl ether, mineral oil (70 cps), mineral oil (350 cps), squalan, castor oil, olive oil, soybean oil
No significant difference	Isostearic acid

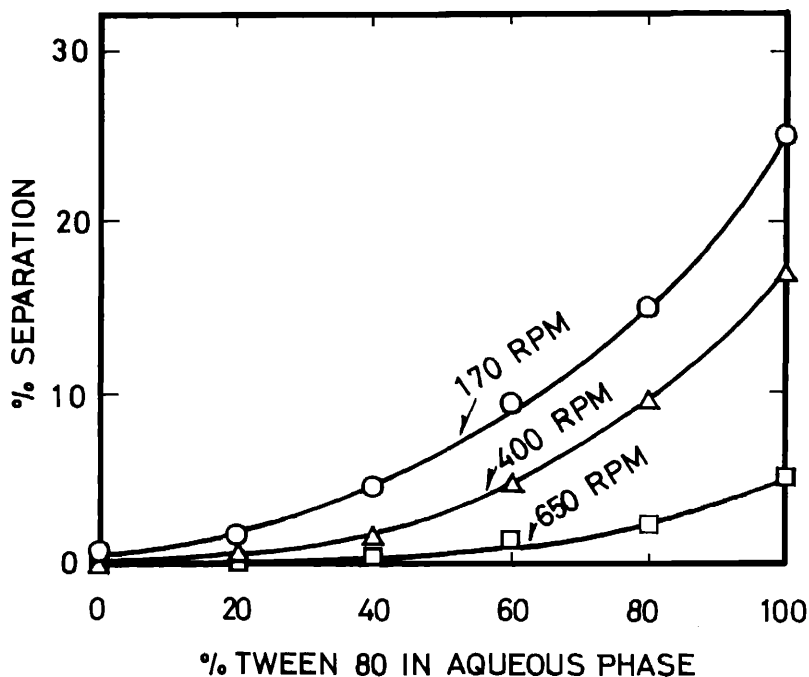


Figure 13. Effect of mixing speed and initial surfactant location on stability of oleyl alcohol emulsions (after 5-min mixing and 3-min standing)

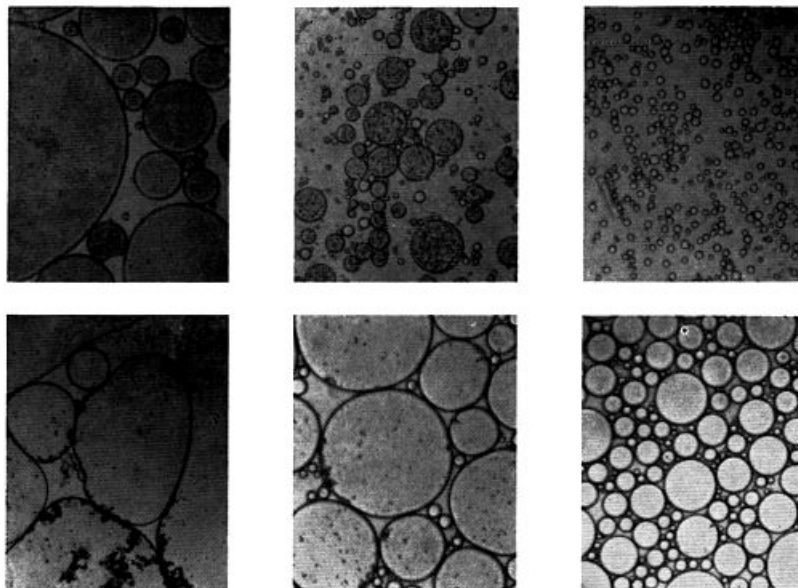


Figure 14. Microphotographs of oleyl alcohol emulsions
 Top. Surfactant initially in oil
 Left to right. Emulsions O-1, O-2, O-3
 Bottom. Surfactant initially in water
 Left to right. Emulsions W-1, W-2, W-3

at various stages of emulsification. Some of the examples are shown in Fig. 14. Examination of these microphotographs indicates the presence of a large number of double emulsions of (W/O)/W type in the emulsions prepared by initially placing the surfactant in the oil phase (i.e., Emulsion O series). As shown in the photograph O-1, which was taken at an early stage of emulsification, extremely small water droplets were observed in very large oil drops. Sometimes the boundaries of these oil drops were not well-defined at this stage. The picture O-2 clearly indicates the presence of double emulsion droplets. These double emulsion droplets disappeared after a prolonged mixing as shown in O-3. Double emulsions were also observed in some emulsions prepared by initially placing the surfactant in the aqueous phase (i.e., Emulsion W series) but the number of droplets containing the double emulsion was much lower.

A close examination of the microphotographs suggests that the formation of the double emulsion might be the reason for the formation of fine emulsion even under very slow mixing when the surfactant was placed in the oil phase. An enlarged photograph of such a double emulsion is shown in Fig. 15. One possible mechanism is that when the emulsion was made by first placing Tween 80 in the oil phase, water initially entered the surfactant micelles in the

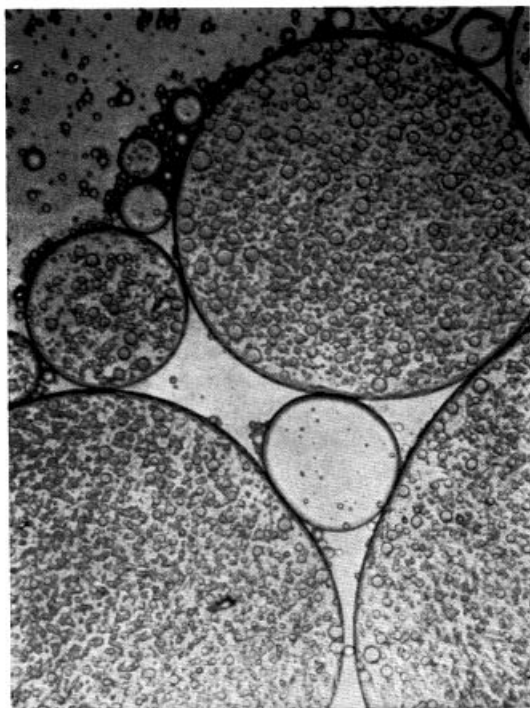


Figure 15. Microphotograph of mineral oil emulsion showing presence of double emulsion

oil phase resulting in the swelling of the micelles. The swelling process continued and a very great number of water droplets were eventually formed in the oil phase. As the Tween 80 molecules migrated out from the oil into the aqueous phase, the mixing action subdivided the oil mass, which contained the microscopic water droplets, to form a double emulsion. The initial formation of a double emulsion could conceivably ease the breaking of the oil drops to produce a finer emulsion that otherwise could not be obtained. As the mixing process continued, the microscopic water droplets grew in size and eventually escaped from the oil droplets, carrying along the dissolved surfactant into the continuous phase. Finally, all microscopic water droplets disappeared and the emulsion became an ordinary single emulsion.

On the other hand, when Tween 80 was first placed in the aqueous phase, the tendency for a double emulsion formation was greatly reduced since the oil phase was initially free of the hydrophilic surfactant. This would then explain the difference in the emulsions obtained as the initial surfactant location was varied.

Under a very high mixing speed, however, the above process was probably carried out in a very short period of time. Furthermore, since the droplets were readily broken by a very high shear rate under a high mixing speed, the

initial formation of a double emulsion was probably no longer an important factor controlling the droplet size of the final emulsion.

CONCLUSIONS

In this work, the surfactant migration was monitored only in the emulsions prepared under very rapid mixing using a Homomixer. Unfortunately, it was not possible to measure the surfactant distribution accurately in emulsions prepared under low mixing speeds as these emulsions were too unstable when subjected to centrifuge. It is hoped that the present technique can be improved in the future to allow handling of emulsions prepared under lower mixing speeds. On the other hand, photographing of the emulsification process was possible only for the emulsions prepared under very gentle mixing conditions.

Most commercial cosmetic emulsions are prepared under neither an extremely high mixing speed, nor a very low speed. Moreover, only liquid oils were used as the internal phase in this work, whereas in commercial cosmetics, various waxes and thickeners are used along with the oils. Hence, the actual migration of the surfactant in a commercial emulsion may be considerably slower than that which took place in the systems studied here. Due to the complex nature of the mechanisms governing the emulsion formation and surfactant migration, the results obtained here cannot be directly applied to commercial emulsions without qualification. However, it seems safe to make a few limited generalizations based on the data obtained.

1. In preparing emulsions, sufficient mixing should be provided not only to reduce the droplet size but also to promote surfactants to attain an equilibrium.

2. If the equilibrium is not attained upon completion of emulsification operation, the surfactant migration thereafter may cause a change in the physical properties or the stability of the emulsion.

3. If an O/W emulsion is made under a moderate mixing speed, it is probably better to place the surfactant initially in the oil phase in order to obtain an emulsion with a finer particle size distribution. However, as pointed out by Lin and Lambrechts, if the HLB of the surfactant mixture is low, this practice may produce a phase inversion which may, in turn, cause emulsion instability (5). Therefore, in making a practical emulsion, the best surfactant location should be decided by carefully controlled experiments.

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