

Prediction of optimum O/W emulsification via solubilization measurements

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*Received August 6, 1976. Presented Ninth IFSCC Congress, June 1976,
Boston, MA.*

Synopsis

In the course of investigating the effects of SURFACTANT LOCATION on O/W EMULSIFICATION, it was discovered that there existed a useful correlation between the maximum amount of aqueous phase that could be solubilized in the oil phase containing the emulsifier and the average droplet size of the emulsion subsequently formed. Experiments were carried out with liquid hydrocarbons and many other oils frequently used in cosmetic emulsions. The emulsifiers used included various nonionic, anionic, cationic surfactants, and their mixtures. Analysis of the solubilization measurements and microphotographically obtained emulsion droplet size distribution data clearly indicated that the point of optimum O/W emulsification, i.e., the point where the finest O/W emulsion was formed in emulsifying with a series of surfactant mixture, corresponded to the point of maximum solubilization provided that the latter fell in a region where O/W emulsion formation was possible. In some systems studied, the maximum solubilization points were found in the region where only W/O emulsions could be formed under the experimental conditions. In such a case, the optimum O/W emulsions were generally found near the W/O–O/W transition point. The correlation held quite well in spite of the differences in the type and ionic nature of the surfactants employed.

INTRODUCTION

In spite of the recent advances in colloid and surface chemistry, the technique of emulsion formulation and manufacturing remains very much an art. Although, it has been 27 years since Griffin (1,2) first proposed the HLB (hydrophile–lipophile balance) method, the selection of an emulsifier system for a practical cosmetic emulsion still requires a tedious trial-and-error procedure. This is chiefly due to the extremely complex nature of emulsions, which often defies systematic scientific treatment.

Fundamentally, HLB is a very useful system in classifying surfactants according to their hydrophilic/lipophilic characteristics. It is, also, recommended as a tool for selecting efficient emulsifiers for preparing emulsions; nevertheless, in this respect, there are many shortcomings which hinder its practical applications.

First of all, to use HLB method for emulsification, one needs not only the “HLB” values of the surfactants but also the “required HLB” values of all the oil phase components to be used in the emulsion. Unlike the HLB values of the surfactants, the

available data on required HLB values are quite limited and the published values are often conflicting. This is partly due to the fact that there is still a lack of a reliable and accurate method to determine the required HLB value of an oil (3).

Second, even for the oils for which required HLB values are available, the HLB method provides only a very rough guide in finding a right emulsifier combination. Even if a formulator knows that he requires a certain HLB to emulsify a given oil, he still needs to carry out many trial-and-error emulsifications, using combinations of surfactants with different chemical types before finding a suitable combination for his practical purpose. The HLB method provides no further guidance in this respect.

Third, the HLB method assumes that like HLB values of the surfactants, required HLB values of oils are also linearly additive. This linear relationship has been found to be questionable in many oil mixtures (4). Furthermore, Griffin's HLB method assumes that both the HLB value of a surfactant and the required HLB value of an oil are *constants* independent of other parameters. This assumption makes the HLB method quite simple to use; however, it also makes the method less precise and sometimes unreliable, since many other factors such as aqueous phase additives, surfactant concentration, phase volume of the oil, emulsification temperature, or even the preparative method can influence the hydrophilic/lipophilic characteristics of emulsions (5,6,7).

Furthermore, the HLB method works fairly well if one uses only ethoxylated nonionic surfactants to emulsify hydrocarbons. It often fails to work satisfactorily, however, in many practical cosmetic emulsions containing a complex mixture of oils, fatty materials, polar substances, and various surfactants. Clearly, there is a need for a better system to aid emulsion formulators to select the most efficient emulsifier combination from the great number of commercial surfactants available today.

During the course of investigating the effects of surfactant location and migration on emulsion properties, it was discovered that there appeared to be a correlation between the maximum amount of the aqueous phase which could be solubilized in the oil phase containing the emulsifiers, and the average droplet size of the emulsion subsequently formed. For a given pair of surfactants, one relatively hydrophilic and the other relatively lipophilic, the most efficient emulsifier combination was generally found at the point where there was the greatest amount of solubilization. After testing over 100 systems with varying oils, surfactants, and other additives, it is believed that this correlation can be very useful in aiding emulsion formulation and to minimize the need for a trial-and-error procedure.

EXPERIMENTAL

For low-speed emulsification, emulsions were prepared by first dispersing the surfactants in the oil phase using a mixer. Sixty-five g of aqueous phase was first placed in a 200 ml beaker, and 35 g surfactant-oil mixture was carefully placed on the top. A 2×6 cm flat blade paddle mixer, set 5 mm above the bottom of the beaker, was turned on immediately to start emulsification. In most experiments, the emulsification was done at room temperature ($21^\circ \pm 1^\circ\text{C}$), and the emulsions were mixed for 3 min at exactly 150 rpm before droplet size measurements. For high-speed emulsification, a rotary homomixer was used. All emulsification operations were carefully done to assure good reproducibility.

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Emulsion droplet size distribution was determined from the Polaroid* pictures taken through an optical microscope. The amount of aqueous solubilization was determined by adding the aqueous phase, drop by drop, into the oil phase containing the surfactant while constantly mixing with a magnetic stirrer. The first sign of permanent turbidity was taken as the end point and the total amount of the aqueous phase added was recorded. In cases where a complete solubilization phase diagram was desired, the oil phase was placed in a large number of capped vials and shaken with varying amounts of water. After equilibration, the vials were observed for any sign of separation or turbidity and a phase diagram was constructed.

RESULTS AND DISCUSSION

CORRELATION OF EMULSIFICATION EFFICIENCY WITH SOLUBILIZATION

There were 2 main purposes in this investigation. The first was to determine the validity and scope of the correlation between the efficiency of emulsification and the maximum amount of aqueous solubilization by the oil phase containing the surfactants. The second aim was to investigate the fundamental role of the solubilization process and its relationship with emulsification.

In this work, emulsification efficiency refers to the efficiency with which a surfactant or a mixture of surfactants emulsify the oil phase to form an emulsion without the use of high-shear equipment. A more efficient surfactant is defined as one which produces an emulsion with a finer average droplet size than a less efficient one under the same degree of mechanical agitation. Generally speaking, an emulsion with a smaller average droplet size is more stable than one with a larger droplet size. However, for this investigation, the emulsification efficiency was directly expressed in terms of droplet size distribution immediately after emulsification rather than the emulsion stability. This choice was made in order to avoid possible confusion in interpreting the data, since emulsion stability is not only a function of droplet size, but also of many other parameters such as the viscosity of the external phase which is often influenced by the presence of the surfactants.

In preparing most emulsions, a moderate mixing speed (150 rpm) was used. The use of an excessively high mixing speed would promote the break-up of droplets caused by mechanical shear and obscure the real effects of the emulsifiers.

The correlation appears to hold both for O/W emulsions prepared with single surfactants and also the emulsions made with combinations of two surfactants, one relatively hydrophilic, and the other relatively lipophilic.

Figure 1 is an example of the data obtained with a series of ethoxylated nonylphenols with ethylene oxide ranging from 2 to 20 moles. Strictly speaking, these are not single surfactants, since they are commercial materials which are expected to have a wide ethylene oxide distribution range. Solubilization limit was defined as the maximum amount of water in milliliters which could be solubilized into a total of 100 g of oil-surfactant mixture. The abscissa represents the average weight percentage of the

*Polaroid Corp., Cambridge, MA.

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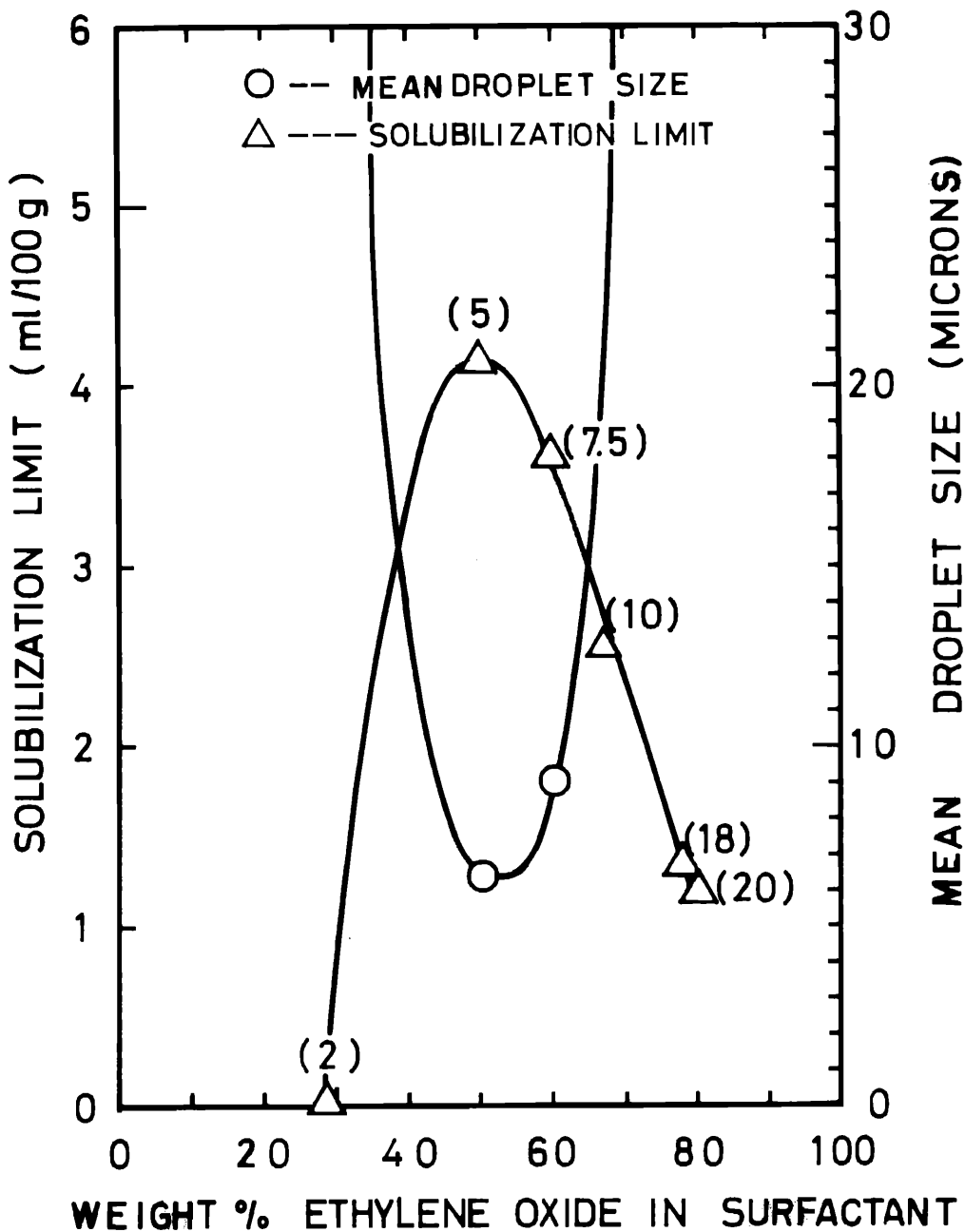
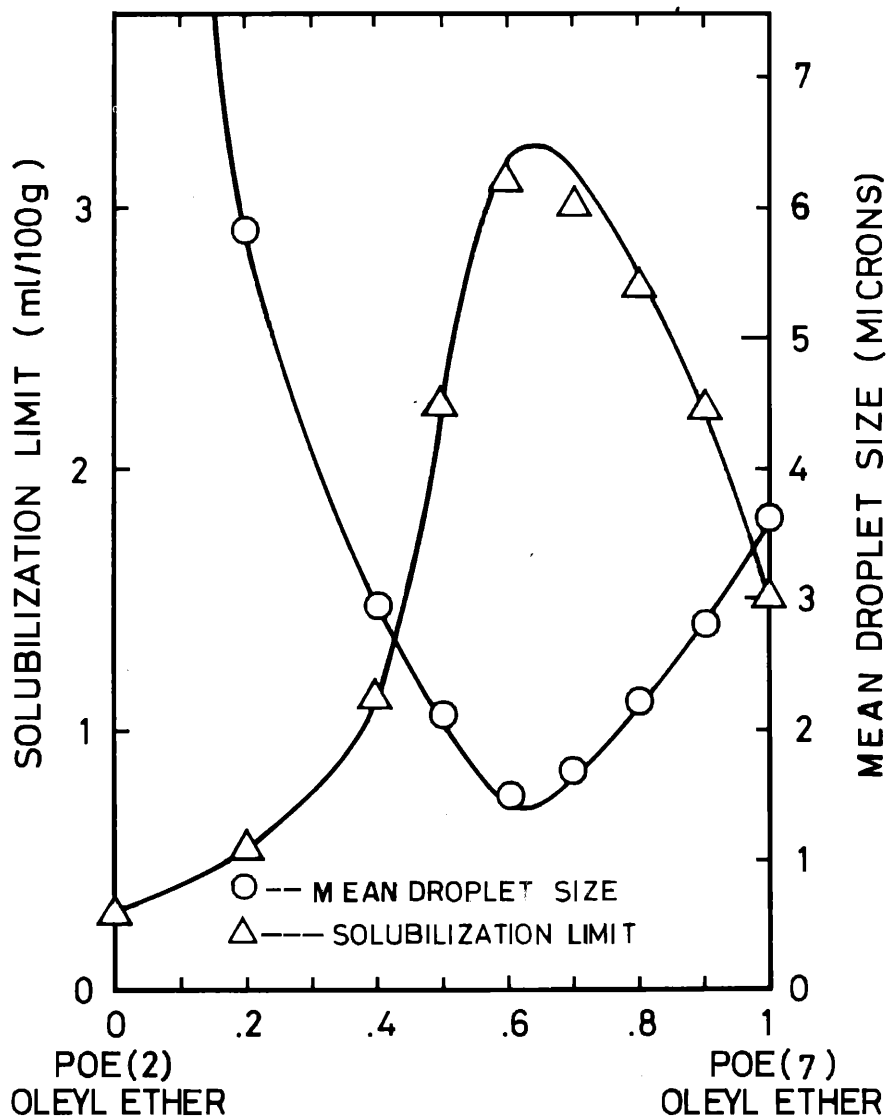


Figure 1. Solubilization-emulsion droplet size correlation for single surfactant systems. (Emulsion contain 30 per cent mineral oil, 65 per cent deionized water, and 5 per cent polyoxyethylene nonylphenyl ethers with per cent ethylene oxide corresponding to abscissa. Number in parenthesis indicates actual mole number of E. O. in each surfactant)



WEIGHT FRACTION OF HYDROPHILIC SURFACTANT

Figure 2. Solubilization-emulsion droplet size correlation for binary surfactant systems. (Emulsions contain 30 per cent mineral oil, 65 per cent deionized water, and 5 per cent nonionic surfactant mixtures. Surfactant mixtures consist of hydrophilic POE (7) oleyl ether and lipophilic POE (2) oleyl ether at ratios indicated by abscissa)

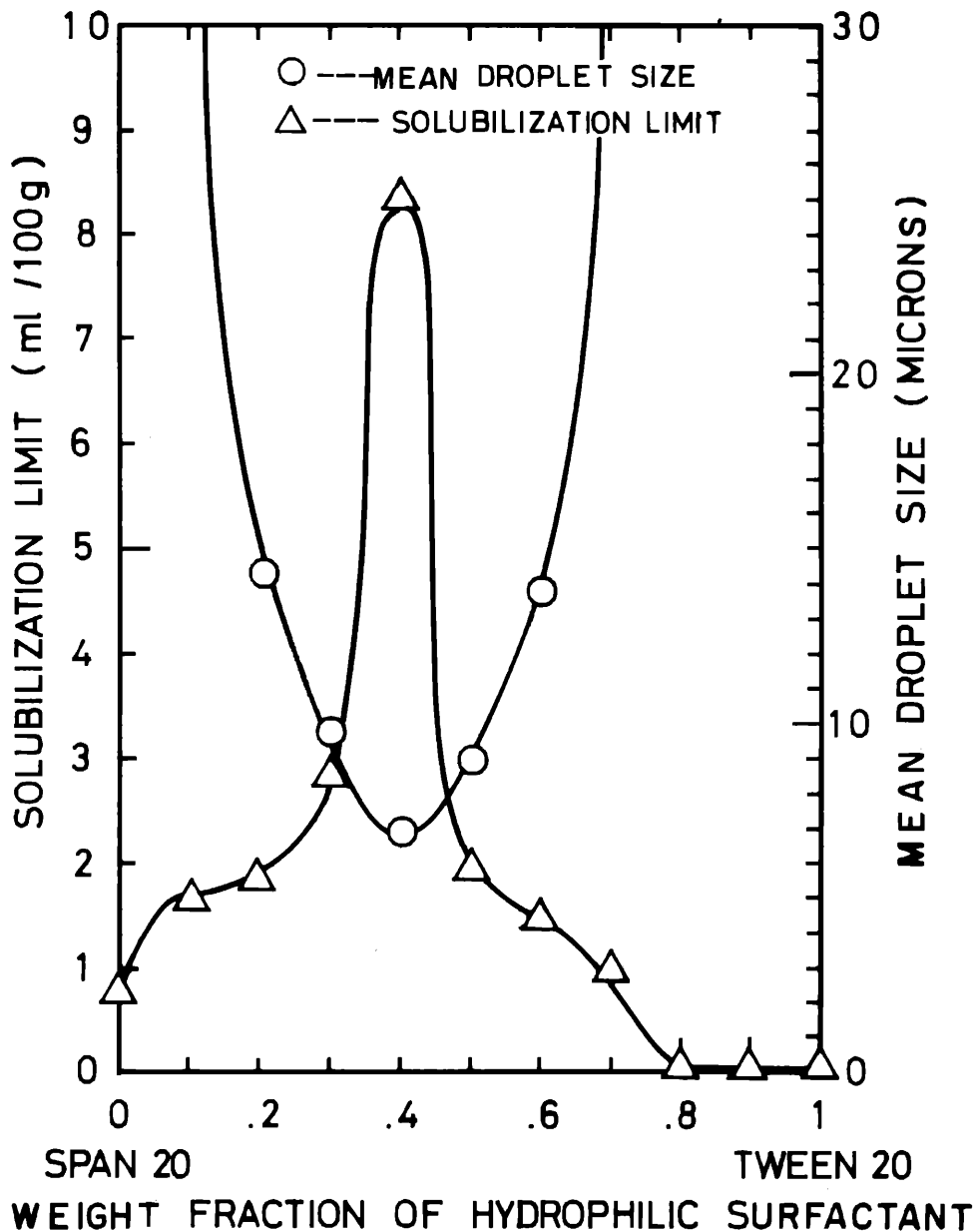


Figure 3. Solubilization-emulsion droplet size correlation for binary surfactant systems. (Emulsions contain 30 per cent mineral oil, 65 per cent deionized water, and 5 per cent nonionic surfactant mixtures. Surfactant mixtures consist of hydrophilic Tween 20 and lipophilic Span 20 at ratios indicated by abscissa)

ethylene oxide in the surfactant. The average droplet sizes of the emulsions obtained from the microphotographic measurements were also indicated in Fig. 1.

It is clearly seen from Fig. 1 that a maximum solubilization in this series of surfactants was obtained when the 5 mol ethylene oxide adduct was used and that this surfactant also gave an emulsion with finest mean droplet size.

Figure 2 shows a similar correlation obtained with various mixtures of 2 and 7 mole ethylene oxide adducts of oleyl ether. Here again, a good correlation between the maximum solubilization point and the minimum droplet size was obtained. The HLB of the surfactant blend at the optimum point was 9.7 calculated from the supplier's experimentally determined HLBs of the 2 and 7 mole adducts, which were given as 7.7 and 10.7, respectively.* This value is fairly close to the literature value of the required HLB of paraffinic mineral oil which is about 10.

Figure 3 shows another example of mineral oil emulsion emulsified with combinations of Tween 20 and Span 20. Here again, a good correlation was obtained at Tween 20/Span 20 ratio of about 40/60. In most systems, the solubilization data were obtained through drop-by-drop addition of water into the oil-surfactant mixture with mixing as described earlier. In a few systems, the solubilization curves were carefully studied by shaking varying amounts of water into vials containing the oil-surfactant mixtures and equilibrating the systems before making observations. Figure 4 shows a photograph taken shortly after the preparation of the representative vials used in the Tween 20-Span 20 system.

TESTING OF THE CORRELATION

In order to test the validity of the correlation, many different types of surfactants, oils, and other additives were employed for solubilization measurements and corresponding emulsification experiments.

In addition to nonionic surfactants, anionic and cationic surfactants and their combinations were also tested. The data for an anionic-nonionic system using 96 per cent active sodium dioctyl sulfosuccinate (SDOS)[†] and sorbitan monooleate (Arlacel 80)[‡] are shown in Figure 5. A fairly good correlation is apparent for this mixed-surfactant system as both the solubilization peak and the droplet size minimum are located around 0.6 weight fraction. It is noted that below approximately 40 per cent of SDOS, the emulsification became extremely poor due to the phase inversion. The point of phase inversion is indicated by the vertical dashed line.

In most of the systems tested, the phase inversion occurred at points near the left end of the diagram and sufficiently removed from the solubilization peaks so that practically no effect on the correlation was observed. However, in some systems, the phase inversion boundary fell on or near the peak as illustrated by Figure 6 which em-

*These are the values given by Nikko Chemicals Co., Ltd. The HLB values of similar surfactants given by ICI United States Inc., are 4.9 and 10.7, respectively. This would give the HLB at the optimum point as 8.7.

[†]Tokyo Kasei Kogyo Co., Ltd. of Tokyo, Japan.

[‡]Kao-Atlas Co., Ltd. of Tokyo, Japan.

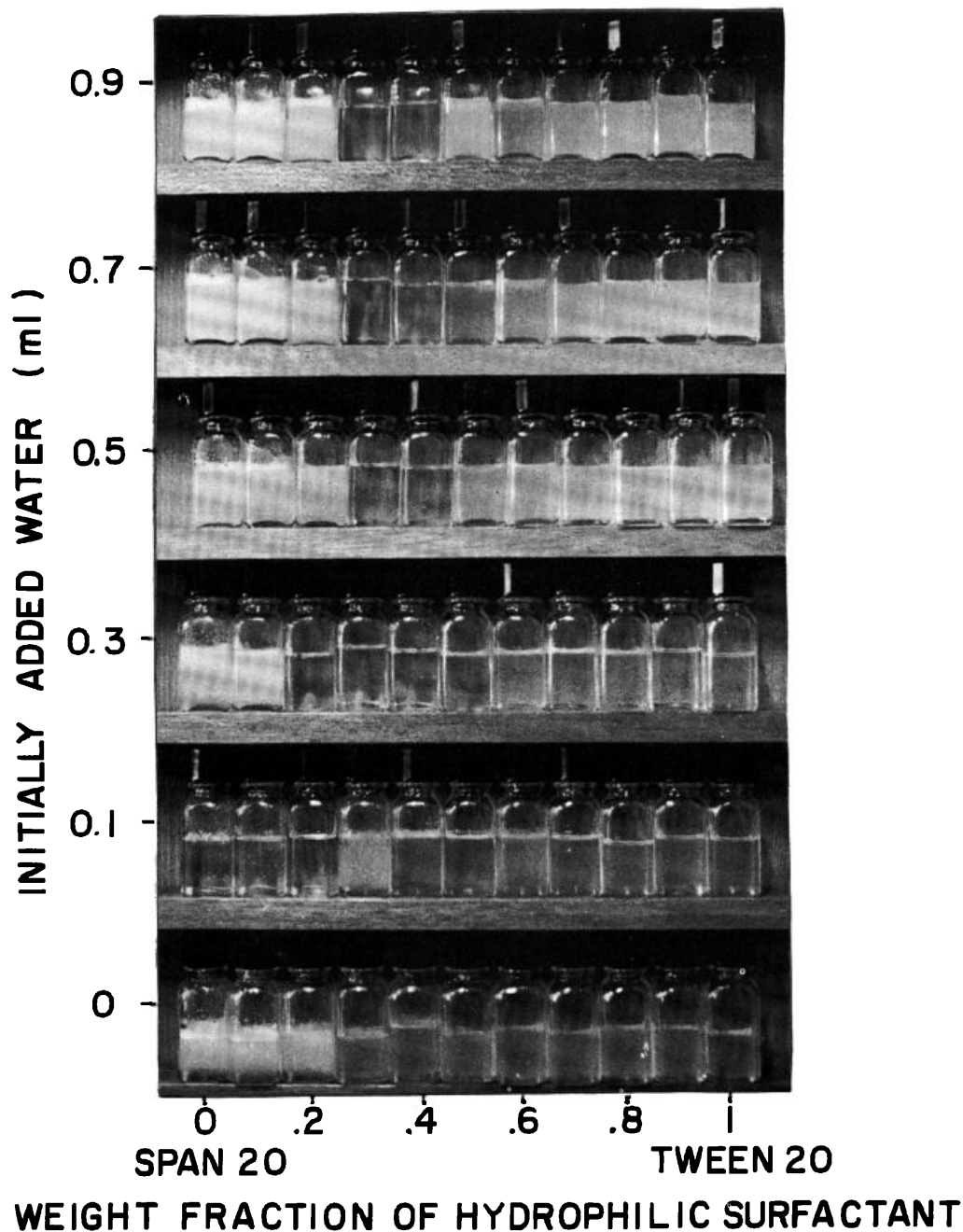


Figure 4. Photograph of vials containing surfactant-oil mixtures. (Each vial contains 15 g mineral oil, 2.5 g mixture of Tween 20 and Span 20, and small amounts of deionized water. Amounts of water in milliliters are indicated by numbers on left-hand edge of photograph. Weight fractions of Tween 20 in the surfactant mixtures are printed under bottom row of vials)

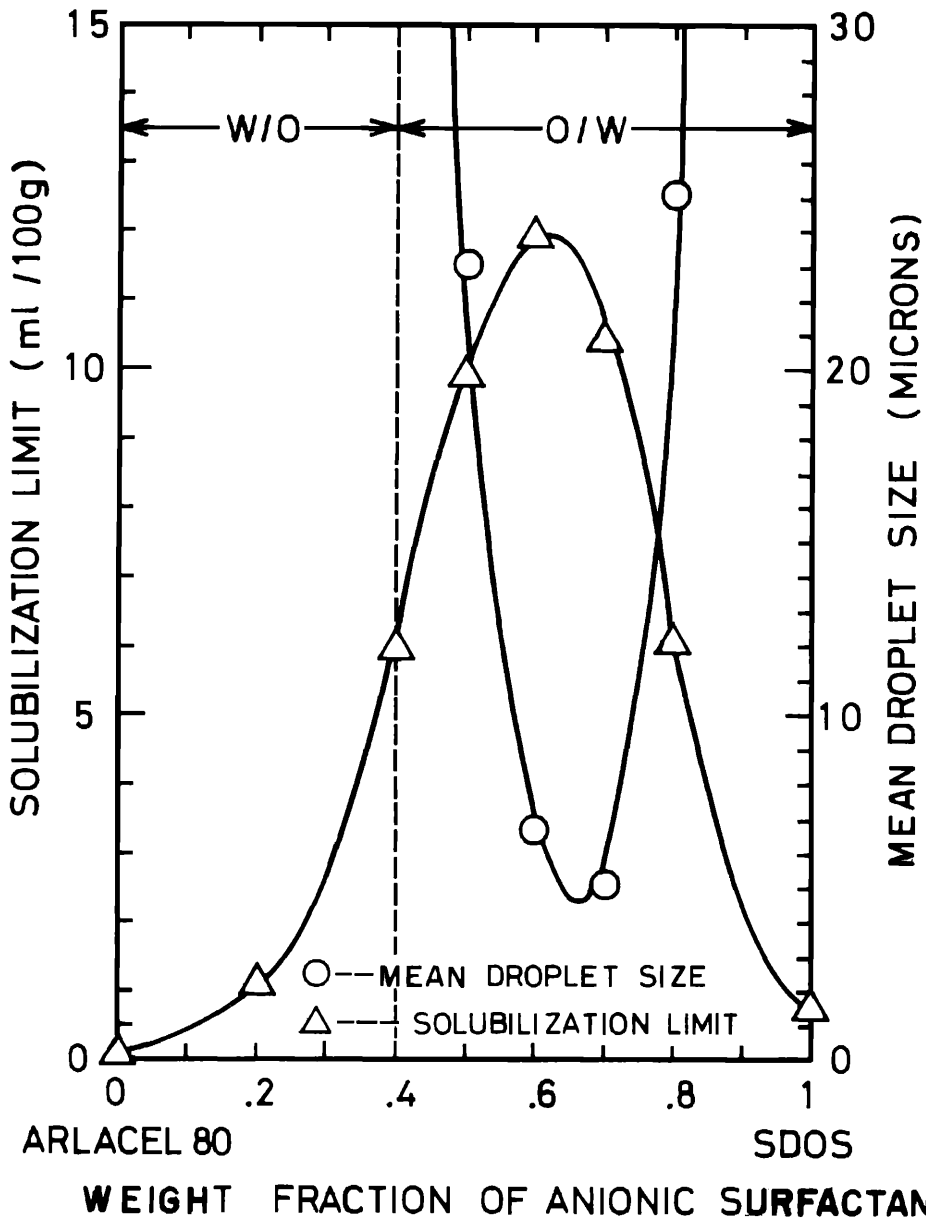


Figure 5. Solubilization-emulsion droplet size correlation for anionic-nonionic systems. (Emulsions contain 30 per cent mineral oil, 65 per cent deionized water, and 5 per cent surfactant mixtures. Surfactant mixtures consist of hydrophilic anionic sodium dioctyl sulfosuccinate, and lipophilic Arlacel 80 at ratios indicated by abscissa)

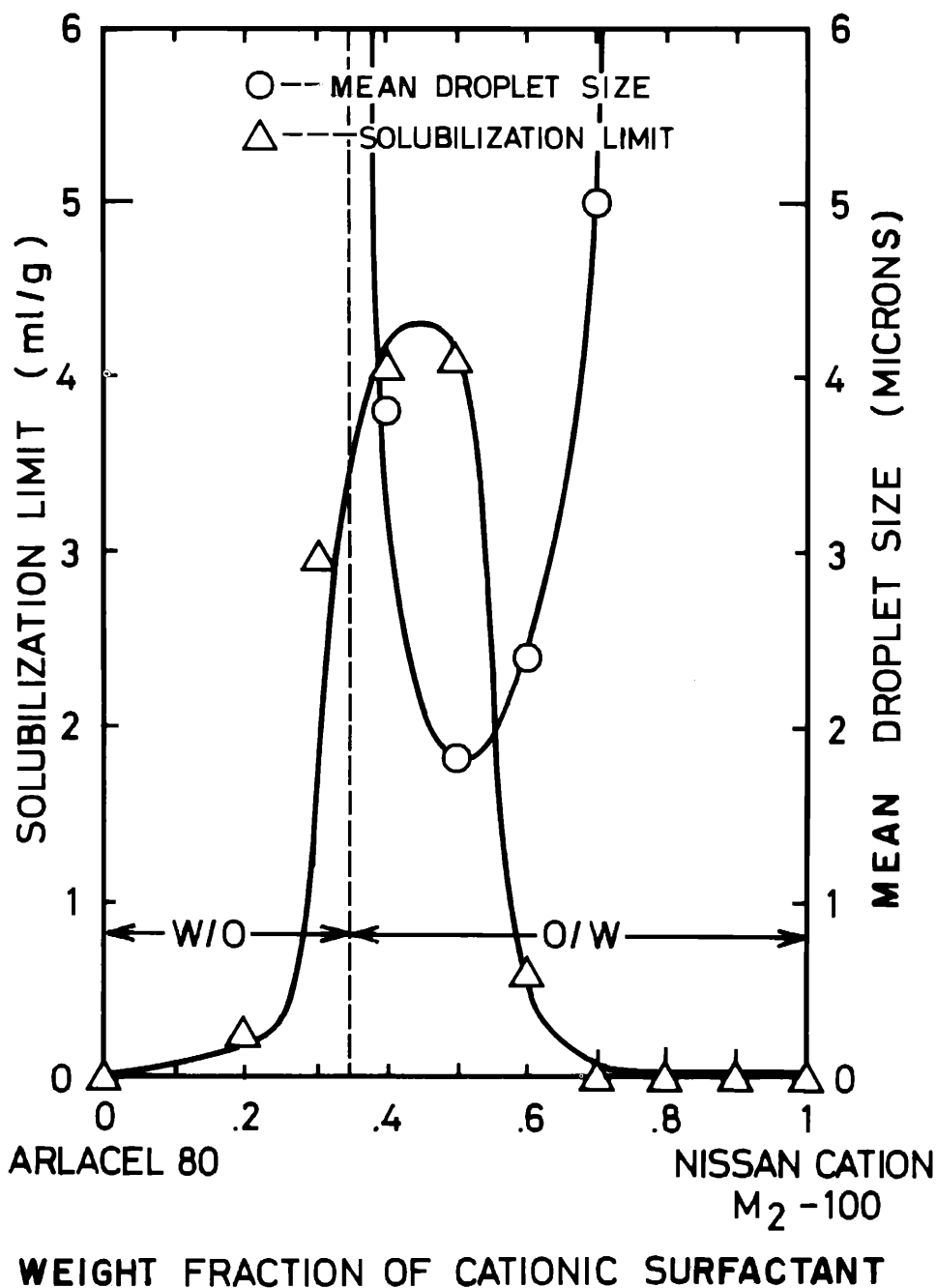


Figure 6. Solubilization-emulsion droplet size correlation for cationic-nonionic systems. (Emulsions contain 30 per cent mineral oil, 65 per cent deionized water, and 5 per cent surfactant mixtures. Surfactant mixtures consist of hydrophilic cationic lauryl dimethyl benzyl ammonium chloride and lipophilic Arlacel 80 at ratios indicated by abscissa)

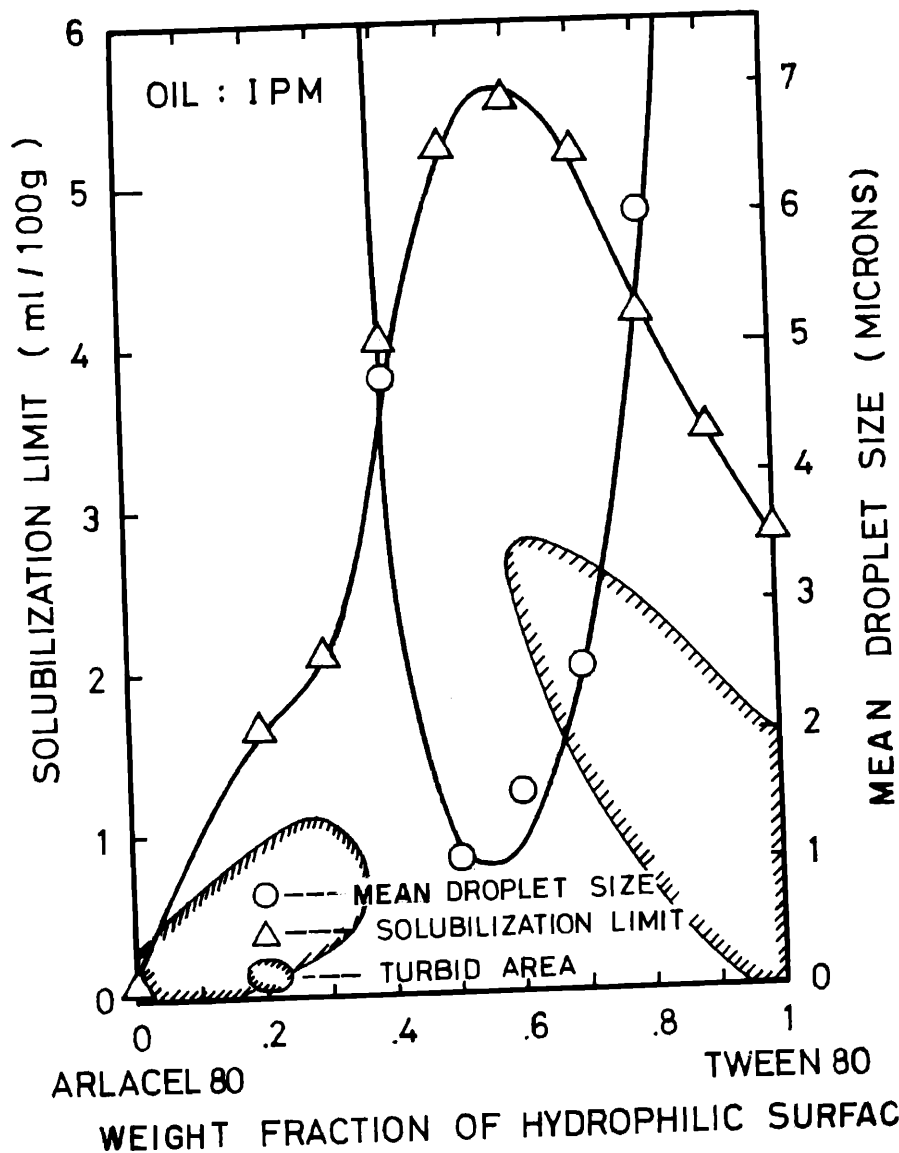


Figure 7. Solubilization-emulsion droplet size correlation for isopropyl myristate systems. (Emulsions contain 30 per cent IPM, 65 per cent deionized water, and 5 per cent surfactant mixtures. Surfactant mixtures consist of hydrophilic, Tween 80, and lipophilic Arlacel 80 at ratios indicated by abscissa)

ployed a cationic-nonionic surfactant combination. The surfactants used were lauryl dimethyl benzyl ammonium chloride* and Arlacel 80. In this example, the point of optimum emulsification does not precisely coincide with the solubilization peak, but is located somewhat to the right of the peak. This is clearly due to a phase inversion, from O/W to W/O, taking place near the solubilization peak.

In addition to mineral oil, many other oils commonly used in cosmetics were tested. Figure 7 gives an example using isopropyl myristate (IPM) and nonionic surfactants. The phase diagram for this system is somewhat more complex due to the appearance of turbid areas under the solubilization curve. In this case, however, the turbid areas did not affect the correlation. In other more complex systems, as will be explained later, the turbid areas could shift the point of optimum emulsification.

The use of the HLB method often does not work satisfactorily in many emulsions containing polar oils. It is believed that a part of the problem is probably related to a flaw in the basic concept. The "HLB-required HLB" emulsifier selection method implicitly divides an emulsion into two parts: a surfactant or a surfactant mixture which is *to emulsify*, and an oil or oil mixture which is *to be emulsified*. In dealing with raw materials for practical emulsions, however, it is not always possible to make such a clear distinction.

For example, lanolin is generally regarded as an oil, but it can also serve as a low HLB emulsifier. Fatty alcohols or fatty acids are commonly used cosmetic ingredients for the oil phase, but they are surface active and can be adsorbed at the oil-water interface. If one considers them as oils to be emulsified, then their required HLB values must be used to calculate the required HLB of the entire oil phase. If one considers them as surfactants, then their HLB values must be included in the surfactant mixture. The problem is that one does not get a consistent result by interchanging the HLB, required HLB values, indicating that there is an inherent inconsistency in this system. This can be best illustrated by considering the following example.

Suppose that it is desired to emulsify an oil mixture consisting of 800 g mineral oil and 200 g cetyl alcohol, using a blend of Tween 80† and Arlacel 80‡.

If one first regards cetyl alcohol as an oil, the "required HLB" of the oil mixture is calculated as follows (8): required HLB of mineral oil, paraffinic = 10; required HLB of cetyl alcohol = 15. Therefore, required HLB of the oil mixture = $0.8(10) + 0.2(15) = 11$.

Taking the HLBs of Tween 80 and Arlacel 80 as 15 and 4.3, respectively (8), one readily determines the optimum ratio of Tween 80/Arlacel 80 for this mixture to be 1.67. If the total amount of the nonionic surfactants is to be 100 g, one needs 62.6 g Tween 80 and 37.4 g of Arlacel 80 to emulsify the cetyl alcohol-mineral oil mixture according to the HLB method.

Alternatively, if one should regard the 200 g cetyl alcohol as a low HLB emulsifier and

*Nissan Cation M₂-100 by Nippon Oils and Fats Co., Ltd., Tokyo, Japan.

†Polyoxyethylene (20) sorbitan monooleate, ICI United States, Inc.

‡Sorbitan monooleate, ICI United States, Inc.

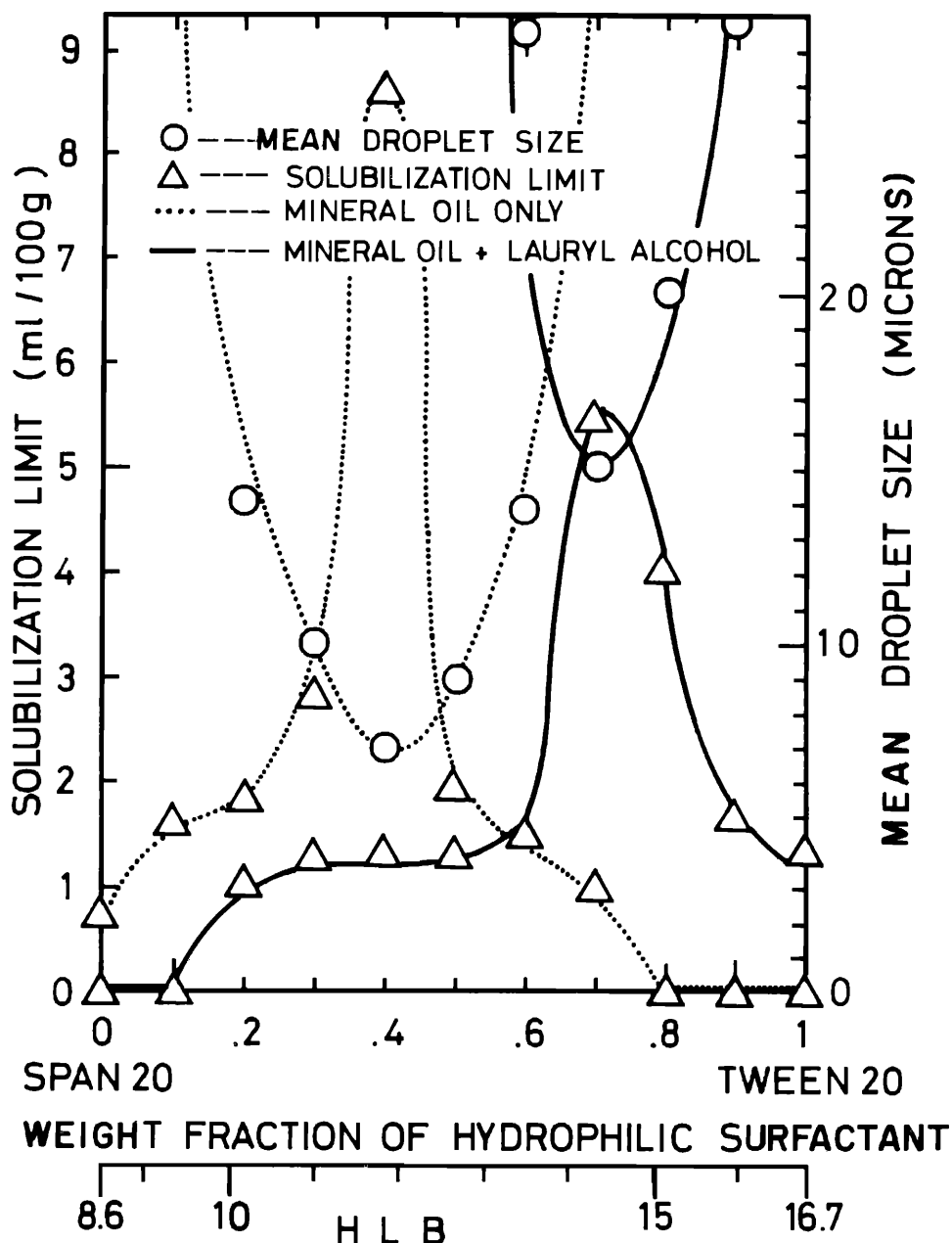


Figure 8. Shifting of optimum emulsification peak by addition of lauryl alcohol. (Emulsions contain 30 per cent oil phase, 65 per cent deionized water, and 5 per cent surfactant mixtures. Surfactant mixtures consist of hydrophilic Tween 20 and lipophilic Span 20 at ratios and corresponding HLB values indicated by abscissa. Dotted lines represent data for pure mineral oil systems. Solid lines represent data for oil mixture consisting of 8 parts mineral oil and 2 parts lauryl alcohol)

use the literature HLB value of 1.15* to repeat the above calculations, one would end up with a result requiring no Arlacel 80 but a very large amount, 354 g, of Tween 80 for the optimum emulsification. This means that by merely altering the functional concept of a component, one can come up with a vastly different surfactant requirement.

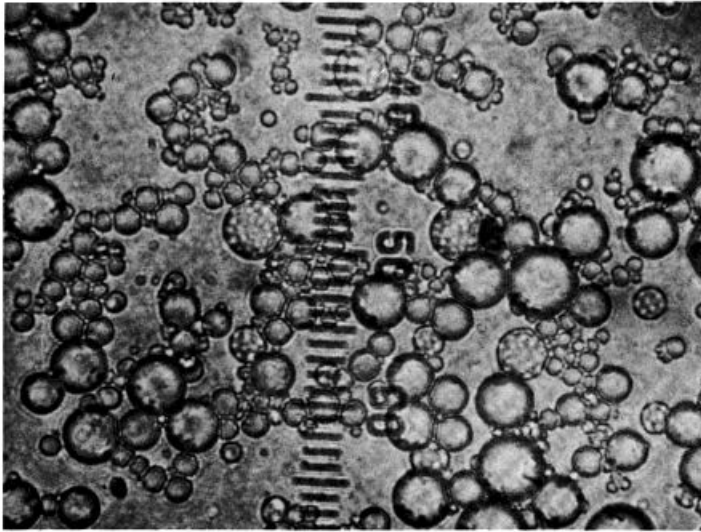
This is a serious problem, since there are so many common cosmetic ingredients like cetyl alcohol, which can be regarded either as oils or auxiliary emulsifiers. In reality, these materials probably function partially as an emulsified oil and partially as surfactant in practical emulsions. In the HLB system, however, one is forced to regard them either as a surfactant to emulsify or an oil to be emulsified, but unfortunately, these 2 alternatives do not lead to a consistent result. This is probably one of the main reasons why the HLB method does not work well for many practical emulsions containing polar substances.

The fact that the addition of a polar oil to a nonpolar oil often affects the required HLB of the system far more than that can be predicted from the simple additive rule can be demonstrated by considering the required HLB of lauryl alcohol which is given in the literature as 14 (8). Thus, a 20/80 mixture of lauryl alcohol/mineral oil has a required HLB value of 10.8 using the linear additivity rule, taking the required HLB value of mineral oil as 10. This means that one should expect no more than 1 unit shift of the required HLB by substituting 20 per cent of mineral oil with lauryl alcohol. However, our emulsification experiments with mixed oils indicated that the shift was considerably greater than one unit. In Fig. 8, the dotted lines indicate the solubilization and emulsification curves for pure mineral oil emulsions prepared with Tween 20 and Span 20. The solid lines on the same figure present the results of substituting 20 per cent of mineral oil with lauryl alcohol. It is clear that the optimum emulsification point shifted about 2.4 HLB units after adding lauryl alcohol to the nonpolar mineral oil. The maximum solubilization point also shifted to the right by the same proportion indicating the reliability of the solubility measurement as a means to predict optimum emulsification. Similar experiments with other polar oils such as oleyl alcohol or oleic acid indicate that the solubilization method can reliably predict the optimum emulsification point even in cases where the HLB system failed.

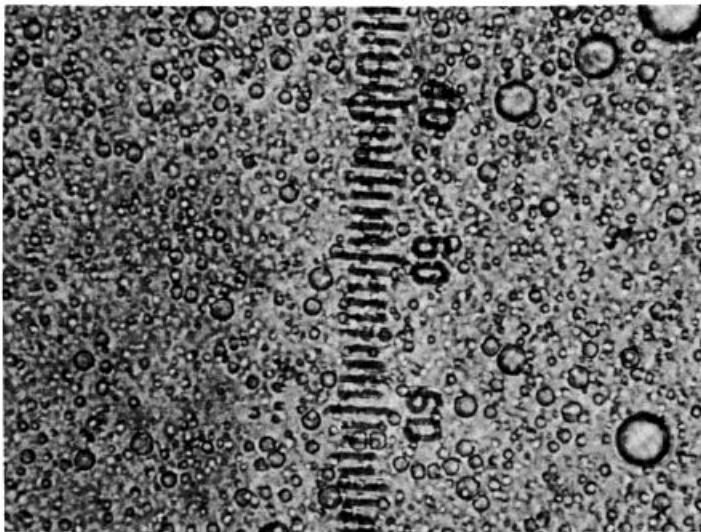
RELATIONSHIP WITH EMULSIFICATION MECHANISMS

In our previous work, we attempted to explain a dramatic difference in O/W emulsification efficiency due to the initial locations of the hydrophilic surfactants by proposing 2 separate mechanisms in emulsification (9). According to our hypothesis based on experimental evidences, mechanism A, which is the mechanism that produces the finer emulsion, *can* control emulsification when a relatively hydrophilic surfactant is initially dissolved in the oil phase. As water is added to this oil-surfactant mixture to start emulsification, the water is first solubilized in the oil phase and a W/O emulsion is formed. As more water is added, the hydrophilic surfactant starts to migrate to the aqueous phase resulting in an emulsion phase inversion to form an O/W emulsion. A short-lived double emulsion of (W/O)/W type may be formed during the transition stage. The phase inversion results in a production of emulsion with a fine droplet size.

*The experimental value of the HLB of cetyl alcohol is given as 1.0 while the calculated HLB according to Davies' group number is 1.3 (5). The average value of 1.15 is used in this calculation.



(A)



(B)

Figure 9. Microphotographs showing improvement of emulsification by adding 2 per cent water to make the oil phase homogeneous. (Emulsions contain 30 per cent mineral oil, 65 per cent deionized water, and 5 per cent surfactant mixtures. Surfactant mixtures consist of Tween 80 and Arlacel 80 at 80/20 ratio.): (A) emulsion made with nonhomogeneous oil phase ($\times 1200$); (B) emulsion made with homogeneous oil phase containing 2 per cent water ($\times 1200$)

When the surfactant is placed in the aqueous phase, phase inversion does not take place, and the oil droplets are broken up by the mechanical shear provided by the mixer. This was referred to as mechanism B, and unless a relatively high speed is used to process the emulsion, the resulting emulsion will have a much larger average droplet size than the same formulation prepared via mechanism A.

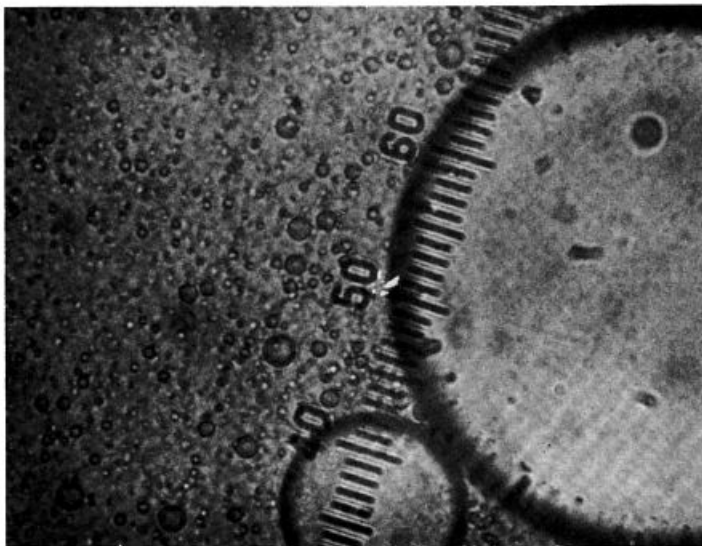


Figure 10. Microphotographs showing mineral oil emulsions with 2 distinct droplet size distributions. (Emulsion contains 30 per cent mineral oil, 65 per cent deionized water, and 5 per cent surfactant mixtures. Surfactant mixtures consist of POE (10) oleyl ether and POE (2) oleyl ether at 40/60 ratio) ($\times 1200$)

There are 3 conditions which must be fulfilled before Mechanism A can operate. They are as follows: (1) the surfactants must be soluble in the oil phase in which it is initially placed; (2) the surfactants in the oil phase must solubilize or emulsify a part of the aqueous phase; and (3) a phase inversion must take place to form an O/W emulsion.

Further work using various oils and nonionic, anionic, and cationic surfactants resulted in no data contradictory to the proposed hypothesis. A careful analysis of the experimental data indicates that wherever any of the above 3 conditions were promoted, the emulsification efficiency improved. On the other hand, whenever a factor was introduced to hinder any of these conditions, the emulsification efficiency often dramatically decreased.

With regards to the first requirement of surfactant solubility in the oil phase, for example, an oil phase containing 14.3 per cent Tween 80/Arlacel 80 mixture at 80/20 ratio does not form a homogeneous phase. Upon standing, a surfactant-rich phase would separate from the mixture and settle to the bottom. The emulsion, prepared by quickly adding water to such a mixture with a moderate mixing, had coarse droplets and was unstable (Fig. 9(A)). However, by initially dispersing about 2 per cent of water in the oil phase, the mixture became homogeneous and the emulsion prepared improved remarkably as can be seen in Fig. 9(B).

The small amount of the water added to the above mentioned mixture apparently had a significant effect on the micellar structure in improving the solubility of the surfactant in the oil phase. Sometimes a similar effect could be achieved by adding a small amount of polar oils such as oleic acid. The result is also a definite improvement of emulsification efficiency.

Another example is a mixture of POE (10) oleyl ether/POE (2) oleyl ether at 40/60 ratio in mineral oil.* If an emulsion is prepared by immediately emulsifying the oil-surfactant mixture right after dispersion, a reasonably fine emulsion is obtained. However, if the oil-surfactant is allowed to stand overnight, it would separate into two layers—the lower oil layer containing most of the surfactant and the top oil layer containing much less surfactant. If an emulsion is prepared with such a two-layered oil phase, the emulsion would contain fine droplets derived from the lower surfactant-rich layer and coarse droplets originated from the upper, surfactant-poor layer. A microphotograph of such an emulsion revealing 2 distinct droplet size distributions is shown in Fig. 10.

The second requirement for the emulsification mechanism is related to the aqueous solubilization by the oil phase. From the experimental results presented so far, it is quite apparent that water solubilization must be related to emulsification efficiency. Other factors being equal, a larger quantity of water solubilization appeared to favor formation of a finer emulsion, although, the quantity of solubilization by itself cannot be regarded as an absolute measure of emulsification efficiency.

Although it is quite possible that a great water solubilization merely indicates the area of favorable condition for emulsification, there is also experimental evidence suggesting that solubilization is one of the necessary steps in the over-all emulsification process. In many systems studied, it was possible to improve emulsification by initially presolubilizing the water into the oil-surfactant mixture before emulsification. For example, a combination of 2- and 10-mole adducts of oleyl ethers in mineral oil forms a fairly complex solubilization diagram as shown in Fig. 11. When an emulsion was prepared in the usual manner using an 80/20 surfactant mixture indicated by a letter "X" in the diagram, the droplets were very coarse and the emulsion unstable. Subsequently, the emulsification procedure was slightly modified by first dispersing and solubilizing a small amount (2.6 per cent) of water into the oil phase to bring the mixture to point "Z" in the diagram. The resulting emulsion was very stable and had a very fine droplet size as shown in the photograph in Fig. 12 (Z).

Another similar presolubilized emulsification was carried out with a slightly reduced amount of initial water (2 per cent instead of 2.6 per cent) corresponding to point "Y" in the turbid area of Fig. 11. The result was an emulsion somewhat better than that of point X, but much inferior to the emulsion prepared at Z.

Since all three emulsions, X, Y, and Z have an identical, final composition, it must be concluded that the presolubilization treatment and the amount of the presolubilized water were positively affecting the emulsification process. In dispersing the water into this oil-surfactant mixture, it was noted that the water was not solubilized instantly, but it required time and considerable amount of mixing work before complete solubilization was obtained. This would suggest that, perhaps, the *rate of water solubilization* too is an important factor in emulsification.

It can be explained that when one starts emulsification from the point X by quickly adding water, even though, compositionwise, the mixture will pass points Y and Z, because of the very slow rate of solubilization, it is not possible for the mixture X to reach

*The total surfactant mixture was 14.3% in the oil phase.

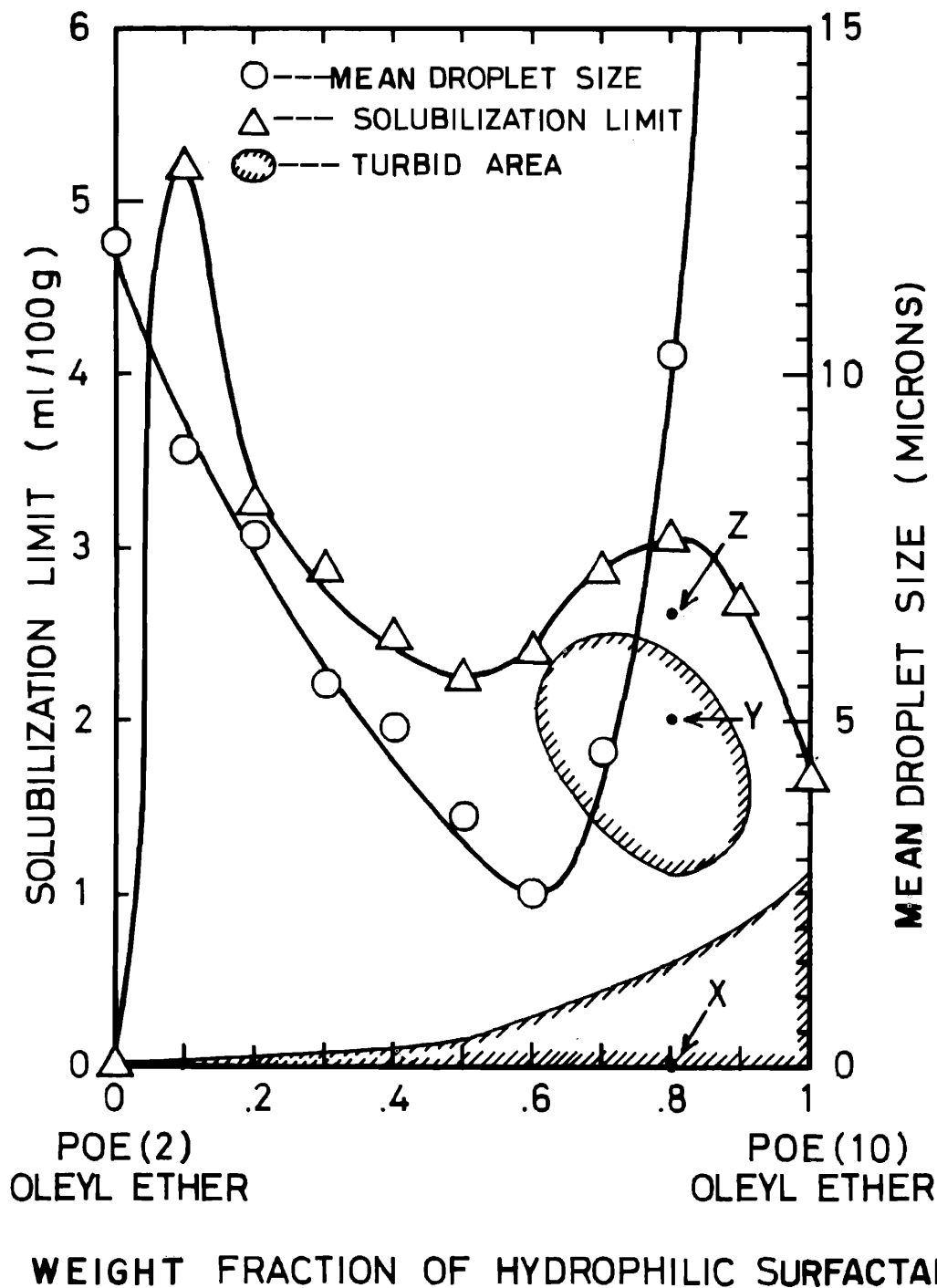


Figure 11. Complex solubilization diagram (emulsions contain 30 per cent oil phase, 65 per cent deionized water, and 5 per cent surfactant mixtures. Surfactant mixtures consist of hydrophilic POE (10) oleyl ether and lipophilic POE (2) oleyl ether at ratios indicated by abscissa)

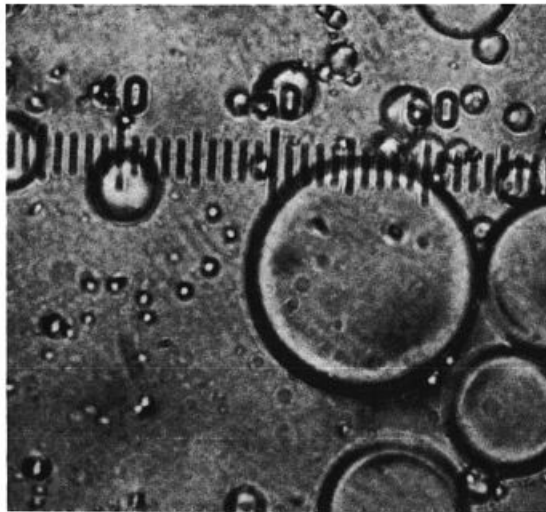
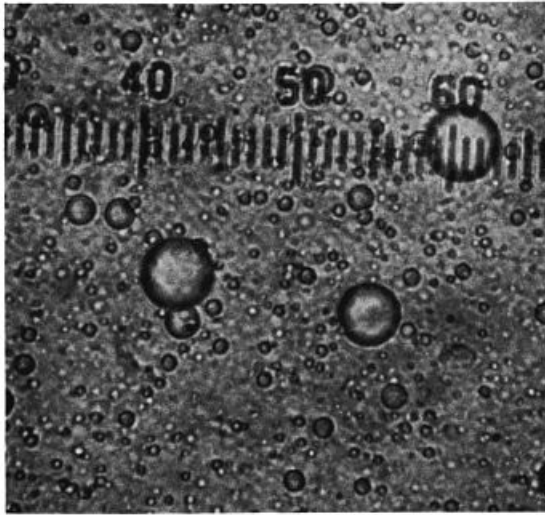
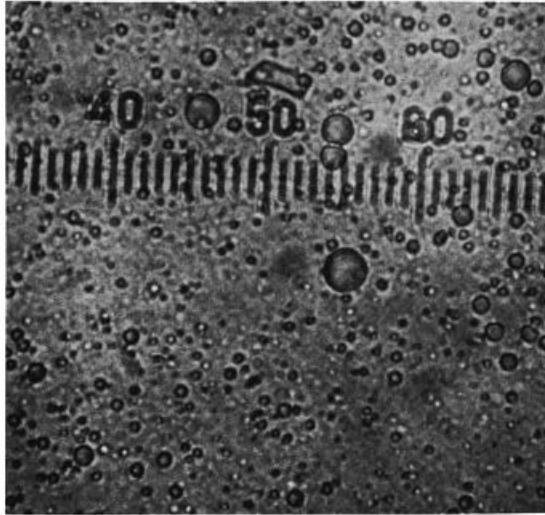


Figure 12. Microphotographs of emulsions prepared from 3 different points in Fig. 11

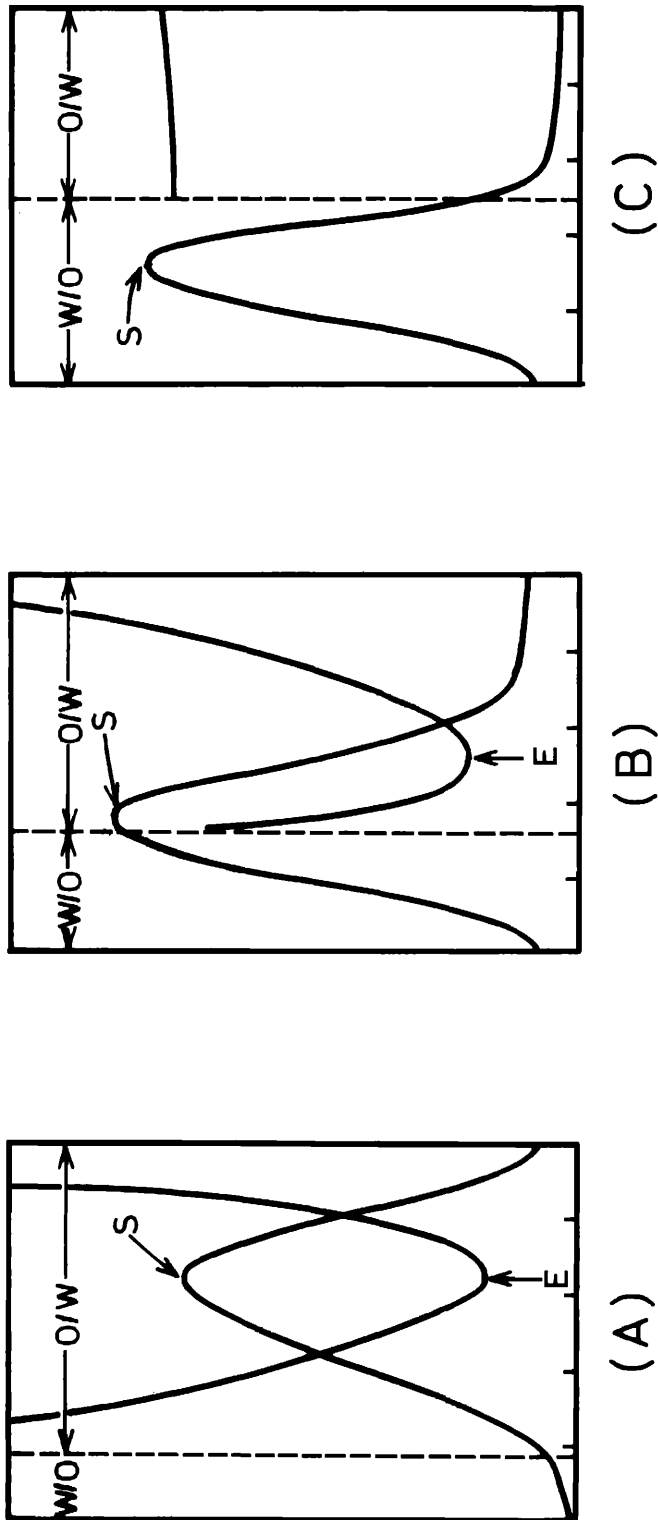


Figure 13. Effect of phase inversion boundary in relation to solubilization peak

the equivalent solubilized state of Z with the method of emulsification employed. With more added water, the hydrophilic surfactant soon migrates to the aqueous phase making it impossible for mechanism A to function.

The third requirement of mechanism A concerns phase inversion. In some systems, poor matching of the solubilization peak and the point of optimum emulsification were believed to be due to the phase inversion effect. As illustrated in Fig. 13 (A), phase inversion has no effect on the correlation when its boundary, indicated by the dashed line, is located on the left-hand side of the solubilization peak S. The optimum emulsification point E generally coincides with the peak in such a case. If the phase inversion boundary should fall on the peak as illustrated by Fig. 13 (B), the optimum emulsification point E generally shifts slightly to the right since an inverted W/O emulsion or mixed emulsion is formed at S. If the peak S occurs within the W/O region and the amount of solubilization is very small in the O/W region as illustrated by Fig. 13 (C), no optimum emulsification point exists as all O/W emulsions made have large droplet sizes.

It should be noted that phase inversion of an emulsion is dependent not only on the hydrophilic/lipophilic nature of the surfactants but also strongly on other variables such as internal phase volume, surfactant location, and the method of emulsion preparation (7, 10). Hence, the phase-inversion boundary can shift depending not only on the formulation, but also on the process variables such as the rate of addition of one phase to the other phase, degree of agitation, emulsification temperature, etc.

In 1964, the PIT (phase inversion temperature) method of selecting emulsifiers was suggested (11, 12) as an alternative to the HLB method. The PIT of an emulsion is dependent not only on the type of surfactants and oils, but also on other parameters such as phase volume, surfactant concentration, or the presence of salts. With regard to this, the PITs are said to provide more accurate information than the HLB, required HLB values which do not account for these effects. However, in practice, the PIT system, like HLB, also has shortcomings. First, systems containing anionic or cationic surfactants do not exhibit PIT and, therefore, the method would not apply. Second, since PIT is dependent on so many parameters, it is more complicated to apply it in a practical system than the HLB method. Finally, the PIT system is also only good as a rough guide, since it merely tells the formulator that he should not use combinations having PITs too close to the temperature at which the product is to be used or stored.

CONCLUSIONS

The obvious value of the solubilization-emulsification correlation here is its application in selecting emulsifiers for product development work. Since a solubilization measurement is relatively simple and the results are reproducible, it provides a quick way to determine the point of optimum emulsification. It can be also used to determine the effects of oil additives on emulsification, since the correlation holds not only for nonpolar oils, but also for many polar oils and their mixtures.

The solubilization and phase inversion data can also be very useful in process development work for emulsion products. They can be helpful in finding the best manufacturing method and also in avoiding manufacturing troubles.

For example, solubilization data obtained at various temperatures are useful in finding an optimum emulsification temperature. If the emulsification is done by the surfactant-in-oil method, it is well to study the oil phase containing various amounts of solubilized water at various temperatures. As it was pointed out earlier, the oil-surfactant mixture containing some water may not be stable and a separation into surfactant-rich and surfactant-poor phases can result in an emulsion with extremely nonuniform droplet size distribution. Therefore, consideration as to when and how rapidly to add the aqueous phase to the oil phase may become a very important factor in preventing manufacturing difficulties.

The method of solubilization measurements used in this work relied upon visual observations and the solubilization limit was defined as the point beyond which a permanent turbidity would develop upon addition of more water. This method is very simple to use, but it does have some disadvantages. In some systems, turbidity does not develop sharply, resulting in a difficulty in determining the endpoint. Another problem is that if the mixture is not completely transparent at the temperature of measurements, it would be very difficult or impossible to judge the endpoint. This would rule out the application of the method to oil mixtures containing two immiscible oils (e.g., mineral oil and silicone fluids) or to the mixture containing a solid suspension.

However, it is believed that such difficulties can be overcome by using other means of determining solubilization. One promising method is the use of vapor pressure measurements which has been successfully used in measuring solubilization of water in nonaqueous systems (14, 15). The vapor pressure of an oil containing solubilized water generally shows an increase with increasing amount of solubilized water until the maximum point is reached. Since the method is not dependent upon a visual observation, the previously mentioned difficulties would not occur.

Unlike emulsion stability which is extremely difficult to define, solubilization is a better-defined phenomenon and can be related to the physical and chemical properties of the materials involved. Therefore, it is believed that the correlation presented here can be a very valuable basis for developing a useful tool for emulsifier selection, which is more accurate and reliable than other existing methods.

ACKNOWLEDGMENT

The authors gratefully acknowledge many valuable suggestions given by Dr. T. Moroe of Takasago Perfumery Co., Ltd.

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