

## **Low-energy emulsification II: evaluation of emulsion quality**

T. J. LIN 628 *Enchanted Way*, Pacific Palisades, CA 90272;  
Toshiyuki Akabori, Shoji Tanaka and Katsuyuki Shimura,  
Arimino Chemical Co., Ltd., Tokyo, Japan.

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### **Synopsis**

LOW-ENERGY EMULSIFICATION (LEE), an emulsification technique proposed by Lin (1, 2) to conserve mechanical and thermal energies in the processing of emulsions, was EXAMINED in terms of EMULSION QUALITY and compared with similar emulsions made with a conventional hot process.

Experimental data obtained from prototype cosmetic formulations consisting of W/O and O/W emulsions stabilized with various cationic, anionic and nonionic surfactants and their mixtures indicate that the technique is extremely flexible and is capable of producing emulsions with varying droplet sizes. The key to success in applying the technique lies in understanding and controlling the physical variables responsible for causing a droplet size variation.

The key variables found were: first stage emulsification temperature, mixing intensity, ratio of external phase added during the first stage of emulsification to that of the second stage dilution, rate and the mode of phase combination. By effectively controlling these variables, it has been demonstrated that it is possible to produce emulsions with smaller and more uniform droplet size distribution using the low-energy technique than similar emulsions obtained with the conventional hot emulsification. In many instances, withholding of a large amount of external phase for later addition resulted in a sharp reduction of the droplet size. This effect is apparently related to the solubilization effect observed by Lin, Kurihara and Ohta (3, 4) and a proper control of this effect allows processing of finer emulsions with a substantial reduction of not only thermal and mechanical energies but also processing time.

### **INTRODUCTION**

The basic principles and the economical advantages of low-energy emulsification (LEE) have been thoroughly discussed by Lin in his earlier publications (1, 2). Basically the technique involves withholding a portion of the emulsion's external phase and first making an emulsion concentrate at an elevated temperature. The withheld external phase is kept at a lower temperature and added to the concentrate with mixing during the second stage (diluting) operation.

Since a portion of the external phase is added at a lower temperature (usually room

temperature), a significant amount of thermal energy can be conserved particularly if the amount of withheld external phase is substantial relative to the amount of emulsion concentrate processed in the first stage. In addition to conserving thermal energy, the technique also allows a considerable reduction in processing time by effectively reducing the time required for batch cooling. Mechanical energy expended during the cooling period is, as a result, also reduced.

It should be emphasized that LEE differs substantially from ordinary, low-temperature emulsification in that the entire process is not carried out at a constant, low temperature. First-stage emulsification can be carried out at almost any desired temperature to obtain the necessary sterilization, dispersion, blending or promotion of a chemical reaction in the low-energy method. The diluting liquid to be added to the batch at the second stage is usually kept at ambient temperature but may be adjusted to any desired temperature, if necessary. LEE is, therefore, much more versatile compared to the conventional, low-temperature method as it allows processing of a wide variety of cosmetic emulsions even when they contain waxy substances such as cetyl alcohol, stearic acid and beeswax. By applying thermal energy only when and where needed, LEE offers a great flexibility with a definite economical advantage.

Whereas the economy of LEE cannot be disputed for the mass production of emulsions when applicable, the quality of emulsions so produced has not been critically examined. The main purpose of this investigation is to systematically evaluate the qualities of typical O/W and W/O cosmetic emulsions prepared by LEE against similar emulsions prepared by a conventional hot process. The quality of a cosmetic emulsion is an ambiguous term and is obviously dependent on its end purpose and one's definition. For the purpose of this presentation, nevertheless, the quality of an emulsion is defined such that the finer the droplet size, the better the quality. This definition is consistent with most applications of cosmetic emulsions as a finer droplet size is usually associated with a finer texture, higher gloss and, generally, but not absolutely, with a better stability. The definition is an arbitrary one, however, as a finer droplet size does not always guarantee a better stability or better performance. Emulsion stability is dependent not only on the droplet size distribution of the internal phase but also on many other factors such as rheological and electrical properties. Moreover, in some cosmetic applications, an excessive stability may not even be desirable from the product performance viewpoint.

## EXPERIMENTAL

All emulsions were prepared in a 500-ml glass beaker equipped with four baffles as shown in Figure 1. A six-blade, stainless steel turbine with 50 mm diameter and 20 mm height, set 15 mm above the bottom of the beaker, was used for mixing. The mixer, driven by a powerful motor, rotates at exactly preset speeds virtually unaffected by viscosity variations during the mixing operation. In most instances, the internal phase of the emulsion was first heated to a desired temperature in the 500-ml beaker. A predetermined amount of the external phase, heated to the same temperature as the internal phase, was then added to start first-stage emulsification at a preset speed. The portion of the external phase withheld for second-stage addition was kept at approximately 20°C and later added to the emulsion concentrate at an approximately constant rate of 150 ml/min through a funnel. The finished emulsion was then mixed to uniformity and the droplet size distribution was

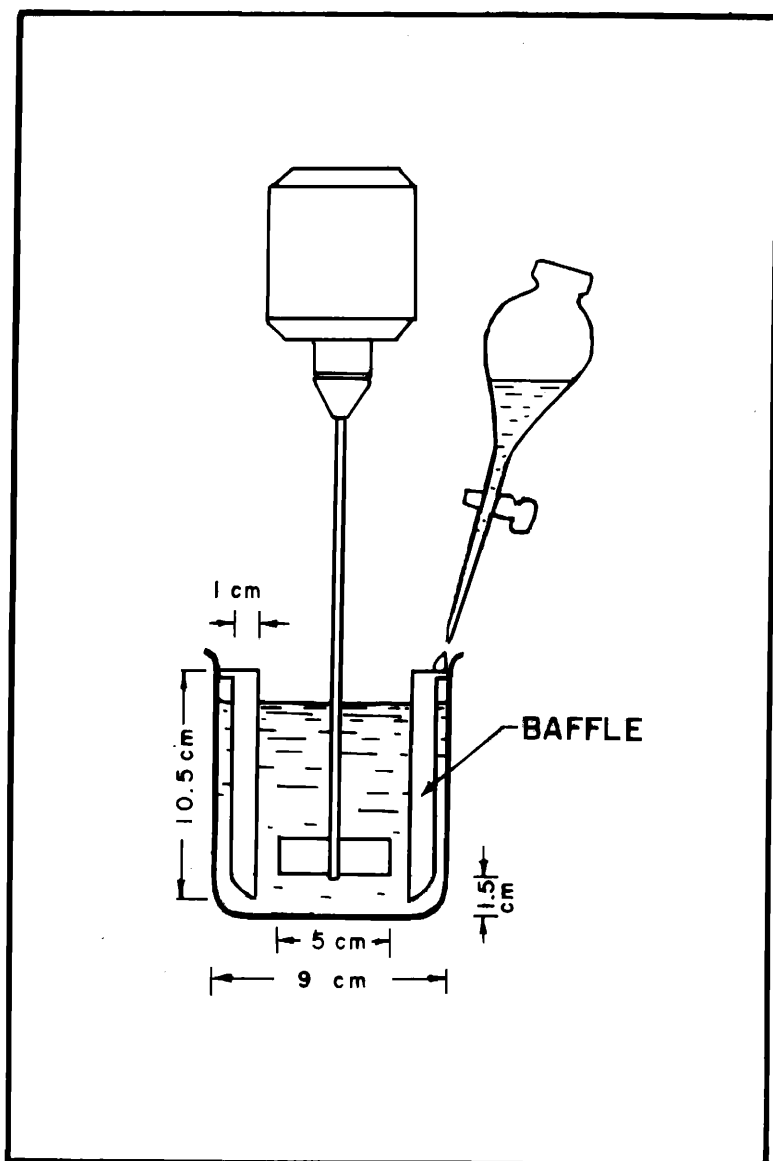


Figure 1. Experimental apparatus

obtained photomicrographically. The average droplet size represents an arithmetic average of approximately 200 droplets.

A parameter,  $\alpha$ , was defined as the percentage of a given phase withheld for a later addition. Thus  $\alpha = 0$  represents no withholding, i.e., conventional hot processing. Specifically,  $\alpha_O$  and  $\alpha_H$  represent, respectively, the percentages of the oil and aqueous phases withheld.

A thermometer placed in the beaker registered temperature changes and viscosity of the finished emulsion was measured at room temperature with a Brookfield-type viscometer

(Type B Viscometer, Model BL, by Tokyo Keiki Seizosho, Tokyo, Japan) at 30 rpm using spindle No. 3. Viscosity measurements were taken after a 1-min rotation. All emulsification operations were done carefully to assure good reproducibility. All surfactants, oils and waxes used in the formulations were cosmetic grade materials without further purification, and deionized water was used in all experiments.

## RESULTS AND DISCUSSIONS

Although a great number of formulations representing a wide range of cosmetic emulsions and nonemulsions were tested by LEE in this series of investigations, because of the space limitation only the results from several representative formulations will be shown. These formulations are simplified prototype cosmetic emulsions including a cationic O/W emulsion, a nonionic W/O emulsion, a nonionic O/W emulsion and an anionic/nonionic O/W emulsion.

The cationic O/W emulsion shown in Table I represents a prototype cationic hair rinse emulsion stabilized with a popular quaternary surfactant, stearyl dimethyl benzyl ammonium chloride.

The results obtained with this cationic O/W emulsion are shown in Figure 2 where the arithmetic mean droplet diameters are plotted against  $\alpha_H$ , the percentages of water withheld for second-stage dilution. The initial temperatures of first-stage emulsification,  $T_e$ , are also indicated in the figure. It is clear from Figure 2 that the emulsion becomes coarser as the emulsification temperature,  $T_e$ , is lowered. The mean droplet size also increases somewhat as  $\alpha_H$  is increased beyond 50%. Below 50%  $\alpha_H$ , the variation in the mean droplet sizes was within the experimental error.

The result is not surprising since it is expected that as emulsification temperature is lowered, emulsification becomes less efficient due to a viscosity build-up. However, for this system, no significant increase in the mean emulsion droplet size is observed until  $\alpha_H$  is well over 50%. This means that as much as 50% of the external phase (water) of this emulsion could be withheld for a later addition at room temperature to save a considerable amount of thermal energy without adversely affecting the emulsion quality.

In general, it is easier to carry out LEE on O/W emulsions containing low solids such as a moisturizer with 70% or more external, aqueous phase. However the applicability of LEE is by no means restricted to O/W emulsions. It also works satisfactorily for W/O emulsions containing a large amount of mineral oil. An example of such a W/O emulsion is given in Table II.

Table I  
Cationic O/W Emulsion

	Wt. %
Stearyl Dimethyl Benzyl Ammonium Chloride (21% active) <sup>a</sup>	4.0
Light Mineral Oil	4.0
Stearyl Alcohol	1.6
Water	90.4
	100.0

<sup>a</sup>Rohm & Haas Co., Philadelphia, Pennsylvania.

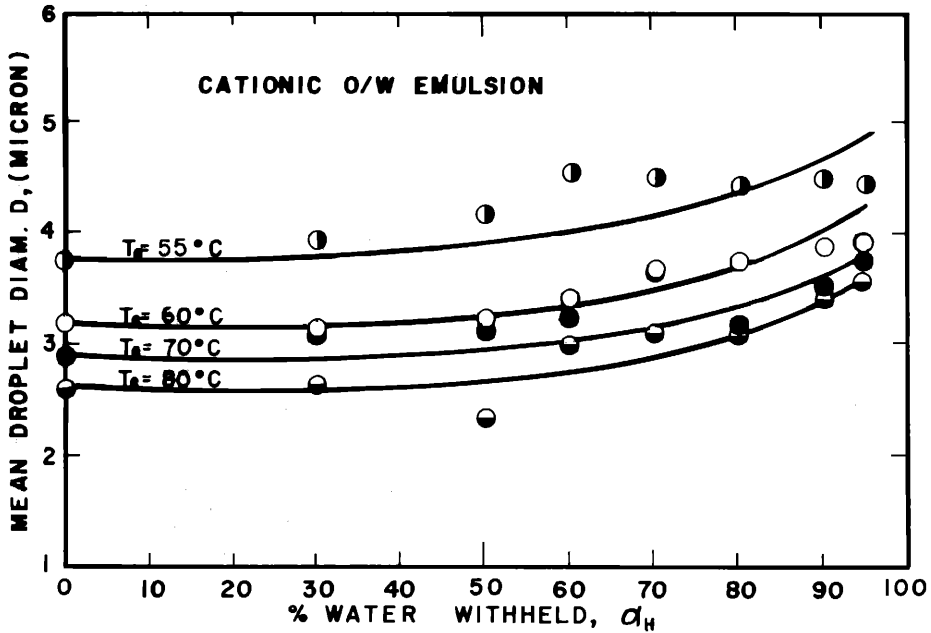


Figure 2. Effect of  $\alpha_H$  and emulsification temperature on droplet size of the cationic O/W emulsion

The external phase of this W/O emulsion is mostly mineral oil. Varying amounts of pure mineral oil were withheld for later dilution at room temperature after completion of the first stage emulsification. It is clear from Figure 3 that LEE worked satisfactorily at an emulsification temperature of 80°C up to  $\alpha_0 = 70$ .

A sharp increase in mean droplet size, indicating a degradation of the emulsion, was observed between  $\alpha_0 = 70$  and  $\alpha_0 = 80$ . From conductivity measurements it was found that the emulsion inverted from a W/O type to an O/W type at  $\alpha_0$  values above 70. Since the intended emulsion was a W/O type, the phase inversion resulted in the formation of coarse emulsions.

The reason for the phase inversion at a high  $\alpha_0$  value is readily understood from the illustration in Figure 4. The dashed line in the figure represents the boundary between the first portion of the external phase used for the emulsification and the second portion used for dilution. As  $\alpha_0$  is increased, the boundary is lowered and the ratio of the first-stage

Table II  
Nonionic W/O Emulsion

	Wt. %
Water	30
Diethyleneglycol Distearate	1
Polyoxyethylene (20) Sorbitan Monostearate <sup>a</sup>	4
Sorbitan Sesquioleate <sup>a</sup>	8
Light Mineral Oil	57
	100

<sup>a</sup>Kao-Atlas Co., Ltd., Tokyo, Japan.

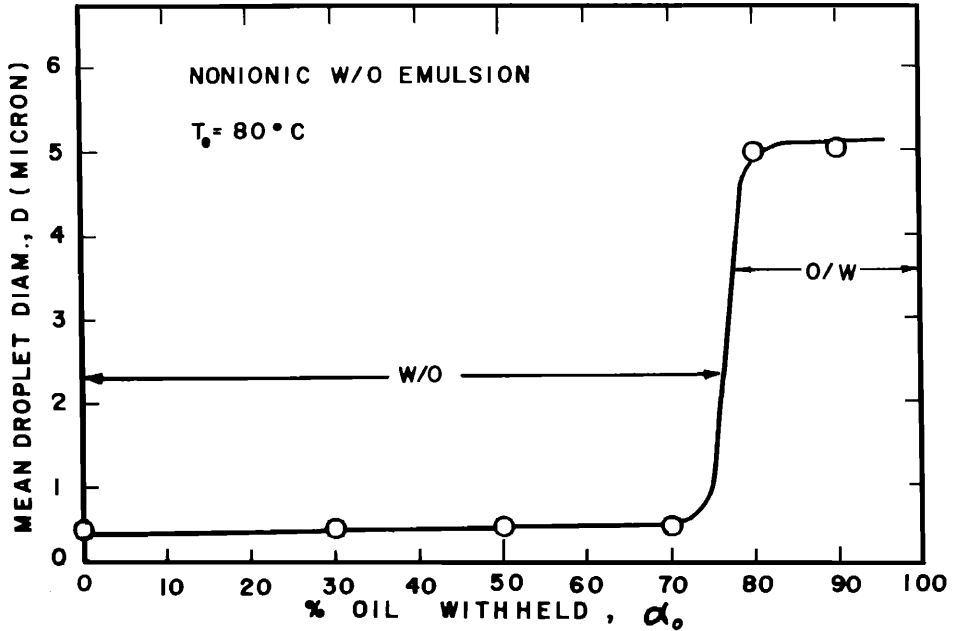


Figure 3. Effect of  $\alpha_o$  on droplet size of the nonionic W/O emulsion

external phase to internal phase reduces accordingly. Eventually the ratio becomes too small to form the desired W/O emulsion concentrate initially and a phase inversion occurs. The subsequent addition of the cold external phase to the inverted emulsions, shown in Figure 3 for  $\alpha_o > 70\%$ , did not reinvert the emulsion and the final emulsion remained O/W type in high  $\alpha_o$  range. Generally, when an inverted emulsion concentrate

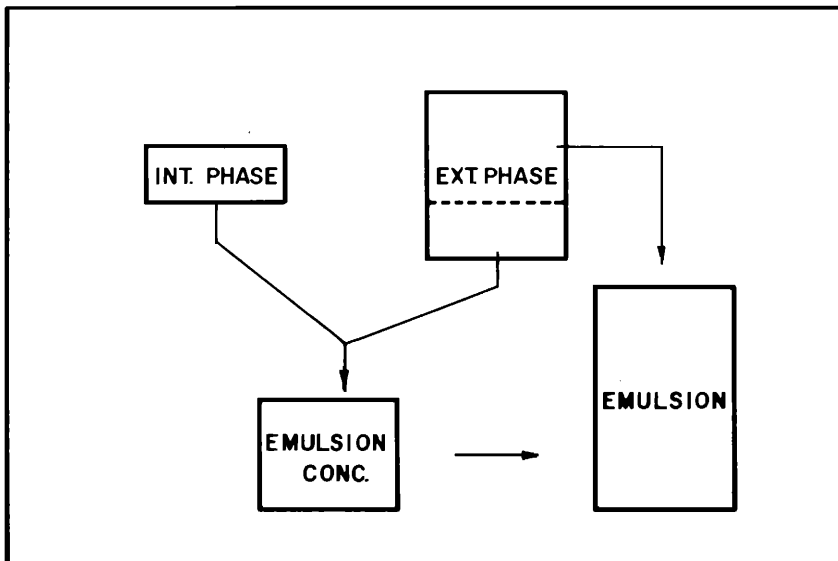


Figure 4. Illustration on  $\alpha$  variation in LEE

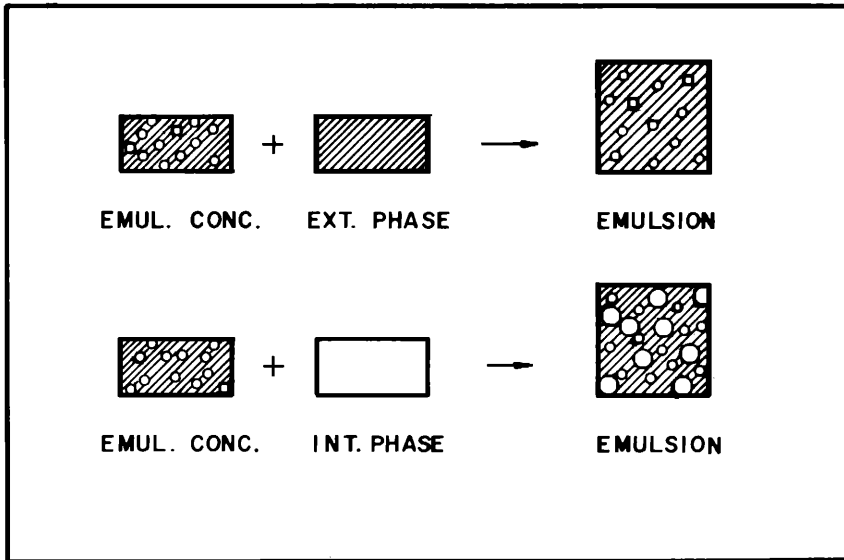


Figure 5. Illustration of adding external phase and internal phase liquids to the emulsion concentrate

fails to reinvert to form the intended type, an emulsion with poor stability or large droplets will form. This happens more frequently with emulsions having a fairly large amount of internal phase and is true with both W/O- and O/W-type emulsions.

Figure 5 illustrates the difference in diluting an emulsion concentrate with an external phase liquid and an internal phase liquid. In general a dilution with an external phase liquid at the second stage is more desirable as dilution proceeds more smoothly and the droplet size of the final emulsion does not change significantly from that of the emulsion concentrate. On the other hand, when an emulsion concentrate is diluted with the internal phase liquid, as illustrated by the lower emulsion of Figure 5, a coarse emulsion or an emulsion with a wider droplet size distribution can result. This is easily understood since, during the addition of the cold phase, the temperature of the batch is lowered considerably and unless a high-shear mixer or a homogenizer is used in the second stage the resulting emulsion will be coarse.

As a general rule in carrying out LEE, it is advisable to add the external phase liquid in the second stage after the completion of the first stage emulsification. If a homogenizing operation is desired, it is generally best to carry it out during the first stage since total batch volume at this stage is smaller and temperature is higher, making homogenization more effective.

In executing LEE, the higher the value of  $\alpha$ , the greater is a conservation of energy expended to process the emulsion. Thus, it is of interest to determine the limit of  $\alpha$  within which emulsions can be prepared without significantly sacrificing the emulsion quality. In most LEE applications, the greater the  $\alpha$  value, the more concentrated and more viscous will be the emulsion concentrate. A practical limit of  $\alpha$  is thus dependent not only on the formulation but also on the process equipment, particularly the geometry of the kettles and the type and power of the mixers. For example, a marine-type propeller mixer can handle low-viscosity emulsions adequately, but not moderate- to high-viscosity emulsions.

Table III  
Nonionic O/W Emulsion

	Wt. %
Light Mineral Oil	10.0
Stearyl Alcohol	3.0
P.O.E. (5.5) Cetyl Ether	1.2
P.O.E. (10) Cetyl Ether	2.0
Propylene Glycol	5.0
Water	78.8
	100.0

A turbine mixer will handle a moderately high viscosity emulsion but probably not a heavy cream. A paddle-type mixer will handle a fairly viscous cream and allows LEE processing at a relatively high  $\alpha$ , although the rate of shear provided by such a low-speed mixer may not be sufficient for an adequate dispersion. Thus, in a practical operation, the limit of  $\alpha$  will be decided by a number of factors.

It is, nevertheless, of interest to determine the upper limit of  $\alpha$  by carrying out experiments up to a very high  $\alpha$  region in the laboratory where a sufficient mixing can be provided. Table III shows an example of a low-solids, O/W emulsion stabilized with nonionic surfactants used in this series of experiments.

A rather surprising result was obtained with this emulsion at high  $\alpha_H$  range as shown in Figure 6. As  $\alpha_H$  increased beyond 50%, the emulsion droplets became smaller and extremely fine emulsions having averaged droplet diameter in submicron range were obtained for  $\alpha_H$  values greater than 70%. The sharp improvement in the emulsion quality at

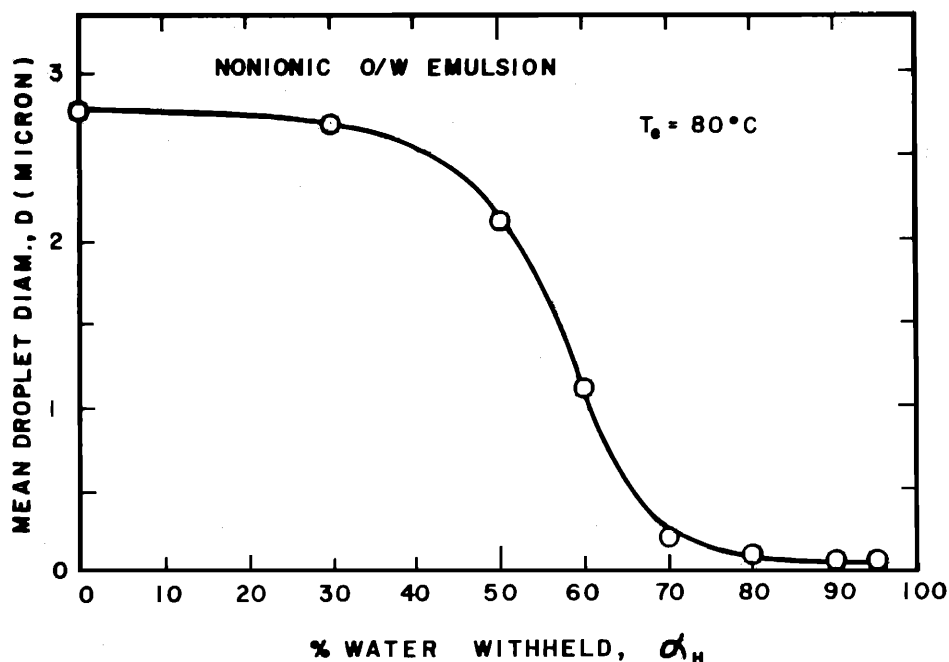


Figure 6. Effect of  $\alpha_H$  on droplet size of the nonionic O/W emulsion



Table IV  
Anionic/Nonionic O/W Emulsion

	Wt. %
Light Mineral Oil	10.0
Stearic Acid	5.0
Cetyl Alcohol	0.2
P.O.E. (5.5) Cetyl Ether <sup>a</sup>	0.6
P.O.E. (10) Cetyl Ether <sup>a</sup>	1.0
Triethanolamine	1.0
Propylene Glycol	5.0
Water	77.2
	100.0

<sup>a</sup>Nikko Chemicals Co., Ltd., Tokyo.

$\alpha_H = 50 \sim 70\%$  is particularly surprising and interesting. This is in contrast to the result of the W/O emulsion shown in Figure 3 where the droplet size shows an increase with  $\alpha_O$ .

The remarkable reduction of droplet size at high  $\alpha$  value was observed, not only in this nonionic O/W emulsion, but also in many other kinds of emulsions. Another example of this effect can be seen from the data obtained with an O/W emulsion stabilized with a mixture of anionic and nonionic surfactants, shown in Table IV.

As it is clearly shown in Figure 7 for emulsions obtained at an initial emulsification temperature of 70°C, a sharp decrease of the mean droplet size of the emulsion occurred when  $\alpha_H$  increased beyond 50%. The viscosities of the emulsions, shown by the broken

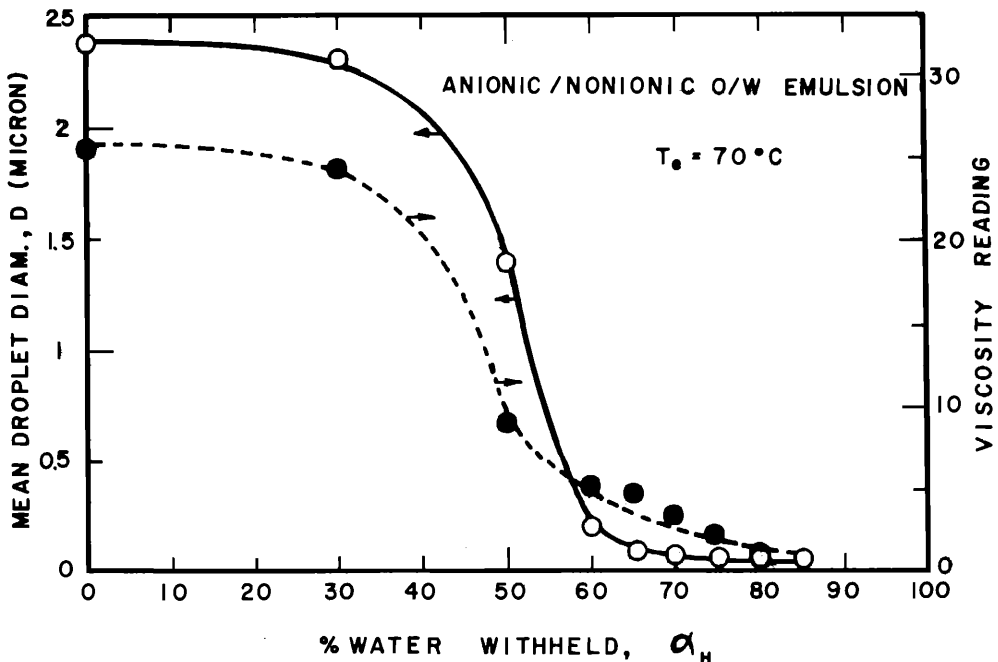


Figure 7. Effect of  $\alpha_H$  on droplet size of anionic/nonionic O/W emulsion

line, also showed a sharp drop at about the same  $\alpha_H$  value. The viscosities in Figure 7 are the viscosities of the final emulsions after they were cooled to room temperature approximately 2 hr after emulsification and they are represented by the Brookfield viscometer reading obtained with No. 3 spindle at 30 rpm. In making this series of emulsions, propylene glycol was placed with the first portion of the water. All other ingredients, including the nonionic surfactants, were initially placed in the oil phase.

The remarkable improvement of the emulsion at high  $\alpha$  values is rather intriguing as it offers a possibility of making better emulsion while conserving energy. In practical applications, emulsification at a high  $\alpha$  value means there is practically no need for cooling the batch after dilution. Not only a great saving of energy is possible, but a substantial reduction in processing time can also be achieved.

Further investigation of this effect revealed that it occurred in many systems, particularly in O/W emulsions. The cationic O/W emulsion of Table I did not show the effect at high  $\alpha_H$  values. However, when this system was reexamined by using a similar but more concentrated cationic surfactant, a very different result was obtained. The revised formula used in this study is shown in Table V.

Stearyl dimethyl benzyl ammonium chloride (80%) is similar to stearyl dimethyl benzyl ammonium chloride (21%), except that the content of active stearyl dimethyl benzyl ammonium chloride is 80% instead of 21%. The constituents of the other components, however, may be significantly different in these two surfactants. The amount of stearyl alcohol was increased in the revised formula to compensate for the lowered viscosity.

The data for this emulsion obtained at emulsification temperature of 80°C are shown in Figure 8. Here again a sharp decrease in the droplet size is observed in the high  $\alpha_H$  region. Interestingly, an optimum point appears to exist at  $\alpha_H$  value of about 83% for this cationic emulsion. This means that above or below 83%  $\alpha_H$ , the emulsions became coarser.

The existence of an optimum point is not completely surprising in view of a previous finding by Lin, Kurihara and Ohta (3). The authors pointed out the importance of a small amount of solubilized water present in the oil phase prior to forming O/W emulsions under a low mixing speed. They discovered that by initially solubilizing a small amount of water in the oil phase containing the surfactant, a remarkable improvement of emulsification efficiency could be achieved in some systems. The amount of the presolubilized water was found to be very critical, as an insufficient or excessive amount would make emulsification less efficient. They suggested that the solubilization was the first step in forming a (W/O)/W type double emulsion which allowed a more efficient emulsification mechanism to function. This mechanism was said to be responsible for the

Table V  
Cationic O/W Emulsion, Revised

	Wt. %
Stearyl Dimethyl Benzyl Ammonium Chloride (80% active) <sup>a</sup>	2.0
Light Mineral Oil	4.0
Stearyl Alcohol	2.5
Water	91.5
	100.0

<sup>a</sup>Toho Chemical Industry Co., Ltd., Tokyo, Japan.

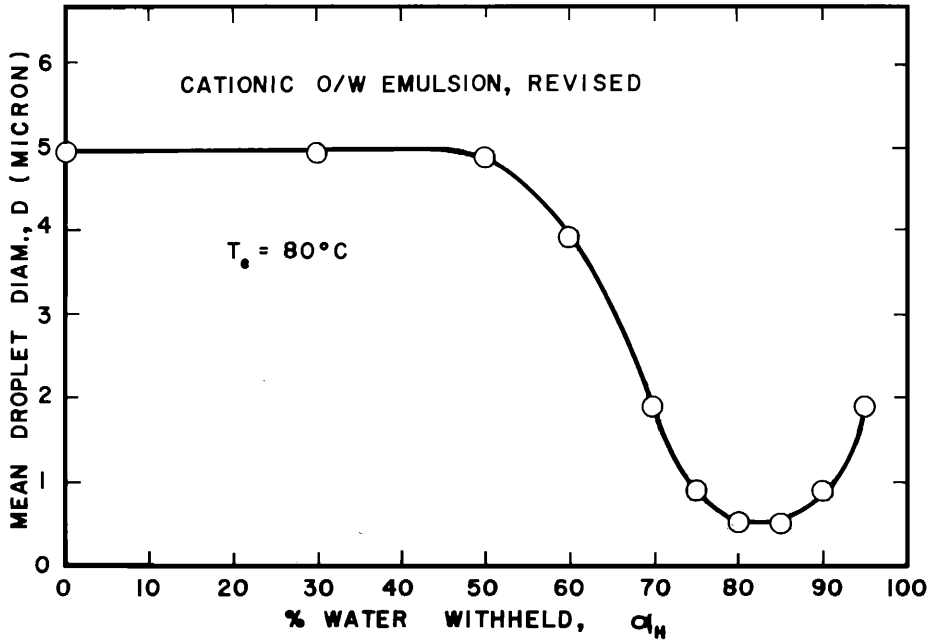


Figure 8. Effect of  $\alpha_H$  on droplet size of cationic O/W emulsion

observed marked difference in the droplet size distributions of the emulsions made with different initial surfactant locations.

In their later work, Lin, Kurihara and Ohta (4, 5) further examined the role of the solubilized water in O/W emulsification. They reported that in many emulsified systems stabilized with various surfactants, the point of optimum emulsification corresponded to the point of maximum solubilization. It was suggested that a solubilization measurement could be utilized to predict the location of the optimum emulsification point.

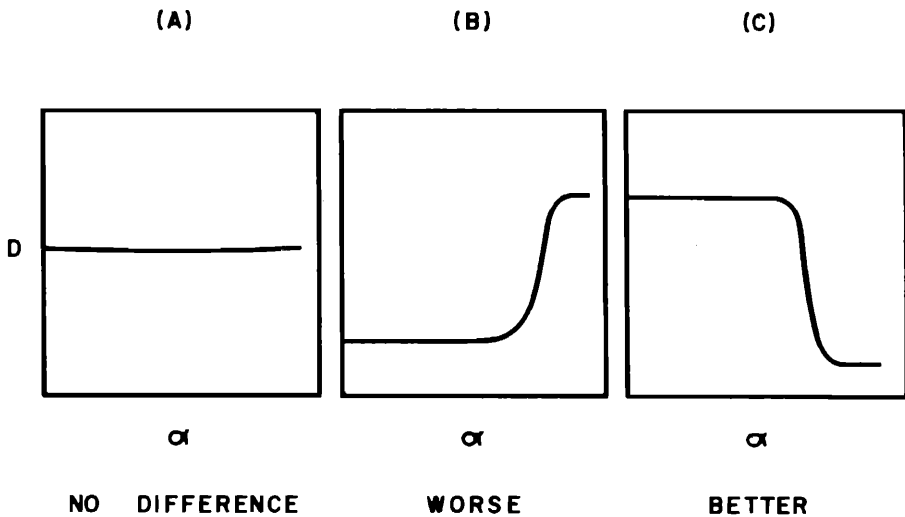


Figure 9. Three types of emulsions

When LEE is carried out for O/W emulsification in a high  $\alpha_H$  region, the amount of the initial water in the emulsion concentrate will be relatively small. It is probable that at some point corresponding to a certain  $\alpha_H$  value, the mechanism mentioned above will function most effectively, resulting in a formation of very fine emulsions.

In summary, the effect of  $\alpha$  varies greatly depending on the emulsion system, but may be roughly classified into the three categories shown in Figure 9. The emulsion (A) shows little or no difference in the emulsion droplet size with respect to  $\alpha$ . Emulsion (B) becomes coarse at a certain  $\alpha$  value due to a phase inversion. In some systems such a degradation of the emulsion is not due to a phase inversion, but rather to the excessive viscosity build-up of the concentrate in high  $\alpha$  region making mixing and first-stage emulsification ineffective. Emulsion (C) illustrates a sharp improvement of emulsification in higher  $\alpha$  range. In some systems, optimum points were observed at a high  $\alpha$  value, which may be regarded as a variation of the type (C).

## CONCLUSIONS

It has been demonstrated that LEE can be applied effectively in commercially processing a wide variety of emulsions. An investigation of the qualities of emulsions made by such a technique revealed that not only the initial emulsification temperature is an important factor, but also the amount of the diluting phase withheld and the extent of mixing. A proper control of these variables will enable one to process a desired emulsion by LEE with a definite economical advantage. The finding of a marked reduction of droplet size in high  $\alpha$  region opens an intriguing possibility of making a very fine emulsion with LEE while conserving a great deal of energy and reducing considerably the required processing time.

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