

Low-energy emulsification. Part VI: Applications in high-internal phase emulsions

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Synopsis

Low-energy emulsification (LEE) is a novel emulsification method by which thermal energy is selectively applied to only a portion of the external or internal phase instead of to the entire emulsion as in conventional emulsification. Although LEE has proven to be extremely energy-efficient and very practical in processing a wide-range of commercial emulsions, it has been difficult to apply the technique to emulsions with large internal phase volumes because of potential irreversible phase inversion. The inversion problem is particularly acute when LEE is carried out at relatively high ratios of unheated phase to heated phase.

The modified LEE technique involves withholding of a portion of the internal phase liquid as well as a portion of the external phase. The emulsion is made in three stages, with application of thermal energy only during the first-stage concentrate preparation.

Tests on O/W emulsions stabilized with anionic and nonionic surfactants indicate that the new method can effectively prevent permanent phase inversion in high-internal phase emulsions and allow LEE processing at higher ratios of unheated phase to heated phase than did the original LEE method. It was discovered that mixing time and mixer rpm as well as the bulk temperature and the size of the withheld phase have significant effects on the mean droplet size of finished emulsions.

INTRODUCTION

Low-energy emulsification (LEE), as originally introduced by Lin, involves a two-stage processing of emulsions (1). A portion of the emulsion's intended external phase fluid is withheld and an emulsion concentrate is first made with application of thermal energy. Generally, the withheld phase (alpha phase) is not heated and serves to cool the bulk during the second stage processing which involves a dilution of the emulsion concentrate. Hence the greater the ratio of the unheated withheld phase to the heated external phase (beta phase), the greater will be energy conservation and cost-reduction. In this work, α and β are defined as the weight fractions of the unheated and heated phases respectively. Subscripts *i* and *e* are used to denote the emulsion's internal and external phases.

It has been demonstrated in pilot plants as well as in many manufacturing plants in different parts of the world that LEE can be extremely useful in processing a wide range of cosmetic, food, and pharmaceutical emulsions with significant reduction of energy and processing costs. The increase in productivity due to a reduction in the cooling

time as the result of adopting LEE can be very substantial. In some cases, the reduction of cooling requirements can be so great that the use of a refrigerated system can be entirely eliminated in designing a new plant (2).

Previous experimental work indicated that when correctly processed, the quality of the emulsions made with LEE was virtually indistinguishable from that of the emulsions made with conventional hot processing (3). Although it is clear that the greater the ratio of α to β , the greater will be the energy conservation, there is a practical limit to the size of the alpha phase because of potential, irreversible phase inversion as pointed out in an earlier work (4).

Uncontrolled phase inversions and the resulting reduction in emulsion stability or coarsening of the emulsion texture are also the main reasons why it has been difficult to apply LEE on emulsions containing relatively high solids or emulsions having internal phases exceeding 30% of the total volume. Emulsions stabilized with nonionic surfactants may undergo phase inversion at temperatures near the phase inversion temperature (PIT). LEE processing may lead to the formation of a coarse emulsion if phase inversion is not controlled (5). On the other hand, when the key variables are properly controlled, LEE can produce very fine emulsions having significantly smaller mean droplet sizes than the emulsions prepared with a conventional high-energy method (6).

The purpose of this work was to test a new technique of double withholding which was designed to expand the utility of LEE beyond low-internal phase O/W emulsions and also to allow LEE processing in a relatively high α range.

In the original LEE method, only a portion of either the external or internal phase is withheld during the initial emulsification process. The new technique now involves withholding portions of both phases. To avoid confusion, the withheld, unheated portions of the internal and external phases will be designated as α_i phase and α_e phase respectively. Similarly, the heated portions of the internal and external phases will be respectively referred to as β_i phase and β_e phase.

In the original method, emulsification is carried out in two stages, including a concentrate preparation stage and a dilution stage as indicated below:

Original LEE

First Stage: Concentrate Preparation

Internal Phase (heated) + $\beta_e \rightarrow$ EC (Emulsion Concentrate)

Second Stage: Concentrate Dilution

EC + $\alpha_e \rightarrow$ E_f (Final Emulsion)

The new LEE technique to be introduced here involves withholding of both α_i and α_e and hence requires a three-step operation as indicated below:

New LEE (Double Withholding)

First Stage: Concentrate Preparation

$\beta_i + \beta_e \rightarrow$ E₁ (First Emulsion Concentrate)

Second Stage: α_e -Phase Addition

E₁ + $\alpha_e \rightarrow$ E₂ (Second Emulsion Concentrate)

Third Stage: α_i -Phase Addition

E₂ + $\alpha_i \rightarrow$ E_f (Final Emulsion)

The advantage of the double withholding technique can be readily seen from Figure 1. In this illustration, the internal phase volume is approximately equal to one third

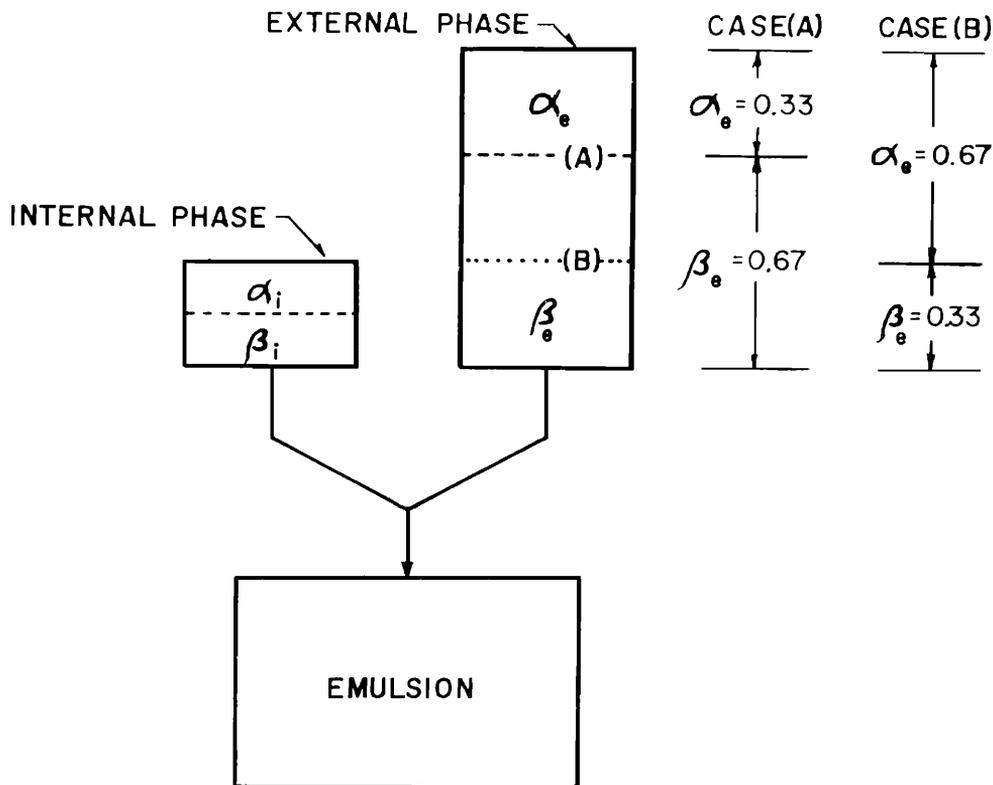


Figure 1. Comparison of two double withholding LEE processes. In both cases internal phase equals one third of external phase; α_i and α_e are withheld internal and external phases respectively; β_i and β_e are heated internal and external phases respectively. Case B is more energy efficient due to a larger withheld external phase α_e . Splitting of the internal phase into α_i and β_i and using only β_i for the initial emulsification reduce the danger of phase inversion.

of the external phase volume. For LEE processing, the external phase is predivided into withheld α_e phase and heated β_e phase. If the division of the external phase were made at $\alpha_e/\beta_e = 0.33/0.67$ as in the Case (A), indicated by a dashed line, the volume of β_e phase would be significantly larger than the total internal phase and generally there would be no great danger of phase inversion. To achieve even greater energy conservation, the division of the external phase may be made at a higher α_e/β_e ratio. In Case (B) shown with a dotted line, the α_e/β_e ratio is chosen at $0.67/0.33$. This means that the β_e phase is now roughly equal to the total volume of the internal phase. From phase volume considerations, there is now a greater danger of unintended phase inversion during the first stage of the emulsion concentrate preparation.

One way to minimize the chance of unintended phase inversion is to add the external phase liquid slowly to the internal phase liquid. In a plant-scale operation, however, such a method is not only time-consuming, but may be unreliable. Controlling the initial surfactant location as proposed by Lin and Lambrechts may be useful in borderline cases, but it is not a sure way to control phase inversion (7).

A better method proposed here is to divide the internal phase into α_i and β_i . If, for

example, the internal phase were subdivided into two equal parts as shown in Figure 1, and if only the β_i phase were used to prepare the emulsion concentrate, the ratio of the external phase to the internal phase volume for the concentrate would now be about two instead of one for Case (B). For Case (A), the ratio would now be approximately four. The substantial increase in the ratio of the external phase volume to the internal phase volume in the first-stage concentrate preparation will greatly reduce the chance of phase inversion during this stage. Since the second stage operation involves only the addition of an external-phase fluid (α_e phase) there is little danger of phase inversion. Although the third stage operation requires addition of the remaining internal phase (α_i phase) there is no great danger of phase inversion since an additional amount of the external-phase fluid was added to the bulk in the second stage operation. Hence, the new double-withholding procedure effectively reduces the danger of irreversible phase inversion during the manufacturing process and allows LEE processing at relatively high α/β ratios to achieve substantial energy conservation.

EXPERIMENTAL

Experiments were carried out in 250-ml glass beakers with no baffles. A six-blade turbine mixer driven by a high-torque, variable speed motor was used to prepare the emulsions. The dimensions of the turbines are indicated in Figure 2. Since the rate of phase addition was found to affect phase inversion, the rates of adding the α_e and α_i phases were carefully controlled by introducing the fluid through a buret with a constant orifice. Other experimental details, including heating and combining the phases, were similar to those of the procedure used in previous reports (3-5). Droplet size distributions were obtained photographically. The mean droplet diameter represents an arithmetic average of approximately 200 droplets. The β_e and β_i phases were heated to 75°C before addition, and the α_e and α_i phases were kept at 26°C before addition.

RESULTS AND DISCUSSION

EFFECTS OF α_e AND α_i

According to an earlier theory advanced by Ostwald, emulsion phase inversion occurs when the internal phase volume exceeds 74.02% of the total volume (8). However, this argument is based on closely packed uniform spheres, which does not necessarily represent a real emulsion. For non-uniform droplets, the critical volume fraction of the internal phase, ϕ , may far exceed the 0.7402 limit without phase inversion.

In commercial processing of emulsions, however, phase inversion depends not only on phase volume but also on many complex factors, including surfactant HLB, processing temperature, method of preparation, mixer geometry, mixer speed, and the rate of phase combination. Generally, the phase-inversion problem becomes more troublesome to control in a plant operation when ϕ values exceed 0.4.

For our experiments, we selected O/W formulations having approximately 50% internal phase volumes. One example of such a formulation is in Table I.

Using the above formulation, one hundred emulsions were prepared with α_e and α_i values ranging from 0 to 0.9. In this series of experiments, all waxy substances as well

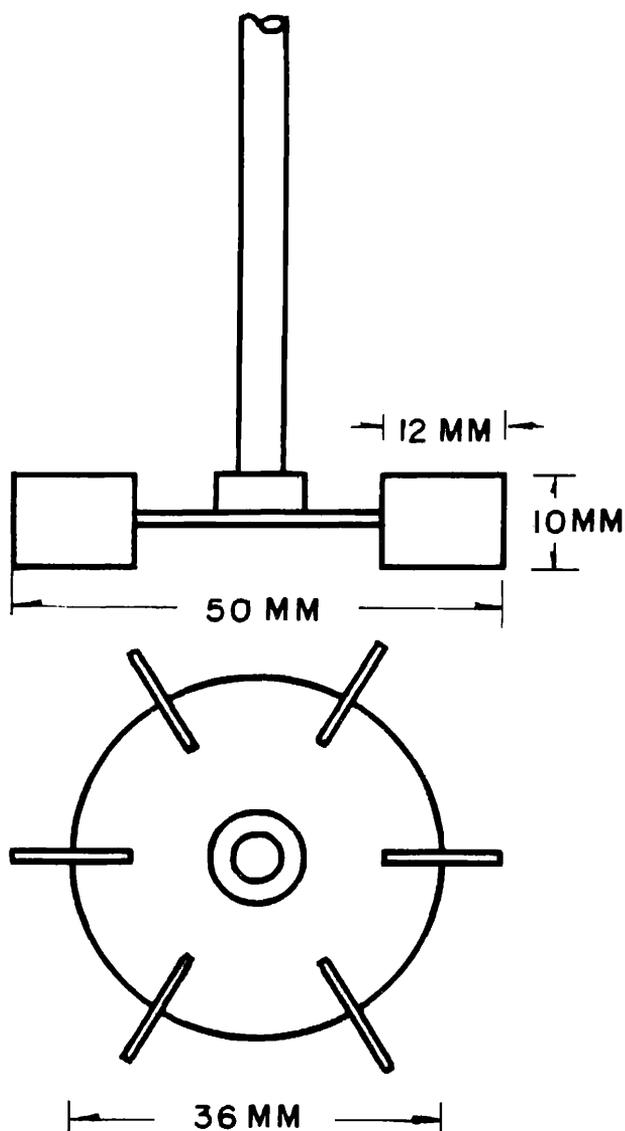


Figure 2. Mixer dimensions.

as the oil-soluble surfactants were initially placed in β_i phase and the water-soluble surfactant as well as the water-soluble polymer were placed in the β_e phase as indicated in Table I. Mineral oil and deionized water were divided into both α and β phases. The rate of addition of β phase was set at 14 ml/min. and the mixer speed was set at 400 rpm. All other process variables were carefully controlled to assure a good reproducibility. The emulsion type for each run was determined with an electrical conductivity tester, and the results are summarized in Table II.

The test formulation contains 48.5% of the oil phase by weight (>50% by volume). By a deliberate choice to test the utility of the modified method, this formulation does not lend itself to easy LEE processing. The data presented in the first row of Table

Table I
Anionic O/W Emulsion

	Wt. %	Phase
Oil Phase (Internal Phase)	40.0	β_i and α_i
Mineral oil	3.0	β_i
Stearic acid	2.0	β_i
Glyceryl stearate SE	1.0	β_i
Cetearyl alcohol	2.0	β_i
Sorbitan sesquioleate	0.5	β_i
Triethanolamine		
Aqueous Phase (External Phase)		
Deionized water	50.9	β_e and α_e
Sodium lauryl sulfate	0.4	β_e
Carbomer 934	0.2	β_e
Total	100.0	

Table II
Type of Emulsions Prepared at Varying α_e and α_i *

$\alpha_i \backslash \alpha_e$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	O/W	O/W	W/O							
0.1	O/W	O/W	O/W	W/O						
0.2	O/W	O/W	O/W	W/O						
0.3	O/W	O/W	O/W	W/O						
0.4	O/W	O/W	O/W	O/W	O/W	O/W	W/O	W/O	W/O	W/O
0.5	O/W	W/O	W/O	W/O						
0.6	O/W	W/O	W/O							
0.7	O/W	W/O	W/O							
0.8	O/W	W/O								
0.9	O/W									

* All emulsions were prepared in 250-ml Griffin beakers. The batch size was 200 g. α_i and α_e were kept at 25°C while β_i and β_e were heated to 75°C before addition. The bulk was mixed at 400 rpm for 5 min each time during the first-, second-, and third-stage operations. Conductivity was measured at the end of the third-stage addition. Most of the W/O emulsions formed were quite unstable and separated within an hour. Most O/W emulsions formed were relatively stable with no visible separation within one hour.

II at $\alpha_i = 0$ represent the original LEE method. Examination of the data indicates that the O/W emulsion inverts to a relatively unstable W/O type when the amount of withheld water exceeds 10% of the total aqueous phase.

By inspecting the data in the second row, third row and further rows down, it is clear that withholding of the internal phase liquid, α_i , effectively prevented phase inversion and expanded the useful range of LEE processing.

When the data in Table II are plotted on a graph, as shown in Figure 3, the boundary of phase inversion shows a roughly straight-line relationship. For this particular O/W emulsion, the relationship can be approximately expressed by the following linear equation:

$$\alpha_i = 1.2\bar{\alpha}_e - 0.15$$

where $\underline{\alpha}_i$ = minimum α_i value for O/W emulsion)

$\bar{\alpha}_e$ = maximum α_e value for O/W emulsion

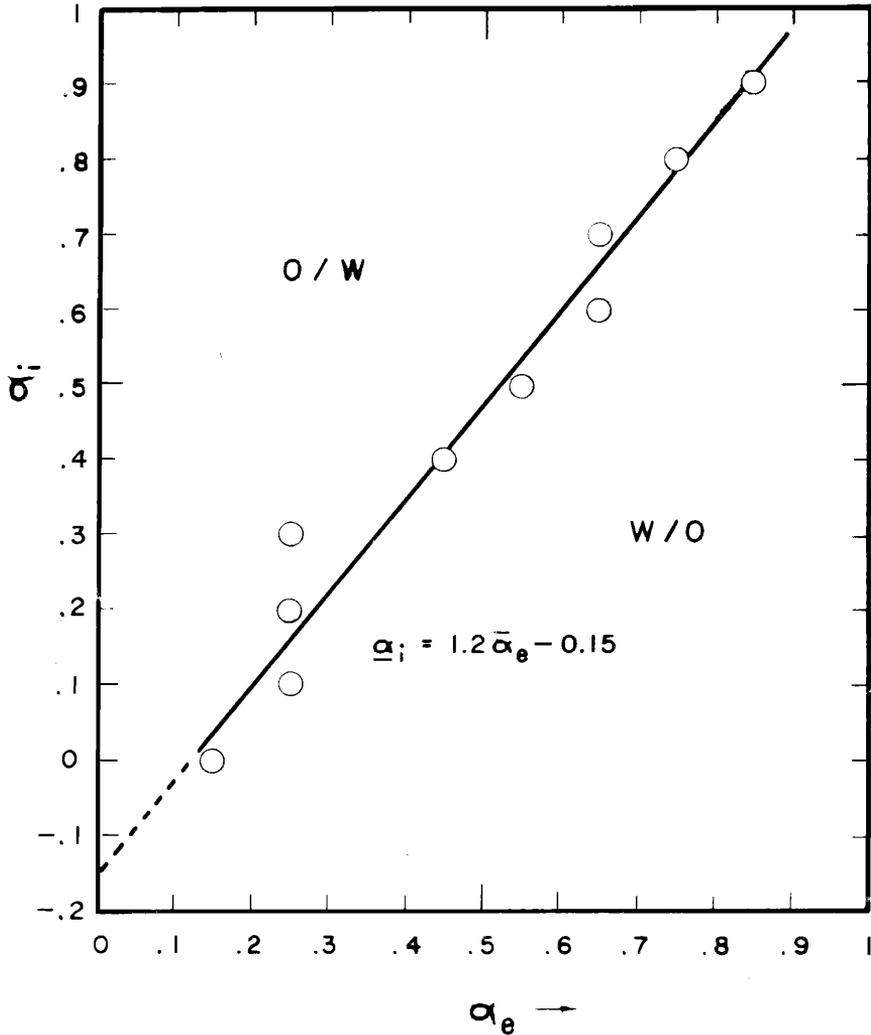


Figure 3. Relationship between amount of external phase withheld (α_e) and the minimum amount of internal phase which must be withheld (α_i) to produce O/W emulsions. Emulsions below line are W/O and above are O/W.

The slope of the line (1.2) in Figure 3 reflects the effectiveness of the double-withholding technique. In this case, the smaller the slope of the line, the greater is the effectiveness of withholding α_i in preventing phase inversion to form W/O type emulsions.

Clearly, when the y-intercept is zero or greater, no O/W type emulsion can be formed with either the conventional emulsification method or the original LEE method at any α_e value and the use of the double-withholding technique becomes essential in making an O/W emulsion.

It is to be noted here that the data in Table II represent only the emulsion type without regard to emulsion quality or droplet sizes. LEE processing at different α_e and α_i values

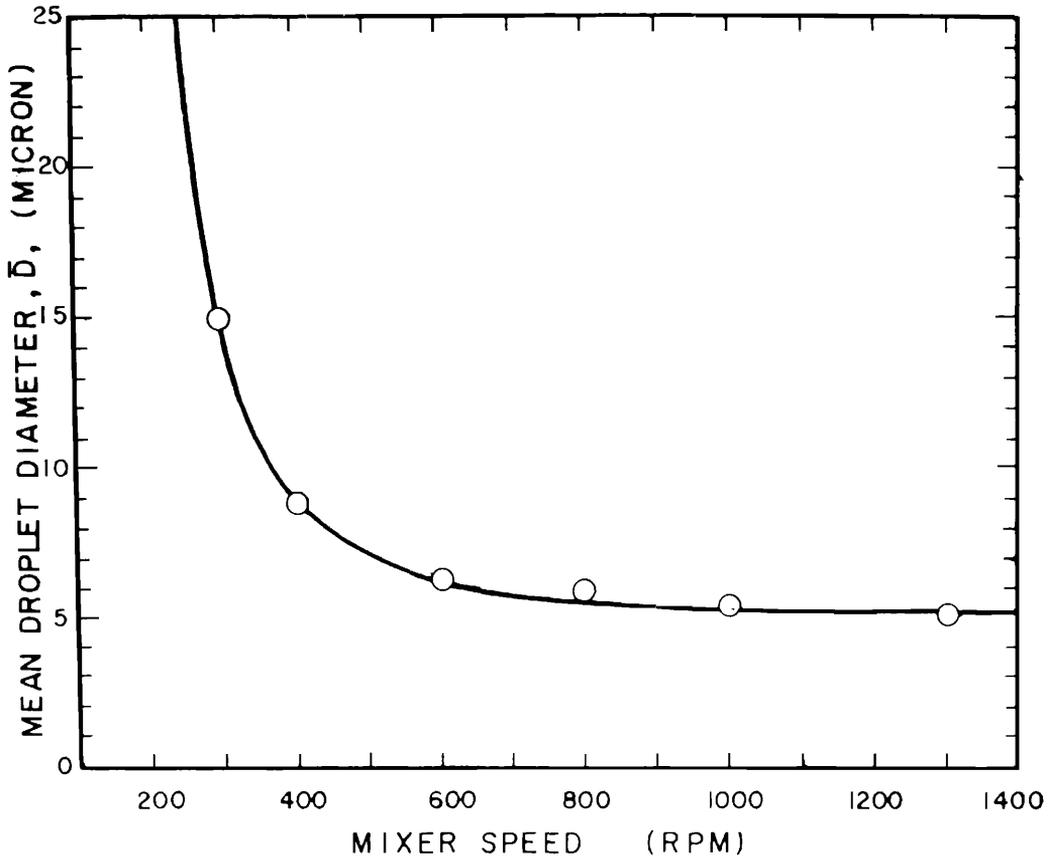


Figure 4. Mean droplet size in a final emulsion as a function of mixing speed. (\bar{D} represents the mean droplet diameter of a final emulsion having the composition shown in Table I, immediately after the E_2 emulsion concentrate was mixed with α_1 for 8 minutes at 27°C . The E_2 emulsion concentrates were prepared identically at $\alpha_c = 0.2$, $\alpha_i = 0.8$, and cooled to 27°C before the addition of α_1 . The E_2 emulsion concentrate had a mean droplet size of 2.5 microns.)

represent a significant variation in processing conditions and thus a large variation in the properties of the emulsions can be expected. In addition to α values, emulsion temperature, mixing time, and the rate of mixing can also have significant influence on the final emulsion.

EFFECTS OF MIXING

The major difference between the modified LEE and the original LEE is the third-stage operation in the new technique which involves an addition of α_1 phase into the emulsion concentrate, E_2 . Although adding oil into a preformed O/W emulsion may represent a radical departure from a normally employed emulsification method, there are no theoretical grounds to believe that such a procedure would not produce a commercially-acceptable emulsion.

Actually, the addition of an oil into an O/W emulsion is not really an unusual industrial practice since in making most hand creams, the cold fragrance oils are often directly added to preformed O/W emulsions at bulk temperatures around or below 40°C .

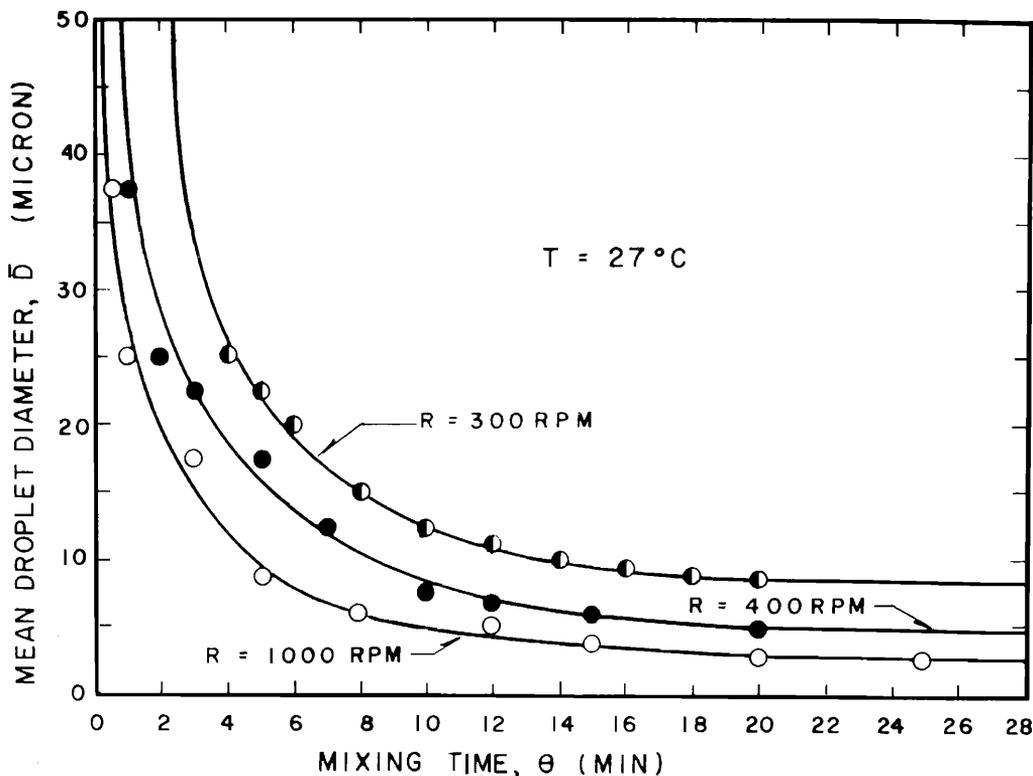


Figure 5. Mean droplet size as a function of mixing speed and time after α_i addition. (\bar{D} represents the mean droplet diameter of a final emulsion having the composition shown in Table I, immediately after the E_2 emulsion concentrate was mixed with α_i at mixer speed R and mixing time θ . The E_2 emulsion concentrates were prepared identically at $\alpha_c = 0.2$, $\alpha_i = 0.8$, and cooled to 27°C before the addition of α_i . The E_2 emulsion concentrate had a mean droplet size of 2.5 microns.)

The important question here is how long and at what speed the final emulsion, E_6 , must be mixed after the addition of the α_i phase. Addition and mixing in of the α_i phase results in not only a size reduction of emulsion droplets but also mass-transfer of surfactants and other components between the newly formed interfaces. Microscopic examinations indicate that as α_i phase is added to the E_2 emulsion, the size distribution initially shows dual peaks. With further mixing, the size distribution initially shows dual peaks. With further mixing, the emulsion droplets change to a near-Gaussian distribution.

The rate at which droplet-size reduction takes place depends heavily on the mixing conditions. As can be seen from Figure 4, the mixer speed is a very important factor, as mixing of an E_2 emulsion concentrate below 300 rpm produced extremely coarse final emulsions. In this example, however, increasing the mixer rpm beyond 1,000 does not appear to accomplish further size reduction within an eight-minute period. The effect of mixing speed can be also seen from the data presented in Figure 5, which shows both the rpm and mixing-time effects. As expected, size reduction is more rapid at a higher mixing speed. Since the mean droplet size of the E_2 emulsion before the addition of α_i was about 2.5 microns, the data indicate that it would require about 20

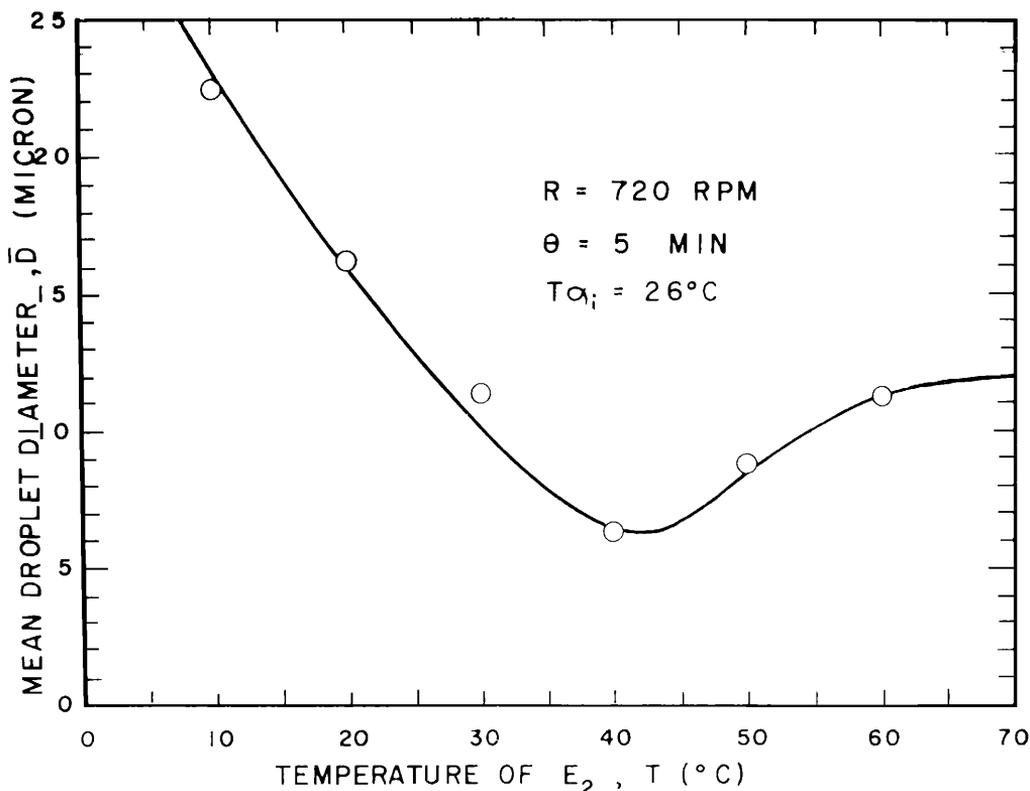


Figure 6. Effect of initial E_2 temperature on mean droplet diameter. (\bar{D} represents the mean droplet diameter of a final emulsion having the composition shown in Table I, immediately after the E_2 emulsion was mixed with α_i at 720 rpm for 5 minutes. The temperature of the α_i phase was 26°C . The E_2 emulsion concentrates were prepared identically at $\alpha_c = 0.2$, $\alpha_i = 0.8$, and cooled to 26°C . Each E_2 emulsion concentrate was heated or cooled to the temperature indicated on the abscissa before α_i addition. The E_2 emulsion concentrate had a mean droplet size of 2.5 microns.)

minutes of mixing time at 1,000 rpm to reduce α_i droplets to the same average size as E_2 droplets.

EFFECT OF TEMPERATURE

Temperature is, of course, a very important factor in all emulsion processing. An example showing the effect of the initial temperature of the E_2 emulsion on the mean droplet size of the final emulsion is shown in Figure 6. It is interesting to note that the mean droplet size shows a minimum at an E_2 temperature of about 40°C . It is believed that the existence of the minimum point is probably due to a viscosity effect. At a constant mixer rpm, size-reduction is most efficient at a moderately high viscosity range for a shear-thinning, time-dependent emulsion. As can be seen from the viscosity data in Figure 7, the viscosity of the emulsion drops sharply at around 50°C , resulting in a lowered shear action by the mixer rotating at a constant rpm. On the other hand, as the temperature drops below 40°C , the increased viscosity and the yield value probably make the mixing less efficient, resulting in the formation of coarser emulsions.

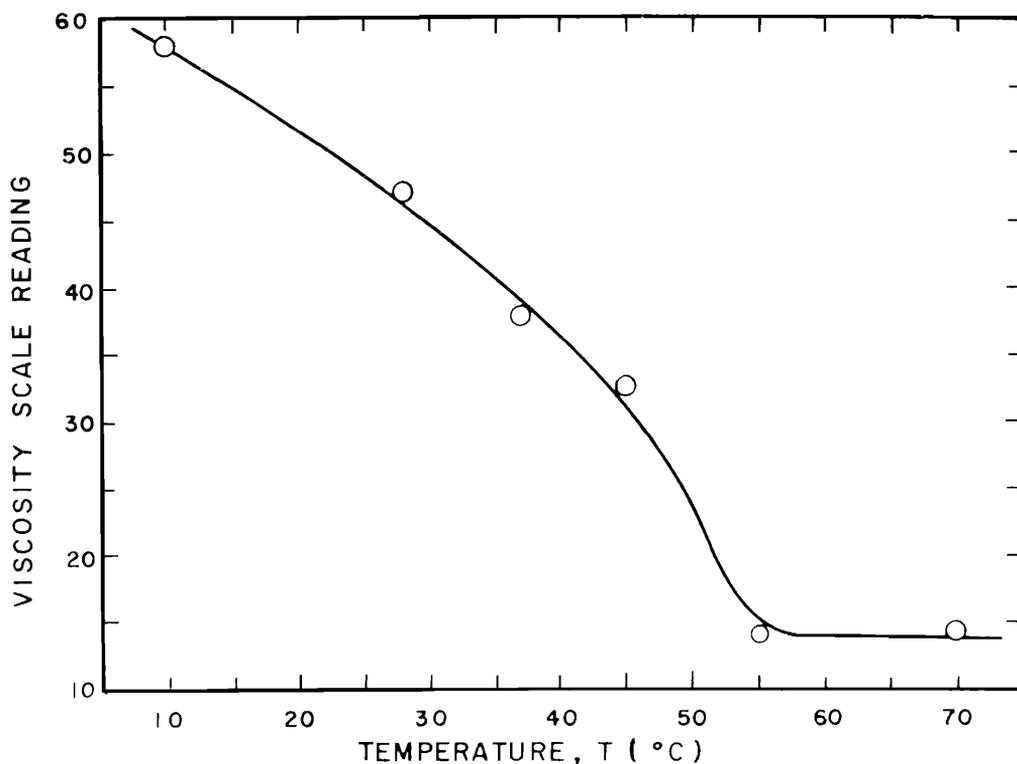


Figure 7. Effect of temperature on the viscosity on an E_2 emulsion concentrate. (Viscosity is the scale reading on a Brookfield Sychroelectric Viscometer, model LVT, spindle #4, at 0.6 rpm. The E_2 emulsion concentrate was prepared at $\alpha_e = 0.2$, $\alpha_i = 0.8$, based on the composition in Table II and cooled to 26°C. The emulsion concentrate was heated or cooled to the indicated temperature before viscosity measurements.)

This is another example showing a probable reason why sometimes one can make a finer emulsion with LEE than using a conventional hot emulsification method (6).

CONCLUSIONS

Experimental data presented here indicate that the modified LEE technique can be used to process O/W emulsions with relatively large internal phases or to carry out LEE in a higher α range without encountering the usual complication of unintended phase inversion.

Although all experimental data presented here were obtained on laboratory scale equipment, some pilot plant work on different formulations was carried out to demonstrate the feasibility of using such a technique on a commercial scale. When carried out at correct α_i and α_e values, emulsification proceeded very smoothly to yield stable emulsions with very fine texture.

In addition to saving more energy, the new technique is even less susceptible to unintended phase inversion, as can be seen from the data in Figure 3; it can be used

to control the phase inversion problem in a commercial operation even if energy conservation is not the purpose.

The success of adopting the method, however, may be dependent on proper selection of the size of α_c and α_i as well as the mixing equipment and mixing conditions. As a rule, α_c and α_i values should not be selected at points too close to the phase-inversion boundary line.

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