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# Dynamics of Transitional Phase Inversion Emulsification: Effect of Addition Time on the Type of Inversion and Drop Size

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Emulsification processes are very sensitive to the time scale during which the dispersed phase is introduced into the continuous phase. A series of experiments were conducted across a transitional phase inversion path, which often leads to formation of nanoemulsions, with the speed of incorporation of the second phase (water) into the first phase (oil) being altered. The optimum condition could only be achieved if the optimum composition was maintained for a critical time. A slow addition (addition time > 60 s) of water to the oil allows the transitional phase inversion to become operative, leading to formation of sub-micrometer droplets. A very fast addition of the water phase (<5.0 s) caused the catastrophic phase inversion mechanism to become dominant, leading to formation of rather large drops. In the intermediate range of addition time, 20–40 s, both inversion mechanisms have contributed to drop formation, at least locally, and as a result skewed or bimodal drop size distributions were formed. The results indicate that while spontaneous emulsification is fast, it is not instantaneous. At a low surfactant concentration, the droplet size was only slightly affected by the rate of addition.

## 1. Introduction

Emulsions are dispersion of an immiscible liquid in another in the form of droplets with the aid of a surfactant, and emulsification is the science and technology of bringing these three components together to form an emulsion. While the properties of the emulsion-forming components used in an emulsion can be determined with a high accuracy, the properties of the final emulsions do not lend themselves easily to predictions and will change significantly with the type of emulsification process used. Perhaps for the same reason, emulsification is still considered as a sophisticated science by many simply because of ambiguities involved in the interpretation of phenomena occurring during this process despite recent developments in understanding of emulsification processes.<sup>1</sup>

Emulsification processes can be carried out in different ways. There are several ways that emulsion components can be brought together.<sup>2</sup> While manual shaking or the use of mechanical shakers are traditional techniques widely used for laboratory or small-scale preparation, more effective techniques are required for making stable emulsions at large-scale production. Commercial emulsions are produced by using a number of emulsification techniques ranging from the use of turbine mixers, rotor-static mixers, high-pressure homogenizers, and ultrasonic devices. In many emulsification processes, all ingredients are instantaneously exposed to a high-intensity mixing or homogenization, and in most instances, the history of emulsion morphology is not known. It is not clear how components are brought into contact in an emulsification chamber in a short period of time and whether equilibration is achieved. The poor reproducibility in some of these processes may point to the lack of equilibration. Full equilibration of water–oil–surfactant systems may require a finite period of time during which the three components, if not more, should be kept in contact. The equilibrated or delayed emulsification allows equilibrium to be

reached between surfactants in different phases and makes the emulsion system less vulnerable to start-up procedures.<sup>3</sup> This is one of the reasons that some emulsification processes in industry, as well as in academia, are carried out under pre-equilibrated conditions.

In many emulsification processes, a fine emulsion can only be achieved if emulsion formulation/composition changes in the course of emulsification time. *Phase inversion emulsification* is a technique in which emulsion composition is directed toward conditions at which formation of fine drops, as well as complex ones,<sup>4,5</sup> is enhanced. This technique has been shown to be an applied and powerful method to produce emulsions with superior properties.<sup>6</sup> The size of droplets in typical equilibrated emulsions is mainly determined by the intensity of mechanical agitation and interfacial properties of the surfactant such as interfacial tension, as well as physical properties of the oil and water. In dynamic methods such as phase inversion emulsification, however, the emulsion properties would change with time and therefore should be considered as a dynamic property.<sup>3</sup>

In a typical phase inversion process, emulsification starts with a given emulsion morphology that inverts to an opposite emulsion by variations in emulsion properties. There are two types of phase inversion, *catastrophic phase inversion* and *transitional phase inversion*.<sup>7</sup> Catastrophic phase inversion (CPI) usually occurs when the starting emulsion is an *abnormal one*; emulsion whose morphology does not correspond to its formulation.<sup>6,8</sup> Therefore, the inversion to proper (normal) emulsion morphology is the ultimate fate. CPI occurs via a large increase in the rate of drop coalescence so that the balance between the rate of drop coalescence and drop break up cannot be maintained any further.<sup>9</sup> This can be brought about by adding the dispersed phase, a surfactant or a salt, as well as altering the emulsification temperature or any parameter that can significantly enhance drop coalescence. Drops formed via CPI are usually above micrometer. Sub-micrometer droplets may only form if CPI of abnormal to normal emulsion occurs in the vicinity of the locus of ultralow interfacial tension.<sup>9</sup> Transitional phase inversion (TPI) occurs when the curvature of the oil–water interface gradually changes from positive to negative,

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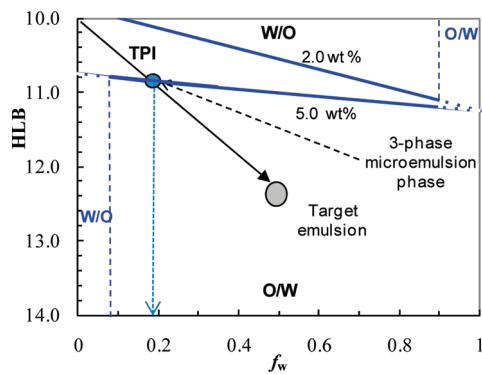
passing through a zero curvature at the inversion point. This is associated with a shift in the surfactant nature from water-soluble to oil-soluble, or vice versa. At the inversion point, the surfactant has similar affinity toward both phases. As a result, the interfacial tension passes through an ultralow value.<sup>10–12</sup> This results in formation of emulsions with very small drop size, sometimes called miniemulsions and nanoemulsions.<sup>13</sup> Transitional inversion occurs by variation in the surfactant HLB (hydrophilic–lipophilic balance), caused by altering temperature (phase inversion temperature, PIT)<sup>14</sup> or by altering surfactant properties via addition of a salt or a surfactant with a different HLB (isothermal or composition phase inversion).<sup>15,16</sup> HLB indicates the degree to which a surfactant is water-soluble or oil-soluble.<sup>17</sup>

Before transitional phase inversion can occur, the surfactants in both phases must diffuse toward the interface, adsorb at the interface, and conform into a mixed surfactant layer at the optimum conditions. The rate of diffusion of the surfactants depends on many parameters, including their size, the viscosity of the phase, and the intensity of mixing, etc. For oil-in-water emulsions containing a pair of water-soluble and oil-soluble surfactants, it was found that the addition of the water phase containing the water-soluble surfactant to the oil phase containing the oil-soluble surfactant may produce very fine emulsions if it is associated with interfacial tension lowering in the course of addition.<sup>2</sup> The rate of addition of the second phase is of paramount importance in achieving an emulsion with desired properties. This is because the dynamic of phase inversion emulsification is very fast, and the emulsion properties change quickly with further addition, contrary to some conventional emulsification methods. Therefore it is important to find and maintain a semiequilibrated state in the course of emulsification during which sufficient surfactant diffusion/adsorption can occur and thus drop rupturing is enhanced. In this research, we aim to investigate how the speed of addition of the second phase to the first phase for the same protocol can affect the final size of drops. This is carried out by the precise control of the rate of addition of the second phase to the emulsion using a syringe pump.

## 2. Experimental Section

**2.1. Chemical.** Cyclohexane was used as the oil phase. Two grades of Igepal (polyoxyethylene nonylphenylether, NPE), supplied by Aldrich, were used as surfactants. They are Igepal co520 and Igepal co720 with nonyl phenol ethoxylate chain lengths of 5 (NPE5) and 12 (NPE12), respectively. NPE5 has the HLB of 10 and is an oil-soluble grade. NPE12 has a HLB of 14.2 and is a water-soluble grade.

**2.2. Apparatus.** Emulsifications were carried out in a 0.25 L jacketed glass reactor with a diameter of 7 cm equipped with four baffles, with the width of 0.5 cm, equally spaced at 90° intervals, a four-blade flat turbine with a diameter of 3.0 cm. The stirring speed was controlled at 500 rpm during emulsifications. The emulsification temperature was controlled at 22 °C. The second phase was added to the vessel using a syringe pump at different feed rates (i.e., addition time or  $t_{\text{add}}$ ). The shortest addition time was an instantaneous one, which was arbitrarily taken as the addition time of 2 s, and the slowest one was 1200 s. In most experiments, mixing was continued for around 1200 s after the completion of addition. The water phase contained 0.50 wt % potassium chloride. Emulsion inversions were determined from measurements of emulsion conductivities and where a large change in conductivity occurred.



**Figure 1.** Simplified dynamic phase inversion map for water–cyclohexane–(NPE5 and NPE12) system for different surfactant concentrations ( $[S] = 2.0$  and 5.0 wt %).

**2.3. Target Emulsion.** The target emulsion was defined as a model cyclohexane-in-water (O/W) emulsion with a volume ratio of oil to water equal to 1 ( $f_w = 0.50$ ). Volumes of 50 mL of cyclohexane and 50 mL of deionized water were used. Each phase contained the same percentage of an appropriate grade of the surfactant, NPE5 or NPE12. This produced an HLB value of 12.3, which can provide a good stability for the target cyclohexane/water (O/W) emulsion. Note that the stability of emulsions depends on the drop size that is determined by the emulsification method. Equilibrated emulsification of the target emulsion, as explained in the next section, produced a rather stable emulsion which underwent phase separation by 25% only during 1 week. Weight averages were used for calculation of the average HLB. Application of a mixture of oil-soluble and water-soluble surfactants can enhance drop stability by producing fine emulsions via interfacial tension lowering. However, a very low interfacial tension may adversely affect the stability of emulsions by boosting drop coalescence. In an extreme case, an ultralow interfacial tension may result in the formation of an emulsion which is extremely unstable and susceptible to instantaneous phase separation. Note that the formulation adopted in this research is similar to that described in previous works,<sup>2,16</sup> but the emulsion composition and the mixing system used in this work are different.

**2.4. Dynamic Phase Inversion Map.** To be able to track the time evolution of phase inversion emulsification for the cyclohexane–water–NPE system, a dynamic phase map, on which the location of the target emulsion is specified, was prepared, as shown in Figure 1. The abscissa in this figure indicates the water volume fraction ( $f_w$ ). The HLB at which transitional phase inversion (TPI) occurs is called  $\text{HLB}_{\text{op}}$ . The locus of the optimum HLB value is shown by solid lines for different surfactant concentrations. The locus of transitional phase inversion for any phase ratio was determined by altering the surfactant HLB of the emulsion by adding oil and water with the same ratio as that of the emulsion. Both added phases, however, contained the appropriate surfactant with the same concentration as that of the emulsion so that the overall concentration of the surfactants in the emulsion was kept constant. The addition was continued with an extremely low rate until phase inversion to opposite emulsion occurred. The runs were repeated for different surfactant concentrations. The locus of inversions obtained for a given surfactant concentration is in fact a zone or a region. The lines shown in Figure 1 represent average values for the corresponding regions. These lines are usually sloped due to higher solubility of nonionic surfactants in the oil phase. The transitional line divides the domains of normal O/W and W/O emulsions; O/W emulsions

below the transitional line ( $\text{HLB} > \text{HLB}_{\text{op}}$ ) and W/O emulsions above the transitional line. The range of HLB at which TPI occurs varies with surfactant concentration. The domain of catastrophic phase inversion (CPI) from normal W/O to abnormal O/W morphology and from normal O/W to abnormal W/O morphology are shown by dotted vertical lines at the extreme  $f_w$  values. The boundaries of catastrophic phase inversion from abnormal morphologies to normal ones are very vague and depend strongly on the surfactant concentration and mixing conditions (not shown). It is evident that the target formulation corresponds to a Winsor-1 O/W emulsion, which is defined as a surfactant-rich aqueous phase in equilibrium with an excess oil phase.

**2.5. Phase Inversion Emulsification Procedures.** Phase inversion (PI) experiments started with the intended dispersed phase (oil) initially placed in the stirred vessel, followed by the gradual addition of the water phase to the mixing vessel using a syringe pump. The water-soluble and oil-soluble surfactants were placed in the water phase and oil phase, respectively. Because the surfactant mixture (at  $\text{HLB} = 12.30$ ) favored formation of O/W emulsion, the addition of the water phase over time resulted in a phase inversion to O/W emulsion morphology. This process is characterized by a variable-HLB operating line and represents a transitional phase inversion if the surfactant concentration is relatively high (i.e.,  $[S] \geq 3.0$  wt %) but a catastrophic phase inversion if the surfactant concentration is low ( $[S] \leq 2.0$  wt %).<sup>16</sup>

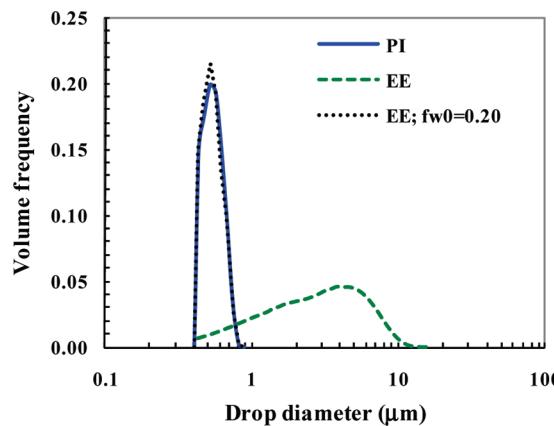
**2.6. Drop Size Measurement.** The average diameter and distribution of the oil drops in O/W emulsions were obtained by a laser diffraction method (Coulter LS130). Samples were diluted with water, which was saturated with cyclohexane and contained 0.25 g/L of an anionic surfactant: sodium lauryl sulfate. The drop sizes were checked by processing images obtained from emulsions by a video-camera connected to an optical microscope and computer. Observation of emulsion morphology was also made by the optical microscope system. The reproducibility of results was satisfactory but improved with increasing addition time.

**2.7. Interfacial Tension Measurement.** Measurements were carried out with Du Nouy tensiometer. The oil phase containing NPE5 was gently placed on the water phase containing NPE12, and the interfacial tensions between the water and cyclohexane phases were measured as a function of time.

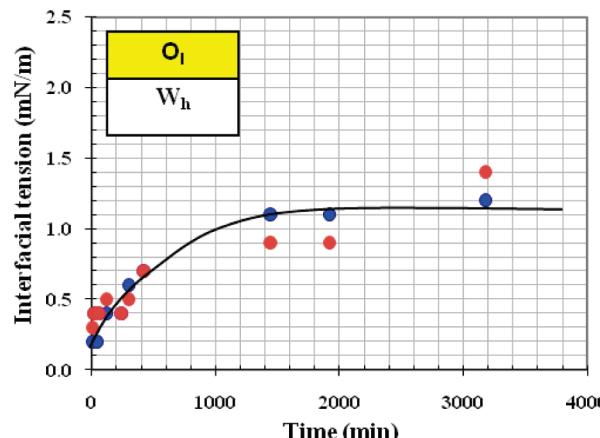
### 3. Results and Discussion

**3.1. Equilibrated Emulsification versus Transitional Phase Inversion Emulsification.** The equilibrated emulsions were produced according to the following procedure; the two phases each containing the appropriate surfactant were placed in a sealed flask and stored for 48 h while being gently shaken. The resulting mixture was then placed in the emulsification vessel and stirred for 1200 s. No significant variations in the emulsion drop size were observed for storage beyond 48 h.

The size distribution of the equilibrated emulsion is compared with that of an emulsion obtained using the PI method in Figure 2. The addition time for the PI method was 1200 s. The PI method produced by far smaller drops with sharper size distribution than equilibrated emulsification of the target emulsion ( $f_w = 0.50$ ). This is because equilibrated emulsification occurred at the emulsion HLB of 12.30 (HLB of the target emulsion), which has an equilibrium interfacial tension of around 1.3 mN/m, as shown in Figure 3. It appears that semiequilibrium is established after 24 h even in the absence of mixing. This is consistent with the equilibrium interfacial tension for a similar



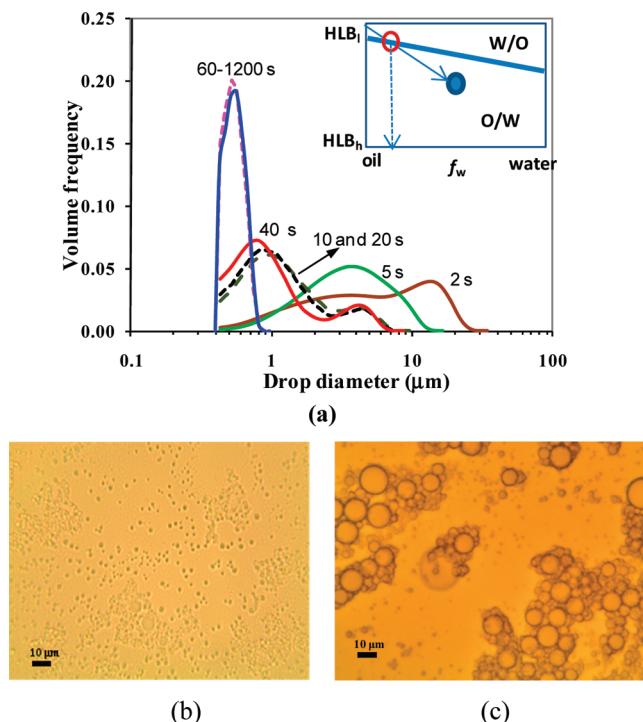
**Figure 2.** Drop size distribution of the final emulsions prepared with 5 wt % surfactant using equilibrated emulsification (EE) and phase inversion (PI) methods. The EE method with  $f_{w0} = 0.20$  indicates that equilibration was achieved with an initial water phase ratio of  $f_{w0} = 0.20$  followed by the addition of the remainder of water ( $f_w = 0.50$ ,  $\text{HLB} = 12.3$ , and  $t_{\text{add}} = t_{\text{emulsification}} = 1200$  s).



**Figure 3.** Variations in interfacial tension as a function of time for the cyclohexane–water–NPE system with  $f_w = 0.50$ . The oil-soluble and water-soluble surfactants were placed in the oil and water phases, respectively. Each phase contained 5.0 wt % of the appropriate surfactant. Two experiments were conducted and are shown by red (light) and blue (dark) symbols.

system as reported elsewhere.<sup>16</sup> The interfacial tension at the optimum conditions ( $\text{HLB}_{\text{opt}} \approx 10.8$ ), where PI emulsification using a long addition time occurs, is close to zero (on the order of  $10^{-1}$ – $10^{-2}$  mN/m).<sup>2</sup> A low interfacial tension enhances drop rupturing and produces finer emulsions. This clearly indicates while application of the equilibrated emulsification method may improve reproducibility, it may not necessarily improve emulsion properties. The emulsion formulation adopted in this work has a potential for producing fine emulsion which can be exploited by PI methods.

It is worth noting that the prior equilibration of certain quantities of oil, water, and surfactant (not the whole recipe) may improve emulsification. The emulsion with  $f_w \approx 0.20$ , as shown in Figure 1 for example, is at optimum composition corresponding to the value of  $\text{HLB}_{\text{opt}} \approx 10.8$ . Therefore, the equilibrated mixture of the oil containing NPE5 and 20 vol % water ( $f_w = 0.20$ ) containing NPE12 surfactant (5.0 wt %), if followed by gradual addition of the remainder of water, could theoretically produce similar emulsions as those by phase inversion emulsification. An experiment was carried out to investigate this hypothesis by using a moderate addition time ( $t_{\text{add}} = 1200$  s). Note that in this case no precise phase inversion

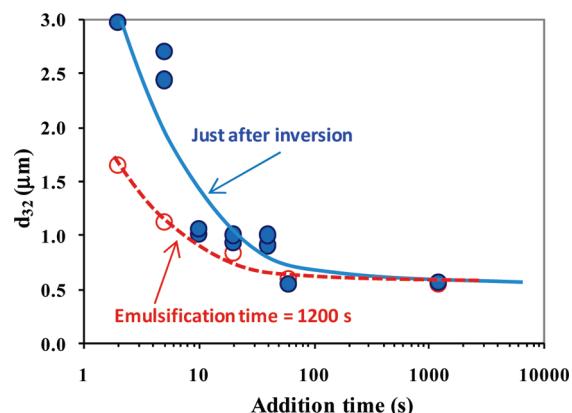


**Figure 4.** (a) Drop size distribution of the final emulsions prepared with 5 wt % surfactant with different addition times. Panels b and c show typical graphs for emulsions made right after inversion with  $t_{\text{add}} = 1200$  and 5 s, respectively ([S] = 5.0 wt % and  $f_w = 0.50$ ).

was detected as the starting mixture was a Winsor-III microemulsion, which is defined as a surfactant-rich phase in equilibrium with excess water and oil. A drop size distribution similar to that obtained by the PI method resulted, as shown in Figure 2 (this is indicated by the initial water volume fraction of  $f_{w0} = 0.20$  in the figure). This clarifies that prior equilibration could be useful if there exists sufficient information regarding the phase behavior of a water–oil–surfactant mixture so that a proper initial composition can be selected for the equilibration stage.

**3.2. Transitional Phase Inversion Protocol Using a High Surfactant Concentration ( $[S] \geq 3.0$  wt %).** The surfactant concentration of 5.0 wt % was selected to study the effect of addition time on the mechanism of inversion. The optimum composition for this [S] can be found from the intersection of the operating line with the transitional line as shown in Figure 1 ( $\text{HLB}_{\text{op}} \approx 10.8$  for  $[S] = 5.0$  wt %). According to the map, the three-phase microemulsion is expected to form when around 12 mL of the water phase is added to the initial oil ( $f_w \approx 0.20$ ). Due to continuous addition of the water phase, the optimum conditions can only be maintained for a short time because emulsion composition departs from that of optimum composition with further addition.

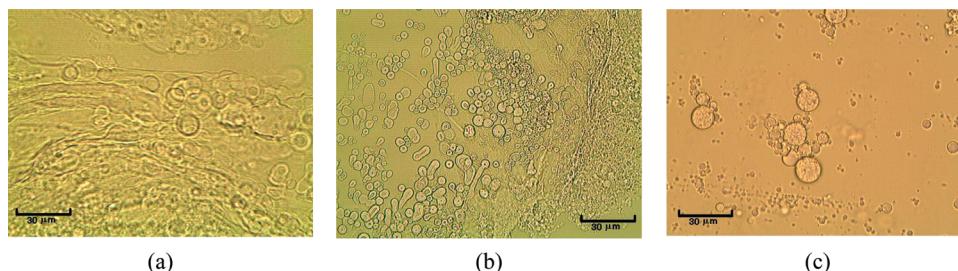
Figures 4 and 5 show the drop size distribution (DSD) and average ( $d_{32}$ ) just after inversion to O/W morphology, respectively, for different addition times ( $t_{\text{add}}$ ). The DSDs narrowed as the average drop size decreased. The micrographs for the emulsions obtained using two different addition times are also shown in Figure 4. With a very fast rate of addition,  $t_{\text{add}} = 2–5$  s, the size of the resulting drops was large and their distributions were very broad. It can be stated that for mixing protocols in which the three-phase microemulsion state is on the trajectory of the emulsification process, as is the case here, a fast rate of addition may lead to elimination of such a state.



**Figure 5.** Variations in the average diameter ( $d_{32}$ ) of oil drops (●) just after the onset of inversion and (○) at the overall mixing time of 1200 s including the addition time ([S] = 5.0 wt % and  $f_w = 0.50$ ).

The adsorption of nonionic surfactants onto the oil–water interfaces is often diffusion-controlled. The diffusion process is triggered by creation of new interfaces introduced by continuous addition of the water phase to the emulsification vessel. The time evolution of interfacial tension has been shown to be of crucial importance in emulsification processes.<sup>18</sup> For nonionic surfactants, the interfacial tension depends on the oil–water phase ratio because of their significant solubility in the oil phase. Therefore, the data presented in Figure 3 are not equally valid for the PI process for which the phase ratio varies with time. Furthermore, the evolution of interfacial tension within the first few seconds of measurements, which is comparable to the length of the addition period used in the PI experiments, could not be recorded. The initial fall in the interfacial tension, typically observed in systems with low concentrations of surfactant,<sup>18</sup> is possibly completed within the first few seconds because of the presence of a high concentration of surfactants in the current system. The application of pendant drop method to monitor dynamic interfacial tension was also not successful due to very low interfacial tension encountered during measurements. Despite these drawbacks, however, still some general inferences can be drawn from the interfacial tension data presented in Figure 3. NPE5 is more mobile than NPE12 so its migration to the interface is relatively rapid. The initial interfaces, therefore, are richer in NPE5 that has an HLB (=10) close to  $\text{HLB}_{\text{op}} = 10.8$ . This can produce a low interfacial tension, as shown in Figure 3, in the first few minutes. It has been shown before that for the current system a minimum interfacial is achieved around  $\text{HLB} = 10.8$ , which corresponds to the optimum composition.<sup>2</sup> This may imply that even a short contact between the two phases could be sufficient to result in a significant interfacial lowering and thus enhanced drop rupturing. This is supported by the fact that a significant number of sub-micrometer droplets are formed even with instantaneous addition (see Figure 4). As more NPE12 surfactant molecules (with  $\text{HLB} = 14.2$ ) are adsorbed at the interface with time probably by the displacement of NPE5, the surfactant HLB at the interface progressively deviates from that of optimum HLB and consequently the interfacial tension increases until equilibrium is reached (see Figure 3). Emulsification under equilibrium conditions, as previously stated, resulted in formation of large drops.

With long addition times, generally the drop size averages and distributions were small and narrow, respectively, and did not significantly change with addition time if  $t_{\text{add}} > 60$  s. These size distributions correspond to TPI. It can be concluded that the minimum addition time required to allow a thermodynamic



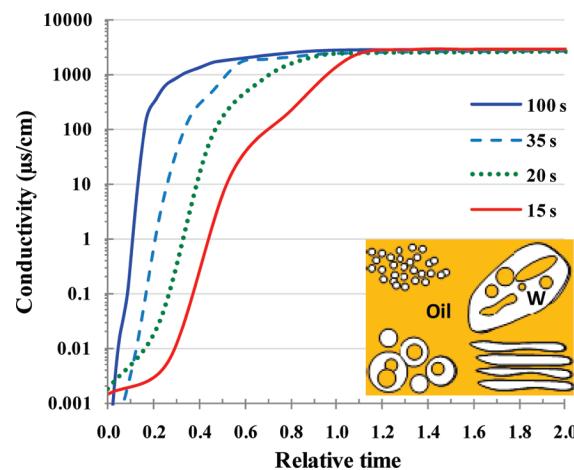
**Figure 6.** Micrographs of W/O emulsions prior to inversion for a fast addition experiment: (a) domains of bicontinuous nature, (b) domains of continuous and discontinuous natures, and (c) domains of multiple drops (or regions) in the continuous phase ( $t_{\text{add}} = 20$  s,  $[S] = 5.0$  wt %, and  $f_w = 0.50$ ).

semiequilibrium to be achieved at the optimum compositions is around 60 s. For addition times shorter than 60 s, the average size of drops increased significantly with decreasing addition time. The drop size distribution showed similar results for addition times between 20 to 40 s but significantly different from those obtained at shorter addition times.

One may argue that the difference in the size of the final drops originates from the different mixing times. To address such a possibility, emulsions were kept under continuous agitation after the completion of addition for the total emulsification time of 1200 s. The average drop sizes of such emulsions are also shown in Figure 5. It is clear that the difference between the size of the resulting drops is damped when all emulsions are exposed to mechanical mixing for the same period of time. However, while the average drop size for the emulsions with fast addition rates (short addition times) shows a sharp reduction with further mixing, no significant disparity can be observed for emulsions with lower rates of addition ( $t_{\text{add}} > 60$  s).

To monitor the pattern of evolution of emulsion morphology during phase inversion, samples from W/O emulsions (prior to inversion) were carefully examined using optical microscopy. For  $t_{\text{add}} = 1200$  s, the typical bicontinuous morphology of the three-phase microemulsion was observed.<sup>19</sup> Typical images from the run with  $t_{\text{add}} = 20$  s, as shown in Figure 6, clearly indicate that there was no single pattern predominant prior to phase inversion, but there were (a) domains that represent bicontinuous emulsions, (b) domains of continuous and discontinuous natures, and (c) domains of large water drops (or regions) containing some oil droplets dispersed in the oil continuous phase or vice versa, which the latter may be considered as a local phase inversion.

Figure 7 shows variations in conductivity with relative time for various addition times. The relative time indicates the time after the onset of addition over the addition time. The relative time of 1.0 indicates the end of addition. The overall compositions of emulsions at any one relative time are the same. For the slow addition (i.e.,  $t_{\text{add}} = 100$  s), phase inversion was completed at the relative time of 0.20 that corresponds to optimum composition ( $f_w \approx 0.20$  and  $\text{HLB}_{\text{opt}} \approx 10.8$ ) and TPI. For the fast additions (small  $t_{\text{add}}$ ), however, phase inversion occurred after the optimum composition (not optimum condition) was achieved. The conductivity of emulsions usually changes vigorously across a phase inversion process. However, it is clear from Figure 7 that the slopes of the conductivity curves only become steep for the long addition times. Similar conductivity profiles were obtained when  $t_{\text{add}} > 60$  s (not shown). The phase inversion was delayed, in terms of relative time or emulsion water-phase ratio, with decreasing addition time due to insufficient contact time. For the addition time of 15 s, the phase inversion was completed right at the end of addition ( $t =$



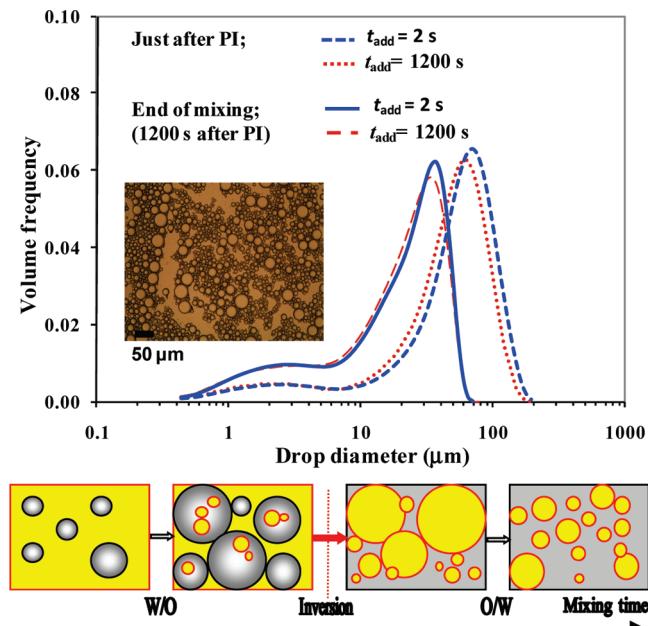
**Figure 7.** Variations in conductivity versus relative time for several addition times ( $[S] = 5.0$  wt % and  $f_w = 0.50$ ). The schematic of different domains of emulsion morphology before phase inversion is shown in the inset.

15 s). This implies that phase inversion would possibly occur after the completion of addition for  $t_{\text{add}} < 15$  s.

It is worth noting that the experiments were carried out using the agitation speed of 500 rpm, which is within the typical range normally used for laboratory vessels. It is quite likely that a higher rate of agitation can improve mixing and alleviates the disparity of different runs. On the other hand, the system might be more sensitive toward the rate of addition at a lower surfactant concentration such as  $[S] = 3.0$  wt %, which is the minimum  $[S]$  that can deliver TPI for the current system.

TPI and CPI are characterized by decreasing and increasing drop size variations, respectively, prior to inversion.<sup>19</sup> The presence of small droplets in the presence of large drops for intermediate addition times just after inversion, as inferred from photographs and bimodal size distributions of drops shown in Figure 4, suggests that TPI has been accompanied by CPI, at least locally. This occurs despite the fact that the emulsification operating line passes through the optimum compositions.

In a recent publication, we showed that the intensity of mixing, as well as location of the impeller, can be used to control the rate of addition of the second phase in a batch operation.<sup>2</sup> An interesting result was that a smaller droplet size could be achieved at a lower impeller speed. At the low impeller speed, the water phase was slowly sucked into the oil phase, leading to occurrence of ultralow interfacial tension and a small droplet size. At a high agitation speed, the intensive mixing of emulsions did not allow the three-phase microemulsion structure across the emulsification path to form, and as a result large drops were formed. The results presented here, which are based on the controlled addition of the second phase, can be considered complementary to those published elsewhere in which the rate of addition was controlled by the rate of agitation.

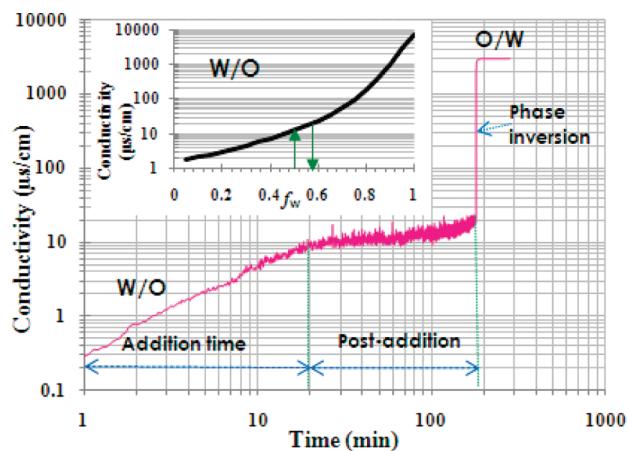


**Figure 8.** Drop size distributions of oil drops with  $[S] = 1.0 \text{ wt } \%$  just after phase inversion and 1200 s after phase inversion for different addition times. Phase inversion occurred at  $t = 2$  and 11150 s for  $t_{\text{add}} = 2$  and 1200 s, respectively ( $f_w = 0.50$ ). The inset photograph represents the final emulsion (1200 s after PI) for  $t_{\text{add}} = 1200 \text{ s}$ . The schematic of phase inversion process is shown underneath.

**3.3. Catastrophic Inversion Protocol Using Low Surfactant Concentration ( $[S] \leq 2.0 \text{ wt } \%$ ).** A surfactant concentration of 1.0 wt % was selected for this study. Two addition times of 2 and 1200 s were considered. For  $t_{\text{add}} = 2 \text{ s}$ , the addition of the water phase was associated with an abrupt phase inversion to O/W emulsion morphology. After the addition was completed, the emulsions were kept under stirring for 1200 s, and then final size measurements were also made. With  $t_{\text{add}} = 1200 \text{ s}$ , phase inversion occurred after 11150 s (186 min.). Stirring continued for another 1200 s after phase inversion (i.e., total emulsification time of 12350 s). Figure 8 shows the variations in drop size distribution of the final drops with addition time using a surfactant concentration of 1.0 wt %. The interesting result is that the size distribution of drops in the resulting O/W emulsions just after inversion changed slightly with the addition time, in contrast with that observed for TPI at higher surfactant concentrations.

One should note that TPI is not always possible across the selected operating line. At  $[S] \leq 2.0 \text{ wt } \%$ , the initial W/O emulsion is in fact an abnormal emulsion (the emulsion composition corresponds to a region where O/W emulsion morphology is favored, as seen in Figure 1). Consequently, phase inversion from abnormal W/O emulsion to O/W morphology can only occur through catastrophic phase inversion. Catastrophic phase inversion of abnormal emulsions under a wide range of conditions has been studied in detail by several groups,<sup>4,6,7,9,20–23</sup> and it is not the subject of this study. However, the CPI encountered across the selected operating line is a special case which deserves an explanation.

Catastrophic phase inversion is usually associated with formation of multiple drops. Multiple O/W/O drops are formed by inclusion of the oil phase by water drops.<sup>20</sup> This occurs because the emulsion morphology is in conflict with its formulation. The dispersed water phase forms an internal phase emulsion morphology which is normal and corresponds to the emulsion formulation. In a typical CPI, the dispersed phase continues to grow while the continuous phase shrinks. The



**Figure 9.** Variations in conductivity of W/O emulsion versus time for  $t_{\text{add}} = 1200 \text{ s}$ ,  $[S] = 1.0 \text{ wt } \%$ , and  $f_w = 0.50$ . The inset shows the predicted conductivity of the W/O emulsion versus water volume fraction using Bruggeman's equation.<sup>24</sup> The conductivities of emulsions at the end of feeding and postaddition stages are shown by two reverse arrows in the inset.

gradual increase in the *effective volume fraction* of the dispersed phase with time because of inclusion,<sup>4</sup> as well as with further addition of the dispersed phase, eventually leads to a phase inversion.<sup>21</sup> After inversion, the internal oil droplets are released into the inverted emulsion and constitute oil droplets. These oil droplets are in fact emulsified in the interior of the dispersed phase in the preinversion regime; so-called *internal phase emulsification*.<sup>22</sup> The internal oil droplets are usually smaller than those that can be achieved via direct emulsification (i.e., addition of oil to water). The formation of multiple emulsions has been found as one of the perquisites to formation of fine emulsions by catastrophic phase inversion.<sup>23</sup> The formation of similar average drop sizes just after inversion suggests that only a small number of complex drops have been formed during the preinversion emulsification stage for both short and long addition times ( $t_{\text{add}} = 2$  and 1200 s, respectively). This is not surprising for  $t_{\text{add}} = 2 \text{ s}$  as at this rate there is not sufficient time for formation of fine internal droplets,<sup>23</sup> but  $t_{\text{add}} = 1200 \text{ s}$  needs more explanation.

Figure 9 shows that the conductivity of W/O emulsion increased significantly with the disperse phase (water) ratio during the addition time, as was expected. The disperse phase ratio was constant (i.e., 50%) during the postaddition stage. However, the conductivity during the postaddition stage showed a small increase (in terms of the degree of magnitude of the change) from  $10 \mu\text{s}/\text{cm}$  after the end of the addition to  $20 \mu\text{s}/\text{cm}$  at the onset of PI. The latter conductivity corresponds to an effective internal phase ratio of 58% (see inset of Figure 9), indicating that multiple drops have been formed only to a limited extent. The CPI encountered in this work is inherently confined to a low range of surfactant concentration (as a high surfactant concentration can lead to TPI). It has been shown before that formation of multiple drops is depressed with decreasing surfactant concentration.<sup>22</sup> This result clearly confirms that the rate of formation of multiple drops was not significant for  $[S] = 1.0 \text{ wt } \%$ . If the internal oil drops are not formed to a great extent, then the size of the oil drops in the inverted O/W emulsion is governed by rupturing the (oil) continuous phase in the preinversion regime.<sup>23</sup> As a result, the variations in the addition time could only slightly affect the size distribution of oil drops at the onset of phase inversion. This can be easily inferred from Figure 8.

The drop size average of emulsions reduced and their distribution narrowed with time during postinversion. Figure 8 also shows that the comparative standing of the size distribution of oil drops during postaddition (1200 s after PI) remains similar to that just after the inversion. For both runs, the history of preinversion emulsification (i.e., addition time) was not very important and the size of drops was mainly determined in the postinversion region.

#### 4. Conclusions

The influence of the speed of incorporation of the water phase into the oil phase on the properties of the emulsions was found to be related to the surfactant concentration. At the high surfactant concentration, the slow addition resulted in reduction of the droplet size because it allowed the transitional phase inversion to occur, which produced fine droplets. Large drops with broad size distributions were formed via catastrophic phase inversion if the addition time was very short (or the rate of addition was high). In the intermediate range of rate of addition, both inversion mechanisms were possibly involved, and as a result bimodal drop size distributions were produced. It has been stated in the literature that equilibrium may be reached instantly in an emulsification process if the emulsion composition is close to that of optimum composition. It can be concluded that while spontaneous emulsification is fast, is not instantaneous.

At the low surfactant concentration, the speed of addition of the second phase only slightly affected the final size of droplets. At this concentration, transitional inversion was not probable and a catastrophic one was predominant. The limited formation of multiple drops during the slow addition rate was the main reason that particle size did not change with the rate of addition.

The conclusion can be extended to conventional nonequilibrated emulsification. The results clearly indicate that any irregularity in mixing procedure or mixing time, even on the order of a few seconds, can lead to a significant change in the drop size of resulting emulsions. While equilibrated emulsions can deliver reproducible emulsions, they cannot necessarily produce fine emulsions.

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