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Evolutionary behaviour of miniemulsion phases: II. Growth mechanism of miniemulsion droplets

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Received 2 November 1999, in final form 6 March 2000

Abstract. The growth mechanism of droplets of hexadecane-in-water emulsions stabilized by heptaethylene glycol mono-*n*-dodecyl ether was studied by means of photon correlation spectroscopy. When the water-to-oil ratio (WOR) was varied from 4 to 10, a translucent oil in water emulsion (a so-called 'miniemulsion') was obtained, while an opaque oil in water emulsion (O/W emulsion) was prepared when WOR was equal to 3. The *z*-average hydrodynamic radius of droplets, r_z , was measured over the 24 days after preparation. Plotting the cube of the *z*-average radius as a function of time, we found that r_z^3 varies linearly with time in the system of the O/W emulsion (WOR = 3). This suggests that the process by which the droplets grow is that of Ostwald ripening. On the other hand, the same plot for the system of miniemulsions ($4 < \text{WOR} < 10$) shows two regimes in the process. In both regimes, r_z^3 varies linearly with time. The rate obtained for the earlier stage is smaller than that of the latter stage. The droplet size distribution became too broad compared with the prediction of Lifshitz–Slezov–Wagner theory for Ostwald ripening ~ 10 days after preparation. Then it approached the predicted distribution again ~ 20 days after preparation.

1. Introduction

Emulsions are usually produced by processes that apply a vigorous agitation using turbines or colloid mills. When the droplet diameter of emulsions is of the order of a few micrometres, the systems appear milky. In general, making small droplets of the order of a submicrometre in diameter uses a large amount of energy. In many cases, therefore, a high pressure homogenizer is required.

Recently, we have developed a thermal protocol that allows us to produce translucent oil in water (O/W) emulsions under gentle agitation [1]. Being optically clear, the characteristic size of the obtained O/W emulsion droplets is ~ 20 nm. These features are quite similar to that for a microemulsion. However, the systems obtained are not thermodynamically stable. It was observed that the obtained O/W emulsion approached a thermodynamically equilibrium state over time. Hence, this translucent O/W emulsion is considered as a miniemulsion. In the previous paper [2], the physical properties of the miniemulsion made up of water/*n*-hexadecane/heptaethylene glycol mono-*n*-dodecyl ether ($C_{12}EO_7$) were investigated by using

light scattering techniques. The obtained miniemulsion phase turns to Winsor's I phase gradually, i.e. the miniemulsion is separated into two phases after a certain time interval. At the initial state, miniemulsion droplets experience hard sphere interactions in terms of the Percus–Yevick approximation [1]. The droplet diameter of the obtained miniemulsion was about 20 nm and the ratio of the hydrodynamic diameter to the hard sphere diameter was about 1.2. It was suggested that the bound water on miniemulsion droplets plays an important role in obtaining a homogeneous miniemulsion [1]. In the destabilization process of miniemulsion, the miniemulsion developed gradually from a monodisperse system to a polydisperse one over 8 days [3]. Plotting the normalized droplet number as a function of time, it was considered that the growth of miniemulsion droplets obeyed a diffusion-controlled process [3].

In the present paper the growth mechanism of miniemulsion droplets is discussed. In general, four distinct mechanisms are considered as major instability processes of an emulsion [4]. These are known as flocculation, coalescence, creaming, and Ostwald ripening. The basic features of these processes are as follows.

- (i) Flocculation kinetics may be described as a second-order reaction process, so-called 'diffusion limited aggregation' [5, 6]. Flocculation occurs when there is a net attractive force between droplets, which is large enough to overcome thermal agitation and cause persistent aggregation. Flocculation may be reversed by the input of much less energy than was required to disperse the droplets in the initial emulsion.
- (ii) Coalescence of two droplets occurs after they have combined to an aggregate [7]. When the thin layer between two neighbouring droplets is ruptured, they form a new larger droplet mixing their contents. Thus coalescence is a first-order reaction process, and this is essentially an irreversible process. The rate of coalescence is dependent on the droplet encounter rate (controlled by the droplet diffusion) and the properties of the droplets' surface [8].
- (iii) Creaming is due to the difference between the densities of the dispersed and continuous phases. Under the influence of gravity, the separation takes place with the most dense phase collecting at the bottom and the less dense phase at the top.
- (iv) Ostwald ripening is the growth of one droplet at the expense of smaller ones due to the difference in their chemical potential arising from their radii of curvature [9, 10]. The growth of droplets occurs by the molecular diffusion of solutes through the continuous phase over time.

Finally, an emulsion reaches the eventual equilibrium state, which is completely separated into the two phases.

In a previous work [3], it is reported that the reciprocal of the normalized total number of miniemulsion droplets, $N(0)/N(t)$, increases linearly with time as shown in figure 1. Both Smoluchowski's theory for the diffusion limited aggregation (mechanism (i)) [5] and Lifshitz–Slezov–Wagner (LSW) theory for Ostwald ripening (mechanism (iv)) [9, 10] deduce the same formula as follows:

$$\frac{N(0)}{N(t)} = 1 + \frac{t}{\tau} \quad (1)$$

where τ is the characteristic time of the growth process. Using equation (1), the characteristic times were estimated as 2.3×10^5 s (2.62 days) and 1.6×10^5 s (1.90 days) for miniemulsions of $WOR = 4$ and 9, respectively. The order of the characteristic time, τ , is quite different between mechanisms (i) and (iv). According to Smoluchowski's theory [5, 6], the characteristic time of mechanism (1) is calculated as

$$\tau_{smol} = \frac{3\eta}{4kTN(0)} \quad (2)$$

where k , T and η are Boltzmann's constant, the absolute temperature and the viscosity of the disperse medium, respectively. According to LSW theory [9, 10], on the other hand, the characteristic time of mechanism (iv) is represented by

$$\tau_{LSW} = \frac{3\phi}{4\pi\omega N(0)} \quad (3)$$

where ϕ and ω denote the volume fraction of dispersed droplets and the rate of Ostwald ripening, respectively. The theoretical values for τ_{smol} and τ_{LSW} in the obtained hexadecane in water miniemulsions stabilized by $C_{12}EO_7$ are calculated to be of the order of 10^{-6} s and 10^4 s, respectively. The characteristic times observed here have a similar magnitude to the theoretical one predicted by LSW theory. Thus, it may be concluded that the growth process of the miniemulsion droplets is that of mechanism (iv) (Ostwald ripening).

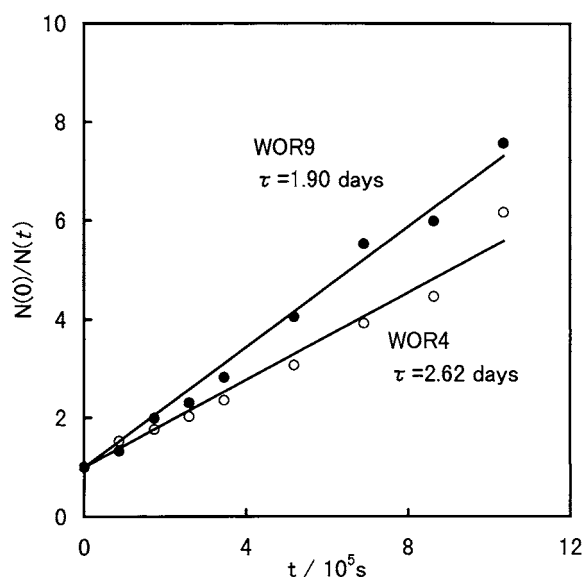


Figure 1. Time evolution of the total number of droplets, $N(0)/N(t)$, for miniemulsions for which WOR is 4 (open circles) and 9 (full circles).

In the present paper, we try to discuss the growth mechanism of miniemulsion droplets in terms of Ostwald ripening.

2. Experimental details

2.1. Materials and sample preparation

Mergital LT7 (with main component heptaethylene glycol mono-*n*-dodecyl ether, $C_{12}EO_7$) was furnished by Sidobre Sinnova, and *n*-hexadecane was purchased from Fluka. All chemicals were used as received without any further purification. Distilled water was used in the preparation of emulsions. Referring to the PIT (phase inversion temperature) method proposed by Shinoda and Saito [11], miniemulsions are prepared by a thermal protocol under gentle stirring. The role of PIT for the preparation of miniemulsions was reported in our previous paper [2]. The volume ratio of water to oil (WOR) was varied from 3 to 10, and the surfactant mass fraction was fixed at 0.12 in all samples. Note that we obtained a monophasic but

opaque emulsion when WOR was equal to 3. The physical property of this oil in water (O/W) emulsion is obviously different from miniemulsions [2]. In order to distinguish this emulsion from miniemulsions, it is called 'the O/W emulsion' in this paper. The samples, which have been maintained at a temperature of 25 °C, were diluted by the dispersion medium (water) about 30 min before each measurement.

2.2. Dynamic light scattering measurements

Dynamic light scattering measurements were accomplished by using a device which is constructed by a He–Ne laser ($\lambda = 632.8$ nm) of 15 mW, a photon counting photomultiplier and a MALVERN 7032 Multi-8 with 64 channels as the digital correlator. All experiments were performed at a scattering angle of 90°, and the sample temperature was controlled at 25 °C with an accuracy of ± 0.1 °C. In order to carry out these measurements under a condition of infinite dilution, we imposed the dispersed phase volume fraction to 0.01. The relationship between the normalized first-order electric field autocorrelation function $g^{(1)}(q, \tau)$ and the single-clipped photoelectron-count autocorrelation function $G_k^{(2)}(q, \tau)$ is represented by [12]

$$G_k^{(2)}(q, \tau) = B(1 + \beta |g^{(1)}(q, \tau)|^2) \quad (4)$$

where q and β are the scattering vector $q = (4\pi n_0/\lambda) \sin(\theta/2)$ and the coherent factor which are dependent on instrumental conditions, respectively. Note that n_0 , λ and θ denote the refractive index of the medium, the wavelength of the incident light and the scattering angle. From the dynamic light scattering experiments, a z -averaged diffusion coefficient and a second-order moment were obtained by means of a second-order cumulant analysis [13]. The z -averaged radius of dispersed droplets, r_z , is calculated by Stokes–Einstein relation $r_z = kT/6\pi\eta D_z$, where k , T and η denote Boltzmann's constant, the absolute temperature and the viscosity of the disperse medium, respectively.

The autocorrelation functions were analysed further using a histogram method. For a polydisperse system, $g^{(1)}(q, \tau)$ is related to the characteristic line width distribution $s(\Gamma)$ through the following expression:

$$g^{(1)}(q, \tau) = \int_a^b s(\Gamma) \exp(-\Gamma\tau) d\Gamma. \quad (5)$$

The relation $\Gamma = q^2 D$ can be assumed in an infinite dilute solution. The histogram method [14] is employed in order to solve this inversion problem of equation (5) with the numerical calculation. Equation (2) is the Fredholm integral equation of the first kind [15]. To carry out the numerical calculation, we employed the constraint regularization algorithm proposed by Twomey [16], Phillips [17] and Provencher [18, 21]. Combining these algorithms with a nonlinear least-squares method [19], we made curve fitting programs by use of the PASCAL language (Borland: Turbo PASCAL) based on the quasi-Marquardt algorithm [20]. These calculations were carried out on a personal computer (PC-9821Xn).

3. Result and discussion

3.1. Time evolution in the cube of the droplet radius

Figures 2–9 show the increases in the cube of the z -average radius, r_z^3 , as a function of time. r_z^3 of the O/W emulsion droplets (WOR = 3) varies linearly with time as shown in figure 2. In the system of miniemulsions ($4 \leq \text{WOR} \leq 10$), figures 3–9 imply that the experimental data are not reproducible with a straight line but are well represented by two straight lines. The full and dashed lines in these figures indicate the initial and second slopes, respectively. The obtained

slopes for initial and second processes, ω_1 and ω_2 , are listed in table 1. Figures 3–9 show the same tendency for the time evolutions of r_z^3 . That is, r_z^3 increased gradually in an earlier stage, then the growth rate changed at a certain point. After this cross-over, $d(r_z^3)/dt$ became larger than that in the earlier stage. In other words, the growth of miniemulsion droplets was accelerated after a cross-over point. The values obtained for ω_1 and ω_2 decreased significantly with increasing WOR.

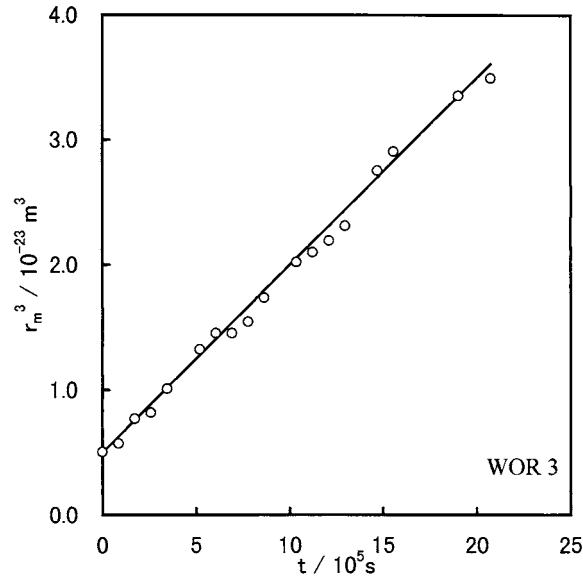


Figure 2. Increase in the cube of the z -average radius as a function of time in O/W emulsion with WOR = 3. The full line represents the result of a least-squares fit.

Table 1. Obtained growth rates, ω_1 and ω_2 , in miniemulsions and the O/W emulsion, for which WOR is varied from 3 to 10.

WOR	ϕ'	$\omega_1 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$	$\omega_2 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$	$\omega_1/\omega_1^{\text{WOR}10 \text{ a}}$	$\omega_2/\omega_2^{\text{WOR}10}$
10	0.1983	0.12	0.34	1.00	1.00
9	0.2061	0.20	0.41	1.67	1.21
8	0.2156	0.23	0.48	1.92	1.41
7	0.2277	0.27	0.62	2.25	1.82
6	0.2433	0.35	0.80	2.92	2.35
5	0.2636	0.60	0.90	5.00	2.65
4	0.2924	0.80	1.30	6.67	3.82
3	0.3358	1.50	—	—	—

^a $\omega_1^{\text{WOR}10}$ and $\omega_2^{\text{WOR}10}$ denote the obtained ω_1 and ω_2 values at WOR = 10.

When r_z^3 varies linearly with time, the growth mechanism of droplets may be explained in terms of Ostwald ripening [22]. The theory in its contemporary form was initially formulated by Lifshitz and Slezov [9] and independently by Wagner [10] (i.e. LSW theory). The basic assumptions of LSW theory are as follows.

- (a.i) The mass transport is ascribed to the molecular diffusion through the continuous phase.
- (a.ii) The dispersed phase particles are spherical and fixed in space.

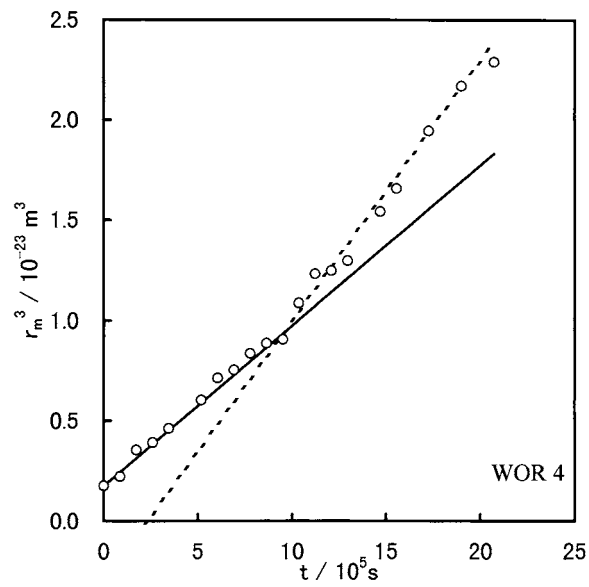


Figure 3. Increase in the cube of the z -average radius as a function of time in a miniemulsion with $\text{WOR} = 4$. The full line and the dashed line indicate the first and second stages in the growth process, respectively.

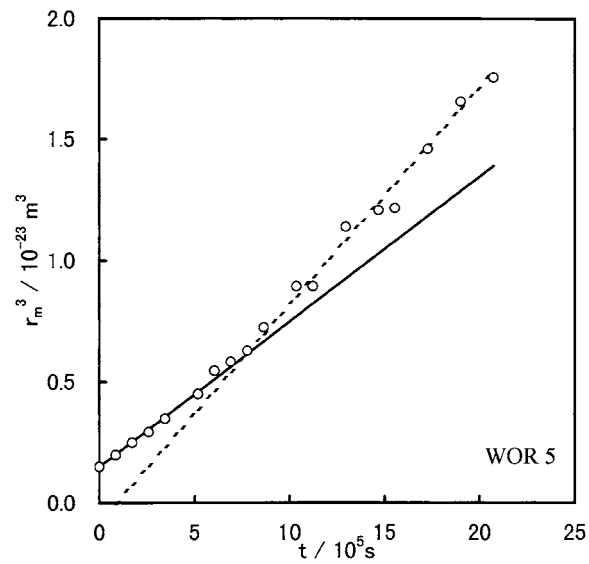


Figure 4. Increase in the cube of the z -average radius as a function of time in a miniemulsion with $\text{WOR} = 5$ (same representation as figure 3).

- (a.iii) There are no interactions between neighbouring particles, i.e. the particles are separated by distances much larger than the diameter of droplets.
- (a.iv) The concentration of the molecularly dissolved species is constant except when adjacent to the particles boundaries.

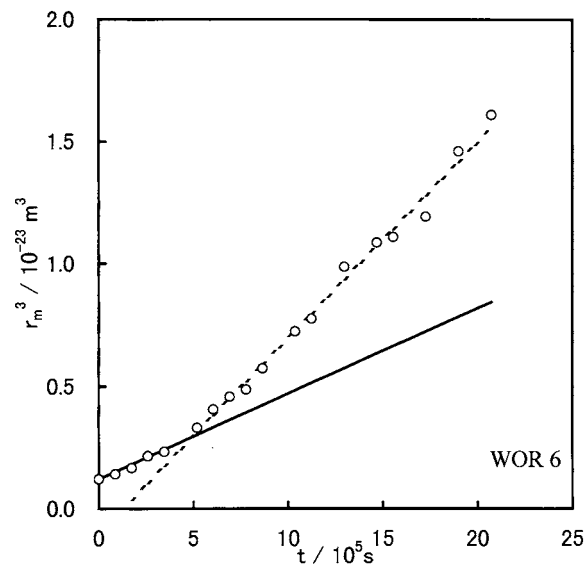


Figure 5. Increase in the cube of the z -average radius as a function of time in a miniemulsion with $\text{WOR} = 6$ (same representation as figure 3).

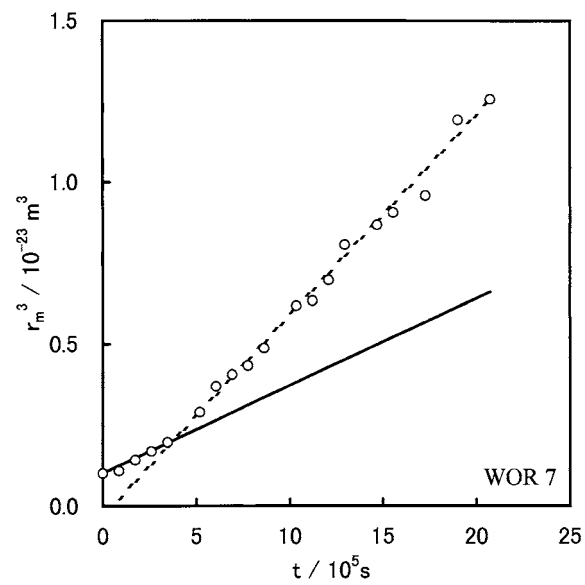


Figure 6. Increase in the cube of the z -average radius as a function of time in a miniemulsion with $\text{WOR} = 7$ (same representation as figure 3).

It follows then that the rate of Ostwald ripening, ω , is given by the increment of r_z^3 with time as follows:

$$\omega = \frac{d}{dt}(r_c^3) = \frac{8\gamma^i C^\infty DV_m}{9RT} \quad (6)$$

where r_c is the critical radius of a droplet which is neither growing nor decreasing in size,

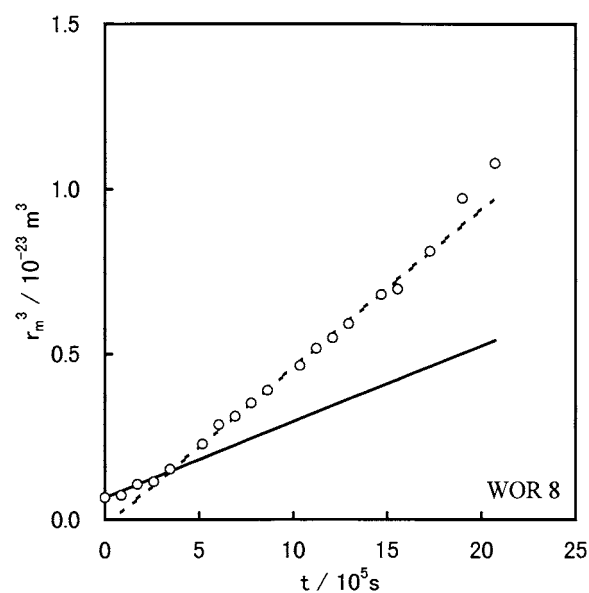


Figure 7. Increase in the cube of the z -average radius as a function of time in a miniemulsion with WOR = 8 (same representation as figure 3).

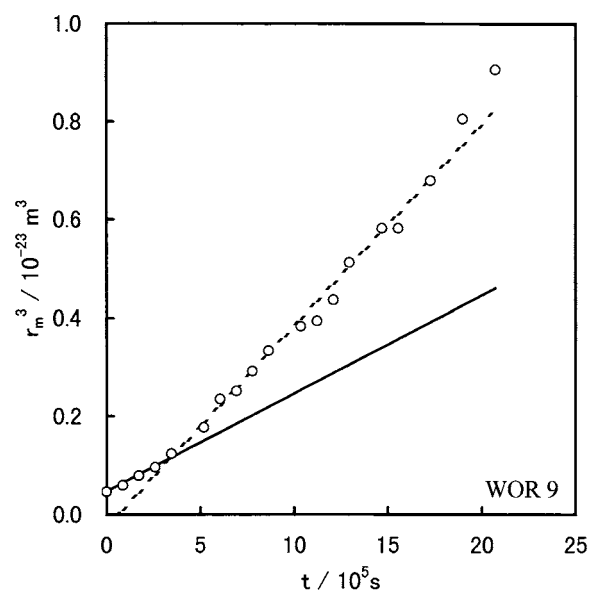


Figure 8. Increase in the cube of the z -average radius as a function of time in a miniemulsion with WOR = 9 (same representation as figure 3).

γ^i is the interfacial tension between the dispersed and continuous phases, D is the diffusion coefficient of solute molecules in the continuous phase, C^∞ is the aqueous solubility of the dispersed phase, V_m is the molar volume of the dispersed phase, R is the molar gas constant and T is the absolute temperature.

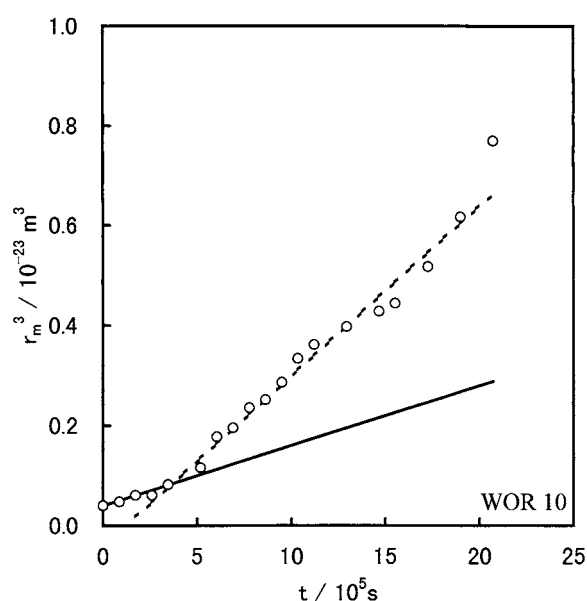


Figure 9. Increase in the cube of the z-average radius as a function of time in a miniemulsion with WOR = 10 (same representation as figure 3).

It is worth comparing the experimental rates obtained here with the theoretical one obtained by LSW theory. The theoretical rate of Ostwald ripening in water/*n*-hexadecane/ $C_{12}EO_7$ miniemulsion is estimated using the following parameters [23]: $T = 298 \text{ K}$, $C^\infty = 1.4 \times 10^{-11} \text{ cm}^3 \text{ cm}^{-3}$, $V^m = 2.91 \times 10^2 \text{ cm}^3 \text{ mol}^{-1}$, $D = 4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $\gamma^i = 1.0 \times 10^{-3} \text{ N m}^{-1}$. The estimated value for the rate of Ostwald ripening is $6.54 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$. The observed ω_1 and ω_2 varied from 0.1 to $1.5 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$. The rates obtained in this work for Ostwald ripening in miniemulsions were of a similar magnitude to the calculated value. Kabalnov *et al* reported $8.7 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$ as the experimental Ostwald ripening rate at 25°C in *n*-hexadecane in water emulsion stabilized by 0.1 M of sodium dodecyl sulphate [24].

According to our previous paper [2], however, it has been suggested that miniemulsion droplets can move freely within the bulk liquid phase and undergo hard sphere interactions. It is clearly against the assumptions (a.ii) and (a.iii), while many researchers have indicated the LSW theory can be applied to emulsions with reasonable accuracy [22, 25, 26]. These deviations from LSW theory are discussed in the next section.

3.2. Deviations from LSW theory

Firstly, the deviation between LSW theory and experiment has been ascribed to the effects of Brownian motion of miniemulsion droplets. Recall the above-mentioned assumption of LSW theory (a.ii). If droplets can move freely in the disperse medium, the mass transfer will in fact be accelerated with respect to that predicted by LSW theory [24]. In this case, the contributions of the molecular and convective diffusion were considered. According to simulation studies [27], thermal and convective contributions can enhance the growth rate without influencing the fundamental nature of Ostwald ripening. However, the observed ω_1 and ω_2 had small values compared with the theoretical rates estimated by LSW theory without taking into account of

the effects of Brownian motion. The experimental result obtained here is in disagreement with the above-mentioned prediction for the effect of Brownian motion.

Secondly, LSW theory assumes that there are no interactions between droplets (recall the assumption (a.iii)). Therefore, the application of this theory is restricted to a low disperse phase volume fraction, ϕ' . At a higher volume fraction of the disperse phase, it is believed that the rate of ripening is dependent on the interaction between neighbouring diffusion fields surrounding droplets [28]. The volume fraction dependence included in LSW theory has been of great interest over the past decade [29]. Using numerical solutions, Enomoto *et al* showed that the rate increases by a factor of 2.5 in the range $\phi' = 0.01$ – 0.30 [30]. We found a strong dependence of ω_1 and ω_2 on the volume fraction of the disperse phase. The obtained ω_1 and ω_2 values increased by a factor of ~ 7 and 4 in the range $\phi' = 0.198$ – 0.292 , respectively (see table 1). This increment is much larger than for any other proposed theories [30–33].

Several authors have recently investigated the role of micellar solubilization in the Ostwald ripening process [22, 23, 34, 35]. They have indicated that micelles play a role in mediating the mass transfer between emulsion droplets, and micelles may facilitate mass transfer by acting as carriers of oil molecules. In this case, the molecular solubility term found in LSW theory (equation (6)) is replaced by the micellar solubility. Thus large increases in the rate of mass transfer would be expected with increases in micelle concentration. Taylor [22] and Kabalnov [35] found increases in the mass transfer rate of by a factor of two to five with increasing micelle concentration. If the micelles exist in an emulsion, Weiss *et al* indicated that one has to contend not only with the Ostwald ripening process, but also with the solubilization of oil into the micelles [34]. It is therefore probable that the earlier stage can be explained by taking into account the competition between oil solubilization and Ostwald ripening. However, the existence of surfactant micelles could not be confirmed in miniemulsions at the present state. According to our previous paper [2], the observed size of droplets is monodisperse and the droplet interaction is completely explained by the hard sphere of interaction of monodisperse droplets. Thus we postpone this question until more detailed data are obtained.

3.3. Single-step and double-step growth processes

As shown in figures 3–9, there were two distinct stages in the coarsening process of miniemulsions of $WOR = 4$ – 10 . On the other hand, only one stage was observed in the system of the O/W emulsion of it $WOR = 3$ (see figure 2). In order to discuss this dissimilarity of the growth process, it is worth recalling the difference between initial states of the prepared emulsion.

In the previous paper [2], we reported that a translucent O/W emulsion, a so-called ‘miniemulsion’, is obtained when WOR is varied from 4 to 10. Plotting the variation of the scattering intensity with ϕ' , it was elucidated that the droplets undergo the hard sphere interaction and there are no droplet size polydispersity in these miniemulsions. On the other hand, the same plots for the O/W emulsion with $WOR = 3$ showed a quite different feature compared with that for a miniemulsion. Thus it is concluded that the physical property of the O/W emulsion with $WOR = 3$, the polydispersity and/or the interaction between droplets, was different from that of the other obtained miniemulsions. While the double-step process was observed in miniemulsions of $WOR = 4$ – 10 , the O/W emulsions of $WOR = 3$ showed the single-step process. It seems probable, then, that the coarsening processes of the obtained O/W emulsion or miniemulsion are strongly dependent on their physical properties at the initial state.

The cross-over time, t_c , is defined as the time at the intersection of the two lines for the earlier (the full line in figures 3–9) and the latter stages (the dashed line). The estimated values for t_c are listed in table 2. t_c did not change significantly in the range $WOR = 7$ – 10 . When

WOR became smaller than 7, t_c increased abruptly as WOR decreased. We guess that the dependence of t_c on WOR can be explained by the amount of bound water on miniemulsion droplets V_{bw} at the initial state of miniemulsions [2]. Referring to V_{bw} listed in table 2, it could be considered that the dependence of t_c is quite similar that of V_{bw} on WOR. V_{bw} is not varied when $7 \leq \text{WOR} \leq 10$, and it shows a strong dependence on WOR when WOR is smaller than 7. It is therefore presumed that the duration of the earlier stage becomes longer with decreasing V_{bw} . It is implied again that the physical properties of miniemulsion droplets at the initial state affect the growth process of droplets.

Table 2. Cross-over time, t_c , and the amount of bound water, V_{bw} at $t = 0$.

WOR	t_c (10^5 s)	ω_2/ω_1	V_{bw}^a
3	—	—	—
4	9.5	1.63	0.32
5	7.6	1.50	4.70
6	4.9	2.29	7.13
7	3.8	2.30	8.00
8	3.4	2.09	8.04
9	3.4	2.05	7.73
10	3.7	2.83	7.37

^a Taken from [1].

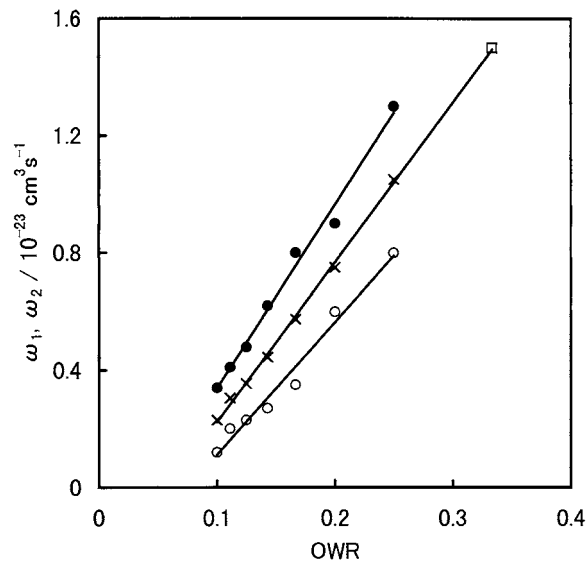


Figure 10. Variations of the obtained growth rates, ω_1 and ω_2 , with oil-to-water ratio (OWR). The full and open circles represent ω_1 and ω_2 , respectively. The open square and cross symbols indicate the growth rate for the system of $WOR = 3$ and the average rates $(\omega_1 + \omega_2)/2$, respectively.

Figure 10 shows the variation of ω_1 and ω_2 with oil-to-water ratio (OWR). Plotting the obtained rates against OWR , some curious points can be suggested. Firstly, it is considered that the ω_2 value increases linearly with OWR , while the variation of ω_1 seems to have small distortion with respect to a straight line. These behaviours indicate a strong dependence of ω_1 and ω_2 on the volume fraction of oil in miniemulsions. Secondly, it is shown that the average rates calculated by $(\omega_1 + \omega_2)/2$ are approximately on a straight line. The growth rate of the

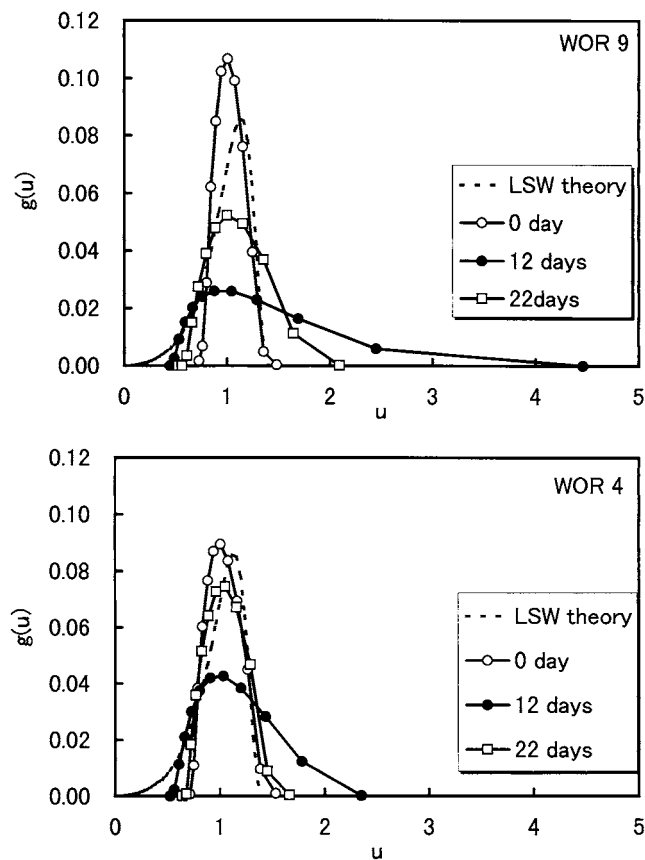


Figure 11. Comparison of the obtained droplet size distribution at 0 days (the open circles), at 12 days (the full circles) and at 22 days (the open squares) with that predicted by the LSW theory (the dashed curve).

O/W emulsion with $\text{WOR} = 3$ ($\text{OWR} = 0.33$), which shows a monotone increase, is found to be on the extension of this straight line. It is therefore supposed that a balance between ω_2 and ω_1 determines the entire stability of miniemulsions. The ratio of ω_2 to ω_1 , which is listed in table 2, decreases with decreasing WOR. This diminution implies that ω_2/ω_1 approaches 1 as WOR decreases. This tendency suggests again that the monotonically increase of r_z^3 will be observed at lower WOR.

3.4. Droplet size distribution and growth mechanism in the first and second stages

Another consequence of LSW theory is the prediction that the size distribution function $g(u)$ for the normalized droplet radius $u = r/r_c$ adopts a time-independent form given by

$$g(u) = \begin{cases} \frac{81e}{31^{1/3}} \frac{u^2}{(u+3)^{7/3}(3/2-u)^{11/3}} \exp\left(\frac{1}{2u/3-1}\right) & \text{for } 0 < u \leq 1.5 \\ 0 & \text{for } u \geq 1.5. \end{cases} \quad (7)$$

In our previous work [4], temporal changes in the droplet size distribution function of miniemulsions were investigated over 12 days. It was revealed that the variance of the

normalized size distribution increased in the early stage, then ceased to develop after ~ 8 days. The mean hydrodynamic diameter grew over the 12 days. The normalized size distribution of the miniemulsion had a time-independent form after 8 days.

Figure 11 shows the comparison between the observed size distribution and the predicted one (equation (7)). The droplet size distributions of miniemulsions, for which WOR is 4 and 9, were calculated from the measured $g^{(1)}(\tau)$ by using the histogram method. The variance of the size distribution function predicted by LSW theory is 0.046. The variance of the obtained size distribution at 0 days was 0.016, that at 12 days was 0.19 in the miniemulsion with WOR = 9. In the miniemulsion with WOR = 4, the variance was 0.022 at 0 days and 0.11 at 12 days. It is obvious that the obtained size distribution function broadens extremely when compared with the predicted one. Simulation studies of Enomoto *et al* indicated that the droplet size distribution function is broadened at the earlier stage, then it approaches the time-independent form predicted by LSW theory over time [30]. The results obtained here are opposed to these simulation studies. Thus we conclude that the growth mechanism of the earlier stage deviates from the fundamental mechanism of LSW theory.

At 22 days after preparation, the normalized size distribution function became narrow again as shown in figure 11 (the open squares). The obtained size distributions were slightly broad compared with the predicted one. The broadening of the time-independent particle size distribution has been reported and discussed by some researchers [26, 30, 32]. For example, Ludwig *et al* have suggested that the broadening of the time-independent size distribution can be ascribed to stochastic effects on the coarsening due to thermal noise [26]. At higher volume fractions of the disperse phase, it is generally expected that the broadening of particle size distributions will be observed [30, 32]. Miniemulsion droplets can move freely in the disperse medium. Thus, it may be reasonable that the broadening of the time-independent size distribution was observed at 22 days. In the latter stage of the growth process, therefore, we can clearly catch sight of fundamental features of Ostwald ripening with the LSW theory.

As the results of our discussions, the scheme of the growth mechanisms in the first and second stages are inferred as follows.

- (1) At the earlier stage, r_z^3 varies linearly with time. At an initial time, the droplet size distribution function is narrow, then it broadens over time until 12 days after preparation. The growth mechanism of the first stage may deviate from the fundamental mechanism of LSW theory.
- (2) At the latter stage, r_z^3 varies linearly with time. At 22 days after preparation, the droplet size distribution approaches again the time-independent form predicted by LSW theory. This process has several preferable features of fundamental mechanisms of LSW theory.

4. Conclusion

The growth mechanism of droplets of *n*-hexadecane-in-water emulsions stabilized by heptaethylene glycol mono-*n*-dodecyl ether was studied by means of photon correlation spectroscopy. Referring to Shinoda's PIT method, the system was emulsified. The water-to-oil ratio (WOR) was changed from 3 to 10. When WOR is varied from 4 to 10, a translucent oil in water emulsion (a so-called 'miniemulsion') was obtained, while an opaque oil in water emulsion (O/W emulsion) was prepared when WOR was equal to 3. The *z*-average hydrodynamic radius of droplets, r_z , was measured over 24 days after preparation. Plotting the cube of *z*-average radius as a function of time, we found that r_z^3 varies linearly with time in the system of the O/W emulsion (WOR = 3). This suggests that the process by which the droplets grow is that of Ostwald ripening. On the other hand, the same plot for the system

of miniemulsions ($4 < \text{WOR} < 10$) shows two regimes in the process. In both of these two regimes, r_z^3 varies linearly with time. After a cross-over point, the growth of droplets was accelerated.

The obtained growth rates of the earlier and second processes, ω_1 and ω_2 , varied from $0.12 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$ to $0.80 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$ and from $0.34 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$ to $1.30 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$, respectively. A strong dependence of ω_1 and ω_2 on the volume fraction of oil in prepared miniemulsions was observed. The theoretical value for the rate of Ostwald ripening is calculated as $6.54 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$. The observed rates had a similar magnitude to the theoretical value. It was suggested that the coarsening processes were strongly affected by the initial state of emulsions, for example the polydispersity and the interaction between droplets. At the earlier stage, r_z^3 varies linearly with time. The droplet size distribution becomes broad over time. At 12 days, the broadening of the distribution is too large when compared with that predicted by LSW theory. At the latter stage, r_z^3 varies linearly with time. The droplet size distribution approached the predicted one again at 22 days. Some characteristic features of LSW theory could be found in the latter stage.

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