



Ostwald ripening of oil drops in a micellar solution

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Abstract

A model for Ostwald ripening of oil-in-water emulsion in the presence of small amount of surfactants is presented. It accounts for the transfer of oil from small to larger drops when the interfacial resistance is rate controlling. In this case, the continuous breakdown and reformation of the micellar structure during mass transfer through the interface, is assumed to be the rate-controlling step. A discretized population balance equation for the change in the number concentration of drops due to Ostwald ripening is solved using the method of characteristics. The third moment of the distribution (average volume) is found to increase linearly with time, consistent with available experimental observations, before reaching an abrupt equilibrium. The rate of change of drop volume is found to be strongly dependent on the solubility and is fairly insensitive to the volume fraction. The transients of the drop size distributions indicate an initial rapid decrease in the small droplets with a corresponding increase in the larger drops followed by a very slow change in the number distributions at longer times. The rate constants involved can be roughly correlated with the components of several experimental measurements, and allow comparison with the data of Kabalnov (Langmuir 10 (1994) 680), but only at small surfactant concentrations. The numerical agreement is not good but it is able to predict the anomalous direction of change with increased surfactant concentrations. The basis of the lack of numerical agreement is discussed. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

A dispersion changes with time, where the small droplets disappear and the larger ones grow. This phenomenon, called Ostwald ripening (Ostwald, 1896, 1897), has been observed even in solid–solid dispersions. The essential reason for such behavior is that surface tension increases the chemical potential of a species in the dispersed phase over that in the dispersion medium. This is called the Kelvin–Thompson effect. Consider a dispersion of oil droplets in water. Water is taken to be insoluble in oil, but oil is assumed to be sparingly soluble in water. By equating the chemical potentials of oil in the droplets to that of molecularly dissolved oil in water, it is possible to show that the solubility of oil in water in the presence of a dispersion of droplets of diameter d , is $c_\infty \exp(D/d)$, where c_∞ is the solubility in the absence of any curved interface and $D = 4\gamma/(RTc_o)$, where c_o is the

molar concentration of pure oil and γ is the oil–water interfacial tension. Hence for some amount of molecularly dissolved oil in water greater than c_∞ , it is possible to find a drop of sufficiently small size for which the oil concentration in water is lower than saturation, and it is also possible to find a sufficiently large drop where the same oil concentration is above saturation. Hence, the large drop grows and the small drop disappears. The final outcome is a single drop, a configuration that offers the largest possible diameter and smallest possible surface area and interfacial energy. The striking feature in Ostwald ripening is not the final outcome but the dynamics. In the observable time, the average drop size keeps increasing. This phase is called coarsening. In particular, the average drop volume or the third moment of the distribution of the diameters is seen to increase linearly with time. Taylor (1998) and Kabalnov (1998) have reviewed both traditional and recent literature. They have also discussed many practical applications of the process.

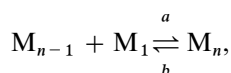
Since the small droplets disappear by dissolving into water, and large droplets grow by absorbing oil from water, it appears that the solubility of oil in water is critical to the rate process. In particular, if the water contains surfactant micelles, the solubility of oil in the

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micellar solution would greatly increase. The surfactants chosen are oil insoluble. However, Kabalnov's (1994) experiments showed practically no change in the rates of coarsening with increasing surfactant concentrations. According to Kabalnov, the rate of coarsening does not improve with surfactant concentration because the surfactant at oil–water interface provides a resistance arising from electrical charge, to micelles swollen with oil from approaching the interface. A different mechanism is used here to model the interfacial resistance as explained below.

Experiments performed to perturb an equilibrium micellar solution indicate that the system relaxes back to equilibrium through two first-order processes. The first is very rapid and is not of interest here. The second time constant τ_2 which ranges from microseconds to below one second and describes the full-blown micellization–demicellization process. The key reactions that describe the growth of micelles are



where M_1 is a singly dispersed amphiphile and M_n is a micelle of n amphiphiles. The polydispersity is important and the rate constants a and b are also functions of n . The model of Lessner, Teubner, and Kahlweit, (1981a) shows clearly that τ_2^{-1} is directly proportional to some average of the *demicellization* rate constants. Experimental data (Lessner et al., 1981b) show that τ_2^{-1} decreases with increasing concentrations of SDS at low SDS concentrations. At large SDS concentrations, τ_2^{-1} increases with increasing surfactant concentrations. A schematic diagram in Fig. 1 illustrates different regions of τ_2^{-1} versus surfactant concentration.

Carroll (1981) measured the rates of solubilization of oil in a micellar solution of nonionic surfactants at relatively high surfactant concentrations. It was seen that the rates, expressed as the rates of transfer of moles of oil per unit interfacial area across the interface k_i , did not change with time. Diffusion cannot be responsible for such a time dependence. Carroll also suggested that diffusion-related mechanisms could not explain the order of magnitude of the rate constant. These results implied that demicellization followed by micellization, could be a plausible mechanism of oil uptake governing the rate process. Carroll (1981) observed that the rate constants increased with surfactant concentrations. Williams, Bhakta, and Neogi (1999) measured the mass transfer rates of oil (nitrobenzene) from a micellar solution to a bulk oil phase. They found that the interfacial resistance was controlling. The surfactant (sodium dodecyl sulfate, SDS) was dilute and the solubilize (nitrobenzene) was even more dilute. They found that on increasing the concentration of a surfactant three times, the interfacial resistance rose by about 20 times, that is,

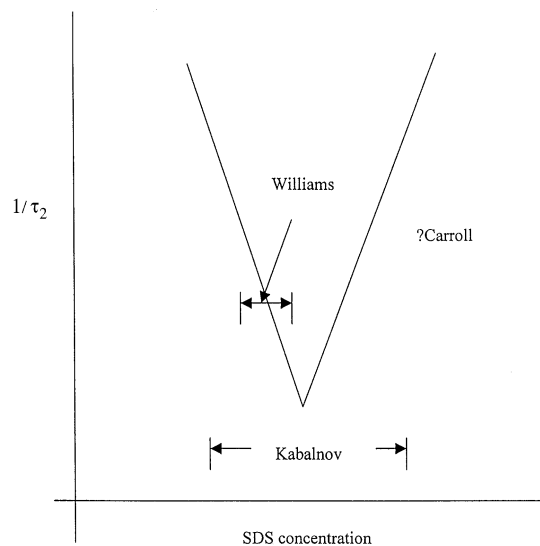


Fig. 1. Schematic diagram of τ_2^{-1} versus concentration of SDS from Lessner et al. (1981b). Also shown are the ranges over which data are available for interfacial resistance from Williams et al. (1999) and Ostwald ripening data from Kabalnov (1994). Although the range for Carroll's (1981) work on interfacial resistance has been included, the surfactant used were nonionics.

k_i fell. This large rise could not be explained through conventional mechanisms. They also showed that if micellization–demicellization was rate controlling, then the rate constant describing interfacial resistance should be proportional to the time constant measured in micellization kinetics. Therefore, the rate constant k_i is to the first approximation proportional to τ_2^{-1} . For SDS in this concentration range, they found that it could explain a decrease in rate constant by a factor of 10 instead of 20 using the data of Lessner et al. (1981b) which show a 10-fold decrease over the same change in SDS concentration with increasing concentration. They also suggested that the presence of a hydrophobic solubilize can account for the larger interfacial resistance since the τ_2^{-1} data of Lessner et al. (1981b) have been obtained in the absence of a solubilize, and those of Williams et al. (1999) in the presence of a small amount of solubilize, which may explain the remaining differences in the numerical values of the rate constant and τ_2^{-1} .

However, for nonionics used by Carroll, very little is known (Lang & Zana, 1987) and in general at high surfactant concentrations other phases (such as lamellar liquid crystals) can appear transiently in systems containing oil (see Friberg, Mortensen, & Neogi, 1985; Raney, Benton, & Miller, 1985). A comparison between the model prediction and Kabalnov's (1994) data using SDS at low surfactant concentrations will have to be made. A model is presented below for Ostwald ripening in the presence of small amounts of surfactants when the interfacial resistance is rate controlling. Substituting the expression from Williams et al. (1999) for the flux of oil

from the micellar solution to the oil drops, into the boundary condition at the moving boundary of the drop surface, one has

$$c_o \dot{d} = 2k_i(c - c_\infty e^{D/d}), \quad (1)$$

where k_i is the rate constant and \dot{d} is the rate of change of the drop diameter. It is evident in Eq. (1) that there is a droplet diameter d_c for which the mass transfer is zero. Drops larger than this size grow and those smaller than this diminish in size. When the interfacial resistance is controlling, the concentration c is uniform in the dispersion medium.

Population balance equation for Ostwald ripening based on the proposed model is solved using discretization. The evolution of the third moment of the distribution with time is then evaluated and compared with the experimental data of Kabalnov (1998), Lessner et al. (1981b) and the solution of LSW scheme as discussed in the appendix.

2. Population balances

A monodisperse sample cannot show Ostwald ripening. Polydispersivity is important and the changes in the distribution of diameters of the drops as a function of time need to be tracked. The population balance equation (Hulburt & Katz, 1964) in dimensionless form is

$$\frac{\partial n}{\partial T} = -\frac{\partial}{\partial x}(\dot{x}n), \quad (2)$$

where $T = 2k_i t/D$, $x = d/D$, $n = n^*D/N$ where n^* is the dimensional population density per unit volume and N is the initial number of droplets per unit volume. In addition, from Eq. (1)

$$\dot{x} = \theta - \theta_\infty e^{1/x}, \quad (3)$$

where $\theta = c/c_o$ and $\theta_\infty = c_\infty/c_o$. Eq. (2) can be rewritten as

$$\frac{\partial f}{\partial T} = -\dot{x} \frac{\partial f}{\partial x}, \quad (4)$$

where the cumulative distribution $f = \int_x^\infty n dx'$ or $n = -\partial f/\partial x$. Eq. (3) is the well-known Burger's equation. The following simplifying assumptions have been made in writing the above population balance equations: ionic surfactants adsorb on the drop surfaces and the charged drops repel each other. The rate of coalescence is reduced or even eliminated over very large time scales. Consequently, it is assumed that there is no drop coalescence. In general, all surfactants make the interface inextensible and the thinning of the film intervening between two drops and leading to coalescence more difficult. The possibility of nucleation has also been ignored. It has been assumed that the change in the bulk surfactant concentration because of Ostwald ripening is negligible.

A material balance for oil in a closed system is

$$\frac{d\theta}{dT} = -3\phi \int_0^\infty \dot{x} x^2 n dx, \quad (5)$$

where $\phi = F(\pi/6)D^3$. Obviously ϕ is a measure of the initial volume fraction of the dispersed phase. According to Eq. (5) the rate of change of oil in the aqueous phase is the negative of the rate of change of oil in the dispersed phase. The object now is to solve Eqs. (3)–(5) subject to $n = -\partial f/\partial x$ and the initial distribution of f and the initial value of θ . Eventually, it is necessary to obtain the third moment of the drop-size distribution as a function of T .

Approximate solutions where the mass transfer is controlled by diffusion in the dispersion medium were first given by Lifshitz and Slezov (1959, 1961) and by Wagner (1961). Kahlweit (1975) has provided a unified treatment of what is now known as the LSW solution. It predicts that the third moment increases linearly with time in keeping with much of the experimental data including those by Kabalnov (1994) under consideration here. In the appendix, we have followed the procedure given by Kahlweit (1975) to determine what the rate law is during the coarsening process when interfacial resistance controls the mass transfer. The result is unsatisfactory in the form of the second moment increasing linearly with time, which is not in keeping with the data for such systems.

Next an attempt was made to solve the problem using the method of moments (Hulburt & Katz, 1964). It is not possible to formulate the problem unless the term $e^{1/x}$ in Eq. (3) is approximated by $1 + 1/x$ and even then a problem results that an appropriate closure cannot be found.

A third method discretizes f in x . That is, f is replaced with f_i and $\partial f/\partial x$ with its forward difference $(f_{i+1} - f_i)/\Delta$ where Δ is the step size in x . This gives rise to a set of coupled ordinary differential equations for f_i in time. Stable solutions can be obtained using upwind differencing (Chang & Cooper, 1970), which also introduces an “artificial viscosity” and has not been used here.

The method that was successful integrates Eq. (4) along the characteristic. One has

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial T} dT$$

on using the chain rule. At constant f , it reduces to

$$\frac{dx}{dT} = -\frac{\partial f/\partial T}{\partial f/\partial x}.$$

On using Eq. (4)

$$\frac{dx}{dT} = \dot{x} \quad (6)$$

results. Consider the initial distribution $f = g(x)$. It is discretized to $\{g_i, x_i\}$ and for a fixed g_i , x_i is updated by integrating Eq. (6). Along with Eq. (5), one solves

M ordinary differential equations where M represents the total number of points $\{i\}$. Eventually, $1/x$ was replaced with $10^3x/(10^3x^2 + 1)$ which becomes $10^3 x$ for very small values of x , and $1/x$ for large values of x . These two regimes are separated approximately at the maximum located at $x = 0.03$. That is, the function $1/x$ is replaced by similar function which is well behaved in the immediate vicinity of $x = 0$. Another problem appears due to the discretization. Over time, values of some x_i increase and some decrease. The ones that reach zero and move to negative values, actually represent drops that have disappeared and should not be counted anymore. This is implemented in the algorithm.

$$\frac{d}{dT}f(0, T) = \dot{x}n(0, T), \tag{7}$$

where the zero in the parentheses denotes $x = 0$. Note that the dimensionless total number of drops $f(0, T)$ decreases with time since \dot{x} at $x = 0$ is negative. Due to discretization, the drops move out of the domain in discrete packets. Now Eq. (5) requires one to calculate an integral from $x = 0$. However, due to the movement of points out of the domain in packets, the smallest positive x_i is some distance away from $x = 0$, and the value of the integral jumps when it disappears and the algorithm moves to x_{i+1} as the current smallest positive value. To prevent these jumps, a linear interpolation has been done

to locate the value of f at $x = 0$. Thomaidis, Zygourakis, and Wheeler (1988) note in their comprehensive treatment of nearly hyperbolic equations by integrating along the characteristics, that points do get convected out of the domain but offer no systematic method for handling this problem. Their stability criterion shows that the present case is unconditionally stable.

The initial cumulative distribution is represented with the Fermi function

$$g = \frac{1}{1 + e^{\alpha(x-x_0)}}. \tag{8}$$

The function falls from 1 to 0 around $x = x_0$. The steepness of the fall increases with α . The value of the mean is a little higher than x_0 and becomes x_0 as α increases, and α can be decreased to increase the polydispersivity.

3. Results and discussion

The value of M was equal to 41, that is, 41 points in x , giving rise to 41 characteristic equations from Eq. (6), plus the conservation equation, Eq. (5), leading to 42 differential equations. The two parameters describing the initial distribution in Eq. (8) were taken to be $x_0 = 10.0$ and $\alpha = 1.0$, that is, the distribution is quite steep. The solubility θ_∞ was taken to be 0.1 or 0.2 and the initial

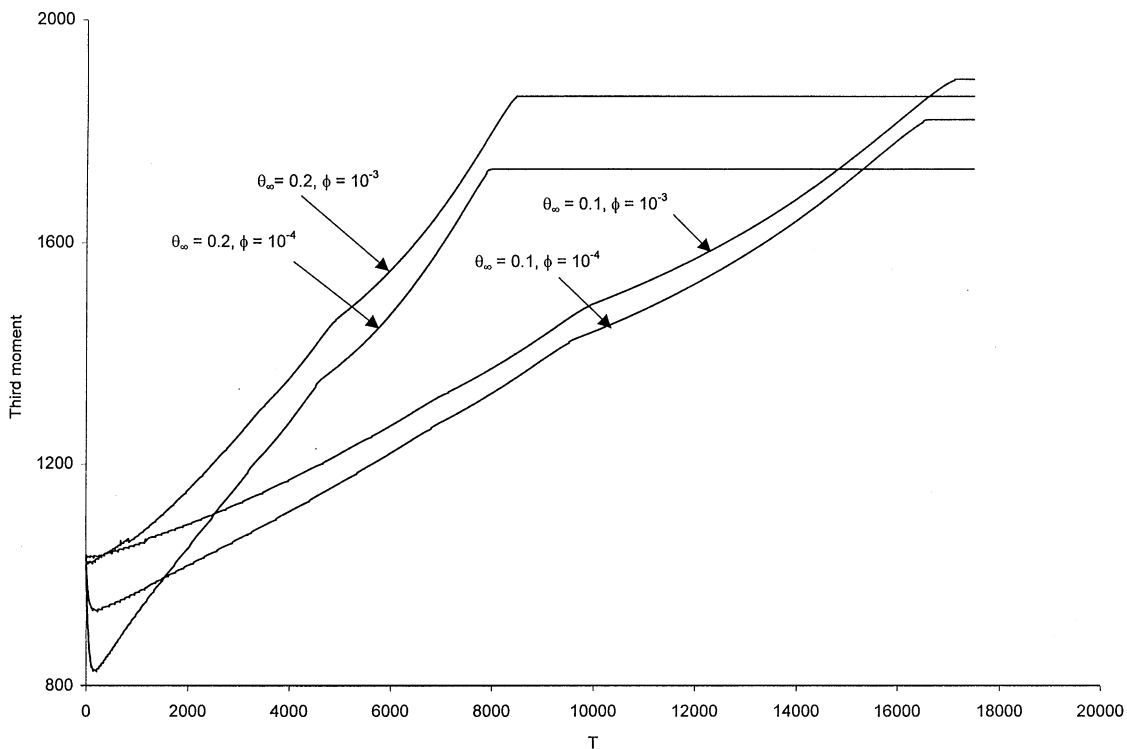


Fig. 2. Dimensionless third moments plotted against dimensionless time T . The common feature is the initial distribution. The two which equilibrate rapidly are for $\theta_\infty = 0.2$ and the slower ones are for 0.1. For a particular θ_∞ the one with $\phi = 10^{-3}$ equilibrates first and one with $\phi = 10^{-4}$ equilibrates last.

amount of concentration θ was also set to θ_∞ to cut down the size of initial transients. The realistic range of values for the last parameter ϕ was found to lie between 10^{-3} and 10^{-4} . Such a number, which is quite apart in magnitude from the rest, makes the equations very stiff, and Gear's subroutine in double-precision DIVAPG was used from the IMSL package. The time period chosen was 0.1.

Fig. 2 shows the third moments as functions of time. Initially, the third moment decreases rapidly at very small times, which is followed by a linear increase at larger times. The response also exhibits abrupt equilibration at larger times. Since one is accustomed to relating the linear relation between the third moment and time to the diffusional resistance as the controlling resistance, the present result that the linearity is preserved in this case is surprising. Possibly, the linear dependence on the concentration difference, which is common to the two rates, plays the key role. Very small waves can be seen in the plots in Fig. 2, which arise due to discrete packets reaching $x = 0$ as explained earlier. It is seen that ϕ has a small impact on the solution, but θ_∞ has a strong effect. Increasing θ_∞ by a factor of two decreases the equilibration time by a factor of two. Investigation into the details of the distribution f showed that packets of drops reached $x = 0$ only very slowly and stayed in the immediate vicinity. Thus, the present interpolation scheme can be expected to succeed.

Fig. 3 shows how the supersaturation (as measured by the increase over θ_∞) increases with time and then drops slowly to an equilibrium value. Changes in the value of θ_∞ does not change the shape of the curve significantly and a change in ϕ has even less effect. In Fig. 4a are shown the cumulative distribution functions at short times. The initial distribution is quite steep. Coarsening, that is, the increase in diameters of the larger drops can be easily seen. Also visible is a quick fall in values of f at $x = 0$ with time. These values are the dimensionless

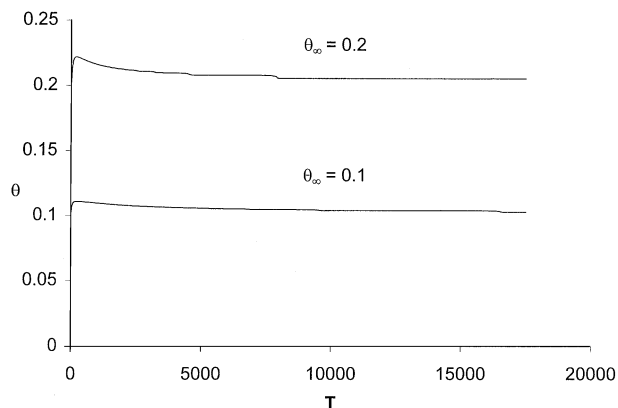


Fig. 3. Dimensionless concentration θ is shown against time. The initial value of θ is θ_∞ . On this plot the responses for the two values of ϕ , 10^{-3} and 10^{-4} , are indistinguishable.

number of drops and equal to 1 at $T = 0$. The distributions at large times are given in Fig. 4b. The two at the largest times occur after equilibration shown in Fig. 2. It is seen that in this phase there is not much change in the number of drops but some coarsening is still taking place. Not shown is the comparison between $\alpha = 1.0$ and 0.5. In the latter case the distribution is broader, leading to a larger initial value for the third moment, but it increases at the same rate as the $\alpha = 1.0$ case.

From Fig. 2, one has to the first approximation that the equilibration time T_e is proportional to $1/\theta_\infty$, or in terms of dimensional variables t_e is proportional to $Dc_0/2k_i c_\infty$. Alternatively for the zeroth-order rate process considered here, the rate is proportional to $2k_i c_\infty/Dc_0$. This is also found to be the case for the rate of change of the second moment with time for LSW method shown in the appendix. As shown in Fig. 1 schematically, only some of Kabalnov's (1998) experiments fall in the low-concentration range, two to be precise: one at 10 mM and the other at 33 mM of SDS. The ratio between these two rates is about 2.0. From the present theory, these rates should be proportional to $k_i c_\infty$, where it can be assumed that k_i is proportional to τ_2^{-1} and that c_∞ is proportional to the amount of surfactant present. Using the value of τ_2^{-1} reported by Lessner et al. (1981b) to estimate k_i , the ratio of the two rates works out to be 33.3! Even though this value does not agree with the experiments, the model is able to predict the correct trend, i.e. the rates should decrease with surfactant concentration and not increase. It also shows that the data of Kabalnov (1994) at low surfactant concentrations are indeed controlled by interfacial resistance.

There are many sources that introduce the inaccuracies seen above. The system of Lessner et al. (1981b) contain no solubilize, that of Williams et al. (1999), where the expression for the interfacial resistance has been developed contain very small amount of a solubilize and the system of Kabalnov (1998) contain significant-to-large amount of solubilize. Solubilizes perturb equilibrium as well as nonequilibrium properties (Lang & Zana, 1987; Friberg et al., 1985; Raney et al., 1985). In spite of these problems, all other features at low surfactant concentrations can be predicted well. This is of importance as some of these run counter to intuition.

The curious observation to make of the research in this area is that very little effort appears to have been made in solving the population balance problem beyond the LSW scheme. The governing equations are difficult to solve, but a lot of progress has been made in numerical solutions, which appear to have been obtained here for the first time. A wealth of details has now emerged on the coarsening process. No shocks appear to form. We also attempted to solve the problem where the diffusion in the dispersion medium is rate controlling. As the Sherwood number is 2 in such system, the mass transfer coefficient is inversely proportional to the drop diameter. At large

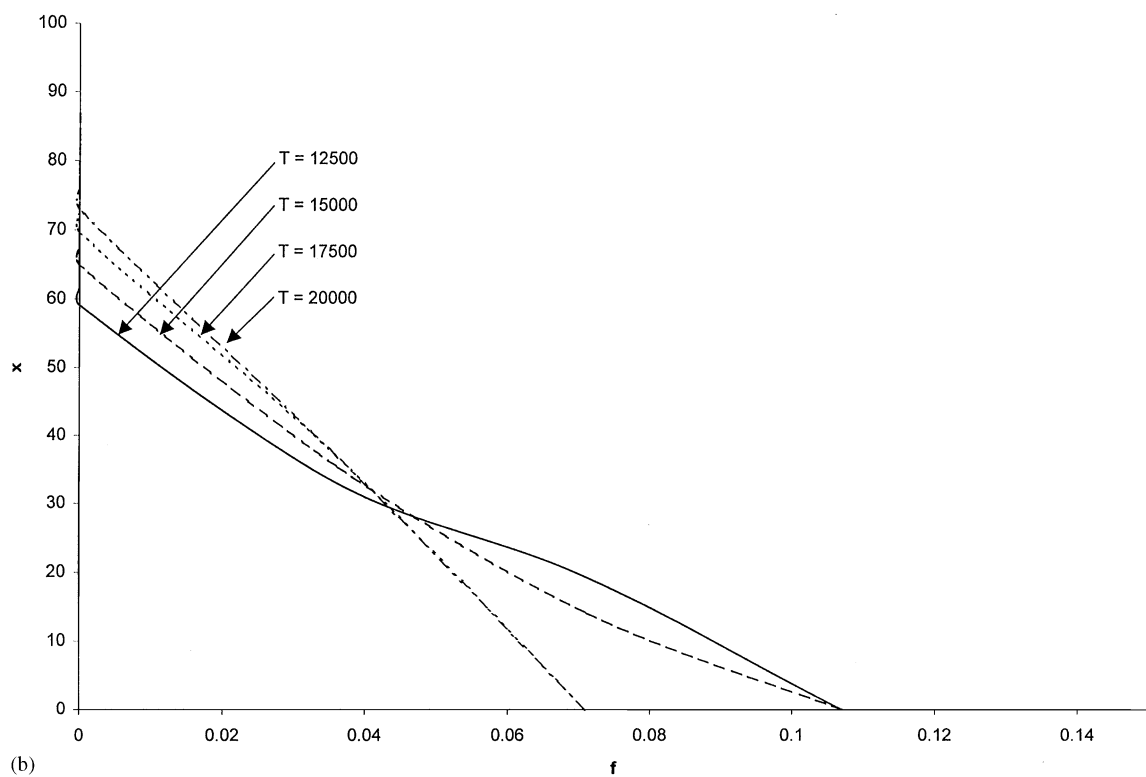
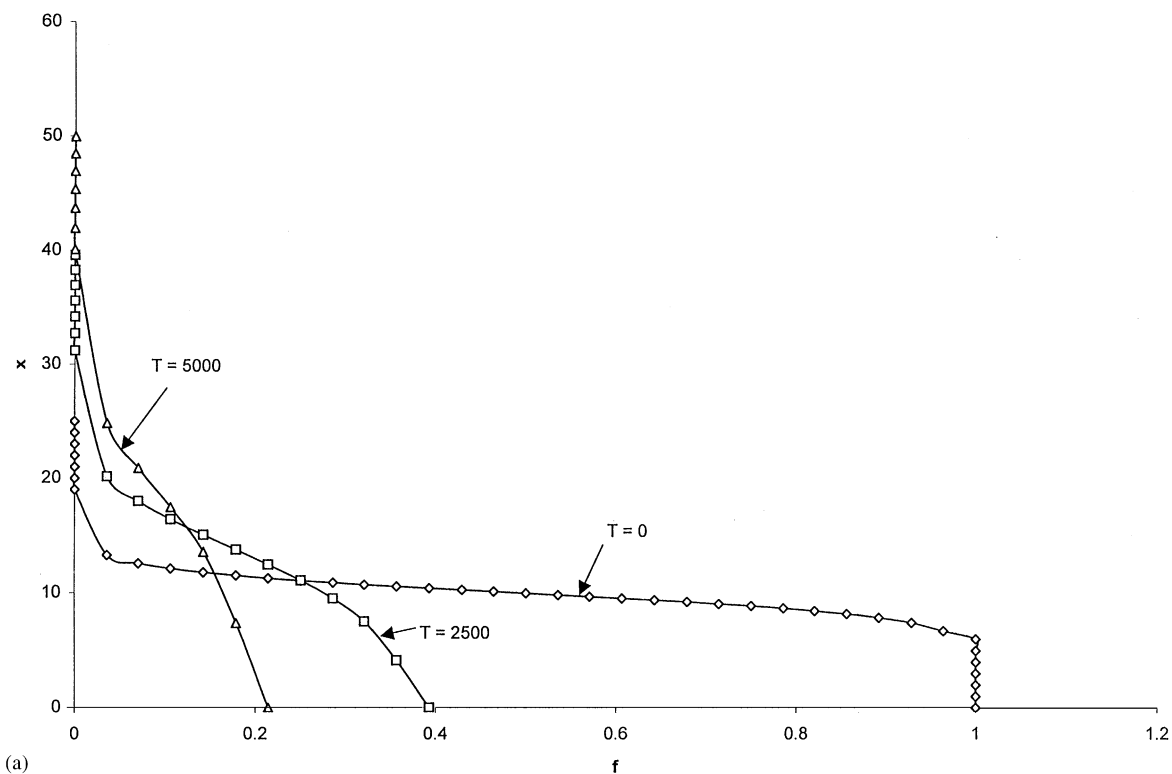


Fig. 4. a. The distributions f have been plotted as a function of x , at $T = 0, 2500$ and 5000 . The values of parameters are $\theta_\infty = 0.1$, $\phi = 10^{-4}$, $x_0 = 10$ and $\alpha = 1.0$. b. The distributions f have been plotted as a function of x , at $T = 12,500, 15,000, 17,500$ and $20,000$. The values of parameters are $\theta_\infty = 0.1$, $\phi = 10^{-4}$, $x_0 = 10$ and $\alpha = 1.0$. In Fig. 2, it is seen that at the last two times equilibration has been reached.

values of x , therefore, mass transfer becomes very small. The numerical solutions show that the coarsening is very slow. In fact at $T = 20,000$ in Fig. 2, where all systems have reached equilibrium, the diffusion limited systems has just overcome the initial transients. Consequently, we need to rescale the problem and rewrite the computer codes to solve this case, which is a large amount of work that has not been undertaken. But if the response is very slow, it suggests that Kabalnov's (1994) data at large surfactant concentrations may indeed be limited by diffusion (with electrostatic repulsion) as suggested by him.

Appendix

The LSW method as generalized by Kahlweit (1975) is used to characterize the coarsening process. Eq. (3) is expanded to read

$$\dot{x} = \Delta\theta - \theta_\infty/x, \quad (\text{A.1})$$

where $\Delta\theta = \theta - \theta_\infty$ is the supersaturation and a critical diameter is defined as

$$x_c = \theta_\infty/\Delta\theta. \quad (\text{A.2})$$

When $x = x_c$, $\dot{x} = 0$.

Now, the basic premise of LSW theory is that during steady coarsening

$$\rho = \frac{x}{x_c} \sim 1. \quad (\text{A.3})$$

Differentiating Eq. (A.3) with T ,

$$\frac{d}{dT} \left(\frac{x}{x_c} \right) = \frac{\Delta\theta}{x_c} \left[\frac{(\rho - 1)}{\rho} - \frac{\dot{x}_c \rho}{\Delta\theta} \right] \sim 0, \quad (\text{A.4})$$

where Eq. (A.1) has been used. The expression within square brackets when set to zero yields two roots for $\rho = \frac{1}{2}[q \pm \sqrt{q^2 - 4q}]$ where $q = \dot{x}_c/\Delta\theta$. Kahlweit (1975) argues that the maximum in ρ (as indicated in Eq. (A.4)) should be picked for that value which produces the highest value, which occurs when the two roots are equal, or $q = 4$. One has

$$\dot{x}_c = 4\Delta\theta = \frac{4\theta_\infty}{x_c} \quad (\text{A.5})$$

or

$$\frac{dx_c^2}{dT} = 8\theta_\infty$$

and substituting Eq. (A.1)

$$\frac{dx^2}{dT} = 8\theta_\infty.$$

Averaging this equation, one has the LSW equivalent that

$$\frac{dx^2}{dT} = 8\theta_\infty. \quad (\text{A.6})$$

Using dimensional time

$$\frac{dx^2}{dt} = \frac{16k_t c_\infty}{Dc_o}. \quad (\text{A.7})$$

References

- Carroll, B. J. (1981). The kinetics of solubilization of non-polar oils by nonionic surfactant solution. *Journal of Colloid and Interface Science*, 79, 126.
- Chang, J. S., & Cooper, G. (1970). A practical difference scheme for Fokker-Planck equations. *Journal of Computational Physics*, 6, 1.
- Friberg, S. E., Mortensen, M., & Neogi, P. (1985). Hydrocarbon extraction into surfactant phase with nonionic surfactants. I. Influence of phase equilibria for extraction kinetics. *Separation Science and Technology*, 20, 285.
- Hulburt, H. M., & Katz, S. (1964). Some problems in particle technology. A statistical mechanical formulation. *Chemical Engineering Science*, 19, 555.
- Kabalnov, A. (1994). Can micelles mediate mass transfer between droplets?. *Langmuir*, 10, 680.
- Kabalnov, A. (1998). Thermodynamic and theoretical aspects of emulsions and their stability. *Current Opinion Colloid Interface Science*, 3, 270.
- Kahlweit, M. (1975). Ostwald ripening of precipitates. *Advances in Colloid and Interface Science*, 5, 1.
- Lang, J., & Zana, R. (1987). Chemical relaxation methods In R. Zana *Surfactant solutions* (p. 405). New York: Marcel Dekker
- Lessner, E., Teubner, M., & Kahlweit, M. (1981a). Relaxation experiments in aqueous solutions of ionic micelles. 1 Theory and experiments on the system H₂O-sodium dodecyl sulfate-NaClO₄. *Journal of Physical Chemistry*, 85, 1529.
- Lessner, E., Teubner, M., & Kahlweit, M. (1981b). Relaxation experiments in aqueous solutions of ionic micelles. 2 Experiments on the system H₂O-sodium dodecyl sulfate-NaClO₄ and their theoretical interpretation. *Physical Chemistry*, 85, 3167.
- Lifshitz, I. M., & Slezov, V. V. (1959). Kinetics of diffusive decomposition of supersaturated solid solutions. *Soviet Physics J.E.T.P.* 35, 331 (English translation); 8, 479 (original).
- Lifshitz, I. M., & Slezov, V. V. (1961). The kinetics of precipitation from supersaturated solutions. *Journal of Physics and Chemistry of Solids*, 19, 35.
- Ostwald, W. (1896). *Lehrbuch der Allgemeinen Chemie*, vol. 2, part 1, Leipzig, Germany.
- Ostwald, W. (1897). Studien uber die Bildung und Umwandlung fester Korper. *Zeitschrift fuer Physikalische Chemie*, 22, 289.
- Raney, K. H., Benton, W. J., & Miller, C. A. (1985). Use of videomicroscopy in diffusion studies of oil-water-surfactant systems. In D. O. Shah, *Macro- and Microemulsions* (p. 193). Washington, D.C: American Chemical Society.
- Taylor, P. (1998). Ostwald ripening in emulsions. *Advances in Colloid and Interface Science*, 75, 107.
- Thomaidis, G., Zygourakis, K., & Wheeler, M. F. (1988). An explicit finite difference scheme based on the modified method of characteristics for solving convective-diffusive problems in one space dimension. *Numerous Methods for Partial Differential Equations*, 4, 119.
- Wagner, C. von (1961). Theorie der Alterung von Niederschlagen durch Umlosen (Ostwald-Reifung). *Zeitschrift fuer Elektrochemie*, 65, 581.
- Williams, C. L., Bhakta, A. R., & Neogi, P. (1999). Mass transfer of a solubilize in a micellar solution across an interface. *Journal of Physical Chemistry*, 103, 3242.