

SEPARATIONS

Phase Separation of Liquid Mixtures in the Presence of Surfactants

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The presence of surface-active compounds does not influence the settling time of a partially miscible liquid mixture as it phase separates. On the other hand, when the same mixture is agitated isothermally while in its two-phase state, its settling time greatly increases if surfactants are added. This phenomenon is monitored microscopically through a series of direct visualizations and is explained theoretically by applying the model H, showing that phase separation is governed by the convective motion due to capillary forces. These forces induce a net attraction between droplets which greatly dominates the repulsive forces due to the presence of surfactants.

1. Introduction

In recent years, our research group has developed a new solvent extraction process^{1–3} that is based on the fact that phase separation of partially miscible solvent mixtures is very rapid, irrespective of the presence of emulsifying compounds within the solution. On the other hand, surfactants strongly retard the coalescence rate of two-phase liquid mixtures after isothermal mixing, causing the formation of stable emulsions. The applications of these results can be found in any liquid–liquid operation involving phase separation, both when emulsions are the final product of the process and when they are detrimental to it. In the first case, emulsions are actively looked after, such as in cosmetics and food industries, while in the second case, as in most extraction processes, they must be broken using coalescers, centrifuges, and skimmers.

Separation and extraction via phase transition is an interesting alternative, because it does not introduce unwanted side effects as, for example, in centrifuging, where the products may degrade because of the high shear stresses involved. In fact, as shown in Gupta et al.² and Ullmann et al.,³ our approach can be used to perform a two-stage liquid extraction process. First, the system is brought to the one-phase region of its phase diagram, where ideal mixing is achieved and the solute can be extracted very efficiently from the native solvent. Then, the system is brought rapidly into its two-phase region, by changing either its temperature or its composition, resulting in rapid phase separation. The macroscopic characteristics of this process were studied in a previous work by Gupta et al.,² using a water–acetonitrile–toluene mixture with a 65 °C critical temperature, to which 20 ppm of surface-active, crystal violet dye was added. Two methods of phase separation were considered. In the first, the system was heated to 75 °C and then quenched back to ambient temperature, whereas in the second method the two-phase liquid mixture was agitated isothermally at ambient temper-

ature. We referred to the former method as TIPS (temperature-induced phase separation), while the latter is well-known in the chemical engineering literature⁴ and is generally referred to as LLE (liquid–liquid extraction). Surprisingly, we found that in the TIPS process phase separation was completed within 20 s, while for LLE a stable emulsion was formed, which remained suspended for more than 2 h. In addition, when solutes were dissolved within the mixture, their concentrations within the two phases at the end of the separation process were equal to their equilibrium value. Finally, when the above experiments were repeated with higher surfactant concentration, we found that the settling time for the TIPS process was almost unchanged, while for the LLE process it increased enormously. This result was somewhat unexpected because deeply quenched, partially miscible mixtures start to phase separate by forming microscopic droplets, and therefore one would expect that TIPS should be more, not less, influenced by the presence of surfactants.

In this work, we complement the previous macroscopic experiments with microscopic observations, describing the dynamics of the separation process and the influence of surfactants on the mechanism of drop coalescence. In fact, our result that coalescence is not slowed down by the presence of emulsion-forming compounds was previously explained by the conjecture¹ that there are no stable or well-defined boundaries between the different phases, to which emulsifier molecules can adhere. Here, we provide a more convincing explanation of that phenomenon, based on the fact that phase separation of deeply quenched liquid mixtures is driven by the motion induced by capillary forces. In fact, because this transport process is convection-driven, we will show that various compounds can be extracted equally fast, independently of their molecular weights, as opposed to the slower extraction rate of heavy molecular weight compounds occurring in the diffusion-driven phenomenon of LLE. Finally, we present a dimensional analysis and try to explain theoretically the role of attractive and repulsive forces during phase separation in the presence of surfactants.

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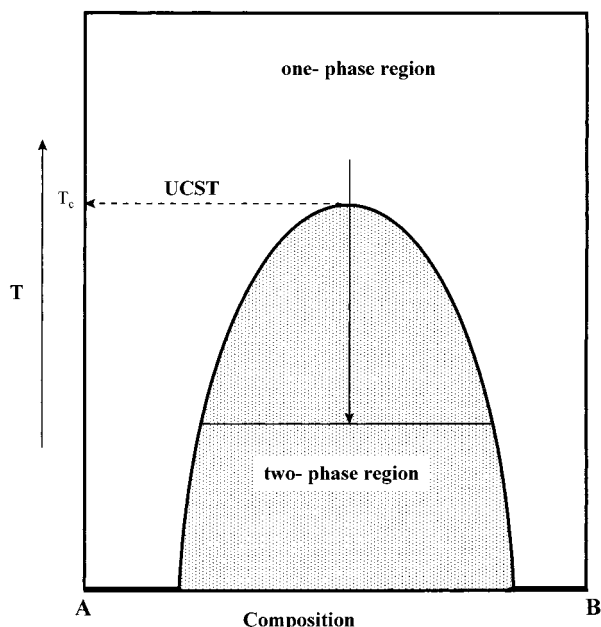


Figure 1. Typical phase diagram of partially miscible mixtures.

2. Background

When an initially single-phase binary mixture is brought across its miscibility curve into the two-phase region at temperature T , it phase separates (see Figure 1). This process can occur either by nucleation (both heterogeneous and homogeneous) or by spinodal decomposition (see Debenedetti⁵ and references therein). The former process describes the relaxation to equilibrium of a metastable system, while the second one is typical of unstable systems. Therefore, nucleation is an activated process, where a free energy barrier has to be overcome in order to form embryos of a critical size, beyond which the new phase grows spontaneously; in most practical cases, suspended impurities or imperfectly wetted surfaces provide the interface on which the growth of the new phase is initiated.⁶

Contrary to nucleation, spinodal decomposition occurs spontaneously, without any energy barrier to be overcome, and involves the growth of fluctuations of any amplitude that exceed a critical wavelength.^{7,8} In principle, nucleation and spinodal decomposition are fundamentally different from each other, as metastable systems relax via the activated growth of localized fluctuations of large amplitude, whereas unstable systems do so via the spontaneous growth of long-wavelength fluctuations of any amplitude. However, for deep quenches, the distinction between the two processes is rather murky, because both the critical nucleus size and the critical fluctuation wavelength decrease as the temperature quench increases.

Experimental studies on spinodal decomposition have shown that, at the end of an initial, very fast (i.e., a few milliseconds) separation process, small microdomains appear, which later grow by diffusion and coalescence,⁹ until they become large enough to sediment. Because the early stages of spinodal decomposition in fluids tend to be extremely rapid, in most of the experimental studies the process is retarded by considering very shallow quenches ΔT below the critical temperature T_c , i.e., for $\epsilon = |T - T_c|/T_c < 10^{-5}$. At these conditions, fluid mixtures start to separate by diffusion only, leading to the formation of well-defined patches

(Chou and Goldberg,¹⁰ Wong and Knobler,¹¹ and Gueunon et al.¹²), separated from one another by sharp interfaces. These single-phase domains are at local equilibrium with each other, with their typical size growing with time as $r(t) \sim t^{1/3}$, as has been shown both experimentally¹⁰ and theoretically.⁹ This initial, diffusion-driven stage is followed by a convection-driven stage, during which a linear growth, $r(t) \sim t$, is observed,¹⁰⁻¹² in agreement with the theoretical estimate by Siggia.¹³ More recently, the numerical simulation of Tanaka and Araki¹⁴ and Vladimirova et al.,^{15,16} together with the experimental investigation of Gupta et al.,¹⁷ has shown that in phase-separating fluid systems convection is driven by a concentration-gradient-induced capillary force, which is responsible for the enhanced coarsening rate among droplets. In addition, these studies have shown that deeply quenched liquid mixtures are never at local equilibrium, because the two stages of phase segregation and domain growth, which for shallow quenches occur successively with one another, now take place simultaneously. Finally, in the so-called, "late" stage of coarsening, phase-separating drops become large enough that buoyancy dominates convection, and the mixture separates by gravity. This occurs when the size of the domains is $r_{\max} = O(\sigma/g\Delta\rho)$, where σ is the surface tension, g the gravity field, and $\Delta\rho$ the density difference between the two separating phases.¹³ In the case of our liquid mixture, that would correspond to $r_{\max} \sim 1$ mm.

When surface-active compounds are dissolved within a liquid mixture, the phase-separating process becomes, obviously, more complex, because coalescence tends to be retarded by surfactants. This phenomenon, however, has been studied extensively only for systems at local equilibrium, where the compositions of the dispersed and continuous phases are constant and equal to their equilibrium values. On the other hand, there are no published data on the influence of surface-active solutes on the coalescence rate of the single-phase domains that form in deeply quenched, phase-separating liquid mixtures.

Stable emulsions in mixtures of mutually immiscible liquids are usually composed of small, 1- μm -size droplets. In this case, as phases are in equilibrium with one another, droplet coalescence is driven only by interfacial tension, i.e., the higher the tension, the more rapid is the coalescence rate. This is why two pure liquids rarely form a stable emulsion and a third substance nearly always must be present, i.e., to lower the surface tension. These modifiers can be of two types, inducing the formation of either electrical double layers (charge stabilization) or protective layers (steric stabilization) on the droplet surface.^{18,19} Ionic surface-active agents belong to the first type of surfactants, inducing charge stabilization through the adsorption of ions or polyelectrolytes at the surface of the drops. In this case, droplets are stabilized because, on the one hand, these electrical double layers tend to prevent the flocculation of equally charged droplets and, on the other hand, they retard the draining of the liquid film, because of the electroviscous effect (i.e., the electrostatic attraction between droplet interfaces and flowing films).^{18,19} The second type of surfactants is far less efficient, because they simply form a protective layer at the surface of the drop, thus obstructing mass transport across the interfaces, as happens with nonionic emulsifiers, polymers, or finely divided solids.

3. Experimental Setup

An experimental setup was designed and built to allow the observation of the phase separation process in the size range of 10 μm to 7 mm. It consisted of a temperature-regulated, 1-mm-thick, 40-mm-high sample cell, and a video camera (Sony XC-711) or still camera (Nikon F-5 with Data Back MF-28) mounted on an optical microscope (Nikon Optiphot-2). Alternately, instead of the microscope, we used bellows to get a field of view of 2.5 mm to 4 cm. The Nikon F-5 camera was chosen for its high-speed film advance (up to 8 frames/s). The temperature was regulated by placing the sample cell into an 8-mm-thick water jacket, into which temperature-controlled water was circulated. Initially the solution, having an upper critical temperature (UCT), was kept at a temperature above its critical point of miscibility, where, at equilibrium, the system is one-phase and homogeneous. Then, the solution was quenched below its critical point of miscibility by quickly changing the temperature of the water circulating within the jacket.

This experimental setup allowed us to obtain an initial quenching rate of 3 $^{\circ}\text{C}/\text{s}$. Temperatures were measured by inserting 350- μm thermocouples, with 0.04-s response time, at various locations inside the cell and connecting them with a data acquisition system. All of the pictures, obtained through both the microscope and the bellows, were taken with a fast shutter speed of $1/100$ s or more, and professional Kodak Gold 100 film was chosen for all of the exposures. A video camera was used to capture up to 20 frames/s, using a Matrox Meteor frame grabber. Matrox Inspector software was used to grab images, make movie files, enhance the image quality, and analyze the images.

In our experiments we used a liquid mixture composed of water, acetonitrile, and toluene, whose thermodynamic properties were determined in previous works.^{1,2} Two types of solutions were considered, with critical temperatures of 35 and 67 $^{\circ}\text{C}$, respectively. The first mixture had a critical volumetric composition of 38% water, 58% acetonitrile, and 4% toluene, undergoing a phase transition at 35 $^{\circ}\text{C}$, while the second solution was off-critical, with a volumetric composition of 54% water, 41% acetonitrile, and 5% toluene, undergoing phase transition at the same 35 $^{\circ}\text{C}$ temperature as the critical mixture. All of the solvents were HPLC grade, while the water was double distilled. The analysis of the phase composition was conducted using an HP 5890 gas chromatograph.

Two types of solute were added to the liquid mixture, namely, 50 ppm of crystal violet and 100 ppm of blue dextran. Crystal violet has a 407 molecular weight and dissolves preferentially in the solvent-rich phase, while blue dextran has a 2 000 000 molecular weight and dissolves preferentially in the water-rich phase. Both crystal violet and blue dextran have strong colors, which facilitate the visualization of the phase separation process. In addition, crystal violet is a cationic emulsifier compound, which makes it ideal to study coalescence during the phase separation of liquid mixtures. In fact, as we have shown in previous works,^{1,2} when our solvent mixture is agitated at ambient temperature (i.e., in the two-phase region), the presence of the crystal violet dye strongly increases the settling time from 10 s (with no dye) to 2 h (with 20 ppm dye). On the other hand, when the same mixture is heated and cooled across its

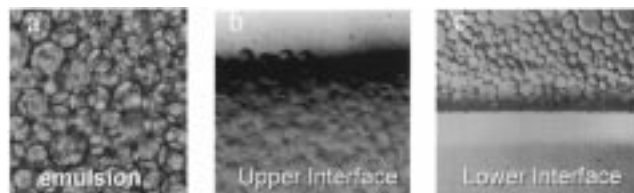


Figure 2. Morphology of the liquid mixture in its two-phase state after it has been mixed isothermally.

miscibility curve, it separates rapidly, irrespective of the presence of the dye.

In all of our experiments, we started with the mixture in its phase-separated state at a constant temperature of 15 $^{\circ}\text{C}$. Then, the solution was first heated from 15 to 38 $^{\circ}\text{C}$, mixed thoroughly, and finally quenched back to 15 $^{\circ}\text{C}$.

4. Experimental Results

We first visualized the settling process, following the mixing of the critical liquid mixture at constant, 15 $^{\circ}\text{C}$, temperature. Because of the presence of 50 ppm crystal violet dye, the surface tension was lowered and small drops were stabilized as soon as they formed, thereby causing a stable emulsion to form. Figure 2a presents a typical morphology of the emulsion formed in such cases. Microscopically, we saw that the emulsion region was filled with micron-size drops within the continuous phase, which slowly moved upward toward the upper interface, where they coalesced (Figure 2b). The lower interface, which looked macroscopically similar to the upper one (see Figure 2c), in reality was quite different. In fact, no coalescence occurred there, and the interface was simply the dividing line between the emulsion region, which shrank as drops coalesced at the upper interface, and the lower, water-rich clear phase, which grew as the drops moved up. Therefore, both upper and lower phases grew as the result of the coalescence of the drops at the upper interface. On the contrary, hardly any coalescence between drops was observed in the middle emulsion region, primarily because of the presence of the coalescence retarding dye on the drop surface.

Completely different morphologies were observed when the critical mixture was quenched from 38 to 15 $^{\circ}\text{C}$, as shown in Figure 3. All pictures were taken using either a digital camera or a 35-mm camera, as explained earlier. Using a field of view of 300 μm , in Figure 3 we see at first the appearance of ~ 10 - μm microdomains (smaller objects cannot be observed, because of limitations in the optical resolution of our apparatus), which subsequently grow to form a bicontinuous structure. Similar growth patterns were observed also when the field of view was changed from 300 μm to 2.5 mm. After reaching millimeter size, domains started to experience gravitational effects and the system rapidly separated into two gravity-stabilized regions. The final equilibrium state was reached in no more than 20 s, except for the presence of some small drops that remained in both phases. The same behavior was obtained with different surfactant concentrations.

For off-critical mixtures, we obtained results similar to those for critical ones, with the basic difference that, as one would expect, in the off-critical case we observed the formation of isolated drops of the minority phase, instead of the bicontinuous structures of the critical case.

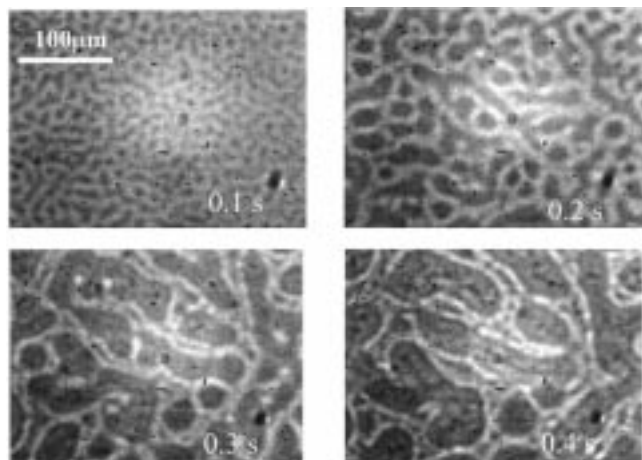


Figure 3. Phase separation in a critical liquid mixture with a 300- μm field of view. Time is measured from the moment when $T = T_c$.

The growth rate of these fast-coarsening structures can be determined by defining the equivalent radius of the domains as a function of time

$$r(t) = \frac{\int \phi(\mathbf{k}, t) d^3\mathbf{k}/|\mathbf{k}|}{\int \phi(\mathbf{k}, t) d^3\mathbf{k}} \quad (1)$$

where $\phi(\mathbf{k}, t)$ is the Fourier transform of the composition $\phi(\mathbf{x}, t)$ of the mixture at location \mathbf{x} and time t . Experimentally, we verified that, in the range of concentrations considered in our experiments, the dye concentration was proportional to the solvent volume fraction, so that $r(t)$ can be evaluated using eq 1, with $\phi(\mathbf{x}, t)$ denoting the degree of grayness of the pixel located at \mathbf{x} . As we see in Figure 4, for critical mixtures the drop size grew linearly in time from 10 to 400 μm , indicating that phase segregation is governed by convective forces (see the next section). The growth rate was 76 $\mu\text{m/s}$ as long as the phase domains were separated from each other and 200 $\mu\text{m/s}$ for times $t > 1$ s, where the morphology was bicontinuous. For off-critical mixtures, the linear growth was 68 $\mu\text{m/s}$, which is comparable with that of the critical case.

Although it was well-known experimentally^{10–12} that the size of the microdomains grows linearly in time, this is the first time that this growth was measured for large temperature quenches (i.e., $\epsilon = |T - T_c|/T_c \sim 0.1$) and that its value was linked to the morphology of the system.

At this point, we wanted to test the assumption that phase separation is governed by convection. To do that, we performed an experiment similar to that performed by Eliyahu and Ludmer,²⁰ to show that during phase separation heavy molecular weight compounds can move with the same speed as lighter solutes. To do that, we studied the phase separation of the liquid mixture described above using, as the solute, 100 ppm of blue dextran dye, which has a molecular weight of 2 000 000. We found again that the separation time was short, i.e., about 10 s, and, in addition, the amount of blue dextran present in each phase immediately after phase separation was equal to its equilibrium values, showing that any solute can be extracted equally fast, independent of its molecular weight. Now because in the absence of convection, a high molecular weight solute would move very slowly, here we have proven that diffusion does

not play any role in extracting the solute and the extraction process is entirely controlled by convection. Accordingly, as the solute molecules follow the bulk flow, it is not surprising that the time needed for the solute to reach its equilibrium concentrations within the two phases is independent of the solute molecular weight.

5. Theoretical Model

5.1. Capillary Forces during Phase Transition.

The motion of an incompressible binary fluid mixture composed of two species A and B is described through the so-called model H (Hohenberg and Halperin⁷). Here, A and B are assumed to have equal viscosities, densities, and molecular weights, with the composition of the system uniquely determined through the molar fraction ϕ of, say, species A.

If the flow is assumed to be slow enough to neglect the dynamic terms in the Navier–Stokes equation, conservations of mass and momentum lead to the following system of equations:

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = -\frac{1}{\rho} \nabla \cdot \mathbf{J} \quad (2)$$

$$\eta \nabla^2 \mathbf{v} - \nabla p = \mathbf{F}_\phi \quad (3)$$

$$\nabla \cdot \mathbf{v} = 0 \quad (4)$$

where \mathbf{v} is the average local fluid velocity, \mathbf{J} is the diffusion flux,²¹ and \mathbf{F}_ϕ is a body force. As shown in previous works,^{22,23} \mathbf{J} is determined via the relation

$$\mathbf{J} = -\rho \phi(1 - \phi) D \nabla \tilde{\mu} \quad (5)$$

where ρ is the density of the system, while D is the molecular diffusivity, which is approximately constant even in the vicinity of the consolute point (see Cussler²⁴). In addition, $\tilde{\mu} = \mu_A - \mu_B$ is the generalized chemical potential, which is defined in terms of the Gibbs free energy g .^{8,25}

$$\tilde{\mu} = \frac{\delta(g/RT)}{\delta \phi} \quad (6)$$

with

$$g = [g_A \phi + g_B(1 - \phi)] + RT[\phi \log \phi + (1 - \phi) \log(1 - \phi)] + RT\Psi\phi(1 - \phi) + \frac{1}{2}RTa^2(\nabla\phi)^2 \quad (7)$$

Here g_A and g_B are the molar free energies of the pure species A and B, respectively, at temperature T and pressure P , R is the gas constant, Ψ is the Margules parameter, and a is a characteristic microscopic length. As shown by Van der Waals,²⁶ a is proportional to the surface tension at equilibrium σ , because σ is the energy stored in the unit interfacial area at equilibrium, i.e.,

$$\sigma = \frac{1}{2} \frac{\rho RT}{M_w} a^2 \int_0^1 (\nabla\phi)^2 dx \approx \frac{\rho RT}{M_w} a \sqrt{\Psi - 2} (\Delta\phi)_{\text{eq}}^2 \quad (8)$$

where $(\Delta\phi)_{\text{eq}}$ is the composition difference between the two phases at equilibrium, M_w is the molecular weight of species A and B, and $l \approx a\sqrt{\Psi - 2}$ is the thickness of the interface.^{22,26} Considering that $(\Delta\phi)_{\text{eq}} \sim \sqrt{\Psi - 2}$, we obtain

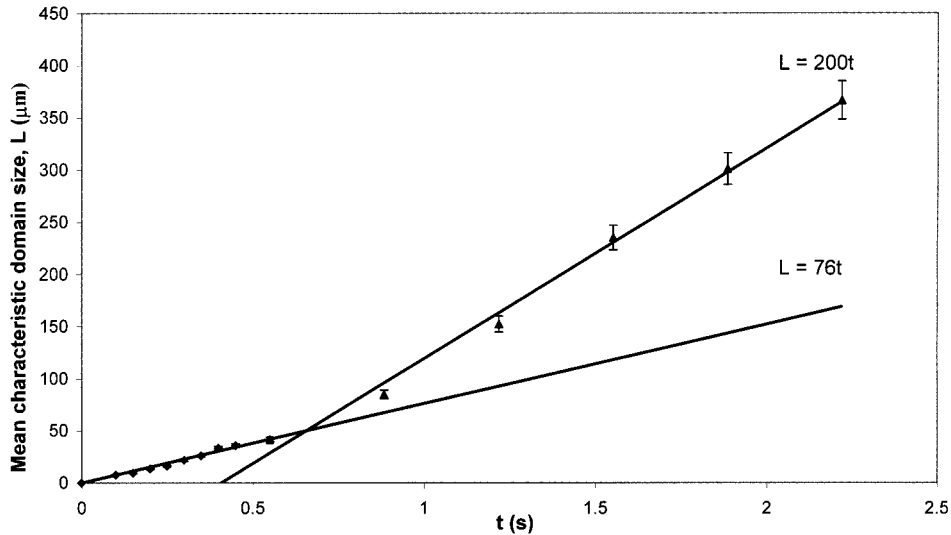


Figure 4. Domain growth during the critical quench.

$$a \sim (\Psi - 2)^{-3/2} \frac{\sigma M_W}{\rho RT} \quad (9)$$

The body force \mathbf{F}_ϕ appearing in eq 3 equals the gradient of the free energy,⁷ and therefore it is driven by the concentration gradients within the mixture (see Farrell and Valls²⁷ and Jasnow and Viñals²⁸).

$$\mathbf{F}_\phi = \frac{\rho}{M_W} \nabla g = \left(\frac{\rho RT}{M_W} \right) \bar{\mu} \nabla \phi \quad (10)$$

Physically, \mathbf{F}_ϕ tends to minimize the energy stored at the interface, driving, say, A-rich drops toward the A-rich region; therefore, it is an attractive force, enhancing the coalescence of droplets. In addition, being proportional to $\bar{\mu} = \mu_A - \mu_B$, the body force is driven by the surface energy and, therefore, can be interpreted as a capillary force, whose magnitude in nondilute cases, i.e., for $\phi = O(1)$, can be estimated via the expression

$$F_\phi \sim \frac{\rho RT \sqrt{\Psi - 2}}{a M_W} \sim \frac{\sigma}{\ell^2 (\Psi - 2)^2} \quad (11)$$

which, as expected, vanishes at the critical point. This force induces a bulk convection of the fluid mixture, characterized by the Peclet number, $N_{Pe} = Va/D$, where V is a characteristic velocity, $V \sim F_\phi a^2 / \eta$ [cf. eq 3],

$$N_{Pe} = \alpha \sqrt{\Psi - 2}, \quad \text{where } \alpha = \frac{a^2 \rho RT}{D \eta M_W} \quad (12)$$

is similar to the “fluidity” parameter defined by Tanaka and Araki.¹⁴ For systems with very large viscosity, α is small, so that the model describes the diffusion-driven phase separation of polymer melts and alloys. For most liquids, however, α is very large. In our case, for example, at $T = 15^\circ\text{C}$ we have $a \sim 10^{-5}$ cm [cf. eq 9, with $\sigma = 10$ dyn/cm] and $D \sim 10^{-5}$ cm²/s, so that $\alpha \sim 10^5$. Clearly, at the critical point $\Psi = 2$ the Peclet number vanishes, because both the body force and the concentration gradient are zero; however, when $\Psi - 2 > \alpha^{-2}$, i.e., when the temperature is at least 0.01°C below the miscibility curve, convection dominates diffusion. Therefore, it appears that in our case diffusion is important only at the very beginning of the separation process. Then, as soon as concentration gradients

develop within the system, the capillary forces take over and lead to the formation of single-phase domains separated by sharp interfaces (see Tanaka and Araki¹⁴ and Vladimirova et al.^{15,16}). When the typical size of these microdomains is denoted by r , a simple mass balance allows us to estimate the growth rate as $dr/dt = \rho^{-1} |\mathbf{J}|$, where \mathbf{J} is the antidiffusive flux [cf. eqs 2–7]

$$|\mathbf{J}| \sim \rho(\Delta\phi)[2\phi(1-\phi)\Psi - 1](a/l)(D/a)$$

obtaining

$$\frac{dr}{dt} \sim \beta \left(\frac{D}{a} \right) \quad (13)$$

with $\beta \sim (\Psi - 2)^2$. Now, considering that for our solvent mixture $\Psi \sim 2.1$, this dimensional analysis predicts a growth rate $dr/dt \sim 100$ $\mu\text{m/s}$, in excellent agreement with our experimental results.

The above dimensional analysis can be rewritten by substituting eq 9 into eq 13, obtaining

$$\frac{dr}{dt} = k_b \frac{\sigma}{\eta} \quad (14)$$

where

$$k_b \sim \alpha^{-1} \sqrt{\Psi - 2}$$

Equation 14 was obtained by Siggia¹³ and San Miguel et al.,²⁹ although their prediction, $k_b \sim 10^{-2}$, far overestimates our growth rate results.

5.2. Colloidal Forces in Liquids. Colloidal particles, when dispersed within our liquid mixture, experience repulsive forces, either electrostatic or steric. Initially, when there are no sharp interfaces within the system, the surfactants will distribute uniformly and, therefore, will not influence the process of phase separation (see Figure 5). Later, however, after droplets have formed, surfactants are swept away by the fluid, moving at speeds exceeding 1 mm/s¹⁷ and clustering on the droplet interfaces (see Figure 5).

Let us compare the magnitude of the attractive capillary force with that of the electrostatic repulsion between two droplets of radius r , assuming that the distance between the droplets is equal to the thickness of their interface, $l \sim a/\sqrt{\Psi - 2}$. Note that for water-

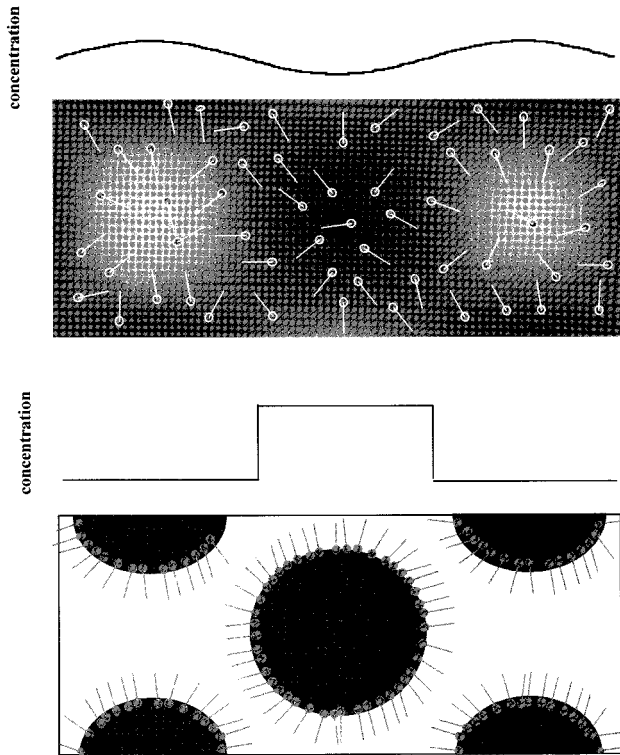


Figure 5. Distribution of surfactant molecules at the early stage of phase separation (above) and after the formation of single-phase domains (droplets), separated by sharp interfaces (below).

based solutions, as in our case, where $a \sim 0.1 \mu\text{m}$, this distance is on the order of the Debye length, i.e., $l \sim \lambda_D$.¹⁹ As the typical repulsive energy V_R between the two droplets in a stable emulsion is of order $10kT$,^{18,19} where k is the Boltzmann constant, the repulsive force is

$$f_R \sim \frac{V^{\max}}{\lambda_D} \sim \frac{10kT}{l} \quad (15)$$

attractive capillary force f_A is equal to the product between the body force F_ϕ and the interfacial volume $V \sim 8\pi r^2 l$, i.e.,

$$f_A \sim \frac{8\pi r^2 \sigma}{l} \quad (16)$$

where we have substituted eq 11 with $(\Psi - 2) = O(1)$. Finally, defining the ratio ξ between the attractive capillary force (16) and the repulsive electrostatic force (15), we obtain

$$\xi = \frac{f_A}{f_R} \sim \frac{r^2 \sigma}{kT} \quad (17)$$

which does not depend on the thickness of the interface l . This analysis reveals that, because $\xi \gg 1$ even for submicron-size drops, the attractive forces due to capillary effects are always dominant with respect to the electrostatic repulsion between drops, caused by surfactants.

Obviously, when, on the other hand, the mixture is agitated isothermally (i.e., without phase transition), the resulting drops are at equilibrium with the continuous phase, so that $\tilde{\mu} = 0$ and $\mathbf{F}_\phi = 0$. Therefore, because there is no attractive force, drops are easily stabilized

by any surface-active compound present within the system, resulting in the formation of stable emulsions.

6. Discussion and Conclusions

In previous studies,² we compared two different processes involving mixtures of two partially miscible liquids, initially in their two-phase state: in the former, the mixture is agitated isothermally, while in the latter, it is heated and cooled across its miscibility curve, inducing phase transition. The most important result of that study is that, while, as expected, the coalescence rate and settling time in the first case are strongly influenced by the presence of emulsifiers, this is not so when the mixture undergoes phase transition. In fact, in this case we found that phase separation is rapid, irrespective of whether or not surface-active compounds are added.

In this work, we offer a clear explanation of this phenomenon. First, we show by microscopic direct visualization that the morphologies of a liquid mixture after isothermal agitation and during phase separation are radically different from each other. In fact, the emulsions that form after isothermal mixing are composed of tightly packed suspensions of micron-size drops, which hardly move and coalesce only at the edge of the emulsion region. This accounts for the slow settling time observed macroscopically and the fact that the presence of surface-active compounds does stabilize the emulsion. On the other hand, when the mixture is brought across its miscibility curve, it appears to be composed of drops moving rapidly and coalescing, revealing that the process is driven by convection and not by diffusion. In fact, we saw that the characteristic size $r(t)$ of the microdomains during phase separation grows linearly with time t , with typical growth rate $dr/dt \sim 100 \mu\text{m/s}$, while it is well-known⁹ that in a diffusion-driven process the characteristic size is expected to grow like $t^{1/3}$. This conclusion is confirmed by the fact that, at the end of the phase separation process, the concentration of a solute within the two phases equals its equilibrium value, irrespective of its molecular weight. In fact, we saw that the extraction times of crystal violet and blue dextran were the same, although these compounds have 407 and 2 000 000 molecular weights, respectively.

Our experimental results are explained, at least qualitatively, using the model H, where fluid convection is driven by a body force \mathbf{F}_ϕ , which is proportional to the local composition gradient. The model H predicts that after an initial stage, characterized by long-range concentration fluctuations, the system separates into single-phase domains, separated by sharp interfaces. At this point, the body force can be identified with the traditional capillary interaction, which drives the motion of the single-phase domains and acts as an attractive interparticle force. As surfactant molecules are convected by fluid motion, they rapidly cluster at the droplet interfaces, inducing electrostatic repulsion. A simple dimensional analysis shows that for micron-size and larger particles the coalescence-enhancing attractive capillary force is much larger than this repulsive force, thereby explaining why indeed surface-active compounds do not appear to influence the settling time of phase-separating liquid mixtures.

Acknowledgment

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