Phase segregation of metastable quenched liquid mixtures and the effect of the quenching rate

by

Filomena Califano[1] and Roberto Mauri[2]

[1] Department of Chemistry and Physics, St Francis College, 180 Remsen Street, Brooklyn Heights, New York 11201, USA, fcalifano@sfc.edu

[2] Department of Civil and Industrial Engineering, Laboratory of Reactive Multiphase Flow, University of Pisa, 56126 Pisa, Italy, roberto.mauri@unipi.it

Abstract

The effect of the quenching rate on the phase separation of partially miscible liquid mixtures of acetonitrile, water and toluene is studied, showing that it may influence the growth rate of single-phase domains. In particular, the phase separation of metastable binary mixtures in the presence of strong emulsifiers appears to be heavily retarded. These effect constitute an important limitation to the phase transition extraction process (PTE) introduced by the authors in previous works, which is based on the fact that phase separation of unstable mixtures is rapid, even in the presence of surface active compounds.

Introduction

When an initial single-phase binary mixture is brought across its miscibility curve into the two-phase region at a temperature below the critical point, it phase separates. This process can occur either by nucleation (both heterogeneous and homogeneous) or by spinodal decomposition [1]. The former describes the relaxation to equilibrium of a metastable system, while the second process is typical of unstable systems. Many theories have been developed to describe the kinetics and dynamics of phase separation; most of these efforts were spent in describing the growth of the domain size in terms of a power law time dependence, $R(t) = t^n$.

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 [2]. 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 [3]. In principle, nucleation and spinodal decomposition are fundamentally different from each other, as metastable system relaxes via the activated growth of localized fluctuations of large amplitude, whereas unstable systems do so via spontaneous growth of long-wavelength fluctuations of any amplitude [4]. However, for deeply quenched systems, the distinction between the two regimes becomes murky, as both the critical nucleus size and the critical fluctuation wavelength decrease. In fact, following a rigorous treatment based on the diffuse interphase (aka phase field) approach, Lamorgese and Mauri [5] have shown that phase separation of both unstable and metastable binary mixtures can be studied using the same procedure, namely by perturbing them with delocalized random fluctuations. This imposed white noise perturbation has an arbitrarily small intensity for unstable mixtures, while, in the metastable case, it has a finite magnitude, showing that, as the mixture composition approaches its value at the coexistence curve, the intensity of the perturbation that is needed to trigger the instability grows exponentially.

In general, following a rapid temperature quench into its unstable region, a partially miscible mixture first quickly attains a spinodal state, and then reaches equilibrium, consisting of two coexisting phases having compositions lying on the coexistence curve. Therefore, the process of phase transition is usually divided in two steps: an early spinodal decomposition stage, consisting of the exponential growth of long-wavelength concentration fluctuations [6], and a late, much longer stage which, for liquid mixtures, consists of the coalescence-driven growth of the localized micro-domains.

The dynamics of the phase separation process has also been observed directly [7], showing that, right after the temperature of the system has crossed that of the miscibility curve, the solution starts to separate by diffusion and coalescence, leading to the formation of well-defined patches, whose average concentration is near its equilibrium value. The shape of these patches appears to depend strongly on the composition of the system: for critical mixtures, they are dendritic, interconnected domains, while for off-critical systems they appear to be spherical drops. Then, in the so-called late stage of coarsening, these patches grow by diffusion and coalescence, until they become large enough that buoyancy dominates surface tension effects and the mixture separates by gravity. This occurs when the size of the domains exceeds the capillary length, $\mathrm{R}_c = O(\sqrt{\sigma}/(g\Delta\rho)$, where σ is the surface tension, g the gravity field, and $\Delta\rho$ the density difference between the two separating phases [8]. In the case of a liquid mixture that would correspond to $Rmax = O(1mm)$. Now, when diffusion is the driving force of the phase separation process, it is well known, both experimentally [6] and theoretically [9] that the typical size of a nucleating drop grows with time as $R(t) \propto t^{1/3}$; for strongly off-critical mixtures, this same $1/3$ exponent law is also the signature of coalescence driven by Brownian motion [10]. Consequently, in this case, we would predict that it takes a very long time for the nucleating drops to become large enough (i.e. to exceed the capillary length) and sediment. Obviously, while similar times are needed to phase segregate polymer melts and alloys, liquid mixtures separate within seconds of the temperature quench, and therefore diffusion and buoyancy alone cannot explain the segregation process of liquid mixtures.

The other mechanism of growth is convection-driven coalescence, which implies that drops move against each other under the influence of an attractive force. Like all convective mechanisms, this coalescence predicts a linear growth law, $R(t) \propto t$, which agrees with most of the experimental measurements [7,8]. The nature of this convective driving force in phase separating systems is well explained by the so-called model *H* [3,11] (also referred to as the phase field, or diffuse interface, model) as the result of the minimization of the interfacial energy, inducing a (non-equilibrium) body force that is proportional to the gradient of the chemical potential. In particular, at the late stages of phase separation, after the system has developed well-defined phase interfaces, this body force reduces to the more conventional surface tension [12], so that the driving force can be thought of as a non-equilibrium capillary force. Applying this model, it has been shown (see the review article by Lamorgese *et al*. [13]) that the enhanced coarsening rate is due to the strong coupling between concentration and velocity fields. This result was confirmed by the experimental observation of Gupta *et al*. [14] that the coarsening rate of phase separating liquid mixtures is almost independent of the presence of surface-active compounds, indicating that the non-equilibrium forces that induce drop coalescence are much larger than any surfactant-driven repulsive interactions. In fact, due to the dominance of convection over diffusion, the presence of surface-active compounds within the phase-separating mixtures does not hinder the coalescence among drops, and therefore it does hardly retard the process of phase segregation [14].

In our experimental works [14-16], after quenching a low-viscosity partially miscible liquid mixture *15℃* below its miscibility curve, we found that the typical size of single-phase domains grows with a constant growth rate *dR/dt = 100mm/s*, which is much larger than that for shallow quenches. In addition, we measured the typical velocity of *10 mm* phase-separating liquid droplets as *v = 0.2-0.7mm/s*, which is a fewer of magnitude larger than their speed due to either gravity or molecular diffusivity. This process was named Phase Transition Extraction (PTE) by Ullmann *et al.* [17], who subsequently studied its application in enhancing the heat transfer [18,19,20].

The main objectives of this work is to investigate experimentally the limitations of the PTE phase separation process. First, we investigate whether the quenching rate has any influence on the phase separation of critical liquid mixtures. In addition, since in many applications we are interested in the behavior of mixtures quenched in the vicinity of their metastable region, we intend to study what happens when we quench strongly off-critical mixtures. Clearly, in this case, we plan to determine at which point phase separation ceases to be convection-driven and start to be diffusion-controlled, therefore becoming much slower. Finally we plan to determine the thresholds of the surfactant concentration and composition beyond which surfactants start to slow down significantly the separation process, just as they do in the absence of phase transition. In our previous work [14-16] we only tested a few emulsifiers and coalescence retardant compounds, as the solute had to be transparent. However, as we died the solution to improve visualization, we noted that there was no difference between different dies, provided that they form slowly coalescing emulsions when the two phases are agitated, and consequently they have almost no impact on the coalescing rate. In this work, we use much stronger and more concentrated emulsifiers, observing their impact on the phase separation rate. We also studied the effect of emulsifiers when the mixture was quenched into its metastable region, where convection and diffusion are comparable. As some of these emulsion stabilizers produce non-transparent systems, we had to limit ourselves to observing only the time needed to complete the separation.

Experimental Setup and Experimental Procedures.

An experimental setup was designed and built to allow the observation of the phase separation process in the size of $10\mu m$ and up (Figure 1). It consisted of a temperature-regulated, *1mm* thick, *40mm* high sample cell. Placing the sample cell into a *8mm* thick water jacket, into which temperature-controlled water circulated, we could regulate the temperature.

Since we were interested to investigate the effect of quenching rate on phase separation process, we used two different volumetric pumps, with flow rates equal to *43.5cc/s* and *9.7cc/s*. Using the former pump, we achieved a cooling rate of $3\,°C/s$ which, being relatively fast, was denoted as “fast cooling”. Using the other pump, instead, we obtained a so called "slow cooling", equal to $1.3°C/s$. Temperatures were measured by inserting $350\ \mu m$ thermocouples, with $0.04\ s$ response times, at various locations inside the cell and condenser, and connecting them to a data acquisition system.

The experimental setup has a digital camera (FinePix S1 Pro) that was chosen for its high-resolution and high-speed continuous shooting at *1.5 frames/s* (for up to five frames). This digital camera employs *3.4-megapixel*, *23.3x15.6 mm* sized Super CCD image sensor. The combination of the enlarged pixel size through the use of octagonal shaped photodiodes and the larger size of Super CCD captures a great deal of light, resulting in superior image sensing capability and ultrahigh resolution image files with up to *6.13 million pixels* (*3,040x2,016 pixels*). The digital camera is provided with a resolution monitor with *200,000 pixels* and it can be used to playback and to check images.

In our experiments we used a liquid mixture of water, acetonitrile and toluene, whose thermodynamic properties were determined in previous works [15]. This mixture has a critical volumetric composition of *38%* water, *58%* acetonitrile and *4%* toluene, undergoing phase transition at a critical temperature $Tc = 35°C$. Its x-T diagram is shown in Figure 3, where x represents the sum of the mole fractions of acetonitrile and toluene. The composition of the mixtures used in this work are reported in Table 1: mixture A with a critical composition and mixtures B and C with strongly off-critical compositions.

As shown in Table I, mixture B phase separates forming 90% of an organic phase and 10% of an aqueous phase, while mixture C forms 90% of an aqueous phase and 10% of an organic phase. We obtained these off-critical solutions starting to heat a solution with critical composition to a temperature above the critical point and then cooling it down to room temperature. As an Oil 0 Red dye is added to the mixture, the lighter organic phase is red colored, while the heavier aqueous phase is colorless, as the dye dissolves preferentially with the organic components. When dissolved in such small percentages, the dye does not change the characteristics of the phase separation process. In the off critical cases, the temperature at which phase separation starts to occur is *28 °C* instead of the *35 °C* of the critical case.

In all experiments (see Figure 2) the mixture was initially in its phase-separated state below the miscibility curve, at a constant temperature T_1=25°C, then it was heated to a temperature Th ≈ Tc + 5°C, that in our case is Th = 40°C, mixed thoroughly and finally it was cooled down, back to temperature T_1. Mixing the solution before the quench is extremely important because, if we do not do it, as it is shown in Santonicola *et al*. [21], after the system is kept at T_1 for two hours, the mixture is still mostly de-mixed, with the exception of a thin, few millimeters thick layer around the phase interface, where a sharp concentration gradient is present.

In our previous work we studied the phase separation of only two liquid mixtures, in which two types of emulsifiers were dissolved at given concentration [14]. Here we want to generalize our results to a wider range of emulsifiers, investigating whetther the phase separation rate is affected by the concentration of strong emulsifiers. Finding the right emulsifiers was a crucial problem and after trying many of them, we found the right candidate in a surfactant named IGEPAL CO-730. The emulsion formed by this surfactant was stable for more than one hour.

Experimental Results and Discussion

a. Influence of quenching rate on phase separation.

In this paragraph, we describe the morphology of critical mixtures during phase separation applying a fast quenching and a slow quenching. Figure 4 shows a selection of pictures fom a typical sequence obtained for the phase separation of the critical mixture A. During the fast cooling, we see that single-domains grow very rapidly, as a result of convection-induced coalescence. When the gravitational crossover is reached, the domain size is so large that gravitational effects start playing a role. Figure 3 shows also a typical sequence for the phase separation of the critical mixture during a slow cooling. Here, the dynamics of phase separation is the same, it just takes longer time for nuclei to grow. However, in both cases, after an initial period, gravity takes over and the heavier phase starts sedimenting formimg a clear interface.

As already predicted by Poesio *et al.* [22] and Ullmann *et al.* [20], the growth rate of single phase domains, *dR/dt*, is a function of the quenching rate. Figure 5 reveals that increasing the quenching rate, the growth rate of single domains increases until it reaches an asymptotic value. When repeating the experiments using a slow cooling, we observed that the dynamics of phase separation was the same but complete phase separation was much slower. From this result, it appears that the quenching rate can be used to manipulate the separation process and obtain domains of the desired size. On the other hand, the separation process can be sped up by increasing the quenching rate.

b. The influence of emulsifiers on phase separation

This set of experiments allowed us to understand how the phase separation rate is affected by the presence of a strong surfactant in critical and strongly off-critical mixtures at different cooling speeds. We used two different surfactant amounts *(2%,* and *5%)* and cooled the system from a temperature $T_h=40\,°C$ to $T_l=25\,°C$, using a fast cooling of $3\,°C/s$ and a slow cooling of $1\,°C/min$.

The results of complete phase separation applying a fast cooling are summarized in Table II. We see that the emulsion-promoting compound has almost no effects on the phase separation rate when the mixture has a critical composition, so that it is quenched well into the unstable region of its phase diagram. On the other hand, the emulsifiers have a strong effect in the off-critical cases, when the mixture is quenched into its metastable region. In this case, the phase separation process slows down dramatically.

Figure 5 shows phase separation for off-critical mixtures in the presence of *2%* of surfactant. We see that phase separation is completed within about one minute. Then, we repeated the experiments using a slow cooling (see Table III), observing that, although the dynamics of phase separation is the same as that of fast cooling, it is much slower. This results are in agreement with Vladimirova *et al.*'s numerical simulations [12], predicting that the process is driven by diffusion when the effective capillary number is large. We conclude that changing the mixture composition to metastable region in presence of surfactant, convection ceases to be a dominant factor in phase separation process and diffusion becomes dominant.

Conclusions

In this paper, we investigated whether the quenching rate affects the phase separation. We showed that domains grow linearly with time up to when gravitational effects take over. We confirmed the experimental observations of Poesio et al. [22], who investigated the effect of quenching rate on the growth rate of single domains, finding that the growth rate increases with increasing quenching rate, until it approaches an asymptotic value. The possibility to influence the growth rate has implications in many industrial problems as it can be used to produce domains of desired size.

We also investigated phase separation of very strong off-critical mixtures. Phase separation of these mixtures is slow, representing a limitation of the PTE process, as the dispersed nuclei can be easily stabilized, due to the presence of even tiny quantities of surfactants. Diffusion is the driving force of this separation process: the typical size of nucleating drop grows with time as $R(t) \propto t^{1/3}$. Consequently, it takes a very long time for nucleating drops to become large enough and sediment.

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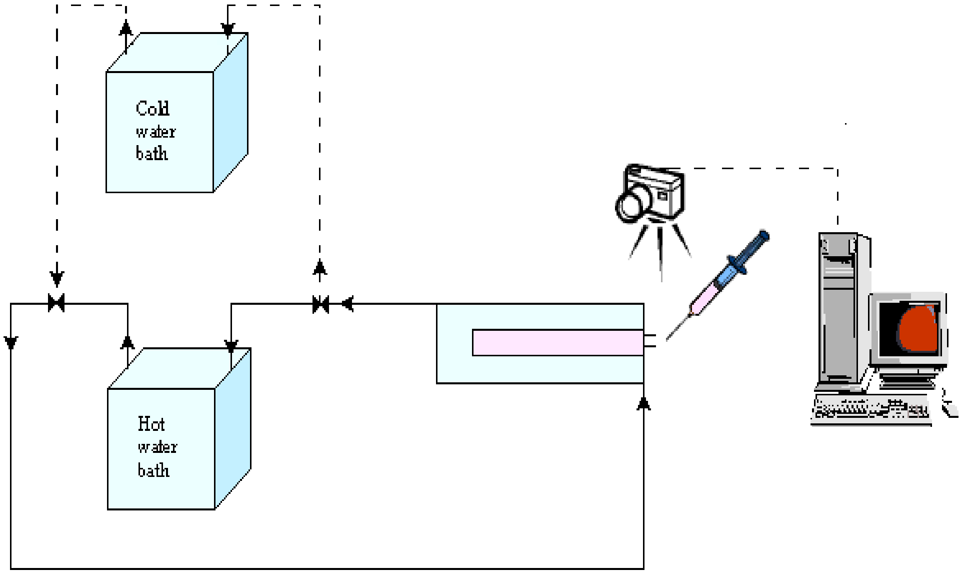


Figure 1: Sketch of the experimental Setup

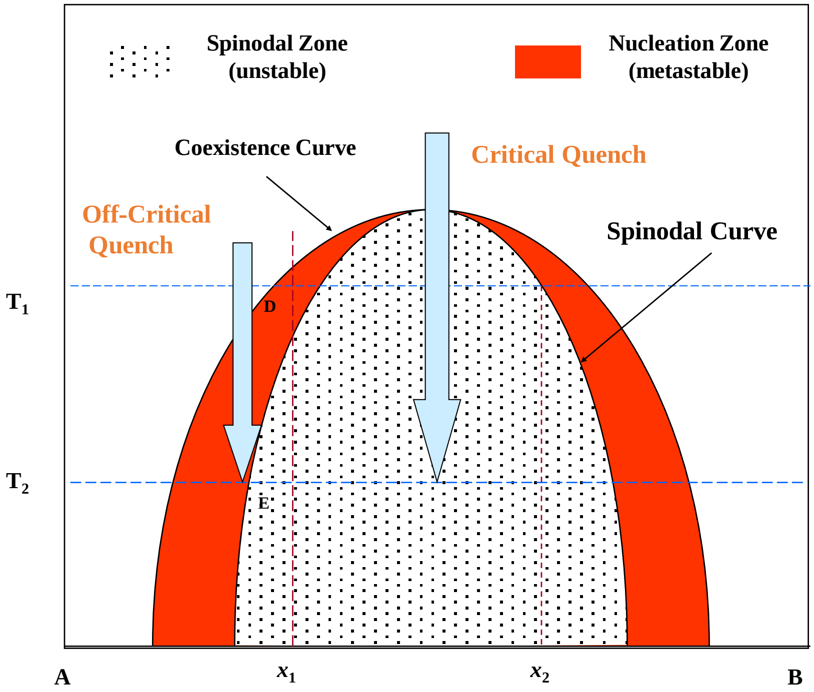
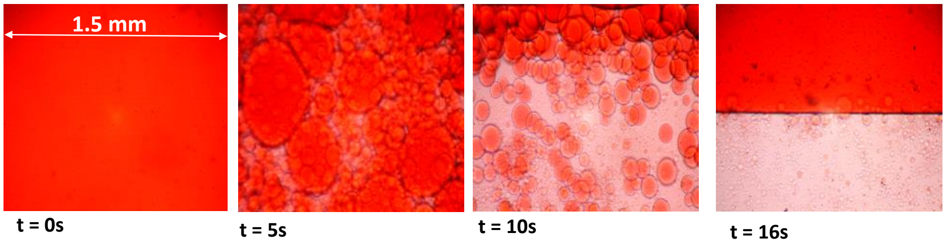


Figure 2: Phase diagram of a water-acetonitrile-toluene mixture and experimental procedures

Fast Cooling Mixture A



Slow Cooling Mixture A

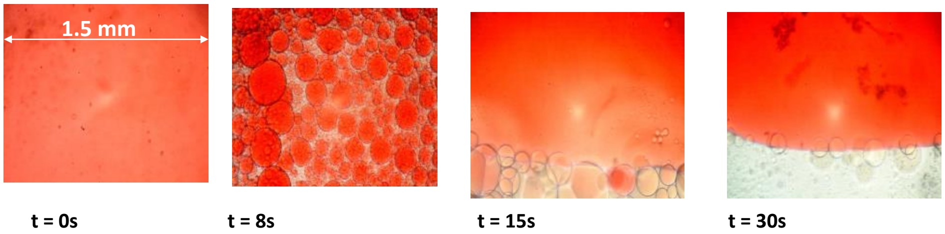


Figure 3: Phase separation of critical mixture A during a fast and a slow cooling.

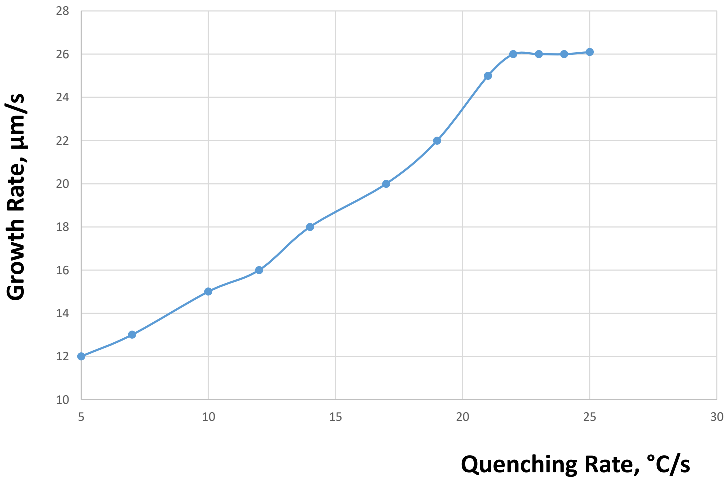
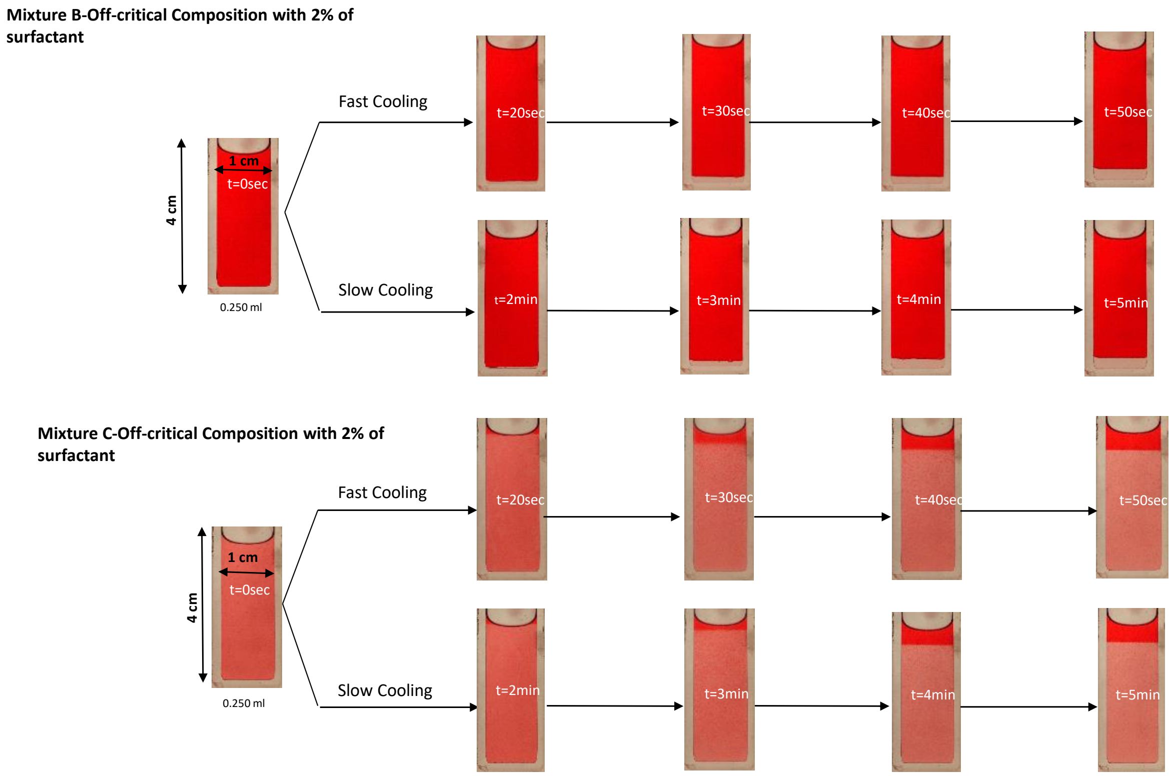


Figure 4: Growth rate as a function of quenching rate



Mixture B-Off-critical Composition with 2% of surfactant

Mixture C-Off-critical Composition with 2% of surfactant

Figure 5: Phase Separation of Off-Critical Mixtures during fast and slow cooling

Table I: Overall volumetric compositions of the mixtures

Mixture	**Water**	**ACN**	**Toluene**
A	38%	58%	4

Mixture	**Organic (ORG)**	**Aqueous (AQ)**
B	90%	10%
C	10%	90%

Table II: Separation Time using a Fast Cooling from Th = 40° to Tc = 25°C.

Mixtures	+2% Surfactant	+5% Surfactant
Mixture A-Critical composition *38%Water,* *58% Acetonitrile, 4%Toluene*	23s	28s
Mixture B-Off-critical composition *90% ORG, 10% AQ*	50s	90s
Mixture C-Off-critical composition *90% AQ, 10% ORG*	50s	90s

Table III: Separation Time using a Slow Cooling from Th = 40° to Tc = 25°C.

Mixtures	**+2% Surfactant**	**+5% Surfactant**
Mixture A-Critical composition *38%Water,* *58% Acetonitrile, 4%Toluene*	50s	2min
Mixture B-Off-critical composition *90% ORG, 10% AQ*	5min	15min
Mixture C-Off-critical composition *90% AQ, 10% ORG*	5min	15min