Full Length Research Paper

Effects of viscosity on phase separation of liquid mixtures with a critical point of miscibility

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After quenching a high-viscosity partially miscible critical liquid mixture to a temperature far below the critical point, we observed the formation of rapidly coalescing droplets, whose size grew linearly with time, indicating that phase separation process is driven by convection. As predicted by the diffuse interface model, this experimental work showed that the viscosity did not have any effect on the growth rate and the speed of the nucleating droplets. Eventually, when the droplets size reached its critical length, they started to sediment and separated by gravity. At this point, the viscosity influenced the settling speed and the total separation time.

Key words: Phase separation, spinodal decomposition, viscosity, convection.

INTRODUCTION

Liquid-liquid extraction (LLE) is a mass transfer operation in which a liquid solution (the feed) is contacted with an immiscible or nearly miscible liquid (solvent) that exhibits preferential affinity or selectivity towards one or more of the components in the feed. LLE has important uses in many industries and has been extensively studied by Treybal (1963), Hanson (1971), Lo et al. (1983), and Alegert (1988). Such processes are used both for the extraction of one compound as well as for the separation between two or more compounds (fractional extraction). In one sense there is a strong similarity between the distillation and the LLE processes. In both cases the operations generally rely upon the unequal equilibrium distribution of substances to be separated between two phases. However, while in the distillation operation the two phases are generated from the original solution by addition of heat, and the components of the original solution then distribute unequally between the liquid and vapor phases, in the LLE process, the second phase is created by addition of extraction solvent, and the solutes are distributed between two liquid phases (Treybal, 1963).

The LLE process procedure is simple in concept and usually requires contacting of feed containing the solute to be extracted with a solvent; this solvent/feed mixture is usually immiscible but may be partially miscible in some cases (Schweitzer, 1975). After forward extraction, the solute remains in the solvent phase and depleted feed becomes the raffinate. In fractional extraction the extract is scrubbed with an immiscible phase (usually involving the same phase type as the original feed) in order to improve the purity of final product. After scrubbing, the solvent is stripped of its solute and the regenerated solvent returned as solvent feed to the process. Often the returned solvent is washed to remove breakdown products. The strip solution provides a product stream (Blumberg, 1988).

Despite the extensive application of liquid extraction over the past several years, and an extensive amount of research, liquid extraction is nevertheless a relatively immature research area and improvements in the process are required. For example, since intense mixing is required in the LLE process in order to form small drops and achieve good contact between the two liquid

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phases in slow mass-transfer systems, the shear stress induced by such a mixing can, in many cases, damage high molecular weight molecules (Hsien-Wen, 1980). In addition, the intense mixing forms fine dispersions which reduces the coalescence rate, or in the presence of surface active impurities, may even cause a "stable emulsion", one of the operating hazards of solvent extraction equipment. Although centrifuges are generally used to disrupt emulsions, this process requires intense agitation, which may be detrimental to the product. Thus, improvements that address these concerns are necessary.

To ameliorate this problem, a new separation technique, the Phase Transition Extraction (PTE) process, was proposed (Ullmann et al., 1993, 1995). In this process, partially miscible binary liquids were used that form a homogeneous, one-phase mixture at one temperature and, form two phases, one solvent-rich and the other water rich, at higher or lower temperature (Ullman et al., 1993), The temperature at which both phases separate is called the critical temperature.

Partially miscible binary fluids with either upper or lower critical solution temperatures (UCST or LCST) have been studied extensively (Kumar et al., 1983; De Benedetti, 2006). Several such systems exhibit critical behavior at ambient conditions, which is particularly convenient for experimental studies. Within the critical region several properties of a fluid vary rapidly as the critical point is approached; for example, the interfacial tension and density difference between phases tend to zero (Williams and Dawe, 1986, 1989a).

The PTE process consists of two steps: 1. Extraction is performed in the homogeneous region of the phase diagram of a mixture with a critical point of miscibility. 2 Separation is performed by rapidly cooling at a temperature below the coexistence curve. Both steps eliminate the need for intense agitation.

When an initial single-phase binary mixture is brought across its miscibility curve into the two-phase region at temperature T, it separates. This process can occur either by nucleation (both heterogeneous and homogeneous) or by spinodal decomposition (Debenedetti, 1996). The former process describes the relaxation to equilibrium of a metastable system, while the second is typical of unstable systems. Many theories have been developed to describe the kinetics and dynamics of phase separation and studies have been carried out on various systems, including those containing polymers (Cumming et al., 1992), fluid systems (Chou and Goldburg, 1979; Siggia, 1979). Most of the efforts have gone into describing the growth of domain size R, after the system is brought into the two-phase region, by the power law dependence in time, $R(t) = t^n$.

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 (Williams and Dawe, 1988b; Zettlemoyer, 1969).

In most practical cases, suspended impurities or imperfectly wetted surfaces provide the interface on which the growth of the new phase is initiated (Frankel and Sarkies, 1974). Williams and Dawe (1988a) investigated the pore-scale behavior of near-critical fluids and found that near the critical point, phase separation takes place through the emergence and subsequent growth of droplets of the second phase from a metastable supersaturated phase. The process is started by localized fluctuation (droplets) that have exceeded a certain size; droplets smaller than a critical size fail to climb over the barrier and shrink back into a supersaturated phase, while droplets larger than the critical size cross over the barrier and the free energy is lowered by their continued growth. This process of nucleation is normally divided into two different mechanisms: homogeneous nucleation, where droplets emerge from within the bulk of the supersaturated phase, and heterogeneous nucleation, where the droplets nucleate on the third phase. Williams and Dawe (1988a, b) presented an approach for studying the critical behavior of phase separating fluids in porous media. Experimental results, using 2, 6-lutidine-water mixtures, with lower critical solution temperature systems (LCST), illustrated the distribution of the phases within the pore space following a quench of a few degrees above the critical point into the two-phase region. Separation appeared to occur by the growth of wetting layers into the bulk; a process which bypasses the nucleation barriers which have to be crossed before droplets appeared.

Contrary to nucleation, spinodal decomposition occurs spontaneously, without any energy barrier to overcome and involves the growth of fluctuations (droplets) of any amplitude that exceed a critical wavelength (Hohenberg and Halperin, 1977; Gunton et al., 1983). The theoretical basis of this process is the Cahn and Hilliard (1958) theory, later extended by other authors (Gunton et al., 1983). In principle, nucleation and spinodal decomposition are fundamentally different from each other; a 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. However, for deeply quenched systems, the distinction between the two regimes becomes less clear, since both the critical nucleus size and the critical fluctuation wavelength decreases.

When low (that is, water-like) viscosity liquid mixtures are quenched to a temperature far below their critical point of miscibility, the process of phase separation is much faster and is driven by convection, which implies that forming drops move against each other under the influence of the non-equilibrium capillary force FΦ (Chou and Goldburg, 1979; White and Wiltzius, 1995; Guenoun

et al., 1992; Siggia, 1979; Hohenberg and Halperin, 1977). This force and, in general, the convective transport induced by the phase transition, is well described by the so-called H model (Hohenberg and Halpering, 1977), also known as the diffuse interface model.

Experimental evidence (Guenoun et al., 1992), for the critical role of convection in the phase separation of liquid mixtures was reported when applying the PTE method. It was found that, under certain circumstances, phase separation was extremely rapid even in the presence of emulsifiers and impurities that tend to slow down the coalescence of droplets. These results indicated that the driving force is much larger than any surface interactions, which would tend to keep the droplets apart.

In another previous study by Califano and Mauri (2004), the formation of rapidly coalescing droplets was observed. Since the droplet size grows linearly with time this indicated that the phase separation process is driven by convection. Eventually, when their size reached a critical length, a size approximately equal to one-tenth of the capillary length, the nucleating drops started to sediment and the two phases rapidly segregated by gravity. This behavior was observed in two different liquid systems (Califano et al., 2005), in a density-segregated system and in a quasi-isopycnic system (that is, a system that separates into two phases having, approximately, the same density). This indicates that gravity cannot be the driving force responsible for the enhancement of the coalescence among the nucleating drops but that gravity takes over only after the drops reached their capillary length. This result is consistent with previous theoretical works (Vladimirova et al., 1999, 2000), based on the diffuse interface model, which predicted that the phase separation of low-viscosity liquid mixtures is a convection-driven process and is induced by a body force proportional to chemical potential gradients. Additionally, it was shown that following the evolution of isolated drops of the secondary emulsion, the size of the droplets grows in time as $t^{1/3}$. The importance of convection relative to diffusion is controlled by the Peclet number, *Pe,* which is defined as the ratio between convective and diffusive mass fluxes $Pe = VL/D$, where *V* is the characteristic speed and *L* a characteristic size of the typical single- phase patches, and *D* the molecular diffusivity.

In the work presented here, we investigated whether viscosity has any influence on the linear growth of the single-phase domains. We expected that coalescence could eventually be retarded by increasing the viscosity of the mixtures. Therefore we determined the thresholds of the mixture viscosity beyond which the separation process starts to slow down significantly. Our results indicate that viscosity does not affect the early stage of separation, only when droplets reach their critical size; viscosity slows down the complete separation.

The motivation of this research lies in the possible industrial applications of the phase separation process. The solvents that are used in industrial applications are often viscous and the influence of viscosity on the phase separation process is of industrial relevance.

MATERIALS AND METHODS

Two experimental setups were designed and constructed to allow for the micro and macro observation of the phase separation process, both for bulk flows and the motion of droplets of size 10 μm to 10 mm. The first experimental setup consisted of a temperature-regulated, 1 mm thick, 40 mm high sample cell for micro visualization, and the second was a 20 cm long and *1cm* diameter condenser tube for macro visualization. Both setups are shown in Figure 1. A digital camera (Fuji FinePix S1 Pro) with high resolution and high-speed continuous shooting (up to five frames per second) was used. Both the cell and the condenser tube were used to allow for the circulation of temperature controlled water, giving a *3°C/s*-quenching rate. Quenching was achieved by circulating cooling water at 2°C through the outer chamber of the cell or of the condenser. Califano et al. (2005) showed there was no detectable temperature difference along the radial direction by inserting three thermocouples within a cross section of the condenser tube. Instead, this rapid quench resulted in a small temperature gradient along the axial direction. The temperature profile along the axial direction of the condenser revealed that during phase separation there was, at most, a 0.28°C/cm temperature gradient. The temperature gradient was almost uniform in the cell. Temperatures were measured by inserting 350 μm thermocouples into the sample cell and condenser.

An optical microscope (Nikon Optiphot-2) with Xenon illuminator (Nikon XBO Lamp 75 W) was used for micro observation.

The sample composition used in our study has been extensively studied previously by Califano et al. (2003, 2005), Califano and Mauri (2004), Gupta et al. (1999), and has a volumetric composition of 38% water, 58% acetonitrile, and 4% toluene. This mixture undergoes phase transition at a critical temperature of 35°C. Figure 2 shows the phase diagram for a water-acetonitrile-toluene mixture (Santonicola et al., 2001).

All the solvents used in our experiments were HPLC grade, while water was double distilled. Within the critical region many properties of a fluid vary rapidly as the critical point is approached: the interfacial tension and the density different between phases tend to zero (Williams and Dawe, 1986). At room temperature, the sample mixture separates into two phases with a density difference $\Delta\rho = 7 \times 10^{-2}/cm^3$. Water is the continuous phase; acetonitrile and toluene are the discontinuous phase. The viscosity of the discontinuous phase (acetonitrile and toluene) was 1.2 cp at room temperature. The surface tension of this mixture is $\sigma = 1.3$ dyn/cm so that its capillary length, $R_C = \sqrt{\sigma/(g\Delta\rho)} = 1.3$ mm. In addition, 50 ppm of Oil 0 Red was added to our mixture to enhance the visualization of the two phases as they separate. When dissolved in such small amounts, this dye does not change the phase diagrams of the mixture, or the characteristic of the phase separation process.

Due to the nature of the experimental design, we were unable to investigate polymers. So in order to study phase separation of high-viscosity mixtures we created mixtures similar to polymers. We added different amounts (up to 4% in weight) of carboxyl-methyl-cellulose (CMC) to our mixtures because CMC is soluble in both hot and cold water, thereby increasing its viscosity, but is completely insoluble in the organic phase. The viscosity of our mixture increased up to 15 times its original (water-like) value. We tested that the CMC added did not act as a modifier and did not alter the coexistence curve. The viscosity was measured
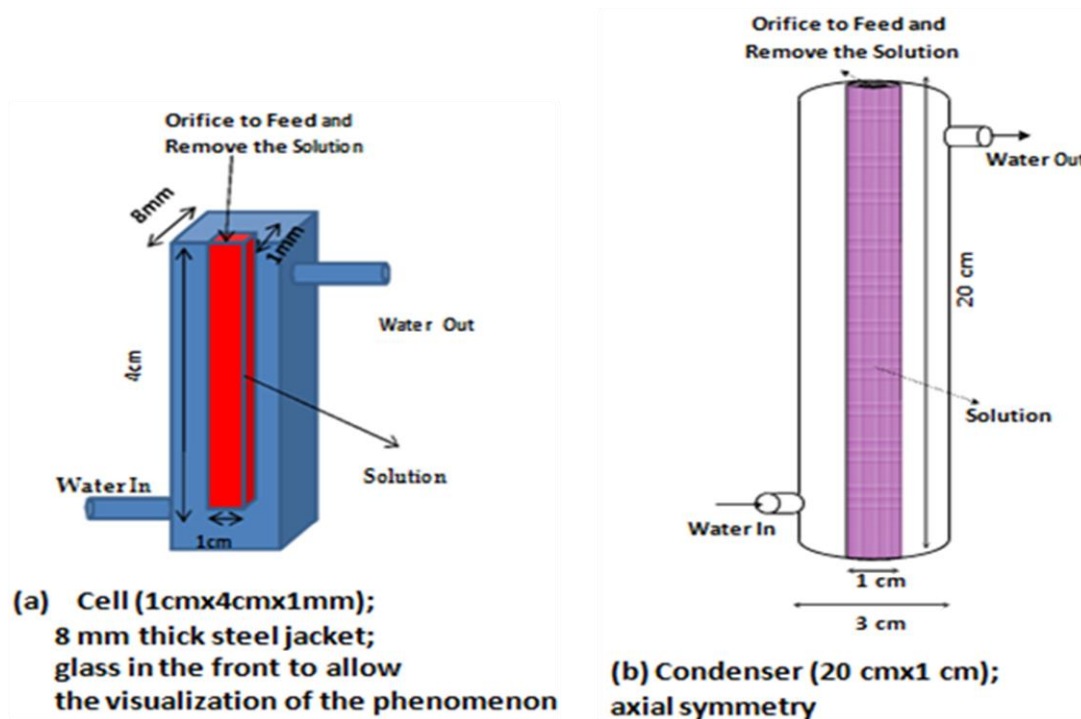
Figure 1. Experimental setups (a) Cell (b) Condenser Tube.
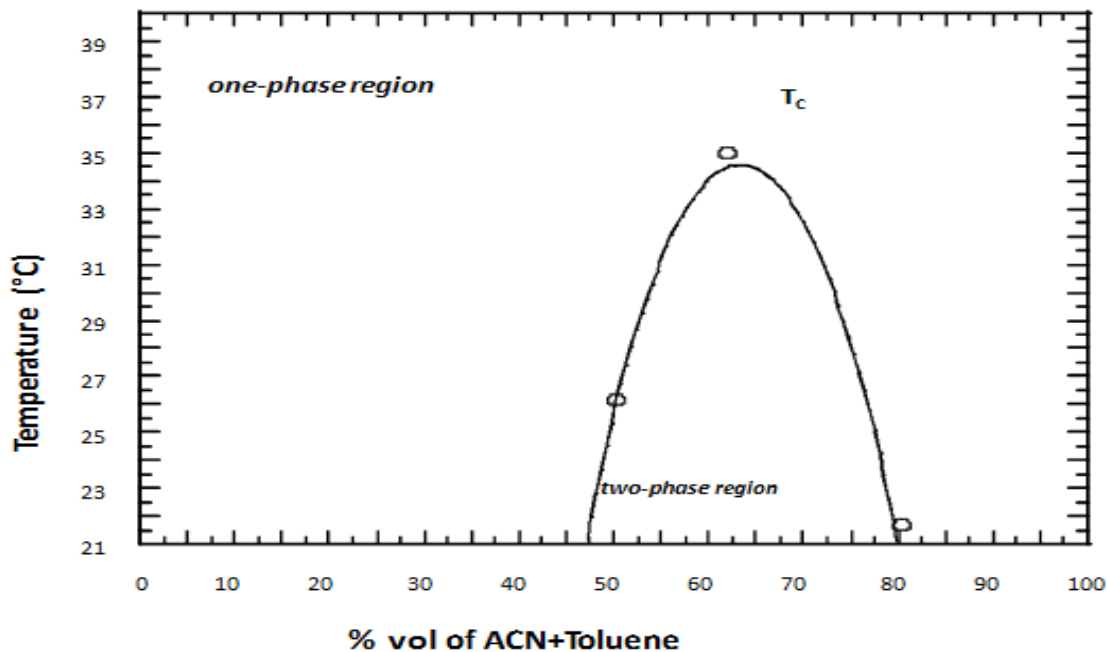

Figure 2. Phase diagram of a water-acetonitrile-toluene mixture (Santonicola et al., 2001).

using a *TA* instrument viscometer (model AR 1000). Data was collected using the following procedure (Califano et al., 2003, 2005; Calfano and Mauri, 2004; Gupta et al., 1999); the sample solution was first heated to a temperature above the critical point (about 5°C above the critical temperature), then mixed thoroughly and finally quenched to 2°C with a cooling rate of about 3°C/s. Thoroughly mixing the solutions before quenching was necessary since we wished to study the behavior of initially
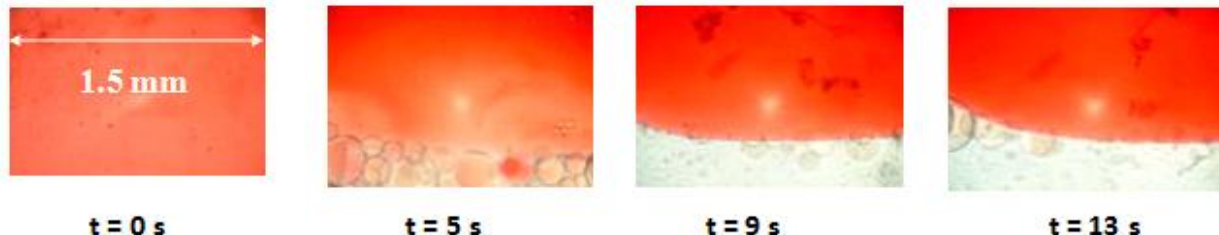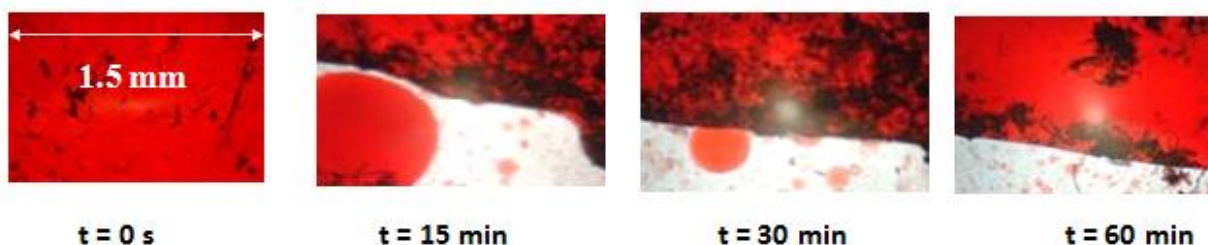
Case 1: System with no CMC, magnification 67X

t = 0 s   t = 5 s   t = 9 s   t = 13 s

Case 2: System with 1.5% of CMC in water, magnification 67X

t = 0 s   t = 15 min   t = 30 min   t = 60 min

Figure 3. Phase separation for Acetonitrile 58%, Water 38%, Toluene 4% system in small cell. t = 0 s corresponds to the moment when the temperature is 35°C. Case 1) the mixture is without CMC, the separation is complete in 13 s. Case 2) the mixture is with 1.5% of CMC, the separation is complete in 1 h.

Table 1. Percentage of CMC dissolved in water and times for complete phase separation.

% CMC dissolved in water	Complete separation time
0.0	15 s
0.3	3 min
0.5	5 min
1.0	20 min
1.5	1 h
2.5	2 h
3.0	> 4 h
4.0	No separation observed

homogeneous mixtures.

EXPERIMENTAL RESULTS

The results of our macroscopic visualization of phase separation of both systems, with and without CMC, are shown in Figure 3, and separation times summarized in Table 1. Time point $t=0$ s corresponds to the moment when the temperature of the mixture crossed the miscibility curve, that is, 35°C. As our previous work showed (Califano et al., 2003, 2005; Calfano and Mauri, 2004; Gupta et al., 1999), in the low viscosity system (that is, in the absence of CMC), we initially see the appearance of isolated micro domains of the dispersed phase (acetonitrile), which grow mainly by coalescence. At later time points, when the size of the nucleating drops becomes comparable to the capillary length $R_C = 1$ mm, the two phases separate rapidly by sedimentation. When 1.5% in weight of CMC was added to our system, we saw that the dynamics of phase separation and the final morphology did not change significantly from the sample without CMC. Complete phase separation occurred after 1 h. The higher the percentage of CMC the longer it took to achieve complete separation. In the case of 3% CMC, it took more than four hours for complete separation, whereas using 4% in weight of CMC; we could not see any separation. Thus complete phase separation of mixtures with a higher viscosity is much slower, and occurs because viscosity slows down the convective motion between the droplets during phase separation.

In the presence of CMC, at the early stage of phase separation, the motion of the drops appeared to have, approximately, random directions and did not depend strongly on the drop size. The movement of a typical nucleating droplet with radius $R<R_C$ has been monitored (Gupta et al., 1999) who showed that 0.5 s after crossing the miscibility curve, a drop with radius $R \cong 30$ µm can move at a speed exceeding 100 µm/s. This indicates that strong convection exists within the system even after drops with sharp interfaces have formed and before the drops have become large enough to
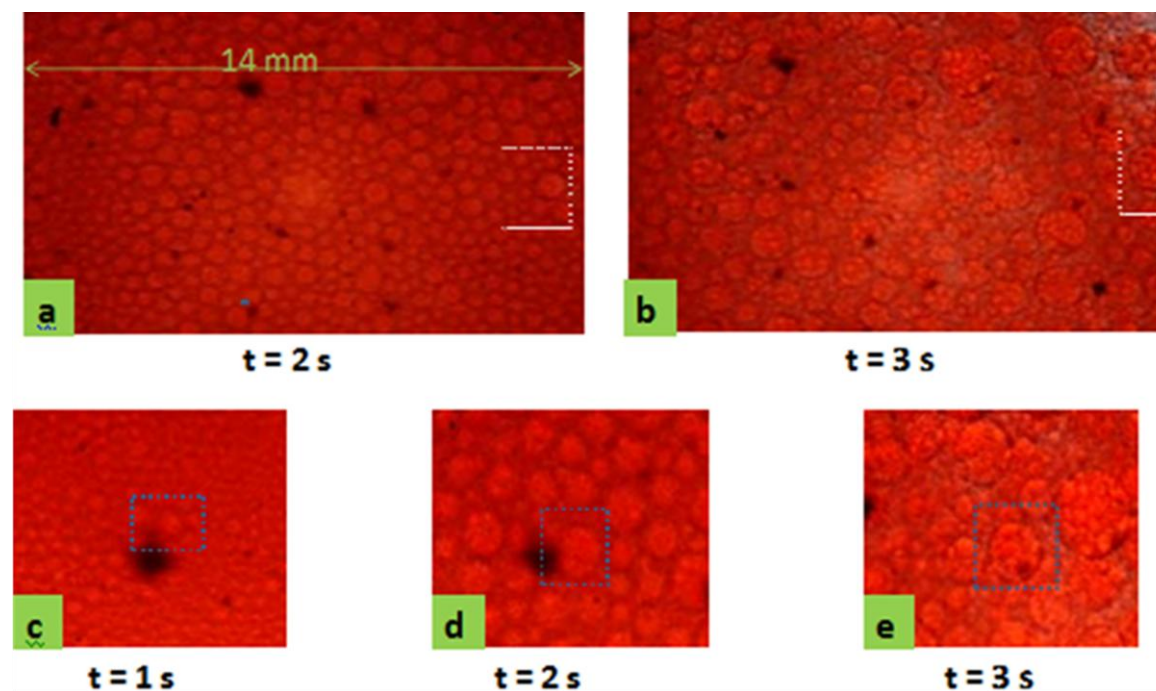
Figure 4. Pictures a-b show the upward movement of a droplet during phase separation; Pictures c-e show the growth of a droplet during phase separation.

sediment. We observed the same behavior in the presence of CMC, which is shown in Figure 4. We followed the movement of 0.91 mm size droplet two seconds after crossing the miscibility curve and found that the droplet moved upward at a speed of 280 µm/s.

The source of this rapid movement cannot be molecular diffusion, as that would predict drop velocities a few orders of magnitude smaller than those observed experimentally. Such strong convection cannot be gravity-driven either, since in that case the motion would be directed preferentially downward and, in addition, it would be of smaller magnitude. In fact, considering the

Stokes sedimentation speed $v_{St} = (2/9)R^2g\Delta\rho/\eta$, which is the terminal velocity at which a sphere of density ρ will sink (or rise) in a medium of density ρ', Stokes (1966), it was found that 0.5 s after the quench, when the temperature of the system is about 33°C, corresponding to a density difference between the two phases $\Delta\rho = 7\times10^{-3}$ g/cm^3, this sedimentation speed was two orders of magnitude smaller than the measured drop velocity. Increasing the viscosity up to 15 times its original (water-like) value, the measured speed was higher than the Stokes speed.

As for the fact that the drop speed did not depend strongly on the drop size, that seems to indicate the existence of a bulk convection, induced by some type of body force acting on the whole system.

Figure 4 also indicates that the drop size increases linearly with time and the growth rate does not depend on

viscosity during the convective stage of phase separation. This behavior is well predicted using the diffuse interface model (Hohenberg and Halpering, 1977), determining that the typical droplet size R grows linearly in time and it is independent of viscosity.

Figure 5 shows the phase separation of the critical mixture with 1.5% of CMC in the condenser tube: acetonitrile-rich droplets formed in the whole tube. Later these droplets started to move along the vertical direction, towards a horizontal interface formed. Then, as more droplets moved towards the interface, separation was complete in one hour.

DISCUSSION AND CONCLUSION

In this paper we present experimental data that demonstrates the influence of viscosity on phase separation of liquid mixtures with a critical point of miscibility. In this set of experiments we used a critical mixture with composition 58% acetonitrile, 38% water, 4% toluene whose continuous phase is water (aqueous phase). We studied the behavior of this mixture with a critical point of miscibility in a low viscosity system (water-like) and modeled higher viscosity systems by adding CMC.

In the low viscosity system we observed that, after cooling, the system remained unchanged for a few seconds before droplets of an acetonitrile-rich phase started forming and moving to a formed interface (Figure

3). This behavior has been observed in previous studies of mixtures with a critical point of miscibility (Califano et al., 2003, 2005; Califano and Mauri, 2004; Gupta et al., 1999; Vladimirova et al., 1999, 2000).

We further observed that droplets form and grow linearly until they reach a critical size, whereupon they start to sediment and the mixture separates by gravity. In the case of phase separation of mixtures with higher viscosity, we observed that the droplet size growth rate does not change significantly when the viscosity of the continuous phase is increased. Additionally, the same steps observed in lower viscosity systems, namely initial formation of acetonitrile drops, followed by interface formation, and then slow movement of droplets towards the interface, are also observed with 1.5% of CMC added. Therefore, we may conclude that the growth rate, the droplet speed, and the general morphology of the mixture are unaffected by addition of CMC.

When gravitational effects become relevant, that is, when droplets become big enough, phase separation is much slower. This happens because viscosity slows down the convective motion between the droplets during phase separation. In the case with *2* and *3%* of CMC we saw that the dynamics of phase separation and the final morphology did not change significantly when compared to the low viscosity system. The hydrodynamic effects on the late stage kinetics of phase separation in liquid mixtures are studied using the model H. Mass and momentum transport are coupled via a no equilibrium body force, which is proportional to the Peclet number α, that is, the ratio between convective and diffusive molar fluxes. Calculations based on this theoretical model show that phase separation in low viscosity, liquid binary mixtures is mostly driven by convection, thereby explaining the experimental findings that the process is fast, with the typical size of single-phase domains increasing linearly with time (Vladimirova et al., 1999, 2000; Lamorgese and Mauri, 2002). However, as soon as sharp interfaces form, the linear growth regime reaches an end, and the process appears to be driven by diffusion, although the condition of local equilibrium is not reached. As the Peclet number increases, the transition between convection- and diffusion-driven regimes occurs at longer times, and therefore for larger sizes of the nucleating drops. In higher viscosity systems, diffusion supersedes convection and the separation process slows down.

In summary, these experiments are totally reproducible and controllable, therefore offering a challenging subject for theoretical and experimental investigations of separation processes, as well as for separation of emulsions.

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