

## Effects of Commercial Surfactants on Phase Separation of Liquid Mixtures

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

### 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 industrial processes that are used both for the extraction of one compound from a solvent as well as for the separation between two or more compounds (fractional extraction).

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. 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.

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 phases, the stress induced by such a mixing can damage high molecular weight molecules. 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, Dr. Califano research group has developed a new separation technique, called Phase Transition Extraction (PTE) process. In this process, partially miscible binary liquids are 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 temperature. The temperature at which both phases separate is called the critical temperature.

The advantages of this new process over the conventional liquid-liquid extraction, or LLE, process are:

- (1) Improved extraction yield: the amount of the final product extracted is much higher than in conventional methods. This is particularly important in the extraction of natural products and fermentation broths.
- (2) Ability to handle emulsion-forming systems: no stable emulsions are formed that usually slow down the extraction process.
- (3) Equipment saving: since there is no need to use centrifuges to break stable emulsions, as we do when using the traditional LLE process, the equipment required to perform PTE is only a tank. PTE is significantly cheaper to perform than LLE.
- (4) Lower product degradation. Any possible shear stress damage to large solute molecules is prevented in the PTE process, where only a mild mixing is required, as opposed to the high centrifugation of traditional LLE. In addition, the fact that in the PTE



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process a small amount of the native solvent is contained in the extract will help prevent the unfolding of large solute molecules, such as proteins.

(5) Replacement of chlorinated solvents. The PTE process is more powerful and versatile and also permits the use of solvents which are environment friendly.

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 low (i.e., water-like) viscosity liquid mixtures are quenched to a temperature far below their critical point of miscibility, the process of phase separation is fast and is driven by convection, which implies that forming drops move against each other under the influence of a non-equilibrium capillary force. Experimental evidence for the critical role of convection in the phase separation of liquid mixtures is reported when applying the PTE method. It was found that, under certain circumstances, phase separation is extremely rapid even in the presence of emulsifiers and impurities that tend to slow down the coalescence of droplets. These results indicate that the driving force is much larger than any surface interactions, which would tend to keep the droplets apart.

In our research, the formation of rapidly coalescing droplets has been observed. Since the droplet size grows linearly with time this indicated that the phase separation process is driven by convection. When the droplet size reaches a critical length, it starts to sediment and the two phases rapidly segregate by gravity. This behavior has been observed in two different liquid systems: in a density-segregated system and in a quasi-isopycnic system (i.e. 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 reach their capillary length.

### Methods and Materials

An experimental setup was designed and constructed to allow for macro observation of the phase separation process. The experimental setup consists of a temperature-regulated, 20cm long and 1cm diameter condenser tube. The setup is 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. The condenser tube was 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. 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. Temperatures were measured by inserting 350µm thermocouples into the condenser.

The mixture used in our study 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. All the solvents used in our experiments were HPLC grade, while water was double distilled. At room temperature, the sample mixture separates into two phases with a density difference  $\Delta\rho = 7 \times 10^{-2} \text{ g/cm}^3$ . Water is the continuous phase; acetonitrile and toluene are the discontinuous phase. 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, and dissolves in acetonitrile. Because we intended to investigate how the phase separation rate was affected by the concentration of emulsifiers, we had to find the right emulsifiers that could dissolve in our system and was appropriate for our purposes. We first used Oil 0Red as surfactant and added increased concentrations to our mixture, then we found a surfactant named IGEPAL CO-730. This surfactant was the right candidate since the emulsion formed was stable for more than one hour.

Data was collected using the following procedure: 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/sec. Thoroughly mixing the solutions before quenching was necessary since we wished to study the behavior of initially homogeneous mixtures.

### Experimental Results

The results of our macroscopic visualization of phase separation of our systems are shown in Figure 3, and separation times summarized in Table I. Time point  $t=0 \text{ s}$  corresponds to the moment when the temperature of the mixture crossed the miscibility curve, i.e. 35°C. In our system, 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  $R_c = 1\text{mm}$ , the two phases separate rapidly by sedimentation.

We initially used Oil 0 Red as surfactant and used five different surfactant amounts (5mg, 10mg, 15mg, and 20mg) and cooled the system from a temperature  $T_h = 40^\circ\text{C}$  to  $T_l = 25^\circ\text{C}$ .

Surfactant amount	5mg	10mg	15mg	20mg
Time for complete separation	50s	60s	70s	75s

**Table 1:** Separation Time using a Fast Cooling from  $T_h = 40^\circ$  to  $T_c = 25^\circ\text{C}$ .

Same results were obtained when we used a commercial and more powerful surfactant: Igepal. We increased the number of droplets of this surfactant and in all cases phase separation was complete within a minute, Figure 4.

The same mixtures were studied after isothermal agitation and isothermal separation. The separation was completed after one hour.

The source of the rapid movement in PTE 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  $\rho$  will sink (or rise) in a medium of density  $\rho'$ , Stokes (1966), it was found that 0.5s after the quench, when the temperature of the system is about  $33^\circ\text{C}$ , corresponding to a density difference between the two phases  $\Delta\rho = 7 \times 10^{-3}\text{g/cm}^3$ , 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.

### Discussion and conclusions

In this paper we present experimental data that demonstrates the influence of surfactants 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,

The results are summarized in table 1. This table shows the time required for complete phase separation. We can conclude that the emulsion-promoting compounds have almost no effects on the phase separation rate in the mixture with critical composition. In fact, phase separation seems to occur at a rate that is independent of its presence, Figure 3.

38% water, 4% toluene whose continuous phase is water (aqueous phase).

In our 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. 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.

First, we show by macroscopic 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 micronsize 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  $t$ . While it is well-known that in a diffusion-driven process the characteristic size is expected to grow slowly. 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 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.

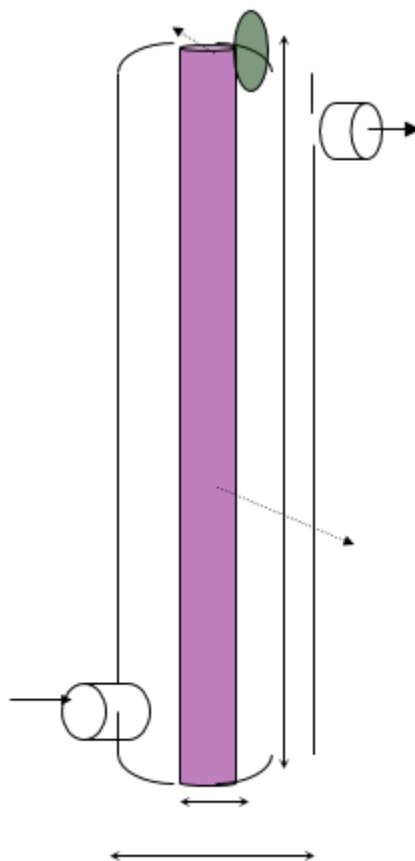


Figure 1: Condenser Tube

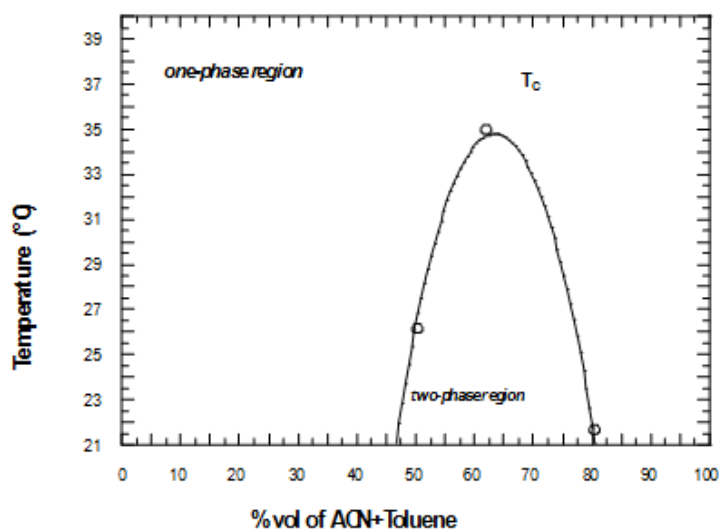
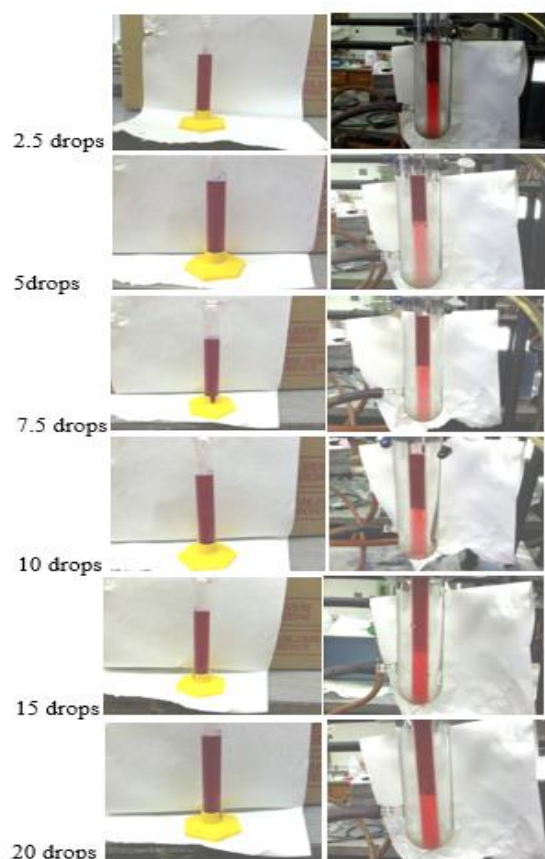


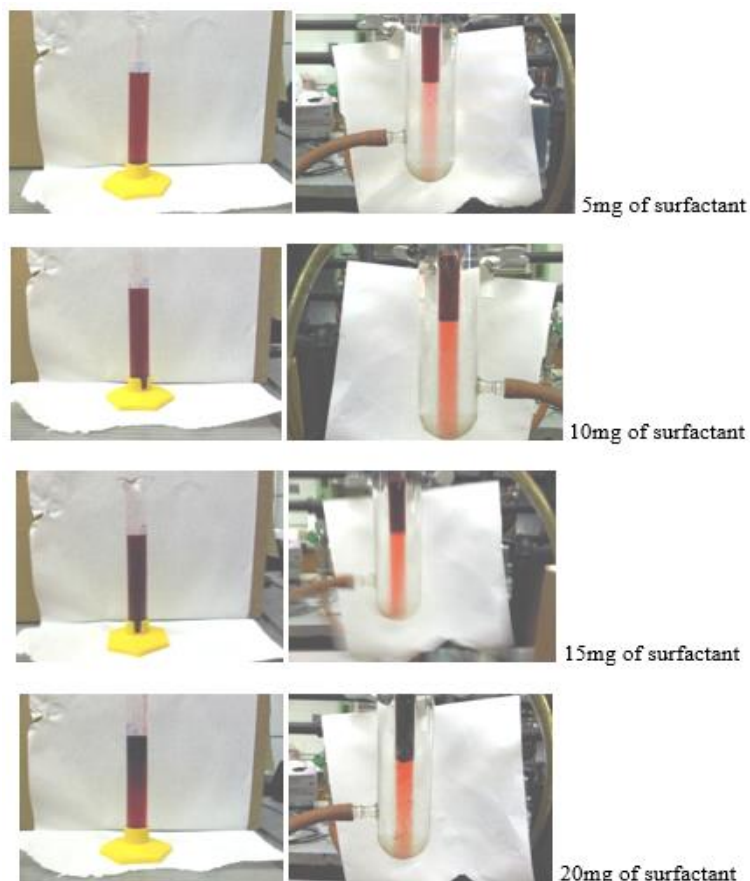
Figure 2: Phase diagram of a water-acet onitrile-toluene mixture, Santonicola et al. (2001)



**Figure 4:** Phase separation in presence of Igepal surfactant

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**Figure 3:** Phase separation in presence of Oil 0 Red

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