

Full Length Research Paper

Study of miscibility of liquid mixtures with a critical point: A new experiment for a physical chemistry course

Filomena Califano*, Guram Nozadze, Alexander Ly van Manh and Ahmed Farhat

Department of Chemistry and Physics, St. Francis College, USA.

Received 10 June, 2013; Accepted 5 February, 2014

This paper describes a new experiment for undergraduate students in physical chemistry. This experiment describes a separation process of liquid-liquid extraction using mixtures with a critical point of miscibility. In this experiment, students will learn how to measure solute concentration, and a new liquid-liquid extraction technique that we called Phase Transition Extraction (PTE). In this experiment, a liquid mixture, together with the solute to be separated, is first heated above its critical temperature, where it forms a uniform solution, and then cooled to the region below the miscibility curve, where it separates. Students will understand that this separation process has the advantage that the resulting separation of the solvents is very rapid. In addition, the extraction speed of it may be 10 times higher than that of the traditional liquid-liquid extraction. The new process is thought of having significant advantages in the extraction of products from fermentation broths, plants, and other natural sources. In this paper, miscibility of binary liquid mixtures of methanol-cyclohexane and acetonitrile-water-toluene will be studied. A two-phase distribution ratio will be determined. Temperature and composition of the liquid-liquid critical point will be determined.

Key words: Miscibility, liquid mixtures, methanol-cyclohexane, acetonitrile-water-toluene.

INTRODUCTION

Liquid-liquid extraction process

Liquid-liquid extraction (LLE) has important uses in many industries and has been extensively studied (Treybal, 1963; Hanson, 1971; Lo et al., 1983; 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.

In general, LLE will be preferred either where distillation

*Corresponding author. E-mail: califano_filomena@yahoo.com

Author(s) agree that this article remain permanently open access under the terms of the [Creative Commons Attribution License 4.0 International License](https://creativecommons.org/licenses/by/4.0/)

fails or where, despite some disadvantages, it provides a less expensive overall process than the distillation process. The following list indicates some typical examples where LLE has demonstrated its unique abilities as a separation method.

a) As a substitute for distillation process where LLE is less expensive.

i) Separation of liquids whose boiling point is very close. An example is the separation of butadiene (b.p. - 4.75°C) from Butylenes (b.p. - 6°C).

ii) Separation of liquids of poor relative volatility. An example is the separation of acetic acid and water, which, despite their relatively large difference in boiling point, have poor relative volatility.

iii) For mixtures with very high boiling point where high vacuum is essential for the distillation process, like long-chain fatty acids and vitamins.

b) As separation means where distillation fails.

i) Separation of heat-sensitive substances such as antibiotics.

ii) Separation of solvents that form azeotropes.

iii) Separation according to chemical type, where boiling points overlap. An example is the separation of aromatic hydrocarbons from paraffin hydrocarbons.

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. The strip solution provides a product stream.

It is important at this stage to recognize certain features of the process that the present work will seek to change. The extraction and the stripping involve liquid-liquid contact in which the droplets of one phase are dispersed in a second phase and mass-transfer has to take place across liquid-liquid boundary. There are several types of contact-equipment in industrial use; basically there are two types of units. Those in which each individual stage is a separate unit and those in which several stages are integrated into one column. Multistage-columns can be simple spray or packed columns or can have stages equipped with various types of mixing devices separated by coalescence sections. The stage efficiency and the

throughput of such devices are a strong function of the mass-transfer and the coalescence rate.

Another important point worth mentioning is the fact that high intensity mixing is required in order to form small drops and good contact between the phases in slow mass-transfer systems. However, the shear stress induced by such a mixing can, in many cases, 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. In the presence of surface-active impurities, this intense mixing may even cause emulsion formation, which is a common problem in the pharmaceutical industry, where the desired products are frequently extracted from fermentation broths containing surface-active impurities. Furthermore, the active compounds to be extracted from the fermentation broths are often "imprisoned" in cell debris, which makes the penetration of solvents even more difficult to achieve.

It would be a novel approach with significant advantages to have contacting equipment and solvent systems that will operate with minimal or without any mechanical agitation and in which there will be no stable boundaries to slow down the mass-transfer and the coalescence rates.

Properties of solvent system with critical point of miscibility

As our whole approach, the present work is based on using partially miscible liquid solvents. A short review of their properties is as follows:

Two-component liquid system may be classified according to whether the components are completely or only partially miscible.

Consider two liquids A and B, exhibiting only partial miscibility. While complete miscibility is obtained whenever a small amount of A is added to B, as more A is added to the solution, eventually the limit of solubility of A in B at the current temperature is reached. Then, further addition of A will result in the appearance of two liquid phases that are saturated solutions of A in B and of B in A. Finally, sufficient addition of A will again bring the system to a condition of one liquid phase. Thus, for a substantial range of the system composition at a given temperature, two liquid phases of constant composition, the saturated solutions, will coexist. The variation in the composition of these saturated solutions with temperature is conveniently shown graphically in the so-called miscibility curves (sometimes also called solubility or coexistence curves).

In the case described in Figure 1 (Ullmann et al., 1995) which is typified by the system butanol-water, the

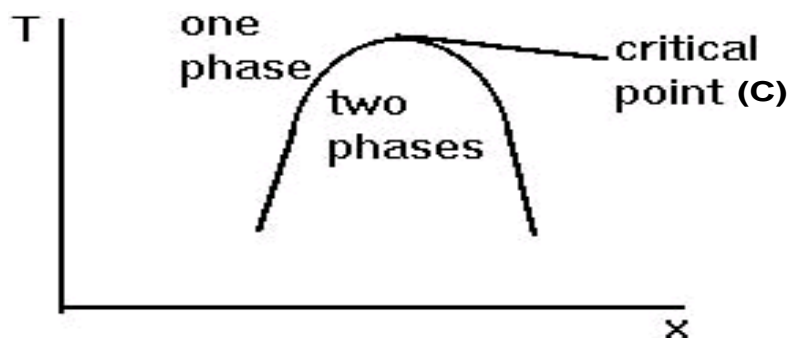


Figure 1. Upper critical solution temperature (UCST) (Ullmann et al., 1995).

solubilities of component A in component B and B in A increase with increase in temperature; so at some elevated temperature, at point C, the two conjugate solutions become identical and the interface between them consequently disappears. This point is termed the critical solution temperature (CST), or consolute temperature, and in the case described in Figure 1, point C is in fact an upper critical solution temperature (UCST). The physical explanation of the critical miscibility phenomena is based upon the interplay of intermolecular forces (Rowlinson, 1969; Domb and Green, 1972).

For example, the existence of UCST can be explained assuming that the A-B molecular bond is weaker than the individual interaction A-A and B-B; then at high temperatures (above UCST) the entropy effects are favored and complete miscibility results. At low temperatures the free energy of interactions is favored and phase separation occurs.

Explanations of the LCST (Domb and Green, 1972) revolve around the highly directional short-range interaction of the entities A and B as in the hydrogen bonding case. At low temperatures the decrease in free energy of solution due to specific interaction of A with B gives rise to miscibility. However, as temperature rises above the LCST, the entropy effects take over favoring a more random orientation of the entities.

The addition of even a small amount of a third component to a two-component liquid system may alter the CST considerably. Typically, when the third component is much more soluble in one of the binary mixture components, its addition raises the UCST (Hales and Green, 1966). When the third component distributes in roughly equal proportions between the two components, its addition tends to lower the UCST (Snyder and Eckert, 1973). Therefore water, for example, raises the UCST of methanol/n-hexane mixture (Rogers, 1969), whereas acetone, as a third component, lowers the UCST of methanol/cyclohexane by 3.5°C% of acetone dissolved (Cohen and Jacobs, 1984). In a similar way, the addition of a third component that is soluble in both liquids raises the LCST, and addition of a third component that is mainly soluble in one of the binary solution mixture components

lowers the LCST. Due to the addition of a third component to a two-liquid system and its distribution between the equilibrium phases, the critical composition will be altered as well. However, for a small amount of third component, the solvents mixture can be regarded as a pseudo two-component system, and the changes in the critical temperature and critical composition can be considered linear (Gunton et al., 1983; Cohn and Jacobs, 1984).

Solvent and solute distribution following phase transition

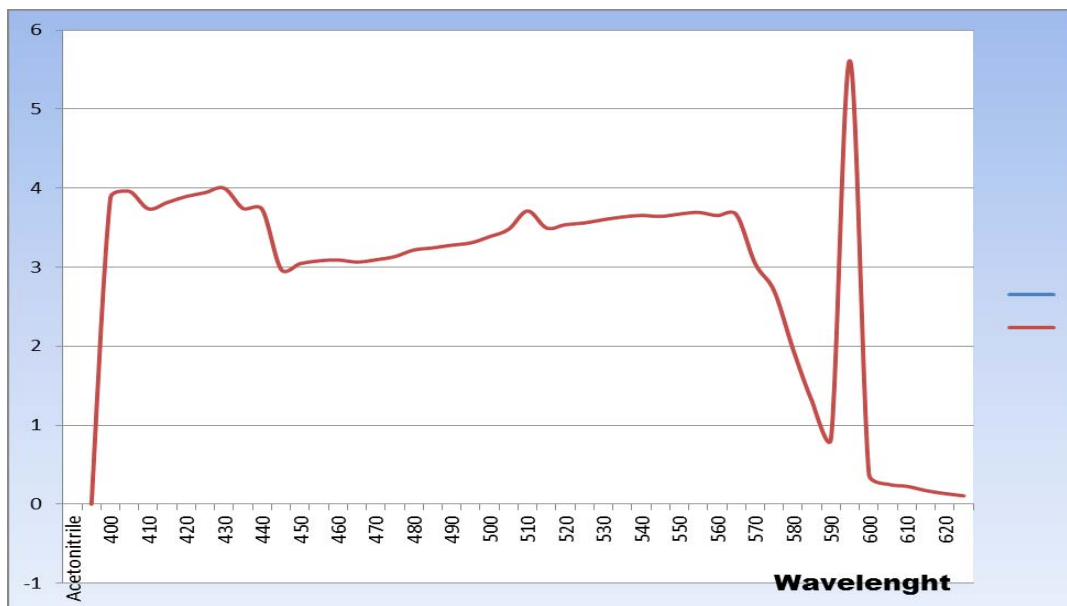
Selection of solvents and solute systems

Generally, the selection of solvent for liquid-extraction processes involves criteria such as capacity, selectivity, availability, physical properties, safety, and cost. When choosing a solvent for the PTE process two additional features are important. First, the deviation of the critical temperature of the mixtures from the ambient temperature should be small, since a large deviation would make the PTE process energy intensive. Secondly, it is advantageous to have as low a solvent concentration in the feed-rich phase as possible; this will minimize the need for solvent separation by distillation, and will also increase the distribution coefficient (Table 1).

In our experiments, the selection of a solvent system for the experiments is mainly affected by our need for easy and accurate experimental operation. Most experiments were conducted with a water-acetonitrile-toluene system. Water was selected as one of the components of our experimental system since it is frequently used as a feed solvent in many commercial extraction processes. Acetonitrile, which is commonly used as a solvent for HPLC analysis and to extract fatty acids from animal and vegetable oils, was selected as the second component. The acetonitrile-water system has an UCST at -0.5°C with 0.36 acetonitrile molar fraction (Figure 2 and Table 2). Toluene has been used as a third component to increase the CST to the desired operational level. Oil 0 Red was chosen as a model solute.

Table 1. Wavelengths, Transmittances and Absorbances.

Wavelength (nm)	100ppm of dye in acetonitrile		100ppm of dye in methanol	
	%T	A	%T	A
400				
405				

**Figure 2.** Absorbance vs Wavelength for Acetonitrile.

The use of a dye as a solute allows as easy, accurate and fast measurement of even very low dye concentration by means of light absorption spectrophotometry. A low solute concentration was preferred because it has a negligible effect on the solvents mutual miscibility and thus simplifies the performance computation of multi-stage extraction processes.

EXPERIMENTS

Measurement of solute concentration

The light absorption spectroscopy method is used to measure the dye concentration in the solvents. A Perkin Elmer UV/Vis spectrophotometer needs to be utilized for this purpose. Absorption spectra of the dye dissolved in methanol showed a maximum at a wavelength (Figure 3 and Table 3). This wavelength is unchanged whether the dye is dissolved in the acetonitrile-rich phase or water-rich phase of the acetonitrile-water-toluene system. Thus, the dye concentration, in each of the phase, can be obtained by diluting the sample with methanol as a reference solvent.

We will use the Beer-Lambert law to have absorbance data for our solutions. Beer-Lambert law states that the absorbance values for a particular solution are directly proportional to the concentration values of this solution and the path length of the light beam over

which the absorbance takes place.

Mathematically, this relationship can be written as:

$$A = \epsilon bc$$

Where A is the absorbance value for a solution at a particular wavelength, ϵ is the molar absorptivity of the solute at this wavelength in $\text{L mol}^{-1}\text{cm}^{-1}$, b is the length of the path of light through the solution in cm, and c is the concentration of the solution being analyzed in mol L^{-1} . Beer's law has many useful applications in analytical chemistry and related disciplines. It can be used in calculating concentrations of unknown solutions when molar absorptivity values are provided.

Experiment 1

- 1) The spectrophotometer should be turned on at least 20 min before any measurements are made.
- 2) Construct graphical plots of absorbance vs. wavelength (absorption spectra) for two different solutions.
- 3) Determine the wavelength at which maximum absorbance occurs for each solution.

Procedure

- 1) Dissolve 1 mg of Oil 0 Red in 10 mL of acetonitrile,

Table 2. Wavelengths and Absorbances for Acetonitrile.

Wavelength	Absorbance (A)
400	3.88
405	3.96
410	3.738
415	3.819
420	3.895
425	3.943
430	4
435	3.741
440	3.732
445	2.972
450	3.045
455	3.08
460	3.091
465	3.065
470	3.093
475	3.134
480	3.217
485	3.244
490	3.278
495	3.307
500	3.386
505	3.479
510	3.711
515	3.495
520	3.538
525	3.56
530	3.601
535	3.635
540	3.655
545	3.642
550	3.672
555	3.693
560	3.653
565	3.666
570	3.044
575	2.699
580	1.959
585	1.301
590	0.839
595	5.61
600	0.372
605	0.253
610	0.226
615	0.172
620	0.134
625	0.105

and 1 mg of Oil O Red in 10 mL of methanol. Now, you have two solutions with 100 ppm concentration of dye. Mix well by inverting the flask about 15 times.

2) Set the wavelength dial of the Spec 20 at 375 nm; perform 0%T adjustment with no test tube and 100% adjustment with distilled water in the test tube.

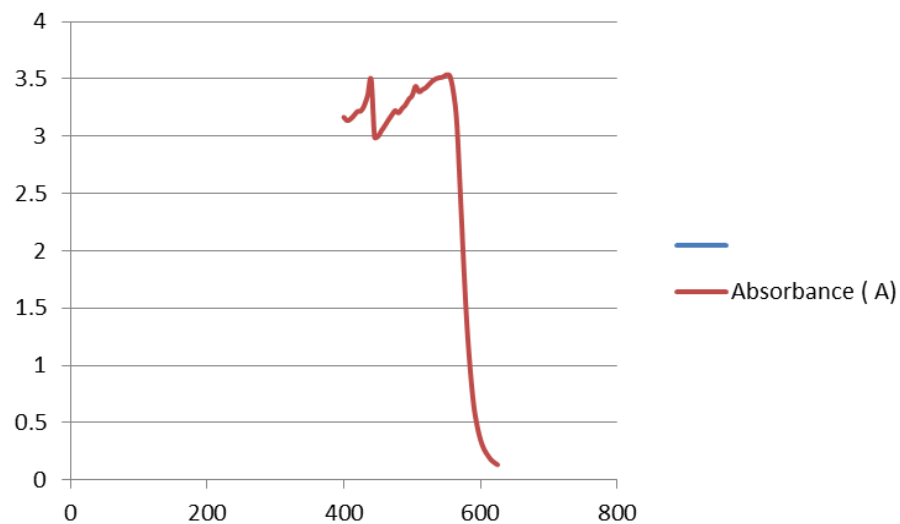


Figure 3. Absorbance vs Wavelength for Methanol.

Table 3. Wavelengths and absorbances for methanol.

Wavelength	Absorbance (A)
400	3.166
405	3.137
410	3.152
415	3.183
420	3.217
425	3.222
430	3.271
435	3.362
440	3.493
445	2.991
450	3
455	3.049
460	3.092
465	3.141
470	3.184
475	3.224
480	3.205
485	3.241
490	3.272
495	3.323
500	3.356
505	3.436
510	3.388
515	3.408
520	3.424
525	3.455
530	3.484
535	3.503
540	3.512
545	3.517
550	3.536

Table 3. Contd.

555	3.528
560	3.397
565	3.142
570	2.568
575	1.921
580	1.367
585	0.963
590	0.658
595	0.475
600	0.351
605	0.272
610	0.222
615	0.180
620	0.154
625	0.134

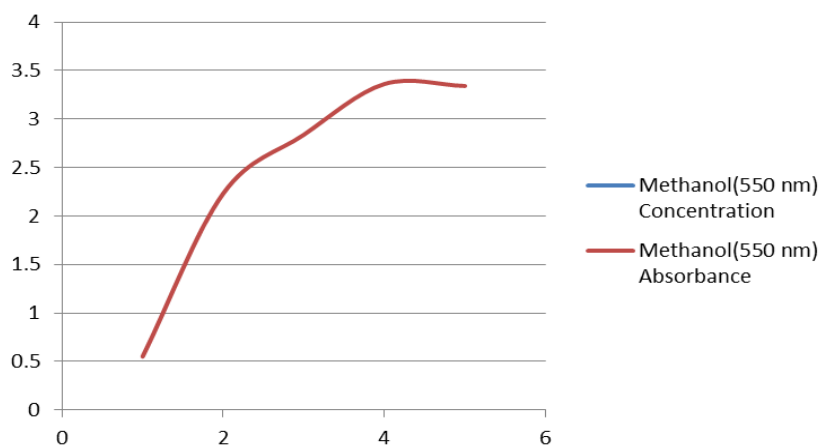


Figure 4. Absorbances vs Concentrations of methanol.

- 3) Obtain %T readings for each solution and record them in your notebook.
- 4) Turn the wavelength dial to 400 nm.
- 5) Repeat the adjustments and the procedure to obtain %T reading for each solution at 5 nm increments from 400 to 625 nm.

Treatment of data

1) You have to make a table in which you record %Transmittance (%T) and Absorbance values (A) for both solutions, using the formula

$$A = 2 - \log\%T.$$

2) Then, you have to plot the absorbance values versus the wavelength values for both solutions. Through this plot, you can determine the values of maximum

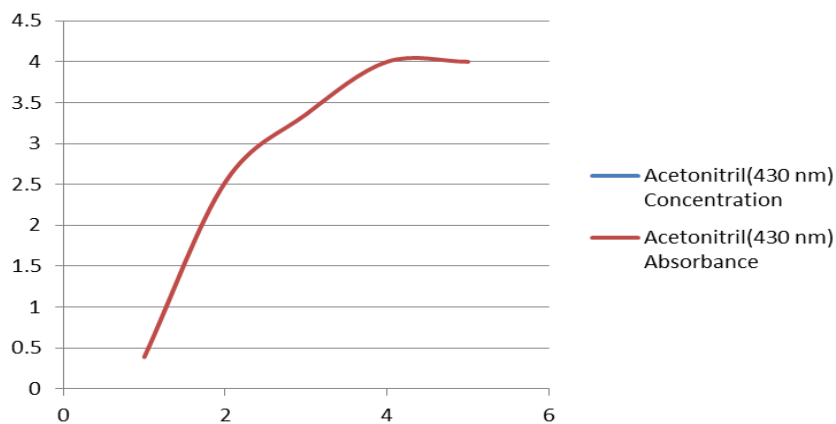
absorbance for both solutions. You have to record these values of maximum absorbance, since you have to use them in future experiments. Since Beer's law is more accurate, when absorbance for each concentration is measured around the wavelength of maximum absorbance, we have to include these values in future studies. We also need to include the values of wavelengths at the intersection points of the two curves. In addition, we include the minimum value of the wavelength for both solutions.

Results of Experiment 1

Values of absorbances were collected for acetonitrile and methanol using different wavelengths with increments of 5 nm (Figure 4 and Table 4). The wavelength at which

Table 4. Concentrations vs Absorbances for Methanol and Acetonitrile.

Concentration (ppm)	Absorbance
Methanol (550 nm)	
50	0.552
100	2.233
150	2.839
200	3.362
250	3.342
Acetonitrile (595 nm)	
50	0.389
100	2.528
150	2.017
200	4
250	4

**Figure 5.** Absorbances vs Concentrations of acetonitrile.

the absorbance has the maximum value was picked for the next experiment.

Experiment 2

- 1) Construct Beer's Law plots (absorbance vs. concentration) for different concentrations of Oil 0 Red in acetonitrile and methanol at different wavelength (Figure 5).
- 2) Determine whether linear relationship between absorbance and concentration is true for these solutions of different concentrations.

Procedure

- 1) Prepare samples of 50, 100, 150, 200 and 250 ppm solutions.
- 2) Use the HP diode array spectrophotometer to obtain absorbance values for the five solutions mentioned above

- at the wavelength at which the absorbance is maximum.
- 3) Record the absorbance values for each concentration and construct Beer's law plots (absorbance versus concentration).

Treatment of data

You have to make two tables in which you record absorbance values for different concentrations for both solutions at the wavelength maximum. Then, you can plot absorbance values versus concentration values.

Results of Experiment 2: Phase transition extraction (PTE)

Representation of concept: Based on the properties of mixtures with critical point of miscibility, a new separation

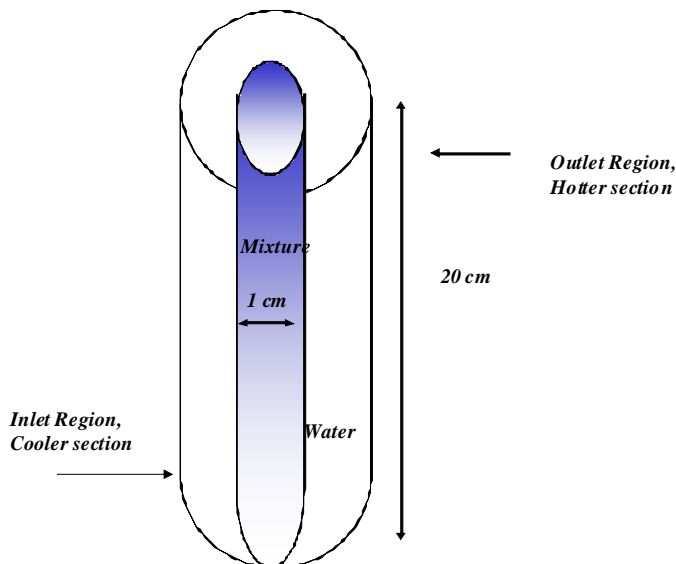


Figure 6. Condenser tube.

process (PTE) is used to separate our mixtures. The novel process capitalizes on the phase transition of such mixtures, especially on the fact that with a relatively small change in temperature one can go from one completely mixed phase to two phases with differing compositions (Figure 1). Our liquid systems form a homogeneous solution above the critical point and two separate phases below the critical point.

Phase separation rate during phase transition: We can test the phase separation rate by performing a series of batch experiments. In these experiments we measure the time needed to complete a full phase separation of a mixture of solvents following a phase transition, and we compare this time with the separation time of the isothermally-mixed mixture.

For all the solvent systems, when the homogenous solvent mixtures are separated by temperature quench, the phase separation is very fast and is complete in one minute.

An experimental setup was designed and built to allow the observation of the phase separation process consisting in a condenser tube (Figure 6) which is 20 cm long and 1 cm in diameter. This experimental setup allows the observation of the motion of individual droplets in a size range of 0.5 mm of diameter and up. The condenser tube is closed on both ends; the temperature is controlled by currently heat transfer liquid trough the cooling system of the condenser, using two constant temperature reservoirs- one hot and one cold, keeping the temperature of each reservoir constant at the desired value and allowing a fast switch between the hot and the cold loops.

In our experiments we use a liquid mixture composed

of water, acetonitrile and toluene; it has a critical volumetric composition of 38% water, 58% acetonitrile, 4% toluene and it undergoes phase transition at critical temperature of 35°C. At ambient temperature, this mixture separates into two phases with a density difference $\Delta\rho_l = 7 \times 10^{-2} \text{ g/cm}^3$ and surface tension $\sigma_l = 1.3 \text{ dyne/cm}$, so that its capillary length is $Rc_l = 1.3 \text{ mm}$. Here, water is the continuous phase. In addition, 50 ppm of Oil 0 Red is added to the mixture to enhance the visualization of the two phases as they separate. When dissolved in such small percents, this dye does not change the phase diagrams of the mixture, or the characteristic of the phase separation process. All the solvents must be HPLC grade, while water is double distilled.

Procedure

- 1) We start with the mixture in its phase-separated state at a constant temperature of 20°C. Then, the solution is first heated to 38°C (that is, well above its critical temperature), mixed thoroughly and finally quenched back to 7°C, with a quench rate of about 3°C/s. This quenching is achieved by circulating cooling water at 7°C through the outer chamber of the condenser.
- 2) The mixture reaches complete separation before it becomes completely cooled. The time reported in all experiments is measured from the moment the temperature crosses the miscibility curve.
- 3) Prepare the same mixture, and heat it up to 38°C; then let it cool down at room temperature. Compare the times of complete separation with the PTE times of separation (Figure 7).

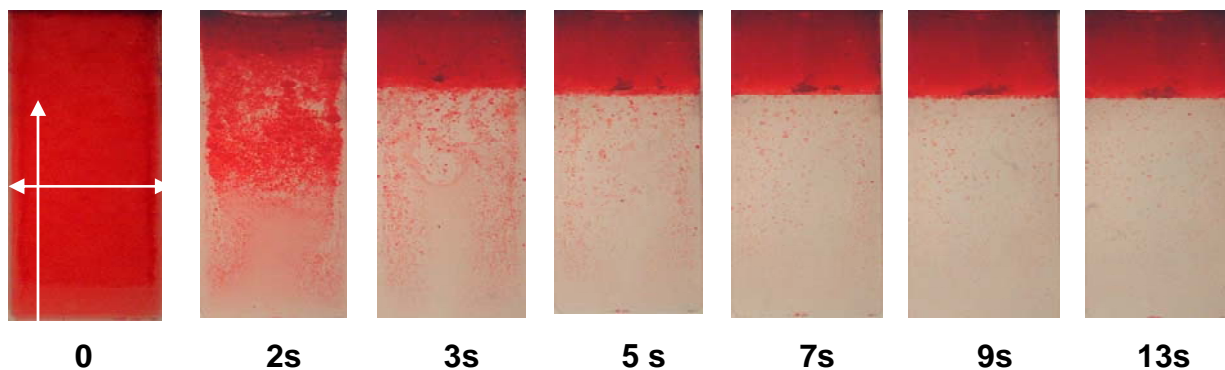


Figure 7. Phase transition extraction process (PTE).



Figure 8. Liquid liquid extraction process (LLE).

Results of Experiment 2

In this study 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 (LLE) (Figure 8), while in the latter, it is heated and cooled across its miscibility curve, inducing phase transition (PTE). 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.

Conflict of Interest

The authors have not declared any conflict of interest.

REFERENCES

Alegert S (1988). Developments in solvent extractions. *J. membrane sci.* P. 35.

- Cohen P, Jacobs C (1984). The clinician's illusion. *Arch. Gen. Psychiatry* 41(12):1178-1182. <http://dx.doi.org/10.1001/archpsyc.1984.01790230064010>
- Domb C, Green MS (Eds.) (1972). Phase transitions and critical phenomena. Academic Press, London and N.Y. 2:18.
- Gunton J, SanMiguel M, Sahni P (1983). Phase transition and critical phenomena, Domb and Lebowitz Eds, Academic press, P. 8.
- Hales AL, Green RWE (1966). Seismic refraction measurements in the southwestern Indian Ocean. *J. Geophys. Res.* 71:1637-1647. <http://dx.doi.org/10.1029/JZ071i006p01637>
- Hanson C (1971), Handbook of solvent extraction, Wiley-Interscience, New York, ISBN 0471041645.
- Lo T, Baird I, Hanson C (1983). Handbook of solvent extraction, Wiley-Interscience, New York.
- Rogers CR (1969). Freedom to Learn. Columbus, OH: Merrill.
- Rowlinson JS (1969). Liquids and liquid mixtures. 2d ed. Plenum Press in New York . P. 371.
- Snyder RB, Eckert CA (1973). Chemical kinetics at a critical point. *AIChE J.* 19:1126-1133. <http://dx.doi.org/10.1002/aic.690190608>
- Treybal RE (1963). Liquid extraction, McGraw Hill, New York, NY. P. 666.
- Ullmann A, Ludmer Z, Shinnar R (1995). Phase transition extraction using solvents mixtures with a critical point of miscibility. *AIChE J.* 41:489. <http://dx.doi.org/10.1002/aic.690410307>