Experimental Investigation of Phase Inversion of Liquid-Liquid Systems in a Spray Extraction Column

Torab Mostaedi, Meisam

Nuclear Science Research School, Nuclear Science and Technology Research Institute, Tehran, I.R. IRAN

Khadiv Parsi, Parissa*[+]; Moosavian, Mohammad Ali

School of Chemical Engineering, University College of Engineering, University of Tehran, Tehran, I.R. IRAN

ABSTRACT: *An experimental study of the phase inversion behavior of liquid-liquid dispersion has been conducted in a spray extraction column for systems of toluene / water, n-hexane/water, CCl_4/water, toluene /water + glycerol (25 % wt), toluene + CCl_4 (25 % wt) / water and toluene / acetic acid (5 % wt)/water. The effects of physical properties, mass transfer and column geometry on phase inversion have been investigated. The results show that the dispersed phase hold up sufficient for phase inversion increases in o/w dispersion and decreases in w/o dispersion by increasing interfacial tension. Also, it was found that by increasing the viscosity of aqueous phase, dispersed phase hold up decreases at phase inversion point in both o/w and w/o dispersions. The tendency to phase inversion increases in o/w dispersion with an increase in density difference of two phases. It was observed that dispersed phase hold up at phase inversion point decreases in the presence of mass transfer, when the direction of mass transfer is from dispersed phase to continuous phase. The results show that dispersed phase holdup increases with drop size at phase inversion point and column diameter has an important effect on phase inversion because of wall effect.*

KEY WORDS: *Phase inversion, Hold up, Liquid-liquid dispersion, Ambivalence region, Mass transfer.*

INTRODUCTION

Two phase flows are very common in industrial processes. Liquid-liquid flows are found in a wide range of applications, such as, column contactors and mixer-settlers. In the petroleum industry, two-phase oil-water flows occur in production wells and sub-sea pipelines.

In a system of two immiscible liquids, usually water and an organic liquid, there are two general types of dispersions which can occur in the system. Water-in-oil (w/o) dispersion is a dispersion formed when the aqueous phase is dispersed in the organic phase and oil-in-water

(o/w) dispersion is a dispersion formed when the organic phase is dispersed in the aqueous phase.

Phase inversion is the phenomenon whereby an interchange occurs between the phases of a liquid-liquid dispersion: the dispersed phase inverts to become the continuous phase and vice versa under conditions determined by system properties, phase ratio and energy input [1-5]. The point at which phase inversion occurs corresponds to the holdup of the dispersed phase for a system at which the transition occurs after an infinitesimal change is made to the properties of the system. Although, phase inversion is a spontaneous phenomenon, it was found that when a small amount of the dispersed phase (sufficient to cause inversion eventually) is added to a system already close to inversion, phase inversion occurs some significant time after the addition. The delay time varies from 5 to 1500s depending on a wide range of parameters [6].

In liquid-liquid extraction, phase inversion is highly undesirable since the design of the contacting equipment is based on a preferred direction of transfer of the solute to give optimum mass transfer rates. On the other hand, phase inversion is an integral process step in the manufacture of butter, which consists of water drops in a fat continuum, from milk, which essentially consists of fat globules in a water continuum phase.

The detailed mechanism underlying phase inversion is not well understood despite over 40 years of research and many attempts to observe the phenomenon by flow visualization techniques [7]. There has also been a considerable amount of experimental work investigating the various physical and physicochemical parameters influencing the inversion process such as the volume ratios of the immiscible liquids, the interfacial tension and the density difference between these two liquids, impeller speed, vessel geometry and materials of construction, as well as temperature.

Previous work has shown that in a system of two immiscible liquids, there is so-called ambivalent range of volume fractions over which either component can be the stable dispersed phase [8-12]. The extent of the ambivalent range depends on how the dispersion is produced [4]. The ambivalent range is defined by the volume fraction of the dispersed phase and the level of energy input into the system. *Luhning* and *Sawistowski* [9] suggested that the asymptotic phase holdup of the

dispersed phase at inversion for the upper and lower inversion curves could be related linearly to the impeller Weber number and they also proposed that the interfacial tension is one of the principal factors affecting the width of the ambivalent region.

An alternative method for plotting ambivalence behavior was proposed by *Kumar et al.* [13]. They plotted the volume fraction of the initially dispersed phase at phase inversion, regardless of which phase was initially dispersed, as a function of the stirrer speed; this method of plotting clearly illustrates the hysteresis effect that accompanies the inversion process [14]. *Brauner* and *Ullmann* [15] investigated the effects of surface rewetting and contaminants on the ambivalent range. They found that, for a hydrophobic surface, the critical holdup of the organic phase increased. They also suggested that a significantly larger oil holdup might be required to invert contaminated o/w dispersion to w/o dispersion compared to the critical oil holdup obtained in a pure system. *Deshpande* and *Kumar* [16] suggested that the inversion holdup for sufficiently intense turbulence is independent of all the operational parameters associated with stirrer tank, e.g., stirrer speed, vessel volume and impeller type; but it depends only on the properties of the liquid-liquid system.

Sarker et al. [17] have been investigated mechanisms of phase inversion in a rotary agitated extraction column. They found that phase inversion took place near column flooding points and occured either simultaneously in different sections of a column contactor, or at the compartment nearest to the light phase inlet.

In the present work, a number of behavioral features relevant to phase inversion in liquid-liquid dispersions have been investigated. Phase inversion curves are experimentally determined for liquid-liquid systems of various physical properties. The effect of mass transfer on ambivalence region has also been examined. Also, the effect of column geometry on phase inversion behavior has been investigated.

EXPERIMENTAL
Liquid-Liquid Systems

The liquid-liquid systems studied were toluene/water, n-hexane/water, CCl_4/water, toluene/water + glycerol (25 % wt), toluene + CCl_4 (25 % wt)/water and toluene / acetic acid (5 % wt)/water. All the materials were Merck products with purities of more than 99 % and distillated

Table 1: Physical properties of the liquid-liquid systems at room temperature (20 ^{o}C).

Liquid-Liquid system	ρ_{org} (kg/m^3)	ρ_{ag} (kg/m^3)	μ_{org} (mPa.s)	μ_{aq} (mPa.s)	σ (mN/m)
Toluene/water	898	996	0.57	0.96	36.1
n-hexane/water	659	995	0.304	0.97	49.7
Toluene /water + glycerol (25 % wt)	865	1020	0.58	2.31	27.9
CCl$_4$/water	1584	997	0.90	0.97	46.5
Toluene/ acetic acid(5 % wt)/ water	858	995	0.643	0.98	23.1
Toluene+CCl$_4$(25 % wt) /water	1045	996	0.66	0.97	23.4

water was used in all experiments. Physical properties of the liquid-liquid systems used in these experiments are listed in table 1. In mass transfer condition, the mass transfer direction was from dispersed phase to continuous phase.

Apparatus

The experiments described here were conducted in a spray extraction column of 72 mm internal diameter and 650mm height and it was made of pyrex glass. For investigating the effect of column diameter on phase inversion another spray column with 110 mm internal diameter was used. Drop forming was provided by means of variety of glass nozzles located at the bottom of the column. The dispersed phase flowed through a tube to the glass nozzles, whereas the spray column was filled with the continuous phase. The column was washed by chromic acid, acetone and distilled water after each run. In all experiments, two phases were mutually saturated before the experiments by repeated circulation through the column.

Procedure

The experimental procedure involved operation of the column with a number of nozzles having different diameters. At a certain value of dispersed phase flow rate, when the column reached near flooding condition as indicated by creation of a dense layer of droplets between coalesced dispersed phase and adjacent continuous phase, when the layer height reached one centimeter, inversion was observed to occur [17, 18]. At inversion point, the dispersed phase inlet valve was quickly shut and the holdup of dispersed phase was determined by displacement method.
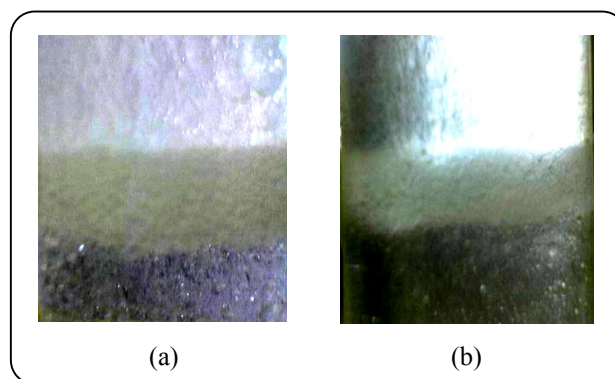

(a)   (b)

Fig. 1: a) Illustration of dispersion bed of (o/w) in n-hexane / water system. b) Illustration of dispersion bed of (w/o) in water/n-hexane system.

Fig. 1 shows typical phase inversion behavior of n-hexane/water system for o/w and w/o dispersions. As it is shown in Fig. 1(a) the dispersion bed of organic phase (n-hexane) is formed between continuous phase (water) and dispersed phase (n-hexane) at phase inversion point and as it can be seen in Fig. 1 (b) the dispersion bed of aqueous phase (water) is formed between continuous phase (n-hexane) and dispersed phase (water) at phase inversion point.

RESULTS AND DISCUSSION

The majority of the experiments conducted to investigate phase inversion in liquid-liquid dispersions have demonstrated the existence of an ambivalence region, which corresponds to a range of volume fractions over which either component can be the stable dispersed phase. Fig. 2 shows the effect of interfacial tension on behavior of ambivalence region. As it is shown in this figure, the organic phase holdup increases at phase inversion point with an increase in interfacial tension for

both dispersions and the ambivalence region is shifted upward as the interfacial tension increases. It is known that, by increasing the interfacial tension, the sizes of drops are increased and the rate of drop coalescence decreases. Consequently the dispersed phase hold up will increase at phase inversion point. According to Fig. 2, it can be concluded that the value of organic phase holdup at inversion point in n-hexane/water system is higher than that in toluene/water system due to higher interfacial tension. The experimental results of *Norato et al.* [14] show that the lower curve of the ambivalent range undergoes significant drop as the interfacial tension decreases. Similar investigations were also carried out by *Reeve* and *Godfrey* [19]; their experiments show that the width of the ambivalent range is unchanged with variation of the interfacial tension. The experimental results, shown in Fig. 2, seem to agree better with the findings of Reeve and Godfrey.

Fig. 3 shows the influence of density difference on ambivalence region. As it is shown in this figure, the lower curve of the ambivalent range undergoes significant fall as the organic phase density increases. The results also show that the density differences between organic and aqueous phase do not affect significantly the upper curve of the ambivalent range. These results are in agreement with those reported by *Norato et al.* [14]. But some investigators have reported that density differences between phases do not affect the phase inversion behavior [8, 11].

Viscosity of a given phase has been shown to play an important role on phase inversion point and to affect directly the width of the ambivalent range. In general, it has been found that as the viscosity of a liquid phase increases its tendency to be the dispersed phase also increases [8]. Fig. 4 shows the effect of viscosity on ambivalence region. It shows that the upper and lower curves of the ambivalent range move towards higher and lower organic phase volume fractions, respectively, with increasing viscosity ratio, or more dispersed phase is required to invert a dispersion as its viscosity increases. This is due to the fact that the coalescence probability increases with decreasing viscosity of dispersed phase [20]. Similar trends were also found by *Yeh et al.* [21], *Yeo et al.* [7] and *Hu et al.* [22].

Fog. 5 shows the effect of mass transfer on phase inversion for d→c mass transfer direction. This figure
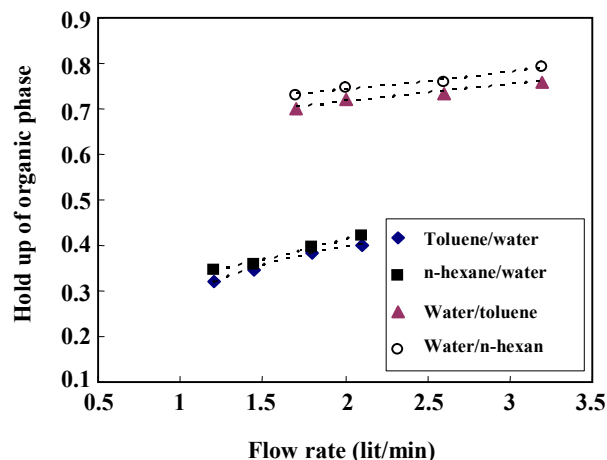

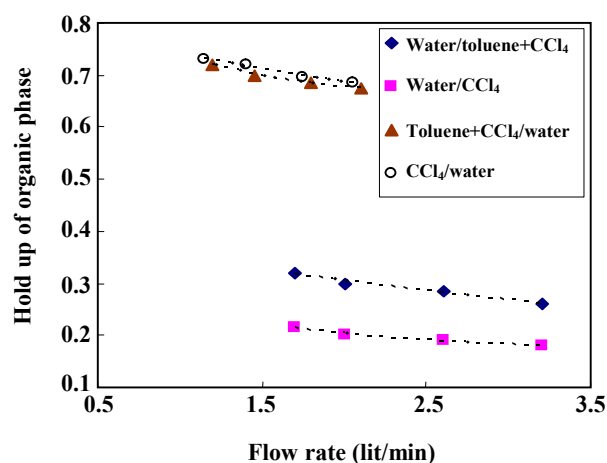**Fig. 2: The effect of interfacial tension on phase inversion behavior.**

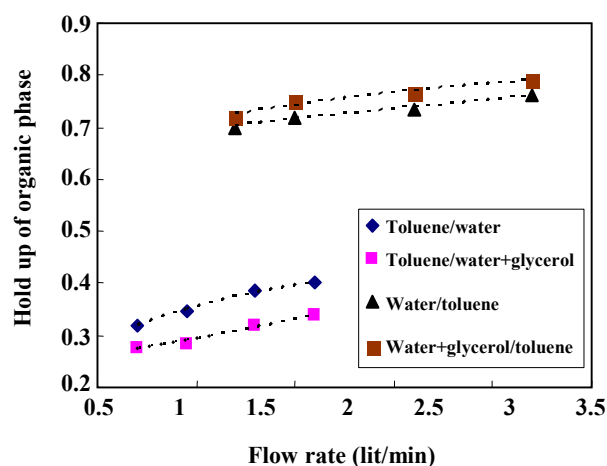**Fig. 3: The effect of density difference between the two phases on phase inversion behavior.**

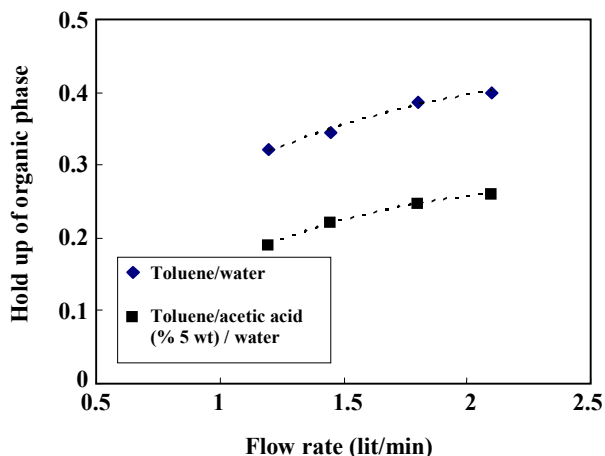**Fig. 4: The effect of aqueous phase viscosity on phase inversion behavior.**

Fig. 5: The effect of mass transfer on phase inversion behavior.

Fig. 6: The phase inversion behavior using different nozzles.

shows that the organic phase hold up at inversion point will decrease when the solute is added to the system. This variation could be explained qualitatively in terms of interfacial phenomena and variation of interfacial tension with mass transfer. The solute concentration near the interface decreases during the drop formation when the direction of mass transfer is from dispersed phase to continuous phase. Mass transfer stops at the contacting interface when the droplets are in contact. As a result, the concentration at the contacting interface increases and is higher than that at the non-contacting interface. Except for this contact point, the solute concentration decreases, and the concentration difference between the contacting interface and the non-contacting interface increases. The concentration difference results in the difference of interfacial tension, which in turn works as a driving force for film drainage. Therefore, the coalescence is promoted and consequently phase inversion occurs at lower organic phase hold up [23, 24].

Apart from liquid physical properties (e.g. viscosity, interfacial tension and density), the effect of column geometry on phase inversion has also been studied. Fig. 6 shows the phase inversion behavior of different nozzles diameter. As it is indicated in this figure, the dispersed phase hold up increases at phase inversion point by increasing the nozzle diameter, because the surface area per unit volume decreases by decreasing drop diameter and consequently lower drop coalescence rates lead to higher dispersed phase hold up for phase inversion. This observation is in agreement with those reported by *Yeo et al.* [7].
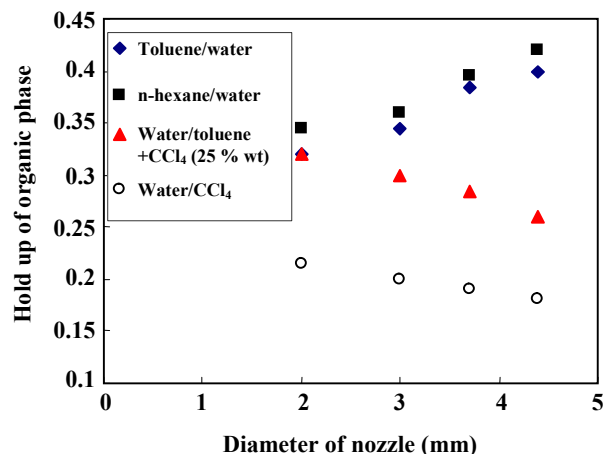
The effect of column diameter on phase inversion has also been investigated by using two different columns of 72 mm and 110 mm diameters. It was observed that by increasing the column diameter, phase inversion may not occur by increasing the dispersed phase hold up. So, it can be concluded that wall effect has an important effect on phase inversion and it can promote the rate of drop coalescence.

CONCLUSIONS

The behavior of phase inversion has been investigated in a spray extraction column. In these experiments, phase inversion is characterized as the rejection of a fraction of dispersed phase as a dense layer of droplets between the coalesced dispersed phase and the adjacent continuous phase.

The results show that interfacial tension has significant effect on phase inversion and the ambivalence region is shifted upward as the interfacial tension increases. The increase in density difference between the dispersed and continuous phases results in the decrease of organic phase holdup at inversion for o/w dispersion, while it does not affect phase inversion for w/o dispersion. According to the results, the ambivalent region becomes wider as the viscosity of aqueous phase increases. Investigation of the mass transfer conditions show that the organic phase holdup decreases at inversion, when the direction of mass transfer is from dispersed phase to continuous phase. It was found that phase inversion is largely affected by the diameter of nozzle as well as the column diameter.

Nomenclatures

o/w	Oil-in-water dispersion
w/o	Water-in- oil dispersion

Greek Letters

μ	Viscosity (mPa.s)
ρ	Density (kg/m^3)
σ	Interfacial tension (mN/m)
ϕ	Hold up

Subscripts

aq	Aqueous phase
org	Organic phase
inv.	Inversion

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