Experimental Study on Phase Inversion in Liquid – liquid Batch System

Abstract

In many industrial processes involving liquid-liquid dispersions, the phenomenon of phase inversion will be encountered.

The aid of this research is the study of speed of rotation or energy input in the range of 400 to 800 rpm in a batch liquid-liquid system of toluene and water. It was also studied the presence of sodium chloride and magnesium sulphate in the system.

It was shown that the increase of energy input had more obvious effect on O/W dispersion at lower values of holdup. Also, shown that the ambivalence region of phase inversion curve was shifted down ward and became wider as a result of decrease in interfacial tension.

It was observed that inorganic salt used in both single and dual (mixed) shapes enhanced phase inversion for O/W dispersion. Therefore, the more the ionic strength, the more the tendency to inversion is.

Keywords: phase inversion, holdup, ambivalence region, delay time, dispersed phase, drop.

Introduction

Liquid-Liquid dispersions have been extensively used in chemical, petrochemical, pharmaceutical, food … industries [1, 2].

Due to the different natures of molecular forces existed in aqueous and organic phases, there is a noticeable difference between O/W and W/O dispersion when separation of two phases occurs. Therefore, it is very important to select exactly the dispersed or drop phase [3].

At steady state condition, equilibrium exists between the processes of coalescence and breakage of drops, which leads to a rather constant drop size distribution with an average drop size [4-6].

Depending on some circumstances, the rate of coalescence of drops exceeds that of breakage in such a manner that dispersed phase places the continuous phase and vice versa. In other words, the experimental studies indicate that the drop holdup can be increased only up to a critical value, beyond which the dispersion undergoes phase inversion [3, 7, 8].

Phase inversion may be of some interest in some cases such as production of Margrine or in producing fine emulsion through the process under successive heating and cooling [6,9].

But, it is the most important factor for emulsion instability in sense.

Usually, phase inversion takes place spontaneously, though some experiments showed a delay time between 5 and 1500 seconds needed to complete this phenomenon which is mainly due to the chemical properties of system [10].

Critical dispersed phase holdup or volume fraction of drop phase at phase inversion point depends mainly to some factors as follow [3, 6].

- Physico-chemical properties of system i.e. viscosity, interfacial tension… It has been already shown that viscosity has high influence compared to other properties.
- Operating condition such as energy input, type of impeller…
- Initial condition or history of system, i.e. whether the impeller first placed in aqueous or organic phase, or, if it is the first run of successive experiments or not … .
- Mass transfer, especially from drops to continuous phase which enhances the drop-drop coalescence.
- Wall effect and wetability of impeller,
- Effect of additives and surface active agents.
- Temperature, mainly effective for the case of nonionic surfactants.

Most of works have been done in stirred vessels and columns with mechanical parts. The main purpose of these works was the determination of ambivalence region related to the curve of critical hold up versus speed of rotation [13-17].

Phase inversion has been recognized to be a very sophisticated one, so a single mechanism governing this phenomenon cannot be specified. Overall, it is obvious that it is a true function of rates of drop coalescence and breakup.

The aid of present research is to investigate the phase inversion in a batch stirred vessel.

Materials and Methods

Materials

All the chemicals were purchased from Merck and used as received. Distilled water was used in all the experiments. Purity of chemicals was all above 99%.

Density of each phase was measured with a Picnometer with volume of 25 ml. Viscosity was measured by a Cannon-Fensk viscometer with the aid of a stepwatch having a precision of 0.1 s. Interfacial tension was measured by a digital Wilhelmy plate Kruss tensiometer.

Before measuring the properties, proper volumes of two phases was brought about together in order to saturate mutually from each other and then separated. Physical properties of chemical which are measured at room temperature are shown in table 1.

Table1. Physical properties of liquid-liquid system used in experiments at room temperature.

Liquid-Liquid System	Water/Toluene	Water/n- Heptane
$\rho_{org}\,(kg/m^3)$	867.0	683.7
$\rho_{aq}\,(kg/m^3)$	996.84	997.0
$\mu_{org}\,(mPa.s)$	0.668	0.450
$\mu_{aq}\,(mPa.s)$	0.814	0.856
$\sigma(mN/m)$	36.1	50.1

Apparatus

The experiments were conducted in a batch mixed vessel or contactor. The vessel was made of pyrex glass which contained an stainless steel impeller and its shaft in the shape of hollowed cylinder, comprising two parallel disks attached by vertical rods. The speed of rotation was set between 50 and 1400 rpm. Figure (1) shows the apparatus and Table (2) illustrates the characteristics of it.

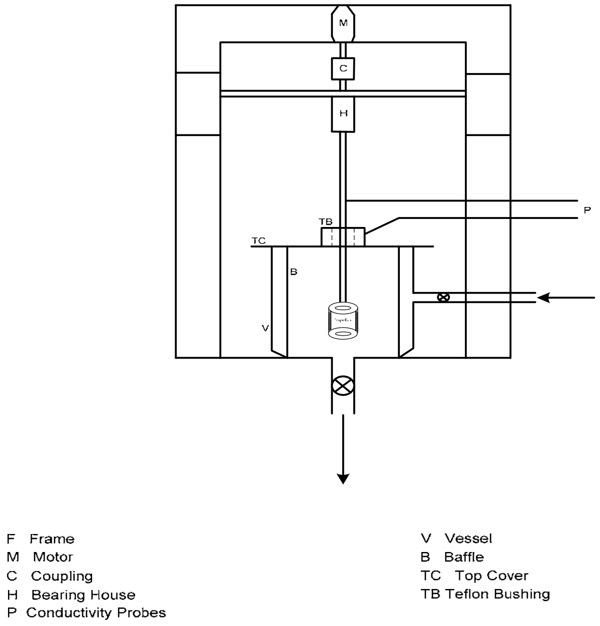

Figure (1). Diagram of equipment.

Table (2). Characteristics of mixed vessel.

Internal diameter of vessel (cm)	9.5
External diameter of vessel (cm)	10.0
Height of vessel (cm)	16.0
External diameter of central shaft (cm)	0.8
External diameter of impeller (cm)	4.6
Height of impeller (cm)	4.0

Since, the observation and registration of phase inversion is difficult at high speeds of rotation, we used a digital conductivity meter, type WPA England CMD510, It is clear that at phase inversion from W/O to O/W, conductivity of system falls significantly [6].

Experimental

The influence of impeller speed (energy input), critical drop phase holdup and interfacial tension on ambivalence curve were studied. Two chemical systems of water/toluene and water/n-heptane were examined. Two cases of absence and presence of inorganic salts of NaCl and $MgSO_4$ were investigated in the shape of single and dual (Mixed). All the experiments were done in the absence of any surfactants.

Before each run, two phases were mixed completely in a separate beaker, becoming mutually saturated. It prohibited the undesirable mass transfer which might be one of the important factor responsible for phase inversion [18,19]. After separating the two phases, a definite volume of prescribe continuous phase (aqueous phase), say about 70% by volume was added to vessel.

Then, the second phase (drop phase) was added gradually to the continuous phase while the shaft of impeller rotated at a definite rate. Addition continued till the commencement of inversion that was shown by change of conductivity property of system.

By this way, the critical holdup at a fixed and definite rotation speed was obtained. Experiments were conducted and carried out for other speed of rotation and hence, we obtain the other points of the upper curve of ambivalence region (O/W → W/O).

These processes also carried out at fixed holdup while increasing rotating speed in order to be assured from the accuracy of obtained curve.

All the aforementioned steps were done for lower curve of ambivalence region (W/O→O/W) through selection of organic phase as the continuous phase. In addition, presence of salts as single and mixed forms were examined on phase inversion.

Results and discussion

- Effect of energy input

Figures 2 and 3 show the behavior of the ambivalence region for systems of W/n-C_7 and w/toluene, respectively.

As written earlier, the upper curve represents inversion of O/W to W/O dispersion and the lower one represents vice versa.

Clearly, ambivalence region is a function of operating and hydrodynamic circumstances which represents an interval between O/W and W/O called hystersis.

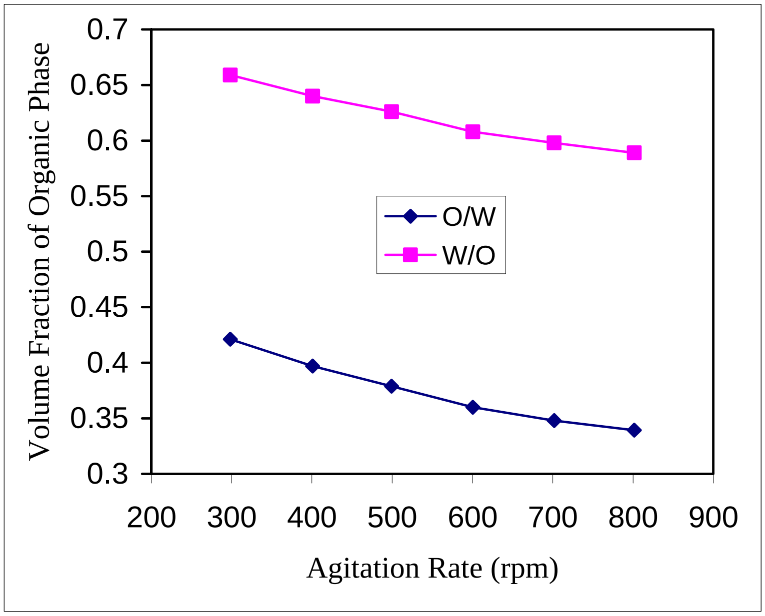

Figure 2 – Ambivalence region for the system of W/n-C7.

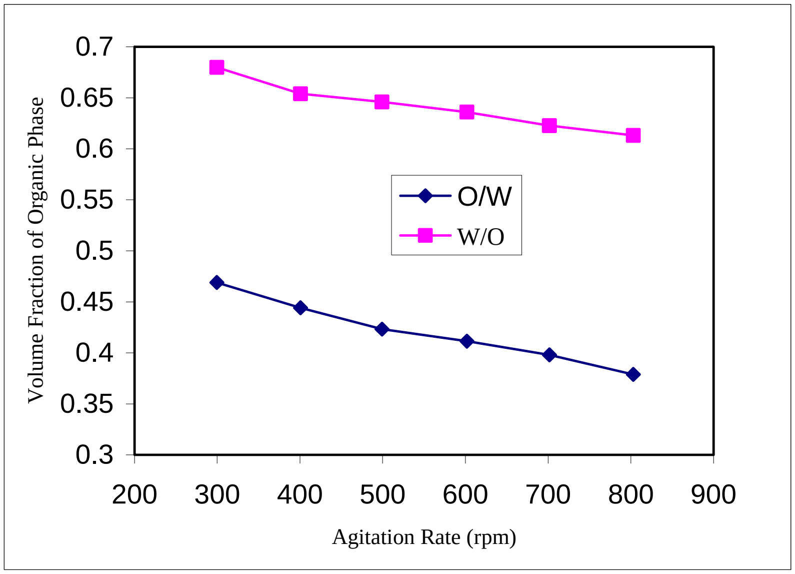

Figure 3 – Ambivalence region for the system of W/Toluene.

As seen from these figures, for drop holdups less than 0.5, phase inversion does not take place, neither for the organic drops (upper curve) nor for the aqueous phase drops (lower curve).

Based on these figures, the characteristics of two types of inversion is primarily different from each other. It was observed that drop holdup required for upper curve (critical holdup) was reduced while increasing rotor speed. But for the lower curve, it had an increasing trend. One of the reasons might be due to the repulsive electrostatic forces between aqueous drops in continuous organic phase [1,8].

Secondary dispersion takes place in W/O dispersion which leads to an O/W/O dispersion or fine droplets of organic phase in aqueous drops. Hence, increasing rate of mixing causes fine droplets that reduces the secondary dispersions inside the dispersed phase and consequently reduces the effective holdup.

- Effect of interfacial tension

Comparison of two chemical systems as seen in figure 4, explains that for the system of w/toluene, the ambivalence region shifts downward with an increase in width of this region. Effect of reduction of interfacial tension is more pronounced in upper curve (O/W→W/O).

It might be due to the absence of secondary dispersion in O/W. it was found that reduction of interfacial tension did stabilized O/W dispersion with respect to W/O one [20]. This is because of producing smaller drops accompanied with a reduction in coalescence rate.

Figure 4, shows that phase inversion holdup of w/toluene at a fixed rotor speed is more than the case of W/n-C7 when W/O inverts to O/W. But, this is not true for O/W inversion to W/O. this may reveals the effect of other physical properties such as density and viscosity.

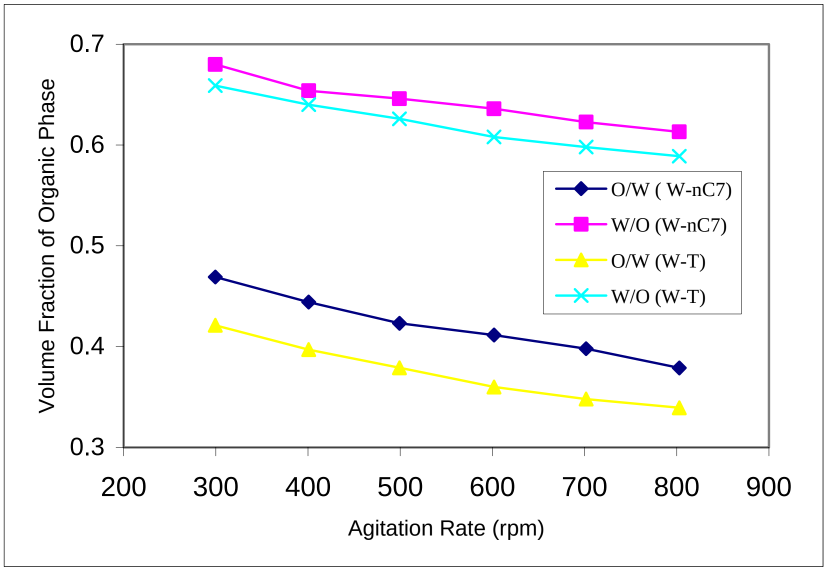

Fig.4. Comparison of ambivalence curve for two systems of w/toluene and W/n-C7

- Effect of inorganic salts

Tables 3 to 6 explains the behavior of the systems of w/toluene and W/nC7 in presence of NaCl and $MgSO_4$, separately.

For an average drop holdup of 0.6, increasing the salt concentration reduced the energy input needed for phase inversion of O/W.

It means that inversion becomes simpler and the upper curve of ambivalence region moves to the left for other values of holdups. As a result curve becomes small in length. This effect is more observable for the salt of $MgSO_4$.

Table 3.The effect of addition of NaCl on Phase Inversion in Toluene/ Water System in $\phi_0 = 0.6$

NaCl Concentration (mol/lit)	Speed of Rotation (rpm)
0	565
0.5	525
1	495
1.5	465

Table 4. The effect of addition of NaCl on Phase Inversion in n-Heptane/ Water System in $\phi_0 = 0.6$

NaCl Concentration (mol/lit)	Speed of Rotation (rpm)
0	775
0.5	720
1	685
1.5	650

Table 5. The effect of addition of $MgSO_4$ on Phase Inversion in Toluene/ Water System in $\phi_0 = 0.6$

$MgSO_4$ Concentration	Speed of Rotation

(mol/lit)	(rpm)
0	565
0.5	485
1	455
1.5	415

Table 6. The effect of addition of $MgSO_4$ on Phase Inversion in

n-Heptane/ Water System in $\phi_0 = 0.6$

$MgSO_4$ Concentration (mol/lit)	Speed of Rotation (rpm)
0	775
0.5	685
1	615
1.5	575

The effect of salt on drop holdup may be related to one of two reasons i.e. effect on interfacial tension and/or effect on electrostatic interactions.

It was observed that the surface tension of an electrolyte solution in contact with air is larger than that of pure water . The surface tension increase is caused by negative adsorption (depletion) of electrolyte ions at the air/water interface due to the electrostatic repulsive interaction between ions and their images with respect to the air/water interface. Agreement with experiment, however is good only at very low electrolyte concentration [21-25]. When the system has no ion, organic drops regardless of degree of polarity have a considerable zeta potential which becomes more negative with pH. Hence, drops become charged. The reason is not exactly clear and known. Some investigators attributed it to the absorption of hydroxyl group at drop-continuous phase interface [8].

Addition of salt to a dispersion, increases ion strength of aqueous phase and reduces electrostatic repulsion forces between adjacent organic drops. The ions make a dense double electrical layer in such a manner that Van der Waals attraction force and electrical repulsive force overlap each other. These results in drop-drop coalescence and O/W dispersion inverts at low holdup [6].

In other words, salt increases ionic strength of aqueous phase which influence on phase inversion through reduction of repulsive forces among organic drops. The more the concentration of salt, the simpler the phase inversion occurs at low speeds of rotation for a fixed holdup.

Adding the second salt at a fixed holdup, reduces the energy input. Which relates to increase in ionic strength of continuous phase. Then results of using mixture of salts of NaCl and $MgSO_4$ are observed in tables (7) and (8).

Table 7.The effect of addition of NaCl and $MgSO_4$ simultaneously with equimolar ratio on phase inversion in n-heptane/ water system

in $\phi_0 = 0.6$

Concentration (mol/ lit)	Speed of Rotation (rpm)
0	775
0.5	700
1	635

Table 7.The effect of addition of NaCl and $MgSO_4$ simultaneously with equimolar ratio on phase inversion in toluene / water system

in $\phi_0 = 0.6$

Concentration (mol/ lit)	Speed of Rotation (rpm)
0	775
0.5	510
1	470

Conclusion

Experiments showed a difference between phase inversion behavior of two initial dispersions of O/W and W/O. The O/W dispersions inverted to W/O dispersion at lower holdup when rotation or energy input increased, while this was vice versa for W/O dispersion. It was strongly related to secondary dispersions formed in W/O.

It was found that the interfacial tension widened the ambivalence region accompanied with a downward shift.

Adding salt to an O/W dispersion enhanced the phase inversion which was more obvious for salt with higher charge. Also, mixture of two salts of NaCl and $MgSO_4$ was examined and revealed that mixed salts behaved well with respect to a separate salt.

Nomenclature

Greek letters

ρ	density	(kg/m^3)
μ	viscosity	(mPa.s)
σ	interfacial tension	(mN/m)
ϕ	-	

Subscripts

aq	aqueous phase
o, org	organic phase
w	water

Reference

[1] Hu, B.; Angeli, P., Matar, O. K., Hewitt, G. F., *Chem. Eng. Sci.*, **60**, p. 3487 (2005).

[2] Ioannou, K., Nydal, O. J., Angeli, P., *Experimental Thermal and Fluid Sci.*, **29**, p. 331 (2005).

[3] Yeo, L. Y., Matar, O. K., Perez de Ortiz, E. S., Hewitt, G.F., *Multiphase Sci. Technol*, **12**, p. 51 (2000).

[4] Tsouris, C., Dong, J., *Chem. Eng. Sci.*, **55**, p. 3571 (2000).

[5] Deshpande, K. B., Kumar, S., *Chem. Eng. Sci.*, **58**, p. 3829 (2003).

[6] Norato, M. A., Tsouris, C., Tavlarides, L. L., *Can. J. Chem.Eng*., **76**, p. 486 (1998).

[7] Noui-Mehdi, M. N., Wu, J., Zhu, Y., *AIChE J.*, **50**, 3281-3283 (2004).

[8] Kumar, S., *Chem. Eng. Sci*, **51**, p. 831 (1996).

[9] Walde, A., Tesmann, H., Leonard, M., Förster, T., “Phase Inversion in Emulsions: CAPICO- Concept and Application”, in M. M. Rieger and L.D.Rhein, “ Surfactants in Cosmetics”, 2nd ed, Marcel Dekker, NewYork (1997).

[10] Gilchrist, A., Dyster, K. N., Moore, I. P. T., Nienow, A. W., Carpenter, K. J., *Chem. Eng. Sci.*, **44**, p. 2381 (1989).

[11] Sajjadi, S., Zerfa, M., Brooks, B. W., *Colloids Surf. A: Phys. Eng. Aspects,* **218**, p. 241 (2003).

[12] Bouchma, F., Van Aken, G.A., Autin, A. J. E., Koper, G. J. M., *Colloids Surf. A: Phys. Eng. Aspects*, **231**, p. 11 (2003).

[13] Davis, G. A., “Mixing and Coalescence Phenomena in Liquid-Liquid Systems”, Science and Practice of Liquid-Liquid extraction, Vol. 1, Thornton, J. D., Ed., Oxford, London (1992).

[14] McClarey, M. J., Mansoori, G. A., *AIChE Symposium Series*, **74**, p. 134 (1978).

[15] Arashmid, M., Jeffreys, G. V., *AIChE J.*, **26**, p. 51 (1980).

[16] Khadiv-Parsi, P. and M.-A. Moosavian, *Can. J. Chem. Eng., 82, 256-264 (2004).*

[17] Yeo, L. Y.; Matar, O. K.; Perez de Ortiz, E. S.; Hewitt, G. F., , *Chem. Eng. Sci.*, **57**, 1069-1072 (2002).

[18] Khadiv-Parsi, P. and M.-A. Moosavian, *Iran. J. Chem. & Chem. Eng., 23,79-88 (2004).*

[19] Khadiv-Parsi, P. and M.-A. Moosavian, *Iran. J. Chem. & Chem. Eng.,23,89-96 (2004).*

[20] Brösel, S., Schuber, H., *J. Chem. Eng. Proc.*, **38**, p. 533 (1999).

[21] L. Lobo, A. Svereika, J. Colloid Interface Sci, 261 (2003) 498 .

[22] H.Ohshima and H.Matsubara, Colloid Polym. Sci., 282 (2004) 1044-1048

[23] G. G. Palazolo, D.A. Sorgentini, J.R.Wagner, food HydroColloids, 19 (2005) 595

[24] G.Urbina-Villalba, M. Garcia-Sucre, Colloids surfaces A: Physicochemical Eng.
Aspects, 190 (2001)111.

[25] A. Koh, G. Gillies ,J. Gore, B. R. Saunders, J. Colloid Interface Sci,227 (2000)390.