

# A Simple Theoretical Model for Prediction of Phase Inversion

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**ABSTRACT:** *Phase inversion in liquid-liquid dispersions corresponds to the transitional boundary between Oil-in-Aqueous dispersion and Aqueous-in-Oil dispersion. A theoretical model based on simple assumptions was proposed to predict phase inversion point, ambivalence region and the hysteresis effect of inversion. Experimental data from the literature were used to validate the model and results were compared with those obtained by the Yeo et al. model. Comparison shows that there is a reasonable agreement between the suggested model and the experimental results taken from the literature. It is also pointed out that this model generates smaller relative errors than the previous work of Yeo et al. does.*

**KEY WORDS:** *Phase inversion, Liquid-liquid dispersion, Ambivalence region, Model.*

## INTRODUCTION

Liquid-liquid extraction is an important separation process that is widely used in the chemical, biochemical, petrochemical, pharmaceutical, and food industries [1, 2]. A dispersion of two immiscible liquids, where one of the liquids forms a continuous phase and the other is dispersed in it, is often observed in liquid-liquid extraction. In general, a given phase is required to be always the dispersed phase with very large holdup so that the productivity is maximized. Experimental studies indicate that the holdup,  $\phi$ , can be increased only up to a critical value,  $\phi_1$ , beyond which the dispersion undergoes phase inversion [3, 4].

Phase inversion is the phenomenon in which the dispersed phase becomes continuous and vice versa. The phase inversion point is therefore the dispersed phase holdup at which this interchange occurs. Inversion of

agitated oil-in-water (O/W or O/A) dispersion to water-in-oil (W/O or A/O) at one volume fraction and that of W/O to O/W at a different value of volume fraction of the dispersed phase are known in the literature for a long time.

The change of the continuous phase will lead to a system with different properties which can be desirable in some cases like production of margarine but in other cases are unwanted, for example in exothermic aromatic nitrations, phase inversion can cause a sudden increase in the reaction rate and produced heat [1].

Therefore it is particularly important in industrial applications to control the dispersion behaviour under operational conditions. Furthermore, inversions in O/W and W/O dispersions are of significant importance, both from an applied point of view as well as for fundamental research.

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It has been found that if the volume fraction of the organic phase is plotted versus energy input via agitation, there is a region which is called the ambivalent region.

The ambivalent region is defined by two curves. The system can exist only as W/O above the upper curve and as O/W below the lower curve. In the gap between the two curves, any configuration is possible, depending on whether the region is reached from a W/O configuration, by addition of water, or from an O/W configuration, by addition of organic phase. In both cases, it has been reported that no inversion will occur until the second limit of the ambivalent region is reached, so that a hysteresis effect exists [5-7].

Despite the work carried out on phase inversion over the past four decades, however, very few studies have reported good agreement between theory and experiment in terms of the width of the ambivalent region. Due to the difficulties in understanding the mechanism which is responsible for phase inversion, the ability to predict the inversion point is severely limited. Various empirical correlations have been proposed to determine the phase inversion point, but unfortunately, there has been a considerable amount of variation between the predictions of these correlations and a satisfactory model [7-9]. Since phase inversion is a spontaneous phenomenon, it was suggested that its prediction can be based on the criterion of minimization of the total free energy of the system [5, 9, 10].

By using this criterion, Yeo et al. proposed a model to predict the limits of the ambivalent region of a phase inversion process. Dispersed phase holdup at inversion,  $\phi_{o,i}$ , is given by the following equation [9]:

$$\frac{\phi_{o,i}}{1 - \phi_{o,i}} = \frac{d_{32O/A}}{d_{32A/O}} \quad (1)$$

Where  $\phi_{o,i}$  and  $d_{32}$  represent respectively the organic phase holdup at inversion and the drop Sauter mean diameter (i.e. the surface area to volume weighted average). In this work, a theoretical model of phase inversion using simple assumptions is proposed to predict the inversion holdup and also to describe the hysteresis of phase inversion.

## METHOD

1- Since liquid-liquid extraction columns are essentially mass-transfer units, the volume-to-surface mean diameter, also known as the Sauter mean diameter,  $d_{32}$ , was chosen in this work to characterize the drop population.

2- All nearest dispersed phase droplets simultaneously coalesce into the continuous phase at the phase inversion point. The coalesced dispersed phase droplets entrap the continuous phase as discrete droplets. This entrapped sub-volumes of the pre inversion continuous phase become the newly formed drops of the post inversion dispersed phase.

3- It is conceivable that a high concentration of the dispersed phase leads to high collision and coalescence rates, and therefore to a larger characteristic size of the droplets [11].

In other words, the collision probability generally increases with an augmentation of holdup. This increases the coalescence rate, thereby commensurately increasing the Sauter mean diameter.

4- Since phase inversion is a catastrophic phenomenon and a swarm of a very large number of both the dispersed and continuous phase droplets will be obtained at phase inversion point, the population of the droplets of the dispersed and continuous phases at inversion is theoretically infinite.

According to assumptions 2, 3 and 4, as a good approximation, it can be supposed that the value of the dispersed phase droplet population relative to that of the continuous phase, just at phase inversion point is 1, as expressed in Eq. (2):

$$N_A/N_O \approx 1 \quad (2)$$

According to assumptions 1 and 2, the volumes of the dispersed phase and the continuous phase droplets in the vicinity of phase inversion point are expressed as in Eqs. (3) and (4):

$$V_A = N_A (\pi d_{32A/O}^3 / 6) \quad (3)$$

$$V_O = N_O (\pi d_{32O/A}^3 / 6) \quad (4)$$

The volume fraction of the organic phase at the phase inversion point is expressed as follows:

$$\phi_{o,i} = V_O / (V_O + V_A) \quad (5)$$

Combining Eqs. (2)-(5) results in:

$$\begin{aligned} \phi_{o,i} &= \frac{V_O}{V_O + V_A} = \frac{N_O d_{32O/A}^3}{N_O d_{32O/A}^3 + N_A d_{32A/O}^3} \\ &= \frac{d_{32O/A}^3}{d_{32O/A}^3 + d_{32A/O}^3} \end{aligned} \quad (6)$$

After a simple transformation, the above equation can be simplified to:

$$\phi_{o,i} = \frac{1}{1 + \left(\frac{d_{32A/O}}{d_{32O/A}}\right)^3} \quad (7)$$

The Sauter mean diameter is directly related to the interfacial area per unit volume, which determines transfer rates of energy, mass and/or chemical reaction in dispersions [12, 13].

Generally, in dilute dispersions where the drop size is determined by the turbulent breakage, the Sauter mean diameter is given by:

$$d_{32} = C_1 We_1^{-C_2} D_1 \quad (8)$$

Where  $We_1 = \frac{\rho_c N_1^2 D_1^3}{\sigma}$  is the Weber number representing the ratio of the external destructive force over the restoring surface tension force,  $\rho_c$  is the density of continuous phase,  $N_1$  is the agitation speed,  $D_1$  is the impeller diameter and,  $\sigma$ , the interfacial tension. Since phase inversion often occurs in concentrated dispersions where drop size is determined by both break-up and coalescence processes, the influence of drop coalescence must be considered. Therefore a modified form of Eq. (8) must be taken into account to describe the increase in drop size:

$$d_{32} = C_1 (1 + C_3 \phi_d) We_1^{-C_2} D_1 \quad (9)$$

To extend the drop sizes to liquid-liquid systems over a wide range of viscosities, a viscosity correction factor is used in a modified form of Eq. (9) as follows:

$$d_{32} = C_1 (1 + C_3 \phi_d) We_1^{-C_2} D_1 \left(\frac{\eta_d}{\eta_c}\right)^{C_4} \quad (10)$$

Where  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are adjustable constants, varying with the nature of the dispersed system [9, 13]. Previous experiments performed mainly in baffled stirred vessels have indicated that [9]:

$$0.05 \leq C_1 \leq 0.08, C_2 = 0.6, C_3 \leq 22 \text{ and } C_4 \leq 0.25$$

The proposed model provides an envelope of predicted ambivalence curves which bracket the experimental results of Selker and Sleicher. In other words if the volume fraction of the organic phase is

plotted as the ordinate, for plotting the upper ambivalence curve, the organic phase is concentrated and the aqueous phase is dilute. Hence, for plotting the lower ambivalence curve the organic phase is dilute, when the aqueous phase is concentrated. In this study, we solve the presented model (equation 7) for the organic phase holdup at phase inversion,  $\phi_{o,i}$ , using the Eq. (10) where  $C_1 = 0.07$ ,  $C_2 = 0.6$ ,  $C_3 = 0$  (for dilute dispersions) or  $C_3 = 3$  (for concentrated dispersions) and  $C_4 = 0.2$

## RESULTS AND DISCUSSION

Many experimental observations on various aspects of phase inversion are reported but no satisfactory and credible theoretical model is available as yet. Current models that predict the onset of phase inversion of liquid-liquid dispersions integrate two distinct approaches: (i) theoretical considerations to relate the volume fraction of the onset and the size of dispersed drops; (ii) calculation procedures to obtain the size of dispersed drops produced by an impeller. What is new in the work is that in approach (i) the relationship between the volume fraction and size is derived from a strikingly simple geometric consideration in contrast to past works in which an interfacial energy balance is considered. In the second part of the work, dealing with approach (ii), the scope is limited to high agitation speeds. Although arguing that 55 % holdup dispersion is a concentrated one and has high effect of drop coalescence on mean drop size and 45 % holdup dispersion (formed after inversion) is dilute, and has marginal effect of drop coalescence on mean drop size is difficult to justify but we act as in previous works. It is markedly obvious that refinement of the phase inversion models to achieve greater agreement with experimental results needs precise drop size correlations which are concerned with the effect of drop coalescence on mean drop size accordingly.

Fig.1 illustrates the plot of the ambivalence limits given as a function of the ratio of the oil-to-water kinematic viscosities, denoted by  $V_o$  and  $V_w$ , respectively. It can be seen that the simple model presented in this work provides reasonable agreement with the results of Selker and Sleicher [8]. The hysteresis effects which are normally present in systems undergoing phase inversion can be described by the presented model.

In general, the inversion holdups are slightly under-predicted for lower ambivalence curve and slightly over-

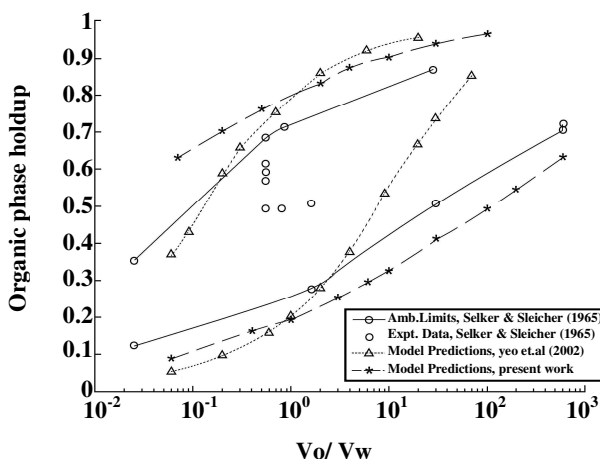


Fig. 1: Ambivalence limits predicted by the present model compared to the results of Selker and Sleicher (1965) and the Yeo et al. model (2002).

predicted for upper ambivalence curve. Salient features observed by Selker and Sleicher can be seen in Fig. 1. For example, the tendency for a phase to be dispersed as its viscosity increases and the lack of symmetry between the upper and lower ambivalence curves. It is seen that the ambivalence curves are independent of the agitation speed. This observation is in agreement with the findings of investigators who reported that the inversion holdup for sufficiently intense turbulence (high agitation speed) is independent of energy input (agitation speed) [15-17]. Restricting the model to high Weber numbers or high agitation speeds is due to the fact that in the derivation of the model, the Sauter mean diameter was used to characterize the drop population.

This may hold good at high impeller speeds, but at low speeds a wide size distribution of the droplets exists. Drop sizes are controlled by the ratio of buoyancy to interfacial tension forces under the conditions of no agitation or low levels of kinematic viscosity of the continuous phase [18].

Decarre and Fabre gathered some useful experimental data from the literature [19]. These experimental data are used to validate the model. Fig. 2 illustrates the relative error,

$$RE = \frac{|\phi_{o(\text{experimental})} - \phi_{o(\text{model})}|}{\phi_{o(\text{experimental})}}$$

, given as a function of the organic phase viscosity. The model compares favourably with that of the Yeo et al. and it can be seen that the presented model gives better results relatively.

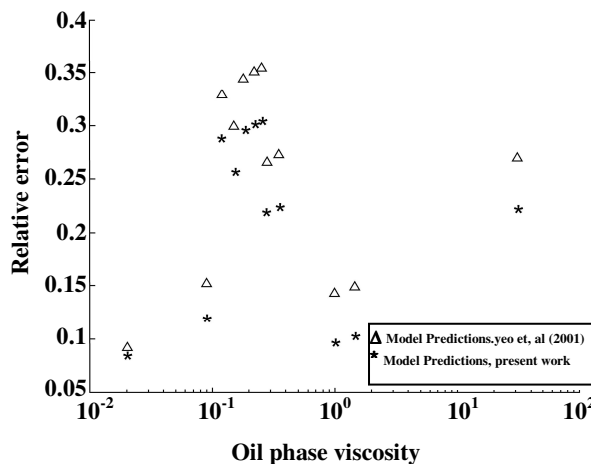


Fig. 2: Relative error versus oil viscosity for proposed model and Yeo et al. model (2002).

### CONCLUDING REMARKS

At high agitation speeds, this model can qualitatively describe both the hysteresis effect of phase inversion and the phase inversion point dependence on dispersed phase holdup value. The approach to phase inversion holdup value was based on simple assumptions resulting in Eq. (7), which is a novel relationship between the volume fraction of the inversion and the characteristic size of the dispersed phase drops. The present model uses the ratio of the dispersed phase droplet population to that of the continuous phase equal to 1 as inversion criterion. It is noteworthy that phase inversion is a complicated phenomenon. Thus, a theoretical model based on the simple assumptions to predict the limits of the ambivalent range of phase inversion is precious. Although there have been relatively few attempts to predict the phase inversion point theoretically, the complexities that accompany the phenomenon motivate for more theoretical work. The model results are in reasonable agreement with the experimental data and those of the Yeo et al. In addition, experimental data from the literature are used to validate the model. Despite the model is concerned with the high agitation speed only, yet it is valuable. The reason is that improving the mass transfer is possible by increasing the agitation speed, because it reduces the stagnant zone and also intensifies the drop breakage rate with a concomitant increase in interfacial area, thereby causing the efficiency of the liquid-liquid extraction to ameliorate. Therefore, in reality high agitation speed occurs in many cases.

The simplicity of the model and its agreement with the findings of Selker and Sleicher (1965) and Yeo *et al.* (2002) gives it an advantage to be later developed and its use may be extended for other systems. Using different drop size correlations, this model can be easily extended to various systems.

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