

PHASE INVERSION AND ASSOCIATED PHENOMENA

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Abstract. Phase inversion in liquid-liquid dispersions is a common phenomenon that occurs in a range of industrial processes. However, the mechanisms responsible for phase inversion and the effect of the physical and geometrical parameters on this phenomenon are not well understood.

In this paper, the significant developments over the past forty years of phase inversion research are critically reviewed. While the majority of phase inversion studies have largely concentrated on agitated vessel systems, the paper also includes a summary of phase inversion research in pipeflow and in contacting equipment.

The main mechanisms of drop coalescence and break-up, which directly influence phase inversion, are discussed in detail. Emphasis is placed on the postulation that the formation of secondary dispersions acts as a mechanism for the enhancement of drop coalescence and hence phase inversion. Particular attention is therefore paid to the existence of these secondary dispersions as well as the mechanisms by which they are formed and destroyed.

The paper also provides a comprehensive review of studies investigating the effect of various physical, geometrical and flow parameters on phase inversion. When conflicting views occur, a critical discussion on each view is presented and, where possible, conclusions are drawn. Crucial areas of future research arising from the ambiguities of previous findings are also identified.

1. INTRODUCTION

Multiphase flow is the simultaneous flow of two or more fluid phases (gas, liquids or solids) in direct contact in a given system. These flows are encountered in a diverse range of industries ranging from the petroleum and chemical industries to nuclear and geothermal power plants. Thus, the study of multiphase flows is pertinent to the design and operation of industrial processes and the equipment associated with these industries.

Two-phase flows are the simplest of the multiphase flow systems. Given that two-phase flows are extremely common in industrial processes and that they are the precursor to more complex multiphase flows, it is not surprising that the fundamentals of multiphase flow research have been focussed on two-phase flow. Liquid-liquid two-phase flows are found in a wide range of applications, such as in solvent extraction equipment e.g. column contactors and mixer-settlers. In the petroleum industry, two-phase oil-water flows are important in production wells and in subsea pipelines. Compared to gas-liquid flows, which have been the subject of much attention, the experimental data and theoretical models for liquid-liquid flows cover only a restricted range of flow configurations and fluid properties. Much of the previous work on liquid-liquid systems has been concentrated on liquid-liquid dispersions in agitated vessels. There is substantially less material on liquid-liquid flow systems.

Phase inversion, the subject of the present review, occurs when, in an immiscible liquid-liquid dispersion, the continuous phase changes; for example, with a change of water fraction or other conditions in an oil-in-water dispersion, the system changes from a dispersion of oil drops in water to a dispersion of water drops in oil. Very little is known about the detailed mechanism of the phase inversion phenomenon despite the fact that phase inversion has been studied for the past 40 years. In recent years, there has been a revived interest in this area especially for liquid-liquid flow in pipes, because of the abrupt and significant changes that occur in the frictional pressure drop and the rheological characteristics of the dispersion at or near the phase inversion point. Nevertheless, much research is still urgently required in order to fully understand the phase inversion process and the mechanisms behind it.

The purpose of this paper is to present a concise but comprehensive general review on phase inversion and its associated phenomena. The review will begin with a general introduction to phase inversion. The following chapter highlights important concepts of phase inversion in agitated vessels followed by a discussion on the theoretical and experimental work carried out to investigate the effects of various parameters on the phase inversion process in agitated vessels. In the next chapter, the postulated mechanisms of the phase inversion process in agitated vessels to date are reviewed. Subsequently, the review will deal with phase inversion as it occurs in pipeflow and in various other contacting equipment such as column contactors and static mixers.

2. THE PHASE INVERSION PHENOMENON

In a system of two immiscible liquids, usually water (or an aqueous solution) and an organic liquid (e.g. an oil), there are two general types of dispersions which can be formed depending on the system's conditions. A water-in-oil dispersion is a dispersion formed when the aqueous phase is dispersed in the organic phase and an oil-in-water dispersion is a dispersion which is formed when the organic phase is dispersed in the aqueous phase.

Phase inversion is the phenomenon whereby the phases of a liquid-liquid dispersion interchange such that the dispersed phase spontaneously inverts to become the continuous phase and *vice versa* under conditions determined by the system properties, phase ratio and energy input. This is illustrated in Figure 1. Thus, by definition, the

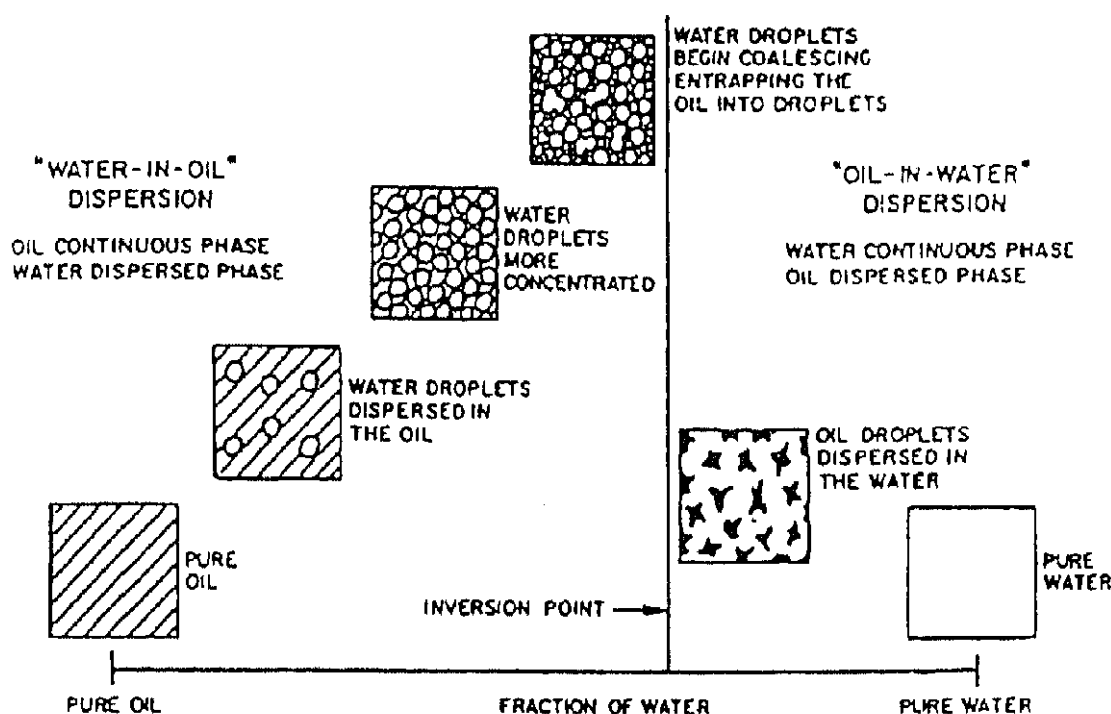


Figure 1 Phase Inversion Process for an Oil-Water Dispersion System (Arirachakaran *et al.*, 1989). Reproduced from 'An Analysis of Oil/Water Flow Phenomena in Horizontal Pipes', Arirachakaran *et al.* (1989), Paper SPE 18836 with the permission of the Society of Petroleum Engineers. Copyright © 1989 Society of Petroleum Engineers Inc.

phase inversion point is the holdup of the dispersed phase for a system at which the transition occurs i.e. when the dispersed phase becomes the continuous phase after an infinitesimal change is made to the system's properties, phase ratio or energy input.

Phase inversion can be regarded as a form of the instability of a system, the stability of the dispersion being the least at the point of phase inversion. Phase inversion is thus a very important factor to consider in liquid-liquid extraction since it can be used effectively in the separation of two immiscible phases. On the other hand, knowledge of the phase inversion point is essential in the preparation of dispersions in order to obtain the desired dispersion. In some operations, spontaneous inversion can be extremely undesirable, especially for mixer-settlers, since the settling times are very different for oil-in-water systems and for water-in-oil systems. Knowing which phase will be the dispersed phase is important in these circumstances. For oil/water flows in pipes, it is important to predict the phase inversion point since it is in this vicinity that the extremes of the pressure gradients will often be found.

The fundamental difficulty in understanding phase inversion lies in the problem of conceptualising the actual mechanism behind the phase inversion process. Much is left to be desired on understanding the actual mechanism of phase inversion although there have been attempts to observe the phenomenon by flow visualisation techniques. On the other hand, there has been a considerable amount of experimental work based on investigating the various physical and physicochemical parameters influencing the phase inversion process. Among these possible parameters are the phase volume ratios of the

immiscible liquids, the interfacial tension and the density difference between these two liquids. Impeller speed, position and shape, vessel geometry and materials of construction, as well as the temperature can also affect the phase inversion of the system due to their effect on the properties of the liquids. In pipeflow, the inlet conditions have been reported to influence phase inversion. Despite the work that has been done on phase inversion over the past decades, systematic relationships between phase inversion and the factors influencing it have yet to be established.

3. PHASE INVERSION IN AGITATED VESSELS

3.1 *Ambivalent Range*

In a system of two immiscible liquids, there is a range of volume fractions over which either component can be the stable dispersed phase (Selker and Sleicher, 1965; Eftimiadu *et al.*, 1994; McClarey and Mansoori, 1978). This region, which represents the existence of a hysteresis effect, is known as the *ambivalent range* or *range of ambivalence*, the extent of this range depending on how the dispersion is produced (Arashmid and Jeffreys, 1980). It is defined by the volume fraction of the dispersed phase and the level of energy input into the system. The ambivalent range is a metastable region (Clarke and Sawistowski, 1978); any perturbation to the system leads to instability of the dispersion producing phase inversion at the boundaries of this region.

A typical graphical representation of the ambivalent region for the hexane-water system is shown in Figure 2. If the volume fraction of the organic phase is plotted as the ordinate, the system can only exist as an organic phase continuous dispersion above the upper ambivalence curve and as an aqueous phase continuous dispersion below the lower ambivalence curve. In between the curves, any of the above two configurations are possible depending on the system's previous history.

McClarey and Mansoori (1978) also included a third phase inversion curve, the *intermediate inversion curve*. While the upper and lower inversion curves were obtained by increasing the dispersed phase holdup at constant agitation speed, the intermediate inversion curve was determined by adding predetermined amounts of both immiscible liquid phases to the mixture and initiating mixing from rest with different impeller speeds. This is seen in Figures 3 and 4.

The ambivalence limits vary between systems. The physical phenomena defining these limits are extremely complex. Any factor which influences the phase inversion process will affect the boundaries i.e. the width of the ambivalent range. Many investigators have attempted to measure the limits of the ambivalent range by correlating data and producing a physical model to interpret this data. While experimentation to produce and correlate data has been successful, a satisfactory model has not been presented to date. According to Davies (1992), this problem is highly non-linear and the phase trajectory within the ambivalent range appears to depend essentially upon the initial conditions of the system. He suggests that this is a problem which may well be approached by chaos theory. Luning and Sawistowski (1971) correlated the width of the ambivalent range as functions of agitation speed and interfacial tension. This work is reviewed in Section 3.3.

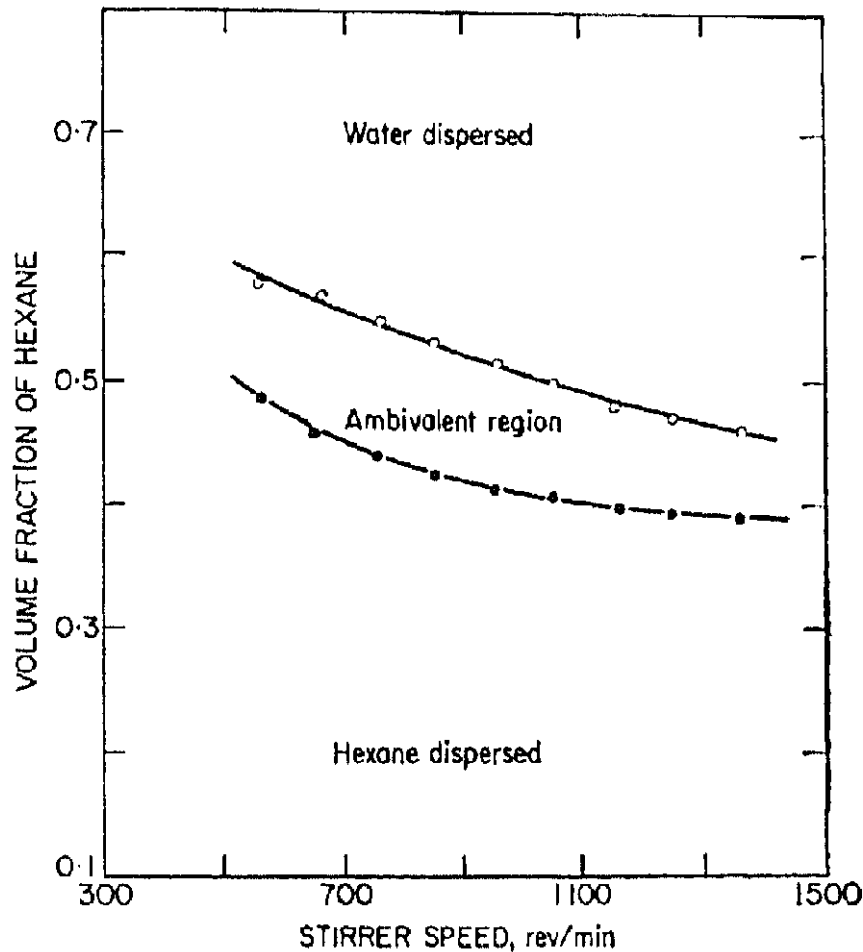


Figure 2 General Ambivalence Behaviour for a Hexane-Water system (Luhning and Sawistowski, 1971). Reproduced with the permission of the Society of Chemical Industry. Copyright © 1971 Society of Chemical Industry.

An alternative method for plotting ambivalence behaviour has been presented by Kumar *et al.* (1991). They plot 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, as seen in Figure 5. While the conventional method of plotting the organic phase volume fraction against the agitation speed is useful for showing the conditions under which only a single dispersion morphology may be maintained (i.e. phase inversion does not occur), the alternative method of Kumar presents the hysteresis effect in a clearer way. By focussing directly on the characteristics of the dispersed phase behaviour, the method of Kumar explicitly shows that the post phase-inversion dispersion can be quite different from the initial dispersion with respect to its dispersed phase holdup and physical properties. Unlike the conventional method where the initial dispersion morphology is important in determining the behaviour of the system, the method of Kumar illustrates the behaviour of the initially dispersed phase regardless of how the system is initiated (Norato *et al.*, 1998).

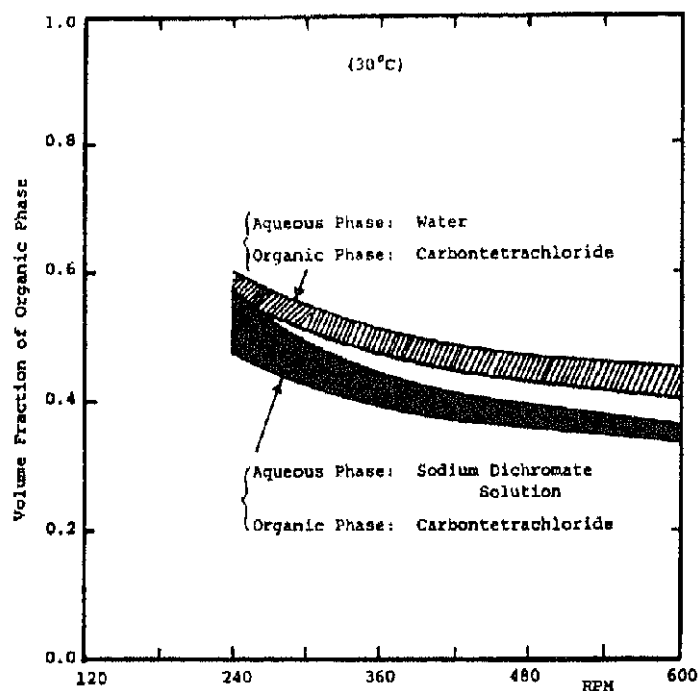


Figure 3 Intermediate Inversion Curves for Two Immiscible Liquid-Liquid Pairs with Substantial Density Differences (McClarey and Mansoori, 1978). Reproduced with the permission of the American Institute of Chemical Engineers. Copyright © 1978 AIChE. All rights reserved.

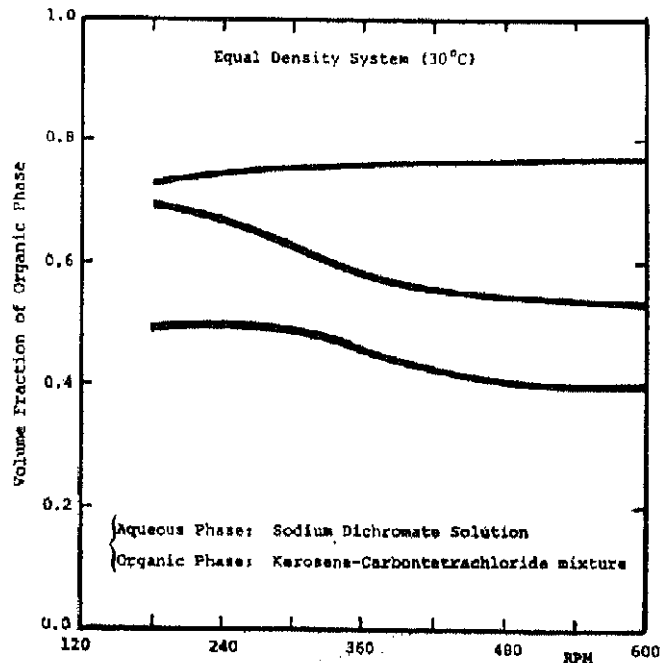


Figure 4 Upper, Lower and Intermediate Phase Inversion Curves for Two Immiscible Liquid-Liquid Pairs with Zero Density Difference (McClarey and Mansoori, 1978). Reproduced with the permission of the American Institute of Chemical Engineers. Copyright © 1978 AIChE. All rights reserved.

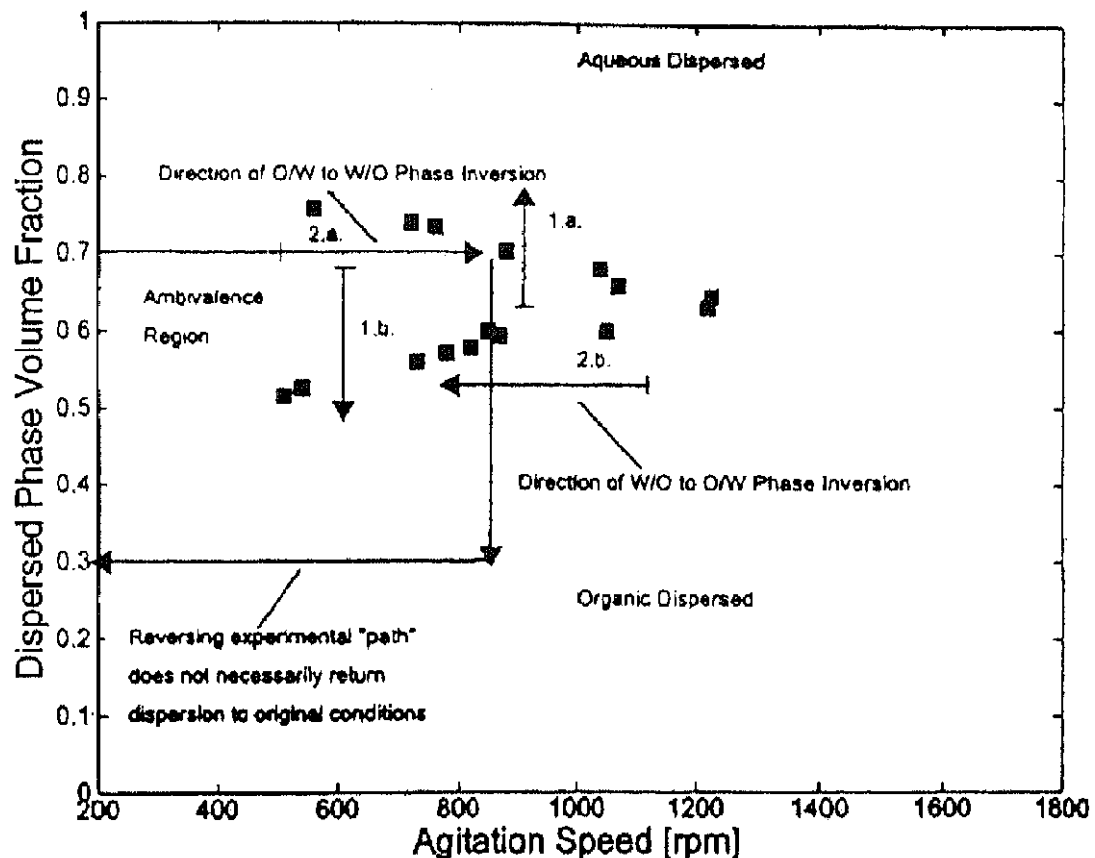


Figure 5 Ambivalence Behaviour Plotted by the Method of Kumar *et al.* (1991) (Norato *et al.*, 1998). Reproduced with the permission of the Canadian Society of Chemical Engineering. Copyright © 1998 Canadian Society of Chemical Engineering.

The hysteresis loop can be seen more clearly in the general ambivalence plot shown in Figure 6 (Norato *et al.*, 1998). In their example, increasing the agitation speed to approximately 1100 r.p.m. for an oil-in-water dispersion (with an initial dispersed phase holdup of 0.55) causes phase inversion to occur. This results in the dispersed phase holdup falling to 0.45 immediately. In order to invert this dispersion back to an oil-in-water dispersion, the agitation speed must be decreased below 900 r.p.m., thus creating a hysteresis loop.

Local reversible behaviour in phase inversion is achievable by crossing both ambivalence curves, but this is only limited to the region in the 'cusp'. The 'cusp' region is formed by the intersection of the two ambivalence curves and is dependent on the physical properties of the system. Far from the 'cusp' region, phase inversion is literally irreversible. Merely adjusting a single parameter (e.g. the agitation speed) is insufficient to invert the dispersion back to its original morphology.

3.2 Critical Dispersed Phase Holdup

Until now, theoretical explanations for the critical dispersed phase holdup have been based on surface energetics or on the geometrical considerations of the system. The

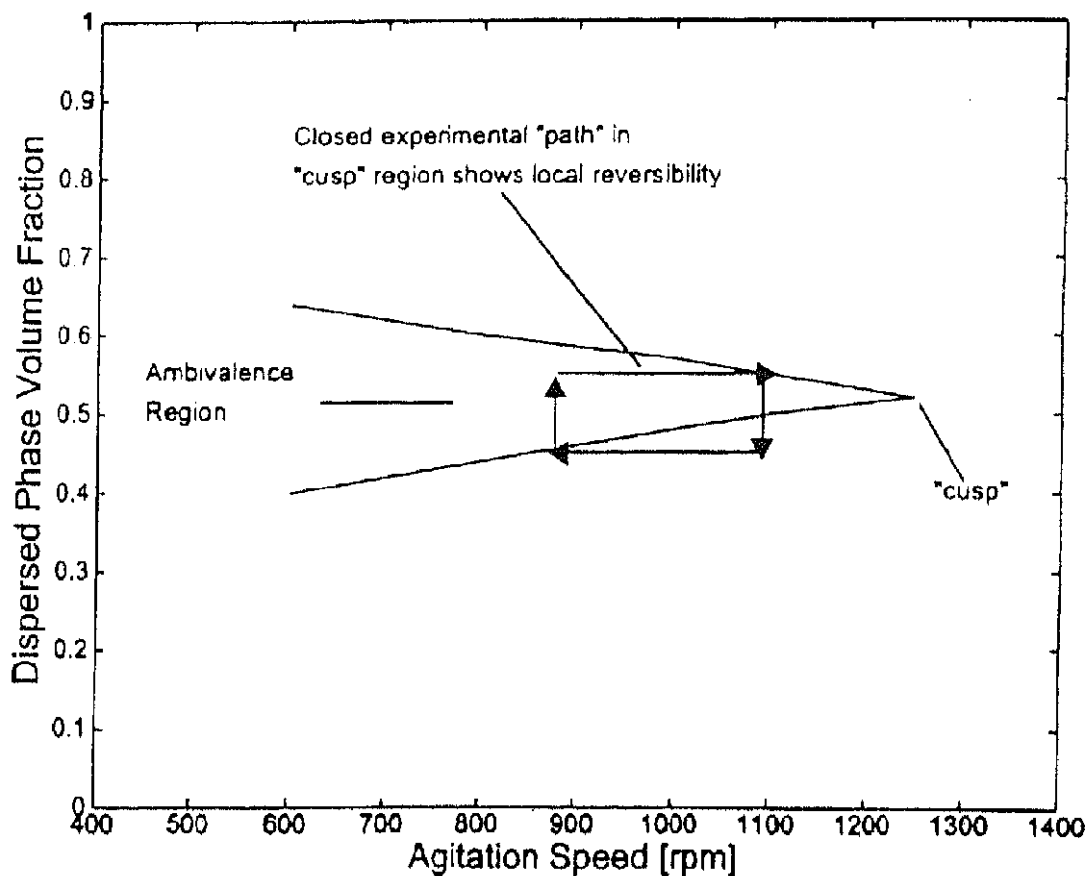


Figure 6 Ambivalence Behaviour Plot Using the Method of Kumar *et al.* (1991) Showing a Closed Experimental Path in the Cusp Region (Norato *et al.*, 1998). Reproduced with the permission of the Canadian Society of Chemical Engineering. Copyright © 1998 Canadian Society of Chemical Engineering.

surface energetics approach is based on the assumption that the surface energy at inversion is minimised. A further assumption is that the drop size distributions are equal before and after phase inversion (Luhning and Sawistowski, 1971). This approach leads to a predicted dispersed phase holdup of 50% at inversion. In other words, in the absence of forces other than static forces, surface tension causes inversion at 50% dispersed phase holdup. This does not seem to be supported by the experimental data of several investigators (Luhning and Sawistowski, 1971; McClarey and Mansoori, 1978; Arashmid and Jeffreys, 1980). Furthermore, by showing that inversion is accompanied by either an increase or a decrease in the interfacial energy, Luhning and Sawistowski have also invalidated the assumption of surface energy minimisation as a criterion for phase inversion. They claim that to use this approach, the total energy content of the system should be considered. This would require additional assumptions concerning the nature and hydrodynamics of the dispersion i.e. knowledge of the drop sizes and their distribution is required. With this in mind, Sarkar *et al.* (1980) have suggested that Kolmogorov's assumption of local isotropic turbulence may hold in this case, the drop diameter being the characteristic length of the turbulent flow field.

An alternative proposal based on geometric considerations assumes that droplets can be represented by uniform hard spheres and thus, if a monodispersion was assumed in addition, then phase inversion would occur by complete coalescence of the dispersed phase when the volume fraction representing the optimum packing efficiency of the spheres has been exceeded. This volume fraction is given by Ostwald's ratio which corresponds to the packing efficiency of a rhombohedral face centred cubic structure i.e. 74.06%. Early workers assumed that this upper limit represented the phase inversion point which could then be determined if the volumes or volume flows of each phase were known.

However, dispersed phase volume fractions for phase inversion exceeding 74.06% and even exceeding 90% have been reported (McClarey and Mansoori, 1978; Arashmid and Jeffreys, 1980; Pal *et al.*, 1986; Guilinger *et al.*, 1988; Plegue *et al.*, 1989; Mewes *et al.*, 1997). Moreover, it has already been established in the previous section that ambivalence limits vary from system to system. Many investigators believe that dispersed phase concentrations at phase inversion may exceed 74.06% because of the deformation that the dispersed drops experience. High dispersed phase holdups are possible for oil droplets which are polyhedral in shape and separated by a thin interfacial aqueous film (Nädler and Mewes, 1997). In addition, Nädler and Mewes also suggest the possibility of multiple emulsions (i.e. droplets-in-drops or secondary dispersions) characterised by water-in-oil-in-water drops or *vice versa* to explain the high dispersed phase holdups obtained at inversion. Secondary dispersions will be discussed in Section 4.4.

It has been proposed that the critical dispersed phase holdups for an oil-water system having similar phase densities and viscosities should remain the same for a given set of operating conditions (Luhning and Sawistowski, 1971; McClarey and Mansoori, 1978; Kumar *et al.*, 1991; Pacek *et al.*, 1994b). Selker and Sleicher (1965) claim that should no liquid physical property other than viscosity affect the system, there would be symmetry between the lower and upper ambivalence curves (i.e. the polar and non-polar phases would invert at identical holdups). However, it is found in all cases that the critical dispersed phase holdups for inversion from oil-in-water dispersions to water-in-oil dispersions are much higher than those for the reverse inversion (Selker and Sleicher, 1965; Arashmid and Jeffreys, 1980; Guilinger *et al.*, 1988; Kumar *et al.*, 1991; Nienow *et al.*, 1994). Pacek *et al.* (1994b) attribute this behaviour to the effect of secondary dispersions which are present in water-in-oil dispersions but absent from oil-in-water dispersions. They claim that since part of the oil continuous phase is trapped in the dispersed phase as oil droplets within the water-in-oil dispersion, the effective holdup of the continuous phase decreases and that of the dispersed phase increases. Thus the system approaches the same close packing volume fraction in the water-in-oil case as in the oil-in-water case just before phase inversion.

Kumar (1996), goes a step further in explaining this asymmetric behaviour by postulating that in liquid-liquid systems, drops carry charge due to the large difference in the dielectric constants of the two immiscible phases, even when there are no ionic additives present. Thus because of the substantial difference in the dielectric constants of the two immiscible phases, the interaction of oil drops in water should also differ from that of water drops in oil. The oil drops in water experience repulsion due to the overlapping of the electrical double layers leading to low coalescence efficiencies (i.e.

the fraction of collisions leading to coalescence). Conversely, water drops in oils of low dielectric constant are not found to experience any repulsive forces and are thus associated with high coalescence efficiencies. Thus, asymmetry in the behaviour of oil-in-water and water-in-oil drops is introduced, even in the case of systems with equal phase densities and viscosities. In addition, the high coalescence efficiencies of the water drops in oil lead to the possible formation of secondary dispersions which are not seen in oil-in-water dispersions, which is in agreement with the hypothesis of Pacek *et al.* above. Nevertheless, the hypotheses of Pacek *et al.* and Kumar are only valid if their observations that secondary dispersions are present only in water-in-oil dispersions and not oil-in-water dispersions are true. It will be seen in Section 4.4 that secondary dispersions in oil-in-water dispersions have occasionally been observed by some investigators.

3.3 Prediction of the Phase Inversion Point

The ability to predict the point of phase inversion has been a common pursuit since the infancy of phase inversion research. A theoretically based correlation relating the phase inversion point with the physical and physicochemical parameters influencing the inversion process would substantially decrease the amount of experimentation required to predict the inversion point for a particular system. Nevertheless, despite the extensive research efforts carried out on phase inversion, there have been relatively few attempts to predict the phase inversion point theoretically. Rather, empirical correlations have been proposed but, unfortunately, there is a considerable amount of variation between the predictions of these correlations.

Quinn and Sigloh (1963) were among the first investigators to attempt a prediction for the phase inversion point for agitated vessels, by proposing that the inversion curves follow a relationship whereby the organic phase volume fraction at inversion, $\phi_{o,i}$ is inversely proportional to the power input, P (W),

$$\phi_{o,i} = \phi_{o,i}' + \frac{\alpha}{P} \quad (3.1)$$

where α is a constant and $\phi_{o,i}'$ is the asymptotic value at high impeller speeds (constant). From dimensional considerations, the rate of energy input, P , is given by the following relationship with the impeller speed for turbulent mixing:

$$P = K\rho_m N^3 \quad (3.2)$$

where K is a constant and N is the impeller speed (r.p.m.). ρ_m is the volume fraction mean mixture density (kg/m^3) and is given as follows

$$\rho_m = \rho_d \varepsilon_d + \rho_c (1 - \varepsilon_d) \quad (3.3)$$

In this equation, ρ_c and ρ_d are the continuous and the dispersed phase densities respectively (kg/m^3) and ε_d the holdup of the dispersed phase.

In a more extensive study, Luhnig and Sawistowski (1971) suggested that the asymptotic phase holdup of the dispersed organic phase at inversion (at high impeller speeds) for the upper and lower inversion curves, $\phi_{o,i}^U$ and $\phi_{o,i}^L$, could be related linearly to the impeller Weber number, We_I :

(i) Upper inversion curve

$$\phi_{o,i}^U = 0.160 + 6.0 \times 10^{-5} We_I \quad (3.4)$$

(ii) Lower inversion curve

$$\phi_{o,i}^L = 0.470 + 2.0 \times 10^{-5} We_I \quad (3.5)$$

The impeller Weber number is defined by

$$We_I = \frac{\rho_c N^2 D_I^3}{\sigma} \quad (3.6)$$

ρ_c being the continuous phase density (kg/m^3), D_I the impeller diameter (m) and σ the interfacial tension (N/m), the impeller Weber numbers examined being in the range between 350 and 4000.

In the same paper, Luhnig and Sawistowski (1971) also present a correlation for the width of ambivalent region, in which they propose that the interfacial tension is one of the principal factors affecting it. The width of the ambivalent region (as volume fractions of the dispersed phase), W , was given by

$$W = \phi_{o,i}^U - \phi_{o,i}^L = (0.094N - 64.0)\sigma^{-(0.82+0.66 \times 10^{-3}N)} \quad (3.7)$$

Fakhr-Din (1973) noted that the equation of Luhnig and Sawistowski (1971) above yielded negative values for the ambivalent region width W for agitation speeds N of less than 680.85 r.p.m. The width is zero if $N = 680.85$. He noted that if this is not an error on Luhnig and Sawistowski's part, then presumably this value is related to the critical agitation speed in their apparatus. In addition, he also proposed two correlations to predict the inversion points for the upper and lower inversion curves based on the criterion that the total energy content of the system has to be minimised since phase inversion is a spontaneous process:

(i) Upper inversion curve

$$\phi_{o,i}^U = 1.32 \times 10^6 \left(\frac{\eta_d}{\eta_c} \right)^{0.32} \left(\frac{\Delta\rho}{\rho_c} \right)^{-0.11} Fr_I^{0.71} Re_I^{1.06} We_I^{-0.25} \quad (3.8)$$

(ii) Lower inversion curve

$$\phi_{o,i}^L = 12.2 \left(\frac{\eta_d}{\eta_c} \right)^{0.31} \left(\frac{\Delta\rho}{\rho_c} \right)^{0.04} Fr_I^{0.13} Re_I^{0.22} We_I^{-0.03} \quad (3.9)$$

η_c and η_d are the continuous phase and dispersed phase viscosities (Pa.s), $\Delta\rho$ is the density difference (kg/m^3), Fr_I is the impeller Froude number [$Fr_I = N^2 D_I^3 / g$ where N is the agitation speed (s^{-1}), D_I the impeller diameter (m) and g the gravitational acceleration (m/s^2)] and Re_I is the impeller Reynolds number. Fakhr-Din also suggests that the correlations above can be generalised further by including the effects of the ratio of the impeller diameter to the vessel diameter.

By concluding that phase inversion, promoted by the rapid coalescence of droplets, was controlled by viscous rather than inertial forces, Yeh *et al.* (1964) proposed a direct relationship between the phase holdup at inversion and the viscosity ratio. This was supported with evidence from their experiments where pairs of liquids were shaken in a flask. Their proposal is further supported by the work of Selker and Sleicher (1965) whose results indicate that the ambivalence limits are primarily dependent on the kinematic viscosity ratios between the two phases. In their work, the dispersed phase holdup at inversion, $\phi_{d,i}$, is given by the following equation:

$$\frac{\phi_{d,i}}{1 - \phi_{d,i}} = \sqrt{\frac{\eta_d}{\eta_c}} \quad (3.10)$$

where η_d is the viscosity of the dispersed phase (cp) and η_c that of the continuous phase (cp). Yeh *et al.* suggested however that the above predictions could be improved if the interfacial viscosity, η_i (cp), is used in place of the continuous phase viscosity η_c .

There is a considerable amount of variation between the correlations reported above. It should be noted that there is no single equation among those proposed on which equipment design can be based upon. It should be further noted that each of the correlations discussed above are based on equilibrated systems whereas in practice, mass transfer has to be accounted for. Rowden *et al.* (1975) demonstrated that mass transfer did affect the limits of ambivalence in their work on mixing and phase inversion in a copper extraction system. While variations in the ambivalence limits in systems with mass transfer have been discussed qualitatively and found to be dependent on the direction of solute transfer with respect to the actual phase continuity, no quantitative studies have been reported so far.

3.4 *The Effects of Various Parameters on Phase Inversion Behaviour*

Phase inversion behaviour is affected by both the physical properties of the liquids that make up the system as well as the geometric factors of the vessel that the liquids are contained within. Fluid physical properties such as viscosity, density and interfacial tension are among those that affect the phase inversion process. Various geometrical factors such as the agitation speed, the number and type of impellers, the materials of construction and their wetting characteristics are found to influence phase inversion and the ambivalence range. This section reviews published investigations of the effects of these factors. A summary table listing experimental studies to investigate the various parameters affecting the inversion behaviour is given in Table 1.

3.4.1 Agitation Speed

Agitation is perhaps one of the oldest and most basic ways of enhancing mass transfer between two immiscible liquids. The power input to the impeller, found to be related to the cube of the agitation speed, produces mechanical energy, which is transmitted to the liquids in the form of turbulent shear causing the break-up of one phase into small drops. The purpose of agitation is thus to create as large as possible an interfacial area between the two liquid phases in order to facilitate the mass transfer.

At low agitation speeds, Selker and Sleicher (1965) observed that the ambivalence limits decreased with increasing agitation speed. This finding was also noted by Quinn and Sigloh (1963), Luhning and Sawistowski (1971), Guilinger *et al.* (1988) and Kumar (1996). Hossain *et al.* (1983) suggested that this effect of the agitation speed on the lower ambivalence curve stems from a considerable increase in the coalescence rate with high energy inputs resulting in larger mean drop sizes. McClarey and Mansoori (1978), while observing the same trends for the intermediate and lower inversion curves, found however that the inversion points on their upper inversion curve increased with increasing agitation speed. This can be seen in Figure 4. Kumar (1996) attempts to explain this trend for the upper ambivalence curve by considering the fact that secondary dispersions are only observed for water-in-oil dispersions. He proposes that the increased agitation speed, which produces smaller drops with a large restoring force and more frequent fluctuations, results in a decrease in the amount of trapped external phase within the dispersed phase and hence the effective holdup of the dispersed phase. This is seen to be supported by the work of Luhning and Sawistowski (1971) who show in their results that, at increased agitation speeds, there is sharp decrease in the difference between the mean drop sizes for the oil-in-water and water-in-oil dispersions, a quantity that is directly related to the amount of external phase trapped in the dispersed water phase in an oil-in-water dispersion (Pacek *et al.*, 1994b). Therefore, it can be seen that phase inversion at increased agitation speeds can only be achieved if more dispersed phase is added to increase the effective holdup of the dispersed phase, thus leading to higher critical dispersed phase holdups.

In all cases, the inversion curve finally tends to an asymptotic value, ϕ_{oi}' , with increasing agitation speed, the volume fraction reaching a constant value when the agitation is fast enough to prevent settling as seen in Figure 7 for the lower ambivalence

Table 1 Summary Table of Experimental Studies Carried Out in Agitated Vessels to Determine the Phase Inversion Holdup as a Function of Various Physicochemical Parameters

Investigators	Physicochemical Parameters Studied	Range	Technique for Determining Phase Inversion	Impeller Type	Impeller to Tank Diameter
Quinn & Sigloh (1963)	1. Agitation Speed	1. 150-900 r.p.m.	Conductivity Probes	4-Flat Bladed	0.54-0.66
	2. Impeller Type and Size			Paddle (and Double Paddles)	
Selker & Sleicher (1965)	1. Viscosity Ratio	1. 0.02-130	Conductivity Probes & Visualisation (Dyes & Settling of Dispersion)	2-Blade Vertical	0.09-0.86
	2. Impeller Type & Size			Paddle & 3-Blade Axial	
	3. Tank Size & Shape			Flow Propeller	
Luhning & Sawistowski (1971)	1. Agitation Speed	1. 600-1360 r.p.m.	Conductivity Probes	4-Bladed Double Turbine	0.435
	2. Interfacial Tension	2. 0.0157-0.0511 N/m			
	3. Mass Transfer				
Clarke & Sawistowski (1978)	1. Agitation Speed	1. 500-1500 r.p.m.	Conductivity Probes	4-Bladed Double Turbine	0.435
	2. Mass Transfer				
McClarey & Mansoori (1978)	1. Agitation Speed	1. 120-600 r.p.m.	Conductivity Probes	2-Pitch Bladed Turbine	0.598
	2. Viscosity Difference				

Table 1 (Continued)

Arashmid & Jeffreys (1980)	1. Agitation Speed	1. 100-800 r.p.m.	Conductivity Probes	4-Bladed Open Turbine	0.49
Gülinger <i>et al.</i> (1988)	1. Impeller & Tank Materials	1. Stainless Steel & Plexiglass	Conductivity Probes & Visualisation	4, 6 and 8-Bladed Turbines	0.130-0.531
	2. Agitation Speed	2. 300-600 r.p.m.			
	3. Impeller Characteristics				
Kumar <i>et al.</i> (1991)	1. Impeller Material	1. Stainless Steel & Glass	Conductivity Probes	Rushton Turbine	
	2. Agitation Speed	2. 600-1250 r.p.m.			
Nienow <i>et al.</i> (1994)	1. Agitation Speed	1. 400-700 r.p.m.	Conductivity Probes & Visualisation	4-Pitch Bladed Turbine	0.5
	2. Viscosity	2. 1-50 cSt			
Chiang & Chen (1994)	1. Density Difference	1. ~0.6-1.6	Conductivity Probes	6-Flat Bladed Turbine	0.448
	2. Surfactants	2. 600-1400 r.p.m.			
	3. Mass Transfer				
Norato <i>et al.</i> (1998)	1. Density	1. 867-1180 kg/m ³	Conductivity Probes	6-Bladed Rushton Turbine & Marine Propeller	0.417-0.619
	2. Viscosity	2. 0.00096-0.00378 Pa.s			
	3. Interfacial Tension	3. 0.0089-0.0323 N/m			
	4. Agitation Speed	4. 400-2000 r.p.m.			
	5. Impeller Type & Size				

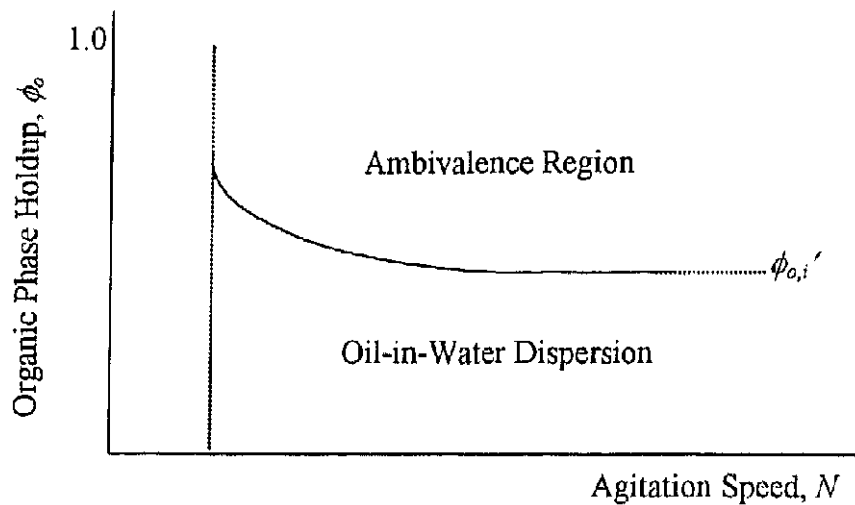


Figure 7 Schematic Representation of the Lower Ambivalence Curve as a Function of Agitation Speed.

curve (Selker and Sleicher, 1965; Luhnig and Sawistowski, 1971). Luhnig and Sawistowski propose a linear relation for this asymptotic holdup of the organic phase for both the upper and lower ambivalence curves as functions of the Weber number, We , as seen previously in equations (3.4) and (3.5).

While the majority of investigators have observed some effect of agitation speed on the ambivalence limits, Groeneweg *et al.* (1998) have reported that there were no observable effects of agitation speed on the ambivalence curves in their experiments. Nevertheless, they admitted that it is possible that this was the case because their experiments were carried out under conditions in which creaming or sedimentation was prevented.

It has been shown by Pacek *et al.* (1994a) that under certain circumstances phase inversion does not occur at all if the agitation is commenced at very high speeds. Nevertheless, they observe that inversion will occur after a reduction from that speed. Pacek *et al.* also noted the reverse case in other circumstances, where phase inversion does not occur when low agitation speeds were adopted to begin with but only occurred after the agitation speed was increased.

3.4.2 Geometrical Considerations

Since the early work of Rodger *et al.* (1956), many investigators have observed that the way in which an agitation is initialised can affect the phase inversion point. Treybal (1958) found that when an impeller is placed in one phase while at rest, that particular phase will become the continuous phase upon the commencement of agitation with the condition that the phase volume ratios are within the range of 1:3 to 3:1. Should the impeller be placed at the interface of the two phases, then it was observed that either of the phases could be dispersed. In some cases, it has been reported that when the impeller is placed at the interface of the two phases, the aqueous phase becomes the continuous phase for oil-water systems whereas the organic phase takes its place as the continuous phase for kerosene-water systems (Laity and Treybal, 1957). In yet other cases, it has

been found that usually one phase is dispersed at low agitation speeds while the other phase is the dispersed phase at high agitation speeds (Rodger *et al.*, 1956; Treybal, 1958; Quinn and Sigloh, 1963; Clarke and Sawistowski, 1978). It follows that the positioning of the impeller thus determines the past history of the dispersion. However, according to Luhning and Sawistowski (1971), the dispersion type for high agitation speeds, where stratification is not possible, can only be determined in this way if the holdup of the system corresponds to a value within the ambivalent region. Should the holdup fall outside the values defined by the ambivalent region, the determination of the dispersion type is not dependent on the positioning of the impeller.

Kato *et al.* (1991) demonstrated that it is possible to form any type of dispersion by controlling mechanical factors such as the agitation speed, the organic phase holdup and the impeller height. They thus show that the observation of Rodger *et al.* (1956), Treybal (1958), Quinn and Sigloh (1963) and Clarke and Sawistowski (1978) that the organic phase is dispersed at low agitation speeds and the aqueous phase is dispersed at high agitation speeds, is not always true. Opposite configurations are claimed to be possible by certain combinations of the agitation speed, organic phase holdup and impeller height.

Both Yeh *et al.* (1964) and Quinn and Sigloh (1965) attempted to eliminate the effect of the impeller position and geometry on phase inversion by carrying out a series of experiments in which the mixture was shaken in a flask to produce the dispersion. However, McClarey and Mansoori (1978) have commented on the method of Yeh *et al.*, questioning their method of shaking a flask manually in order to produce the liquid-liquid dispersion. According to McClarey and Mansoori, the intensity of mixing is uncontrollable and the nature of the dispersion had to be determined by visual inspection. McClarey and Mansoori also claimed that the results of Quinn and Sigloh were not completely reproducible and that the dispersion was only uniform at high agitation speeds.

Guilinger *et al.* (1988) studied the effect of impeller clearance above the vessel base on phase inversion. They found from their experiments that for the range of impeller heights investigated, phase inversion was not dependent on this parameter. However, they note that while impeller height was not important in phase inversion, the positioning of the impeller for batch systems does have an effect on the dispersion type, as discussed above. They also found that a continuous system behaves differently from a batch system in this respect as it was found that the impeller position is irrelevant to phase inversion as long as the impeller is placed such that there is adequate turbulence generated to prevent settling of the heavier phase and rising of the less dense phase.

The effects of the impeller to vessel diameter ratio and the impeller type on phase inversion were investigated by Norato *et al.* (1998). They found that there was no profound effect on phase inversion in varying the ratio of the impeller diameter to that of the vessel (in the range 0.417 to 0.619) but conclude that their study could have been undefinitive due to the limited range of impeller diameters used. Norato *et al.* also found that for constant impeller to vessel diameter ratios, the type of impeller used did not affect the ambivalence limits significantly.

Selker and Sleicher (1965) studied the effects of the size and shape of the vessel on the ambivalence limits but found no systematic effects. They concluded, however, that the variation of vessel shapes in their experiments were limited and that it is possible that

very unconventional vessel and baffle shapes could exert an influence on the ambivalence limits.

3.4.3 Wetting Characteristics

Since it has been established that the coalescence phenomena plays an important role in phase inversion, it is possible that in the absence of any surfactants the materials of construction of the vessel could affect the phase inversion process through the preferential wetting of the vessel by one of the liquid phases. Groeneweg *et al.* (1998) pointed out that wetting affects the collision frequency and hence the coalescence rates, leading to a change in the inversion holdup. McClarey and Mansoori (1978) suggested that when the effect of other factors (such as the differences in the density and the viscosity between the fluid phases) were eliminated, the discrepancies in their inversion curves could be attributed to the difference in the wettability of the vessel surface by the liquids. In agitated vessels, there are indications (see Section 4.2) that the break-up processes take place in the vicinity of the impeller whereas coalescence occurs primarily in regions further away from the impeller. However, if the impeller is preferentially wetted by the dispersed phase, Kumar *et al.* (1991) proposed that there is a possibility that drops approaching the impeller could coalesce with it at sufficiently high dispersed phase holdups. The drops leaving the impeller zone would then be smaller or larger than those coalescing with the impeller leading to a different drop size distribution. It would then follow that wetting results in additional break-up and coalescence mechanisms which could in turn affect the characteristics of phase inversion.

Guilinger *et al.* (1989) carried out experiments using identically shaped stainless steel and Plexiglas impellers, baffles and vessels in order to study the effects of wetting characteristics on phase inversion. They reported that the organic phase, since it preferentially wets the Plexiglas, tends to be continuous over higher water phase holdups than when stainless steel was used. They also noted that the effect of the materials of construction becomes less pronounced at higher power inputs and as the size of the mixer increases. They concluded, however, that the basic nature of the phase inversion characteristics remained unchanged.

On the other hand, Kumar *et al.* (1991) have suggested that the nature of the phase inversion characteristics can be altered by the wetting characteristics of the impeller material. They propose an additional mechanism of drop coalescence onto the impeller leading to the formation of a thin dispersed phase film on the impeller. The subsequent breakage of this film either at the impeller or at its outer edge could alter the phase inversion characteristics of the system. Their work involved using both a stainless steel impeller and a glass impeller, in which they show that coalescence occurs at the impeller through inertial impaction. This was deduced from their observations that the trend for inversion for water-in-oil dispersions was reversed (i.e. the critical dispersed phase holdup increasing with agitation speed for a stainless steel impeller but decreases for a glass impeller) when the impeller material was changed from stainless steel to glass whereas the inversion of oil-in-water dispersions remained identical.

When the oil is dispersed, the oil drops cannot come into contact with the impeller and coalesce there by inertial impaction to form a thin film. This is due to the requirement that the dispersed phase density has to be larger than that of the continuous

phase for the drops to reach the impeller. In this case, the oil density is lower than the water density. The wetting of the impeller therefore would not have any effect on the inversion and hence the inversion of oil-in-water dispersions exhibit the same trends for both impellers. For water-in-oil dispersions, the dispersed phase density is greater than that for the continuous phase and hence the water drops are able to reach the impeller surface by inertial impaction. Since water preferentially wets glass, the water drops will not remain as drops on the impeller but will form a continuous film and subsequently breakage to form drops occurs. There is thus a significant change in the inversion characteristics in this case as observed. In addition, Kumar *et al.* also observed that the asymptotic value of the critical dispersed phase holdup at high agitation speeds was changed by the wetting characteristics indicating that the effects are not just significant at low agitation speeds as found by Guilinger *et al.* (1989).

3.4.4 Viscosity

The viscosity of a given phase, whether dispersed or continuous, plays an important role in the ambivalence behaviour of a system of two immiscible liquids. A survey of the literature on dispersion viscosity is given by Guilinger *et al.* (1989). Selker and Sleicher (1965) showed how the ratio of the kinematic viscosities influenced the limits of ambivalence. Their results are reproduced in Figure 8 in which ν_A represents the kinematic viscosity of the hydrocarbon phase *A* and ν_B represents that of the polar phase *B*. Selker and Sleicher noted that as the viscosity of a phase increased, its tendency to be dispersed increases. They also note the lack of symmetry between the curves, which was expected to be evident if no other fluid property other than the viscosity affected the curve. This lack of symmetry was suggested to be due to the non-isotropy of one of the coefficients of interfacial viscosity, possibly a result of the differences in polarities between the phases or a result of contaminants.

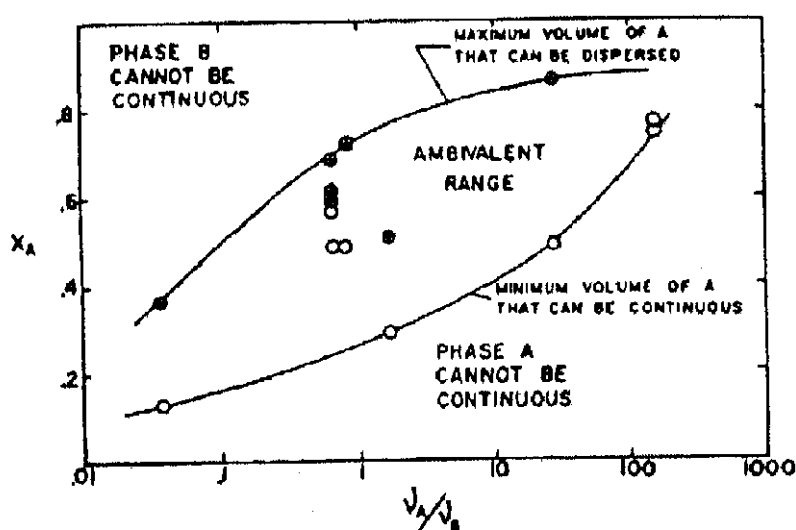


Figure 8 Ambivalence Limits as a Function of the Ratio of Kinematic Viscosities (Selker and Sleicher, 1965). Reproduced with the permission of the Canadian Society of Chemical Engineering. Copyright © 1965 Canadian Society of Chemical Engineering.

On the other hand, earlier work by Treybal (1963) suggested that the high viscosity of one of the phases favoured it becoming the continuous phase. Recent studies by Norato *et al.* (1998) have also suggested this trend. In this work, Norato *et al.* plotted the ambivalence curves for different viscosities and found that the ambivalence region is widened with increases in the viscosity of the fluids. They suggest that higher dispersed or continuous phase viscosities result in longer film drainage times for the continuous phase between two drops in collision, resulting in lower coalescence rates. The dispersed phase holdup must then be increased in order to accelerate the coalescence rate to a value that phase inversion can occur and hence the ambivalence region is widened. This has been confirmed by the findings of Groeneweg *et al.* (1998).

McClarey and Mansoori (1978) also demonstrated the effect of the viscosity difference between the phases by performing experiments on equal density, binary, immiscible systems with and without viscosity differences between the phases. They showed that the viscosity difference was very effective in influencing phase inversion and ambivalence region behaviour. In the absence of viscosity differences, it was shown that the intermediate inversion curves were located at the equivolume line for all agitation speeds. McClarey and Mansoori thus conclude that any deviation of that particular curve from the equivolume location for the dispersed phase holdup is a result of the viscosity difference between the two liquids alone. In another work, large ratios of the dispersed to continuous phase viscosity ratio are postulated to cause secondary dispersions (Treybal, 1963).

In their experiments on kerosene-water dispersions in stirred tanks, Guilinger *et al.* (1989) indirectly measured the dispersion viscosity by monitoring the impeller power input to the dispersion as a function of the dispersed phase holdup. They observed that agitation became less efficient as the dispersed phase holdup approaches the phase inversion point. Conversely, after the inversion point a high degree of turbulence was noticed suggesting more efficient agitation. These observations show that there is a maximum in the dispersion viscosity at or near the region of phase inversion. Guilinger *et al.* thus conclude that the dispersion viscosity is a property which indicates when phase inversion occurs but is not a factor which controls the phenomenon. Falco *et al.* (1974) reported a similar viscosity maximum in the phase inversion region in their work on microemulsions (optically transparent oil-water dispersions). They attribute this to a change in the dispersed water phase structure from spheres to cylinders to lamellae and subsequently to a continuous phase, which they postulate to be the mechanism for which phase inversion occurs. A schematic representation of these structures is shown in Figure 9.

3.4.5 Density

Early work on liquid-liquid dispersions has established that large density differences between the aqueous and continuous phases makes a dispersion more difficult to achieve. More stirring power is required in order to produce a homogeneous dispersion (Treybal, 1963; McClarey and Mansoori, 1978). This is particularly true at low agitator speeds.

Selker and Sleicher (1965) reported that they did not observe any effects of density on phase inversion. However, they used liquids whose densities did not vary widely.

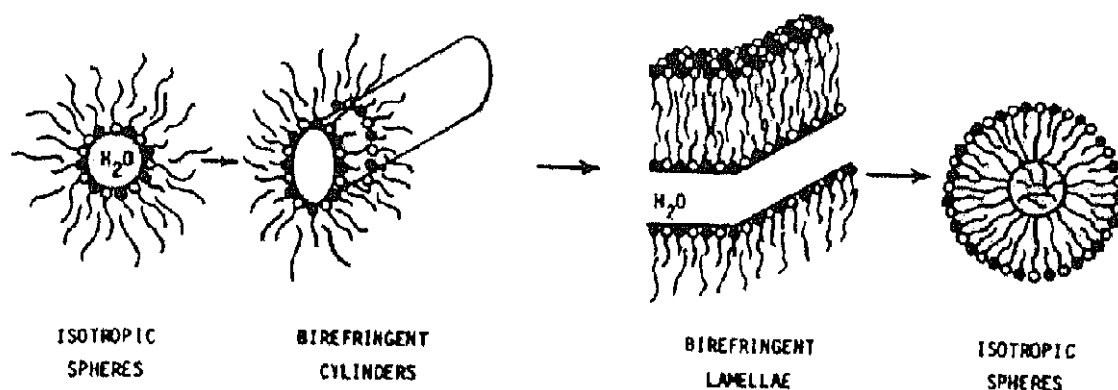


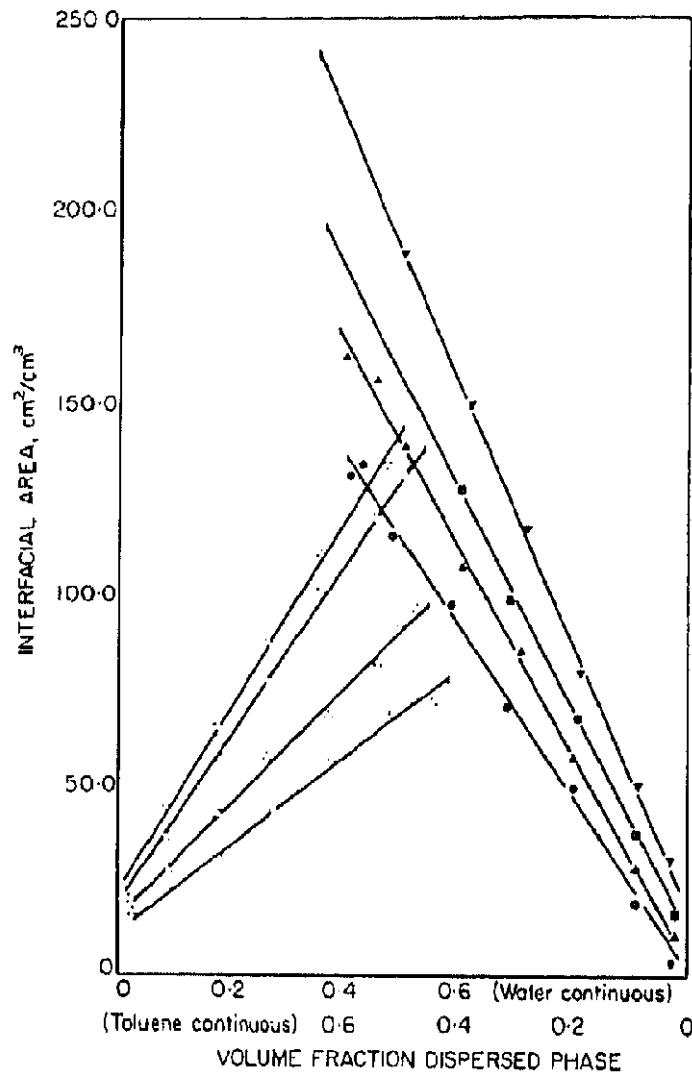
Figure 9 Schematic Representation of the Change of the Dispersed Water Phase Structure at Phase Inversion for Microemulsions (Falco *et al.*, 1974). Reproduced with the permission of the American Institute of Chemical Engineers. Copyright © 1974 AIChE. All rights reserved.

Norato *et al.* (1998) also found that there is little effect of density on the ambivalence behaviour, for small differences in the density between the phases. In general, other investigators have found that systems in which there are large density differences between the phases show increased tendencies to invert (Rodger *et al.*, 1956; Kumar *et al.*, 1991). This is due to the fact that an increase in the density difference between the phases leads to higher relative velocities between the dispersed and the continuous phases. As a direct result, the shear in the system is increased causing more drop breakage in the system, leading to an exponential increase in the interfacial area (Rodger *et al.*, 1956). Chiang and Chen (1994), on the other hand, found that systems with large density differences showed increased tendencies to invert if the organic phase is the dispersed phase and a lower tendency to invert if water is the dispersed phase. It was also observed that when the density difference was removed, the uncertainty range of inversion was diminished (McClarey and Mansoori, 1978).

3.4.6 Interfacial Tension and the Presence of Impurities, Solutes & Surfactants

Interfacial tension is perhaps the least understood of all the factors that could possibly influence the phase inversion phenomenon. Selker and Sleicher (1965) maintained that the magnitude of interfacial tension is unlikely to influence ambivalence behaviour, since to suggest otherwise would imply that the interfacial tension between a pair of fluids is a function of the interfacial curvature. However, they did not pursue further investigations on interfacial tension to prove this argument. Yeh *et al.* (1964), on the other hand, have suggested that the interfacial tension plays a small role in phase inversion behaviour since, in the absence of other forces, the interfacial tension will cause inversion to occur only for equivolume mixtures.

Later work seems to suggest that the interfacial tension has a more significant influence. In the work of Luhnig and Sawistowski (1971), interfacial tension is shown to affect phase inversion. They showed that the inversion process was accompanied by either an increase (inversion from oil-in-water to water-in-oil dispersion) or a decrease (inversion from water-in-oil to oil-in-water dispersion) in the interfacial area and hence a respective increase or a decrease in the interfacial energy as shown in Figure 10.



● 560 r.p.m. ▲ 760 r.p.m. ■ 960 r.p.m. ▼ 1160 r.p.m.
 Solid symbols indicate the o/w configuration;
 open symbols indicate the w/o configuration

Figure 10 Interfacial Area Per Unit Dispersion Volume as a Function of the Dispersed Phase Volume Fraction (Luhning and Sawistowski, 1971). Reproduced with the permission of the Society of Chemical Industry. Copyright © 1971 Society of Chemical Industry.

Clarke and Sawistowski (1978) later showed that the width of the hysteresis gap is critically affected by the interfacial tension; the lower the interfacial tension, the wider the hysteresis gap implying an increased difficulty in inducing inversion. Using a light transmittance technique to measure the interfacial area, they observed that the interfacial area increased from the inversion of the oil-in-water dispersion to a water-in-oil dispersion whereas the interfacial area decreased with inversion in the opposite direction. Their work thus confirms the earlier findings of Luhning and Sawistowski (1971) that phase inversion could be associated with a change in the interfacial energy. As a consequence, they suggest that the minimisation of interfacial energy is not a valid

criterion for phase inversion since phase inversion results in a different phase configuration, which leads to a different effective dispersion viscosity and also to a change in the system's total energy content. From a phase inversion perspective, interfacial tension is thus not the critical component of energy.

Recent work by Norato *et al.* (1998) established that a decrease in the interfacial tension led to the widening of the ambivalence curves as found by previous investigators, in particular the lower ambivalence curve being shifted downward significantly. This suggests that lowering the interfacial tension promotes the formation of new interfacial surfaces and indicates a greater resistance of the system to inversion with the widening of the hysteresis gap. They explain this by referring to the work of Coualoglou and Tavlarides (1977). Since a deformed drop undergoes break-up when the turbulent kinetic energy transmitted to the drop by turbulent eddies exceeds the drop surface energy which is dependent on the interfacial tension, it follows that a decrease in the interfacial tension would enhance drop break-up. On the other hand, decreasing the interfacial tension would result in a decrease in the drop size as well as an increase in the drainage times for the film between two drops in collision. These in turn results in a decrease in the drop coalescence rates. With the enhanced rates of drop break-up and suppressed drop coalescence rates, it thus follows that higher dispersed phase holdups are required to invert the system.

There is a high possibility that even the slightest impurities, for example dust particles, could contaminate a system. Contaminants are usually found to accumulate at the phase interface, observable by a dull, grey film at the interface. If on the other hand, pure liquids are used, the interface will be mirror-like with a distinct and regular meniscus at the walls of the vessel, around the impellers and the baffles (Rodger *et al.*, 1956). In addition, surfactants are usually present at the liquid-liquid interface in most practical systems. These contaminants or additives would result in a change in the interfacial tension of the dispersion and could very well affect the phase inversion behaviour. As a result, several research efforts have been made to study the effects of their presence on phase inversion.

Brooks and Richmond (1994a) who studied the effects of the addition of non-ionic surfactants on phase inversion and Vaessen (1996) have suggested that phase inversion could be brought about by either changing the dispersed phase holdup (catastrophic phase inversion) or by changing the surfactant's affinity for the oil and water phase (transitional phase inversion). At transitional phase inversion, they suggest that a surfactant phase may be present. They also suggest that in non-ionic surfactant oil-water systems, catastrophic phase inversion can only occur when the water-oil ratio is moved in one direction. Unlike surfactant-free oil-water systems, inversion hysteresis in this case is not possible (Brooks and Richmond, 1994b). The mechanisms behind transitional phase inversion and catastrophic phase inversion will be discussed briefly in Section 4.1.

Selker and Sleicher (1965) suggested that the presence of interfacially active contaminants could change the inversion characteristics of a system or affect the tendency of a particular phase to be continuous by considerably widening the ambivalence region. Luhning and Sawistowski (1971) proposed similar effects for the presence of solute in phase equilibrium in the dispersion as seen in their results which are reproduced here in Figure 11. They observed that the presence of propionic acid in phase equilibrium with the system resulted in a large upward shift of the upper

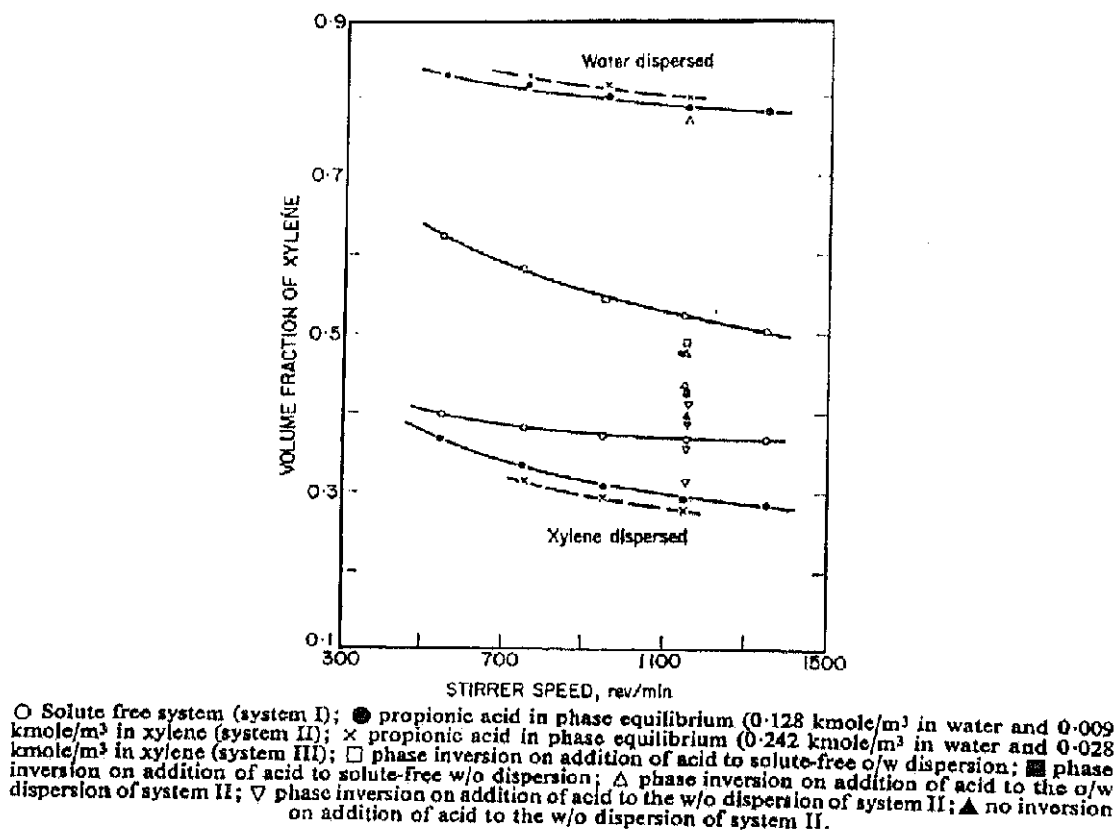


Figure 11 Effect of the Presence of Solute on the Phase Inversion Characteristics (Luhning and Sawistowski, 1971). Reproduced with the permission of the Society of Chemical Industry. Copyright © 1971 Society of Chemical Industry.

ambivalence curve and a smaller corresponding downward shift of the lower ambivalence curve. Since the presence of surfactants generally lowers the interfacial tension, their results are in agreement with those of Clark and Sawistowski (1978) and Norato *et al.* (1998) who showed that the ambivalence region widened as the interfacial tension is lowered. This is also confirmed by Groeneweg *et al.* (1998) who showed that the film drainage times increased with the addition of emulsifying surfactants thereby causing the coalescence rate to decrease, making inversion more difficult. In addition, drop coalescence can be further suppressed by the Marangoni effect (the spreading of liquids from points of low surface tensions onto those of higher surface tensions due to the presence of surface tension gradients) which induces a counterflow in the draining liquid film thereby prolonging the film drainage time (Walstra, 1983; Vaesen, 1996). Moreover, it is possible that certain surfactants can also deliver a steric hindrance in the last stages of the film drainage process. This is a result of a repulsive force generated between two approaching drops due to the presence of the adsorbed surfactant layers at the drop interfaces (Tadros and Vincent, 1983; Campbell *et al.*, 1996). As a whole, the retardation of coalescence due to the combination of these different effects is mirrored in the widening of the ambivalence region.

Clarke and Sawistowski (1978), following on from the work of Luhning and Sawistowski (1971) demonstrated the importance of a solute both in equilibrated

systems and in systems with mass transfer. In their work on equilibrated systems, they attempted to compare the effect of two solutes, propionic acid and acetone. It was observed that propionic acid produced a wider hysteresis gap indicating that its presence in phase equilibrium increased the resistance for the system to invert, probably due to the polar nature of propionic acid. Clarke and Sawistowski also found a corresponding decrease in the mean drop diameter (i.e. an increase in the interfacial area) for the propionic acid system. This increase in the interfacial area results in the lowering of the interfacial tension, shifting the dynamic equilibrium between coalescence and break-up towards smaller drop sizes leading to the widening of the hysteresis gap as observed. They thus suggest that it is the drop size rather than the interfacial tension that is the primary factor in consideration of the resistance to inversion.

In his work on mass transfer (non-equilibrated system) effects, Sawistowski (1971) suggested that in the presence of mass transfer it is expected that transfer into the dispersed phase should increase the rate of drop break-up while retarding the rate of coalescence due to the Marangoni effect. Thus, for given agitation speeds, drop sizes should be smaller and the interfacial area larger than those in the absence of mass transfer. On the other hand, subsequent to phase inversion when mass transfer takes place out of the dispersed phase, the Marangoni effect would act to retard drop break-up and accelerate coalescence. This results in a shift of the dynamic equilibrium towards larger drops and smaller interfacial areas. The Marangoni effect would then decay with time as the system approaches equilibrium whereby a new drop size distribution is obtained (Clarke and Sawistowski, 1978). In summary, Sawistowski concludes that phase inversion occurs at lower dispersed phase holdups for a given agitation speed with mass transfer out of the dispersed phase than if mass transfer were to occur in the opposite direction. Alternatively, for fixed phase ratios, phase inversion is expected to occur at lower agitation speeds. This behaviour, however, is expected to vary for different physical properties, in particular, the interfacial tension and the viscosity.

Clarke and Sawistowski (1978) reported a significant narrowing of the ambivalence region when both acetone and propionic acid were injected into the continuous phase. In addition they observed that for most dispersions the sudden introduction of solute caused permanent phase inversion to occur (i.e. the system did not re-invert when the transient effects of the solute faded away). In the case of the addition of acetone, however, they observed an unstable region in which the subsequent injection of additional amounts of solute caused re-inversion to occur as shown in Figure 12. They thus claim that while the addition of solute in phase equilibrium reduced the interfacial tension and hence increased the resistance to inversion, the injection of a small amount of solute into the continuous phase under mass transfer or non-equilibrium conditions enables the system to invert more easily, virtually eliminating the hysteresis effect.

However, the narrowing of the ambivalence region due to mass transfer of the solute from the continuous phase into the dispersed phase cannot be explained by the Marangoni effect as proposed by Clarke and Sawistowski (1978). The transfer of solute from the continuous phase film between two dispersed drops into these dispersed drops would result in a lower concentration of solute and thus a higher interfacial tension in the continuous phase film. As a consequence of the Marangoni effect, there will therefore be a flow of the continuous phase from the bulk region where interfacial tension is lower

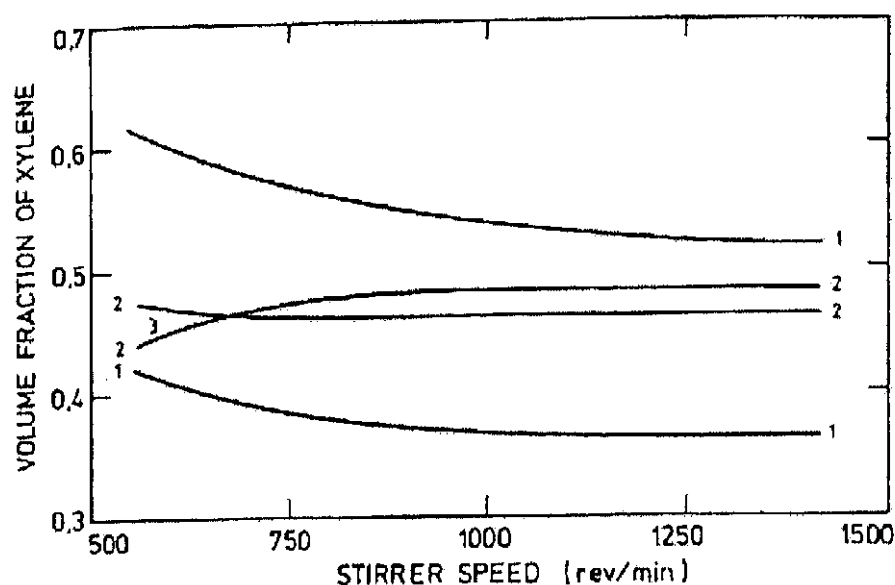


Figure 12 Ambivalence Behaviour of Xylene/Water System with Mass Transfer of Acetone. 1 – Solute Free Inversion Curve; 2 – Inversion Curve for 15cm³ of Acetone Added; 3 – Unstable Region (Clarke and Sawistowski, 1978). Reproduced with the permission of the Institution of Chemical Engineers. Copyright © 1978 IChemE.

into the region of the film between the two drops where interfacial tension is higher. The drops will then be separated, preventing their coalescence as mentioned previously.

Since the coalescence rate is retarded, higher inversion holdups would be required leading to a widening of the ambivalence curves, contradictory to the observations of Clarke and Sawistowski.

It would seem that the apparent narrowing of the hysteresis region could be due to hydrodynamic factors. It has already been established above that the mass transfer of solute into the dispersed phase would leave the film between the drops relatively devoid of surfactant and thus result in a high interfacial tension for the film. This would serve to reduce the film drainage time thereby increasing the coalescence rate and hence reducing the dispersed phase holdup for inversion. A narrowing of the hysteresis region would thus be obtained. As a whole, there could therefore be two competing phenomena arising from the mass transfer of solute out of the continuous phase: the Marangoni effect which serves to prevent drop coalescence and the decreasing film drainage times which serve to enhance it. It thus seems that in Clarke and Sawistowski's case, the decrease in film drainage times occur at timescales faster than the Marangoni effect thereby overriding it and hence causing the ambivalence region to narrow. Localised re-inversions could then be probable, as observed, since subsequent to the first inversion the solute would then be in the dispersed phase and mass transfer would occur into the continuous phase thereby enhancing coalescence and hence the probability of re-inversion. It is possible that the re-inverted system would then invert repeatedly depending on the outcome of the two competing phenomena.

Increasing the salt concentration in the water phase is seen to decrease the critical dispersed phase holdup for oil-in-water dispersions and to increase that for water-in-oil dispersions (Selker and Sleicher, 1965). In the past, this behaviour was explained by

either the effect of interfacial tension, the interfacial tension gradient or the electrostatic interaction between drops. Kumar (1996) views the first two alternatives as unfeasible because they predict the same effect regardless of the configuration of the dispersion or because they predict minimum coalescence in the absence of salt which are in conflict with the observations of Selker and Sleicher (1965). Kumar thus proposes a model whereby drops in liquid-liquid systems are charged. He postulates that the addition of salt reduces the electrostatic repulsion between two charged oil drops in aqueous medium, thus increasing the coalescence efficiency and therefore the oil-in-water dispersion inverts at lower values of the dispersed phase holdup. On the other hand, the addition of salt to water-in-oil dispersions enhances the coalescence of the oil droplets in water drops with other oil droplets within the same drop and with the external oil phase. This reduces the quantity of oil phase trapped in the water drops thereby reducing the effective water phase holdup. Inversion can then occur only when the effective water phase holdup is increased by increasing the holdup of the continuous water phase. The effect of adding salt to systems will be discussed further in Section 4.5 in which the effects of drop electrostatic charge on phase inversion are examined.

3.4.7 Temperature

Only a few investigators in the past have focused part of their research efforts on the effects of temperature on phase inversion. McClarey and Mansoori (1978) found that for constant agitation speeds, phase inversion approaches higher aqueous phase holdups with increasing temperatures. Mao and Marsden (1977) reported that an increase in temperature favours the formation of water-in-oil dispersions and *vice versa*. Given that temperature affects most of the physical properties of liquids, it would follow that any change in temperature would affect phase inversion by changing some other physical parameter of the liquid which has a direct effect on phase inversion.

Temperature effects are important in oil-water systems where surfactants are present. There exists a temperature at which the hydrophilic and oleophilic natures of the surfactant are in balance which is known as the phase inversion temperature. As temperature is increased through the phase inversion temperature, a surfactant alters from stabilising a certain dispersion configuration (e.g. oil-in-water dispersion) to the other (e.g. water-in-oil dispersion). Dickinson (1982) explains the existence of the phase inversion temperature by suggesting that the interaction of the polar group of a non-ionic surfactant with the surrounding water molecules is temperature dependent. He goes on to imply that the existence of a phase inversion temperature is therefore indicative that phase inversion is a spontaneous process and has a strong relationship with thermodynamic behaviour.

3.5 Summary

In this chapter, a brief review of the fundamentals of phase inversion in agitated vessels has been presented. In general, there are two theoretical approaches to determining the critical dispersed phase holdup; the surface energetics approach and the consideration of the dispersion geometry. While the geometrical approach is more widely accepted at present, the surface energetics approach remains an important factor in phase inversion.

Luhning and Sawistowski (1971) have suggested that the total energy content of the system be minimised as a criterion for phase inversion. However, this has not been pursued due to the complexities involved in obtaining a reliable model for the dispersion hydrodynamics, in particular, the drop size distributions.

Some investigators have attempted to correlate the phase inversion holdup with various system parameters that influence the inversion process. However, there have been considerable variations among the correlations which have been reported and a satisfactory model has yet to be presented. In addition, these correlations were obtained for different liquid-liquid systems and physical conditions making comparisons between them difficult. While most of these correlations have been substantiated by experimental data, these have been highly selective. It is often found that the correlations are only applicable to certain experimental configurations. As a result, the proposed correlations have been severely limited in application.

In spite of important findings in previous work, systematic relationships between the various parameters that influence the phase inversion process have not been fully elucidated. In some cases, conflicting observations have been noted. The competing effects of the Marangoni effect and the film drainage times in systems with mass transfer taking place that has been proposed to explain the findings of Clarke and Sawistowski (1978) requires further verification. As a whole, further investigations and experimental work are required before a thorough understanding of phase inversion and the mechanisms associated with it can be achieved.

4. THE MECHANISMS OF PHASE INVERSION IN AGITATED VESSELS

4.1 *Postulated Mechanisms of Phase Inversion*

The phenomenon of phase inversion is very complex and hence little is known about the actual mechanism governing the inversion process. With the large amount of experimental information that has been gathered on phase inversion, many investigators have in the past attempted to postulate the underlying mechanism of phase inversion. It is possible to recognise two distinct approaches to the formulation of the mechanism behind phase inversion. The traditional models have their roots in colloid science which tend to focus on research into phase inversion in emulsions where surfactants are present. More recently, in the field of chemical engineering, efforts have been made to postulate mechanisms based on a kinetic approach. However, until present there has not been a united view favouring one single mechanism.

In colloid science, two mechanisms of phase inversion in emulsions have been proposed, transitional phase inversion and catastrophic phase inversion. Transitional inversion is based on a thermodynamical framework and focuses on the role of the surfactant in microemulsions (thermodynamically stable mixtures of an oil and an aqueous phase in the presence of a surfactant), the preferred morphology of an emulsion gradually inverting to the non-preferred one upon changing the equilibrium distribution of the surfactant over the phases. Catastrophic inversion, on the other hand, is a discontinuous process induced by altering the dispersed phase holdup in kinetically

stabilised liquid-liquid dispersions and coarse emulsions. Dickinson (1982) first suggested the applicability of catastrophe theory to emulsion phase inversions based on the fact that the process displayed qualitative characteristics of elementary catastrophe theory. The occurrence of a hysteresis gap, which could not be explained by other theories at that time, was found to be the most important characteristic. This approach was also followed in later work by Lim and Smith (1991). Vaessen and Stein (1995), however, suggested that the use of thermodynamic treatments, though justified in transitional phase inversion is an insufficient quantitative basis for explaining catastrophic inversion. Whilst in transitional inversion the stability before and after inversion are comparable, this is not true for catastrophic inversion which involves the inversion from a highly unstable morphology to a more stable one. In addition, coalescence plays a more significant role in catastrophic inversion than in transitional inversion in the breaking of unstable emulsions. Vaessen and Stein thus propose a kinetic treatment as a basis in catastrophe theory.

This approach to modelling phase inversion based on drop dynamics has been investigated by workers such as Pacek *et al.* (1994a), Kumar (1996) and Groeneweg *et al.* (1998), who have proposed that drop coalescence plays a significant role in phase inversion. Vaessen (1996) showed that both transitional and catastrophic inversion can be interpreted in this single framework since the coalescence kinetics are determined by both the surfactant characteristics and the phase volume ratio of the drops.

4.2 Drop Coalescence & Break-Up

In turbulent liquid-liquid dispersions, the dispersed phase drops are randomly moving about and continually colliding resulting in some drops coalescing with one another. If the turbulence is isotropic, break-up (redispersion) of drops will also occur simultaneously due to the effect of turbulent shear applied by the continuous phase on the dispersed phase in the system. For very dilute systems (< 1% dispersed phase holdup), coalescence can be neglected and drop break-up is considered to be the dominant feature. At moderately low dispersed phase holdups, the two competing phenomena of drop coalescence and break-up will always reach a dynamic equilibrium. On the other hand, if the system deviates from equilibrium (e.g. if the dispersed phase holdup is increased) such that the coalescence rate becomes increasingly dominant over the rate of drop break-up, there will be an abrupt increase in drop sizes leading to the coalescence of the dispersion drops into a single continuum, i.e. phase inversion occurs. The post phase-inversion dispersion can be quite different from the initial dispersion in terms of the dispersed and continuous phase physical properties, but equilibrium will again be attained between drop break-up and coalescence. Thus phase inversion can be seen as the lack of a stable equilibrium between the coalescence and break-up processes.

For coalescence to occur, the intervening continuous phase film separating the collided drops has to drain to the critical film rupture thickness so that agglomeration occurs. In order for this to be achieved, the contact time between the drops must exceed the drainage time to critical film thickness. The drainage time depends on the nature of the compression force (Coulaloglou and Tavlirides, 1977; Das *et al.*, 1987) as well as the film flow characteristics e.g. the approach force, the degree of interface flattening and the interfacial mobility (Chesters, 1991; Calabrese *et al.*, 1993). In addition, it has

been postulated that turbulent fluctuations can separate the drops during drainage. Therefore, not every collision would result in coalescence. The coalescence rate depends on the coalescence efficiency as well as the collision frequency, which increases with the increase in the number density of drops (Coulaloglou and Tavlarides, 1977). This is confirmed by Quinn and Sigloh (1963) who suggest that the rate of coalescence is proportional to the concentration of the dispersed phase, which in effect will increase the number density of the drops. The coalescence rate is therefore given as

$$\text{Coalescence Rate} = \text{Collision Frequency} \times \text{Coalescence Efficiency} \quad (4.1)$$

In summary, coalescence can generally be viewed as a consequence of forces exerted on the colliding drops which act to drain out the intervening liquid film to a critical thickness. Several researchers have proposed models to calculate the collision frequency (Howarth, 1967a; Shiloh *et al.*, 1973; Coulaloglou and Tavlarides, 1977). A review of these including the limitations of each model is given by Das *et al.* (1987). At low holdups, Groeneweg *et al.* (1998) suggest that the collision frequency is proportional to the holdup squared and the shear rate in laminar flow, and to an equivalent parameter in turbulent flow. At higher holdups, they proposed that the collision frequency would vary with a higher power of the holdup since the drops are surrounded by many other neighbouring drops. The coalescence efficiency, λ , in general can be described by the following expression (Coulaloglou and Tavlarides):

$$\lambda = \exp\left(-\frac{t_{\text{drain}}}{t_{\text{contact}}}\right) \quad (4.2)$$

where t_{drain} is the film drainage time (s) and t_{contact} the contact time between the colliding drops (s). In this expression, Coulaloglou and Tavlarides specify the drainage time to be a function of the continuous phase viscosity and density, the agitation speed, the impeller diameter, the drop size (or volume) and the interfacial tension. The contact time is given as a function of the agitation speed, impeller diameter and drop size. On the other hand, Das *et al.* (1987) proposed a model for the coalescence efficiency based on film drainage as a stochastic process.

For equal drops and uniform energy dissipation, the coalescence rate, N_c (s^{-1}), given by Coulaloglou and Tavlarides (1977) is as follows

$$N_c = K_1 v^{7/9} N D_I^{2/3} \lambda_1 N_d^2 \quad (4.3)$$

where

$$\lambda_1 = \exp\left[-\frac{K_2 \eta_c \rho_c D_I^2 N^3 \left(\frac{v^{1/3} v'^{1/3}}{v^{1/3} + v'^{1/3}}\right)^4}{\sigma^2}\right] \quad (4.4)$$

K_1 and K_2 are dimensional coalescence constants related to the collision frequency and the coalescence efficiency (and particularly to the film thickness at coalescence) respectively. In equation (4.4), v and v' denote the volumes of the coalescing drops (cm^3), N the agitation speed (s^{-1}), D_I the impeller diameter (cm), η_c the continuous phase viscosity (g/cm.s), ρ_c the continuous phase density (g/cm^3), σ the interfacial tension (dynes/cm) and N_d the total number of drops. Sovová (1981), however suggested that the coalescence efficiency of Coualoglou and Tavlarides given by the exponential term in equation (4.4) above only allows for the preferential coalescence of small drops. He proposes the following expression as an alternative for the coalescence efficiency based on an analysis of the impacting drops:

$$\lambda_2 = \exp \left[- \frac{K_3 \sigma (v^{2/3} + v'^{2/3})(v + v')}{\rho_d N^2 D_I^4 v v' (v^{2/9} + v'^{2/9})} \right] \quad (4.5)$$

where K_3 is a dimensionless constant and ρ_d the dispersed phase density (g/cm^3). Sovová suggests that this expression allows for the small drops arising from break-up to be preserved. It is also possible that a combination of both mechanisms be used as found in the following expression for the overall coalescence efficiency, λ , which could replace λ_1 in equation (4.3):

$$\lambda(v, v') = \lambda_1(v, v') + \lambda_2(v, v') - \lambda_1(v, v') \lambda_2(v, v') \quad (4.6)$$

A white-noise band model for the coalescence efficiency has also been proposed by Muralidhar and Ramkrishna (1986) to take into account the coalescence of larger drops. In this model, the film drainage between two colliding drops is modelled as a stochastic process driven by a suitably idealised random process for the fluctuating force applied on the drops.

Thus it can be seen that, as the dispersed phase holdup is increased, there is consequently an increase in the collision frequency and hence in the coalescence rate. In order to obtain a new steady-state condition, it follows that the probability for drop break-up in the turbulent impeller region should also increase. This is obtained at relatively larger drop diameters since for this larger drop there will be an increased number of streamlines in the impeller region having sufficiently intense flow for turbulent break-up. Therefore, an increase in the dispersed phase holdup would eventually lead to a new steady-state equilibrium with larger drop sizes where the drop coalescence and break-up rates are again in equilibrium. This continues until drop sizes are attained for which the increase in the break-up probability is insufficient to balance that for coalescence and hence inversion occurs. This is because the intrinsic duration for drop break-up is too long for it to occur in the intense turbulent region within the vicinity of the impeller leading to insufficiently deformed drops in that region. Efficient drop break-up would thus only take place in a region of lower turbulence intensity further away from the impeller. This results in larger drops and hence a severely disturbed balance between drop coalescence and break-up in the impeller region (Groeneweg *et al.*, 1998).

However, there is still some disagreement about the actual locations where drop coalescence and break-up occur in agitated vessels. Most researchers have suggested that the process of drop break-up occurs in the impeller region, as a result of the pressure fluctuations arising from turbulence and the blade-tip vortices (Gilchrist *et al.*, 1989). Very little is known however on the location in which coalescence is dominant. Park & Blair (1975) found that far from the impeller the collision efficiency is extremely low, approximately 10% of the collisions resulting in coalescence. They suggested that coalescence rates are relatively independent of drop size but are dependent on the turbulence. This lead to the conclusion that the coalescence rate is greater in the impeller region. On the other hand, Hoffer and Resnick (1979) assumed that coalescence occurs in the quiescent regions of the vessel away from the impeller whereas drop break-up mainly occurs in the impeller discharge region.

Arashmid and Jeffreys (1980) suggested that at the inversion point the rate of drop coalescence equals the rate of drop break-up. In other words, as the dispersed phase holdup increases (at constant agitator speed), the proportion of the drop pairs coalescing with each other at each collision increases until, at phase inversion, coalescence will occur at every collision i.e. the coalescence frequency equals the collision frequency. Thus, at the inversion point

$$N_T = N_C \quad (4.7)$$

where N_T is the collision frequency (s^{-1}) and N_C is the coalescence frequency (s^{-1}).

Arashmid and Jeffreys used the expression developed by Misek (1964) to obtain the collision frequency for drops of initial size p (m):

$$N_T = \frac{K' \phi_d^2 \eta_d \rho_d \rho_c N^{9/4}}{p^2 \eta_c^{9/4}} \quad (4.8)$$

where ϕ_d is the dispersed phase holdup, ρ_c and ρ_d are the continuous and the dispersed phase densities (kg/m^3) and η_c and η_d are the continuous and the dispersed phase viscosities (Pa.s). N is the stirrer speed (r.p.m.) and K' is a dimensional proportionality constant characteristic of the agitator type. Arashmid and Jeffreys used the correlation of Bouyatiotis and Thornton (1967) to estimate the mean drop size p . The expression for the coalescence frequency that Arashmid and Jeffreys used was that of Howarth (1967b) and is given by

$$N_C = \frac{6.0 \phi_d \left[\frac{dp}{dt} \right]}{(2.0 - 2.0^{0.667}) p^4} \quad (4.9)$$

where t is the time (s). Using the results of Miller *et al.* (1963), a relationship for the derivative of drop size with respect to time can be estimated whereby

$$\frac{dp}{dt} \propto N^{1.8} \quad (4.10)$$

At phase inversion, when N_T calculated from equation (4.8) equals N_C calculated from equation (4.9), the following expression is obtained from which the dispersed phase holdup at inversion can be predicted:

$$\frac{N_C}{N_T} = \frac{K'}{\phi_d p^2 N^{0.46}} = 1 \quad (4.11)$$

Arashmid and Jeffreys found that the theory described above agreed well with their experimental results. However, the validity of the prediction method of Arashmid and Jeffreys has been questioned by Guilinger *et al.* (1988). In their paper, Guilinger *et al.* suggested that incorrect forms of Misek's correlation and Bouyatiotis and Thornton's correlation have been used.

Pacek *et al.* (1994a) used a stereo microscope with a very shallow depth of field connected to a video camera to visualise the phase inversion process. On the basis of their observations, they postulated that a simultaneous mechanism of the break-up of the continuous phase is required to explain the inversion process. By monitoring the change in the full drop size distribution and the mean drop size, they show that both the continuous phase break-up to produce droplets-within-drops (i.e. secondary dispersions) and the enhanced coalescence of the dispersed phase to give larger drops play a significant role in phase inversion.

Much more investigative work is required before a definitive mechanism for phase inversion can be ascertained. New methods of flow visualisation are needed, allowing the actual inversion process to be visualised and hence forming a basis for the development of a theoretical model for phase inversion. In the meantime, until more advanced models are proposed, it is generally accepted that phase inversion is a function of the drop coalescence and break-up rates, and any factor affecting these will influence the inversion process.

4.3 Phase Inversion Time Delay

Investigations of the delay time associated with phase inversion have been carried out by Gilchrist *et al.* (1989) who suggest that such studies may be a useful way of gaining an insight into the dynamics of the process. A study of the time delay is seen as a possible path to understanding the relative importance of the coalescence and break-up processes which are so closely related to the mechanism of phase inversion. Using a simple video system and a conductivity probe to detect the phase inversion (low conductivity for water-in-oil dispersions and high conductivity for oil-in-water dispersions), Gilchrist *et al.* observed that over a narrow range of holdups, the delay time could vary from zero (instantaneous inversion) to infinity (phase inversion never occurred i.e. the dispersion is stable). A typical dynamic conductivity trace is shown in Figure 13. The delay time was found to be dependent on the fluid dynamic parameters (e.g. agitation speed, liquid height, baffle gap etc.) and on the liquid physical properties.

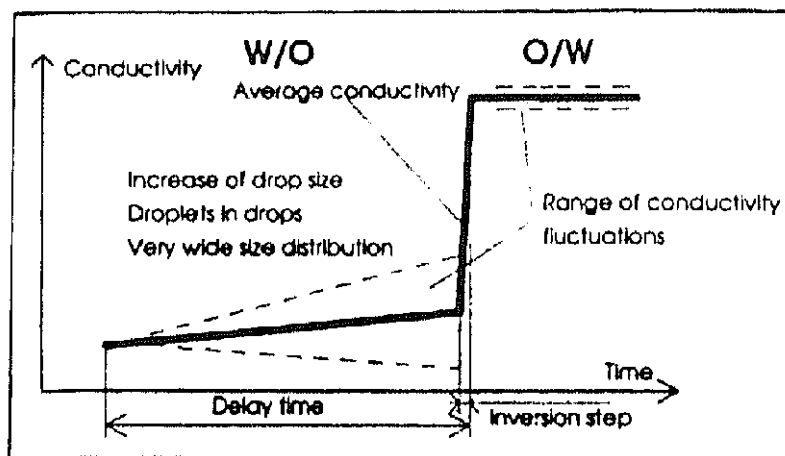


Figure 13 Typical Transient Conductivity Response to the Phase Inversion Process (Pacek *et al.*, 1994a). Reproduced with the permission of the American Institute of Chemical Engineers. Copyright © 1994 AIChE. All rights reserved.

During the initial delay period (ranging from several minutes to several seconds) from the change in the operational parameter and leading up to the final catastrophic instability transient, Gilchrist *et al.* (1989) observed significant increases in the number density of the larger drops in the dispersion. This is an observation which was discussed in the previous section where the increase in drop sizes lead to the coalescence of the dispersion drops into a single continuum. In addition, secondary dispersions of oil-in-water-in-oil droplets were observed in this period of time prior to inversion. The final catastrophic instability transient resulting in the complete phase inversion of the dispersion then occurred in a time span of only a few seconds as seen by the conductivity response in Figure 13. After inversion, the drop sizes noted were much smaller and more uniform.

Gilchrist *et al.* (1989) used their results to postulate that the growth of drops during the phase inversion delay period is controlled by the relative rates of break-up and coalescence, phase inversion occurring once a critical number concentration of drops is exceeded. Any effects favouring the break-up of drops would increase the time delay whereas any effects favouring drop coalescence would reduce the time delay.

Kato *et al.* (1991) reported the phenomenon of time delays in their experiments on dynamic phase inversion. By instantaneously increasing the agitation speed, they observed a time delay of 1.2 minutes for an oil-in-water dispersion to invert. In reversing the experimental pathway by an instantaneous decrease in the agitation speed, they found that the water-in-oil dispersion inverted back only after 3.4 minutes.

Pacek *et al.* (1994b), using a video microscopy technique to visualise phase inversion, also observed time delays. However, in trying to reproduce the experiments of Gilchrist *et al.* (1989), they found that delay times could not be measured for oil-in-water dispersions inverting to water-in-oil dispersions. The inversion was either instantaneous or it never occurred at all. They also did not observe any secondary dispersions of water-in-oil-in-water droplets for this case.

In general, the time delay decreases with increasing dispersed phase concentration. Nienow *et al.* (1994) attribute this observation to dramatically enhanced coalescence as

well as a rapid approach to the critical dispersed phase holdup. They also found that the direction of impeller rotation is an important factor on the time delay. When the pumping direction of the second liquid phase into the agitation vessel is downwards, there is a rapid rate of change in the direction of the flow due to the sharp angle between the vessel wall and floor. Gilchrist *et al.* (1989) suggest that the sharp turn that the flow makes results in inertial effects, which causes an enhancement in the coalescence rate. When the pumping direction is upwards, this effect is much smaller since the change in the flow direction is more gradual and hence the time delay is longer. Ganguly *et al.* (1992) however commented that these observations only refer to partially filled vessels. They note that should the vessel be completely full, the effect of the pumping direction would be the opposite. Nevertheless, the time delay decreases in both cases with increasing impeller speeds as seen in Figure 14. In addition, Pacek *et al.* (1994a) also found that the delay time was influenced by the initial state of the impeller, whether it was at rest or whether the agitation speed was altered in a stepwise manner.

In addition, Gilchrist *et al.* (1989) found the delay time to be a function of the liquid height. They ascribed the increase in the delay times to the inhomogeneity in the system which became increasingly apparent with increasing liquid height at constant agitation speeds. At higher speeds however, the spatial inhomogeneity disappears and consequently the delay time no longer depends on the liquid height.

The effects of the gap between the baffles and the vessel wall have also been investigated by Gilchrist *et al.* (1989). They reported that at low impeller speeds, increasing this spacing would reduce the overall coalescence rate and thus prolong the delay period for phase inversion. This follows from their view that the local quiescent region behind the baffle near the wall is one of the regions where coalescence takes place. At higher impeller speeds, the gap spacing has little effect on the time delay because the regions

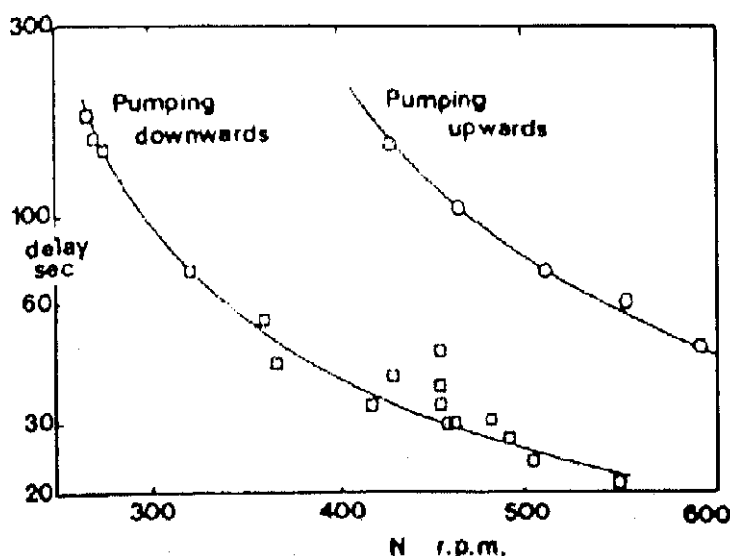


Figure 14 Time Delay as a Function of Agitation Speed and Pumping Direction (Gilchrist *et al.*, 1989). Reprinted from *Chemical Engineering Science* 44(10): 2381-2384 (1989), Gilchrist *et al.*, 'Delayed Phase Inversion in Stirred Liquid-Liquid Dispersions'. Copyright © 1989 with permission from Elsevier Science.

behind the baffles are well agitated even when the spacing is small resulting in the two liquid phases from all regions of the vessel being equally involved in the coalescence process.

Increasing the viscosity of the phases or the surfactant concentration is found to increase delay times. Nienow *et al.* (1994) ascribe this observation to a reduced coalescence rate as a result of the increasing viscosity or surfactant concentration. The increase in the resistance to continuous phase break-up and its incorporation into dispersed phase drops (i.e. to produce a secondary dispersion) is also a consideration in this case.

Norato *et al.* (1998) also reported observations of time delays and secondary dispersions in phase inversion. Measuring the conductivity, Norato *et al.* were able to confirm the results of previous investigators that the final catastrophic instability transient which resulted in the complete phase inversion of the dispersion occurred very rapidly over a timescale of the order of a few seconds. It was suggested that although the overall time delay between the time when the operational parameter was altered and the time at which inversion actually occurs is dependent on the experimental pathway, the time of the final catastrophic instability transient is independent of the path taken.

It has already been established that the prerequisites of phase inversion are:

- (i) an enhanced rate of coalescence i.e. the rate of coalescence exceeding the rate of break-up;
- (ii) a high dispersed phase holdup.

Thus if the final catastrophic instability transient which results in phase inversion is extremely rapid, it can be assumed that the rate-controlling mechanism for phase inversion is the coalescence process (Sarkar *et al.*, 1980). The rate at which phase inversion occurs thus depends on the coalescence rate which is a function of the collision frequency and the turbulence intensity as discussed in the section above.

Sarkar *et al.* (1980) have proposed an expression to predict the time required to invert a phase. In their work on countercurrent agitated columns, they used an analogy to the coagulation of a colloidal suspension to develop their model, noting that the only difference between this system and coalescence in liquid-liquid systems is that while coagulation in colloidal dispersions is influenced by electrostatic forces, liquid-liquid dispersions are brought about by surface interactions. Assuming Fick's second law of bulk diffusion to apply to drops under homogeneous turbulent conditions and assuming a simple mechanism for the drop collision and growth mechanisms, they propose the following equation to predict the time required for inversion, t_I (s):

$$t_I = 0.048V^{0.66}\phi_d^{-0.33}D_{tr}^{-1.0} \quad (4.12)$$

where V is the volume of the vessel or compartment of the contactor (m^3), ϕ_d the dispersed phase holdup and D_{tr} a turbulent diffusion coefficient (m^2/s) to characterise the eddy diffusion in a turbulent field. D_{tr} is predicted from the following expression (Levich, 1962):

$$D_{ir} = \alpha' \bar{\varepsilon}^{-0.33} \lambda^{1.33} \quad (4.13)$$

where α' is a dimensional constant, $\bar{\varepsilon}$ the mean energy input per unit mass (J/kg) and λ' the eddy length (m). Equation (4.12) is based on the assumption that the total time for drops of different species to attain inversion through a series of drop combinations is the time taken for a drop to grow continuously with the addition of fresh surface elements (drops).

The cause of the time delay phenomenon is not well understood. Gilchrist *et al.* (1989) attributed the time delay to the inhomogeneity of turbulence causing variations of coalescence rates at different regions of the stirred vessel. On the other hand, Pacek *et al.* (1994b) seem to believe that secondary dispersions are required for a finite delay time to be observed. This follows from their observation that neither time delays nor secondary dispersions were observed for oil-in-water dispersions inverting to water-in-oil dispersions. They thus postulate that the delay time is the time required for sufficient droplets of the continuous phase to be incorporated into the dispersed phase until the critical packing fraction is sufficient to cause phase inversion. Nienow *et al.* (1994) further propose that the presence of these structures would suggest that both drop coalescence and break-up are processes that contribute to the mechanism of phase inversion.

4.4 Secondary Dispersions

The presence of secondary dispersions (otherwise known as dual dispersions, double dispersions or multiple dispersions) of oil droplets in water drops in water-in-oil dispersions at phase inversion was observed in early studies such as those of Rodger *et al.* (1956), Quinn and Sigloh (1963), and Luhning and Sawistowski (1971). In these studies, pure systems were used. For systems containing surfactants, observations of secondary dispersions for water-in-oil systems were reported by Brooks and Richmond (1991).

On the other hand, secondary dispersions of water droplets in oil drops have never been observed, until recently with the exception of the ciné photographs produced by Luhning and Sawistowski (1971) which were claimed to show water droplets in toluene drops. However, Pacek *et al.* (1994b), having failed to reproduce such observations in toluene-water systems, dismissed these photographs as unclear. Later work by Pacek and Nienow (1995) seems to suggest that this non-symmetrical behaviour of oil-in-water and water-in-oil dispersions subject to the same hydrodynamic conditions is not dependent on which phase is more viscous or dense.

Groeneweg *et al.* (1998), however, report observations of water droplets in oil drops for a triglyceride-water system. They attribute this to the low viscosity of the water continuous phase which results in inertia-dominated coalescence of flattened oil drops in the turbulent impeller region. This is said to be the cause of the inclusion of the secondary water droplets into the oil drops. For highly viscous oil continuous phases, on the other hand, the viscosity-dominated coalescence of flattened water drops is unlikely in the impeller region because the film drainage times are too long. Groeneweg *et al.* note that the coalescence of spherical drops still occurs in this case but this does not lead

to the incorporation of secondary droplets. Groeneweg *et al.* thus concluded that secondary dispersions do occur in both oil-in-water and water-in-oil dispersions but that their occurrence would depend on whether the incorporation of secondary droplets is counteracted by their escape back into the continuous phase. In addition, water droplets in oil drops have been reported in systems containing surfactants (Campbell *et al.*, 1996; Hou & Papadopoulos, 1996).

The phenomenon of secondary dispersion is found to intensify as the system approaches inversion and disappears just at phase inversion. The variation in drop sizes with the water concentration indicating a sharp rise in drop sizes as secondary dispersions occur is shown in Figure 15. However, the conductivity trace results of Norato *et al.* (1998), in which secondary dispersions are characterised by large oscillations in the conductivity, seem to indicate that secondary dispersions take a considerable amount of time to disengage after cessation of the agitation. They also found that even for extended periods after bulk phase separation, the aqueous phase remained turbid indicating a suspension of tiny oil drops in the aqueous phase.

As mentioned briefly in Section 3.2, secondary dispersions have been considered to be the reason why higher critical dispersed phase holdups for inversion from oil-in-water dispersions to water-in-oil dispersions are higher than in the reverse case. Phase inversion occurs when a critical packing fraction is reached, the value of this packing fraction depending on each specific system. However, when secondary dispersions are present, the effective dispersed phase holdup is greater than that suggested by the mass balance. In other words, the dispersed phase holdup is increased in accordance with the droplets of the continuous phase trapped within the dispersed phase whereas the continuous phase is reduced by the same amount. This is also postulated to be the reason

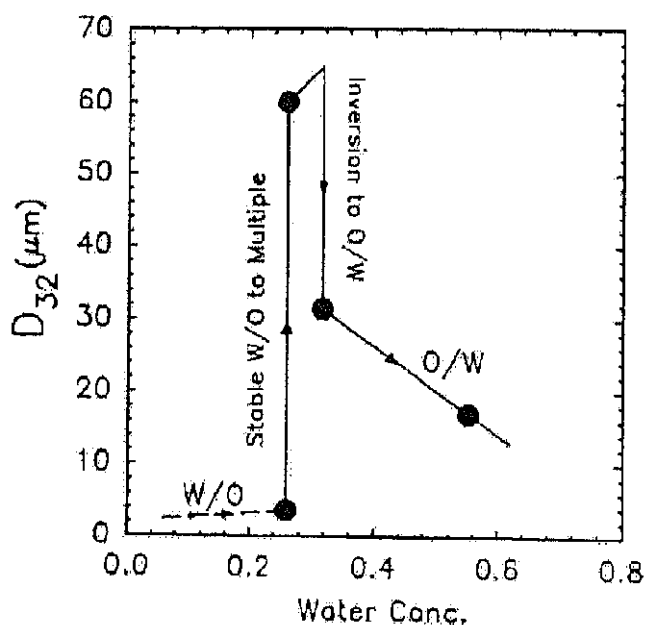


Figure 15 Drop Size Variation with Water Concentration (Pal, 1993). Reproduced with the permission of the American Institute of Chemical Engineers. Copyright © 1993 AIChE. All rights reserved.

why high maximum dispersed phase holdups of up to 90% are possible (Nienow *et al.*, 1994). Nienow *et al.* also obtained an estimate for this effective holdup from their video visualisation technique. However, this argument is based on the assumption that secondary dispersions only exist in water-in-oil dispersions and not in oil-in-water dispersions.

If secondary dispersions in oil-in-water dispersions do occur as suggested by Luhning and Sawistowski (1971) and Groeneweg *et al.* (1998), the influence of secondary dispersions in producing differences in the phase inversion holdup, depending on the direction of change in phase fraction, may be lessened. Groeneweg *et al.* propose a different explanation altogether for high dispersed phase holdups at inversion. They claim that close packing is an insufficient criterion for inversion since it cannot explain how the required inversion holdup can be reached in systems in which inversion is induced by agitation alone. They suggest that the critical dispersed phase holdup is dependent on the coalescence rate, which in turn is a function of the film drainage time. Should the drainage time be high, then the coalescence efficiency and hence the coalescence rate is reduced, as seen from equations (4.2) and (4.3), thus requiring a considerably larger dispersed phase holdup for inversion. Since film drainage time is viscosity dependent, the argument by Groeneweg *et al.* would therefore imply that oil drops have high viscosities and hence high film drainage times. This would lead to low coalescence rates and hence higher critical dispersed phase holdups are required for oil-in-water dispersions to invert than for water-in-oil dispersions to invert.

The role of secondary dispersions in the mechanism of continuous phase break-up has been mentioned earlier in this chapter. As previously noted, the presence of secondary dispersions is also the cause of the time delay in the phase inversion process, the delay arising from the time taken for the droplets to be incorporated into the dispersed phase in order for the critical effective packing fraction to be reached. Since the delay time is extremely sensitive to the hydrodynamics of the system (Gilchrist *et al.*, 1989; Pacek *et al.*, 1993), it follows that the rate of incorporation of the droplets into the drops must also depend on this factor (Pacek *et al.*, 1994b).

The mechanism by which the oil droplets are incorporated into the water drops is not known precisely. Groeneweg *et al.* (1998) propose that the incorporation of secondary droplets does indeed occur for low dispersed phase holdups by the coalescence of two drops. Luhning and Sawistowski (1971) suggest that at high dispersed phase holdups, both the drop coalescence and the continuous phase break-up processes result in the entrainment of the continuous phase by the dispersed phase. This is similar to the mechanism for the phase inversion of emulsions postulated by Schulman and Cockbain (1940).

For increasing dispersed phase holdups, the total drop concentration increases and the inter-drop distance decreases thus increasing the frequency of multi-body collisions (collisions involving more than 3 drops). The simultaneous coalescence of these drops then occurs in such a way that the intervening continuous phase is trapped. Successive coalescence of such drops would then result in drops which have more than a single droplet within them. This mechanism is illustrated in Figure 16.

There are two requirements for secondary dispersions to exist:

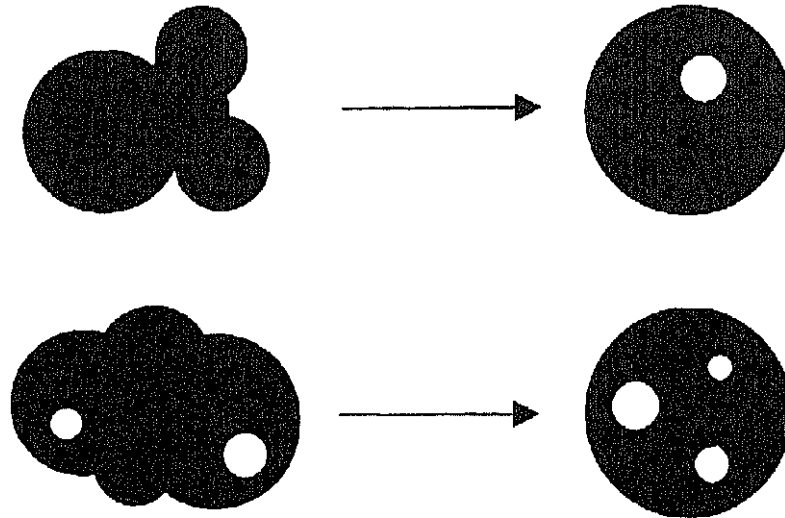


Figure 16 Simplified Representation of Multi-Body Collisions Producing Secondary Dispersions of Continuous Phase Droplets in Dispersed Phase Drops (after Kumar, 1996).

- (i) a sufficiently high coalescence efficiency giving rise to simultaneous coalescence with sufficient flattening of the drops, thereby enabling the entrapment of the flattened continuous phase film between the drops (Groeneweg *et al.*, 1998);
- (ii) stabilisation of the trapped droplets to prevent their escape back into the continuous phase (Kumar, 1996).

Kumar put forward the possibility of drops being charged in order to explain the phenomenon of secondary dispersions and how the above two requirements are met. This will be discussed in Section 4.5 below.

Experimental data on the frequency of the incorporation of secondary dispersions have been presented by Groeneweg *et al.* (1998). By microscopic observation of the size distribution of the secondary droplets and by assuming that each incorporation or inclusion event results in a secondary droplet of 8 μm that could coalesce further to produce larger secondary droplets, they were able to calculate the frequency and hence the rate of droplet incorporation. This was then compared with the average number of droplet circulations around the vessel. In this study, Groeneweg *et al.* conclude that only very few secondary droplets are incorporated into drops during each passage through the turbulent impeller region. Collisions with sufficient intensity to deform and hence flatten the dispersed drops such that the continuous phase can be trapped within them occur only in a small volume just outside the impeller region. Within the impeller region itself, only the drop break-up process will occur whereas far from the impeller region there is again insufficient coalescence for incorporation to occur.

Two mechanisms for the process by which the secondary droplet escapes from their host drop have been postulated by Groeneweg *et al.* (1998). Both stem from the underlying principle that film rupture between the secondary droplet and the continuous phase is required for the droplet to escape:

- (i) The dispersed drop is deformed by shear induced by the flow leading to the incorporation of a large secondary droplet which might be trapped between the walls of the surrounding drop. Subsequently the film between the enclosed secondary droplet and the continuous phase could rupture allowing the droplet to escape;
- (ii) The secondary droplet moving within the surrounding drop reaches the boundary of the drop, remaining there for a sufficiently long period of time for the film between the secondary droplet and the continuous phase to become so thin that film rupture occurs leading to the escape of the droplet.

In addition, a further mechanism has been suggested by Kumar (1996) whereby the secondary droplet coalesces with other secondary droplets and with the external phase causing film rupture thereby destroying the entire secondary dispersion structure. It can thus be seen that the escape process becomes more probable as the size of the secondary droplet approaches that of the surrounding drop.

If the secondary droplet phase contains emulsifying surfactants, or even surface-active impurities, the coalescence of these droplets with each other and with the external phase is strongly suppressed, delaying their escape back into the continuous phase (Hou & Papadopoulos, 1996). In spite of this, recent work by Groeneweg *et al.* (1998) found that this stabilising effect was overridden by the effect of the deformation of the surrounding drop. They suggest that the interfacial area increases following drop deformation temporarily decreasing the concentration of surfactant adsorbed in the deformation region. As a result, the film between the secondary droplet and the continuous phase might no longer be sufficiently stabilised leading to the escape of the droplet. Groeneweg *et al.* thus propose that drop deformation is a necessary requirement for the escape process. However, it should be noted that this would only be true if the adsorption time of the surfactant is larger than the time taken for the drop to deform.

According to Groeneweg *et al.*, (1998), the effective dispersed phase holdup is determined by a delicate balance between the rate of incorporation of the secondary dispersions and the rate of escape by which these structures are destroyed. The effective holdup increases gradually until steady-state is achieved between the incorporation and escape processes or until the critical dispersed phase holdup is obtained at which point phase inversion occurs. They thus propose that the time taken for the effective holdup to reach the critical value constitutes the phase inversion delay time, a view similar to those of Gilchrist *et al.* (1989) and Pacek *et al.* (1994b) which were discussed in the previous section.

4.5 Effects of Drop Electrostatic Charge

Tobin and Ramkrishna (1992), in examining the effect of drop electrostatic charge on coalescence in turbulent liquid-liquid dispersions, reported that surface charge on drops can substantially inhibit the drop coalescence process. Their experimental studies show that electrostatic effects due to hydroxide ion (OH⁻) adsorption at the organic-water interface can significantly stabilise dispersions. They also found that such stabilisation against coalescence occurs even in the absence of surfactants. Since then, Kumar (1996)

has postulated that it is the drop charge that could explain the secondary dispersion phenomenon during phase inversion. It has already been mentioned in Section 3.2 that drops acquire charge due to the large differences in the dielectric constants of the two immiscible phases even when there are no ionic additives present. Oil drops in water experience electrostatic repulsion due to the overlapping of the double layer forces and thus have low coalescence efficiencies whereas water drops in oil have high coalescence efficiencies because no such repulsion exists.

Water-in-oil dispersions meet both the criteria for secondary dispersions to exist as listed in Section 4.4 because of the high coalescence efficiencies of water drops in oil. Therefore, by this argument it follows that dispersions of oil-in-water-in-oil do indeed exist. On the other hand, oil-in-water dispersions do not have sufficiently high coalescence efficiencies to give simultaneous multi-body collisions. In addition, the water droplets engulfed in the oil drops have high coalescence efficiencies thus escaping the oil drops rapidly. Kumar (1996) claims that the requirement of high coalescence efficiencies for the existence of secondary dispersions is supported by the experimental results of Brooks and Richmond (1994a).

It should be noted that the argument of Kumar (1996) seems to suggest an acceleration towards phase inversion. As the coalescence rate increases, Kumar proposed that secondary dispersions are created thereby increasing the effective dispersed phase holdup. Thus, higher collision frequencies are obtained since this is a direct function of the dispersed phase holdup and as a result the coalescence rate is enhanced. This would lead to a start in the cycle again where more secondary dispersions are formed as a result. It is possible that more and more secondary dispersions are thus created enhancing the coalescence rates further and further till they exceed the drop break-up rates, at which point phase inversion occurs.

The role of surface charges on drops was also investigated by Norato *et al.* (1998) who dissolved sodium chloride (NaCl) into the aqueous phase. They found that the fluctuations in the conductivity trace prior to phase inversion occurred with the same magnitude but did not find any of the large fluctuations observed after phase inversion in systems without any NaCl dissolved into the aqueous phase. They also observed that adding NaCl to the system reduced the separation time of the phases after phase inversion when the agitation stopped. The initially turbid aqueous phase for a NaCl free system was clear in the system with added NaCl. It is thus apparent that increasing the ionic strength by adding NaCl eliminated the possibility of secondary dispersions being formed.

Norato *et al.* (1998) suggest that the presence of ions compresses the electric double layer to an extent that the van der Waals forces overlap the repulsive forces. This implies that the addition of NaCl at high concentrations negates any effect of surface charges, thereby increasing the drop coalescence rate. However, by demonstrating that the formation of secondary dispersions is eliminated when NaCl is added despite the enhanced coalescence rate that is caused, the results of Norato *et al.* contradict those of Kumar (1996) who postulated the formation of secondary dispersions as the coalescence rate is increased. Nevertheless, Norato *et al.* admit that further studies, in particular the incorporation of visualisation techniques, are required in order to draw a definitive conclusion.

4.6 *Phase Inversion Modelling*

Juswandi (1995) reports a stochastic model which attempts to simulate phase inversion. The case considered was the phase inversion of a dispersion of spherical drops that exists in a thin annular liquid film flowing around a tube wall. This is done by using a Monte Carlo simulation to model the movement of the drops from their original positions in a lattice. At the new drop positions, Juswandi proceeds to determine the coalescence probability of the drop. Coalescence is assumed to be possible only if the distance between the centres of two drops is less than a given critical distance; no indication, however, is given on how this distance is obtained. The model also incorporates drop break-up by accounting for the drop size, flow conditions and the viscosities of the continuous and dispersed phases. For a given water holdup, the drop size distributions and hence the drop interfacial energy of both the water-in-oil and the oil-in-water configurations are then calculated. Given that the initial condition is a water-in-oil configuration, the criterion for phase inversion is for the energy of the water-in-oil dispersion to exceed that of the oil-in-water dispersion. The model thus uses an iterative process, repeating the procedure with increments in the water holdup until inversion occurs.

Juswandi's model does have its limitations in that it does not accurately reflect the actual mechanisms behind the inversion process; secondary dispersions which play an important role in phase inversion have not been considered. The model also does not take into account the hydrodynamics of the coalescence process; film drainage times and contact times have not been incorporated into the coalescence model. In addition, the coalescence probability depends on more factors than just the dispersed phase holdup. While Juswandi reports that his results are in good agreement with the experimental data of Brooks and Richmond (1994b), he has not shown this in great detail. No extensive attempts to match the conditions (e.g. flow and geometry) with those of Brooks and Richmond were made. In addition, the data of Brooks and Richmond was based on systems with surfactants present whereas the Juswandi model does not take account of this.

Deterministic models derived from the fundamental physical mechanisms governing phase inversion are rare. There is thus a great need for deterministic models which account for drop interaction and hydrodynamics as well as for the effects of secondary dispersions.

4.7 *Summary*

Whilst a single unified mechanism behind phase inversion does not exist, there is little doubt among researchers that the main mechanisms governing the inversion process are drop coalescence and break-up. However, definitive information on the details of the processes remains elusive despite extensive investigations that have been carried out over the years. With the advent of advanced methods of flow visualisation, it is hoped that by direct visualisation of the actual drop coalescence and break-up processes, these mechanisms can be further elucidated. Of importance to phase inversion studies are the factors that affect drop coalescence and break-up and to a slightly lesser extent the location where these processes are dominant. While relationships between the various

factors that control the break-up and coalescence processes have been proposed, further experimental and theoretical verification is required before any generic predictive methods can be developed.

It has been shown that secondary dispersions are postulated to play an extremely important role in drop coalescence and hence in phase inversion. As a result, the existence of secondary dispersions has been used to explain many of the phenomena that are associated with phase inversion. While the existence of secondary dispersions has been well documented, the actual existence of water droplets in oil drops still requires verification. Should this configuration exist, then the use of secondary dispersions by Pacek *et al.* (1994b) as an explanation for the non-symmetrical behaviour of oil-in-water and water-in-oil dispersions may be implausible. At present, the observations of various researchers regarding the existence of water-in-oil-in-water dispersions are inadequate to provide any concrete views on the validity of this dispersion configuration and hence more work is urgently required in this area.

It has been generally accepted that secondary dispersions are formed by the action of drop coalescence. Nevertheless, the mechanism by which the incorporation process occurs is not known precisely. The drop charge hypothesis proposed by Kumar (1996) as a mechanism for the formation of secondary dispersions requires further independent assessment. Conflicting views have been proposed on the effect of salt addition on drop surface charge and hence further investigation is essential before any definitive statements can be made. It seems that phase inversion time delay is strongly related to the existence of secondary dispersions. Further work into this phenomenon should provide clues to a better understanding of the role of secondary dispersions in phase inversion.

Over the past 40 years of phase inversion research, there have been very few models based on a thorough theoretical understanding of the physical processes underlying the inversion process which have been developed to predict the phase inversion holdup. A model which incorporates the fundamentals of drop coalescence and break-up together with the physical properties of the system at both microscopic and macroscopic levels would be an extremely valuable tool for both research workers and for the industry.

5. PHASE INVERSION IN OTHER SYSTEMS

5.1 *Introduction*

Whilst a large proportion of research has been carried out on agitated vessels, a comprehensive review of phase inversion phenomena is incomplete without a survey of the other work carried out for liquid-liquid dispersions in pipeflow and other systems. The next section details the studies of phase inversion in pipeline flows whereas the work carried out for various other systems is discussed in the following section.

5.2 *Phase Inversion in Pipeflow*

One of the most common but least understood types of multiphase flows is that of pipeline transport of two immiscible liquids. In the chemical and petroleum industry,

mixtures of oil and water are transported over long distances in horizontal pipes. Water is often introduced to the oil in the transportation of heavy viscous crude oil in order to reduce the pressure gradient and hence the pumping required to transport the oil through the pipes. The design of these pipelines as well as the pumping equipment requires an understanding of the oil-water flow patterns and the pressure drop for given volumetric flows of the two phases. However, this is very complicated due to the existence of a variety of flow patterns with different mechanisms governing each of them and with a wide range of pressure gradients encountered for each different flow pattern. An added complication is the non-Newtonian rheological behaviour of oil-water flow systems. The phase inversion phenomenon is a key consideration in pipeline flow, particularly because of the abrupt and significant changes in the frictional pressure drop and the rheological characteristics of the dispersion at or near the phase inversion point. Failure to account for the abnormally high pressure drops at the region in which phase inversion occurs may result in substantial decreases in the oil productivity in wells and in the capacity of pipelines.

The main flow patterns observed in liquid-liquid flow can be classified into four categories as follows:

- (i) Segregated Flow – The two fluid phases flow in separate stratified layers with either a smooth or wavy surface depending on the velocities of the phases.
- (ii) Slug Flow – One liquid phase flows as a large spherical or elongated slug in another liquid phase.
- (iii) Dispersed Flow – One fluid forms a dispersion of drops within the continuous phase of the other fluid.
- (iv) Annular Flow – One of the liquids forms an annular core around the pipe wall whereas the other liquid flows in the annulus. This flow regime is common when the two liquids have similar densities or when one liquid has a large viscosity compared to the other.

In practice, the flow often consists of a combination of these categories. The possible flow patterns are given in Figure 17.

The flow pattern observations are often delineated onto flow pattern maps in terms of two independent system parameters, conventionally the superficial liquid velocities, or alternatively, the mixture velocity and the input fraction of one of the liquids. The existing flow pattern maps have been produced for oil-water systems with similar pipe diameters and density differences but for different oil viscosities and pipe materials. The flow pattern maps of Guzhov *et al.* (1973), Arirachakaran *et al.* (1989) and Nädler and Mewes (1997) are given in Figures 18(i) to 18(iii) respectively. There is some similarity between the various flow pattern maps regarding the sequence of flow patterns and the boundaries for stratified flow, but there is some variation in how the various dispersed flow regimes are classified and where their boundaries occur.

Phase inversion in vertical pipes was briefly studied by Luo *et al.* (1997). Nevertheless, more work is required to consolidate any conclusions that have been

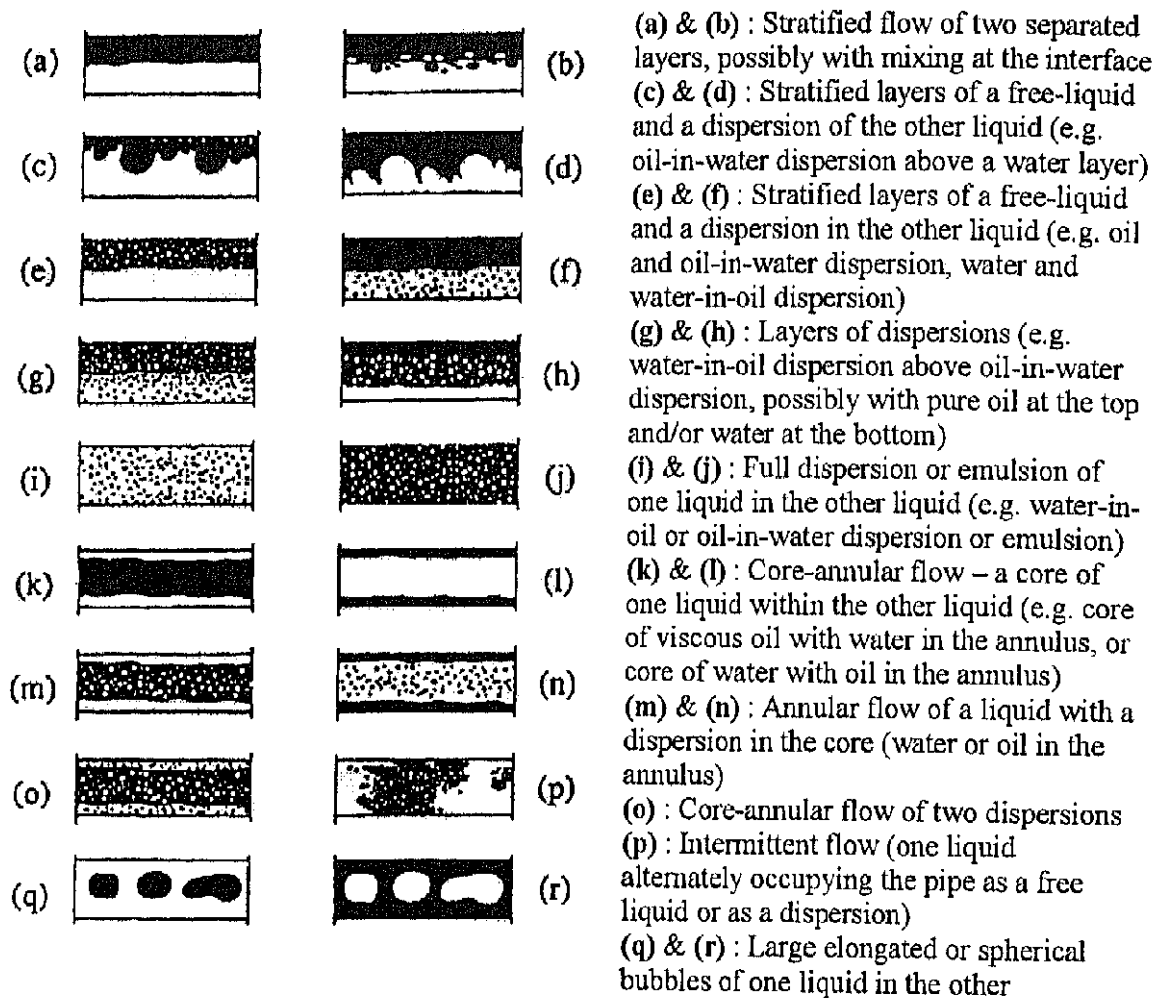


Figure 17 Schematic Representations of Possible Flow Regimes (Brauner, 1998).

found. There exists virtually no detailed information about the mechanism of phase inversion in flow in pipes. This is a subject which still needs more investigation. The relationship between phase inversion and radial concentration gradients across the pipe cross-section is not yet known.

Phase inversion in three-phase gas-oil-water flows was studied by Malinowsky (1975), Laflin and Oglesby (1976), Pan (1996), Donnelly and Behnia (1997), Utvik *et al.* (1998) and Odozi *et al.* (1998). In general, these investigators have found that in addition to the liquid superficial velocity, the inversion point is a strong function of the gas superficial velocity. In early work on three-phase flows, Malinowsky, and Laflin and Oglesby reported a shift in the inversion point to higher input liquid holdups compared to that for two-phase oil-water flows. Furthermore, Laflin and Oglesby and Utvik *et al.* also noted that the inversion point depends on the gas-liquid ratio, shifting toward higher water holdups with increasing gas-liquid ratios. It is thus believed that this phenomenon can be explained by the gas becoming dispersed as bubbles in the oil-water mixture during the flow. These bubbles interfere with the coalescence between the dispersed phase drops and, as a result, higher dispersed phase concentrations are therefore required to overcome the action of the bubbles leading to higher inversion holdups.

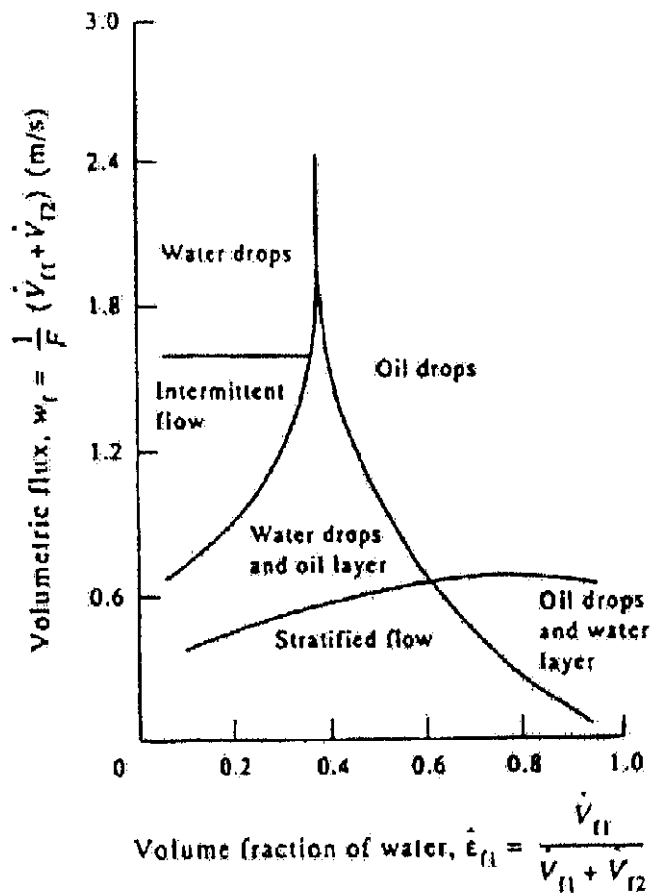


Figure 18(i) Flow Pattern Map for Oil and Water in a 39.4 mm ID Steel Pipe (Guzhov *et al.*, 1973).

5.3 Phase Inversion in Contacting Equipment

Solvent extraction is a widespread operation in the chemical industry. There are two major types of solvent extraction equipment, stagewise equipment generally referring to mixer-settlers and differential equipment usually referring to column contactors. In the design of extraction equipment, the choice and stability of the dispersed phase is often important. While contactor columns with low dispersed phase holdup characteristics will not encounter phase inversion problems under normal operating conditions, mixer-settlers which are frequently operated with high holdups often experience the difficulty of maintaining the desired dispersion phase. Should phase inversion occur in contacting equipment, there would be a change in the direction of mass transfer leading to a change in the overall mass transfer rate. Given that contacting equipment is designed on an assumed identity of the dispersed phase for optimum mass transfer rates, phase inversion would likely lead to a reduction in the transfer rate and would be highly undesirable.

While most of the previous work on phase inversion has been carried out on agitated vessels and hence applies to mixer-settlers, phase inversion studies as it applies to column contactors has attracted relatively little interest. Arnold (1974) studied phase

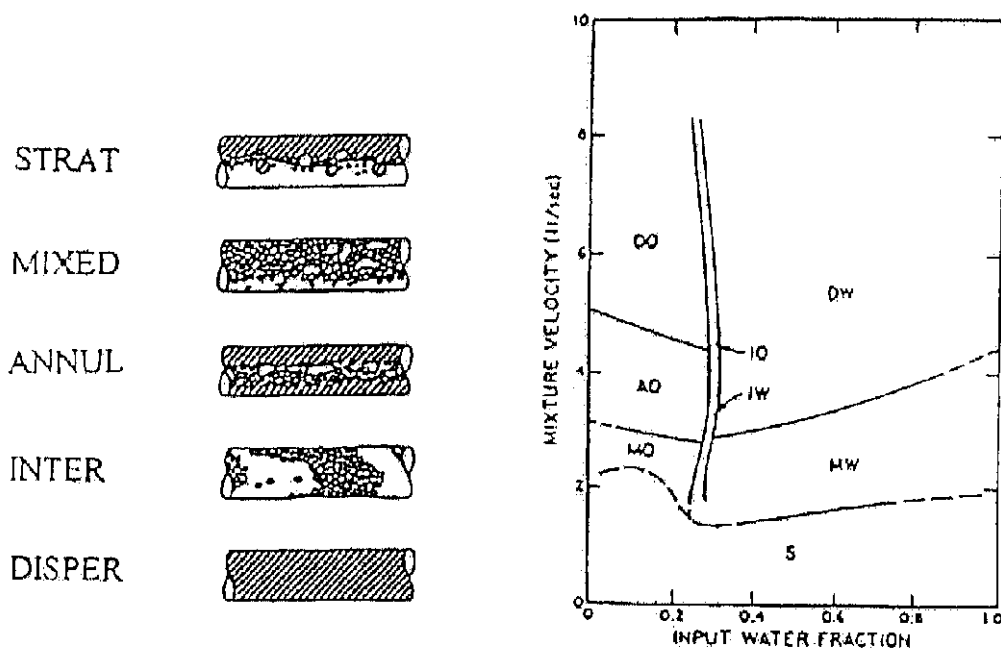


Figure 18(ii) Classification of Oil-Water Flow Patterns and Flow Pattern Map for a 39.3 mm ID Steel Tube (Arirachakaran *et al.*, 1989). Reproduced from 'An Analysis of Oil/Water Flow Phenomena in Horizontal Pipes', Arirachakaran *et al.* (1989), Paper SPE 18836 with the permission of the Society of Petroleum Engineers. Copyright © 1989 Society of Petroleum Engineers Inc.

inversion in an Oldshue Rushton column. Sarkar *et al.* (1980) carried out a study on the mechanisms of dynamic phase inversion in Rotating Disc and Oldshue Rushton contactors, finding phase inversion to occur as a pseudosteady-state phenomenon in time cycles which occurred at high dispersed to continuous phase ratios, being characterised by 'slugs' of the coalesced dispersed phase rising periodically up the column.

There have been even fewer studies on phase inversion in static mixers. The fundamental difference between dispersions formed in agitated vessels and in static mixers lies in the width of the ambivalence region. Tidhar *et al.* (1986) found that the width of the ambivalence range is considerably smaller for static mixers as compared to that for dispersions formed in agitated vessels. In addition, they also noted that the ambivalent zone for dispersions formed in static mixers is not a zone where the dispersion morphology can either be organic continuous or aqueous continuous depending on the system's history or on how the ambivalence zone is reached as in agitated vessels. Rather, it is a region in which the system oscillates between the organic continuous and the aqueous continuous configurations. This is illustrated in Figure 19.

5.4 Prediction of the Phase Inversion Point

In recent years, phase inversion point predictions have been concentrated on applications other than agitated vessels. In particular, predicting the phase inversion point has become of paramount importance in the pipeline transportation of oils, given the fact that there is

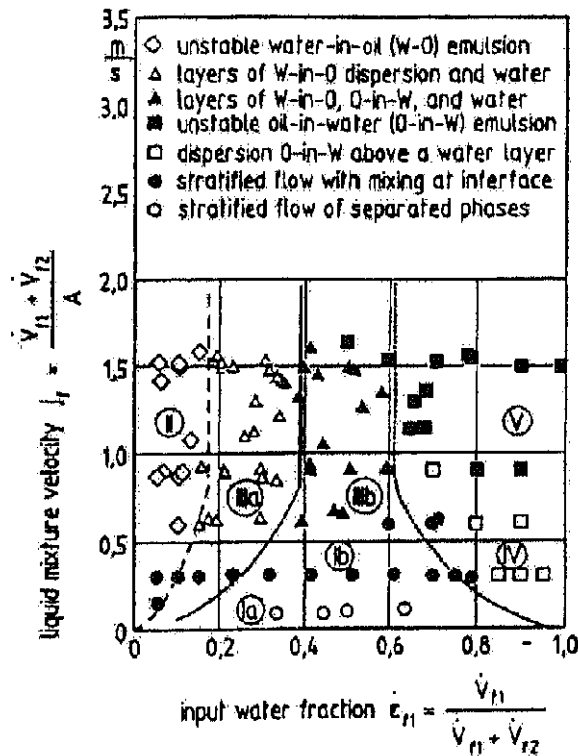
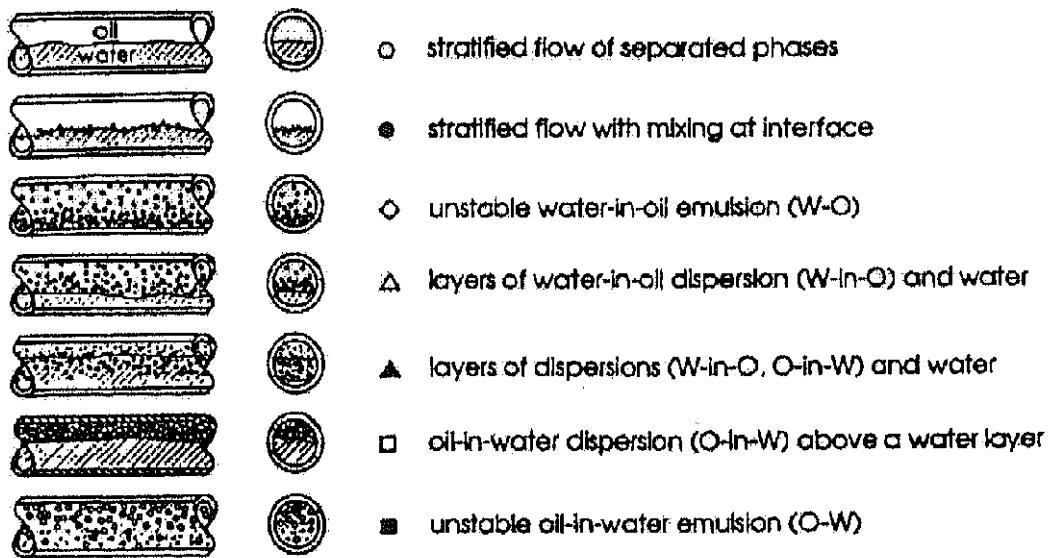


Figure 18(iii) Oil-Water Flow Regimes and Flow Pattern Map for a 59 mm Perspex Tube (Nädler and Mewes, 1997). Reprinted from *International Journal of Multiphase Flow* 23(1): 55-68 (1997), Nädler & Mewes, 'Flow Induced Emulsification in the Flow of Two Immiscible Liquids in Horizontal Pipes'. Copyright © 1997 with permission from Elsevier Science.

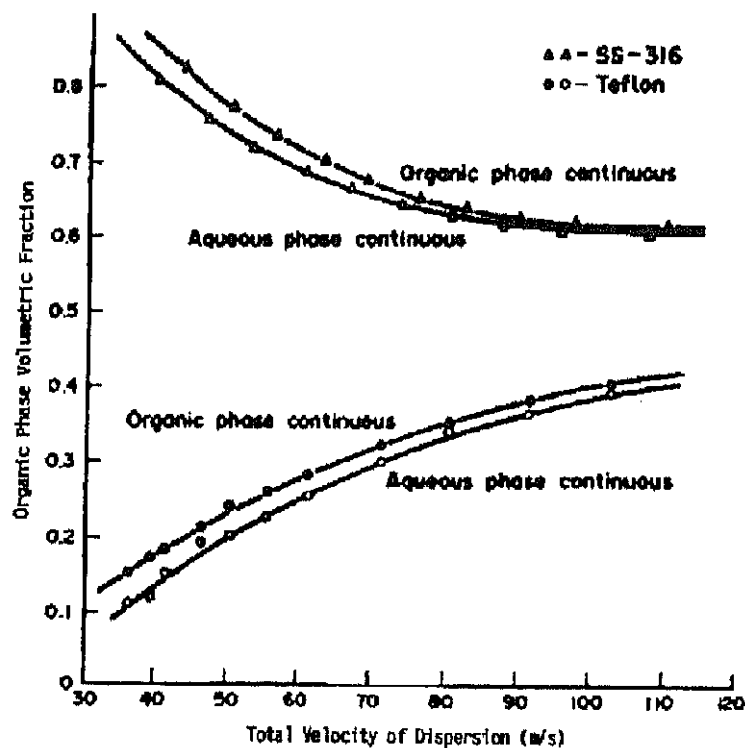


Figure 19 Ambivalence Region for Flow in Static Mixers (Tidhar *et al.*, 1986). Reprinted from *Chemical Engineering Science* 41(3): 457-462 (1986), Tidhar *et al.*, 'Characteristics of a Motionless Mixer for Dispersion of Immiscible Fluids - II. Phase Inversion of Liquid-Liquid Systems'. Copyright © 1986 with permission from Elsevier Science.

often an abrupt and significant increase in the frictional pressure drop associated in the region where phase inversion from oil to water continuous occurs. Knowledge of the critical fraction would then dictate how the pressure gradient increase could be calculated.

Arirachakaran *et al.* (1989) found that the input water fraction required to invert a dispersion decreased with increasing oil viscosity. Using the experimental data of Guzhov *et al.* (1973), Russell *et al.* (1959), Charles (1961), Oglesby (1979) and Arirachakaran (1983), they correlated the following logarithmic relationship between the oil viscosity and in the input water fraction required to invert the system in the fully laminar oil region, $\phi_{w,i}$:

$$\phi_{w,i} = 0.500 - 0.1108 \log \eta_o \quad (5.1)$$

where η_o is the oil viscosity (cp) with reference to the viscosity of water. This equation indicates that for a 1 cp oil, the system would invert at 50% input water fraction.

Arirachakaran *et al.* (1989) observed that mixture velocity had little effect on the inversion mechanism as long as there was no transition in the flow regime. They also note that this correlation was developed for oils with interfacial tensions of 30 ± 2 dynes/cm and caution the use of the correlation for oils with interfacial tensions outside this range.

In contrast, Nädler and Mewes (1995a), in their work on flow in horizontal pipes, proposed that phase inversion is a function of the mixture superficial velocity of the oil-water mixture, v_m (m/s), given by

$$v_m = \frac{1}{A} \left(\dot{V}_d + \dot{V}_c \right) \tag{5.2}$$

where A is the cross-sectional area of the pipe (m^2). This is claimed to be supported by the results of Russell *et al.* (1959), Guzhov *et al.* (1973) and Nädler and Mewes (1994).

Nädler and Mewes (1995a) developed a simplified model based on the combined momentum equations of the two liquid layers for stratified flow, assuming that the interfacial shear stress is zero and that there is no slip (i.e. the in-situ holdup equals the input cut). Using a Blasius type equation for the friction factor f

$$f = C \text{Re}^n \tag{5.3}$$

where C' is a constant, to calculate the shear stresses, the following equation to predict the critical input water cut was calculated:

$$\phi_{w,i} = \frac{1}{1 + k_1 \left(\frac{C_o' \rho_o^{(1-n_o)} \eta_o^{n_o}}{C_w' \rho_w^{(1-n_w)} \eta_w^{n_w}} \frac{1}{[dv_m]^{(n_o-n_w)}} \right)^{\frac{1}{k_2}}} \tag{5.4}$$

In this equation, C_w' , C_o' , n_w and n_o are parameters in the friction factor equation described above in equation (5.3), ρ_w and ρ_o are the densities (kg/m^3), and η_w and η_o are the dynamic viscosities (Pa.s) of the water and oil phases respectively. d is the internal pipe diameter (m), v_m the superficial liquid mixture velocity (m/s) and k_1 and k_2 are parameters.

The parameter k_1 reflects the wall/liquids contact perimeter as determined by the in-situ configuration ($k_1 > 0$). k_2 accounts for the flow regime in each of the phases, the superficial Reynolds number ($\text{Re}_i = \rho_i v_m d / \eta_i$) for each respective phase i being used to predict the flow regime. For laminar flow in both the water and oil phases, $C_w' = C_o' = 16$, $n_w = n_o = 1$, $k_1 = 1$ and $k_2 = 2$ which results in equation (5.4) being in complete agreement with the equation of Yeh *et al.* (1964) described above [equation (3.10)]. For turbulent flow in both phases, $k_1 = 1$ and $k_2 = 1.2$. The prediction of the input water cut at inversion using equation (5.4) would then yield a similar value to that calculated using the correlation of Arirachakaran *et al.* (1989) in equation (5.1) above. Nädler and Mewes (1995a) used equation (5.4) to predict the phase inversion curves in their flow regime map given in Figure 18(iii). The dashed line between regions IIIa and IIIb in the flow regime map marks the transition from an unstable water-in-oil dispersion to layers of water-in-oil dispersion and water is predicted by equation (5.4) with $k_1 = 3$ and $k_2 = 1.2$. The local phase inversion points within the dispersion layer are represented by the solid line which is derived from equation (5.4) with $k_1 = 1$ and $k_2 = 1.2$. The transition to oil-

in-water dispersions is given by the dotted line, derived using $k_1 = 1$ and $k_2 = -1.2$. It should be noted here that the phase inversion curve represented by the solid line was observed visually whereas the other two curves were determined using impedance measurements.

Tidhar *et al.* (1986) predicted the organic phase holdup at phase inversion, $\phi_{o,i}$, in static mixers. Their proposed general expression can be expressed as

$$\phi_{o,i} = 0.5 + C_1 We^{-0.5} Re^{0.15} (\alpha D_H) \cos \varphi \quad (5.5)$$

Here C_1 is a constant, α the static mixer area per unit volume (m^2/m^3), D_H the hydraulic diameter of the mixer (m) and φ the contact angle made between the drop and the surface (rad.). The Weber number, We , is defined by

$$We = \frac{\rho_m v_T^2 D_H}{\sigma} \quad (5.6)$$

ρ_m is the mixture density (kg/m^3), v_T the total velocity of the dispersion (m/s) and σ the interfacial tension (N/m). The Reynolds number, Re , is defined by

$$Re = \frac{\rho_m v_T D_H}{\eta_m} \quad (5.7)$$

where η_m is the mixture viscosity (Pa.s).

Hossain *et al.* (1983), in their work on mixer-settlers, suggest that the dispersed phase holdup at inversion, $\phi_{d,i}$, reaches a maximum. By representing the point of phase inversion as a stationary point and hence applying the following conditions on the input volumetric flows of the dispersed and the continuous phases, \dot{V}_c and \dot{V}_d respectively,

$$\frac{d\dot{V}_d}{d\phi_{d,i}} = 0 \quad (5.8)$$

$$\frac{d\dot{V}_c}{d\phi_{d,i}} = 0 \quad (5.9)$$

they obtain the following expression for the dispersed phase holdup at phase inversion:

$$\frac{\dot{V}_c}{\dot{V}_d} = 1 - \frac{4}{3\phi_{d,i}} + \frac{1}{9\phi_{d,i}^2} + \frac{2}{27\phi_{d,i}^3} + \frac{4}{81\phi_{d,i}^4} \quad (5.10)$$

This was found to be in reasonable agreement for higher holdups, but in poorer agreement as the holdup decreases. Hossain *et al.* claim that in addition to predicting the phase inversion point, this relationship can also be used to predict the maximum capacity of a mixer-settler in which phase inversion occurs in the mixer prior to phase entrainment in the settler. Their predictions are however sensitive to minor fluctuations in flow rate, impeller speed or the presence of impurities.

Salem (1988) developed the following semi-theoretical mathematical model for mixer-settlers based on slip velocities to predict the phase ratio, R , at the ambivalent range where inversion can take place, assuming that the light phase is always the dispersed phase:

$$R = \frac{\dot{V}_c}{\dot{V}_d} = \left(\frac{\rho_c \eta_d}{\rho_d \eta_c} \right)^{0.3} \frac{1}{\theta} \quad (5.11)$$

where the dispersed phase and continuous phase viscosities, η_c and η_d are in centipoise (cp). θ takes a value between 0.5 and 2 and is given by

$$\theta = \frac{\dot{V}_L}{\dot{V}_H} \left(\frac{\rho_L \eta_H}{\rho_H \eta_L} \right)^{0.3} \quad (5.12)$$

in which \dot{V}_L and \dot{V}_H are the volumetric flows of the light and heavy phases respectively (m^3/s). ρ_L and ρ_H are the densities of the light and heavy phases (kg/m^3) and η_L and η_H are the viscosities of these phases (cp). The critical dispersed phase holdup can then be found by the following equation:

$$R = \left(\frac{1 - \phi_{d,i}}{\phi_{d,i}} \right) \left[- \frac{(1 - \phi_{d,i}) + C}{\phi_{d,i} - C} \right] \quad (5.13)$$

where C is a constant that depends on the system and the contactor used (stagewise or continuous).

5.4 The Effects of Various Parameters on Phase Inversion Behaviour

5.4.1 Geometrical Considerations

In pipeflow, it is possible that obstacles present at the wall could cause the dispersed phase to be separated out behind the obstacle due to the recirculation of the fluid. The separation of these drops could possibly have an influence on the coalescence rate and hence on phase inversion. Similar recirculation zones could also be possible in agitated vessels in the wake zone of the impeller. However, this is an area where further research is required.

Hossain *et al.* (1983) examined the relationship between the 'dispersion wedge' geometry and phase inversion in mixer-settlers. Here, the 'dispersion wedge' is the shape of the dispersion band which is distributed in the form of a wedge between the two separated phases in a settler. They found that phase inversion is accompanied by either an increase or decrease in the dispersion wedge length, thus affecting the effective settler length. In industrial settlers which seldom operate under steady-state conditions, there is enhanced mutual phase entrainment since the design of the settler involves the dispersion wedge extending across the entire length of the settler. Minimum entrainment is obtained, on the other hand, by ensuring phase stability.

5.4.2 Wetting Characteristics

It has generally been found that the oil-wetted shearing surfaces favoured strongly the formation of oil-continuous dispersions. The surface roughness is said to have a similar effect since it altered the wettability of the plates. Efthimiadu and Moore (1994) investigated the effect of the material on phase inversion in their work on liquid-liquid dispersions in parallel shearing plates. They found that the wettability of the plates by the liquid was the only dominant factor in the determination of the dispersion type when the viscosity difference between the liquids were negligible. By using glass, Perspex and stainless steel in their experiments, they were able to show that a water continuous phase was favoured when the aqueous phase preferentially wetted the plate material and *vice versa*.

Tidhar *et al.* (1986) studied the effect of the surface material of static mixers on phase inversion. Their results based on stainless steel and Teflon mixers showed that the nature of the surface influences the inversion of the system only when the flowrate is low. At high flowrates, the influence of the surface material on phase inversion is less pronounced.

5.4.3 Pipe Inlet Conditions

In the same way the manner in which a dispersion is initialised can affect the phase inversion point in an agitated vessel system, Efthimiadu *et al.* (1994) found that for pipeflow, the pipe inlet conditions can affect the inversion point if they favour the creation of a film on the pipe wall of a phase that wets the wall. The pipe geometry which determines the mode of flow in the pipe can be an important influence on the phase inversion process since the mechanism by which a dispersion is produced is different under laminar and turbulent conditions. These flow conditions were found to have a large effect on the dispersed phase drop size and hence the coalescence and the stability of the drop (Efthimiadu and Moore, 1994).

5.4.4 Viscosity

Similar peaks for the laminar viscosity at phase inversion were observed for pipeflows by Martinez *et al.* (1988), Arirachakaran *et al.* (1989), Pal *et al.* (1986) and Corlett and Hall (1999). Arirachakaran *et al.* found that the mixture viscosity, calculated from their pressure gradient data assuming the flow to be homogeneous, approached the single-

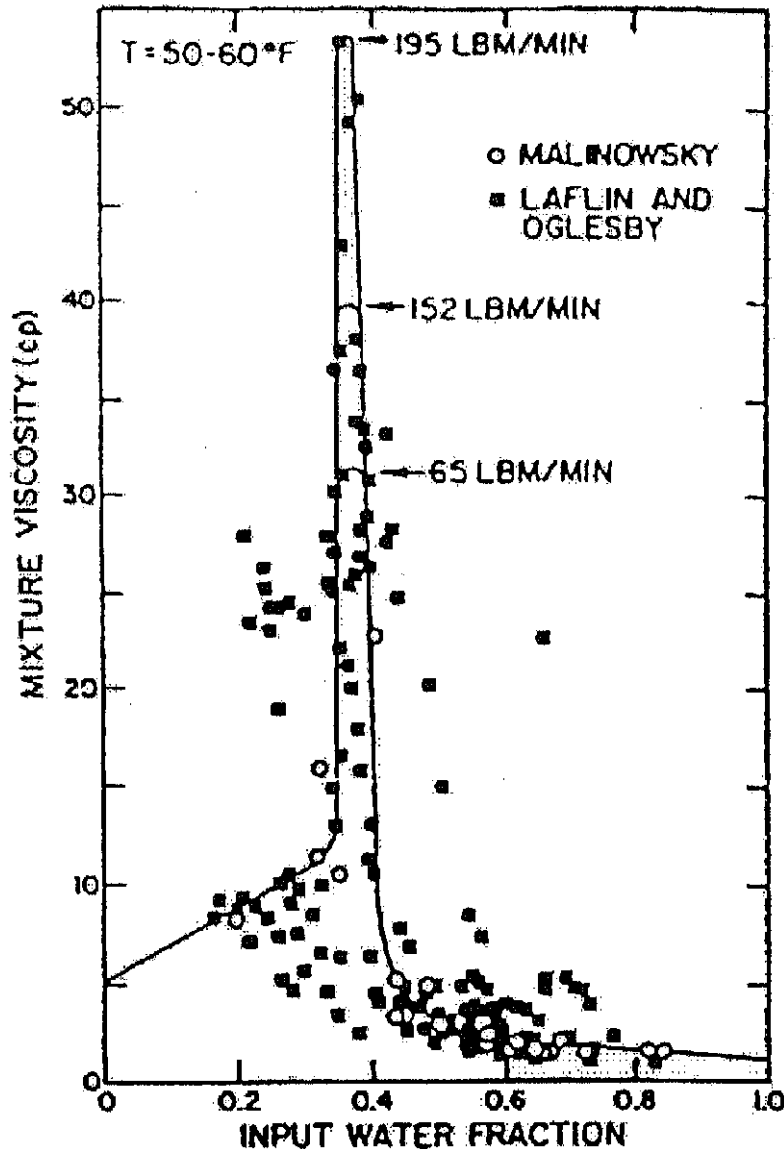


Figure 20 Mixture Viscosity as a Function of Input Water Cut for Low Viscosity Oils (Arirachakaran *et al.*, 1989). Reproduced from 'An Analysis of Oil/Water Flow Phenomena in Horizontal Pipes', Arirachakaran *et al.* (1989), Paper SPE 18836 with the permission of the Society of Petroleum Engineers. Copyright © 1989 Society of Petroleum Engineers Inc.

phase water viscosity when the continuous phase was water. At the inversion point, the maximum viscosity was noted to be of the same magnitude as the single-phase oil viscosity if medium to heavy oils were used. On the other hand, for low oil viscosities they found that the maximum was one order of magnitude higher than the single-phase oil viscosity and attributed this to turbulence in the flow when low viscosity oils were used at the same flowrates. This turbulence caused the oil to disperse into finer drops resulting in a higher mixture viscosity. Pal (1993) attributed the decrease in the viscosity after phase inversion to the effects of dilution. The plot for mixture viscosity as a function of input water cut is given in Figure 20.

5.4.5 Pressure Drop

In the same way that a peak in the mixture viscosity was observed at or in the region of phase inversion for pipeflow, there is a similar peak for the frictional pressure gradient as well. This was observed by all the investigators working on liquid-liquid dispersions flowing in pipes (Charles *et al.*, 1961; Guzhov *et al.*, 1973; Mukherjee *et al.*, 1981; Martinez *et al.*, 1988; Arirachakaran *et al.*, 1989; Nädler and Mewes, 1995b; Soleimani *et al.*, 1997). However, it should be noted that there also exist systems in which the pressure drop increases monotonically with the input water cut up to the inversion point (Valle and Utvik, 1997). In three-phase gas-oil-water flows, shifts in the pressure drop peak corresponding to the inversion point have already been discussed in Section 5.2.

Arirachakaran *et al.* (1989) found that the value for the pressure drop maximum at the inversion point varies with mixture velocity and with oil viscosity, observing that the pressure drop at the inversion point has the same magnitude as the pure single-phase oil pressure drop for the same flow conditions. Nädler and Mewes (1997), on the other hand, observed the abrupt change in the pressure gradient at the inversion point to values of an order of magnitude higher than the pressure drop of pure oil. Martinez *et al.* (1988) also found that the pressure gradient at inversion was substantially higher than that for the pure oil. Mukherjee *et al.* (1981) attributed the pressure gradient peak at inversion to the increase in apparent viscosity of the liquid mixture which peaked in the region where phase inversion occurs.

The pressure drop peak which is associated with phase inversion can often be used to predict the point at which phase inversion occurs. However, care must be taken in this approach because a second pressure drop peak is noticed. Guzhov *et al.* (1973) observed a second pressure drop peak occurring at input oil holdups in the range of 0.8 to 0.9 and assumed it to be due to initial turbulence of the oil phase. Nädler and Mewes (1995b) observed this second peak as well but associated it with a transition from the ambivalence region to oil-in-water dispersions (transition from region III to region V in Figure 18(iii)). After this second pressure gradient peak, the pressure drop was found to decrease down to that for the single-phase flow of water. In systems where high density differences exist between the phases, Valle and Utvik (1997) found unexpectedly that the peak in the pressure drop does not correspond to phase inversion but rather to a transition from oil continuous dispersed flow to stratified flow. It has been suggested that the existence of separated flow is due to the high density differences combined with low water viscosity.

Phase inversion in inclined pipes was studied by Mukherjee *et al.* (1981). They observed that the phase inversion point, as identified by the peak in the pressure drop, was found to lie at input water holdups between 0.4 and 0.5 for all inclination angles except -30° . Phase inversion for that inclination angle was found to occur at input water holdups of 0.7-0.8. This is because this inclination angle coincided with the angle at which the maximum slippage of water past oil occurred, the input water holdup of 0.7 for the inclination angle -30° corresponding to an in-situ water holdup of approximately 0.55. The severe slippage at this inclination angle was also found to be the reason why the frictional pressure gradient was found to be less than those for all other inclination angles.

5.4.6 Temperature

The effects of temperature on phase inversion in pipeflows and in other contacting equipment have not been investigated in detail. In their work on oil-water horizontal flows, Martinez *et al.* (1988) noted that there may be a single temperature at which phase inversion occurs for a given input water holdup and dispersion system, a similar observation to that of Mao and Marsden (1977) which was previously discussed in Section 3.4.7.

5.5 Summary

Whilst phase inversion has been studied extensively in agitated vessels, there is an urgent need for more research into phase inversion as it occurs in pipeflow and in contacting equipment. Physical mechanisms responsible for the occurrence of phase inversion as well as systematic relationships between the various parameters that influence the phase inversion process in these applications have yet to be determined. The widespread occurrence of phase inversion and its substantial effects (e.g. abrupt change in the frictional pressure drop and the rheological characteristics of the dispersion) on processes in these industrial applications justify the concentration of more research effort in this area.

6. CONCLUSIONS

Despite decades of research, phase inversion is still a relatively poorly understood phenomenon. The investigative work on phase inversion has been largely concentrated on agitated vessel systems whereas work in other areas in which phase inversion occurs remains relatively unexplored. While there are certainly many important findings and hypotheses that have been presented, these still need to be verified before any conclusive or definitive theories can be proposed. This is true as well for the vast supply of experimental data that has been gathered. In many instances, observations have been contradictory and limited to the conditions in which the experiments were carried out.

The work to determine the mechanisms by which phase inversion occurs has largely centred on the existence of secondary dispersions, for which the driving mechanism is still subject to debate. Key areas of future research should focus on elucidating and verifying the following issues associated with the role of secondary dispersions in phase inversion:

- The physical mechanism responsible for secondary dispersions;
- The effect of drop electrostatic charge and its role in the formation of secondary dispersions;
- The existence, or non-existence, of water-in-oil-in-water dispersions.

With recent advances in direct flow visualisation techniques, the dynamic visualisation of the actual phase inversion process and in particular the formation and destruction mechanisms of secondary dispersions would undoubtedly provide many clues to unravelling these issues.

There is an inherent difficulty in studying the system parameters in isolation to each other. The tight interrelationships which exist between various parameters could very well be the source of the conflicting views that have been recorded. Viscosity and interfacial tension stand out as possibly the most important parameters that directly affect phase inversion behaviour. However, these parameters have not been studied in detail and much of the ambiguity lies in determining their influence on phase inversion. The study of the system parameters should be focussed on how they would affect the drop interaction processes on a microscopic scale, such as drop coalescence and break-up which are the major mechanisms influencing phase inversion. Although there are a number of models for the collision frequency, coalescence efficiency and drop break-up, improved models based on an understanding of the process are urgently required.

There have been few computational studies to predict phase inversion holdup. There are even fewer deterministic models that have been derived from the fundamental physics governing the phase inversion process. Whilst stochastic models have their use, deterministic models that incorporate drop interaction and secondary dispersion effects would be highly attractive since they provide insight into the mechanisms that govern phase inversion.

Phase inversion is still very much an active field of research. There are many aspects of phase inversion in which little is understood. Urgent work is therefore required in order to gain a better understanding of phase inversion and its associated phenomena. Perhaps with the advances into crucial areas of research which have been identified above, a unified and conclusive view on the mechanism of phase inversion can be elucidated.

NOMENCLATURE

Symbol		Unit
a	Static mixer area per unit volume	m^2/m^3
A	Pipe cross-sectional area	m^2
C, C_1	Constants in equations (5.13) and (5.5) respectively	
C'	Multiplier in the Blasius type equation described in equation (5.3)	
C_o'	Multiplier in the Blasius type equation described in equation (5.3) for the oil phase	
C_w'	Multiplier in the Blasius type equation described in equation (5.3) for the water phase	
d	Internal pipe diameter	
D_I	Impeller diameter	cm or m
D_H	Mixer hydraulic diameter	m
D_{tr}	Turbulent diffusion coefficient to characterise the	m^2/s

	eddy diffusion in a turbulent field	
F	Friction factor	
Fr_I	Impeller Froude number	
g	Gravitational acceleration	m/s^2
k_1, k_2	Parameters in equation (5.4)	
K	Dimensional constant defined by equation (3.2)	
K'	Dimensional proportionality constant characteristic of the agitator	
	type used in equation (4.8)	
K_1, K_2, K_3	Coalescence constants in equations (4.3), (4.4) and (4.5)	
n	Parameter in the Blasius type equation described in equation (5.3)	
n_o	Parameter in the Blasius type equation described in equation (5.3) for the oil phase	
n_w	Parameter in the Blasius type equation described in equation (5.3) for the water phase	
N	Impeller speed	r.p.m. or s^{-1}
N_C	Coalescence frequency/rate	s^{-1}
N_d	Total number of drops.	
N_T	Collision frequency	s^{-1}
p	Drop size	m
P	Rate of energy input	W
R	Phase ratio	
Re	Reynolds number	
Re_I	Impeller Reynolds number	
Re_i	Superficial Reynolds number for phase i	
t	Time	s
$t_{contact}$	Contact time between the colliding drops	s
t_{drain}	Film drainage time	s
t_I	Time required for inversion	s
v, v'	Drop volume	cm^3
v_m	Superficial liquid mixture velocity	m/s
v_T	Total velocity of the dispersion	m/s
V	Volume of vessel or compartment of contactor	m^3
\dot{V}_c	Volumetric flow of the continuous phase	m^3/s
\dot{V}_d	Volumetric flow of the dispersed phase	m^3/s
\dot{V}_H	Volumetric flow of the heavy phase	m^3/s
\dot{V}_L	Volumetric flow of the light phase	m^3/s
W	Width of ambivalent region	
We	Weber number	
We_I	Impeller Weber number	

Greek Symbol		Unit
α	Constant defined by equation (3.1)	
α'	Dimensional constant in equation (4.13)	
$\Delta\rho$	Density difference	kg/m^3
$\bar{\varepsilon}$	Mean energy input per unit mass	J/kg
ε_d	Holdup of the dispersed phase	
η_c	Viscosity of the continuous phase	$\text{cp, Pa}\cdot\text{s or g/cm}\cdot\text{s}$
η_d	Viscosity of the dispersed phase	$\text{cp or Pa}\cdot\text{s}$
η_H	Viscosity of the heavy phases	cp
η_L	Viscosity of the light phases	cp
η_m	Mixture viscosity	$\text{Pa}\cdot\text{s}$
η_o	Oil viscosity	cp or Pas
η_w	Water viscosity	$\text{Pa}\cdot\text{s}$
η_Y	Interfacial viscosity	$\text{cp or Pa}\cdot\text{s}$
θ	Parameter defined by equation (5.12)	
$\lambda, \lambda_1, \lambda_2$	Coalescence efficiencies defined by equations (4.4), (4.5) and (4.6)	
λ'	Eddy length	m
ν_A	Kinematic viscosity of hydrocarbon phase <i>A</i>	m^2/s
ν_B	Kinematic viscosity of polar phase <i>B</i>	m^2/s
ρ_c	Density of the continuous phase	$\text{kg/m}^3 \text{ or g/cm}^3$
ρ_d	Density of the dispersed phase	kg/m^3
ρ_H	Density of the heavy phase	kg/m^3
ρ_L	Density of the light phase	kg/m^3
ρ_m	Volume fraction mean mixture density	kg/m^3
ρ_o	Density of the oil phase	kg/m^3
ρ_w	Density of the water phase	kg/m^3
σ	Interfacial tension	N/m or dynes/cm
ϕ_d	Dispersed phase holdup	
ϕ_o	Organic phase holdup	
$\phi_{d,i}$	Dispersed phase holdup at the phase inversion point	
$\phi_{o,i}^U$	Dispersed organic phase holdup for the upper inversion curve	
$\phi_{o,i}^L$	Dispersed organic phase holdup for the lower inversion curve	
$\phi_{o,i}'$	Asymptotic phase holdup of the organic dispersed phase at inversion (for high impeller speeds)	
$\phi_{w,i}$	Input water fraction required to invert an oil-water dispersion system	
φ	Contact angle	rad.

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