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Manuscript received February 20, 1978; revision received December 7, and accepted January 3, 1979.

Analysis of the Phase Inversion Characteristics of Liquid-Liquid Dispersions

Correlations of the collision frequency and the coalescence frequency of an agitated dispersion are combined with models relating drop sizes and hold-up to agitator speed, to predict the ambivalence range and phase inversion composition of liquid-liquid dispersions. Our model was tested by comparing predicted and experimental phase inversion compositions of the systems toluene-water and carbon tetrachloride-water. In addition, the predicted results have been compared with published results for the system kerosene-water, and in all cases, agreement between predicted and experimental results are excellent.

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Liquid-liquid dispersions are generated in solvent extraction operations, direct contact heat exchangers and in two-phase chemical reactors. The identification of the dispersed phase under all conditions and the limits of stability of these heterogeneous mixtures are most important in these process operations. Hitherto, the limits of the ambivalence range and the phase inversion concentrations have been treated qualitatively, and there has been no attempt to predict either limit or assess the effect of agitator speed and the physical properties of the system on the inversion characteristics. In this article, phase inversion is analyzed in terms of the collision frequency and coalescence frequency of agitated dispersions. It was possible to combine models of these two phenomena with the effects of disperse phase hold-up on drop size, to accurately predict the ambivalence range and the phase inversion compositions.

CONCLUSIONS AND SIGNIFICANCE

The collision frequency and the coalescence frequency of agitated dispersions have been studied extensively, and both have been found to depend on the turbulence level of the agitation, the disperse phase hold-up, and the physical properties of the system. These phenomena can be combined to accurately predict the ambivalence range and the phase inversion concentration. Thus the ambivalence range can vary from 20% dispersed to 90%, depending on how the dispersion was produced. Recently, Arnold (1975) showed that a solvent extractor operates most efficiently under sequential phase inversion conditions. Therefore, it is necessary to be able to predict the ambivalence range and the phase inversion concentrations, and the model presented here has been tested on two systems of widely different physical properties, together with a third studied qualitatively by another researcher (Ali 1969). We found that the ambivalence range and the phase inversion concentration can be predicted accurately as a function of agitator speed, dispersed phase hold-up and the physical properties of the system. This has significance in the design and operation of extraction equipment, direct contact heat exchangers, and two-phase liquid-liquid reactors.

Characterization of a liquid-liquid dispersion is an important requirement in many industrial chemical engineering operations such as solvent extraction, direct contact heat exchangers, and batch and continuous heterogeneous reactors. These dispersions are produced by injecting one phase through a distributor into the second phase, or mechanically agitating the two phases in the equipment in

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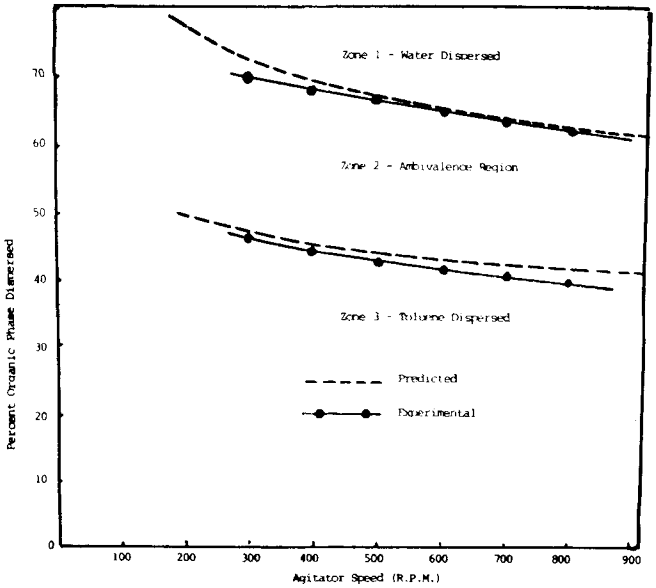

Figure 1. Ambivalence range for system toluene-water.

which the dispersion is to reside. If the energy transmitted to the liquid-liquid system is large, very small drops of the dispersed phase are produced and a metastable emulsion could result, but in the majority of chemical engineering operations this is unlikely and undesirable. In most process operations of the types cited above, a large interfacial area between the phases is essential. This may be achieved by applying mechanical energy to produce small droplets, or by adjusting the phase ratio to increase the number of droplets, albeit larger droplets. In practice, the adjustment of the phase ratio is generally more preferable, because of the subsequent inherent difficulties associated with the phase separation of dispersions consisting of small drops (for example, secondary dispersions). There are, however, limits to which one liquid phase can be dispersed in another. If the droplets remained spherical, the maximum volume fraction of the dispersed phase would correspond to Ostwald's ratio, but because of distortion of the drops in the dispersion, phase inversion ratios in excess of 90% have been reported. Phase inversion is generally presented graphically by plotting the volume fraction of the dispersed phase in the heterogeneous mixture at inversion against the speed of the agitator. A typical plot is shown in Figure 1 for the system water-toluene.

In this figure, two curves separate three zones. These are:

Zone 1—in which the composition of the mixture and agitation rate are such that only water can exist as the dispersed phase.

Zone 3—in which the mixture composition and agitation rate are such that only toluene can exist as the dispersed phase.

Zone 2—where either phase can be dispersed. In Zone 2 the phase dispersed depends on the method by which the dispersion was formed. The difference in the composition of the dispersed phase in this zone, at any agitation rate, is generally termed the "ambivalence range." All agitated heterogeneous liquid-liquid systems exhibit this hysteresis region and, although there are several studies of this phenomenon (Sawistowski 1971, McClarey & Mansoori 1978) no attempt has been made to quantify the parameters controlling phase inversion. We considered this essential, because it has been observed that phase inversion phenomena has a pronounced effect on the performance of mechanically agitated extraction columns (Arnold 1975, Al-Saadi 1978). Therefore we initiated an investigation to identify properties of the system that control the phase inversion characteristics of a heterogeneous liquid mixture in an agitated environment. The results obtained follow.

MATHEMATICAL MODEL

Consider a heterogeneous liquid-liquid mixture to be agitated in a tank of suitable dimensions so that 1) isotropic turbulence persists throughout its contents and that 2) the energy input is sufficient to produce and maintain a dispersion in the tank. When steady state is attained, there will be equilibrium between the kinetic energy transmitted from the agitator causing drop break-up, and the energy of adhesion inducing the drops to coalesce (Shinnar 1960).

Both the break-up and coalescence processes proceed simultaneously throughout the contents of the tank, if the turbulence is isotropic. This will manifest itself through frequent collisions of adjacent drops, and some coalescence will result. Under these conditions, the smaller drops will be coalescing and the larger drops will be breaking up. The scale of turbulence will be such that the collision frequency of the drops in the turbulent regime may be estimated from the expression deduced by Levich (1962). Thus, following Misek (1964) for drops of initial size p, the frequency of collision N_T is

$$N_T = \frac{\rho_d n^2 \epsilon_0^{3/4} p^4}{\rho_c \nu_c^{5/4}} \tag{1}$$

where n is the number of drops per unit volume. Other terms are identified in the nomenclature.

$$n = \frac{6\cdot\phi}{\pi\cdot p^3} \tag{2}$$

The energy per unit volume of mixture transmitted to the liquids is proportional to the density of the continuous phase and the agitator speed, or

$$\epsilon_0 = k_1 \rho_c N^3 \tag{3}$$

where k_1 is the proportionality constant. Substituting Equations (2) and (3) into Equation (1), and introducing the viscosity ratio to allow for the shearing effect of turbulence on the drops in the turbulent field, gives

$$N_T = \frac{K\cdot\phi^2\cdot\mu_d\cdot\rho_d\cdot\rho_c N^{9/4}}{p^2\cdot\mu_c^{9/4}} \tag{4}$$

where $K = 3.65\ k_1^{3/4}$, and k_1 is a constant characteristic of the type of agitator.

The coalescence frequency of drops in a dispersion in an agitated tank has been studied by Howarth (1967), who stated that the coalescence frequency could be estimated by

$$N_c = \frac{6.0\phi[dp/d\theta]}{(2.0 - 2.0^{0.667})p^4} \tag{5}$$

Howarth found that the rate of change of drop size with time following a disturbance was proportional to $N^{1.9\text{-}2.25}$ for agitator speeds in the range 200-400 rpm. Whereas, Maddern and Damerell (1962) found that the coalescence frequency dependence on agitator speed was proportional to $N^{1.5\text{-}3.3}$. This range of the exponent of the agitator speed agrees with the tabulated results of Miller (1963). Extrapolating Miller's results for a turbine agitator and dispersed phase hold-up's greater than 60% gives an exponent of 1.8. That is,

$$\frac{dp}{d\theta} \propto N^{1.8} \tag{6}$$

is the most suitable relationship to substitute into Equation (5) for the variation of drop size with time following a disturbance.

The steady state drop size is a function of both the agitator speed and the dispersed phase hold-up, and the effects of hold-up on drop size have been the subject of a large number of research studies. These are summarized by Tavlarides and Coulaloglou (1976) who stated that the different correlations proposed are equally valid, within the limits of their derivation. The correlations of Thornton and Bouyotiotes (1967) will be applied to estimate the mean drop size at different dispersed phase hold-ups. Thornton and Bouyotiotis showed that the sauter mean drop size at hold-up ϕ is related to the sauter mean drop size at zero hold-up by

$$p = p_0 + m\phi \tag{7}$$

where m is related to the physical properties by

$$m = k_2 \left(\frac{\sigma}{\mu_c{}^2 g} \right) \left(\frac{\Delta\rho\sigma^3}{\mu_c{}^4 g} \right)^{-0.62} \left(\frac{\Delta\rho}{\rho_c} \right)^{0.05} \tag{8}$$

and where k_2 is a geometric constant.
These authors further showed that the drop size at zero hold-up p_0 could be correlated by the expression

$$\left(\frac{p_0 \cdot \rho_c{}^2 \cdot g}{\mu_c{}^3} \right) = 29.0 \left(\frac{P_0{}^3 \cdot g_c}{\rho_c{}^2 \cdot \mu_c \cdot g^4} \right)^{-0.32} \left(\frac{\rho_c \cdot \sigma^3}{\mu_c{}^4 \cdot g} \right)^{0.14} \tag{9}$$

Replacing P_0 by $(k_1 \rho_c N^3)$ and converting to SI units, and then rearranging Equation (9) gives

$$P_0 = k_3 \cdot m_1 N^{-2.88} \tag{10}$$

where the parameter m_1 is correlated to be

$$m_1 = \left(\frac{\mu_c{}^3}{\rho_c{}^2 \cdot g} \right) \left(\frac{\rho_c \cdot \sigma^3}{\mu_c{}^4 \cdot g} \right)^{0.14} \left(\frac{\rho_c}{\mu_c \cdot g^4} \right)^{-0.32} \tag{11}$$

Combining Equations (7) and (10) leads to

$$p = k_3 \cdot m_1 N^{-2.88} + m\phi \tag{12}$$

Expressions similar to Equation (12) can be developed from many of the other correlations quoted by Tavlarides (1976).

When the dispersion is agitated, the drops will collide and some will coalesce. As the disperse phase hold-up increases, at constant agitator speed, the proportion of the pairs of drops coalescing at each collision will increase until, at phase inversion, coalescence will occur at every collision. That is when coalescence frequency is equal to collision frequency, and phase inversion occurs, or when N_T in Equation (4) is equal to N_c in Equation (5). Let the ratio (N_c/N_T) be T or

$$T = \frac{K}{\phi p^2 N^{0.46}} \tag{13}$$

By Equation (13), phase inversion occurs when $T = 1.0$, and the inversion composition for any system should be capable of predicting from Equations (12) and (13) for the condition $T = 1.0$.

EXPERIMENTAL

Batch phase inversion studies were performed in a 0.102 m diameter round bottom glass vessel 0.102 m high, containing four equally spaced stainless steel baffles, 0.01 m wide. The tank's contents were agitated by a four blade stainless steel open turbine, 0.05 m diameter. It is powered by a 10 kW electric motor with a variable speed attachment, and is capable of a maximum agitator speed of 800 rpm. The agitator speed was kept constant during each phase inversion test, and was monitored by an electronic tachometer.

Phase inversion was detected by inserting two electrodes into the side walls of the glass mixing vessel; the inversion point could be detected very accurately by violent deflection of the ammeter placed in the electrode circuit.

SYSTEMS STUDIED

Two immiscible liquid systems were studied: toluene-water, and carbon tetrachloride-water. The toluene and carbon tetrachloride were both of G.P.R. grade and mixed with deionized distilled water until they were saturated. This was accomplished by agitating each organic liquid with the water in an aspirator bottle for three days at 25°C. When the phases had been saturated, the relevant physical properties of each were determined by the usual methods.

EXPERIMENTAL TECHNIQUE

The mixing vessel and all the measuring cylinders used for the experimental work were thoroughly cleaned by soaking in a 1.0% Decon solution overnight, then by rinsing with hot running water, and finally with deionized distilled water. The mixing vessel was cleaned after each six experiments, and the purity of each system studied was tested by immersing 400 mL of each phase in the mixing vessel, agitating at 450 rpm for ten minutes and then switching off the agitator. Time taken for the dispersion to collapse to a clear interface was determined. This time was compared with that for fresh liquids, and if there was a 5.0% deviation from the original value, the particular mixture was rejected and replaced.

Phase inversion experiments were performed by placing the continuous phase in the mixing vessel until the impeller was immersed; the continuous phase volume was noted. Usually this was of the order of 500 mL. The impeller was then started and its speed adjusted to that desired for the particular experiment. After this, small quantities of the dispersed phase were added at frequent intervals to produce a dispersion occupying 800 mL total volume. The phase ratio was then periodically adjusted by adding or removing 3.0 mL portions of either phase, until phase inversion was observed. After phase inversion, the agitator was stopped and the volume of each phase ascertained.

Experiments were conducted at agitator speeds between 300 and 800 rpm. The results are presented in Figures 1 and 2, for the systems toluene-water and carbon tetrachloride-water, respectively.

During a number of experiments, the variation in drop size with hold-up was estimated, and the Thornton-Bouyotiotes correlation up to phase inversion was tested by taking photographs of the dispersion with a 35 mm camera. The photographs were evaluated on a Zeiss particle counter. These results are presented in Figure 3.

RESULTS

In all experiments, we observed that the variation in drop size with hold-up conformed to the Thornton-Bouyotiotes correlation close-up to the phase inversion concentration. But, in the vicinity of phase inversion, the

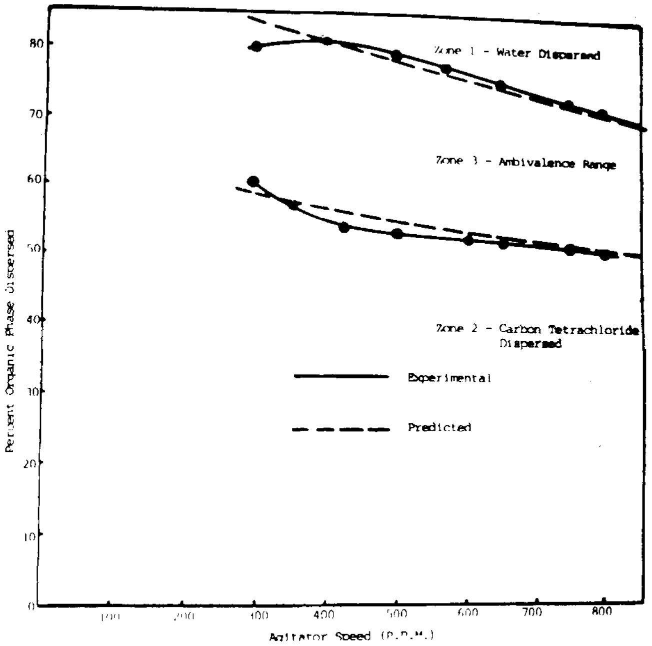

Figure 2. Ambivalence limits for the system carbon tetrachloride-water.

drop size increased rapidly with very small additions of the dispersed phase. Immediately prior to phase inversion, globules of the dispersed phase were discharged from the periphery of the impeller region. This could be expected, since in this region of the mixing vessel, rapidly moving drops discharged from the impeller come into contact with the slower moving dispersion near the walls of the mixer. Phase inversion followed rapidly after these conditions were passed. Still, while the actual phase inversion process was much more abrupt at slow agitator speeds than at high speeds, in all experiments the change occurred quite fast and was accompanied by violent fluctuations through the vessel.

The model describing phase inversion was tested on the two systems studied. In addition, the data of Ali (1969) for the system kerosene-water were also analyzed. Results for this system are presented in Figure 4. The constants in Equations (12) and (13) were evaluated for one experimental result for each system, and these are presented in Table 1. The values of the constants so obtained were then inserted into all the other results. Equations (8), (11), (12) and (13) were solved by an appropriate computer program (Arashmid 1979), and all the results

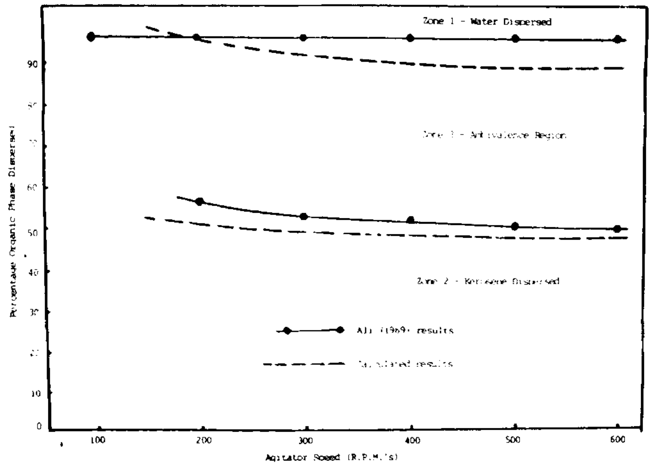

Figure 4. Ambivalence range for the system kerosene-water.

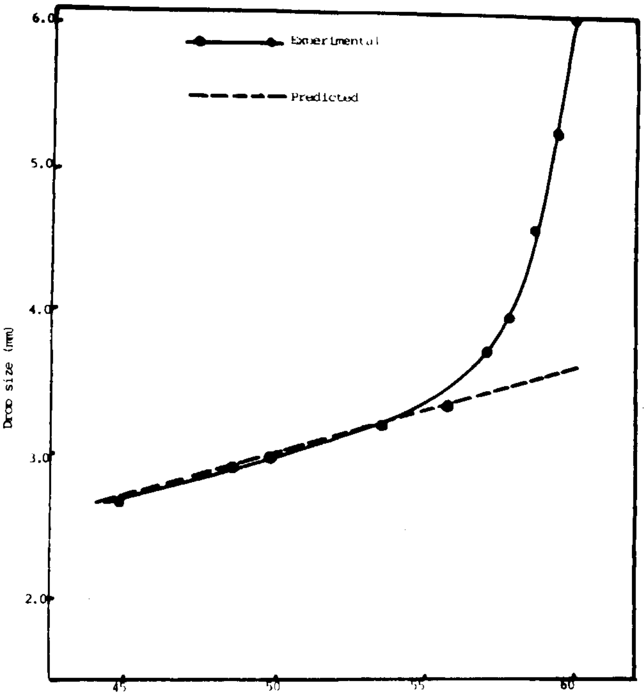

Figure 3. Drop size vs. dispersed phase hold-up for an agitator speed of 400 rpm.

Table 1. Overall Constant for Prediction of Phase Inversion

Dispersed phase	Continuous phase	K
Water	Toluene	2.62×10^5
Water	Carbon tetrachloride	6.85×10^4
Water	Kerosene	1.83×10^{-3}
Toluene	Water	2.91×10^4
Carbon tetrachloride	Water	9.75×10^4
Kerosene	Water	6.09×10^7

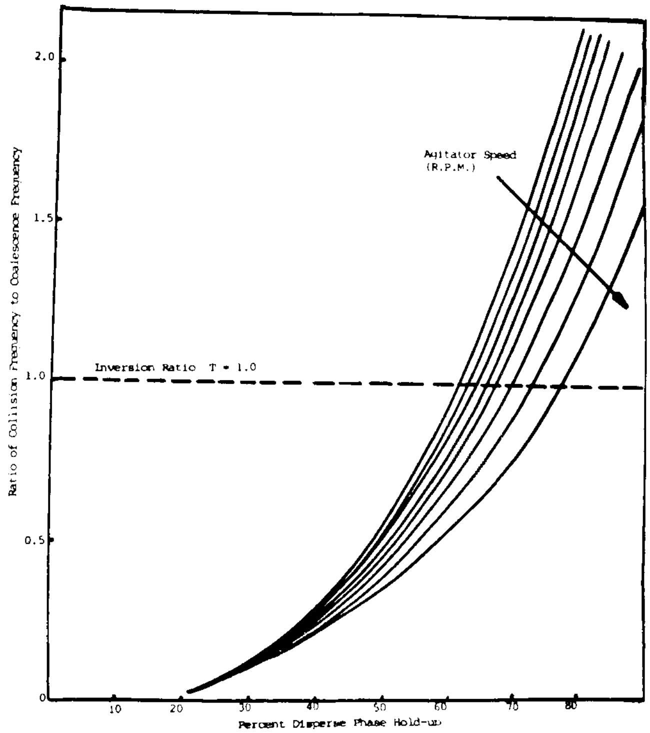

Figure 5. Variation of collision frequency/coalescence frequency with dispersed phase hold-up and agitator speed.

calculated for the three systems are shown in Figures 1, 2 and 4, where they can be compared with the experimental results.

Variation in the value of T with the volume fraction dispersed for the system toluene-water, with toluene dispersed, is plotted in Figure 5, using agitator speed as parameter. The line for "$T = 1.0$" is also shown, and the abscissa for the intersection of this line with each curve gives the inversion point. Corresponding plots for the other systems studied here have been prepared by Arashmid (1979). The points obtained from this type of curve were then transferred to the normal phase inversion curve as shown in Figures 1, 2 and 4. In all cases, the agreement between the predicted phase inversion curve and the experimental curve is exceptionally good. The difference between the experimental and predicted inversion concentration was generally less than 2.0% volume fraction. The greatest difference was observed with the system carbon tetrachloride-water with water dispersed. In that case, differences of the order of 4% were observed. Generally better agreement was obtained when the organic liquid was dispersed, and improved agreement can be seen for each system as the agitator speed increases.

NOTATION

g = gravity acceleration constant
k_1 = proportionality constant characteristic of the agitator
k_3 = combined constant in drop size equation
m = gradient of drop size vs. hold-up relationship
m_1 = parameter correlated by Equation (11)
n = number of drops per unit volume
N = agitator speed in rpm
N_c = coalescence frequency
N_T = collision frequency
p = drop size
p_0 = drop size at zero hold-up
P_0 = power transmitted by agitator
T = ratio of N_c/N_T

Greek Symbols

ζ = energy of turbulence
ν_c = kinematic viscosity of continuous phase
ρ_c = density of continuous phase
ρ_d = density of dispersed phase
θ = time
μ_c = viscosity of continuous phase
μ_d = viscosity of dispersed phase
ϕ = fractional hold-up of dispersed phase

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Manuscript received March 21, 1979; revision received August 2, and accepted August 30, 1979.

Effectiveness and Deactivation of a Diluted Catalyst Pellet

In this article, we analyze the performance of a diluted catalyst pellet consisting of inert and active particles, under diffusion influenced conditions and pore-mouth poisoning. First, we establish the requirements for validity of the analytical solutions of the diluted pellet equations. Secondly, we show that, under pore-mouth poisoning conditions, a diluted pellet can display considerably longer lifetimes than a uniformly impregnated catalyst. Conversely, for the same lifetime, use of a diluted pellet can result in savings of the catalytic agent. These advantages are not offset by difficulties in catalyst manufacture, as is the case for previous designs.

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SCOPE

Many catalytic processes of industrial importance operate in the temperature region where the reaction is essentially diffusion controlled, and only a small fraction of total catalyst volume is effective in the reaction. In situations where shell-progressive or pore-mouth type poisoning describes the deactivation process, the catalyst may suffer a precipitous decline in activity by virtue of the fact that

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