FACTORS AFFECTING THE PHASE INVERSION OF DISPERSED IMMISCIBLE LIQUID-LIQUID MIXTURES

An experimental technique is devised through which effect of various factors on phase inversion of agitated, immiscible, organic -aqueous liquid systems are studied. The factors which are established to be effective on phase inversion are temperature, density difference, and viscosity difference, between the mixed phases. The nature of the effect of these factors on phase inversion is determined through this experimental technique. It is concluded that other factors, which may include wettabilities of phases with the container surface at low mixing speeds, would also be responsible for some of the unusual behavior of phase inversions.

Michael J. McClarey and G. Ali Mansoori

When two immiscible liquids are mixed in a stirred tank, one of the liquids breaks up in the form of droplets suspended in the continuum of the other liquid. The liquid which is in the form of droplets is known as the dispersed phase, and the continuum liquid is known as the continuous phase. The mixing of immiscible liquids to form dispersion is important in several chemical engineering processes. Solvent extraction, heterogeneous liquid-liquid reactions, and interfacial heat transfer are examples cited (2 to 3). Dispersion increases the interfacial area available for the required interfacial transfer operation, and as a result it enhances the rate of these processes. Phase inversion is the transition from one phase dispersed to the other. Knowledge of the conditions under which the phase inversion occurs is important in the design of the contactors and the separators of the immiscible liquids for interfacial processes.

Factors which may influence the phase inversion include the volume ratio of the stirred immiscible liquids, their density difference, viscosities, interfacial tension, and agitator speed. Impeller position, number, and shape, geometry of the mixing vessel, and finally temperature, owing to its effect on the properties of the stirred liquids, may also be effective on the phase inversion. In previous developments concerning the area of dispersion, the dependence of the dispersion shift on some of the factors mentioned above is established. However, the effect of the other factors on the phase inversion is either not established or the conclusions drawn are contradictory, resulting from different conditions at which the experiments were performed. In the present report, an experimental technique is introduced enabling the possibility of singling out the effects of some of the factors mentioned above on the phase inversion.

It has been demonstrated that the location, number, and shape of the impellers are effective on the phase inversion of stirred, immiscible liquids. In the work reported here, the effect of impeller position and number on the phase inversion is eliminated. This is achieved by placing a number of simple, two-bladed impellers in a mixing vessel and varying the number of impellers used until the results are insensitive to the increase of the number of impellers. It is shown that the magnitude of the density difference between the two immiscible liquid phases has a profound effect on the stability of the phase inversion. The effect of impeller speed and temperature on the phase inversion is demonstrated graphically for systems with negligible density difference between two phases. With the increase of impeller speed at a constant temperature, the phase inversion occurs at higher fractions of the aqueous phase. Also, the phase inversion moves toward higher fractions of the aqueous phase with an increase of temperature at a
constant impeller speed. The effect of viscosity difference on the phase inversion is demonstrated by performing experiments on equal density, binary, immiscible systems with and without zero viscosity difference between the two phases. The viscosity difference between the phases is shown to be very effective on the phase inversion and the ambivalence range of the mixed, immiscible, liquid-liquid systems. It is also found that while the magnitude of the interfacial tension might be effective on the width of the ambivalence range of mixed immiscible liquid-liquid systems, the effect of the anisotropic properties of the two phases, such as the polarity difference, on the ambivalence range can not be overlooked.

BACKGROUND AND OBJECTIVE

The previous work in the area of immiscible liquid-liquid dispersion has dealt primarily with the application of one impeller immersed in either of the immiscible liquid phases or at the interface of the two phases. It has been concluded that with the application of one impeller, the phase in which the agitator impeller is placed would at rest be the continuous phase during the mixing (3 to 10). Provided that the volume ratios of the two phases are within the range of 1:3 to 3:1. If the impeller is located at the liquid-liquid interface, either of the phases could be dispersed; seemingly, there is no way to predict which phase would be the dispersed phase (10). Quinn and Sigloh reported that when the impeller is located at the interface, the aqueous phase is the continuous phase for binary systems of water and SAE 10 or SAE 30 motor oil, and the organic phase is the continuous phase for the kerosene-water system (4). In other cases, it is found that when the impeller is located at the liquid-liquid interface, usually one phase is dispersed at low impeller speeds while the other phase is dispersed at high impeller speeds (3, 8, 10). Quinn and Sigloh carried out a series of experiments in which they attempted to eliminate the effect of impeller position on the phase inversion. To obtain results, a mixing vessel was used whereupon one impeller was centered in the upper half of the vessel on the agitator shaft and another impeller centered in the lower half of the shaft. Through the above system the effect of the impeller speeds on the phase inversion of several binary immiscible liquid-liquid systems were investigated. Quinn and Sigloh reported that at low agitator speeds, an organic continuous phase and an aqueous continuous phase could be identified; one in the upper portion and the other in the lower portion of the mixing vessel. This two-phase dispersion persisted up to the agitator speed of 400 rev/min, at which point the dispersion became uniform. Their results, however, were not completely reproducible, and the dispersions were not uniform except at high impeller speeds, Yeh et al. (11) attempted to eliminate the effect of the impeller position and geometry on the phase inversion by producing liquid-liquid dispersion in a flask by shaking the flask manually. However, the intensity of the mixing was uncontrollable, and the nature of the dispersion had to be determined visually.

The effect of agitator speed on the phase inversion has been studied by several investigators (7, 8). It has been found that the power input for mixing is related to the cube of mixing speed and that if the agitator speed is increased, inversion of a dispersion may occur. It is also understood that for most liquid-liquid systems, the stable dispersion at low impeller speeds is the organic phase dispersed in the aqueous phase, and, as the impeller speed is increased, the system would invert to the aqueous phase dispersed in the organic phase. The above results were obtained with the system starting from rest for each agitator speed. Through a series of experiments in which impeller speed was changed without stopping the system, Selker and Sleicher (9) found that once a dispersion had formed, changing impeller position or speed would not cause phase inversion to occur. This holds true if the phases are not permitted to settle.

It has been observed that it is difficult to produce a dispersion containing more than 75% by volume of the dispersed phase (9, 11). In the range from 25 to 75% by volume, either phase can be dispersed, depending on the other conditions. The presumption behind this is that the closest packing of the spherical droplets of the dispersed phase occurs when the dispersed phase volume fraction is about 74% of the total volume. As a result, the coalescence of the droplets will occur. In reality, the dispersion with higher percentage volumes of the dispersed phase can be obtained because the droplets of the dispersed phase are not necessarily spherical, and also the droplet sizes are not uniform (11). Other factors which may influence these proportions to the extent that dispersions containing more than 75% by volume of the dispersed phase may be achieved include large viscosity difference between the phases, the presence of surface-active agents in the system, and the low interfacial tension between the phases (3, 5). The range of volumes in which the phase inversion may occur is called the ambivalence range.

It is understood that the phase inversion of agitated, immiscible, liquid-liquid systems generally depends on the fluid properties. Treybal (3) noted that a large density difference between the aqueous phase and the organic phase makes the dispersion more difficult to achieve, or it takes more stirring power to achieve a homogeneous dispersion in a system having a large density difference between the mixed phases. Selker and Sleicher (9) observed that as the viscosity of a phase increases, its tendency to be dispersed also increases. A large ratio of the dispersed phase viscosity to the continuous phase viscosity can cause dual dispersions (part of the continuous phase encapsulated as small droplets within larger drops of the dispersed phase) to occur (3, 6).

The effect of interfacial tension on the phase inversion is not fully realized. It is generally understood that if no other forces are present, interfacial tension would cause the phase inversions to occur only for equi-volume mixtures of immiscible liquids (9, 11).

The presence of impurities may exert great influence on the dispersion and cause the ambivalence range to be larger than it would be if pure liquids are used (3, 9). Dust particles usually accumulate at the liquid-liquid interface and may affect the
phase inversion of mixed immiscible liquids (2). It is noted that the liquid-liquid interface will contain a dull gray film if contaminated (7, 8). If the liquids are pure, the interface will mirrorlike with distinct and regular meniscus at the walls of the tank, around the baffles, and around the impellers.

In the present report, a method is presented in order to eliminate the effect of the agitator number and position on the phase inversion of binary, agitated, immiscible, liquid-liquid systems. Attempts are made to explain the effects of density difference, viscosity difference, temperature, and the other possible factors relating to the phase inversion.

THE TWO-PHASE DISPERSION SYSTEM

In order to devise a technique for systematic analysis of the effects of different factors on phase inversion, an experimental apparatus was set up (12). For this apparatus, the mixing vessel used was a 2000 ml glass beaker, equipped with a removable four-blade stainless steel baffle assembly. The beaker had a 12.7 cm diameter, and 1500 ml of liquid filled the beaker to a height of 12.6 cm. The baffle blades used were 2 cm wide, 2 mm thick, and 15 cm long. The experiments were performed with the application of different numbers of stainless steel two-bladed impellers for mixing the phases. The blades of half of the impellers used were +60 deg inclined from the horizontal plane, and the blades of the other half of the impellers used were −60 deg inclined from the horizontal plane. +60 deg inclined blade impellers were used in the lower portion of the mixing vessel, and the −60 deg inclined blade impellers were used in the upper portion. As a result of this assembly, the lower portion impellers were pushing the fluid upward, and the upper portion impellers were pushing the fluid downward when rotated clockwise. The dimensions of the impellers are given in Figure 1.

The impeller shaft was driven by a 600 rev/min synchronous motor through a step-function speed reducer, which allowed for mixing speeds of 60 to 600 rev/min, with 60 rev/min intervals. The mixing system was immersed in a constant temperature water bath during all the runs.

By measuring the electrical conductivity of the immiscible liquid-liquid mixture, the dispersed phase and the continuous phase were distinguished, each from the other. For measuring the electrical conductivity, two copper plates with 1.8 X 1.8 cm dimensions, spaced 9 cm apart, were used. The conductivity probe was assembled on a movable support enabling its position, with respect to the height of the vessel, to be changed during a run. This setup allowed for the possibility of checking to determine whether or not the dispersion was uniform with respect to the height of the mixing vessel.

The chemicals used for the preparation of the immiscible phases consisted of distilled water, sodium dichromate (Baker, 3672), benzene (Mallinckrodt, 3856), carbon tetrachloride (Fisher, C-199), kerosene (Texaco Crystallite, LO314-3), and-silicon oil (Dow Corning 200 Fluid).

For all the experiments carried out, the total volume of the liquid system was chosen to be 1500 ml. The temperature was kept constant during the experimentation by a controlled temperature water bath. In the majority of the experiments performed, a dilute sodium dichromate solution (1.2 g of Na₂Cr₂O₇·2H₂O in 1000 ml) was used for the aqueous phase, while the organic phase was varied. The addition of a small amount of sodium dichromate to the aqueous phase increased the contrast between the conductivities of the two mixed phases, and as a result the recognition of the phase inversion was clearer.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of the experimental work are reported in Figures 2 to 7. In all these figures, volume fraction of organic phase vs. revolutions per minute is plotted for different mixtures with constant total volume of 1500 ml and at different conditions.

In eliminating the effect of the agitator position and number on the phase inversion, different experiments were performed with different numbers of impellers ranging from 2 to 12. The impellers were placed in equal distances from the liquid-liquid interface while at rest, both in the upper and in the lower portions of the mixing vessel, and in helical form. It was found that for smaller number of impellers, up to six, the phase inversion was dependent on the impeller number. When eight, ten, or twelve impellers were used, the phase inversion became insensitive to the number of impellers. Accordingly, ten impellers were chosen for all the experiments which were performed and reported here.

Depending on the manner by which the dispersion of a binary immiscible liquid-liquid system is initiated, one may
recognize three different phase inversion curves. We may call these three curves the upper inversion curve, the lower-inversion curve, and the intermediate inversion curve. The upper inversion curve is obtained by keeping the agitator speed and the volume of one of the liquid phases (the continuous phase) constant, while the second liquid phase (the dispersed phase) is added to the mixing vessel until the maximum volume of the second phase for which the phase inversion occurs is determined. By shifting the two liquid phases, and through a similar procedure as the one mentioned above, the lower inversion curve can also be obtained. The intermediate inversion curve is determined by adding certain volumes of both of the immiscible liquid phases to the mixing vessel and initiating the mixing of the two phases from the rest
two phases makes the dispersion more difficult to achieve. This is particularly true at low agitator speeds, as is demonstrated by Figure 2. The inversion curves reported on this figure are the intermediate inversion curves for different mixed, immiscible liquid-liquid systems as indicated. When the density difference between the mixed phases is removed, the uncertainty range of inversion will also be diminished. This is shown by the intermediate inversion curves reported in Figure 5, where the mixed phases have equal densities. To remove the effect of density difference between the phases on the phase inversion, the remaining work was performed on equal density, immiscible liquid-liquid systems.

In Figure 6, the temperature dependence of the intermediate inversion curve for a mixed, immiscible liquid-liquid system is reported. According to this figure, the phase inversion occurs at lower fractions of organic phase with the increase of temperature.

In order to study the relative positions of the upper, the intermediate and the lower inversion curves with respect to each other for a certain mixture, experiments reported in Figures 5 and 6 were performed. In these experiments, temperature was kept constant, and the mixed phases had equal densities. (For both of these figures, the aqueous phases is solution of sodium dichromate, while the organic phase is varied from one figure to the other as indicated.) According to these figures, as the revolutions per minute values are increased, the volume fraction of the organic phase at the inversion points of the upper inversion curve is increased, while for the intermediate and the lower inversion curve it is decreased.

In order to single out the effect of the viscosity difference on the dispersion of binary, immiscible liquid-liquid systems, the experiments reported in Figure 7 were performed. In these experiments, an organic phase with the same density and viscosity as the aqueous phase was used. In making up the organic phase of Figure 7, benzene, carbon tetrachloride, and silicon oil were mixed. The resulting mixture had the same density and the same viscosity as the aqueous sodium dichromate solution. [10.447 g silicon oil (DC 200 Fluid) was brought to the volume of 1 000 ml by adding to it a mixture of benzene and carbon tetrachloride which had the same density as the sodium dichromate solution at 30°C.] According to Figure 7, in the absence of viscosity difference between the mixed immiscible liquid phases, the intermediate inversion curve will be located at the equi-volume line for all the impeller speeds reported. Accordingly, it is concluded that any deviation of the intermediate inversion curve from the equi-volume location is indeed due to the viscosity difference between the immiscible liquid phases only.

It was previously assumed that in the absence of viscosity difference (between the mixed, immiscible liquid phases), the upper and lower inversion curves would be situated at the closed-packed locations (II). (Closed-packed locations correspond to about 74% by volume of the dispersed phase and 26% by volume of the continuous phase.) However, according to Figure 7, the upper and the lower inversion curves are not
situated at the closed-packed locations. There also exists an
asymmetry between the locations of these two curves with
respect to the equivalent line. This is because if we plot
volume fraction of the aqueous phase, vs. revolutions per
minute, we will not retain the same curves for the inversion
curves. As a result, one may conclude that some other factor,
or factors, may be causing the unsymmetric location of the
upper and lower inversion curves. It should be pointed out
that interfacial tension may not be considered a cause for this
asymmetry owing to the nature of its definition (9).

A comparison of Figures 5 and 6, with Figure 7 shows that
the abrupt changes in slopes of the intermediate and lower
inversion curves in Figures 5 and 6 can be due to changes in
mixing regimes of the systems studied (that is, transition
from laminar mixing to turbulent mixing). For the data of
Figure 7, where the viscosity difference between the mixed
phases is diminished, transition in mixing regimes does not
effect the inversion curves. However, for all the systems
studies, Figures 5 to 7, the upper inversion curves are ap-
parently insensitive (or slightly insensitive) to transition in
mixing regimes. Differences in wettabilities of mixed phase,
with the container surface, may also be effective on these
discrepancies only at low revolutions per minute values.

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