z = compressibility factor, Pv/RT
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek Letters

α = dimensionless constant, Equation (9)
μ = absolute viscosity, centipoises
μ^* = viscosity at normal pressures, centipoises
ξ = viscosity parameter, $T_c^{1/6}/M^{1/2}P_c^{2/3}$
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c
$b\rho\chi$ = Enskog modulus

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The Influence of Mass Transfer on a Countercurrent Liquid-Liquid Fluidized System

I. DUNN, LEON LAPIDUS, and J. C. ELGIN

The present work is concerned with an experimental study of the influence of mass transfer on the holdup of countercurrent lqiuid-liquid fluidized systems and the effect of solute on droplet coalescence. Of particular importance in the results obtained is the dramatic demonstration that mass transfer greatly influences the holdup when solute is being extracted from the discontinuous phase loading to strong coalescence.

The prediction of the volume fraction of the discontinuous phase is of particular concern in fluidization studies. The recent development of a generalized theory of fluidization (*14*) has led to a means of carrying out such a prediction. In accordance with this theory the volume fraction of the discontinuous phase or the holdup of any fluidized system is dependent solely on the relative velocities of the slip velocity between the phases for a given set of fluid properties and a given geometry. The theory has been experimentally verified for all regimes of solid-liquid fluidization and a modification of the theory accounting for drop and bubble terminal velocities verified for countercurrent liquid-liquid (*1, 23*) and gas-liquid systems (*3*). This modified theory states that the holdup is a function of the slip velocity-terminal velocity ratio where the added factor of a terminal velocity is defined for an average size drop or bubble. Apparently, drop and bubble motion which might cause a departure from ideal solid sphere behavior does not influence the fluidized system to any measurable degree.

Many observations on the behavior of liquid-liquid extraction systems indicate that solute transfer between the phases may seriously alter the holdup (*12, 13, 18, 19*). Previous work, however, does not provide a means of making quantitative evaluations regarding this point, and no systematic study appears to have been made. Speculation indicates that coalescence, especially when promoted by mass transfer, could cause sufficient nonidealities in flow characteristics which may produce marked deviations from the predictions of the generalized slip velocity theory. The present work is concerned with an experimental study of the influence of mass transfer on the holdup of countercurrent liquid-liquid fluidized systems and the effect of solute transfer on droplet coalescence.

Of particular importance in the results obtained is the dramatic demonstration that mass transfer may greatly influence holdup. This is particularly true when solute is being extracted from the discontinuous phase leading to strong coalescence. In such cases the deviations from the ideal slip velocity theory become so great as to make it invalid.

LITERATURE REVIEW

The behavior of a falling swarm of droplets depends on the individual drop behavior and the interaction effects. Deformations, oscillation, internal circulation, and surface phenomena distinguish a liquid drop from a rigid sphere. Internal circulation patterns in falling droplets have been observed in many instances (*2, 6, 17*). Noncirculating drops result from the presence of surface active contaminants (*6, 17*). These stagnant drops are less likely to oscillate when falling and will fall slower than circulating drops (*6, 15, 22*). Drop terminal velocities are difficult to predict, and correlations of terminal velocities with size and physical properties cannot be expected to be closer than 10%. This is not surprising when one considers the erratic experimental results which have been obtained (*22*).

Phenomena resulting from solute transfer across the drop interface may cause violent pulsating and kicking motions (*9, 16, 20*). Also a falling drop is most likely to display circulation, distortion, and oscillation when solute transfer is occurring. Local variations in interfacial tension seem to provide the forces necessary for all types of surface movement. Apparently a local lowering of the interfacial tension by the solute is a necessary condition for interfacial motion (*10, 20*). The magnitude of the motion will depend on the magnitude of the gradient in interfacial tension. Thus the solute concentrations at the interface and the slope of the solute concentration-interfacial tension curve are the important quantities in this process. A model for the mechanism by which interfacial turbulence is produced has been proposed and investigated analytically (*21*). The results show how it is possible for the stability of some systems to depend on the direction of transfer and how these interfacial phenomena are driven by interfacial tension gradients.

Coalescence of drops is a process which depends on surface properties and interfacial phenomena. Any disturbance of the film of liquid between two drops may promote coalescence. Such a disturbance is apparently responsible for the coalescence promoting effect of solute transfer. Transfer from the droplet hastens coalescence, while transfer into the drop retards coalescence (*4, 7, 19*). Most investigators agree that this phenomena is caused by Marangoni instability, which is a surface flow driven by gradients in interfacial tension; the flow is in the direction of high surface tension. The gradients in interfacial tension are a result of high or low local solute concentrations in the region between the drops, and the dependency of interfacial tension on solute concentration. The interfacial tension of most liquid pairs is reduced by the presence of a solute (except for some inorganic salts); therefore, the higher concentration between the drops which is caused by solute transfer from the drop induces a local lowering of the interfacial tension and drives a surface flow away from that region. It is probable that this surface flow thins the continuous phase film which separates the drops and thus hastens coalescence. In accordance with this mechanism a development of a region of locally high interfacial tension between the drops would tend to build up the interfacial film separating the drops. This could be caused by solute transfer in the opposite direction (into the drop) or the opposite dependency of interfacial tension on concentration.

The mathematical difficulties encountered in describing the motion of a single particle contribute to making the description of a swarm of interacting particles extremely complex. All analyses of falling single spheres (*15*) and two interacting spheres (*11*) have been limited to creeping flow ($N_{Re_T} << 1$). Experimental investigations (*8*) confirmed the theoretical finding that two spheres will fall faster than one and that a trailing sphere will tend to overtake the leading one. These accomplishments do not go far in describing a fluidized system. Certain correlations are available in the literature with which an estimation can be made of the batch fluidization curve for solid spheres in liquid. In the present work the experimental fluidization data are compared with fluidization curves derived from the correlation of Zenz (*24*).

Actually in the range of $1 - \epsilon$ up to 0.10 to 0.15 there is a disagreement among various empirical correlations such as Zenz's and these correlations differ from a number of theoretical treatments (*3*). It was felt, however, that this correlation was adequate for the current work.

EXPERIMENTAL DETAILS

The purpose of these experiments was to determine the influence of solute transfer on the holdup of liquid-liquid countercurrent fluidized systems and to compare the results obtained with a correlation for the batch fluidization of solid spheres with the generalized slip-velocity theory. It was also of interest to measure the effect of surface active additives on these systems with and without mass transfer. The experiments were directed to a general conclusion about the influence of solute transfer on the operation of spray types of extraction columns for all liquid-liquid systems.

Holdup-flow rate data were taken on two countercurrent liquid-liquid systems of radically different interfacial tensions, methyl isobutyl ketone (mibk)-water (γ = 11 dynes/cm.) and toluene-water (γ = 33) with dissimilar solutes acetic acid and acetone, respectively. The organic phases entered through nozzles at the bottom of the column and rose in droplet form countercurrent to the continuous aqueous phase. Dodecyl sodium sulfate was added to some of the runs to determine the effect of this surface active agent on column behavior. A nonsurface active organic dye was added to mark single tracer drops.

The equipment was essentially the same as used previously (23). The column test sections, entry sections, nozzles, and cut-off valves were of the same size and geometry. All metal parts were stainless steel, and all synthetic seals and tubing which contacted the liquid were teflon. Thus the major source of contaminating surface active substances was eliminated. Additions to the earlier equipment consisted of a sensitive manometer arrangement with which steady state conditions could be detected and a separate nozzle through which single dyed tracer drops could be introduced for coalescence studies and terminal velocity measurements (5). Actual holdup values were measured directly by isolating the column with rapidly closing ball valves and allowing the phases to separate. Photographs for drop size data were taken through a plastic cell which minimized distortion.

Holdups were determined for each system at two values of the continuous phase flow rate over a wide range of discontinuous phase rates from very low holdups to nearly flooded conditions. Each system was studied with and without solute transfer in both directions and at high and low concentration levels. Samples were taken and analyzed for solute concentration to determine that solute was being transferred throughout the column length. Terminal drop velocities of each system were measured in the column for use with the slip velocity relation, and a surface active agent was added to the system under all transfer conditions. Table 1 provides the necessary information regarding the runs, including entering solute concentration, surface active agent concentration, direction of transfer, and flow rates.

In order to draw general conclusions on the influence of solute transfer for other liquid-liquid fluidized systems, single drop coalescence studies were conducted. This was accomplished by forming the drops on a hypodermic needle and then contacting two or more of them on a glass or teflon surface which was submerged in the continuous phase. Contact times required for coalescence were measured and related to the column performance. Table 2 summarizes these experiments.

RESULTS AND DISCUSSION

The slip velocity theory previously mentioned for liquid-liquid fluidized systems postulates that for a given terminal velocity V_T the holdup $1 - \epsilon$ is a function of the discontinuous phase velocity V_d, with the continuous phase velocity V_c as a parameter. This may be expressed functionally by

$$1 - \epsilon = f\,[V_d, V_c, V_T]$$

For the ideal solid-liquid system this functionally may be determined from a single, simple experiment, namely the batch fluidization of solid spheres ($V_d = 0$). Many such experiments have already been carried out, and these form the basis of the Zenz correlation. Thus, the Zenz correlation, within its limitations, provides all the information necessary to obtain the functionality above for the fluidization of solid spheres of the size and density of any liquid drop. The resulting solid analogue (the fluidization curve expected if the liquid drops were solid spheres of the same density) provides a means of comparing ideal solid sphere fluidization with the nonideal fluidization of liquid drops. In the present work a large number of photographs were taken of the fluidized systems, and when this information is combined with terminal velocity data, a characteristic terminal velocity of an average size drop can be determined for all the noncoalescing systems. From this information and the knowledge of the flow rates used,

TABLE 1. COLUMN EXPERIMENTS

Methyl isobutyl ketone—acetic acid—water

Series	Discontinuous phase	Transfer	Continuous phase	V_c, cm./min.	Coalescence
I-A	mibk	none	water	56.4	slight
I-B	mibk	none	water	39.9	slight
II-A	0.138 M Hac in mibk*	→	water	56.4	much
II-B	0.138 M Hac in mibk	→	water	39.9	much
III-A	0.045 M Hac in mibk	→	water	56.4	much
III-B	0.045 M Hac in mibk	→	water	39.9	much
IV-A	mibk	←	0.132 M Hac	56.4	none
V-A	mibk	←	0.031 M Hac	56.4	none
I-AS2	mibk	←	0.005% surfactant	56.4	none
II-AS2	0.138 M Hac in mibk	→	0.005% surfactant	56.4	none

Toluene—acetone—water

Series	Discontinuous phase	Transfer	Continuous phase	V_c, cm./min.	Coalescence
I-A	toluene	none	water	56.4	some
I-B	toluene	none	water	39.9	some
II-A	0.123 M acetone in toluene	→	water	56.4	very much
III-A	0.042 M acetone in toluene	→	water	56.4	very much
IV-A	toluene	←	0.137 M acetone	56.4	slight
I-AS2	toluene	none	0.005% surfactant	56.4	none
I-AS1	toluene	none	0.0025% surfactant	56.4	some
III-AS2	0.042 M acetone in toluene	→	0.005% surfactant	56.4	none

* M = g. moles/liter.

TABLE 2. COALESCENCE EXPERIMENTS WITH SINGLE DROPS

System	Discontinuous phase	Transfer	Continuous phase	Coalescence time
Mibk-HAc-H_2O*	1% HAc in H_2O	→	Mibk	2 to 30 sec.
Mibk-HAc-H_2O	2% HAc in H_2O	→	Mibk	immediate
Mibk-HAc-H_2O	H_2O	←	1% HAc in mibk	5 to 80 sec.
Mibk-HAc-H_2O	H_2O	←	2% HAc in mibk	30 to 60 sec.
Toluene-H_2O	H_2O	none	toluene	5 to 10 sec.
Tol-acetone-H_2O	1% acetone-H_2O	→	toluene	immediate
Tol-acetone-H_2O	H_2O	←	1% acetone in tol	3 to 5 sec.
Tol-acetone-H_2O	H_2O	←	2% acetone in tol	3 to 5 sec.
Tol-acetone-H_2O	0.15 M acetone-toluene	→	H_2O	immediate
Organic nonaqueous systems				
aniline-n-heptane	aniline	none	n-heptane	<5 sec.
aniline-methylhexanone-n-heptane	5% solute in aniline	→	n-heptane	immediate
aniline-methylhexanone-n-heptane	aniline	←	5% solute in n-heptane	20 to 30 sec.
aniline-petroleum oil (clear)	aniline	none	oil	<5 sec.
aniline-methylhexanone-petroleum oil (clear)	5% solute in aniline	→	oil	immediate
aniline-methylhexanone-petroleum oil (clear)	aniline	←	5% solute in oil	20 to 30 sec.
aniline-CCl_4-petroleum oil (clear)	5% solute in aniline	→	oil	immediate
aniline-CCl_4-petroleum oil (clear)	aniline	←	5% solute in oil	20 to 30 sec.

* In the ternary systems the solute is named second.

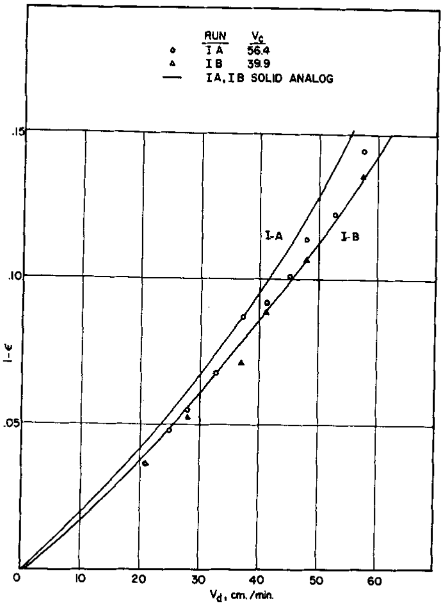

Fig. 1. Comparison of solute-free MIBK system with slip velocity theory.

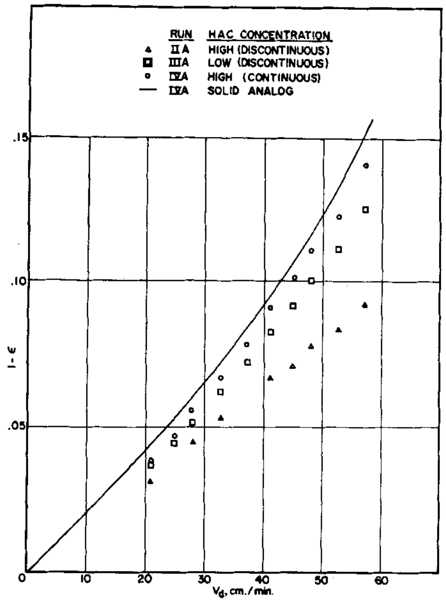

Fig. 2. Influence of direction of transfer and solute concentration, MIBK systems.

the Zenz solid analogues follow by direct calculation; these results are shown as solid lines on all the graphs to be discussed here.

Figure 1 is a plot of the holdup of the mibk system without solute vs. V_d at constant V_c and fixed V_T. As can be seen, there is fairly good agreement with the solid analogue equivalent as predicted by the slip velocity theory for countercurrent liquid-liquid fluidization system. An analogous behavior is obtained with the toluene system, although the data are not shown here. Neither system showed appreciable coalescence in the absence of solute transfer.

When solute is added to the systems so that transfer takes place, the holdup and the coalescence of the system are strongly affected; furthermore, the direction of solute transfer influences this parameter. Solute transfer from the continuous into the discontinuous phase resulted in noncoalescing systems with both toluene and mibk. Almost the same holdup was attained as in the case of no solute. Transfer in the opposite direction, from the discontinuous into the continuous phase, promoted coalescence. Under these conditions the holdup was determined by a competition between drop coalescence and drop breakup. The low interfacial tension of the mibk systems encouraged drop breakup and did not permit the formation of extremely large drops. Contrastingly, the toluene system, with higher interfacial tension, permitted coalescence to build drops which almost filled the column. The overall effect of coalescence on the column for both systems was to lower the holdup drastically. The holdup of the coalescing toluene systems (series II-A and III-A in Table 1) exhibited only a slight sensitivity to solute concentration in the organic phase. Runs at these two concentration levels resulted in approximately the same reduction in holdup, 40% of the holdup of the noncoalescing series I-A and IV-A at the high discontinuous phase flow rates. In each case coalescence created drop sizes which nearly filled the column cross section. Holdups of the coalescing mibk systems (series II-A and III-A) was also influenced by a change in solute concentration. Figure 2 shows the data which demonstrate the influence of direction of transfer and solute concentration for the mibk systems. The violence of the coalescence in such systems indicates that higher concentrations would probably not lower the holdup further.

Addition of a surface active agent, dodecyl sodium sulfate, increased the holdup of all toluene and mibk systems with and without solute transfer. A concentration of 0.005% surfactant added to the toluene and mibk I-A series resulted in holdup increases of 40 and 60%, respectively. This increase can be attributed to the measured 5% reduction in drop terminal velocities; the resulting lower slip velocities gave correspondingly higher holdups. The effect of the addition of surface active agent is well demonstrated by the data for the mibk series I-A and I-AS2 (0.005% surfactant) in Figure 3. A surfactant concentration of 0.0025% in toluene series I-AS1 produced essentially no holdup enhancement over series I-A. This is in agreement with the measurements of terminal velocity. The action of surfactant on coalescing solute systems was much more marked. Coalescing systems were converted to noncoalescing systems with a large increase in holdup. The holdup increase over the coalescing system was as much as 190% for the mibk system and 250% for the toluene system. Experimental data which demonstrate the influence of surfactant on a coalescing toluene system III-A are shown in Figure 4. In Figure 5 the data for two mibk noncoalescing systems with surfactant are plotted in the form $1 - \epsilon$ vs. V_s/V_T. Here the unique functionality between slip velocity ratio and holdup and the agreement with the solid analogue is apparent.

All observations of droplet coalescence tendencies and measurements of variations in interfacial tension support the theory which explains the influence of solute transfer on coalescence in terms of interfacial tension gradients. Measurements of the dependency of interfacial tension on solute concentration for the mibk-acetic acid-water system and the toluene-acetone-water system showed that interfacial tension decreases steadily with solute concentration over the range studied here. This conjecture was further supported by experiments with surfactant systems. It was found that a noncoalescing system was obtained if enough surface active agent was present to make the interfacial tension insensitive to solute concentration, a flattening of the curve. Under these conditions the interfacial tension gradients which apparently promote coalescence are not induced by solute transfer. A dodecyl sulfate concentration of 0.0025% was not high enough to flatten the interfacial tension curve and render the toluene system non-

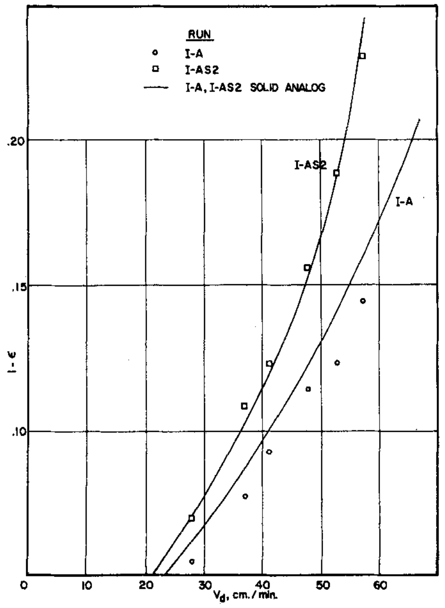

Fig. 3. Effect of surface active agent on solute-free MIBK system.

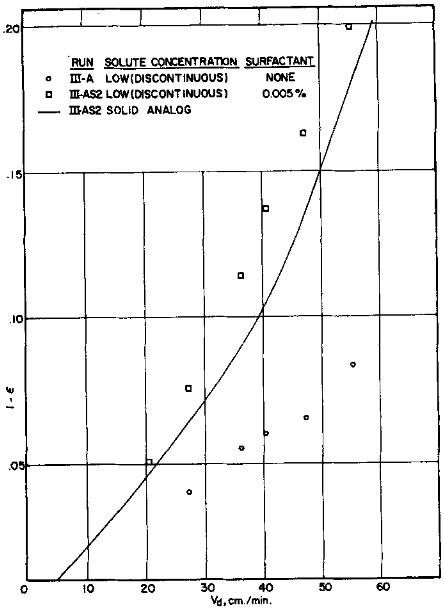

Fig. 4. Effect of surface active agent on solute-free MIBK system.

coalescing, but 0.005% prevented coalescence in the toluene and mibk extraction systems.

A correlation between single drop experiments and the column behavior provided a means of extending the significance of the toluene and mibk studies to other systems. Systems which coalesced instantaneously in the single drop experiments exhibited vigorous coalescence in the column. Experiments on three ternary nonaqueous organic systems revealed that instantaneous coalescence occurred with single drops whenever one component was being transferred from the drop. Transfer in the opposite direction inhibited coalescence. These results firmly suggest the possible occurrence of vigorous mass transfer promoted coalescence in organic fluidized systems. The reduction in holdup would be expected to be similar to that shown by the mibk and toluene systems.

APPLICATION OF RESULTS

The Solid Analogue as a Method of Predicting Holdup in Noncoalescing Liquid-Liquid Systems

This work demonstrates the use of the slip velocity theory with the Zenz solid analogue in predicting the holdup of noncoalescing liquid-liquid systems. Necessary for this comparison is a knowledge of droplet terminal velocities and drop size distributions. A noncoalescing system is obtained under the following conditions: no solute transfer between phases, solute transfer from the continuous phase, and solute transfer from the discontinuous phase with sufficient amounts of surfactant in the system. The maximum error in the predicted holdups would probably be 8 to 10%. Although this work dealt only with countercurrent systems, the generalized slip velocity theory can be applied to all flow regimes. This has been verified for solids fluidization and is probably true for the present case.

The information from single drop experiments demonstrated that coalescence is minimal under the above conditions, regardless of which phase is dispersed. In accordance with the experiments, the behavior of nonaqueous organic systems should be equally predictable under these conditions. This would suggest that whenever a high and predictable holdup is desired, the solute gaining phase should be dispersed.

Predictability of Coalescing Systems

The column and single drop experiments indicate that coalescence is promoted by solute transfer from the discontinuous phase for all systems in which the solute lowers the interfacial tension. This was true regardless of which phase was dispersed and for nonaqueous organic systems as well. Vigorous coalescence in any liquid-liquid fluidized system can be expected with transfer from the drops whenever it is known that the solute lowers the interfacial tension appreciably or whenever single drop experiments show instantaneous coalescence. Again, this applies to organic and aqueous systems regardless of which phase is dispersed.

Predicting the reduction of holdup due to coalescence at given flow rates is rather difficult. The holdup in a coalescing system depends on the competition between drop coalescence and drop breakup processes. The drops of high interfacial tension systems can grow very large before the surface forces are overcome and the drop breaks apart. Thus a system such as toluene-water which is coalescing may attain a holdup which is only 40% of its holdup without coalescence. It is at the high holdups, where a column would most likely be operated, that coalescence severely reduces the holdup. Unfortunately the information obtained on these two systems does not permit

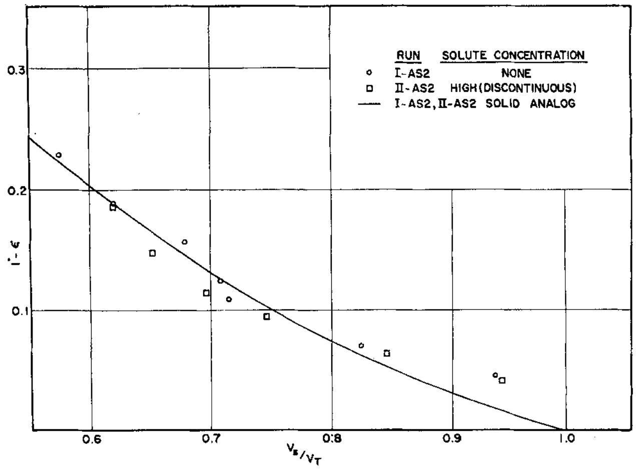

Fig. 5. Slip velocity-holdup curve for noncoalescing MIBK surfactant systems.

formulation of a quantitative prediction scheme for the holdup of coalescing liquid-liquid systems.

The effect of coalescence on the operation of an extraction column or other contacting equipment would make itself most strongly felt through the reduction in interfacial area. The specific interfacial area is proportional to the holdup and inversely proportional to the drop size for spherical drops. While the holdup may be reduced by 50%, the drop size may be increased by fifty times, which results in a one-hundred-fold reduction in interfacial area. The reduction in interfacial area is not as great for systems of low interfacial tension, since the drop size does not reach these proportions.

A rational design of an extraction column is possible with knowledge of the interfacial area, the mass transfer coefficient, and the driving forces, and how these factors vary throughout the column. Only one of these factors is of direct concern in this work, the interfacial area. However, a strong degree of coalescence in a column would certainly influence the others. For instance, the mass transfer coefficient is probably appreciably enhanced by coalescence and would alter the driving forces in the column. The net effect of coalescence would probably be a reduction in the overall efficiency of most liquid-liquid contacting operations, especially in the case of high interfacial tension systems.

The Use of Surface Active Agents

For some purposes the use of surface active agents to eliminate coalescence and increase the holdup of liquid-liquid fluidized systems might be advantageous. As the experimental results demonstrate, addition of these materials to a coalescing system can increase the holdup two to two and a half times. Surfactants can increase the holdup of a noncoalescing system 40 to 60%. Their use would of course be dictated by whether contamination of the system could be tolerated.

The amount of surfactant which should be added for optimum effectiveness can be easily determined. Experiments presented in this work indicated that the most effective surfactant concentration for a solute system will cause a flattening of the interfacial tension-solute concentration curve. This amount of surface active material insures that no coalescence will occur. For a system with no solute, the most effective amount would reduce the terminal velocities to a minimum.

One must consider that surface active agents will reduce the intrinsic mass transfer coefficient of a single drop three to four times and will lower the coefficient for a coalescing system probably even more. It is expected that the gain in interfacial area will usually more than compensate for this decrease in mass transfer coefficient; the overall efficiency of the column will be therefore increased.

CONCLUSIONS

Mass transfer exerts its influence on a liquid-liquid fluidized system through the promotion or inhibition of droplet coalescence. This process depends on the direction of transfer in accordance with a mechanistic theory. Gradients in interfacial tension apparently control this mechanism.

The liquid-liquid fluidized systems with undistributed solutes studied in this work will coalesce strongly whenever the solute is being extracted from the discontinuous phase. Experiments with single drops demonstrated that this will be true for these systems, including nonaqueous organic systems, whenever the solute significantly lowers the interfacial tension. This is found to be independent of which phase is dispersed. The effect of coalescence on a fluidized system is to reduce the holdup approximately 50%. This figure is not quantitatively predictable, but it is shown to be greater for high interfacial tension systems and lower for low interfacial tension systems.

Noncoalescence results for the systems studied whenever there is no mass transfer or whenever the solute is tranferred from the continuous phase into the drop. Coalescing systems can be converted to noncoalescing systems by the addition of enough surfactant to render the interfacial tension insensitive to solute concentration. The holdup of these systems attained values as much as two and a half times greater than coalescing systems and can be predicted by the solid analogue.

All observations on coalescence and measurements of the variation of interfacial tension with solute concentration support the theory that coalescence is promoted whenever solute transfer induces a local reduction in interfacial tension in the region between the drops.

NOTATION

V_c = continuous phase velocity
V_d = discontinuous phase velocity
V_T = terminal velocity
V_s = slip velocity
γ = interfacial tension
$1 - \epsilon$ = system holdup

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