Coalescence Frequencies in Agitated Liquid-Liquid Systems

A. J. MADDEN and GLENN L. DAMERELL

University of Minnesota, Minneapolis, Minnesota

An experimental technique is described for estimating the coalescence frequency of droplets in an agitated liquid-liquid system. Results are presented for dilute aqueous dispersions in toluene. Quantitative estimates of the coalescence frequency are based upon a simple model proposed to describe the coalescence process. The coalescence frequency is shown to increase markedly with increase in impeller speed and to a lesser extent with increase in the dispersed-phase volume.

A great number of studies have been made on the behavior of single, liquid drops in contact with a second, immiscible liquid. However the fact remains that in practice one seldom deals with single, isolated drops but rather with assemblages of drops. This is certainly the case in such applications as liquid-liquid extraction and in chemical reactors involving two immiscible liquid phases. To what extent coalescence and redispersion of drops occurs is a question that must be answered if a better understanding is to be gained of the behavior of such systems. The rate of generation of new interfacial surface and the magnitude of internal mixing of the dispersed drops would be expected to vary greatly depending upon the coalescence and redispersion frequency of the system. These factors in turn could strongly influence interphase mass transfer and chemical reaction rates.

Rietema (*7*) has recently shown that in the case of liquid-liquid reactions which occur in the dispersed phase, the degree of interaction of dispersed drops may greatly influence the productivity of a continuous reactor. Thus to predict the performance of a continuous liquid-liquid reactor from batch reaction data, knowledge of the degree of interaction is essential for proper forecasting.

It is surprising to note that quantitative data on the interaction effect are nonexistent for mechanically agitated systems. This research was undertaken in an attempt to gain some insight into this problem. The present paper has a twofold purpose:

1. to discuss an experimental technique for estimating the coalescence frequency of dispersed aqueous droplets in a stirred-tank system
2. to present quantitative results showing the influence of impeller speed and dispersed phase volume on the coalescence frequency.

A TECHNIQUE FOR ESTIMATING THE COALESCENCE FREQUENCY

The studies reported here were conducted with an aqueous dispersed phase with an immiscible organic liquid as the continuous phase. Water containing an inert electrolyte (sodium nitrate) was first dispersed in toluene containing iodine. This mixture was agitated in a baffled vessel with a constant speed turbine impeller. To trace the progress of coalescence and redispersion of the aqueous phase a small amount of concentrated aqueous hypo (sodium thiosulfate) solution was introduced into the vessel. Samples of toluene (continuous phase) were withdrawn periodically and analyzed as the free iodine was gradually extracted in accordance with

$$2S_2O_3^{=} + I_2 \rightarrow S_4O_6^{=} + 2I^-$$

As a result of the coalescence and redispersion of droplets the sodium thiosulfate originally contained in a few drops is distributed over more and more of the droplets as time progresses. Therefore the extraction begins at a finite low rate and increases as more droplets acquire hypo by coalescence and redispersion. In order to relate the concentration-time data to the magnitude of the coalescence frequency a model for the coalescence process must be advanced.

A SIMPLE MODEL FOR THE COALESCENCE PROCESS

The simplest assumption to make is that, under constant agitation conditions, the dispersed phase is made up of a constant number of drops of equal size. This implies that when, as a result of coalescence, an aggregate drop is formed, it is immediately broken up into two new drops of the original size. It is further assumed that the coalescence frequency is a constant, designated by θ, representing the fraction of all drops coalescing per unit time. With these assumptions an equation can be developed for the number of drops containing sodium thiosulfate (N_s) as a function of time, as related to the coalescence frequency.

The total number of drops containing sodium thiosulfate coalescing per unit time is given by θN_s. The drops containing hypo may either coalesce with other hypo drops or with inert drops. Of the total number of hypo drops coalescing per unit time, the fraction N_w/N represents the probability of coalescences with inert drops. Hence the number of hypo drops coalescing with inert drops per unit time at any time t is given by $\theta\, N_s \cdot N_w/N$. Each time a hypo drop coalesces with an inert drop and the aggregate splits into two new drops, there is a net increase of one hypo drop. Thus the rate of propagation of hypo drops with time is given by

$$\frac{dN_s}{dt} = \theta\, N_s \cdot \frac{N_w}{N} = \theta\, N_s \frac{(N - N_s)}{N} \qquad (1)$$

since $N = N_s + N_w$. Integrating Equation (1) over the limits $t = 0$, $N_s = N_{so}$ and $t = t$, $N_s = N_s$ one gets

$$N_s = N \frac{1}{1 + \frac{1}{X} e^{-\theta t}} \qquad (2)$$

Equation (2) gives the relationship for the number of drops containing hypo (sodium thiosulfate) as a function of time and coalescence frequency. It is next necessary to consider the manner in which this relates to the rate of removal of iodine from the toluene (continuous) phase.

THE RELATIONSHIP BETWEEN COALESCENCE FREQUENCY AND EXTRACTION RATE

It was recently shown by Fujinawa and Maruyama (*1*) that for a fixed interfacial area the rate of extraction of iodine from benzene by an aqueous solution of sodium thiosulfate depends only upon the concentration of iodine in benzene, if the concentration of sodium thiosulfate in the water phase is sufficiently high. When one applies these findings to the present system, the rate of removal of iodine from toluene by aqueous thiosulfate (for a fixed set of agitation conditions) should be given by

$$-V_t \frac{dc}{dt} = ka\, N_s\, c \qquad (3)$$

In a coalescence experiment droplets containing sodium thiosulfate are added to an agitated dispersion of inert drops, and N_s changes with time in accordance with Equation (2). Substituting the expression for N_s given by Equation (2) into Equation (3) one gets

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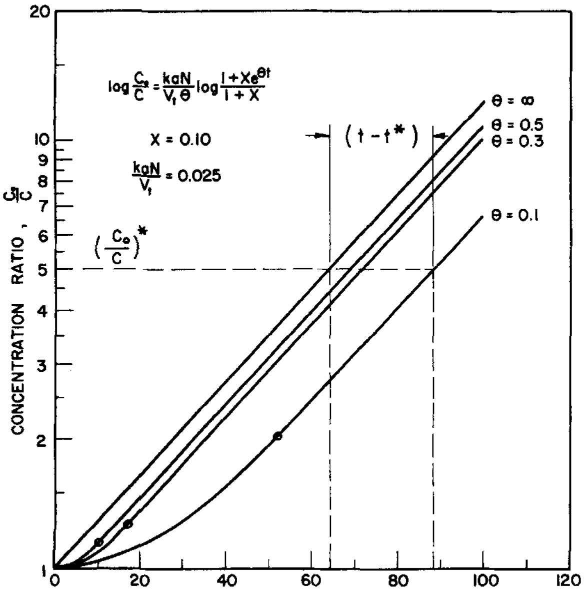
Glenn L. Damerell is with the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.



○ Circle denotes time required for hypo to become distributed over 95 percent of droplets.

Fig. 1. The effect of coalescence frequency on the predicted concentration-time relationship.

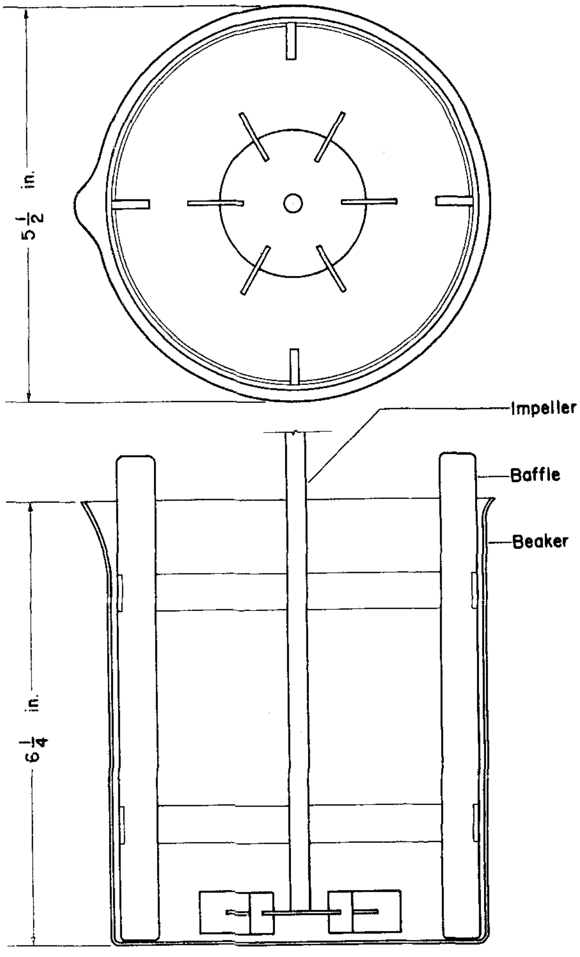


Fig. 2. The assembled vessel for coalescence studies.

$$-\frac{dc}{c} = \frac{kaN}{V_t}\left[\frac{1}{1+\frac{1}{X}e^{-\theta t}}\right] dt \quad (4)$$

For fixed experimental conditions, that is impeller speed and volume of the dispersed phase, the grouping of terms kaN/V_t, which will be called the *extraction rate constant,* should be a constant. With this assumption Equation (4) can be integrated over the limits $C = C_o$, $t = 0$ to $C = C$, $t = t$ to give

$$\ln \frac{c_o}{c} = \frac{kaN}{V_t\theta} \ln \frac{1 + X\,e^{\theta t}}{1+X} \quad (5)$$

where c_o = initial concentration of iodine in toluene. Equation (5) represents the expected concentration-time relationship for a coalescence experiment with the validity of the simple coalescence model and the constancy of the extraction rate constant kaN/V_t assumed.

The magnitude of the extraction rate constant can be determined by performing a companion experiment in which all drops of the dispersed phase contain hypo. This can be accomplished by premixing the hypo solution with the inert aqueous solution before introduction into the reaction vessel. In this case $N_s = N$, and Equation (3) may be integrated to give

$$\ln \frac{c_o}{c} = \frac{kaN}{V_t} t \quad (6)$$

This type of experiment will be referred to as a *direct extraction experiment.* A plot of $\ln c_o/c$ vs. time should yield a straight line the slope of which is kaN/V_t, the extraction rate constant. An alternate scheme for obtaining the value of kaN/V_t involves the use of the data for the coalescence experiment itself. As the coalescence experiment progresses, $Xe^{\theta t}$ eventually becomes much greater than unity, and Equation (5) reduces to

$$\ln \frac{c_o}{c} = \frac{kaN}{V_t\theta} \ln \frac{X}{1+X} + \frac{kaN}{V_t} t \quad (7)$$

Thus in the limit of long times for a coalescence run the plot of $\ln c_o/c$ vs. t becomes a straight line the slope of which is kaN/V_t, the extraction rate constant.

When one has established the value of the extraction rate constant for a particular set of experimental conditions, the coalescence frequency θ can be estimated by assuming values of θ so as to fit Equation (5) to the experimental data. A simplified procedure may be obtained for estimating the coalescence frequency on the basis of the comparative results of the coalescence and companion direct extraction experiments. This will be discussed following a general consideration of the concentration-time data expected from such experiments.

Figure 1 shows the expected variation of the concentration-time relationship as predicted by Equation (5) for various assumed values of θ with X and kaN/V_t fixed by the experimental conditions. It is clear from this that only sufficiently small values of θ may be expected to be determined with any accuracy. As θ becomes very large, the data of a coalescence run become indistinguishable from the results of a direct extraction run. (A direct extraction run corresponds to $\theta = \infty$.) This is to be expected, since the hypo propagates throughout the dispersed phase in a very short time. It is of interest in this connection to have a general idea of the rate of distribution of hypo throughout the dispersed phase and the dependence upon the magnitude of the coalescence frequency θ. The time required for 95% of the dispersed drops to acquire hypo may be determined from Equation (2):

$$\frac{N_s}{N} = \frac{1}{1+\frac{1}{X}e^{-\theta t}} = 0.95$$

If $X = 0.1$, then $\theta t = 5.23$. Thus if $\theta = 0.1$ sec.$^{-1}$, 52.3 sec. are required for 95% of the drops to acquire hypo. This is plotted as the circled point on the curve for $\theta = 0.1$ sec.$^{-1}$ in Figure 1. Corresponding points are also shown for $\theta = 0.3$ sec.$^{-1}$ and $\theta = 0.5$ sec.$^{-1}$. It will be observed that for

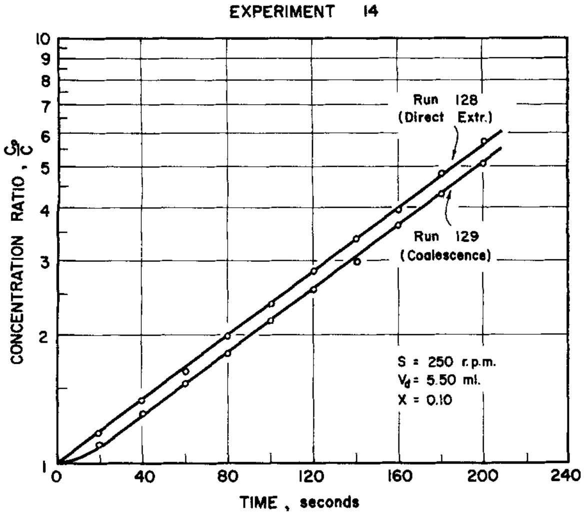


Fig. 3. Typical experimental data for a coalescence run and a companion direct extraction run.

times greater than those corresponding to the circled points the concentration time curves are essentially straight and parallel. The slope in each instance is kaN/V_t.

Experimentally, one may also vary X, the initial ratio of hypo drops to inert drops. The lower the value of X the larger will be the time required for the hypo to be distributed throughout the dispersed phase. Consequently for a given value of θ the time displacement between the direct extraction and the coalescence curves will be increased. It is clear from this that it is desirable to work with as low a value of X as practical. Physically this indicates the volume of added hypo solution should be as small as possible in relation to the total volume of dispersed phase.

The time displacement between the concentration-time curve for a coalescence experiment and for a direct extraction experiment may be utilized for estimating a value for the coalescence frequency. Equation (6) may be rewritten in the form

$$\ln\left(\frac{c_o}{c}\right)^* \Big/ \frac{kaN}{V_t} = t^* \qquad (6a)$$

where t^* is the time required to reach a certain concentration level $(c_o/c)^*$ by a direct extraction run.

The time t required to reach the same concentration level $(c_o/c)^*$ by a coalescence run is assumed to be great enough so that $Xe^{\theta t} >> 1$. For this case Equation (7) applies and may be rearranged to give

$$\ln\left(\frac{c_o}{c}\right)^* \Big/ \frac{kaN}{V_t} = \frac{1}{\theta}\ln\frac{X}{1+X} + t \qquad (7a)$$

Equating the right-hand members of Equations (7a) and (6a) one obtains

$$\theta = \frac{\ln\dfrac{1+X}{X}}{t-t^*} \qquad (8)$$

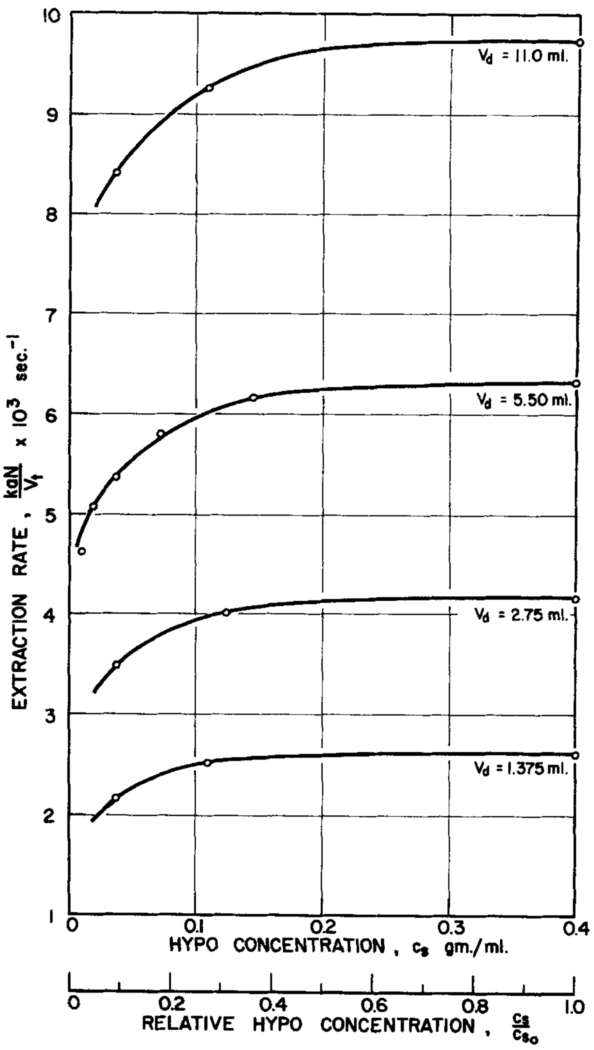


Fig. 4. The effect of hypo concentration on the extraction rate constant.

The term $(t - t^*)$, called the *time lag*, represents the difference in times required for a direct extraction and a coalescence run to reach an arbitrary concentration level which is high enough so that the extraction rates (slopes) are equal. This is shown graphically in Figure 1.

In the experimental work which will be discussed in the following sections the variation of the coalescence frequency with two principal parameters has been investigated. These were the impeller speed and the volume fraction of the dispersed phase. Brief consideration was also given to the influence of changes in the ionic strength of the dispersed phase.

EXPERIMENTAL EQUIPMENT AND MATERIALS

Apparatus

The apparatus used in the experiments consisted of a 1,500 ml. stainless steel beaker, a six-bladed turbine impeller, and a four-bladed removable baffle assembly. These three parts were commercially coated with Teflon. Teflon was chosen for its inertness and to provide a surface which is nonwetting for the aqueous phase in order to eliminate wall effects in the coalescence study. The four baffles were arranged symmetrically and occupied about 10% of the tank diameter. The turbine impeller was 3 in. in diameter and occupied 60% of the tank diameter. The volume swept out by the impeller in each revolution was about 6.5% of the reactor volume. This is a somewhat higher fraction than encountered in most industrial mixing operations (8). The assembled reactor is illustrated in Figure 2, showing two principal dimensions.

The impeller shaft was connected through a gear train to a 75 rev./min. 150 oz.-in. continuous torque synchronous motor. The gears were arranged to give agitating speeds of 150, 200, 250, or 300 rev./min.

A standard 10-ml. pipette was used to withdraw samples of toluene from the reaction mixture. It was equipped on one end with a rubber squeeze bulb and on the sampling end with a Teflon tube. The bottom of the tube was fitted with a fine-mesh, Teflon-coated brass screen to exclude water drops from the toluene samples. Experience with the sampling device showed that very clear toluene samples were obtained. Sampling time was of the order of 1 sec.

The analysis of the toluene samples for determining the iodine content was carried out with a photometer. The toluene samples varied in color from dark red to clear, depending on the iodine concentration. Calibration curves were established for known solution of iodine in toluene.

The reactor assembly was immersed in a recirculating water bath to maintain the temperature constant at 25°C. for all experiments.

Chemicals

The toluene used in all experiments was obtained from a recycle system in which toluene from previous experiments was subjected to a series of water washings followed by distillation. The first run of the distillation was discarded, and the fraction boiling in the range 110° to 110.6°C. was retained. This toluene was water saturated prior to use. Mallinckrodt reagent grade toluene was used for make-up in the recycle system.

All aqueous solutions were prepared with conductivity water. Free iodine was obtained by mixing equal volumes of the following solutions:

Solution A:

5.60 g. KIO_3 and 13.12 ml. 12N HCl/liter

Solution B:

21.84 g. KI/liter

The concentrations were arranged to yield 0.1 g. iodine with 5.0 ml. of each solution. After mixing, the free iodine was extracted with 50 ml. of toluene. The iodine-toluene solution was then washed with a dilute solution of sodium carbonate before being added to the experimental system. The purpose of the sodium carbonate wash was to remove any remaining traces of acid so as to prevent decomposition of the sodium thiosulfate during the course of an experiment.

The hypo solutions were prepared shortly before runs were made, generally with 0.4 g. $Na_2S_2O_3 \cdot 5H_2O$/ml.

Experimental Technique

The reactor assembly was secured in the constant-temperature bath maintained at 25°C. The impeller shaft was centered carefully and adjusted to clear the bottom by ⅛ in. This was to insure breakup of the more dense aqueous phase. The tank was then charged with 950 ml. of water-saturated toluene followed by another 50 ml. containing the appropriate amount of iodine. The amount of iodine used in all runs was one-half the stoichiometric amount required for complete reaction with the sodium thiosulfate to be added to the system. The system was agitated until thermal equilibrium was established and the iodine completely distributed throughout the toluene.

Coalescence Run

The desired quantity of inert aqueous sodium nitrate solution was next introduced. It was found that more reproducible run were obtained when sodium nitrate solution was used as the initial dispersed phase rather than pure water. The concentration of the sodium nitrate solution was adjusted to have the same ionic strength (5) as the sodium thiosulfate solution to be added. Approximately 10 min. of agitation were allowed for dispersion of the aqueous sodium nitrate solution. Then the initial sample of toluene was taken to determine the starting iodine concentration.

The appropriate amount of hypo solution was then quickly introduced and the electric timer started. Toluene samples were then taken at 20-sec. intervals. Sample volumes were about 5 ml., and generally ten samples were taken over the course of an experiment. The iodine content of the various samples was determined with the photometer immediately after each run.

Direct Extraction Run

The procedure in this case differed only at the beginning of the run. Here the hypo and the inert sodium nitrate solutions were premixed in a small Teflon cup before introduction into the agitated toluene.

EXPERIMENTAL VARIABLES

The coalescence frequency was determined for impeller speeds of 150, 200, 250, and 300 rev./min. For each impeller speed, dispersed phase volumes of 1.375, 2.75, 5.5, and 11.0 ml. were investigated. In general, for these experiments, the ionic strength of the dispersed phase was 4.84, and the initial ratio of hypo to inert drops was 0.1. In a limited number of experiments variations in the ionic strength of the aqueous phase from

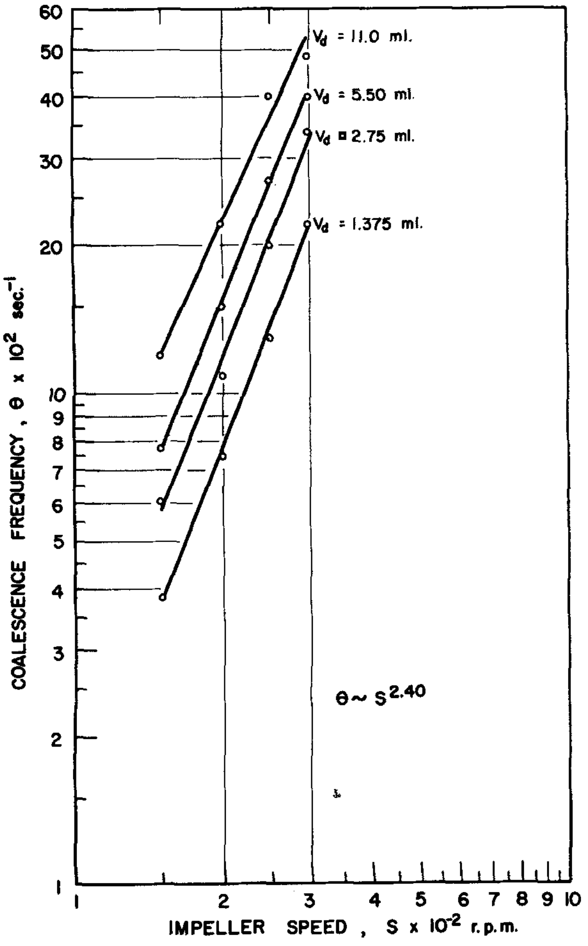


Fig. 5. Variation of coalescence frequency with impeller speed.

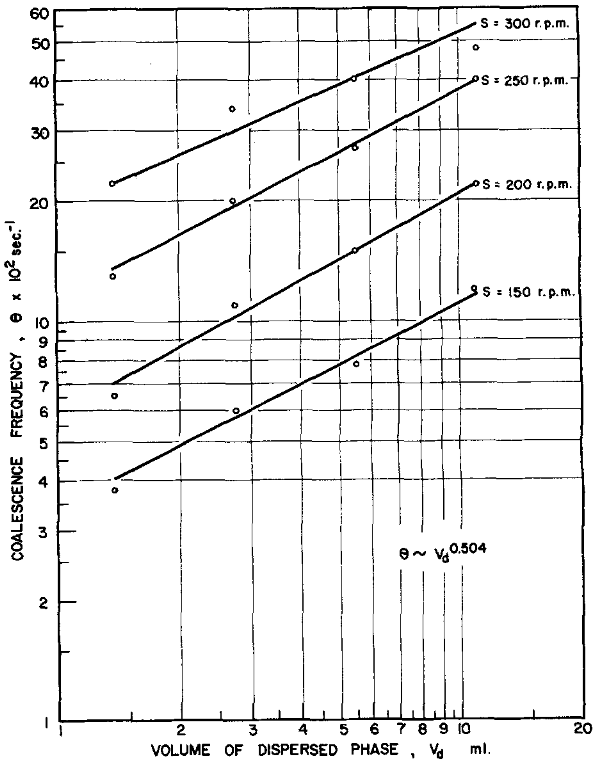


Fig. 6. Variation of coalescence frequency with dispersed phase volume.

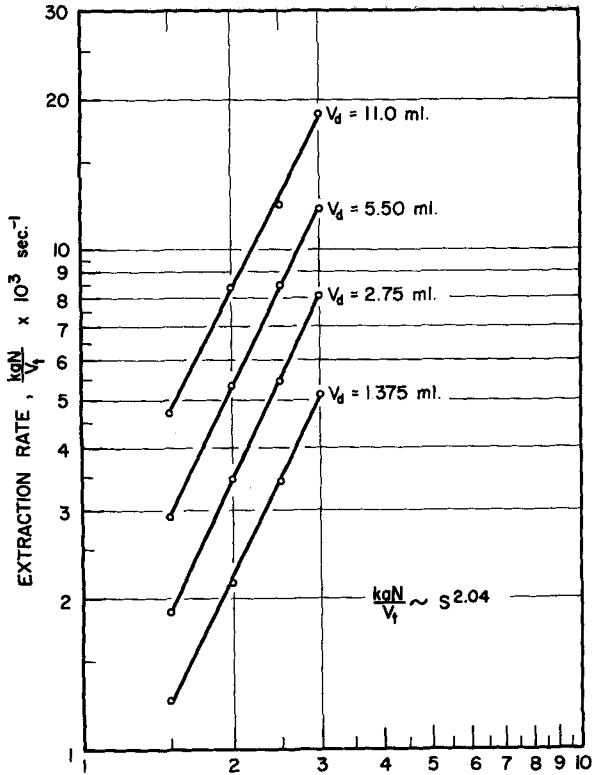


Fig. 7. Effect of impeller speed on the extraction rate constant.

2.42 to 9.68 were considered. Similarly, the initial ratio of hypo to inert drops was varied from 0.0232 to 0.2.

PRESENTATION OF RESULTS

Typical experimental results for a coalescence experiment and for the companion direct extraction experiment are shown in Figure 3. The plot of log C_o/C vs. time for the direct extraction data gives a good straight line in agreement with Equation (6). From the slope the extraction rate constant kaN/V_t was found to be 0.00855 sec.$^{-1}$. The comparable data for the coalescence experiment gives the same limiting slope, as expected from Equation (7).

From Equation (5) the estimated coalescence frequency was found to be 0.27 sec.$^{-1}$. In applying this equation the initial ratio of hypo to inert drops was taken to be the same as the ratio of the volume of hypo solution added to the volume of inert aqueous phase present at the start of the coalescence run. This relates back to the earlier assumption of a constant drop size for the system. Thus 0.5 ml. of hypo solution were added to an initial dispersion of 5.0 ml. of inert (sodium nitrate) solution, and X was equal to 0.1. This procedure was followed in all other cases as well.

THE CONSTANCY OF THE EXTRACTION RATE CONSTANT

Equation (5) was developed on the premise that the extraction rate constant kaN/V_t is a constant for a given set of experimental conditions, that is fixed impeller speed and volume of dispersed phase. This assumption was based upon the findings of Fujinawa and Maruyama (*1*) that for sufficiently high concentrations of sodium thiosulfate the rate of removal of iodine is independent of the sodium thiosulfate concentration. In a coalescence experiment the drops containing sodium thiosulfate initially added to the system were highly concentrated when compared with the concentration prevailing after distribution of the hypo over the entire dispersed phase. In most experiments X was equal to 0.1 Thus the relative concentration of hypo after distribution over all the drops was about 1/11 that of the initial drops. It was important then to the analysis of the data that the validity of the assumption regarding the constancy of the extraction rate constant be confirmed experimentally.

A series of direct extraction experiments was conducted at 200 rev./min. to investigate the possible variation of the extraction rate constant with hypo concentration. In each instance the ionic strength of the dispersed phase was maintained constant at 4.84. The experimental results for various hypo concentration levels at four different dispersed phase volumes are summarized in Figure 4. For hypo concentrations greater than about 0.2 g./ml. the extraction rate constant is essentially independent of the hypo concentration. Some decline in the rate constant is observed at the lower concentrations. As a consequence it might be expected that in the initial stages of a coalescence run iodine would be extracted at a relatively higher rate leading to a permanent upward offset in the concentration-time curve. This, in turn, could lead to an erroneous estimate of the coalescence frequency. In most experiments however it was found that the variation of the extraction rate constant kaN/V_t from the beginning to the end of a coalescence run was only of the order of 20%. This variation had a negligible effect on the estimate of the coalescence frequency. This was substantiated by analyzing a number of experiments in which the variation of the extraction rate constant was taken into account by a step-by-step integration of Equation (4). The resulting estimate of θ differed negligibly from that obtained with Equation (5), where the extraction rate constant was taken to be constant and equal to the value obtained for the terminal part of the coalescence run.

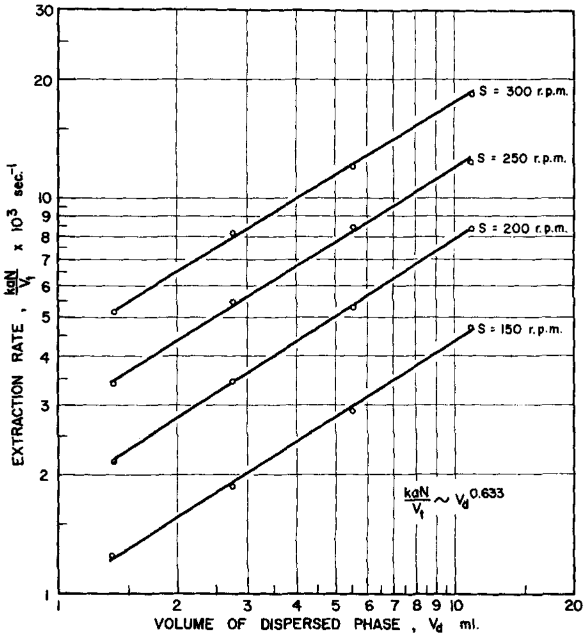


Fig. 8. Effect of dispersed phase volume on the extraction rate constant.

CONFIRMATION OF THE THEORETICAL COALESCENCE MODEL

According to the simple coalescence model proposed for a fixed impeller speed and volume of the dispersed phase, one should obtain experimentally a single value for the coalescence frequency, irrespective of the initial ratio of hypo to inert droplets. To demonstrate this point a series of coalescence runs was made at 200 rev./min. with 5.5 ml. of dispersed

Table 1. The Effect of the Initial Ratio of Hypo to Inert Droplets

Total volume of dispersed phase = 5.5 ml.
Ionic strength = 4.84
Initial conc. of hypo solution = 0.4 g./ml.
Impeller speed = 200 rev./min.

Expt. no.	X	kaN/V_t, sec.$^{-1}$	θ, sec.$^{-1}$
1	0.0232	0.00461	0.15
2	0.0476	0.00508	0.15
3	0.100	0.00535	0.15
4	0.222	0.00582	0.13

phase in each instance but varying the initial ratio of hypo to inert drops from 0.0232 to 0.222. The results are summarized in Table 1. It is seen that the coalescence frequency is essentially the same over a tenfold variation in X. This lends supporting evidence for the approximate validity of the proposed coalescence model.

THE EFFECT OF OPERATING PARAMETERS ON COALESCENCE FREQUENCY

The effects of the impeller speed and the volume of the dispersed phase on the coalescence frequency are shown in Figures 5 and 6. In these experiments the ionic strength of the dispersed phase was 4.84 in all cases. The coalescence frequency is seen to increase with increase in the impeller speed and with increase in the volume of the dispersed phase. θ was found to vary approximately as the 2.4 power of the impeller speed and as the square root of the dispersed-phase volume.

A few experiments were conducted to examine the effect of variations in the ionic strength of the dispersed phase on coalescence frequency. These experiments were for a fixed agitation speed (200 rev./min.) and fixed volume of dispersed phase (5.5 ml.). The results, summarized in Table 2, over a fourfold range of ionic strengths indicate a slight increase in θ with increasing ionic strength.

THE EFFECT OF OPERATING VARIABLES ON THE EXTRACTION RATE CONSTANT

Incidental to the determination of coalescence frequencies, values of the extraction rate constant were also determined. Because of continuing interest in mass transfer coefficients for immiscible liquid systems, these results are also given. The extraction rate constant kaN/V_t was also found to increase with increase in impeller speed and with increase in the dispersed-phase volume. The results are summarized in Figures 7 and 8. From these data kaN/V_t was found to vary approximately as the 2.04 power of the impeller speed and as the 0.63 power of the dispersed-phase volume.

DISCUSSION OF RESULTS

Historically, studies involving liquid-liquid systems have been plagued by impurities in the system, and many anomalous results have been attributed to this source. This work has been no exception. In some of the early runs a thin, skinlike film was observed at the interface after an extraction or coalescence run. This was thought to be partly colloidal sulfur resulting from the decomposition of hypo either by air

$$2\,S_2O_3^= + O_2 \rightarrow 2SO_4^= + 2S$$

or by acidic impurities in the toluene

$$S_2O_3^= + H^+ \rightarrow HSO_3^- + S$$

In subsequent runs the hypo solution was freshly prepared for each day's use, and all acidic impurities were removed from the system. Thereafter no interfacial films were observed, and more consistent results were obtained. Similar interfacial films, noted by Parrett (6) in static coalescence studies, were found to increase the coalescence time by more than 600%.

Early work also showed a significant variation in results when various lots of reagent grade toluene were used as received under the same experimental conditions. It was necessary to eliminate this variable so as to focus attention on the variation of coalescence frequency with the operating parameters, impeller speed, and dispersed-phase volume. For this reason a standardized procedure was adopted for purifying and recycling the toluene. As a consequence it should be noted that the absolute results reported here for the coalescence frequency are unique for this system. Any other toluene, containing traces of different constituents, might be expected to give different values for similar operating conditions. One case can be cited for illustration. An experiment, when conducted with refined toluene at 200 rev./min. with a dispersed-phase volume of 11.0 ml., gave a coalescence frequency of 0.2 sec.$^{-1}$ and an extraction rate constant of 0.00841 sec.$^{-1}$. When toluene was used directly as received under the same experimental conditions, the respective values were 0.13 and 0.00769 sec.$^{-1}$.

The principal conclusion to be drawn from this work is that the coalescence frequency increases rather markedly with increase in impeller speed and to a lesser extent with increase in dispersed-phase volume. At this stage no attempt will be made to explain the specific observed functional dependence. A few qualitative observations may be made, however, relating to the dynamics of the system. Vermeulen, Williams, and Langlois (9) have shown that, for a given dispersed-phase volume, the drop size decreases with increasing impeller speed. Thus increasing the speed leads to an increase in the number of drops in the system. Increase in the dispersed-phase volume also increases the drop population, although probably not in direct proportion, since the drop size is also affected (9). The observed increase of coalescence frequency with both increased speed and increased dispersed-phase volume suggests a relationship to the drop population. At the same time it should be noted that changes in impeller speed, and perhaps to some extent, changes in the dispersed-phase volume will also alter the turbulence level of the system. This too would be expected to influence the coalescence frequency. Since no attempt was made in this work to measure the drop size of the system, it is impossible to consider separately the possible effects of drop population and turbulence on the observed results.

One might raise a further question as to how the mass transfer which occurred in a coalescence experiment influenced the measured coalescence frequency. In this work mass transfer occurred from the continuous phase to the drops. Would the results have been different had mass transfer been in the opposite direction? A considerable body of evidence (2, 3, 4,) exists that coalescence is, indeed, influenced by the direction of mass transfer. These studies suggest that a higher frequency might have been expected had the mass transfer been in the opposite direction. This aspect is being investigated in a continuation of this research.

It is recognized that the simple coalescence model underlying the quantitative results reported here represent a considerable simplification of the dynamic behavior of a stirred liquid-liquid system. Nevertheless it is considered a reasonable starting point in the study of a very complex problem.

SUMMARY

An experimental technique has been described for tracing the progress of

Table 2. The Effect of Ionic Strength on Coalescence Frequency

Volume of dispersed phase = 5.5 ml.
Impeller Speed = 200 rev./min.
$X = 0.1$

Expt. no.	Ionic strength	kaN/V_t, sec.$^{-1}$	θ, sec.$^{-1}$
20	2.42	0.00531	0.13
3	4.84	0.00535	0.15
21	7.26	0.00591	0.15
22	9.68	0.00635	0.16

coalescence and redispersion of dilute aqueous dispersions in toluene in a stirred-tank system. A simple coalescence model has been advanced for purposes of estimating the magnitude of the coalescence frequency. This model assumes a constant drop size in the system, a constant number of drops, and a constant coalescence frequency for a fixed set of experimental conditions. The coalescence frequency is defined as the fraction of all drops coalescing per unit time. The experimental results indicate that the coalescence frequency varies as the 2.4 power of the impeller speed and as the square root of the dispersed-phase volume.

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NOTATION

a = interfacial area per drop, sq. cm.
c = concentration of iodine in toluene at time t, g./cc.
c_o = initial concentration of iodine in toluene, g./cc.
c_s = concentration of hypo in aqueous phase, g. $Na_2S_2O_3 \cdot 5H_2O$/cc.
c_{so} = initial concentration of hypo in aqueous phase, g. $Na_2S_2O_3 \cdot 5H_2O$/cc.
I = ionic strength of dispersed phase
k = mass transfer coefficient, cm./sec.
N = total number of drops of dispersed phase ($= N_s + N_w$)
N_s = number of drops containing hypo at time t
N_{so} = initial number of drops containing hypo
N_w = number of drops containing only inert solute at time t
t = time, sec.
S = impeller speed, rev./min.
V_d = total volume of dispersed phase, cc.
V_t = total volume of toluene (continuous) phase, cc.
X = initial ratio of hypo to inert drops $\left(= \frac{N_{so}}{N - N_{so}} \right)$
θ = coalescence frequency, sec.$^{-1}$

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Axial Solid Distribution in Gas-Solid Fluidized Beds

LIANG-TSENG FAN, CHAU JEN LEE, and RICHARD C. BAILIE
Kansas State University, Manhattan, Kansas

γ-ray attenuation method was applied to determine the axial fluidizing bulk density profile for an air-solid aggregative fluidized bed. Except for beds fluidized at very high air velocities two distinct density zones were noted. The density of the bed in the lower portion of the column was relatively constant for a particular set of operating conditions and did not vary with bed height. The density in the top portion of the bed fell rapidly with bed height.

The average density of the lower zone was correlated as a function of the operating variables. The density in the top zone was represented by a one-tail normal distribution curve. A somewhat better correlation was obtained by a two-parameter equation at high air velocities. The effects of operational variables, such as air velocity, static bed height, particle size, and particle-size distribution on these correlations were investigated.

Friction-factor correlations based on two different definitions of bed height were also obtained.

The major purpose of the present work was to investigate the axial distribution of the fluidized bulk density in an aggregative fluidized bed by γ-ray technique.

During the past years the characteristics of aggregative fluidized beds were studied by several different experimental methods.

1. High speed photographic studies were made by Matheson et al. (*13*), Furukawa and Omae (*9*), and by Massimilla and Westwater (*12*). They took high-speed photographs of bubbles through transparent walls of fluidized columns for gas-solid systems.
2. Shuster and Kisliak (*18*) studied the uniformity of aggregative fluidized beds by using diaphragm plates to measure pressure gradients.
3. Morse and Ballou (*16*) and Dotson (*7*) examined the uniformity of aggregative fluidization by measuring the variation of the electric capacitance between condenser probes. Later Bakker and Heertjes (*4*) applied a similar technique to measure the point porosity of fluidized beds.
4. Yasui and Johanson (*19*) devised a small light probe to study the frequency, thickness, and the rising speed of bubbles in aggregative fluidized beds.

TABLE 1. PARTICLE SIZE OF GLASS BEADS USED

Mesh	Particle range	Average size
40-45 U.S. mesh	0.00138-0.0164 in.	0.0153 in.
80-100 U.S. mesh	0.0049-0.0070 in.	0.00642 in.
60-70 U.S. mesh	0.0083-0.0098 in.	0.00906 in.

Chau Jen Lee is at Oklahoma State University, Stillwater, Oklahoma.