

Dispersed Phase Mixing:

II. Measurements in Organic Dispersed Systems

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When two liquid phases are contacted in a stirred tank reactor, dispersed phase mixing can affect average reaction rate and product selectivity in nonfirst order or mass transfer controlled reactions, as shown theoretically in Part I. This work is concerned with experimental measurement of the dispersed phase mixing rate. Various organic phase dispersions in water were studied in stirred tanks with a dye transfer light transmission technique. Batch experiments were performed in 0.30, 5.5, and 86-gal. vessels. The variables studied were power input per unit volume, phase fraction, impeller type, and vessel scale. Dispersed phase mixing rates were found to be in the range where they can have significant effects on chemical reactions. A typical value of the mixing rate is 10 volumes of dispersed phase/min. at a power input of 10 hp./1,000 gal. The information given here and in Part I shows for the first time the importance of these effects in reactor design.

It is well known that a distribution of residence times occurs in a well-stirred flow reactor. If two immiscible liquid phases are being contacted in such a reactor, a distribution of dispersed phase concentration results. This concentration distribution is modified by interaction between drops due to coalescence and redispersion. The higher the rate of this dispersed phase mixing the more uniform will the drop concentrations become. If a reaction occurs in the dispersed phase then for other than first-order reactions, the dispersed phase mixing rate can have an important effect on the reactor size for a given conversion or on the conversion and selectivity for a given reactor.

This work presents experimental measurements of dispersed phase mixing rates in stirred vessels and an investigation of the variables that affect these rates. This experimental work is complementary to Part I, in which a theoretical model was proposed and solutions obtained for the effect of dispersed phase mixing on conversion for zero order and mass transfer controlled reactions.

The surprising result of the theoretical calculations is that an extremely high ratio of mixing rate to residence frequency is needed if the reaction rate is to be that of a completely mixed

dispersed phase. Therefore the order of magnitude of rate to be expected in practical situations must be measured in order to determine whether the effects of dispersed phase mixing must be considered in design.

The data presented herein are not intended to be used directly for design purposes. In view of the many (and unknown) factors which affect coalescence rates, this would be foolish indeed. These measurements with relatively clean liquid phases showed interaction rates in the range of importance for residence times typical of commercial use of continuous stirred reactors. Thus in many reactors the dispersed phase cannot be considered to be either totally unmixed or perfectly mixed, and consideration of dispersed phase interaction should be included in scale up and design. A further purpose and result of this work is the illustration of how interaction rate depends on several design variables.

Measurements of the dispersed phase mixing rate were made by a light transmission technique following batch addition of a dye. A small quantity of highly colored drops was added to a stirred vessel containing uncolored or weakly colored drops dispersed in the continuous phase. A light transmission model was developed which permits the rate of dispersed phase

mixing to be deduced from measurements of the change of light transmission with time.

There have been only two other pieces of work reported in which dispersed phase mixing rates were measured. Madden and Damerell (5) studied the single system water dispersed in toluene in a 0.3-gal. vessel stirred with a flat blade turbine. They followed the mixing rate by reacting iodine dissolved in the toluene with sodium thiosulfate distributed in the dispersed phase. Matsuzawa and Miyauchi (6) reported negligible mixing rates for water dispersed in benzene in a 0.5-gal. vessel.

Organic liquid dispersions in an aqueous phase were studied in the present work. These included carbon tetrachloride, carbon tetrachloride/isooctane (specific gravity = 1), spray base (a kerosene) in water, and spray base in 65%w potassium nitrite. Power inputs from 1 to 140 hp./1,000 gal. at dispersed phase fractions from 0.1 to 0.4 were covered in 0.3-, 5.5-, and 86-gal. geometrically similar vessels. The impellers used were flat bladed turbines and propellers with and without draft tubes, all with wall baffles.

LIGHT TRANSMISSION THEORY

When a light beam enters a liquid-liquid dispersion, portions of it are re-

TABLE 1. IMPELLER CHARACTERISTICS

Impeller	0.30-gal. vessel					5.5-gal. vessel					86-gal. vessel				
	Diam.	Pitch Diam.	$\frac{D_{imp.}}{D_{tank}}$	Power coefficient Fully baffled	Draft tube	Diam.	Pitch Diam.	$\frac{D_{imp.}}{D_{tank}}$	Power coefficient Fully baffled	Draft tube	Diam.	Pitch Diam.	$\frac{D_{imp.}}{D_{tank}}$	Power coefficient Fully baffled	Draft tube
Marine propeller	2 in.	1.1	0.50	0.66	0.65	5 in.	1.6	0.48	—	0.48	13 in.	0.91	0.50	—	0.16
Flat blade turbine	2 in.	—	0.50	6.0	—	5 in.	—	0.48	4.9	—	13 in.	—	0.50	5.5	—

flected and refracted at the interfaces between the phases. Unless the detailed geometry of the system is given, it is not possible to calculate the intensity of light elsewhere in the emulsion. However it is an observed fact that if the number of drops in the nominal path is large, the transmitted light does not vary greatly in intensity. The apparent optical density of the emulsion must therefore be a statistical property which does not fluctuate widely even though the detailed geometry is continually changing; that is the variance of the distribution of transmitted light intensity is small with respect to the average. This means that in solute-free emulsions (nonabsorbing) there is a distribution of separate paths through drops (involving multiple reflections and refractions) which is relatively fixed. Therefore when drops containing solute are introduced into the system, and these drops distribute themselves spatially at random in the emulsion, one must consider the interaction of the distribution of path lengths through drops and the distribution of concentration among the drops.

A path i of length h_i through absorbing drops will be assumed to cause an attenuation of light in accordance with the Beer-Lambert law:

$$\left(\frac{I}{I_0}\right)_i = e^{-(\alpha + \beta \bar{c}_i)h_i} \quad (1)$$

I_0 includes the light scattering properties of the emulsion. If $p_1(h, \bar{C})$ is the joint probability density distribution of path length h and average concentration $\bar{C}$, then the average light transmission over the composite paths of a beam is

$$\frac{\bar{I}}{I_0} = \int_0^\infty \int_0^\infty e^{-(\alpha + \beta \bar{C})h} p_1(h, \bar{C}) dh d\bar{C} \quad (2)$$

Here $p_1(h, \bar{C}) = p_2(h) p_3(\bar{C}|h)$, where $p_3(\bar{C}|h)$ is the conditional probability density distribution of $\bar{C}$ when h is specified. Equation (2) may be rearranged to give

$$\frac{\bar{I}}{I_0} = \int_0^\infty e^{-\alpha h} p_2(h) \int_0^\infty e^{-\beta \bar{C} h} p_3(\bar{C}|h) d\bar{C} dh \quad (3)$$

The term p_3 is also the sampling distribution of the mean for samples with path length h , from a drop population with a concentration distribution $p_4(\bar{c})$ having mean $\bar{c}$ and central variance μ_2 .

Take h to be a multiple of an average drop path length $\bar{d}$, $h = nd$. Assume that there are r drops in the beam distributed among q paths. If the drops are distributed at random, the distribution of drops among the paths is binomial with the frequency function

$$p_2(n) = \left(\frac{r}{n}\right) \left(\frac{1}{q}\right)^n \left(1 - \frac{1}{q}\right)^{r-n} \quad (4)$$

The function $p_3(\bar{C}|h)$ is the sampling distribution of the mean for samples

$$\frac{\bar{I}}{I_0} = \sum_{n=0}^r e^{-\left[\alpha d + \frac{\bar{c}}{\mu_2} \ln \left(1 + \frac{\beta d \mu_2}{c}\right)\right] n} p_2(n) \quad (7)$$

of size n from a population distribution $p_4(c)$, having mean $\bar{c}$ and central variance μ_2 . The sample average is of course defined as

$$\frac{\bar{I}}{I_0} = \left[1 + \frac{1}{q} \left(e^{-\left[\alpha d + \frac{\bar{c}}{\mu_2} \ln \left(1 + \frac{\beta d \mu_2}{c}\right)\right]} - 1\right)\right]^{-1} \quad (8)$$

$$\bar{C} = \frac{1}{n} \sum_{i=1}^n c_i \quad (5)$$

When n is large and the variance of c

$$\log \frac{\bar{I}}{I_0} = \frac{r}{q} \left(e^{-\left[\alpha d + \frac{\bar{c}}{\mu_2} \ln \left(1 + \frac{\beta d \mu_2}{c}\right)\right]} - 1 \right) \quad (9)$$

not too great, the central limit theorem (2) states that $p_3(\bar{C}|h)$ approaches a normal distribution with mean $\bar{c}$ and central variance $\mu_2^* = \mu_2/n$. However if Equation (3) is evaluated with the binomial and normal approximation, the result is

$$\ln \frac{\bar{I}}{I_0} = \gamma_0 + \gamma_1 \mu_2$$

which cannot hold at large variances. Therefore the central limit theorem is not satisfactory, and a better approximation must be sought. From a mathematical standpoint the Pearson type III (Gamma) distribution (3) is con-

$$\theta = \frac{\log \frac{\bar{I}}{I_1}}{\log \frac{\bar{I}_2}{\bar{I}_1}} = \frac{e^{-\beta \bar{d} \bar{c} \left[\frac{\bar{c}}{\beta d \mu_2} \ln \left(1 + \frac{\beta d \mu_2}{c}\right) \right]} - 1}{e^{-n \bar{d} \bar{c}} - 1} \quad (12)$$

venient as well as having the important property of being nonzero only for positive variables. If the mean of the Pearson type III distribution is set equal to c with variance equal to μ_2/n , it may be written

$$p_3(\bar{C}|n) = \frac{\left(\frac{n\bar{c}}{\mu_2}\right)^{\frac{n}{\mu_2}} \left(\frac{n\bar{c}}{\mu_2} - 1\right)^{\frac{n}{\mu_2} - 1} e^{-\frac{n\bar{C}}{\mu_2}}}{\Gamma\left(\frac{n\bar{c}}{\mu_2}\right)} \quad (6)$$

When this and the binomial distribution are used, the inner integration in Equation (3) is readily performed to give

which is the moment generating function of the binomial distribution with the exponent coefficient as its argument. This becomes

For large q (many paths, or equivalently many drop diameters, in the beam diameter) the logarithm of (8) is simpler:

The initial light transmission of the emulsion prior to the addition of a solute is from (9), when $\bar{c} = 0$

$$\log \frac{\bar{I}_1}{I_0} = \frac{r}{q} [e^{-\alpha d} - 1] \quad (10)$$

while the final light transmission when $\mu_2 = 0$ is

$$\log \frac{\bar{I}_2}{I_0} = \frac{r}{q} [e^{-(\alpha d + \beta d \bar{c})} - 1] \quad (11)$$

Then a normalized light transmission measure (θ) may be defined as [(9) minus (10)] divided by [(11) minus (10)]

which for small final light absorption per single drop ($\beta d \bar{c} \ll 1$) becomes

$$\theta \approx \frac{\bar{c}}{\beta d \mu_2} \ln \left(1 + \frac{\beta d \mu_2}{c}\right) \quad (13)$$

or

TABLE 2. LIQUID PROPERTIES

Liquid	$d^{77/100}$	Solubility of bifluoridene (approx.), g./liter	Viscosity 77°F., centipoise	Interfacial tension with water 77°F., dynes/cm.
Water	0.998	0	0.95	—
65% w KNO ₃	1.56	0	3.0	—
CCl ₄	1.58	50	0.92	45
64% v iC ₈ — 36% v CCl ₄	1.01	8.5	0.58	46
Spray base	0.80	10	1.7	47 (58)*
Spray base + 8 g./l BiF	0.80	—	1.8	47

* Interfacial tension vs. 65% w KNO₃.

$$\theta \cong 1 - \frac{1}{2} \frac{\beta d}{c} \mu_2 + \frac{1}{3}$$

$$\left(\frac{\beta d}{c} \mu_2 \right)^2 - \frac{1}{4} (\dots (14)$$

For small μ_2 this reduces to the same form as from the normal distribution. However the assumption of the Pearson type III distribution (Gamma distribution) gives an equation for θ which does indeed have the limits zero and one for the range of μ_2 from infinity to zero, as is necessary if the equation is to be used in interpreting experiments.

The Pearson type III in turn cannot be the exactly correct form for $p_n(\bar{C}|n)$ as the latter undoubtedly has a non-zero density at $\bar{C} = 0$ for small samples and large initial variance.

The experimental technique involves the observation of light transmission changes after batch addition of a small amount of highly colored dispersed phase. In Part I it was shown that the variance of concentration in a stirred batch emulsion in which coalescences and redispersions are taking place, as calculated with an idealized model, decays exponentially with time in accordance with

$$\mu_2 = \mu_2(o) e^{-1/2\omega_i t} \quad (15)$$

Substituting this into (13) one obtains

$$\theta = \frac{\bar{c}}{\beta d \mu_2(o)} e^{1/2\omega_i t} \ln \left(1 + \frac{\beta d \mu_2(o)}{\bar{c}} e^{-1/2\omega_i t} \right) \quad (16)$$

or into (14)

$$\theta = 1 - \frac{1}{2} \frac{\beta d}{c} \mu_2(o) e^{-1/2\omega_i t} + \frac{1}{3} \left[\frac{\beta d}{c} \mu_2(o) \right]^2 e^{-\omega_i t} - \dots \quad (17)$$

When t is large, this reduces to

$$1 - \theta \cong \frac{1}{2} \frac{\beta d}{c} \mu_2(o) e^{-1/2\omega_i t} \quad (18)$$

Since experimentally the observed light transmission followed Equation (18) closely, it was used to obtain ω_i . Very little difference in results was obtained by using Equation (16).

When this method is used to interpret light transmission measurements through emulsions in terms of a dispersed phase mixing rate, it should be kept in mind that approximations are involved in both the dispersed phase

mixing model suggested in Part I (constant size drops, immediate redispersion after coalescence, internal mixing of the coalesced drop before redispersion, random collisions) and in the present calculation for the light transmission through such a system. The experimental results indicate decay of the logarithm of light transmission even more exactly exponential in most cases than the theory indicates.

In the foregoing, complete mixing of coalesced drops before redispersion has been assumed. However this is no limitation since the light transmission technique measures the inhomogeneity of the dispersed phase, which is the

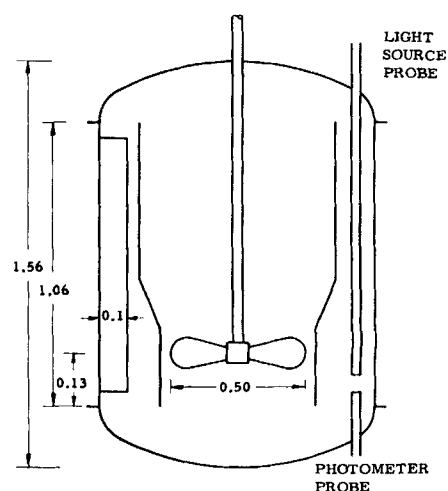


Fig. 1. Vessel with propeller in draft tube. All dimensions are relative to tank diameter.

variable of real interest. Thus ω_i can be interpreted as the mixing rate of the dispersed phase rather than the rate of coalescence and redispersion. Since the mixing rate depends so strongly on the rate of coalescence, ω_i gives information about the latter even if coalesced drops are not completely mixed before redispersion.

APPARATUS

Three vertical cylindrical vessels were used in this study, the volumes of which were 0.30-, 5.5-, and 86-gal. Impellers used were one-half the vessel diameter. The impellers were six-blade turbines and marine (three-blade) propellers and their dimensions and power numbers are given in Table 1. The power coefficient K is defined by the relation power = $K\rho N^3 D^5/g_c$. Figure 1 shows the sketch of one of the vessels with a propeller in draft tube. Turbines were located at one-half the vessel height. Since the three vessels used were geometrically similar, dimensions are given relative to the vessel diameter. The three vessel diameters are 4, 10.4, and 26 in. The vessels were equipped with elliptical heads and had an overall length/

TABLE 3. RANGE OF VARIABLES STUDIED

System	ϕ	Power input range, hp./1,000 gal.							
		0.30-gal. vessel		5.5-gal. vessel		86-gal. vessel		D.T.	W.B.
		Prop. in D.T.*	Prop. in W.B.†	Turb. in W.B.†	Prop. in D.T.	Turb. in W.B.	Prop. in D.T.		
iC ₈ -CCl ₄ in water	0.1	8-100	2-100	9-240	—	—	—	—	—
	0.2	2-100	2-100	9-140	4-110	2-44	10-104	10-132	—
	0.3	1-100	2-100	3-140	—	—	—	—	—
	0.4	1-100	2-100	3-140	4-61	2-44	6-104	10-132	—
CCl ₄ in water	0.2	3-110	—	—	9-112	—	—	—	—
	0.4	10-123	—	—	10-113	—	—	—	—
Spray base in water	0.1	4-96	—	—	—	—	—	—	—
	0.2	2-94	—	8-107	4-100	5-42	6-104	10-130	—
	0.3	2-93	—	—	—	—	—	—	—
	0.4	2-91	—	8-104	4-96	2-40	5-100	10-125	—
Spray base in KNO ₃	0.2	17-140	—	—	—	—	—	—	—

* DT = draft tube + wall baffles.

† WB = four wall baffles.

TABLE 4. DEPENDENCE OF INTERACTION RATE ON POWER INPUT

System	ϕ	Propeller in draft tube		0.30-gal. vessel		5.5-gal. vessel		86-gal. vessel	
		Slope†	ω_t^*	Slope†	ω_t^*	Slope†	ω_t^*	Slope†	ω_t^*
iC ₈ -CCl ₄ in water	0.1	0.85	6.3	0.89	3.2	1.08	1.9	—	—
	0.2	0.78	12.0	0.82	6.4	0.99	3.1	0.84	7.3
	0.3	0.72	15.0	0.80	10.0	1.07	5.1	0.91	4.7
CCl ₄ in water	0.4	0.62	22.0	0.80	13.0	0.96	8.8	0.83	10.0
	0.2	0.63	16.0	—	—	—	—	0.69	8.2
	0.4	0.49	35.0	—	—	—	—	0.80	13.0
Spray base in water	0.1	0.73	1.8	—	—	—	—	—	—
	0.2	0.68	2.5	—	—	0.88	0.85	0.60	2.0
	0.3	0.62	3.6	—	—	—	—	0.78	2.1
Spray base in KNO ₃	0.4	0.59	4.3	—	—	0.74	1.8	0.63	3.2
	0.2	0.83	~0.8	—	—	—	—	0.70	3.1
	—	—	—	—	—	—	—	0.62	1.6

* At 10 hp./1,000 gal.

† Slope defined by $\omega_t = \text{constant} \times (P/V)^{1/\text{slope}}$.

diameter ratio of 1.6. All experiments were made with the vessels completely filled with liquid. Four symmetrically placed wall baffles, one-tenth the vessel diameter in width, were used in all tests. Variable speed drive was provided for the two smaller vessels by DC motors with Thymotrol control units; a gasoline engine

Figure 1) is the best of all arrangements tested in this respect. Also the three impeller arrangements tested cover the range from what is usually called a *high-flow type* (propeller in draft tube) to a *high-shear type* (turbine). Unfortunately geometrically similar propellers of the appropriate sizes were not available at the

gauge stainless steel tubing having sixteen equally spaced holes were used in the large vessel. It was possible to make from four to eight successive injections on each charge before reaching the limit of linearity of the photometer.

The properties of the liquids used in this study are shown in Table 2.

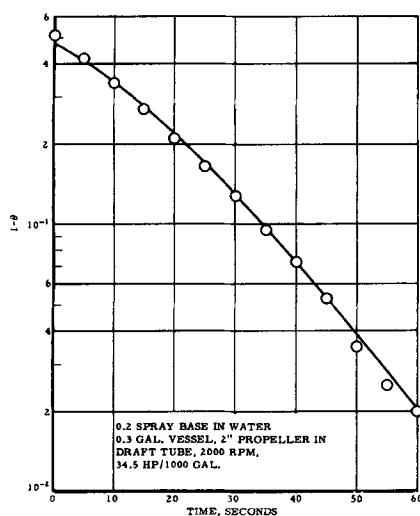


Fig. 2. Results of a dispersed phase mixing experiment correlated by Equation (16), $\omega_t = 6.0 \text{ min.}^{-1}$.

powered the 86-gal. mixer. The power numbers reported were measured experimentally. In the cases where a draft tube was used the wall baffles remained in the vessel. The 2-in. propeller was a flat bladed variety, and the other two were cast marine propellers. The flat bladed turbines had blade lengths of $D/4$ and blade heights of $D/5$.

The impeller sizes and locations used were not chosen as being typical of commercial practice. Rather they were chosen for ability to disperse the organic phase uniformly throughout the vessel at low power inputs. Thus a wide range of power inputs could be covered even with a system as difficult to disperse as carbon tetrachloride-water. The marine propeller in draft tube (of the design shown in

TABLE 5. DEPENDENCE OF INTERACTION RATE ON DISPERSED PHASE FRACTION

System	Value of exponent on ϕ		
	0.30-gal. vessel	5.5-gal. vessel	86-gal. vessel
Spray base in water	0.7	0.6	0.5
iC ₈ -CCl ₄ in water	1.0	1.1	1.1
CCl ₄ in water	1.0	0.9	—

time of the tests. Any effect this may have had on the results is discussed later.

Each vessel was equipped with a unit for examining the emulsion photometrically. The unit consisted of an incandescent light source and probe, photocell, logarithmic amplifier, and high-speed recorder. The location of the light source and probe in the vessel is shown in Figure 1. The light was filtered to give a nearly monochromatic beam of about $455 \text{ m}\mu$, the wavelength of the absorption peak of the dye that was used. The dye used was 9,9'-bifluorylidene, which has a light yellow to orange-red color in the hydrocarbon solvents used.

The light beam was filtered to produce a nearly monochromatic source at $455 \text{ m}\mu$, which is the wavelength of the absorption peak of the dye. At this wavelength the extinction coefficient is $2.3 \times 10^4 \text{ liters/mole cm.}$ A single point injection technique was used on the 0.30- and 5.5-gal. vessels, but owing to the large volume of dye required for the 86-gal. vessel, a multi-point injection was necessary to achieve small drops and rapid injection. Hence circular injection rings of $1/4 \text{ in.} \times 16$

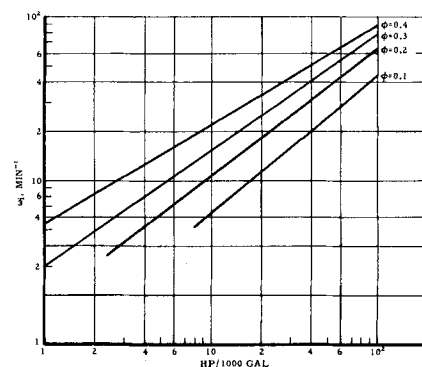


Fig. 3. Effect of power input and dispersed phase fraction 0.30-gal. vessel, propeller in draft tube, iso-octane-carbon tetrachloride in water.

EXPERIMENTS

For measurement of drop interaction rates the vessel was charged with liquids and the impeller speed set. Sufficient time was allowed to reach drop size equilibrium, as indicated by steady light transmission. Then a small amount of a nearly saturated solution of bifluorylidene dye in solvent (same as dispersed phase) was injected quickly ($\sim 1 \text{ sec.}$) from a hypodermic syringe to a point just above the impeller and near the center of the vessel. The light transmission change with time through the emulsion was recorded as the solute distributed among the drops by coalescences and redispersions. Equation (18) was then fitted to the light transmission recording to determine ω_t . This was done by plotting $\log(1 - \theta)$ vs. time t and measuring the slope which will be $\omega_t/2$. The results of a typical experiment are shown in Figure 2. The direct analysis

of the recordings was achieved rapidly by the use of a curve reader. The curve reader consists of an exponential signal generator, whose signal is fed into an oscilloscope, and a mirror for superimposing the generated curve from the oscilloscope screen and the recorder trace.

The light transmission depends upon the drop size distribution as well as the dye concentration distribution. Therefore during an experiment the former must remain constant to obtain meaningful measures of the latter. This was checked by observing the light transmission before and after the dye addition experiment with a filter in the light path that absorbed in the dye range. In a few instances the light transmission with this filter in the light path was measured throughout a complete experiment. In no cases for the data reported here were there any changes in drop size distribution during an experiment.

In earlier experimental work other dyes were found to be surface active which resulted in changes in drop size distribution during a run. The bifluorilidene dye which is nonsurface active was selected after an extensive search. It required careful purification to obtain consistent results. Distilled water was used in the two smaller vessels and tap water in the 86-gal. vessel. The authors found that more consistent results were obtained when salt was added, so that 0.05 moles/liter of sodium chloride was present in the aqueous phase in all of the experiments. Thorough water washing of the carbon tetrachloride before an experiment was also necessary to obtain reproducible results.

The dye solution injected was generally nearly saturated. However a few measurements were made both in the 0.3- and 86-gal. vessels, with twice the volume injection of one-half the concentration to find out if there was an effect of dye concentration. These gave interaction rates in agreement with those with saturated dye, so it is concluded that the effect of dye concentration over a twofold range has a negligible, if any, effect on the measurement of interaction rate.

RESULTS

Table 3 shows the range of the variables covered in the experimental work. To save space only a few representative examples of the results are shown in Figures 3, 4, and 5. The functional dependencies of interaction rate on power input and volume fraction of dispersed phase for the several liquids and vessel sizes are given in Tables 4 and 5, respectively. For clarity data points are given only on Figure 4; their purpose here is to illustrate the number of points used to determine each curve and the spread in the data. Since drop interaction rate is so sensitive to trace contaminants, different experimenters cannot expect to duplicate each other's data, although the order of magnitude of interaction rate and the dependence on design variables should be the same. Hence

there is little purpose in giving each datum.

Effect of Power Input

Interaction rates were measured at power inputs over the range of 1 to 140 hp./1,000 gal. and were found to increase markedly with power input in all cases. One isolated measurement was made at 240 hp./1,000 gal. The dependence on power input varied with the 0.5 to 1.1 power depending on the system and impeller used as summarized in Table 4.

Effect of Dispersed Phase Fraction

The interaction rate was found to be proportional to the dispersed phase fraction to the 0.6 power for spray base and to the 1.1 power for iso-octane — carbon tetrachloride. An ex-

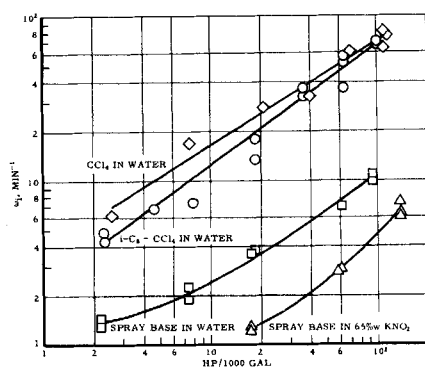


Fig. 4. Effect of system on dispersed phase interaction rate 0.30-gal. vessel, propeller in draft tube, $\phi = 0.20$.

ample of the effect of phase fraction is shown in Figure 3. A summary of the dependence on phase fraction for the three systems and three vessel sizes is given in Table 5.

Effect of System

Interaction rates were measured in all three scales and with two impeller types for the systems spray base in water and iso-octane — carbon tetrachloride in water. In all cases the latter system gave higher mixing rates by two to eightfold than the former for the same phase fraction and power input. Carbon tetrachloride in water gave the same to somewhat higher rates than the iso-octane — carbon tetrachloride mixture. Spray base in 65% potassium nitrite gave about one-half that for spray base in water. The effect of system in the 0.30-gal. vessel is shown in Figure 4, which also gives an idea of the degree of scatter of the data.

The great difference between systems will be due to the differing fractions of collisions that result in coalescence. The effect is quite difficult to

predict, since so many factors are involved. When the drops collide or come close to each other, the coalescence will be influenced by the rate of thinning of the intervening film of the continuous phase. The physical properties of the system and the condition of the interface will have a great effect on the thickness of the film, its stability, and its resistance to rupture. Trace materials that are surface active can also have marked effects on this film, as evidenced by the difficulties experienced with contaminated liquids and dye. Any mass transfer that occurs can also have a marked influence on the behavior of the film between the drops (4). In the experiments reported in this work the authors found lower interaction rates for contaminated systems and when the hydrocarbons were not freshly washed, in agreement with the work of others on individual coalescences and drop sizes in dispersions.

Effects of Scale and Impeller Type

The effects of vessel size and impeller type are inter-related and anomalous. The interaction rate decreased with increasing vessel size with the propeller in draft tube. Yet when the turbine with wall baffles was used, the interaction rate was about one-third that for the propeller with draft tube in the smallest vessel and increased with scale to be threefold greater in the largest vessel. In the intermediate vessel the two impellers gave about the same results. A third impeller arrangement, a propeller with wall baffles (located at the center axially, without draft tube), was tested in the 0.30-gal. vessel only. It produced rates midway between those for the other two impeller arrangements. These effects are shown in Figure 5.

Interaction rate depends on the relative velocity between drops, which probably depends strongly on shear rate. Now it is likely that interaction rate depends on the distribution of shear rates (which is very nonuniform) as well as the average shear rate. This distribution is quite different for the different impeller arrangements. Moreover dynamic similarity, hence distribution of shear rates, is not maintained at the same (P/V) for scale up with geometrical similarity. Therefore it is not surprising that ω_i varies with scale at the same (P/V) or that the impellers have different scale-up rules.

COMPARISON WITH WORK OF OTHERS

One of the two previously reported works on the measurement of dispersed phase interaction is a recent paper by Madden and Damerell (5), who meas-

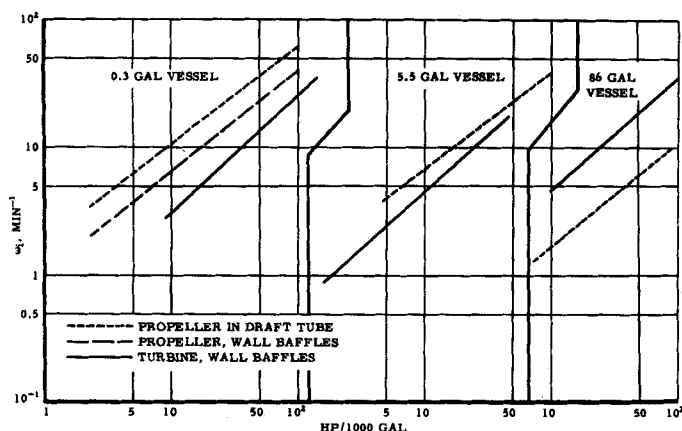


Fig. 5. Effect of impeller type and vessel size on interaction rate, iso-octane-carbon tetrachloride dispersed in water, $\phi = 0.20$.

ured interaction rates in a turbine stirred 0.3-gal. vessel, with wall baffles, for water dispersed in toluene. The toluene contained iodine and the interaction rate was measured by adding a small amount of sodium thiosulfate solution and following the extraction of the I_2 . They investigated the effect of power input from 1 to 7 hp./1,000 gal. and the effect of dispersed phase volume from 0.0014 to 0.011 dispersed phase fraction.

If Madden's results are extrapolated to $\phi = 0.1$ and compared with those reported here, Madden's rates are the greater by about 2 orders of magnitude. Madden used an aqueous dispersion in an organic phase in contrast to the organic dispersions of this study. Aqueous dispersions coalesce much more rapidly than organic dispersions, so the discrepancy is not surprising. Madden found ω_i dependent on power input to the 0.8 power for power inputs between 1 and 7 hp./1,000 gal. which is in the range 0.5 to 1.1 found in this work for power inputs between 1 and 140 hp./1,000 gal. Madden found that ω_i depends on phase fraction to the 0.5 power in the range of ϕ from 0.0014 to 0.011 which is close to the exponent of 0.6 to 1.1 for this work in the range of ϕ from 0.1 to 0.4. Madden found, as was found here, that addition of inorganic salts to the aqueous phase gave more reproducible results.

Matsuzawa and Miyauchi (6) reported experiments in which they attempted to measure the dispersed phase mixing rate for water drops dispersed in benzene. They used a 3-liter vessel with a 70-mm. diameter four-bladed turbine, feeding aqueous ferric chloride and stannous chloride so that the reaction product ferrous chloride could be measured to indicate the mixing rate. They reported negligible mix-

ing at around 1 hp./1,000 gal. power input. This is surprising when compared with the high values reported by Madden at this power input for almost the same system. Perhaps the chlorides present caused a large reduction in coalescence rate.

EFFECT ON REACTIONS

Dispersed phase mixing has no effect on first-order reactions but will increase the conversion for orders less than 1 (and the analogous mass transfer controlled reaction) and decrease the conversion for orders greater than 1. It is rather difficult to make a general statement about the quantitative effects, since these will depend on the particular reaction scheme and rates under consideration. However for a specified reaction system and reaction rate the effect on conversion can be obtained from the results in Part I. Part I contains charts for two cases only, zero-order reaction and the mass transfer controlled reaction. However the same methods can be used to make calculations for other reaction schemes.

A simple illustration follows for the zero-order reaction case. The experiments indicate that ω_i of 10 min.⁻¹ is a reasonable value at a feasible power input of about 10 hp./1,000 gal. If one now turns to the results in Part I, one sees that the parameters to be specified are the dispersed phase mixing modulus ω_i/ω_r and the reaction modulus $k/\omega_r C_o$. If one selects some residence frequencies, say 0.1, 1.0, min.⁻¹, the corresponding values of the mixing modulus are 100, 10. It can be seen from Part I that for a wide range of the reaction modulus considerable increases in conversions would result when compared with zero dispersed phase mixing. Also in some cases the conversion would still be considerably below the 100% conversion that would result from complete dispersed phase

mixing. The conclusion is drawn that the rates of dispersed phase mixing that were measured are in the range where significant effects on conversion are experienced. These effects are most marked in high conversion processes. Also it is concluded that the actual mixing rates have effects significantly different from either the zero or complete dispersed phase mixing limiting cases. Since liquid dispersions in commercial reactors usually contain more contaminants than those studied here, interaction rates should be lower than reported here. In such cases drop interaction effects will be important over a wider range of residence times than in the examples just given.

When kinetic data are being obtained in the laboratory, a batch experiment is often performed. Dispersed phase mixing will have no effect on the reactions in a batch reactor because there is no distribution of concentration in the dispersed phase. However when the results of a batch experiment are used to design a continuous stirred tank reactor, then the dispersed phase mixing effects must be considered.

CONCLUSIONS

The variables studied for a given liquid system were power input, dispersed phase fraction, impeller type, and scale of the apparatus. Quite large differences in dispersed phase mixing rates were obtained with different liquid systems. The dispersed phase mixing rate depends on the power input per unit volume raised to approximately the 0.8 power. This exponent varies between 0.5 and 1.1. The mixing rate is proportional to the dispersed phase fraction to the 0.5 to 1.1 power. These dependencies on power input and phase fraction are in good agreement with the work of Madden and Damerell (5). The different systems have up to a tenfold effect on the mixing rate, spray base in 65% potassium nitrite giving the lowest rates and carbon tetrachloride in water the highest mixing rates. The rates for the organic dispersions are about 2 orders of magnitude smaller (at the same power input) than the rates of Madden and Damerell (5) for an aqueous dispersed system. These great differences in system are undoubtedly due to the different coalescence rates. Mixing rates for the propeller in draft tube design are about two or three times greater than in the baffled turbine at the 0.3-gal. scale. However as the scale increases, the mixing rate decreases for the propeller and increases for the turbine until at the 86-gal. scale the turbine mixing rates are approximately two or three times those of the propeller.

The order of magnitude of the dispersed phase mixing rate is ten volumes interacting per volume of dispersed phase per minute at power inputs of the order 10 hp./1,000 gal. The theoretical analysis in Part I leads to the conclusions that these values of the mixing rates can have significant effects on chemical reactions in stirred vessels, and that such rates are not closely equivalent to either of the two limiting conditions, zero or complete dispersed phase mixing. The value of these results is that some estimate of dispersed phase mixing, and its effect on chemical reactions can now be made in reactor designs, a possibility that has not existed heretofore.

NOTATION

a	= interfacial area per unit volume
c	= dye concentration in a drop
$\bar{c}$	= mean of $p(c)$
$\bar{C}$	= average concentration in light path
D	= impeller diameter
d	= drop diameter

g_c	= conversion factor
h	= length of light path
$I(I_0)$	= light transmission (zero drop absorptivity)
$\bar{I}$	= average light transmission
$\bar{I}_1$	= initial average light transmission before dye added
$\bar{I}_2$	= final average light transmission after dye dispersed
K	= power coefficient of an impeller
N	= impeller rotational speed
n	= number of drops
p	= probability density distribution or frequency function

$p(h, \bar{C})$ = joint probability density distribution of path length h and $\bar{C}$

$p(\bar{C}|h)$ = conditional probability density distribution of $\bar{C}$ when h is specified

P/V	= power input per unit volume
q	= number of light paths
r	= number of drops in the beam

Greek Letters

α	= light absorptivity of dispersed phase prior to dye injection
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β	= extinction coefficient of the dye
γ_0, γ_1	= constants
θ	= normalized light transmission
μ_0	= central variance of $p(c)$
ν	= kinematic viscosity
ρ	= liquid density
ϕ	= volume fraction of dispersed phase
ω_i	= dispersed phase mixing, vol./vol., of dispersed phase/min.
ω_r	= residence frequency

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Drying of Air by Fixed Bed Adsorption with Molecular Sieves

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Fixed bed air drying is representative of many operations including ion exchange and the more general operation of adsorption. All these processes are characterized by the breakthrough phenomenon in which the stream leaving the bed remains at a low concentration for a considerable period and then rises to the value of the stream entering the bed. This rise when plotted against time or cumulative material passed through the bed results in an S-shaped curve and relatively defines the mass transfer zone (MTZ). The mass transfer zone has been precisely defined (14) as that part of the bed or breakthrough curve in which the water concentration change from C_B to C_E is occurring, (C_B

and C_E are arbitrarily chosen as 0.05 C_0 and 0.95 C_0 respectively). A typical breakthrough curve is shown in Figure 1.

Adsorption has been studied extensively, but the manufacture of new adsorbents and recognition of new applications have greatly increased the necessity of finding simple and dependable design procedures. Typical of the new adsorbents are the molecular sieves which are unique in their separating properties. The selectivity of these adsorbents and their high affinity for water make them ideal for removing moisture from air.

One simple design procedure for fixed bed adsorbents is the mass transfer zone (MTZ) method described by

Treybal (14) in which an adsorption zone of constant length and shape independent of fixed bed height is used. It was the purpose of this work to obtain MTZ data for molecular sieves and to further develop the MTZ design method by investigating the effect of inlet air moisture content on the mass transfer zone.

EXPERIMENTAL

All runs were made with a 0.628 in. I.D. fixed bed drier (adsorber). The ranges for the independent variables investigated were as follows: air stream flow rate, 468 to 1,131 lb. dry air/(hr.)(sq. ft.); bed temperature, 65° to 90°F; inlet air water concentration, 0.00571 to 0.01870 lb. water/lb. dry air; adsorbent particle size, 0.065 to 0.093 in.; fixed bed height, 1.156