

Mass Transfer and Chemical Reaction in Liquid-Liquid Agitation Systems

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(Received January 25, 1960)

The objectives of the agitation of liquid-liquid mass transfer systems with or without chemical reaction may be set forth as follows in general:

- (1) increase in the interfacial area by promoting dispersion,
- (2) diminution of the mass transfer resistance in the diffusion film outside the liquid droplets, and
- (3) diminution of the mass transfer resistance in the inner part of liquid droplets or mixing of dispersed phase.

The diameter of liquid droplets was measured to estimate the interfacial area. At the same time, the rate of reaction or the rate of mass transfer was observed for various kinds of liquid-liquid mass transfer systems which were classified according to reaction or no reaction and according to degree of difference in density. Comparison was then made between the increase in the estimated interfacial area and the increase in the rate of reaction caused by the increase in agitator speed.

On the other hand, mathematical analysis were performed on these processes to clarify the effect of agitation for various kinds of fundamental and important liquid-liquid agitation systems. Thus the authors found that the effect of agitation upon the liquid-liquid mass transfer was mainly to increase the interfacial area, that the decrease of the mass transfer resistance in the diffusion film outside droplets was slight, and that the mixing of the inner part of the droplets was rather decreased by the increase in agitator speed.

Part I Effect of Agitation for the Diminution of Mass Transfer Resistance in Continuous Phase.

Introduction

The effect of agitation on reducing the diffusional resistance in continuous phase may be inferred roughly from the results of previous experiments about liquid-solid systems.⁵⁾ In a liquid-solid agitation system, it was ascertained that the smaller the difference in density, the smaller the effect of increasing the agitator speed on reducing the mass transfer resistance in diffusional film. Hence

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for a liquid-liquid system the effect of agitation on reducing the mass transfer resistance in continuous phase may be considered rather small, because the difference in density is generally small.

For liquid-liquid systems in which difference in density is zero and the dispersed phase consists of a single component only, the effect of increase in agitator speed on the diminution of mass transfer resistance on the outside of liquid droplets is assumed to be negligible. In such systems the effect of increase in agitator speed is supposed to increase only the interfacial area. For this reason, these liquid-liquid systems whose density difference is zero ($\Delta\rho=0$) may be considered the most fundamental objects for an investigation of the agitation effect on liquid-liquid mass transfer. Starting from these systems, the more complicated cases may be clarified, for example, systems in which difference in density is not zero and mass transfer is accompanied by chemical reaction. From this point of view, the authors investigated the relation between over-all mass transfer rate, interfacial area and intensity of agitation in the following systems:

- (1) Dissolution of hardly miscible liquids in which the density difference is zero and no chemical reaction occurs (Example: *o*-toluidine-water system).
- (2) Liquid-liquid systems in which the density difference is zero and diffusion resistance in continuous phase is controlling, and chemical reaction occurs (Example: iso-valeryl chloride-water system).
- (3) Liquid-liquid systems in which the density difference is not zero and diffusion resistance in continuous phase is controlling and chemical reaction occurs (Example: benzoyl chloride-water system and fumaric acid chloride-water system).
- (4) Liquid-liquid systems in which the density difference is zero, and chemical reaction and diffusional resistance are comparable in magnitude (Example: *n*-butyric anhydride-water system).

1. Experimental Conditions and Procedure.

a) Experimental Apparatus and Procedure.

The experimental apparatus used is quite similar to that for solid-liquid agitation^{5),6)}. A cylindrical glass vessel with a flat bottom is used. The inside diameter (D) is 10 cm and the liquid depth (H_l) is always equal to the vessel diameter. A paddle agitator with four blades is used. The diameter of the impeller (d) is equal to 5 cm and the width of the impeller blades (b) is equal to 1.5 cm. The pitch angle of the blades (θ) is 75° to the plane of rotation. The elevation of the impeller (H_p) is always 4 cm (refer to Fig. 1).

Somewhat uncommon baffle plates⁶⁾ are used as shown in Fig. 1 (a). Width of the baffle plates, $w_b=1$ cm, submersion length $S_B=2.5$ cm, distance of the baffles from the agitator axis, $\varepsilon_B=2.5$ cm. Two baffle plates are inserted symmetrically,

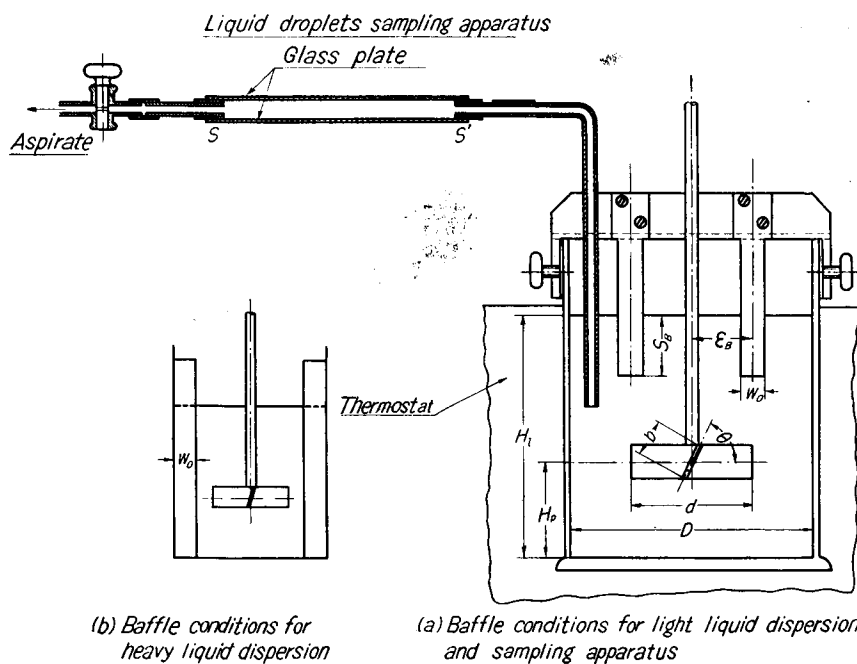


Fig. 1. Diagram showing the agitation equipment.

Table 1. Physical properties of materials

Materials	Mol. formula	Density [g/cm ³]	Surface tension [dynes/cm]	Viscosity [c.p.]	Solubility in water [g/100g·H ₂ O]
water	H ₂ O	1.00	73.9 (12)*	0.895	—
o-toluidine		1.002	—	—	1.50
iso-valeryl chloride	(CH ₃) ₂ CHCH ₂ COCl	1.015** 1.005	28 (12)	0.675	slightly solub.
benzoyl chloride		1.2188 (15)	—	1.23	"
fumaric acid chloride		1.4095	—	—	"
n-butyric anhydride	[CH ₃ (CH ₂) ₂ CO] ₂ O	0.9946 (20)	—	1.43	"
n-butyric acid	CH ₃ (CH ₂) ₂ COOH	0.959	—	—	(any ratio)
α-nitro propane	CH ₃ (CH ₂) ₂ NO ₂	1.003	30.0 (20)	0.709	1.4 (20)
tetraline	C ₁₀ H ₁₂	0.971	—	2.02	very slightly solub.
carbon tetrachloride + paraffine oil	CCl ₄ + C _n H _{2n+2}	1.00	—	19.2	"
diethyl carbonate	CO ₃ (C ₂ H ₅) ₂	0.975 (20)	27.2 (12)	0.777	slightly solub.

* temperature, °C, ** observed value.

in this case, and used for the dispersion of the small amount of lighter liquid.

When the dispersion of heavier liquid is required, four baffle plates of $w_0 = 1.5$ cm are inserted symmetrically as shown by **Fig. 1 (b)**. Both the impeller and the baffle plates are made of stainless steel (SUS-12).

The liquid temperature is held constant within $\pm 0.1^\circ\text{C}$.

In order to trace the change in concentration of solute dissolved, or amount of reaction taking place, a platinum plate electrode of 1×1 cm with the distance of 1 mm was used.

When a steady state condition is reached, a part of the liquid containing some droplets is withdrawn into the sampler $S-S'$ as shown in **Fig. 1 (a)** and a photograph of the droplets is taken to measure the diameter of the liquid droplets.

b) Materials used.

Materials used are all chemically pure and some of their physical properties are tabulated in **Table 1**.

2. Calculation of the Interfacial Area.

Provided that the diameters of droplets in an agitation vessel are denoted as $d'_1, d'_2, d'_3, \dots, d'_i, \dots$ and d'_n [cm] and the number of the droplets of diameter d'_i as n'_i , the interfacial area (A') of this liquid-liquid interface is calculated by the relation,

$$A' = \sum_{i=1}^n n'_i \pi d_i'^2 = \pi \sum_{i=1}^n n'_i d_i'^2$$

However, all of the droplets can hardly be observed. Most probable data must be estimated statistically using the observed data of a part of liquid sample.

Let the total volume of liquid droplets be denoted as U , and the measured diameter and their number of droplets be denoted as:

$$d_1, d_2, \dots, d_i, \dots \text{ and } d_n \\ n_1, n_2, \dots, n_i, \dots \text{ and } n_n$$

Then the total interfacial area A is expressed as follows:

$$A = \pi \sum_{i=1}^n n_i d_i^2 \frac{U}{\frac{\pi}{6} \sum_{i=1}^n n_i d_i^3} = 6U \frac{\sum_{i=1}^n n_i d_i^2}{\sum_{i=1}^n n_i d_i^3}$$

The mean volume diameter d_v and the mean surface diameter d_s is defined by the following equations:

$$d_v = \left\{ \frac{\sum (n_i d_i^3)}{\sum n_i} \right\}^{1/3} \\ d_s = \left\{ \frac{\sum (n_i d_i^2)}{\sum n_i} \right\}^{1/2}$$

Therefore using enough observation data, the interfacial area A is expressed as follows:

$$A = \pi \frac{\sum_{i=1}^n n_i d_i^2}{\frac{\pi}{6} \sum_{i=1}^n n_i d_i^3} U = 6U \frac{d_s^2}{d_v^3} \quad (1)$$

That is, from the values of mean volume diameter (d_v) and mean surface diameter (d_s), the interfacial contact area can easily be obtained. The values of d_v and d_s may be obtained from the observed data as follows.

In the case of the present experiment, the distribution of droplet diameters is expressed by the logarithmic normal distribution. Let the drop diameter be denoted as d (probability variable), then the general form of the distribution curve $F(d)$ is expressed by the following equation.²⁾

$$F(d) = \frac{\sum n}{\sqrt{2\pi} \ln \sigma_g} \exp\left\{-\frac{(\ln d - \ln d_g)^2}{2 \ln^2 \sigma_g}\right\} \quad (2)$$

where d_g is a geometric mean diameter and σ_g is a geometric standard deviation.

Thus the mean surface diameter d_s and the mean volume diameter d_v is derived as follows:

$$d_s^2 = \frac{\sum (nd^2)}{\sum n} = \frac{\sum n}{\sum n \sqrt{2\pi} \ln \sigma_g} \int_{-\infty}^{\infty} d^2 \exp\left\{-\frac{(\ln d - \ln d_g)^2}{2 \ln^2 \sigma_g}\right\} d \ln d$$

$$d_v^3 = \frac{\sum nd^3}{\sum n} = \frac{\sum n}{\sum n \sqrt{2\pi} \ln \sigma_g} \int_{-\infty}^{\infty} d^3 \exp\left\{-\frac{(\ln d - \ln d_g)^2}{2 \ln^2 \sigma_g}\right\} d \ln d$$

Now denoting $\ln d = x$, $2 \ln^2 \sigma_g = 1/a$ and $\ln d_g = b$.

$$d = e^x, \quad \sqrt{2\pi} \ln \sigma_g = \sqrt{\pi/a}$$

$$\therefore d_s^2 = \sqrt{\frac{a}{\pi}} \int_{-\infty}^{\infty} e^{2x} \cdot e^{-a(x-b)^2} dx = \sqrt{\frac{a}{\pi}} e^{-ab^2} \int_{-\infty}^{\infty} e^{-ax^2 + 2(1+ab)x} dx$$

$$= \sqrt{\frac{a}{\pi}} e^{-ab^2} \sqrt{\frac{\pi}{a}} e^{\frac{(1+ab)^2}{a}} = e^{2b+1/a} = e^{2 \ln d_g + 2 \ln^2 \sigma_g}$$

Converting the logarithmic base from e to 10, we have,

$$\log d_s^2 = 2 \log d_g + 4.605 \log^2 \sigma_g \quad (3)$$

Similarly,

$$d_v^3 = \sqrt{\frac{a}{\pi}} \int_{-\infty}^{\infty} e^{3x} \cdot e^{-a(x-b)^2} dx = \sqrt{\frac{a}{\pi}} e^{-ab^2} \int_{-\infty}^{\infty} e^{-ax^2 + 2(3/2+ab)x} dx$$

$$= \sqrt{\frac{a}{\pi}} e^{-ab^2} \sqrt{\frac{\pi}{a}} e^{\frac{(3/2+ab)^2}{a}} = e^{3b+9/4a} = e^{3 \ln d_g + 9/2 \ln^2 \sigma_g}$$

Converting the logarithmic base to 10, we have,

$$\log d_v^3 = 3 \log d_g + 10.362 \log^2 \sigma_g \quad (4)$$

The values of d_v and d_s may be calculated from Eq. (3) or (4) using the values d_g and σ_g .

The following method may be followed. Diameters of more than 500 droplets are observed, and the values are subdivided into about 10 grades, where the upper limit of the i 'th section is expressed as D_i .

The number of droplets in each section N_i is counted and divided by the total number $\sum_{i=1}^n N_i$; thus the normalized cumulative frequency is obtained.

$$\text{normalized frequency} \quad : \quad N_i / \sum_{i=1}^n N_i \equiv N_i'$$

$$\text{normalized cumulative frequency} \quad : \quad \sum_{i=1}^t N_i' \equiv N_i''$$

Plotting the values of N_i versus D_i on log-probability graph paper, we have approximately a straight line. The reading of D_i for $N_i=0.5$ gives a geometric mean diameter (d_g). From the ratio of the reading of D_i for $N_i=0.158$ to d_g , the

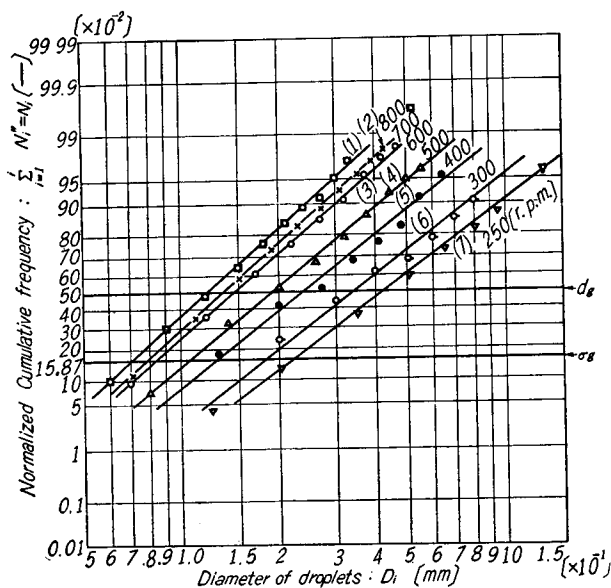


Fig. 2. Plots of N_i vs. D_i on log-probability paper for iso-valeryl chloride-water system.

geometric standard deviation σ_g (*i. e.*, logarithmic mean standard deviation) is obtained (refer to Fig. 2).

$$\log d_g = \frac{\sum(N_i \log D_i)}{\sum(N_i)}$$

$$\log \sigma_g = \sqrt{\frac{\sum\{N_i(\log D_i - \log d_g)^2\}}{\sum N_i}}$$

In the present experiment the authors measure the diameters of droplets at

the intervals of 3~10 seconds after the commencement of reaction, that is, at the conversion x . Denoting the geometric mean diameter, mean surface diameter and mean volume diameter at x as d_{gx} , d_{sx} and d_{vx} respectively, the interfacial area A_0 and the drop diameter d_{g0} at the moment of interfacial contact is derived as follows.

From Eq. (1),

$$A_0 = 6U_0 \frac{d_{s0}^2}{d_{v0}^3} \quad (5)$$

The total dispersed phase volume (U_x) at conversion x is,

$$U_x = U_0(1-x) \quad (6)$$

Assuming that the total number of droplets does not change in the course of the reaction and the change in diameter of all droplets takes place according to the following relation,

$$\frac{d_{gx}}{d_{g0}} = \frac{d_{sx}}{d_{s0}} = \frac{d_{vx}}{d_{v0}} \quad (7)$$

then the following relations are derived:

$$A_x = A_0(1-x)^{2/3} = 6U_0(1-x) \frac{d_{s0}^2}{d_{v0}^3} \quad (8)$$

$$d_{g0} = d_{gx}(1-x)^{-1/3} \quad (9)$$

3. Over-all Rate of Reaction.

In the case where the dispersed phase consists of only one component, and dissolves into a solvent in which a chemical reaction occurs, the over-all rate of reaction is expressed by the following equation just as in the case of gas absorption. According to S. Hatta³⁾, the following reaction is obtained:

$$R = \beta k_{BA} \left\{ C_B^* - \frac{C_B}{\cosh \gamma} \right\} \quad (10)$$

where $\beta = \gamma / \tanh \gamma$ (Hatta number).

(a) In cases where the physical diffusion rate is controlling, Eq. (10) is reduced to,

$$R = k_{BA}(C_B^* - C_B) \quad (11)$$

(b) In cases where the reaction velocity is very large compared with the diffusion velocity, or where the volume of continuous phase is very large compared with the interfacial area, the diffusion resistance becomes rate controlling and Eq. (10) reduces to,

$$R = \beta k_{BA} C_B^* = \beta k_{BA} H C_A^* \quad (12)$$

Therefore, representing the change in interfacial area caused by the chemical

reaction with Eq. (8),

$$R = C_E V \frac{dx}{d\theta} = \beta k_B A_0 H C_A^* (1-x)^{2/3} \quad (13)$$

By integration,

$$1 - (1-x)^{1/3} = k'\theta \quad (14)$$

where

$$k' \equiv \beta k_B A_0 H C_A^* / 3 C_E V \quad (14')$$

In the range where mass transfer coefficient k_B is held constant, $\{1 - (1-x)^{1/3}\}$ is proportional to θ as shown by Eq. (14).

(c) In the case where the chemical reaction velocity is small compared with the diffusion velocity or where the dispersed phase is comparatively large so that the value of $\alpha v = \sqrt{k_w/D_f} \cdot (V/A)$ is nearly equal to 1 (refer to the previous paper of the authors⁶⁾), Eq. (10) reduces to the form where reaction rate is controlling:

$$R = k_w V C_B \quad (15)$$

4. Effect of Agitation on Simple Dissolution Systems whose Density Difference is Zero.

As already discussed, in the case of liquid-solid agitation systems where the difference in density of the two phases is small, the change in diffusion resistance accompanied by the change in agitator speed decreases.

Since the difference in density is generally small in the case of liquid-liquid systems, the diffusion resistance on the outside of droplets may hardly be lowered by increasing agitator speed, especially in cases where the difference in density of the two phases is zero.

To confirm this inference, the authors measured the increase in dissolution velocity and interfacial area of *o*-toluidine (specific gravity=1.002) in water which accompanied an increase in agitation velocity.

In **Fig. 3**, curve (1) representing the change of dissolution velocity has approximately the same slope as that of curve (2) representing the change of interfacial area. The fact that these two curves parallel each other shows that the change in diffusion resistance is almost negligible.

On the other hand, the geometrical mean diameter of the dispersed droplets changes with the increase in agitator speed as shown by the curve (3). The observed points lie on the two hyperbolic curves subdivided by the critical agitator speed (N_a) where suction of air occurs. It is to be noted that the bend points of the curve of interfacial area [curve (2)] and of the curve of dissolution rate [curve (1)] seems to appear at the same agitator speed of N_a .

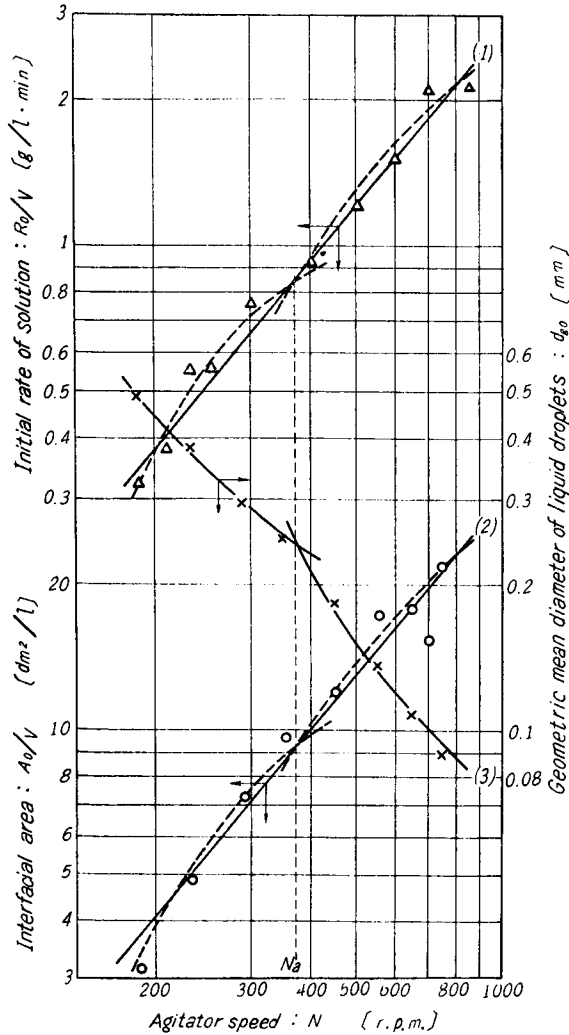


Fig. 3. Plots of d_{g0} , A_o/V and R_o/V vs. N for o-toluidine-water system. With 2 baffle plates for light liquid dispersion, water: 785 [cc], o-toluidine: 5.00 [g], temp.: 26.0°C.

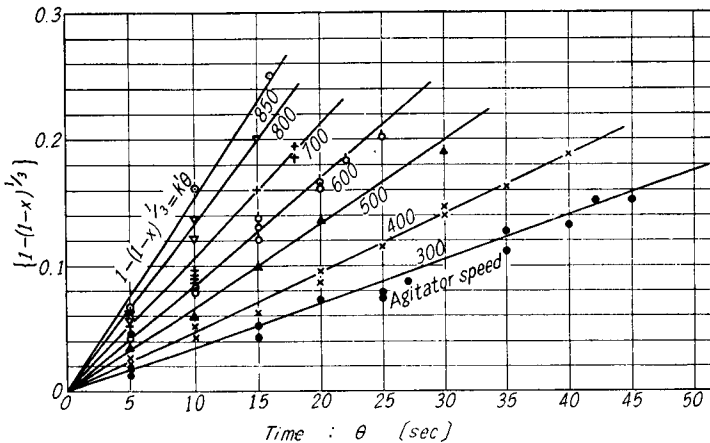
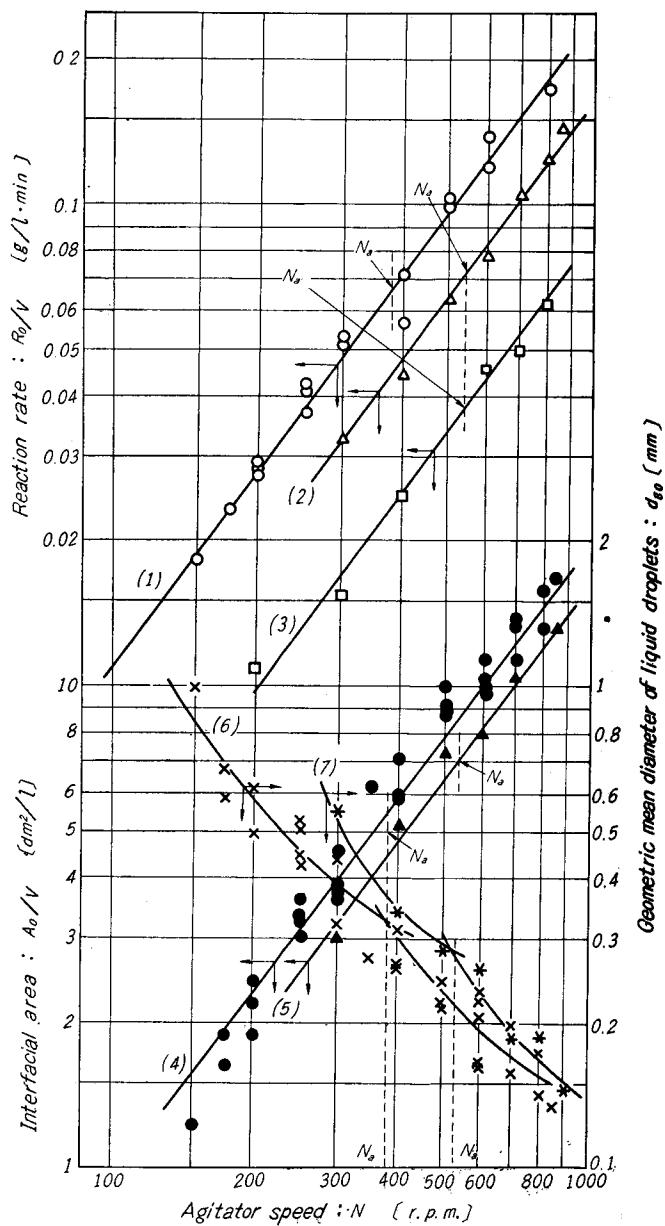


Fig. 4. Plots of $\{1-(1-x)^{1/3}\}$ versus θ for hydrolysis reaction process in iso-valeryl chloride-water system. Without baffle, temp.: 25.0°C.



Baffle condition		Temp.	Symbol		
No		°C	R_0/V	A_0/V	d_{g0}
(1),(4),(6)	2 baffle plates for light liquid dispersion	25	(1) ○	(4) ●	(6) ×
(2),(5),(7)	Without baffle plate	25	(2) △	(5) ▲	(7) *
(3)	Without baffle plate	20	(3) □		

Fig. 5. Plots of d_{g0} , A_0/V and R_0/V vs. N for hydrolysis reaction of iso-valeryl chloride. Water: 785 [cc], iso-valeryl chloride: 5.00 [cc].

5. Effect of Agitation for Reaction Systems Controlled by Diffusion whose Density Difference is Zero.

As an example, the authors took up the hydrolysis reaction of iso-valeryl chloride $[(CH_3)_2\cdot CH\cdot CH_2CO\cdot Cl]$ whose specific gravity is 1.015 and is close to that of water. The rate of hydrolysis of I.V.C. (for simplicity, let us denote iso-valeryl chloride as I.V.C. hereafter) is very large compared with the rate of diffusion. The results of the rate of hydrolysis reaction and the interfacial area is proportional as shown by Fig. 5.

As the solubility of I.V.C. in water is very small and the rate of diffusion is controlling, the relation between conversion x and time θ should be given by Eq. (14). Fig. 4 is a diagram showing the relation of $\{1 - (1-x)^{1/3}\}$ versus θ . The observed data shows a good linearity. The slope of these lines gives the coefficient k' . From these data, it is possible to calculate the over-all rate of reaction. Curve (2) in Fig. 5 is the plot of the experimental data and is parallel

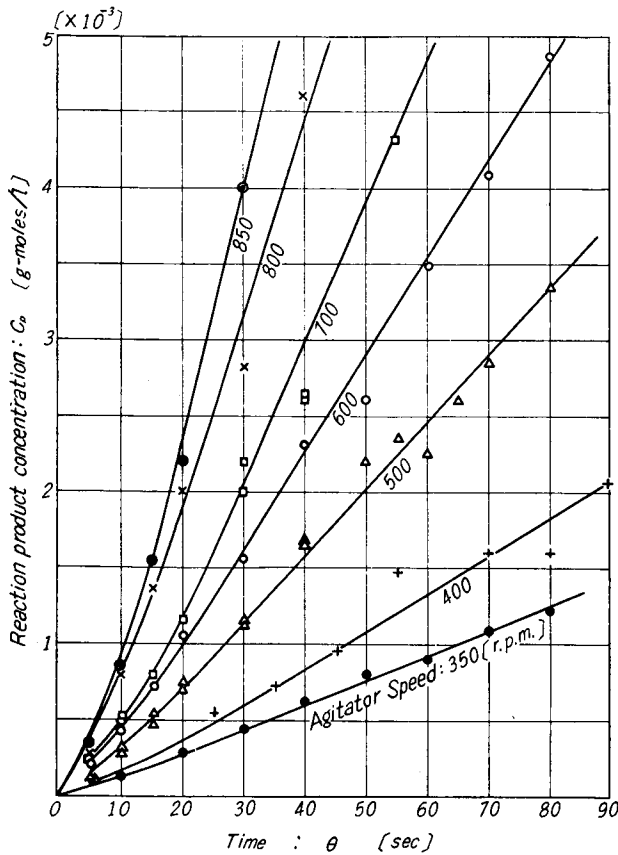


Fig. 6 Plots of reaction product concentration C_p vs. time θ for hydrolysis reaction process in benzoyl chloride-water system.

to curve (5) which shows the interfacial area. Curves (1), (4) and (6) show the results of the experiment with baffle plates for lighter phase dispersion.

6. Effect of Difference in Density.

Fig. 6 is diagram showing the rate of hydrolysis of benzoyl chloride (sp. gr.=1.219). As shown by the curves, pseudo zero order reaction mechanism seems to hold after a steady state is reached. Rearranging and replotting the data of reaction velocity against agitator speed, curve (1) in **Fig. 7** is obtained. Curve (2) shows the observed data of the interfacial area. Thus the slope of curve (1) is slightly larger than that of curve (2). **Fig. 8** is a diagram for the hydrolysis of fumaric acid chloride (sp. gr.=1.410). As shown by these two diagrams, the diffusion resistance on the outside of the dispersed droplets is

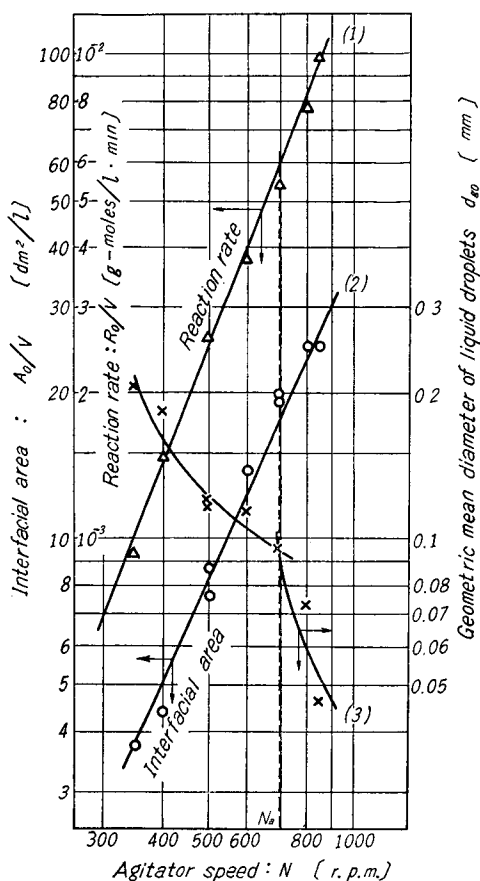


Fig. 7. Plots of d_{g0} , A_0/V and R_0/V vs. N for hydrolysis of benzoyl chloride. 4 baffle plates for heavy liquid dispersion, water: 785 [cc], benzoyl chloride: 5.00 [cc], temp.: 25.0°C.

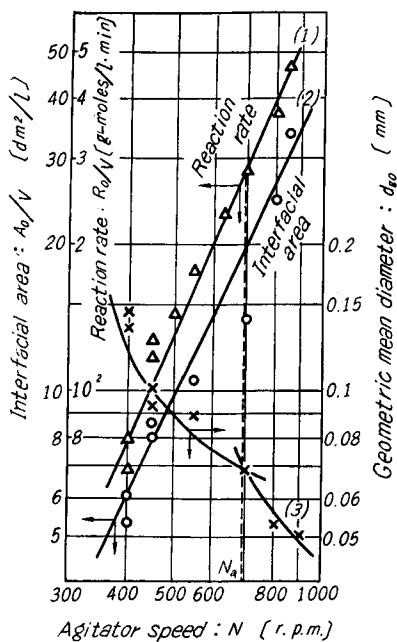


Fig. 8. Plots of d_{g0} , A_0/V and R_0/V vs. N for hydrolysis of fumaric acid chloride. Fumaric acid chloride: 5.00 [cc], temp.: 25.0°C.

lowered by the increase in agitator speed. Generally speaking, however, the difference in density of liquid-liquid systems is rather small, so that the effect of the increase in agitator speed on the decrease in diffusion film resistance is insignificant and its effect on the increase in interfacial area is of overwhelming importance.

7. Effect of Agitation on Reaction Systems of both the Diffusion- and Reaction-Rate Controlling, and of Negligible Difference in Density.

In liquid-liquid mass transfer followed by chemical reaction, if the rate of reaction is very large compared with that of diffusion as in the case of hydrolysis of I.V.C., the over-all rate of reaction is proportional to the increase in the interfacial area of droplets and is similar to the physical dissolution.

On the other hand, if the reaction rate becomes comparable to the diffusion rate, the reaction rate can never keep up with the rate of diffusion in the range of high agitator speed, because the interfacial contact area is very much increased by the agitator speed.

Therefore the authors adopted the hydrolysis reaction of *n*-butyric acid anhydride which has approximately the same density (sp. gr. = 0.9946) as water and has a reaction rate compara-

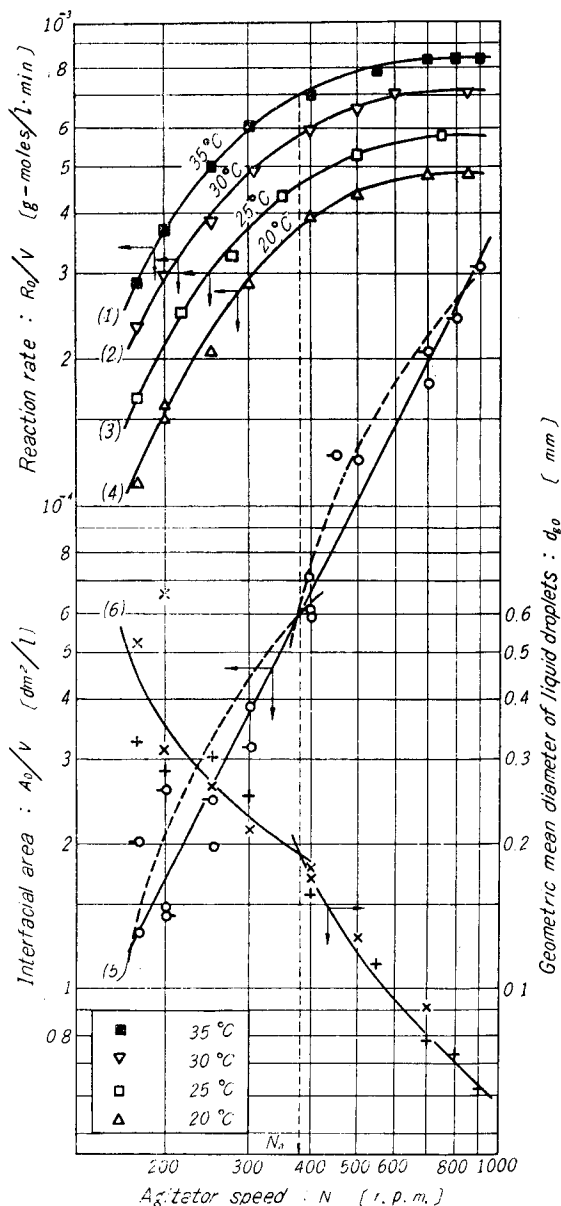


Fig. 9. Plots of d_{g0} , A_0/V and R_0/V vs. N for hydrolysis of *n*-butyric anhydride.

With 2 baffle plates for light liquid dispersion, water: 785 [cc], *n*-butyric anhydride: 5.00 [cc].

ble to its rate of diffusion.

The result of this reaction is shown in Fig. 9. As shown by the diagram, the over-all rate of reaction nearly corresponds to that of diffusion controlling in the range of lower agitator speed, *i.e.*, the curve for (R_0/V) is nearly parallel to the curve for A_0/V . When the agitator speed is increased, the rate of diffusion is increased with an increase in interfacial area, and finally attains a state where the concentration of butyric acid anhydride in the continuous phase comes to saturation. Thus, in this range, the over-all rate of reaction nearly corresponds to the rate of hydrolysis. Therefore, there must be free butyric acid anhydride as well as the butyric acid produced by hydrolysis in the continuous phase. To verify the above, the authors withdrew part of the solution and filtered it through a glass filter to remove undissolved droplets of butyric acid anhydride. The rate of hydrolysis in the filtrate is shown by the curves (1) and (2) in Fig. 10. This hydrolysis reaction shows a form of first order homogeneous reaction, and the reaction velocity constant is determined to be 0.048 [1/min] for $N=800$ r.p.m. and 0.047 [1/min] for $N=215$ r.p.m. by the analysis* of curves (1) and (2). These

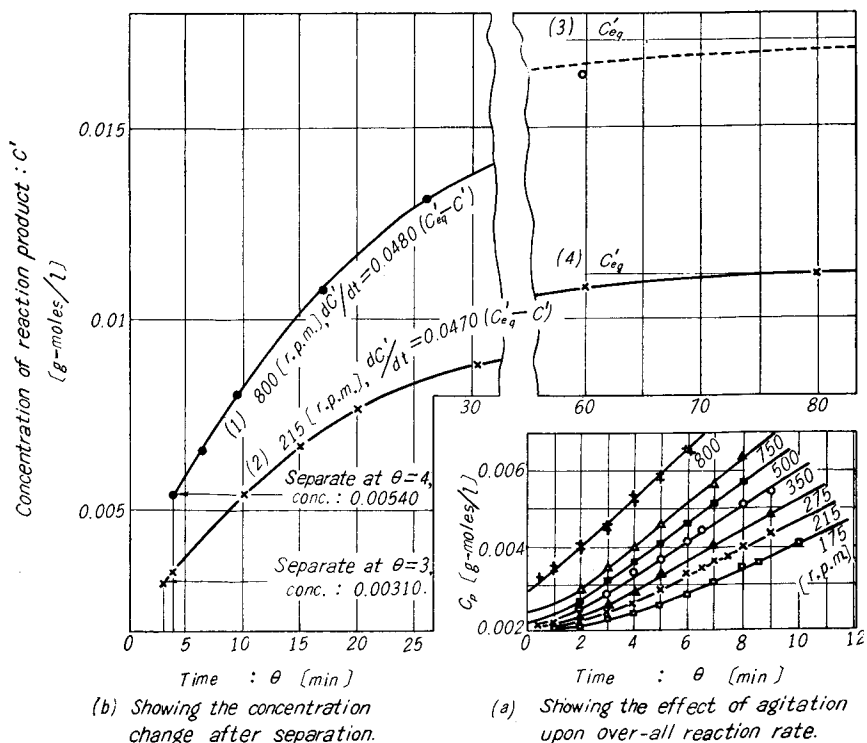


Fig. 10. Hydrolysis reaction process in n-butyric anhydride-water reaction system.

* Details of the analysis to determine the rate constant are the same as reported in a previous paper³⁾.

values agree well with the value 0.047 [1/min] that is stated in the International Critical Tables.

As mentioned above, there is apparently some unreacted butyric acid anhydride in the continuous phase (water), and the quantity is increased with increase in agitator speed. Accordingly the over-all rate of reaction is increased by the increase in agitator speed. But above a certain speed, the range may appear in which reaction rate becomes controlling.

Part II Effect of Agitation on the Mixing of the Inner Parts of Droplets.

Introduction

The effects of agitation on liquid-liquid mass transfer consist of (1) the increase in contact surface area resulting from the break up of dispersed phase, (2) the decrease in the diffusion resistance in continuous phase, (3) the mixing inside the droplets caused by the convection current induced.

As stated above, the authors discussed items (1) and (2). On item (3), the authors made experiments mentioned later.

The authors adopted the liquid-liquid systems in which dispersed phase was diluted with another solvent having equal density, viscosity and interfacial tension. By measuring and comparing the changes in interfacial area and mass transfer rate accompanying the changes in agitator speed, the effect of mixing inside the droplets caused by agitation may be made clear.

Comparisons are made on the observed data (1) with the calculated curve based on perfect mixing, (2) with the calculated curve based on molecular diffusion without convection current.

An experiment was also performed diluting the dispersed phase with solvent of high viscosity in order to reveal the effect of diffusion resistance and convection current occurring inside the droplets.

The physical properties of the samples used are tabulated on **Table 1**.

8. Calculation of Interfacial Area.

The volume of the dispersed phase (U_x) at a conversion x may be related to the initial volume U_0 ,

$$U_x = U_0(1 - mx) \quad (16)$$

where m is the initial weight fraction of solute in the dispersed phase.

Provided that the total number of droplets is unchanged and the following relations (17) are assumed to hold regardless of the conversion, Eqs. (18) and (19) are derived using Eq. (8),

$$\frac{d_{gx}}{d_{g0}} = \frac{d_{sx}}{d_{s0}} = \frac{d_{vx}}{d_{v0}} \quad (17)$$

$$A_x = A_0(1-mx)^{2/3} = 6U_0(1-mx)d_{sx}^2/d_{vx}^3 \quad (18)$$

$$d_{gx} = d_{g0}(1-mx)^{1/3} \quad (19)$$

9. Mass Transfer Coefficient in Continuous Phase.

In the following experiment, the authors deal with the case where the diffusing substance (reactant) is at first dissolved in the dispersed phase. When the dispersed phase comes into contact with water, the reactant diffuses from the dispersed phase into the water (continuous phase) followed by hydrolysis reaction. The concentration of the diffusing substance (B) just outside of the interfacial surface is denoted as C_B^* and the concentration in the liquid bulk C_B . In the case where the rate of hydrolysis is very large, C_B is assumed to be practically zero, and the rate is expressed^{(3), (5)} as an irreversible pseudo first order reaction, *i.e.*,

$$R = \beta k_B A C_B^* \quad (20)$$

where β is the Hatta number which is equal to $\gamma/\tanh \gamma$ for steady state diffusion and is equal to $1/\operatorname{erf} \sqrt{\alpha/D_{fB}}$ for unsteady state diffusion.

In this section, the agitation efficiency inside the dispersed droplets is to be examined. Prior to this main object, it is necessary to make clear the diffusional resistance in the continuous phase. **Fig. 11 (a)** is a schematic diagram showing the concentration gradient adjacent to the interface when the dispersed phase consists of a single phase. The concentration of the continuous phase at the interface C_B^* is assumed to be in equilibrium with the internal concentration $C_A^*(=C_A)$ and C_B^* is assumed to be equal to HC_A^* (for example, the solubility of I.V.C. in water is very small, so that the Henry's law is assumed to hold), then from Eq. (20),

$$\beta k_B H = \frac{R/V}{(A/V)C_A} \equiv K_B \quad (21)$$

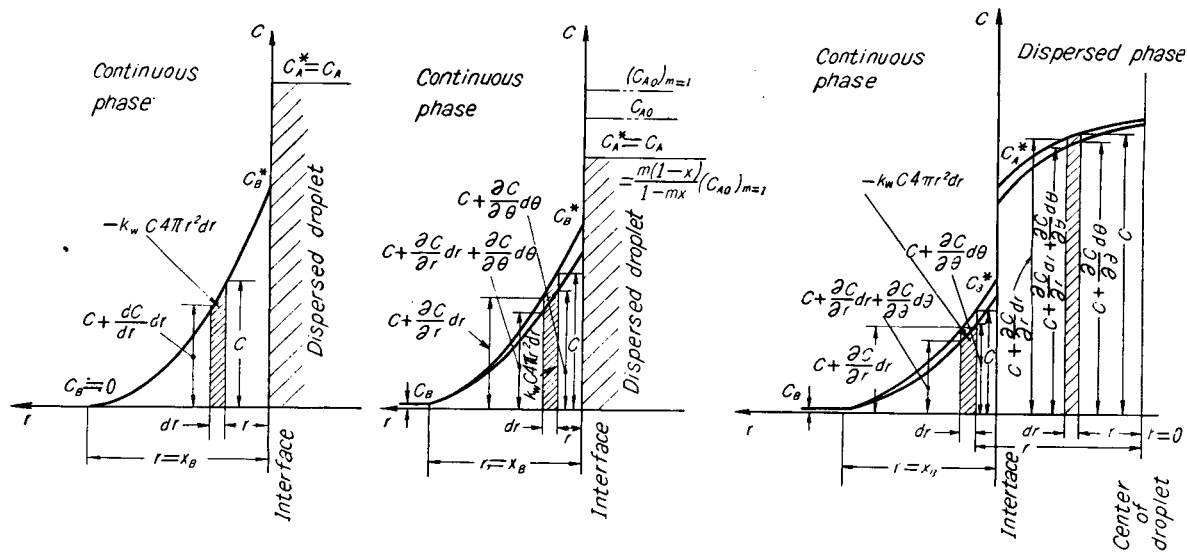
Using Eq. (21), the value of $\beta k_B H$ may be calculated.

10. Derivation of Over-all Rate Equation.

(a) Cases where perfect mixing is assumed in the droplets.

Fig. 11 (b) is a schematic diagram which corresponds to the case where the reactant is completely mixed with the solvent in the droplets and gradually dissolves into continuous phase reacting with water.

The average concentration of reactant in the droplets having weight fraction m and conversion x is expressed:



(a) Dispersed phase is pure solute or reactant of one component.
 (b) A state of perfect mixing in a droplet.
 (c) A hypothetical state of none of agitation in a droplet. (Molecular diffusion only occurs)

Fig. 11. Diagram showing the concentration gradient of reactant or solute in liquid-liquid agitation systems.

where $(C_{A0})_{m=1}$ is the initial concentration of solute in the dispersed phase consisting only of reactant.

By using Eqs. (18), (20) and (22), the rate of reaction at conversion x is

$$C_A = \frac{m(1-x)}{1-mx} (C_{A0})_{m=1} \tag{22}$$

expressed :

$$\begin{aligned} \frac{R}{V} &= \frac{dC_0}{d\theta} = \beta k_B \left(\frac{A}{V} \right) H C_A \\ \frac{R}{V} &= C_E \frac{dx}{d\theta} = \beta k_B \left(\frac{A_0}{V} \right) \frac{Hm(1-x)}{(1-mx)^{1/3}} (C_{A_0})_{m=1} \end{aligned} \quad (23)$$

By integration, we have,

$$\int_0^x \frac{(1-mx)^{1/3}}{(1-x)} dx = \frac{3k_B H m A_0 (C_{A_0})_{m=1}}{C_E V} \theta + I_0 \quad (24)$$

As the coefficient of θ is independent of time, the relation between θ and x can be obtained by integrating the left hand side term. Multiplying the concentration C_E by x , the quantity of the reaction product is obtained.

(b) Cases where the mass transfer is assumed to occur by molecular diffusion only.

Fig. 11 (c) is a diagram which shows that mass transfer occurs by molecular diffusion only, and no convection current takes place in the droplets. The concentration distribution $C(r, \theta)$ inside and outside the droplets next to the interface is assumed to be symmetrical with regard to the center of the droplets.

Taking a material balance between r and $r+dr$, the rate of mass transfer is expressed by Fick's law as follows ;

$$\frac{\partial C}{\partial \theta} = D_{fA} \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (a \geq r \geq 0) \quad (25)$$

$$\frac{\partial C}{\partial \theta} = D_{fA} \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) - k_w C \quad (r \geq a) \quad (26)$$

These two equations are solved under the following initial and boundary conditions ;

$$\left. \begin{aligned} C(r, 0) &= C_{A_0} & (a \geq r \geq 0) \\ C(r, 0) &= 0 & (r \geq a) \end{aligned} \right\} \quad (27)$$

$$\frac{\partial C(0, \theta)}{\partial r} = 0 \quad (\theta \geq 0) \quad (28)$$

$$C\{(a+x_B), \theta\} = 0 \quad (\theta \geq 0) \quad (29)$$

$$HC(a_{-0}, \theta) = C(a_{+0}, \theta) \quad (\theta \geq 0) \quad (30)$$

$$D_{fB} \frac{\partial C(a_{+0}, \theta)}{\partial r} = D_{fA} \frac{\partial C(a_{-0}, \theta)}{\partial r} \quad (\theta \geq 0) \quad (31)$$

$$\beta k_B C_B^* = \beta k_B H C_A^* \equiv K_B C_A^* = D_{fA} \frac{\partial C(a_{-0}, \theta)}{\partial r} \quad (\theta \geq 0) \quad (32)$$

In the course of the solution of these equations, the unknown value of H is

included; however as mentioned above, the value of $\beta k_B H$ is practically held constant regardless of agitator speed N and time θ , and is calculated by Eq. (21). Considering this fact, Eq. (33) may be derived from Eq. (25) by substituting the initial condition of Eq. (27) and the boundary conditions of Eqs. (28), (30) and (32).

$$C(r, \theta) = \frac{2aLC_{A0}}{r} \sum_{n=1}^{\infty} \frac{\exp(-D_{fA}\lambda_n^2\theta/a^2)}{\{\lambda_n^2 + L(L-1)\}} \frac{\sin \lambda_n r/a}{\sin \lambda_n} \quad (a \geq r \geq 0) \quad (33)$$

where $L \equiv a k_B / D_{fA}$, λ_n 's are roots of $\lambda_n \cot \lambda_n + L - 1 = 0$.

The over-all reaction rate R/V is also derived as follows :

$$\frac{R}{V} = D_{fA} \frac{A}{V} \left(\frac{\partial C}{\partial r} \right)_{r=a} = \frac{2L^2 C_{A0} D_{fA} A}{aV} \sum_{n=1}^{\infty} \frac{\exp(-D_{fA}\lambda_n^2\theta/a^2)}{\{\lambda_n^2 + L(L-1)\}} \quad (34)$$

The average concentration in the droplets is obtained :

$$C_m = \frac{1}{(4/3)\pi a^3} \int_0^a C(r, \theta) 4\pi r^2 dr = \frac{3}{a^3} \int_0^a C(r, \theta) r^2 dr \quad (35)$$

The conversion x or the concentration of reaction product C_p is given by the following equation :

$$\frac{C_p}{C_E} = x = 1 - \frac{C_m}{C_{A0}} = 1 - \sum_{n=1}^{\infty} \frac{6L^2 \exp(-D_{fA}\lambda_n^2\theta/a^2)}{\lambda_n^2 \{\lambda_n^2 + L(L-1)\}} \quad (36)$$

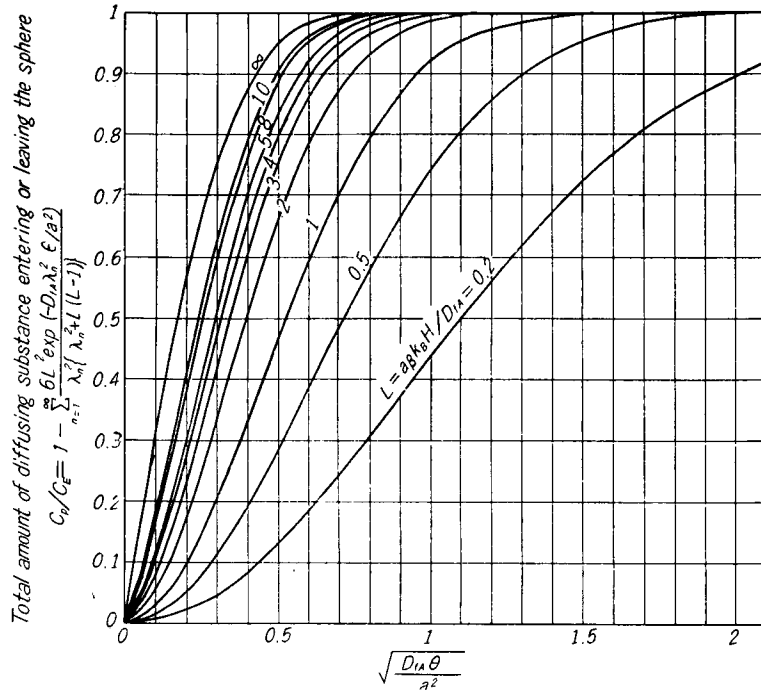


Fig. 12. Sorption or desorption curves for the surface condition : $-D_{fA}(\partial C/\partial r) = \beta k_B H(C_{A1}^* - C_B)$.

A. B. Newman⁷⁾ made a numerical calculation on the relation C_m/C_{A0} and $D_f A^\theta/a^2$ using L as the parameter.

J. Crank¹⁾ made a conversion of the calculated values and drew a diagram showing the relation between $(1-C_m/C_{A0})$ and $\sqrt{D_f A^\theta/a^2}$ (refer to Fig. 12).

Accordingly, the value of K_B is obtained by Eq. (21) and the value L calculated from the value d_s (estimated by the observed value of A_0). Reading the value of conversion $x (= C_p/C_E)$ from Fig. 12 corresponding to the calculated value of $\sqrt{D_f A^\theta/a^2}$ in appropriate time interval, the relation between reaction product concentration C_p and time θ is obtained.

11. Experimental Results and Comparison with the Theoretical Values in the Two Extreme Cases.

I.V.C. is diluted with α -nitropropane which has nearly equal density, viscosity and interfacial tension and has little solubility in water. This mixture is added to water agitated to a steady state. After a certain period (about 2~10 seconds), sample solutions are withdrawn and the size distribution is measured to estimate $d_{g,x}$. Values of d_{g0} are estimated by Eq. (19) and plotted against agitator speed N , thus curve (1) in Fig. 13 is drawn.

The interfacial surface area A_0

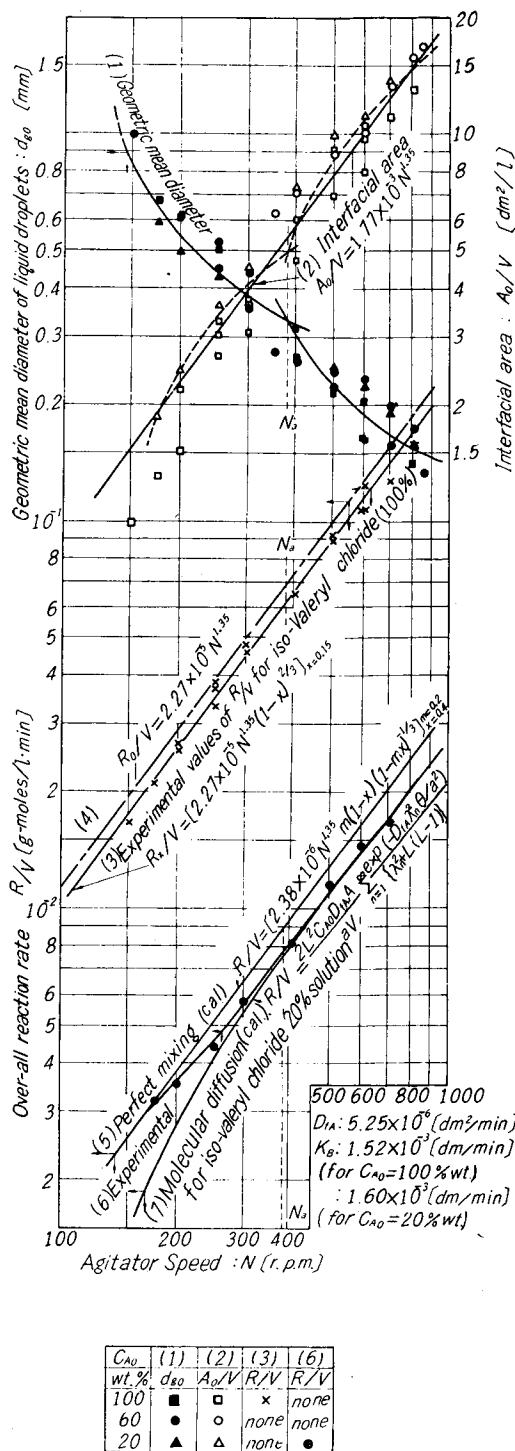


Fig. 13. d_{g0} , A_0/V and R_0/V vs. N for water-(I.V.C. + α -nitro propane) system.

is obtained by Eq. (18) and plotted in **Fig. 13** as shown by curve (2) which is approximated by the following equation :

$$A_0/V = 1.77 \times 10^{-3} N^{1.35} \quad [\text{dm}^2/l] \quad (37)$$

Therefore the interfacial area A_x at the initial concentration of m in weight fraction and conversion x should be given by the following equation :

$$A_x/V = 1.77 \times 10^{-3} N^{1.35} (1-mx)^{2/3} \quad [\text{dm}^2/l] \quad (38)$$

Curve (3) is that which represents the relationship between the over-all rate of reaction at $x=0.15$ and N , when the dispersed droplets consist of pure I.V.C.

The value $(R_x/V)_{x=0.15}$ increases in proportion to $(A_x/V)_{x=0.15}$ against agitator speed and is expressed by the following relation :

$$(R_x/V)_{x=0.15} = 2.03 \times 10^{-5} N^{1.35} \quad [\text{g-moles}/l \cdot \text{min}] \quad (39)$$

The experimental result obtained with pure I.V.C. corresponds to that where perfect mixing is attained inside the droplets and the rate of reaction should be expressed by Eq. (23). In the present case the weight fraction m is equal to 1.00 so that the initial rate of reaction R_0/V is expressed as follows :

$$R_0/V = R_x/V(1-x)^{-2/3} \quad (40)$$

Since Eq. (39) is the observed results at $x=0.15$, substituting the relation into Eq. (40), we have,

$$R_0/V = 2.27 \times 10^{-5} N^{1.35} \quad [\text{g-moles}/l \cdot \text{min}] \quad (41)$$

Curve (4) in the diagram is drawn by Eq. (41). Therefore the general form of reaction rate has the form,

$$R_x/V = 2.27 \times 10^{-5} N^{1.35} (1-x)^{2/3} \quad [\text{g-moles}/l \cdot \text{min}] \quad (42)$$

As $(C_{A_0})_{m=1}$ is equal to 8.43 [g-moles/l], combining Eqs. (38) and (42) the value of K_B in Eq. (21) is calculated :

$$K_B = \beta k_B H = \frac{R/V}{(A/V) C_A} = 1.52 \times 10^{-3} \quad [\text{dm}/\text{min}] \quad (43)$$

Curve (6) is that which represents the relation between the over-all rate of reaction at $x=0.4$ for a mixture of 20% by weight I.V.C. and 80% α -nitropropane *versus* agitator speed N .

Since the solubility of α -nitropropane is 1.35 g/100 g water, the experiment was performed with water saturated with α -nitropropane so that the value H was larger than that used in Eq. (43). Comparing the values of R_0/V at $m=0.2$, 0.6, 0.9 and 1.0, the authors obtained a value of K_B which is 1.05 times as large

as that given by Eq. (43). Denoting the value of H in the case of dilution as H' we have:

$$K_B' = \beta k_B H' = \beta k_B H \frac{H'}{H} = 1.60 \times 10^{-3} \quad [\text{dm}/\text{min}] \quad (44)$$

Therefore the reaction rate calculated on the assumption that the insides of the droplets are always kept uniform, is expressed as follows:

$$\begin{aligned} \frac{R}{V} &= K_B' \frac{A_0}{V} (C_{A_0})_{m=1} m(1-x)(1-mx)^{-1/3} \\ &= 2.38 \times 10^{-6} N^{1.35} m(1-x)(1-mx)^{-1/3} \end{aligned} \quad (45)$$

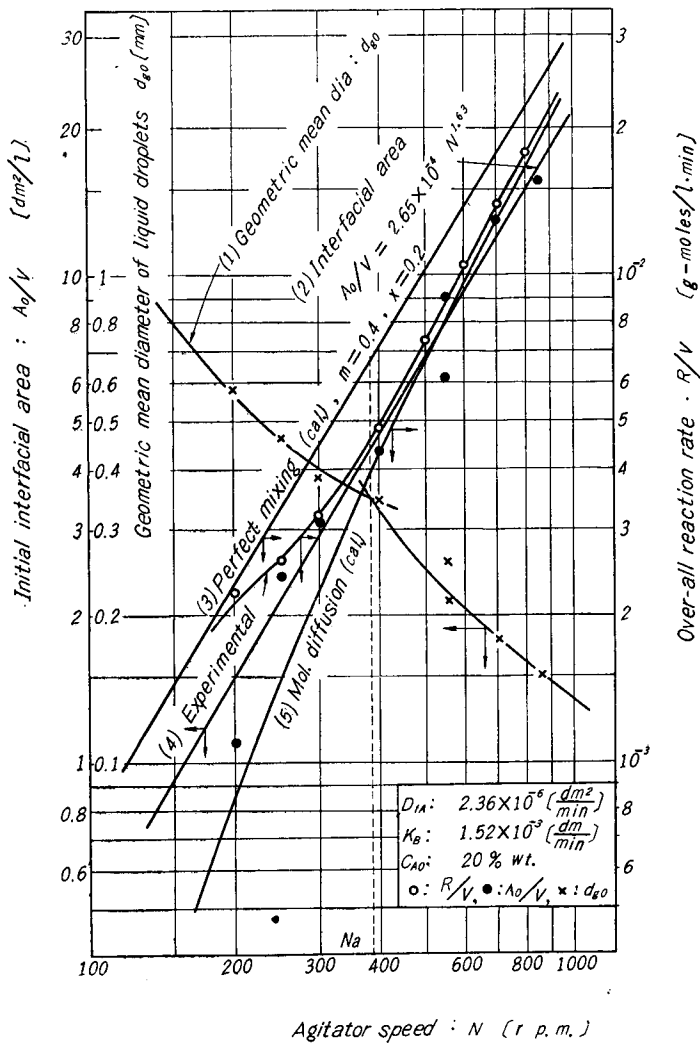


Fig. 14 d_{g0} , A_0/V and $(R/V)_{x=0.4}$ vs. N for water-(I.V.C.+tetraline) system.

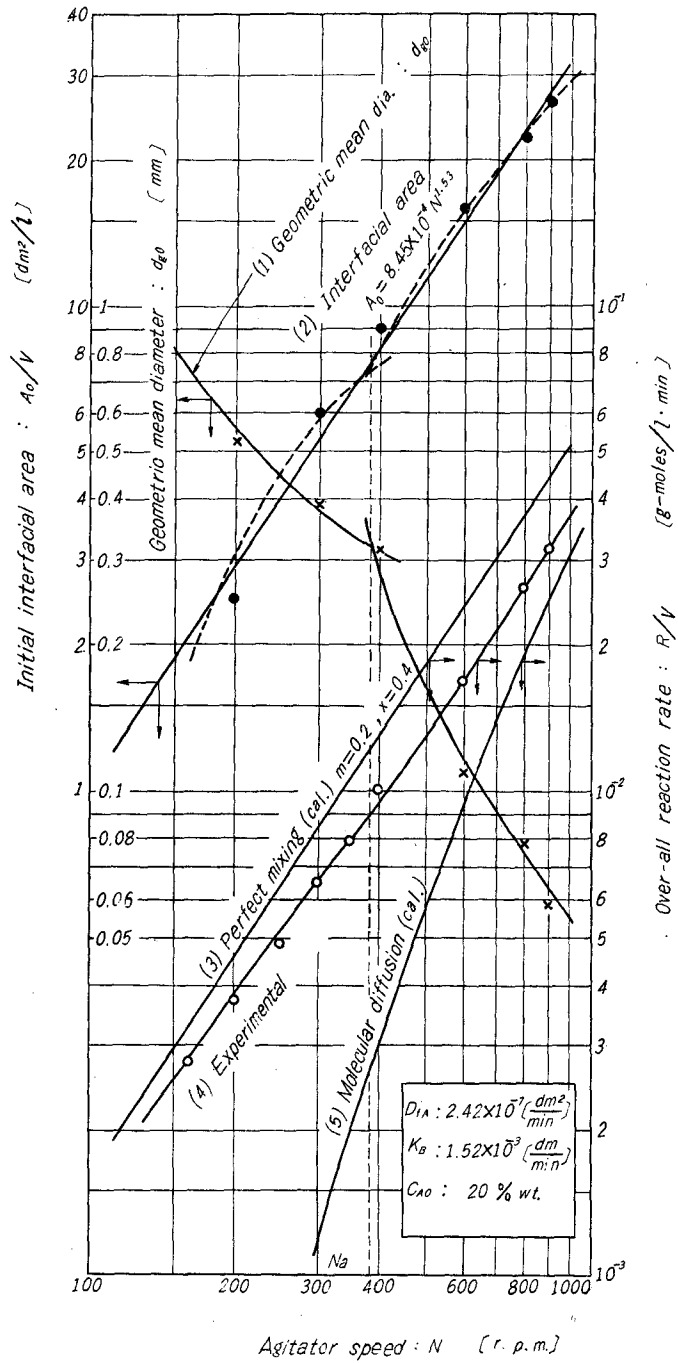


Fig. 15. d_{g0} , A_0/V and $(R/V)_{x=0.4}$ vs. N for water-(I.V.C.+ CCl_4 +paraffine oil) system.

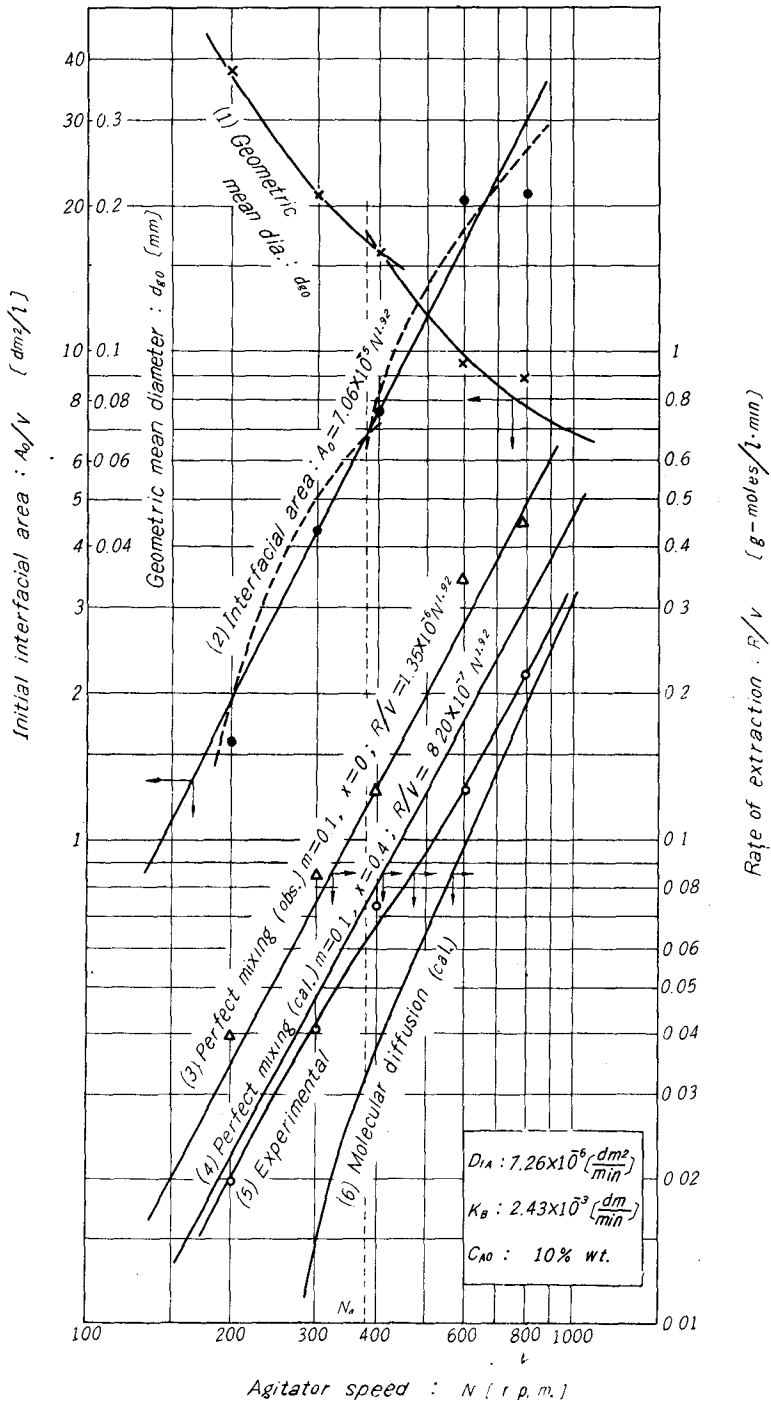


Fig. 16. d_{g0} , A_0/V and R/V vs. N for water-(n-butyric acid)-diethyl carbonate extraction system.

Curve (5) is a plot of Eq. (45) at the condition of $m=0.2$ and $x=0.4$.

Curve (7) is a plot of Eq. (36) which is derived from the assumption that the mass transfer of I.V.C. in the droplets depends only on the molecular diffusion.

As shown by the diagram, the observed data is close to the curve of perfect mixing in the lower range of agitator speed. With the increase in agitator speed, the value of R/V naturally increases, but much less, proportionally, than the interfacial area. The range of higher agitator speed, observed data approaches the theoretical curve of molecular diffusion, though both curves of perfect mixing and molecular diffusion tend to approach each other.

When the viscosity of the diluent becomes higher, using for example tetraline ($\mu=2.02$ c.p.) (refer to Fig. 14) or a mixture of CCl_4 and paraffine oil ($\mu=19.2$ c.p., sp.gr.=1.00) (refer to Fig. 15), those trends mentioned above become more marked. In both cases, the diffusion resistance in the continuous phase is nearly equal. In proportion to decrease in D_{fA} as a result of increased viscosity, the effect of mixing inside the droplets by agitation becomes greater.

As shown by these diagrams, it seems reasonable to say that in the range of lower agitator speed ($N=160$ r.p.m.), the state of mixing is nearly perfect and the concentration in the droplets is comparatively uniform, while at a high agitator speed ($N=800$ r.p.m.) the dispersed droplets become smaller and mechanical agitation cannot cause mixing inside of the droplets.

As an example similar to industrial liquid extraction, the authors added an experiment on the extraction of *n*-butyric acid from diethyl carbonate into water.

Fig. 16 is a diagram showing the result of this experiment. Curve (2) shows the relation between A_0/V and N , and curve (3) shows the observed rate of extraction at the instant of introduction of the reactant (*i.e.*, $x=0$). At the initial state, the inner part of each droplet is in uniform concentration similar to a state of perfect mixing, so that the value of K_B for this extraction system is obtained from curve (3). Curves (4) and (6) are the estimated results of the rate of extraction from Eqs. (23) and (34), cases of perfect mixing and molecular diffusion, respectively, and curve (5) is an observed results at the conversion $x=0.4$.

Conclusions

(1) The effect of agitation on liquid-liquid mass transfer consists in the following three items: (1) increase in the interfacial area, (2) diminution of the mass transfer resistance on the outside of the diffusion film of droplets and (3) diminution of the mass transfer resistance on the inside of liquid droplets.

(2) Measuring the diameters of the droplets, the interfacial surface area

was estimated. On the other hand, the over-all rate of reaction was observed and compared with the change in interfacial surface area.

In a system where diffusion is rate controlling and where densities are nearly equal (*i.e.*, $\Delta\rho \approx 0$), these two lines are parallel which means that the agitation intensity does not affect the diffusion film resistance on the outside of droplets. In cases where the density difference is significant, the slope of the over-all rate curve is greater than that of A_0/V , which means that by increasing agitator speed the diffusion film resistance is somewhat decreased. However, the effect of increasing agitation intensity is mainly an increase of interfacial surface area.

(3) In the case where the reaction rate is controlling or comparable with the rate of diffusion, the main body of the liquid contains a portion of unreacted solute and some reaction product. The higher the agitation velocity, the more abundant is the unreacted solute in the liquid bulk. Beyond a certain agitator speed, there is a range where the increase in agitation has little effect on the over-all rate of reaction, *i.e.*, the chemical reaction is rate controlling.

(4) In the range of lower agitator speed, the diameters of the dispersed droplets are rather large and there seems to be a good convection current which makes the concentration inside the droplets rather uniform.

(5) In the liquid-liquid systems whose density difference is nearly zero, the increase in mass transfer rate does not correspond to the increase in the interfacial surface area. This is because the convection current decreases with the increase in agitator speed.

(6) In the range of higher agitator speed, the diameters of the dispersed droplets become small so that the convection current seems to have difficulty to occurring, and the rate of mass transfer approaches that caused by molecular diffusion only.

On the other hand, the estimated values of the over-all rate of mass transfer on the assumption of perfect mixing, and of molecular diffusion approach each other in the range of high agitator speed, so that the effect of agitation on the mixing inside of the droplets becomes insignificant.

(7) Generally speaking, diffusion resistance outside of the droplets does not change greatly with the increase in agitator speed, because the density difference in liquid-liquid systems is rather small. Moreover the efficiency of mixing inside of the droplets becomes less with the increase in agitator speed. Considering all, the most marked effect of the increase in agitator speed on liquid-liquid systems is the increase in the interfacial contact area.

Notations used

a	: radius of liquid droplet	[mm]
A	: total interfacial area	[cm ²] or [dm ²]
b	: width of impeller blade	[cm]
C	: concentration of solute or reactant in solution at time θ	[g-moles/l]
C'	: concentration of reaction product in the solution after separation from the solid	[g-moles/l]
C'_{θ}	: concentration of reaction product in the separated solution after an infinite time has elapsed	[g-moles/l]
C_E	: concentration of reaction product at equilibrium	[g-moles/l]
C_m	: average concentration of solute or reactant in the inner part of droplets at time θ	[g-moles/l]
C_p	: concentration of reaction product in the liquid bulk at time θ	[g-moles/l]
C_w	: concentration of water	[g-moles/l]
d	: diameter of the impeller	[cm]
d_g	: geometric mean diameter of liquid droplets	[cm]
d_i	: observed values of the diameter of liquid droplets	[mm]
d_s	: surface mean diameter of liquid droplets	[mm]
d_v	: volume mean diameter of liquid droplets	[mm]
D	: diameter of the agitation vessel	[cm]
D_f	: diffusion coefficient of solute	[cm ² /sec] or [cm ² /min]
D_i	: upper limit of the diameter of droplets at the i 'th section	[mm]
F	: mathematical symbols representing "function of"	[—]
H or H'	: constant of Henry's law	[—]
H_l	: liquid depth	[cm]
H_p	: elevation of impeller above bottom	[cm]
I_0	: an integral constant	[—]
k	: hydrolysis reaction rate constant for 2nd order reaction	[l/g-moles·min]
$k' = \frac{k_B \beta A_0 H C_A^*}{3 C_E V}$		[dm ³ /min·l]
k_B	: mass transfer coefficient in continuous phase	[dm/min]
$k_w = k C_w$: hydrolysis reaction rate constant multiplied by concentration of water	[1/min]
$K_B = \beta H k_B$		[dm/min]
$L = a K_B / D_f$		[—]
m	: initial concentration of solute in dispersed phase expressed in weight fraction	[—]
n_i	: number of liquid droplets measured	[—]

N	: agitator speed	[r.p.m.]
N_a	: agitator speed at which suction of air occurs	[r.p.m.]
N_c	: critical agitator speed required to mix two immiscible liquids	[r.p.m.]
N_i	: normalized cumulative frequency	[-]
N_i''	: normalized frequency	[-]
r	: distance from the center of droplet	[cm]
R	: over-all reaction rate	[g-moles/min]
S_B	: submerged length of baffle plate	[cm]
U	: total volume of liquid droplets	[cm ³]
$v = V/A$: volume of liquid per unit interfacial area	[l/cm ²]
V	: liquid volume	[l]
w_0	: width of baffle plates	[cm]
x	: weight fraction of reaction product	[-]
x_B	: thickness of effective diffusional film	[cm]
$\alpha = \sqrt{k_w/D_f}$		[1/cm]
$\beta = \gamma/\tanh \gamma$ or $1/\operatorname{erf} \sqrt{\alpha/D_f}$	"Hatta number"	[-]
$\gamma = \sqrt{k_w D_f}/K$		[-]
ϵ_B	: eccentric distance of baffle plate from agitator shaft	[cm]
θ	: angle of impeller blades	[degree]
θ	: time elapsed from interfacial contact	[sec] or [min]
λ_n	: the roots of the equation; $\lambda_n \cot \lambda_n + L - 1 = 0$	[-]
μ	: viscosity of agitated liquid or solvent	[c.p.]
ρ_l	: density of agitated liquid	[g/cm ³]
$\Delta\rho$: density difference between two liquids	[g/cm ³]
σ_g	: geometrical standard deviation	[-]

Subscript

A	: dispersed phase
B	: continuous phase
0	: initial value
x	: at x (weight fraction of reaction product)
*	: at interface

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