MEASUREMENT OF CONTINUOUS-PHASE MASS TRANSFER COEFFICIENT AT DROPLET SURFACE IN LIQUID-LIQUID MIXING VESSEL BY CHEMICAL REACTION METHOD

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The continuous-phase mass transfer volumetric coefficient $k_L a$ in a liquid-liquid mixing vessel was measured by using the hydrolysis reaction of both n-amyl and n-hexyl acetates with sodium hydroxide. Droplet diameter was also observed by using a videorecorder via a microscope during the reaction period, allowing the continuous-phase mass transfer coefficient, k_L, to be determined. The coefficient obtained was 2-5 times larger than that obtained from the correlation by Calderbank-MooYoung. Dimensionless correlation of the mass transfer coefficient with the droplet diameter and the power input per unit volume was confirmed experimentally to be close to that for the solid suspension system.

Introduction

For the analysis of a mass transfer-controlled heterogeneous reaction, it is necessary to know both the continuous-phase mass transfer coefficient and the effective interfacial area.

For heterogeneous systems, especially solid-liquid systems, mass transfer through the interface in an agitated vessel has been studied by many investigators[2,3,6,8,9,11] and many correlations of the continuous-phase mass transfer coefficient have been proposed.[16] Most were based on the local isotropic turbulence theory of Kolmogoroff, though Kuboi *et al.*[8] used the effective relative velocity for mass transfer. For liquid-liquid dispersions, the continuous-phase mass transfer coefficients were studied by Schindler and Treybal[12] and Keey and Glen[7] for a continuous-flow stirred-thank system and by Skelland and Lee[15] for a batch-stirred tank system. Their experiments were, however, conducted under the condition that the droplet size was not in dynamic equilibrium. Nanda and Sharma[10] and Sharma and Danckwerts[13] proposed a chemical method that gave only the interfacial area of dispersion.

In the present work, the continuous-phase mass transfer coefficient for tiny droplets in dynamic equilibrium is measured by using a reaction method

and is compared with the results of previous works and with correlations for the solid-liquid system.

1. Reaction Model

We consider the hydrolysis of ester with alkali[1] as a slow reaction.

$$RCOOR' + NaOH \rightarrow RCOONa + R'OH \qquad (1)$$

The following assumptions are made for the present analysis:

i) The ester disperses as droplet in the aqueous phase.

ii) The droplet diameter is constant during the reaction period.

iii) The alkali is mixed well instantaneously when added into the aqueous phase to start the reaction.

iv) The reaction in the concentration boundary film on the droplet surface is negligible compared to the reaction in the bulk of the aqueous phase.

v) The reaction is first-order with respect to the ester and the alkali.

The reaction rates of the ester with the alkali can be expressed as

$$dC_A/dt = k_L a(C_{Ai} - C_A) - k_2 C_A C_B \qquad (2)$$

$$dC_B/dt = -k_2 C_A C_B \qquad (3)$$

At low volume fraction of droplet ϕ, the apparent concentrations of the ester and the alkali, $\bar{C}_A$ and $\bar{C}_B$, can be expressed as

$$\bar{C}_A = (1-\phi)C_A + \phi C_A^\circ \fallingdotseq C_A + \phi C_A^\circ \qquad (4)$$

$$\bar{C}_B = (1-\phi)C_B \fallingdotseq C_B \qquad (5)$$

where C_A° is the molarity of pure ester.
Initial conditions at $t=0$ are expressed as

$$C_A = C_{A0} = C_{AS}, \quad C_B = C_{B0} = \bar{C}_{B0},$$
$$\bar{C}_A = \bar{C}_{A0}, \quad \bar{C}_B = \bar{C}_{B0} \qquad (6)$$

where subscript "0" means initial value.

From mass balance the apparent concentration of the ester is related to that of the alkali as follows:

$$\bar{C}_{A0} - \bar{C}_A = \bar{C}_{B0} - \bar{C}_B \qquad (7)$$

From Eq. (4) the following relation can be obtained.

$$\phi/\phi_0 = (\bar{C}_A - C_A)/(\bar{C}_{A0} - C_{A0}) \qquad (8)$$

Where the droplet diameter d_p is constant during the reaction period, the interfacial area per unit volume, a, is proportional to the volume fraction of the droplet, ϕ. Then the following expression can be obtained:

$$a/a_0 = \phi/\phi_0 = (\bar{C}_A - C_A)/(\bar{C}_{A0} - C_{A0}) \qquad (9)$$

Substitution of Eqs. (5), (7) and (9) into Eqs. (2) and (3) gives the following equations:

$$\frac{dC_A^*}{dt^*} = K\left\{\frac{1 - \theta_B(1 - \bar{C}_B^*) - C_A^*}{1 - C_{A0}^*}\right\}(C_{Ai}^* - C_A^*) - C_A^* \bar{C}_B^* \qquad (10)$$

$$d\bar{C}_B^*/dt^* = -C_A^* \bar{C}_B^*/\theta_B \qquad (11)$$

where

$$C_A^* = C_A/\bar{C}_{A0}, \quad \bar{C}_B^* = \bar{C}_B/\bar{C}_{B0}, \quad C_{Ai}^* = C_{Ai}/\bar{C}_{A0}$$
$$\theta_B = \bar{C}_{B0}/\bar{C}_{A0}, \quad K = k_L a_0/k_2 \bar{C}_{B0}, \quad t^* = k_2 \bar{C}_{B0} t \qquad (12)$$

The dimensionless initial conditions are:

$$C_A^* = C_{AS}^*, \quad \bar{C}_B^* = 1 \quad \text{at} \quad t^* = 0 \qquad (13)$$

Equations (10) and (11) were solved simultaneously by the Runge-Kutta method.

The reaction rate constant k_2 and the mass transfer volumetric coefficient $k_L a_0$ were determined by the following method.*

i) The Box complex method is used in obtaining the optimum combination of k_2 and K that best fits the observed curve of alkali concentration vs. time.

ii) The reaction rate constant k_2 depends only on temperature. Hence the reaction rate constant is determined as the average value of k_2 for all runs.

iii) By using the resultant k_2, the optimum K value and the mass transfer volumetric coefficient $k_L a_0$ are obtained for each run.

iv) The mass transfer coefficient k_L is obtained from the values of $k_L a_0$ and a_0, which is calculated from the observed Sauter mean droplet diameter, d_{32}, as

$$a_0 = 6\phi_0/d_{32} \qquad (14)$$

The initial volume fraction ϕ_0 is obtained from the mass balance of ester as

$$\phi_0 \fallingdotseq \left(\frac{V_A}{V_W} - \frac{C_{AS}}{C_A^\circ}\right) \qquad (15)$$

where V_A and V_W are respectively the volumes of pure ester and water added initially to a vessel.

3. Experimental

A schematic diagram of the experimental apparatus is shown in **Fig. 1**. Agitated glass vessels of 17-, 14- and 10-cm ID were used in the present study. Stainless steel six-blade paddle impellers were used, with diameters d of 8.5, 7 and 5 cm. The ratio of impeller to vessel diameter d/D ranged from 0.29 to 0.50.

The ester, n-amyl acetate or n-hexyl acetate, was added to the stirred water to form a dispersed liquid with an apparent ester concentration of 0.025 mol/l. The water was saturated with the ester and the droplet size was in dynamic equilibrium, usually in 10–15 minutes. The initial volume fraction ϕ_0 defined by Eq. (15) was 0.0017 for n-amyl acetate and 0.0035 for n-hexyl acetate. The reaction was started by instantaneous addition of sodium hydroxide aqueous solution, the concentration of which was adjusted to become 0.050 mol/l in the vessel. At this moment no change in droplet size was observed. The progress of the reaction was monitored by measuring the variation of alkali concentration by electric conductivity meter and by titration.*) The reaction temperature was 25°C or 30°C, and the stirrer speed was 175 to 700 rpm.

For the measurement of droplet diameter, the liquid was sucked up into the focus of a microscope and the droplet picture was recorded with a video-recorder during the reaction period. Each droplet diameter was sized on a microcomputer display and its datum was stored in the computer memory. The Sauter mean diameter d_{32} was obtained from 500 droplet diameters

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*) As the solubility of n-hexyl acetate into aqueous phase is very low, an error in measurement of ester concentration has a significant effect on the evaluation of k_2 in a homogeneous system.

*) For the titration, the sampled liquid is poured quickly into acidic solution to stop the reaction, then the resultant acidic solution is titrated with alkaline solution. The time lag for sampling is less than three seconds.
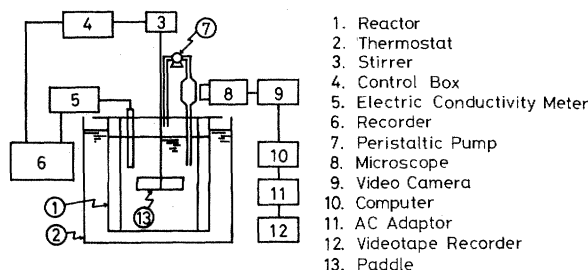
1. Reactor
2. Thermostat
3. Stirrer
4. Control Box
5. Electric Conductivity Meter
6. Recorder
7. Peristaltic Pump
8. Microscope
9. Video Camera
10. Computer
11. AC Adaptor
12. Videotape Recorder
13. Paddle

Fig. 1. Schematic diagram of experimental apparatus

at 5-minute intervals.

The physical properties of the esters are listed in **Table 1.** The diffusivity D_A was estimated from Wilke's equation,[19] and the interfacial tension σ was measured by the Wilhelmy method.[18] The solubility C_{AS} was observed by using an agitated vessel with a flat liquid-liquid interface, in the same manner as in the previous paper.[1]

4. Results and Discussion

Table 1 also shows the reaction rate constant k_2 obtained. The value for n-amyl acetate at 25°C was close to the observed value of 0.0805 l/mol·s for isoamyl acetate by Viallard.[17]

In **Fig. 2** the observed Sauter mean diameter of droplet d_{32} is correlated with the product of impeller diameter and -0.6 power of Weber number. The observed diameter is 0.7 to 2.5×10^{-4} m and is slightly larger than that from the correlation by Chen-Middleman.[5]

The value of d_{32} was almost constant during the reaction period, though the number of droplets in the video-picture decreased with time. Thus the droplet size was presumed to be in dynamic equilibrium.

The value of $k_L a_0$ was determined as the average value during the initial reaction period up to 30 minutes, where the dimensionless concentration of the alkali and the volume fraction ratio, $\bar{C}_B^*$ and ϕ/ϕ_0, decreased from unity to 0.55 and 0.003 respectively.

The observed mass transfer coefficient is plotted against the power input per unit volume in **Fig. 3**, where the solid line shows the correlation by Calderbank-MooYoung[4]:

$$k_L = 0.13(P_V \rho^2/\mu^3)^{0.25} Sc^{-2/3} \qquad (16)$$

The observed mass transfer coefficient is 2–5 times larger than that from Eq. (16). In this figure the experimental data by Schindler and Treybal[12] for the continuous-flow stirred-tank system are also plotted. They are 2–3 times larger than the present experimental data.

The condition under which the chemical reaction occurs in the bulk of the aqueous phase can be expressed as[14]

Table 1. Physical properties and reaction rate constant of esters

Ester	Temp. [°C]	Diffusivity $D_A \times 10^{10}$ [m²/s]	Solubility C_{AS} [mol/l]	Interfacial tension $\sigma \times 10^3$ [N/m]	Reaction rate constant k_2 [l/(mol·s)]
n-amyl acetate	25	7.88	0.0135	14.5	0.082
	30	8.75	0.0135	15.3	0.113
n-hexyl acetate	25	7.32	0.0039	14.0	0.071
	30	8.13	0.0039	14.8	0.097

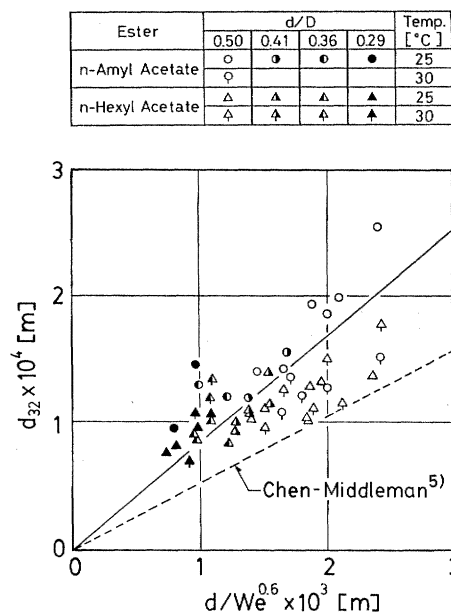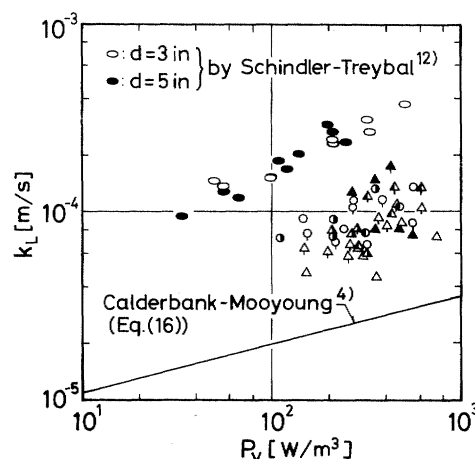| Ester	d/D 0.50	d/D 0.41	d/D 0.36	d/D 0.29	Temp. [°C]
n-Amyl Acetate	O	◑	◐	●	25
	○				30
n-Hexyl Acetate	△	▲	◭	▲	25
	◮	◭	◮	◮	30

Fig. 2. Sauter mean droplet diameter

Fig. 3. Mass transfer coefficient at droplet surface. Keys are the same as in Fig. 2, except for Schindler-Treybal.

$$k_L \gg (k_2 D_A \bar{C}_B)^{1/2} \qquad (17)$$

The value of k_L is larger than 5×10^{-5} m/s in Fig. 3, and $(k_2 D_A \bar{C}_B)^{1/2}$ is smaller than 2.2×10^{-6} m/s from Table 1. Then, the present reaction system satisfies the relation of Eq. (17) and the expressions of Eqs. (2) and (3).
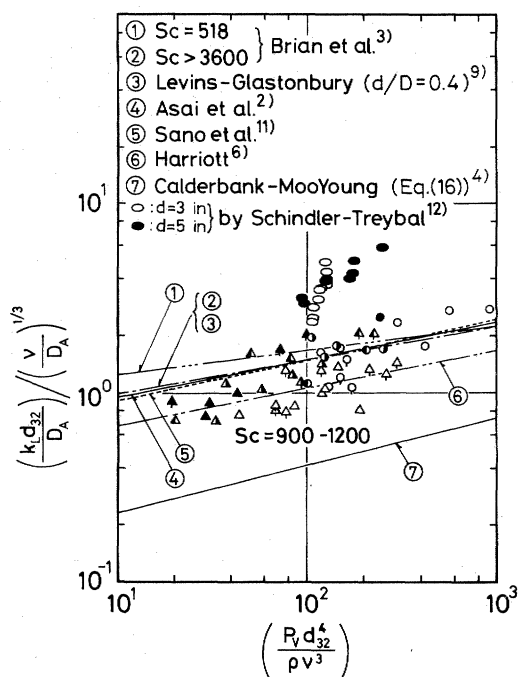
Fig. 4. Dimensionless correlation of mass transfer coefficient for tiny droplet. Keys are the same as in Fig. 2, except for Schindler-Treybal.

solid spheres.

Nomenclature

a	=	interface area per unit volume	$[m^{-1}]$
b	=	impeller width	$[m]$
C_A	=	concentration of ester	$[mol \cdot l^{-1}]$
C_{Ai}	=	concentration of ester at interface	$[mol \cdot l^{-1}]$
C_{AS}	=	solubility of ester in water	$[mol \cdot l^{-1}]$
$\bar{C}_A$	=	apparent concentration of ester	$[mol \cdot l^{-1}]$
C_A°	=	concentration of pure ester	$[mol \cdot l^{-1}]$
C_B	=	concentration of alkali	$[mol \cdot l^{-1}]$
d	=	impeller diameter	$[m]$
d_p	=	droplet diameter	$[m]$
d_{32}	=	Sauter mean diameter	$[m]$
D	=	vessel diameter	$[m]$
D_A	=	diffusivity of ester in water	$[m^2 \cdot s^{-1}]$
H	=	liquid depth	$[m]$
K	=	dimensionless parameter $(= k_L a_0/k_2 \bar{C}_{B0})$	$[-]$
k_L	=	continuous-phase mass transfer coefficient	$[m \cdot s^{-1}]$
$k_L a$	=	mass transfer volumetric coefficient	$[s^{-1}]$
k_2	=	reaction rate constant	$[l \cdot mol^{-1} \cdot s^{-1}]$
n	=	rotational speed	$[s^{-1}]$
P	=	power input	$[W]$
P_V	=	power input per unit volume $(P/(\pi D^2 H/4))$	$[W \cdot m^{-3}]$
P_{VI}	=	power input per unit volume swept by impeller $(= P/(\pi d^2 b/4))$	$[W \cdot m^{-3}]$
Sc	=	Schmit number $(\equiv v/D_A)$	$[-]$
t	=	time	$[s]$
V_A	=	volume of pure ester added to a vessel	$[m^3]$
V_W	=	volume of water added to a vessel	$[m^3]$
We	=	Weber number $(\equiv d^3 n^2 \rho/\sigma)$	$[-]$
θ_B	=	molar ratio $(= \bar{C}_{B0}/\bar{C}_{A0})$	$[-]$
μ	=	viscosity	$[Pa \cdot s]$
v	=	kinematic viscosity	$[m^2 \cdot s^{-1}]$
ρ	=	density	$[kg \cdot m^{-3}]$
σ	=	interfacial tension	$[N \cdot m^{-1}]$
ϕ	=	volume fraction of droplet	$[-]$

⟨Superscript⟩
* = dimensionless

⟨Subscript⟩
0 = initial value

By using the Sauter mean droplet diameter d_{32} as a characteristic length and the power input per unit volume P_V as a factor related to a characteristic velocity, the dimensionless correlation of the mass transfer coefficient is shown in **Fig. 4**. The correlation lines by Brian et al.,[3] Levins and Glastonbury,[9] Asai et al.,[2] Sano et al.[11] and Harriott[6] for the mass transfer of suspended solid sphere, as well as by Calderbank-MooYoung,[4] are shown in the same figure. The observed data are close to the correlation lines for the solid suspension, though the data of Schindler and Treybal[12] are above the correlation lines. The disagreement between the data of Schindler and Treybal and those in the present experiments is probably due to the difference of flow system, continuous vs batch. The result in Fig. 4 shows that the mass transfer behavior of tiny droplets is very similar to that of suspended solid spheres.

Conclusions

For liquid-liquid dispersion of ester in aqueous alkali solution, the continuous-phase mass transfer volumetric coefficient at the droplet surface was measured by using a hydrolysis reaction of the ester with the alkali. The droplet diameter was measured by using a videocamera via a microscope during the reaction period. The continuous-phase mass transfer coefficient was calculated from the observed volumetric coefficient with the droplet diameter. The mass transfer coefficient for the tiny droplet was shown experimentally to satisfy the correlation for suspended

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