$$\frac{(-1)^n I(m,n) \operatorname{Cos}\left[\frac{(2m+1)}{2}\pi y^2\right] \operatorname{Exp}[\phi]}{2_n + 1} \quad (C7)$$

where $I(m, n)$ is obtained from Equations (C5) or (C6) as appropriate and where

$$\operatorname{Exp}\phi = \operatorname{Exp}\left[\frac{-(2m+1)\pi^2(z-z_I) - (2n+1)^2\pi^2 Z_I}{4Pg}\right] \quad (C8)$$

The $I(m, n)$ term simplifies considerably for specified odd or even values of m and n. This is displayed in the following result for $\overline{T}_2(z)$ which is obtained from Equation (23):

$$\overline{T_2}(z) = \frac{16}{\pi^3}\sum_{m=0,2}^{\infty}\sum_{n=0,2}^{\infty}\frac{\operatorname{Exp}[\phi]}{(2n+1)(2m+1)(n+m+1)} + \frac{16}{\pi^3}\sum_{m=0,2}^{\infty}\sum_{n=1,3}^{\infty}\frac{\operatorname{Exp}[\phi]}{(2n+1)(2m+1)(n-m)} - \frac{16}{\pi^3}\sum_{m=1,3}^{\infty}\sum_{n=0,2}^{\infty}\frac{\operatorname{Exp}[\phi]}{(2n+1)(2m+1)(n-m)} + \frac{16}{\pi^3}\sum_{m=1,3}^{\infty}\sum_{n=1,3}^{\infty}\frac{\operatorname{Exp}[\phi]}{(2+1)(2+1)(n+m+1)} \quad (C9)$$

For the transformation corresponding to two-channel, partial flow inversion, Equation (4) gives

$$y_2 = y_1 - y_c, y_2 < q_c$$
$$y_2 = y_1 + 1 - y_c, y_2 > q_c \quad (C10)$$

The following results have been obtained for $I(\lambda_m, \lambda_n)$:

$$I(m,n) = \frac{(-1)^n}{2\pi(n-m)(n+m+1)}$$
$$[(2n+1)\operatorname{Cos}\lambda_m y_c - (2n+1)\operatorname{Cos}\lambda_m y_c - (-1)^m(2m+1)\operatorname{Sin}\lambda_n y_c + (-1)^n(2m+1)\operatorname{Sin}\lambda_m y_c] \quad (C11)$$

for $m \neq n$. As before, this is indeterminate for $n = m$, and an alternate result is needed:

$$I(m,n) = (-1)^n\frac{y_c}{2}\operatorname{Sin}\lambda_n y_c + \frac{(1-y_c)}{2}\operatorname{Cos}\lambda_n y_c \quad (C12)$$

for $m = n$.

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Properties of Recirculating Turbulent Two Phase Flow in Gas Bubble Columns

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The equation of motion for the two phase flow within a bubble column, operated within the recirculation flow regime, has been solved, and the profile of liquid flow has been determined. Nicklin's relation for the bubble flow regime has been extended to the recirculation flow regime.

Data analysis shows that the mean slip velocity between bubble and liquid is approximately constant and that the kinematic turbulent viscosity increases rapidly with increasing diameter of the column. These observations lead to the conclusion that scale-up has but little influence upon the mean gas holdup.

SCOPE

It is well known that a swarm of bubbles rises uniformly within a gas bubble column when the superficial gas velocity is low (usually less than 2 to 4 cm/s) and when bubbles of uniform size are generated at the gas distributor, that is, when the column is operated in the bubble flow regime. Operation of the column in the bubble flow regime has been utilized widely for several gas-liquid contacting operations (Østergaard, 1968; Sada, 1969; Kumar and Kuloor, 1970).

When the gas velocity is increased, the bubble flow ceases to be uniform; it becomes unstable, intense recirculation is observed within the gas-liquid mixed phase,

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and the column operates in the recirculation flow regime (Pavlov, 1965; Yoshitome, 1967; Yamagoshi, 1969). The recirculation is due to the existence of a phase rich on bubbles near the center of the column and a phase relatively lean on bubbles near the wall of the column, and the thus caused difference in buoyancy forces. Operation of bubble columns in the recirculation flow regime has often been utilized for gas-liquid reactions like fermentation. The recent (Takahashi and Washimi, 1976) application to high temperature steam cracking of petroleum asphalt is another successful example for the operation of columns in this flow regime.

For bubble columns of sufficient large aspect ratio L/D_T, operated without continuous liquid feed, theories of recirculation have been presented by Miyauchi and Shyu (1970) and Hills (1974). These authors employ the same equation of motion but different hypotheses for the turbulent viscosity. In earlier work, Koide and Kubota (1966) attempted to employ the mixing length theory to the flow near the wall of the column. More recently, Ueyama and Miyauchi (1976) considered time averages of the Navier-Stokes equations for two phase flow, thus clarifying the physical meaning of the turbulent viscosity in the bubble column operated in the recirculation flow regime.

Experimental results including liquid velocitites, bubble velocities, bubble sizes, radial profiles, and mean values of bubble gas holdup, turbulent viscosities and axial diffusivities of the liquid phase have been reported (Pavlov, 1965; Yamagoshi, 1969; Towell, 1965; 1972; Miyauchi and Shyu, 1970; 1971; Yoshida, 1971; Kato and Nishiwaki, 1971; Hills, 1974; Kato et al., 1975; Ueyama and Miyauchi, 1977*a*, *b*).

The objective of this work is the development of sound bases for the understanding of the flow characteristics within the recirculation flow regime and for the design procedure that permits the scaling-up of columns operated in the recirculation flow regime.

Firstly, the equation of motion which governs the recirculation bubble flow, including continuous liquid feed, has been solved. Secondly, using this solution, available data have been analyzed and correlated while the radial profile of gas holdup, its mean value, mean slip velocity, size of bubbles, and kinematic turbulent viscosity have been studied.

CONCLUSIONS AND SIGNIFICANCE

For the usual low viscosity fluids, recirculation type of flow is observed when the superficial gas velocity is in excess of 0.04 to 0.05 m/s. The equation of motion for an axisymmetric bubble column, operated in the recirculation flow regime, has been solved to yield the profile of the velocity of the mixed phases.

A constant turbulent kinematic viscosity has been assumed for the mixed phase, and a radial profile of the gas holdup has been assumed according to an empirical formula based upon extensive experimental observations. In order to avoid difficulties of defining the thickness of the irregularly bubbled laminar-turbulent buffer layer and to simplify the mathematical treatment, a simplified boundary condition near the wall of the column has been proposed and employed.

The relation for the bubble flow regime by Nicklin (1962) has been extended to include the recirculation flow regime by adding superficial velocity terms arising from the recirculation flow. The new relation has been derived through mass balances for continuously fed gas and liquid streams. The following facts have been clarified through investigation of experimental data, on the basis of the here developed theory:

1. In the recirculation flow regime, the mixed phases are in intensely turbulent flow. For $U_G \gtrsim 0.2$ m/s, the mean slip velocity of the bubbles $\overline{u}_s$ assumes an approximately constant value. Apparently, there is no interaction between bubbles; these seem to move independently.

2. Calculations show that the shear stress near the wall of the column usually is negligible when compared with the buoyancy forces. Consequently, the profile of the velocity is greatly simplified; its predictions are in reasonable agreement with experimentally observed profiles.

3. The turbulent kinematic viscosity increases rapidly with increasing column diameter D_T. ($\nu_t \propto D_T^n$, with n between 1.8 and 1.5.) It shows little dependence upon U_G.

4. Scaling-up of the column seems to have little influence upon the dependence of the mean gas holdup $\overline{\epsilon}_b$ upon U_G. Possibly, this behavior may be explained through the use of the characteristic properties of $\overline{u}_s$ and ν_t.

For design and scale-up of a column operating in the recirculation flow regime, the dependence of ν_t upon D_T, when D_T is increased beyond 0.6 m, is not yet fully measured experimentally. However, our recent experience (Koide et al., 1977) with an industrial bubble column (5.5 m diameter) suggests that the dependence of ν_t upon D_T may be approximately extrapolated to larger size columns. This question as well as the behavior of a column whose aspect ratio L/D_T shrinks towards 1 are still under investigation. All other parameters seem to be sufficiently well correlated to be helpful for practical applications.

THE BASIC EQUATIONS

Figure 1 depicts the profile of the time averaged mean liquid velocity within a bubble column, operated in the recirculation flow regime, whose aspect ratio L/D_T is sufficiently larger than 1. For steady state conditions, the equation of motion is (Miyauchi and Shyu, 1970; Hills, 1974)

$$-\frac{1}{r}\frac{d}{dr}(r\tau) = \frac{d\overline{P}}{dZ} + (1 - \epsilon_b)\rho_l g \qquad (1)$$

Using the molecular kinematic viscosity ν_M, and introducing a turbulent kinematic viscosity ν_t, one can relate the shear stress τ with the mean axial velocity through

$$\tau = -(\nu_M + \nu_t)\rho_l\left(\frac{du}{dr}\right) \qquad (2)$$

The molecular viscosity ν_M is negligibly small compared with the turbulent viscosity ν_t everywhere except in a thin layer next to the wall of the column. Ueyama and

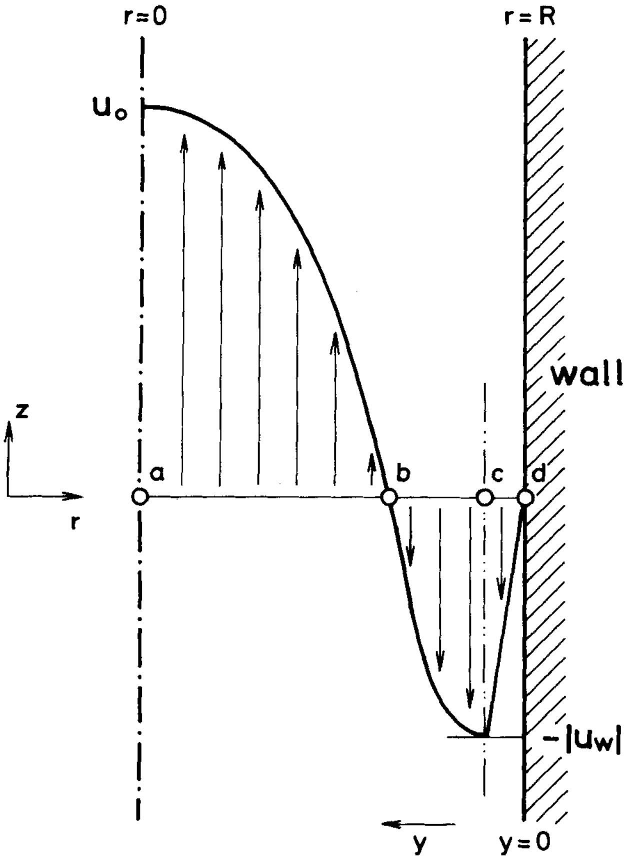

Fig. 1. Flow pattern of liquid in a bubble column.

Miyauchi (1976) have recently studied the time averaged fluctuation velocity components of the Navier-Stokes equations for two phase flow and have demonstrated that for a bubble column with $L/D_T >> 1$, the turbulent shear stress is governed by

$$-\nu_t \frac{du}{dr} = (1 - \epsilon_b)\, \overline{u_r' u_z'} \tag{3}$$

Equations (1) and (2) form the basis of the subsequent theoretical development.

THE BOUNDARY CONDITIONS

The boundary conditions formulated here are essentially those suggested by Miyauchi and Shyu (1970). As illustrated in Figure 1 (for $+ |U_L|$), liquid flow is upwards and turbulent in the innermost region $a < r < b$; it is downwards and fully developed turbulent in the annular region $b < r < c$. In the laminar sublayer $c < r < d$, the flow is downwards and laminar; the radial gradient of the axial velocity is very large in this sublayer. According to the universal, turbulent velocity profile (Schlichting, 1960), there must exist a buffer layer between the turbulent core and the laminar sublayer. However, in this case it is difficult to separate a buffer layer from the turbulent core; bubbles from the turbulent core enter and agitate the buffer layer in an irregular manner. Both to simplify the mathematical development and to comply with a sound physical interpretation of the bubbling buffer layer, the thickness of the laminar sublayer δ will be taken somewhat larger than that for single-phase flow, and the buffer layer will be considered as part of the laminar sublayer.

According to the universal law of the velocity profile (Schlichting, 1960), the velocity profile within the laminar sublayer is described by

$$\frac{|u|}{v_*} = \frac{y v_*}{\nu_M} \quad \text{for} \quad \frac{y v_*}{\nu_M} \lesssim 5 \tag{4}$$

using the friction velocity $v_* = \sqrt{|\tau_w|/\rho}$. The velocity profile within the turbulent core is given by

$$\frac{|u|}{v_*} = 5.75 \log\left(\frac{y v_*}{\nu_M}\right) + 5.5 \quad \text{for} \quad \frac{y v_*}{\nu_M} \gtrsim 70 \tag{5}$$

Evaluating both (4) and (5) at $y = \delta$, and then equating the respective values, one obtains

$$\frac{\delta v_*}{\nu_M} = 11.63 \tag{6}$$

Using Equation (4) with the value (6), one can determine the velocity u_δ at $y = \delta$:

$$u_\delta = -11.63 v_* = -11.63\sqrt{|\tau_w|/\rho_l} \tag{7}$$

According to the results of numerous experimental investigations, which will be presented in subsequent section, the thickness δ is usually much smaller than the radius of the column R; hence, the peripheral velocity of the turbulent core u_w is equal to u_δ at very nearly $r = R$. One can write the boundary condition

$$u_w \doteq u_\delta = -11.63\sqrt{|\tau_w|/\rho_l} \quad \text{at} \quad r = R \tag{8}$$

Another boundary condition is

$$\frac{du}{dr} = 0 \quad \text{at} \quad r = 0 \tag{9}$$

THE SOLUTION OF THE BASIC EQUATIONS

In order to develop the sought solution of the basic Equation (1), one first multiplies this equation by $2\pi r$ and then integrates the product between $r = 0$ and $r = R$; dividing the result by πR^2, one obtains

$$-\frac{d\overline{P}}{dz} = \left(\frac{2}{R}\right)\tau_w + (1 - \overline{\epsilon}_b)\rho_l g \tag{10}$$

employing the mean gas holdup

$$\overline{\epsilon}_b = \int_0^R 2\pi r\, \epsilon_b\, dr/\pi R^2 \tag{11}$$

Substituting in Equation (1) for $d\overline{P}/dz$ by Equation (10) and for τ_w according to Equation (2) (neglecting ν_M in the turbulent core), one obtains the modified basic equation for axial liquid flow in the turbulent core:

$$-\frac{1}{r}\frac{d}{dr}\left(\nu_t r \frac{du}{dr}\right) = \frac{2}{R\rho_l}\tau_w - (\overline{\epsilon}_b - \epsilon_b)g \tag{12}$$

Two simplifying assumptions (Miyauchi and Shyu, 1970) are used with (12). Firstly, ν_t is to be constant throughout the turbulent core; secondly, the profile of the gas holdup ϵ_b is approximated by (Miyauchi and Shyu, 1970; Hills, 1974; Kato et al., 1975; Ueyama and Miyauchi, 1977*a, b*)

$$\frac{\epsilon_b}{\overline{\epsilon}_b} = \left[\frac{(n+2)}{n}\right](1 - \phi^n) \tag{13}$$

using the normalized radius $\phi = r/R$. With these simplifications, one can solve (12). The solution which satisfies both boundary conditions (8) and (9) is given by

$$u + |u_w| = \frac{R^2}{\nu_t}\left[\left(\frac{\tau_w}{2R\rho_l} + \frac{\overline{\epsilon}_b g}{2n}\right)(1 - \phi^2)\right.$$

$$- \frac{\bar{\epsilon}_b g}{n(n+2)} (1 - \phi^{n+2}) \Big] \quad (14)$$

However, this solution (14) incorporates two as yet unknown quantities $|u_w|$ and τ_w.

The superficial liquid velocity, designated by $\pm\ |U_L|$, has a positive sign for concurrent gas and liquid flows and a negative sign for countercurrent flows. $U_L = 0$ corresponds to batchwise liquid operation of the bubble column. A mass balance of the liquid phase yields

$$\int_0^R 2\pi r u (1 - \epsilon_b) dr = \pm\ \pi R^2 |U_L| \quad (15)$$

Equation (8) provides the expression for τ_w:

$$\tau_w = -\ \rho_l (|u_w|/11.63)^2 \quad (16)$$

Substituting in (15), for u by (14) and for τ_w by (16), one obtains a quadratic equation in $|u_w|$. Thus, $|u_w|$ can be determined:

$$|u_w| = (11.63)^2 \frac{\nu_t J_1}{R} \Bigg[-1 + \sqrt{1 + \frac{\{2J_0 - (\bar{\epsilon}_b/2)\}}{(11.63)^2 J_1^2} \cdot \frac{R^3 g}{\nu_t^2} - \frac{(\pm\ 2R|U_L|)}{(11.63)^2 J_1 (1 - \bar{\epsilon}_b) \nu_t}} \Bigg] \quad (17)$$

Substituting, by (16) and (17) for τ_w and $|u_w|$, one obtains

$$u = [J_1(1 - \phi^2) - 1]\ |u_w| - \frac{R^2 g}{\nu_t} [J_0(1 - \phi^2) - I(\phi)] \pm J_1 \left(\frac{|U_L|}{1 - \bar{\epsilon}_b} \right) (1 - \phi^2) \quad (18)$$

using

$$J_0 = \frac{(n+6)\ \bar{\epsilon}_b}{4(n+4)} \cdot \frac{\left[1 - \dfrac{(n^2 + 10n + 20)}{(n+2)(n+6)} \bar{\epsilon}_b \right]}{\left[1 - \dfrac{(n+6)}{(n+4)} \bar{\epsilon}_b \right]}$$

$$J_1 = \frac{2(1 - \bar{\epsilon}_b)}{\left[1 - \dfrac{(n+6)}{(n+4)} \bar{\epsilon}_b \right]}$$

$$I(\phi) = \int_\phi^1 \frac{1}{\phi} \left[\int_0^\phi \phi\, \epsilon_b\, d\phi \right] d\phi = \left(\frac{n+2}{n} \right) \left[\frac{1 - \phi^2}{4} - \frac{1 - \phi^{n+2}}{(n+2)^2} \right] \bar{\epsilon}_b$$

Equations (17) and (18) properly specialize to the earlier (Miyauchi and Shyu, 1970) presented solutions for $U_L = 0$.

SOME PROPERTIES OF THE SOLUTION

Relation Between $\bar{\epsilon}_b$ and $\bar{u}_s$

For uniformly distributed rising bubbles, the relationship between the mean gas holdup $\bar{\epsilon}_b$ and the slip velocity of the bubbles relative to the liquid $\bar{u}_s$ is given by (Nicklin, 1962; Yoshitome, 1963)

$$\frac{U_G}{\bar{\epsilon}_b} - \frac{\pm\ |U_L|}{(1 - \bar{\epsilon}_b)} = \bar{u}_s \quad (19)$$

In order to find the corresponding relationship for the recirculation flow regime, one investigates the mass balance of the gas phase of a continuously bubbled column:

$$\int_0^R 2\pi r (u + \bar{u}_s) \epsilon_b\, dr = \pi R^2 U_G \quad (20)$$

According to experimental observations in the recirculation regime of the slip velocity (Yamagoshi, 1969; Ueyama and Miyauchi, 1976), $\bar{u}_s$ is approximately invariant with r for D_T between 0.25 and 0.60 m and $U_G = 0.058$ and between 0.35 and 0.93 m/s. Taking a mean constant value for $\bar{u}_s$ in Equation (20), and Equations (13) and (18) for ϵ_b and u, respectively, one can integrate that equation:

$$\left(\frac{U_G}{\bar{\epsilon}_b} \right) - \frac{1}{(1 - \bar{\epsilon}_b)} \left[\pm\ |U_L| + \frac{u_o + |u_w|}{(n+4)} \right] = \bar{u}_s \quad (21)$$

An apparent interstitial liquid velocity $(u_o + |u_w|)/(n+4)$ is added to the net liquid feed term $\pm\ |U_L|$; consequently, for any given $\bar{u}_s$, $\bar{\epsilon}_b$ for the recirculation flow regime is lower than that for the bubble flow regime. Equation (21) properly specializes to Equation (19) for no recirculation flow.

Particular Case with $n = 2$. The values for n in the recirculation flow regime reported to date are presented in Table 1; they differ somewhat. Most data indicate a value for n of approximately 2, in the average. For given flow conditions, the empirically adjustable viscosity ν_t assumes different values for different values of n. However, once ν_t is adequately selected, the flow characteristics of the gas-liquid mixed phase vary but little with n. The data of Miyauchi and Shyu (1970), which indicate $n = 8$, were obtained at an early stage of the study; subsequent extensive measurements by Kato et al. (1975) show, for essentially the same column, $n = 2$. Thus, when we use $n = 2$ in the sequel, Equations (17), (18), and (21) may be simplified to read

$$\frac{|u_w|}{u^*} = 12(11.63)^2 \left[\frac{1 - \bar{\epsilon}_b}{3 - 4\bar{\epsilon}_b} \right] \left[-1 + \left\{ 1 + \frac{Gr_t \bar{\epsilon}_b}{1152} \cdot \frac{(3 - 4\bar{\epsilon}_b)(2 - 3\bar{\epsilon}_b)}{(11.63)^2 (1 - \bar{\epsilon}_b)^2} - \frac{(3 - 4\bar{\epsilon}_b)(\pm\ |U_L|)}{6(11.63)^2 (1 - \bar{\epsilon}_b)^2 u^*} \right\}^{1/2} \right] \quad (22)$$

$$\frac{u}{u^*} = \left[\frac{6(1 - \bar{\epsilon}_b)}{(3 - 4\bar{\epsilon}_b)} (1 - \phi^2) - 1 \right] \frac{|u_w|}{u^*} + \frac{Gr_t \bar{\epsilon}_b}{32} (1 - \phi^2) \left(\frac{1 - \bar{\epsilon}_b}{3 - 4\bar{\epsilon}_b} - \phi^2 \right) \pm \frac{6|U_L|}{(3 - 4\bar{\epsilon}_b) u^*} (1 - \phi^2) \quad (23)$$

$$\left(\frac{U_G}{\bar{\epsilon}_b} \right) - \frac{1}{(1 - \bar{\epsilon}_b)} \left[\pm\ |U_L| + \frac{u_o + |u_w|}{6} \right] = \bar{u}_s \quad (24)$$

where $Gr_t = D_T^3 g/\nu_t^2$ and $u^* = \nu_t/D_T$. Figure 2 shows a plot of Equation (22).

Mean Linear Recirculation Velocity of Liquid

Knowledge of this velocity is sometimes useful for the understanding of the intensity of flow of the mixed phases;

Table 1. Experimental Data

(Air-water system; room temperature under atmospheric pressure)

D_T [m]	Gas distributor	U_G [m/s]	n [—]	u_o [m/s]	$\lvert u_w^* \rvert$ [m/s]	u_s [m/s] Data	u_s [m/s] Equation (26)	$\bar{\epsilon}_b$ Data	$\bar{\epsilon}_b$ Calc.	d_{VS} [m]	Reference	Key in Figure 5
0.172	Perforated plate	0.046		0.32	0.25		0.28		0.12		Pavlov (1965)	▼
		0.100		0.52	0.45		0.36		0.18			
		0.171		0.63	0.50		0.50		0.23			
		0.257		0.69	0.58		0.62		0.28			
		0.515		0.78	0.60		0.98		0.38			
		0.710		0.96	0.74		1.15		0.43			
0.15	Perforated plate	0.075		0.40	0.35		0.32		0.16		Yoshitome (1967)	♦
0.25	Single nozzle	0.052	1.6	0.43	0.25	0.18	0.21	0.15			Yamagoshi (1969)	★ ☆
0.10	Single nozzle	0.045	8	0.27	0.12		0.30	0.12			Miyauchi and Shyu (1970)	▲
		0.082	8	0.32	0.30		0.42	0.15				
		0.155	8	0.40	0.40		0.57	0.21				
		0.225	8	0.68	0.50		0.60	0.26				
		0.28	8	0.85	0.65		0.61	0.29				
		0.32	8	0.98	0.75		0.61	0.31				
		0.37	8	1.09	0.85		0.61	0.34				
0.25	Single nozzle	0.082								0.024	Yoshida (1971)	⬢
0.138	Perforated plate	0.019	1.8	0.17	0.20		0.25		0.06		Hills (1974)	■
		0.038	1.3	0.33	0.27		0.23		0.11			
		0.064	1.8	0.44	0.32		0.31		0.14			
		0.095	1.8	0.52	0.34		0.39		0.17			
		0.127	1.8									
		0.169	1.6	0.58	0.34		0.54		0.23			
0.12	Perforated plate	0.02 ~0.15	1.7 ~2.5								Kato et al. (1975)	
0.60	Single nozzle	0.35	2.3	1.80	1.00	0.49	0.41	0.32		0.038	Ueyama and Miyauchi (1977*a*)	○ ◑ ●
		0.53	2.1	2.00	1.20	0.51	0.54	0.38		0.038		
		0.93	1.8	2.50	1.20	0.52	0.50	0.52		0.038		
0.30	Single nozzle	0.46	1.5								Ueyama and Miyauchi (1977*b*)	
0.095	Porous plate	0.01 ~0.1									Nicklin (1962)	
0.15	Perforated plate	0.02 ~0.2									Yoshitome (1963)	— — —

* $\lvert u_w \rvert$ are obtained by extrapolation of the measured distribution of liquid velocity.

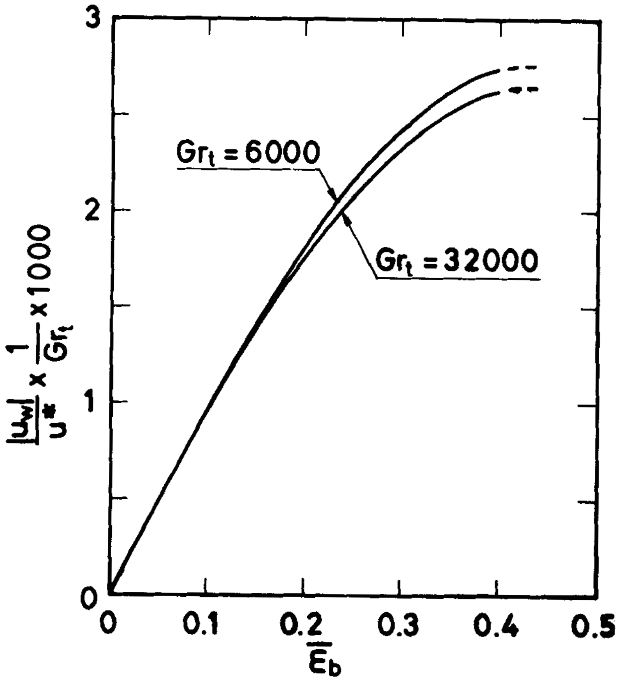

Fig. 2. $|u_w|$ as a function of $\bar{\epsilon}_b$ and Gr_t.

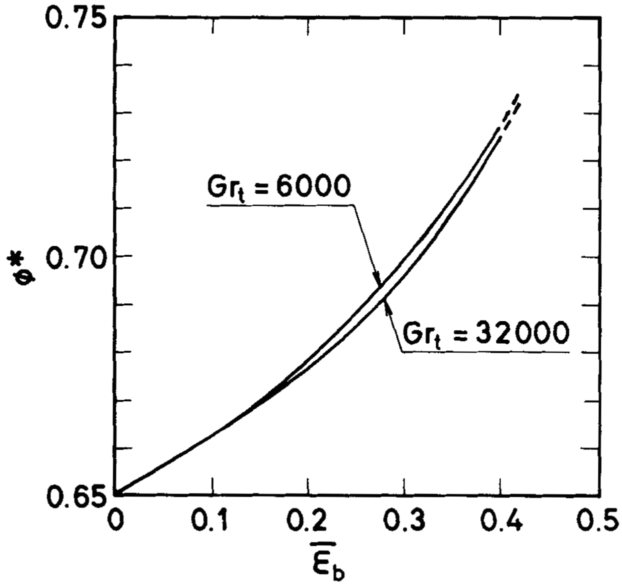

Fig. 3. ϕ^* as a function of $\bar{\epsilon}_b$ and Gr_t.

it is obtained through a knowledge of that radial position $\phi^* = r^*/R$, where the axial liquid velocity has value zero. The value of ϕ^* can be obtained, for $n = 2$, from Equation (23) by setting $u = 0$. The mean upflowing axial velocity of the liquid is, therefore, given by

$$(\bar{u})_{\text{upflow}} = \int_0^{\phi^*} (1 - \epsilon_b) u \phi \, d\phi \Big/ \int_0^{\phi^*} (1 - \epsilon_b) \phi \, d\phi \tag{25}$$

Values of ϕ^* and of $(\bar{u})_{\text{upflow}}$ are shown in Figures 3 and 4, respectively.

COMPARISON WITH EXPERIMENTAL DATA

Available experimental data for the recirculation flow regime are analyzed and compared with the above developed correlations.

Slip Velocity $\bar{u}_s$

When u_o, $|u_w|$, and $\bar{\epsilon}_b$ are known from experiments, then Equation (24) can be used to predict $\bar{u}_s$. Table 1 summarizes such data for columns operated $U_L = 0$. The calculated values of $\bar{u}_s$ are plotted in Figure 5, using solid keys. The Kato-Nishiwaki correlation (1971) has been employed to calculate $\bar{\epsilon}_b$ when experimental data for the latter were not available. Experimentally determined values of the slip velocity $\bar{u}_s$, calculated as the difference between the mean velocities of bubbles and liquid (Yamagoshi, 1969; Ueyama and Miyauchi, 1977), are shown in Figure 5 using open keys. Reasonable agreement exists between calculated and observed data of $\bar{u}_s$, except for Pavlov's data when $U_G > 0.2$ m/s; the cause for this discrepancy is not clear. The influence of the superficial gas velocity U_G upon $\bar{u}_s$ generally seems to be a solid line in Figure 5. Various techniques were employed for the measurement of the liquid velocity. Pavlov (1965), Miyauchi and Shyu (1970), and Hills (1974) used the Pitot tube; Yamagoshi (1969) and Ueyama and Miyauchi (1977*a*, *b*) used the electrolytic tracer method; Yoshitome (1967) measured the drag force on a solid sphere submerged in the gas-liquid mixture.

Table 1 presents the experimentally determined volume-surface mean diameter of the bubbles d_{vs}. The free rising velocity of a bubble of size d_b is given by (van Krevelen and Hoftinger, 1950)

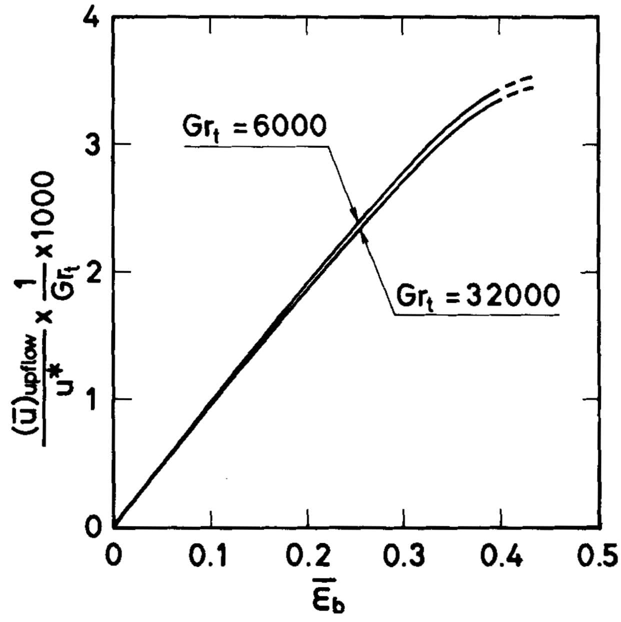

Fig. 4. $(\bar{u})$ upflow/u^* as a function of $\bar{\epsilon}_b$ and Gr_t.

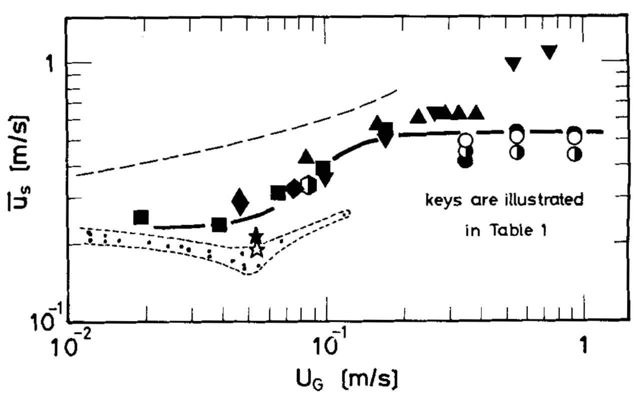

Fig. 5. Slip velocity u_s as a function of U_G.

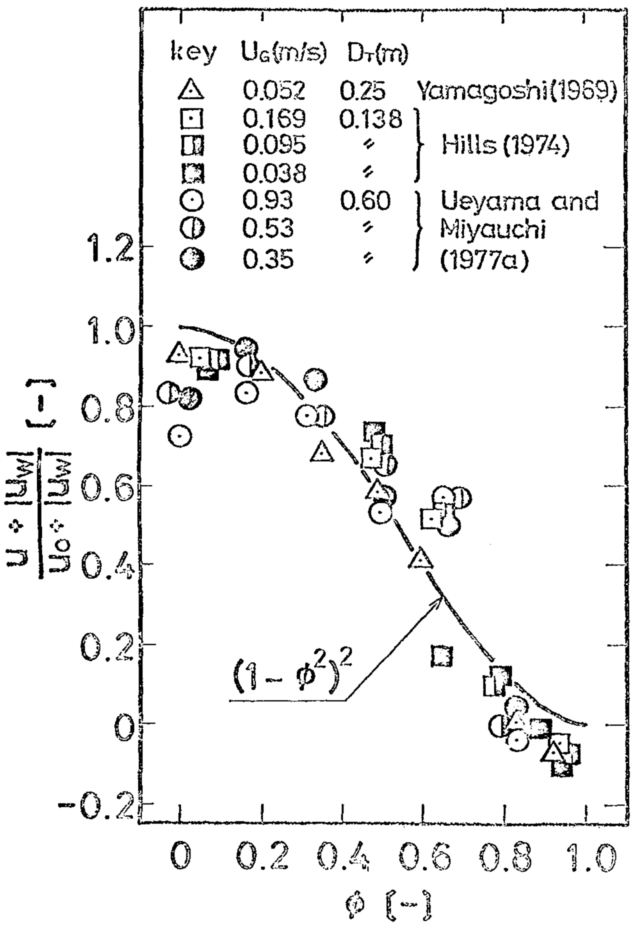

Fig. 6. Normalized distribution of liquid velocity in bubble columns.

$$u_s \doteqdot \sqrt{g\, d_b/2} \tag{26}$$

Velocities calculated using (26) with d_{vs} instead of d_b are entered in Figure 5 using half-open keys. These calculated bubble velocities are in fair agreement with the data plotted using open and closed keys which represent experimentally observed values. One is thus lead to conclude that bubbles in a highly turbulent flow field apparently have very little interaction; each bubble rises independently. Also shown in Figure 5 are the data by Nicklin (1962); these seem to indicate the onset of a recirculation type of flow at approximately $U_G = 0.05$ m/s. Nicklin uses a porous plate type of gas distributor; his bubbles sizes are smaller than those developed in columns with single nozzle type of gas distributor. Yoshitome uses a perforated plate type of gas distributor; his slip velocities are greater, for he uses Equation (19) instead of Equation (21) for the calculation of $\overline{u}_s$ in the recirculation flow regime.

Profile of the Liquid Velocity in the Column

Equation (14) can be modified to provide a simple expression for the profile of the liquid velocity. Shyu and Miyauchi (1971) suggest the correlation $|u_w| = 1.42\, U_G^{0.43} D_T^{0.28}$. Also, in the recirculation flow regime, $\overline{\epsilon}_b = 0.54\, U_G$ for D_T between 0.1 and 0.6 m and for U_G between 0.06 and 0.9 m/s (Ueyama and Miyauchi, 1973). Using these two correlations with Equations (8) and (16), one can express the ratio of the magnitude of the two terms in Equation (14); for $n = 2$, one obtains

$$\left(\frac{-\tau_w}{R\rho_l}\right) \Big/ (\overline{\epsilon}_b g) \approx 0.06 \left(\frac{U_G}{D_T}\right)^{0.4}$$

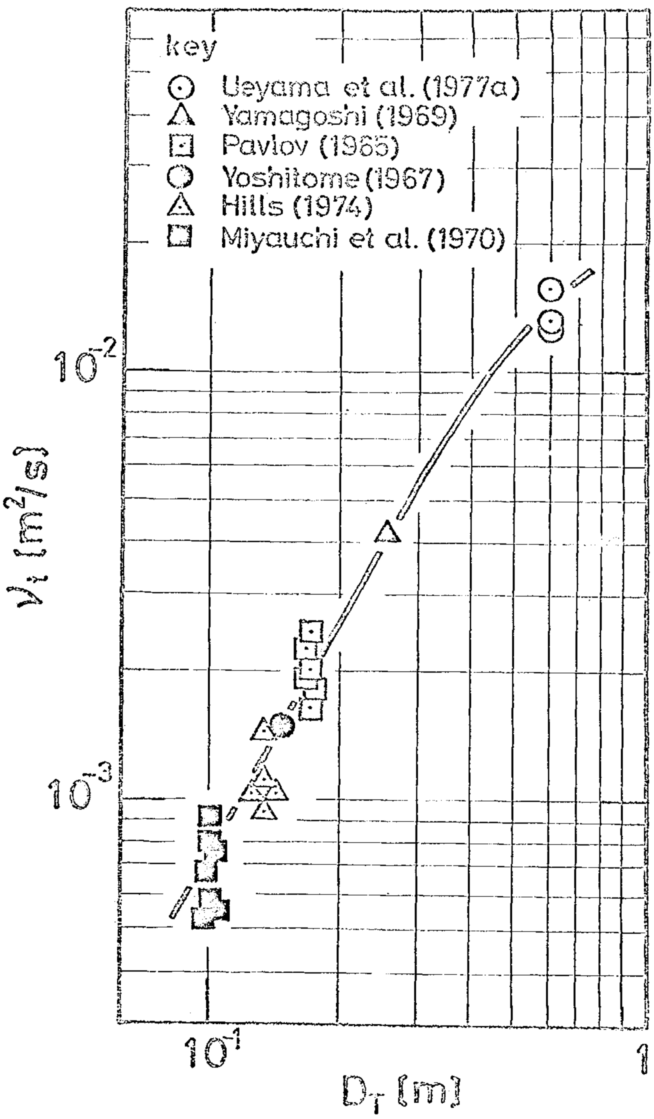

Fig. 7. Turbulent kinematic viscosity ν_t for varying D_T.

Within the usual ranges of bubble column operation, this ratio is much smaller than 1; hence, $|\tau_w/R\rho_l|$ in Equation (14) is much smaller than $\overline{\epsilon}_b g/n$. Thus, one simplifies and obtains

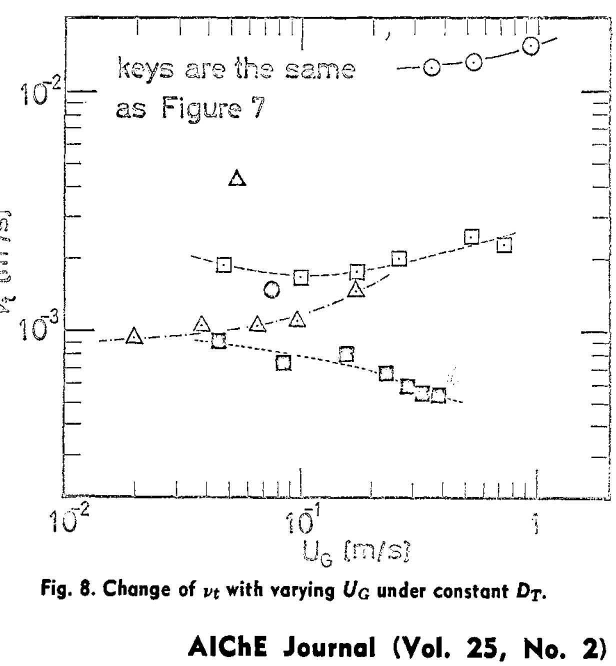

Fig. 8. Change of ν_t with varying U_G under constant D_T.

$$(u + |u_w|)/(u_o + |u_w|) = (1 - \phi^2)^2 \qquad (27)$$

with

$$u_o + |u_w| = \frac{1}{32} \frac{D_T^2 g \bar{\epsilon}_b}{\nu_t} \qquad (28)$$

In order to compare the experimental measurements of the profiles of liquid velocity with those predicted by (27), the following procedures were employed:

1. u_o and $|u_w|$ are determined from experimental velocity profile data. Then ν_t is calculated using (28).

2. The value of ν_t obtained in the first step is used together with Equations (22) and (23) to check u_o and $|u_w|$.

3. With these values of u_o and $|u_w|$, calculate the left-hand side of Equation (27).

The results are plotted in Figure 6; clearly, the equation is well suited to describe the profile of the liquid velocity.

Turbulent Viscosity ν_t

Figure 7 shows a plot of the values of ν_t obtained through the use of experimental data with Equation (28), using D_T as the abscissa. For columns of smaller diameter, ν_t is proportional to $D_T^{1.8}$; this relationship agrees with that reported earlier by Miyauchi and Shyu (1970). However, for larger values of D_T, ν_t appears to increase less strongly with increasing D_T.

Figure 8 shows the influence of the superficial gas velocity U_G upon ν_t. The available data do not yet indicate a clear trend; instead, the dependence of ν_t upon U_G seems to be rather weak. Until more data become available, ν_t may be considered practically invariant with U_G.

Besides a knowledge of ν_t, the knowledge of the mean gas holdup $\bar{\epsilon}_b$ is important for predictions of the flow properties of the bubble column.

Mean Gas Holdup $\bar{\epsilon}_b$

This quantity can be calculated as the solution of a quadratic equation using Equations (24) and (28):

$$\bar{\epsilon}_b = \frac{1}{2}\left(\frac{1+\alpha}{1-\beta}\right)\left[1 - \sqrt{1 - 4\left(\frac{\alpha}{1+\alpha}\right)\left(\frac{1-\beta}{1+\alpha}\right)}\right] \qquad (29)$$

with $\alpha = U_G/\bar{u}_s$, $\beta = D_T^2 g/192\nu_t\bar{u}_s$, and $U_L = 0$. For $U_G \gtrsim 0.2$ m/s, $\bar{u}_s$ is nearly invariant with U_G, as shown in Figure 5; thus, α and β are nearly proportional to U_G and to D_T^2/ν_t, respectively. However, β increases only slightly with D_T, since ν_t increases quite rapidly with D_T (see Figure 7). Therefore, $\bar{\epsilon}_b$ by Equation (29) is nearly proportional to $U_G^{0.5}$ and tends to decrease but slightly with increasing D_T.

The indicated dependence of $\bar{\epsilon}_b$ upon U_G and D_T is generally in good agreement with published data (Miyauchi and Shyu, 1970; Kato and Nishiwaki, 1971; Ueyama and Miyauchi, 1977*a*). It seems to explain the cause why the $\bar{\epsilon}_b$ vs. U_G plot is hardly influenced by scaling-up of the column.

NOTATION

d_b = sphere equivalent bubble diameter, m
d_{vs} = volume surface mean diameter of bubbles, m
D_T = diameter of a column, m
g = acceleration of gravity, ms^{-2}
Gr_t = $D_T^3 g/\nu_t$, nondimensional number
$I(\phi)$ = Equation (18)
J_0, J_1 = Equation (18)
L = height of gas-liquid mixed phases, m
n = exponent in Equation (13)
$\bar{P}$ = static pressure, Pa
r = radial coordinate, m
r^* = r, where $u = 0$, m
R = radius of a column, m
u = time averaged interstitial velocity of liquid, ms^{-1}
u_s = slip velocity of a bubble relative to liquid, ms^{-1}
$\bar{u}_s$ = mean slip velocity of bubbles, ms^{-1}
$|u_w|$ = absolute value of u at the wall of a column, ms^{-1}
u_o = u at the center of a column, ms^{-1}
u^* = ν_t/D_T, parameter, ms^{-1}
u_δ = u at $y = \delta$, ms^{-1}
$(\bar{u})_{upflow}$ = mean upflowing linear velocity of liquid defined by Equation (25), ms^{-1}
u_r', u_z' = fluctuating components of liquid velocity in r and z direction, respectively, ms^{-1}
$\bar{U}_G$ = superficial gas velocity, ms^{-1}
$\bar{U}_L$ = superficial liquid velocity, ms^{-1}
v_* = friction velocity, ms^{-1}
y = distance from the wall, m
z = axial coordinate, m

Greek Letters

α, β = nondimensional parameter in Equation (29)
δ = thickness of the laminar sublayer, m
ϵ_b = gas holdup
$\bar{\epsilon}_b$ = mean gas holdup defined by Equation (11)
ν_M = molecular kinematic viscosity, m^2s^{-1}
ν_t = turbulent kinematic viscosity, m^2s^{-1}
ρ_l = density of liquid, kg m^{-3}
τ = shear stress, kg m^{-1} s^{-2}
τ_w = shear stress at the wall, kg m^{-1} s^{-2}
ϕ = r/R, nondimensional radial coordinate
ϕ^* = ϕ, where $u = 0$

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Kinetics of Step Polymerization with Unequal Reactivities

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The kinetics of step polymerization involving a monomer with unequal reactivities has been obtained. The polydisperity index (PDI) has also been calculated both as a function of conversion and the initial stoichiometric ratio. It has been shown that the usually assumed maximum value of 2 for PDI can lead to erroneous molecular weight.

SCOPE

Step polymers such as polyesters, polyurethanes, etc., can be considered as products of reaction between two difunctional monomers. While it is usually assumed that the two groups of the monomer are equally reactive, many exceptions exist. Thus, a glycol containing a primary and a secondary hydroxyl group is an asymmetric monomer since the two groups may be expected to react at different rates. Similarly, the two functionalities of a cyclic monomer, such as an anhydride, can be expected to react at different rates. Moreover, possibly owing to resonance and conformational effects, reaction of one of the groups of the monomer may induce asymmetry and alter the reactivity of the other group. Such induced asymmetry is found in diisocyanates. In this paper, the effect of the unequal reactivities on the kinetics of polymerization and the evolution of the polymeric product as characterized by the polydisperity index (PDI) will be studied.

CONCLUSIONS AND SIGNIFICANCE

It is shown that the results for monomers with induced asymmetry can be obtained from the results for cyclic monomers necessitating discussion of only one of them. If K, the ratio of the reaction rate constants of the two groups, is increased beyond unity, the rate of consumption of the groups, as may be expected, is found to increase. This is true for both asymmetry and induced asymmetry.

In the asymmetric case, both the number average molecular weight ($\overline{M}_n$) and the PDI increased with conversion or time. The PDI at the end of the reaction is independent of K for $R < 1$. However, the PDI at the end of the reaction goes through a minimum followed by a broad maximum as R is increased beyond 1. This is shown to be due to the presence of unreacted monomer. A modified PDI defined by excluding the contribution of the monomers does not exhibit these extrema and decreases monotonically as R is changed from 1.