Gas Holdup in Bubble Column with Surface-Active Agents: A Theoretical Model

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Surface-active agents such as small concentrations of alcohols in water significantly affect gas holdup and mass transfer in bubble column reactors (Kelkar et al., 1983; Shah et al., 1983; Oels et al., 1978). The surfactants tend to accumulate at the bubble surface and create surface tension gradients that cause tangential stresses along the bubble surface. These stresses retard surface motion, internal circulation within the bubble, and the rise velocity of the bubbles. The magnitude of these effects depends on the flow regime. Theoretical analysis of the effect of surfactants on bubble rise velocity has been presented by Levich (1962) for high Reynolds number ($Re > 1{,}000$) and by Waslo and Gal-Or (1971) for creeping flow ($Re < 1$). Both these analytical treatments are not applicable at intermediate Reynolds numbers ($1 < Re < 1{,}000$), which are encountered in the homogeneous flow regime of bubble column reactors.

For the intermediate Reynolds number range, Levich (1962) analyzed the velocity distribution around an uncontaminated bubble by proposing that the fluid surrounding the bubble exhibits potential flow and that a thin boundary layer exists near the surface of the bubble. While his formulation was in error and his solution was incorrect, as shown by Chao (1962) and Moore (1963), his concept has been well accepted. However, the application of this theory has been restricted to the lower extreme of the intermediate Reynolds number range ($1 < Re < 1{,}000$) for single bubbles, primarily because at higher Reynold numbers boundary layer separation occurs. In dispersed systems, boundary layer separation is suppressed considerably due to the interaction of neighboring bubbles, as pointed out by Waslo and Gal-or (1971). In view of this, and the fact that there exists no theory at present for finite perturbations at higher Reynolds numbers (Harper, 1972), this paper presents analytical expressions for bubble rise velocity and gas holdup using Chao's (1962) approach in conjunction with Lochiel's (1965) modifications. The retardation effect of surfactants is characterized by the retardation parameter (γ). Marrucci's (1965) expression derived on the basis of the spherical cell model is used to relate the single-bubble rise velocity to the bubble swarm velocity.

The retardation parameter for different alcohol solutions is evaluated from experimental measurements of single-bubble rise velocities. The values of γ for different alcohol solutions are compared with those calculated from previously reported experimental results for gas holdup in downflow as well as upflow bubble columns, and the range of applicability of the model is discussed.

Mathematical Model

Terminal rise velocity

The theoretical analysis follows that of Chao (1962). The terminal rise velocity of a single bubble is determined by a force balance on the bubble. For a stationary bubble, the drag force is balanced by the bouyancy force. The drag force on the bubble is evaluated from the knowledge of the velocity distribution around the bubble. The velocity distribution in the boundary layer in the presence of a surface-active agent is obtained by solving the Navier-Stokes equation in the boundary layer.

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The simplified form of the Navier-Stokes equation in dimensionless variables (Chao, 1962), assuming the bubble surface to be planar within the boundary layer, is given by

$$u \cos\theta + \sin\theta \frac{\partial u}{\partial \theta} - 2y \cos\theta \frac{\partial u}{\partial y} = \frac{4}{3} \frac{1}{Re} \frac{\partial^2 u}{\partial y^2} \tag{1}$$

with the boundary conditions:

$$u \rightarrow 0; \quad \text{as } \theta \rightarrow 0 \tag{2}$$

$$u \rightarrow 0; \quad \text{as } y \rightarrow \infty \tag{3}$$

$$\frac{\partial u}{\partial y} = \frac{3}{2} \sin\theta \left(2 + \frac{3\gamma}{\mu_L}\right); \quad \text{as } y \rightarrow 0 \tag{4}$$

The boundary condition given by Eq. 4 is determined by a force balance at the bubble interface, using an approach similar to that of Lochiel (1965). Gal-or and Waslo (1968) and Levich (1962) define the retardation coefficient in Eq. 4 as

$$\gamma = \frac{1}{3} K \frac{d\sigma}{d\Gamma} \tag{5}$$

The boundary condition in Eq. 4 is identical to Moore's (1963) boundary condition for spheres moving in pure liquids, if one neglects the term containing γ. It differs from Lochiel's (1965) and Lochiel and Calderbank's (1964) boundary condition in that the influence of the dispersed phase is neglected in the present analysis. Also, the parameter γ in the present analysis is a generalized retardation coefficient as compared to the surface tension parameter p employed by Lochiel (1965). For surfactants that diffuse slowly, the retardation coefficient γ reduces to (Levich, 1962)

$$\gamma = \frac{1}{3} \frac{R\Gamma_0 R_1 T}{D_i} \tag{6}$$

and the term 3γ in Eq. 4 becomes identical to the surface tension parameter p used by Lochiel.

Equation 1 was solved analytically as suggested by Chao (1962) to give the perturbation velocity in the (θ, y) plane as

$$u = -2\sqrt{\frac{3}{Re}} \left(\frac{2 + 3\gamma/\mu_L}{\sin\theta}\right) \cdot \left(\frac{2}{3} - \cos\theta + \frac{1}{3}\cos^3\theta\right)^{1/2} i \operatorname{erfc}(\eta) \tag{7}$$

where

$$\eta = \left(\frac{3}{4} Re\right)^{1/2} \frac{\sin^2\theta}{\left(\frac{2}{3} - \cos\theta + \frac{1}{3}\cos^3\theta\right)^{1/2}} y \tag{8}$$

and to yield the drag force

$$F_D = 4\pi U_\infty R \mu_L \left[1 + (2 + 3\gamma/\mu_L)\left(1 - \frac{0.628}{Re^{1/2}}\right)\right] \tag{9}$$

Eq. 9 reduces to

$$F_D = 12\pi U_\infty R \mu_L \tag{10}$$

for the case when surfactants are absent and potential flow conditions exist, and is in agreement with Moore's (1963) and Levich's (1962) expression for drag force.

The terminal velocity obtained by equating the drag force and the force due to buoyancy is given by:

$$U_\infty = \frac{R^2 g \Delta\rho / 3\mu_L}{\left[1 + \left(2 + \frac{3\gamma}{\mu_L}\right)\left(1 - \frac{0.628}{Re^{1/2}}\right)\right]} \tag{11}$$

In the absence of surfactants, and if the flow regime is potential flow, Eq. 11 reduces to

$$U_b = \tfrac{1}{9} R^2 g \Delta\rho / \mu_L \tag{12}$$

This expression is identical to that obtained by Levich (1962) for uncontaminated bubbles. Hence, Eq. 11 can be rewritten as

$$U_b^s = \frac{3U_b}{\left[1 + (2 + 3\gamma/\mu_L)\left(1 - \frac{0.628}{Re^{1/2}}\right)\right]} \tag{13}$$

It is apparent from this equation that the magnitude of the decrease in the rise velocity of single bubbles in the presence of a surfactant is dependent on the value of the retardation parameter γ. Also, as pointed by Lochiel (1965), relatively small effect of surfactants on the rise velocity in the presence of viscous liquids is evident from Eq. 13.

Gas holdup

Marrucci (1965) developed a theoretical equation for the rise velocity of a swarm of bubbles based on the spherical cell model for dispersed systems. In the bubble flow regime, the slip velocity can be equated to the bubble swarm velocity, and the following expression can be obtained for the swarm velocity,

$$U_{\text{swarm}} = \frac{3U_b}{\left[1 + (2 + 3\gamma/\mu_L)\left(1 - \frac{0.628}{Re^{1/2}}\right)\right]} \frac{(1 - \epsilon_g)}{(1 - \epsilon_g^{5/3})} \tag{14}$$

Equation 14 allows one to predict the gas holdup in a homogeneous bubble column with surface-active agents. The calculation requires a knowledge of the liquid properties such as

Table 1. Physical Properties of Systems Investigated

System	Conc. vol. %	Density kg/m^3	Surface Tension N/m	Viscosity Pa · s *10^3
Distilled water	—	1,000.0	0.073	0.80
Methanol	0.5%	997.0	0.067	0.83
Ethanol	0.5%	997.3	0.066	0.83
n-Propanol	0.5%	994.8	0.066	0.85
n-Butanol	0.5%	993.5	0.063	0.84

Table 2. Single-Bubble Measurements in Plexiglas Column

System	U_b^s m/s	U_{rel}	γ Pa · s *10^5
Distilled water	0.235	1.0	0.0
Methanol	0.226	0.963	3.074
Ethanol	0.218	0.928	6.207
n-Propanol	0.210	0.895	9.385
n-Butanol	0.204	0.869	12.060

density, viscosity, bubble size, and the value of retardation parameter γ.

The retardation parameter γ can be estimated from the knowledge of the transport properties through similar relationships, such as Eq. 5 and 6, which depend upon the nature of the surfactant and their behavior at the interface. Unfortunately, in many practical cases the absence of such information would limit the use of Eq. 14 for prediction purposes. However, this difficulty can be overcome quite simply for gas-liquid systems through experimental evaluation of the parameter γ. The experimental tests involve only the measurement of the rise velocity of single bubbles.

Experimental Method

The bubble rise velocity of single bubbles was measured in a rectangular Plexiglas column of 0.006 m^2 cross-sectional area and 0.9 m height. Single bubbles were introduced from the bottom of the column through a 3 mm dia. orifice. The bubble rise velocity was determined by measuring the time required by the bubble to travel a distance of 0.85 m. Twenty such measurements were performed for each system investigated. The experiments used air as the gas phase, and the liquid phase consisted of distilled water and aqueous solutions of 0.5 vol. % methanol, ethanol, *n*-propanol, and *n*-butanol. The physical properties of the systems investigated are reported in Table 1.

Results and Discussion

Table 2 illustrates the values of bubble rise velocities of single bubbles, U_{rel} (ratio of bubble rise velocity in the presence of surfactant to bubble rise velocity in pure liquid), and the retardation parameter γ evaluated from Eq. 13. For distilled water, the value of 0.235 m/s for U_b agrees well with the value 0.235 m/s reported by Freedman and Davidson (1969). For aqueous solutions of various alcohols, a definite trend was observed, namely the bubble rise velocity decreased with an increase in the chain length of the alcohol in spite of the fact that the surface tension and other physical properties of all alcohol solutions were very similar. There is strong literature evidence suggesting the possible dependency of the bubble rise on velocity alcohol chain length; Levich (1962), Keitel and Onken (1982a, b), and Keitel and Onken (1982a) have developed an empirical correlation relating the bubble properties to the number of carbon atoms in the molecule of an alcohol.

Table 4. Comparison of Calculated and Reported* Holdup Values in the Presence of Alcohols

Solution	V_g m/s	V_L m/s	ϵ_g Obs.	Pred.
1.0% CH_3OH	0.01	0.022	0.04	0.040
	0.02	0.022	0.08	0.082
	0.03	0.022	0.13	0.128
	0.04	0.022	0.18	0.170
	0.06	0.022	0.32	0.262
1.0% C_2H_5OH	0.01	0.022	0.04	0.042
	0.02	0.022	0.08	0.084
	0.03	0.022	0.135	0.132
	0.04	0.022	0.19	0.175
	0.06	0.022	0.33	0.270

*Oels et al. (1978)

As a result of reduction in bubble rise velocity, the gas holdup in bubble column reactors should increase under upflow conditions and decrease under downflow conditions. Kelkar et al. (1983) reported the gas holdup in various alcohol solutions in an upflow system. The gas holdup was found to increase as follows: methanol < ethanol < *n*-propanol < *n*-butanol. An opposite trend was observed by Shah et al. (1983) in a downflow system. It should be noted that both these authors found no effect of alcohol concentration on the gas holdup, and that the homogeneous bubble flow regime prevailed for *n*-butanol, *n*-propanol, and ethanol solutions. For air-water and methanol solutions, two distinct classes of bubbles (small and large) were observed. Using the experimental data reported by these authors, the average values of U_b^s were calculated; the values are given in Table 3. While the magnitude of these values does not agree with that of values obtained from single-bubble rise velocity measurements, the trend in U_b^s is very similar to that observed for different alcohol solutions in experiments with single bubbles. Since the bubble rise velocities for upflow and downflow bubble columns are extrapolated values, the discrepancy in the magnitude of U_b^s can be expected. This discrepancy may also be due to the impossibility of keeping bubble size constant with increasing gas throughput in dispersed systems, as required for the use of the Marrucci (1965) expression. However, more important is the fact that the

Table 3. Single-Bubble Rise Velocity U_{rel} from Data in Downflow and Upflow Bubble Columns

	Downflow (Shah et al., 1983)			Upflow (Kelkar et al., 1983)		
System	U_b^s m/s	U_{rel}	γ Pa · s *10^5	U_b^s m/s	U_{rel}	γ Pa · s *10^5
Water	0.298	1.0	0.0	—	1.0	0.0
Methanol*	0.290	0.971	2.389	—	—	—
Ethanol*	0.278	0.934	5.653	0.270	0.905	8.40
n-Propanol*	0.265	0.888	10.090	0.264	0.884	10.50
n-Butanol*	0.246	0.826	16.850	0.236	0.800	20.00

*0.5 vol. % in water

values of U_{rel} in Table 3 for various alcohol solutions agreed within approximately 8% and the trend was again similar to that observed for the single-bubble measurements. In the upflow system, Marrucci's expression could not be utilized for air-water and aqueous methanol solutions since the dispersion in these cases was not homogeneous. In view of this fact, U_b for water in this case was assumed to be the same as that for the downflow system.

The calculated values of the retardation coefficient γ are also reported in Table 3. The trends for γ for various alcohol solutions for both downflow and upflow bubble columns are the same as that observed for the single-bubble experiments. Moreover, the agreement in the values of γ is reasonably good.

Using the retardation parameter values reported in Table 2, the experimental data of Oels et al. (1978) were analyzed. The analysis was restricted to the gas holdup values for 1.0% methanol and 1.0% ethanol solutions for a perforated-plate gas distributor. U_∞ for distilled water was reported to be 0.25 m/s. As is evident from Table 4, the predicted gas holdup values match reasonably well at lower gas velocities, whereas at high gas velocities Eq. 14 underpredicts the gas holdup. One would expect that at high gas velocities predicted gas holdup values from Eq. 14 would be higher than experimental values due to the assumption of the homogeneous bubbly flow regime, and also because Marrucci's expression does not consider growth in the bubble size as the gas velocity increases. Moreover, at higher gas velocities, that is, at high bubble Reynolds number ($Re > 1{,}000$), the surfactants are swept away from the surface, boundary layer separation results, and the effect of surfactants on the terminal bubble rise velocity becomes negligible (Levich, 1962). A possible explanation for the discrepancy observed is that the reported experimental data may well have included the foaming effects that tend to be prevalent at higher gas velocities in solutions containing surfactants.

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Notation

C = concentration of surfactant
D_b^s = diffusivity of surfactants in bulk solution, m^2/s
D_i^s = diffusivity of surfactants at interface, m^2/s
F_D = drag force, Eq. 9, N
$K = 2\Gamma_0 R/[2D_i^s + \alpha^* D_b^s R^2/D_b^s + \alpha^*\delta(\partial\Gamma/\partial C)_{eq}]$
R = radius of bubble, m
R_1 = gas constant
Re = Reynolds number for a single bubble, $2RU_\infty \rho_L/\mu_L$
T = temperature, °C
u = dimensionless velocity vector in y direction
U = bubble rise velocity, m/s
U_∞ = bubble rise velocity in medium, m/s
$U_{swarm} = V_g/\epsilon_g \pm V_L/(1 - \epsilon_g)$
V_g = superficial gas velocity, m/s
V_L = superficial liquid velocity, m/s
x = dimensionless coordinate, X/R
y = dimensionless coordinate, Y/R

Greek letters

α^* = overall adsorption rate constant
δ = thickness of boundary layer of diffusion
γ = retardation parameter due to presence of surfactant
Γ' = perturbation in surface concentration of surfactant
$\Gamma = \Gamma_0 + \Gamma'$
Γ_0 = equilibrium surface concentration of surfactant
σ = surface tension, N/m
θ = cone angle between vector radius and vertical at equator
ϵ_g = gas holdup
$(d\Gamma/dC)_{eq}$ = constant of proportionality for small deviations from equilibrium
μ = viscosity, Pa·s
ρ = density, kg/m^3

Superscript

s = surfactant system investigated

Subscript

b = bubble
g = gas
L = liquid
d = dispersed
r = radial component

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