Gas/Liquid Mass Transfer in a Bubble Column with Suspended Nonwettable Solids

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Viscous pseudoplastic solutions of polymers, for example, carboxymethyl cellulose (CMC), are frequently used to simulate the rheological behavior of fermentation broths. The pertinent studies in bubble column reactors have recently been reviewed by Schumpe and Deckwer (1987). When correlating the hydrodynamic and mass transfer parameters, the concept of effective viscosity has commonly been employed. The viscosity as measured in a viscometer and characterized in the form of the Ostwald-de Waele relation

$$\mu = k \cdot \dot{\gamma}^{n-1} \tag{1}$$

is used as a correlating parameter based on an estimate of the effective shear rate in the bubble column. Usually the effective shear rate is assumed to be proportional to the superficial gas velocity:

$$\dot{\gamma}_{\text{eff}} = C u_G \tag{2}$$

The coefficients C suggested in the literature range from 1,500 to 5,000 m^{-1}. When empirically correlating the volumetric mass transfer coefficients $k_L a$ with the effective viscosity, exponents in the range of -0.70 to -1.01 have been found. Based on their comprehensive data set with a particularly wide variation of the flow behavior index ($1 \leq n \leq 0.18$), Schumpe and Deckwer (1987) suggested the optimum coefficient

$$C = 2{,}800 \text{ m}^{-1} \tag{3}$$

and the viscosity exponent of -0.70.

The results of studies in suspensions with a viscous pseudoplastic flow behavior are listed in Table 1 (Eqs. 4–7 are located in this table). In the bubble column slurry reactor, consistently smaller influence of the effective viscosity than in polymer solutions is observed; that is, at the same viscosity measured in a viscometer, polymer solutions and solid suspensions exhibit different mass transfer characteristics. This problem has been addressed in the paper of Godbole et al. (1983), who investigated the specific interfacial areas in suspensions of polystyrene particles (300 μm) by the sulfite oxidation method. They observed only a small effect of the relative viscosity due to the addition of polystyrene particles. It is not clear if this result has to be attributed to the poor wettability of polystyrene or if it refers to the different effect of suspension viscosity as compared to solution viscosity.

It is the purpose of this paper to investigate the effects of suspension viscosity and solid wettability on gas/liquid mass transfer in a bubble column slurry reactor. To this end, the volumetric mass transfer coefficients for oxygen are studied in suspensions of wettable (glass) and poorly wettable (polypropylene) particles in CMC solutions of equal concentrations. At the high viscosities encountered, the bubble column operates in the slug flow regime. For comparison, the effect of polypropylene particles was also investigated in the absence of dissolved polymer at heterogeneous flow conditions. Aqueous suspensions of the glass spheres have been studied previously (Nguyen-tien et al., 1985; Nigam and Schumpe, 1987).

Experimental Method

The measurements were carried out in a Perspex column of 0.14 m ID at a height of the gas-free suspensions of 1.4 m. A ring distributor (29 holes of 1 mm dia.) served as the gas sparger. The superficial gas velocity was controlled with a mass flow meter and ranged from 0.02 to 0.2 m/s. The suspension was operated batchwise; its temperature was 15 ± 1°C.

The gas holdups were determined from the change in dispersion height due to the gas flow. The volumetric mass transfer coefficients were investigated by the dynamic method; that is, the increase of oxygen fugacity by aeration of initially oxygen-

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Table 1. Studies on the Influence of Effective Viscosity on Oxygen Transfer in Bubble Columns with Suspended Solids

Systems	Correlation	Eq.	C m^{-1}	Reference
$Ca(OH)_2 + CaCO_3$	$a \propto \epsilon_G^{1.13}\ \bar{\mu}_{eff}^{-0.042}$	4	4,000	Capuder & Koloini (1984)
Al_2O_3, kieselguhr in sulfite solution	$a = 583\ u_G^{0.81}\ \bar{\mu}_{eff}^{-0.22}$ $a = 651\ u_G^{0.87}\ \bar{\mu}_{eff}^{-0.24}$	5a 5b*	5,000 2,800	Quicker et al. (1984) Schumpe et al. (1987)*
Al_2O_3, kieselguhr, activated carbon in water and sulfate solution	$k_La \propto u_G^{0.82}\ \bar{\mu}_{eff}^{-0.39}$	6	2,800	Schumpe et al. (1987)
Al_2O_3, polyethylene, PVC in ligroin	$k_La \propto u_G^{0.75}\ \bar{\mu}_{eff}^{-0.42}$	7	2,800	Öztürk & Schumpe (1987)

*Recalculated for $C = 2{,}800\ m^{-1}$ by Schumpe et al. (1987)

free liquid was measured with a fast response oxygen electrode. Experimental details have been discussed previously (Schumpe 1985; Nigam and Schumpe 1987).

Glass spheres ($\rho_s = 2{,}770\ kg/m^3$) with a uniform diameter of 50μm and polypropylene particles ($\rho_s = 940\ kg/m^3$) with a volume-mean diameter of 164 μm (standard deviation: $\pm 47\ \mu$m) were studied as the solid. The rheological behavior of the suspensions in CMC solution was investigated with a concentric cylinder viscometer (Contraves 115 with MS 145). The parameters of the Ostwald-de Waele relation, Eq. 1, are listed in Table 2. The viscosity of the CMC-free polypropylene suspensions could not be measured because of floating of the particles in the rheometer. Freshly introduced polypropylene particles tended to stick together. Only after several hours of aeration were the particles well distributed. Then a steady state was reached where k_La was about 30% higher than the initially determined value. All results reported for polypropylene particles were obtained after overnight aeration of the suspension.

The gas/liquid contact angle θ can be used as a measure of the specific solid/liquid surface energy $\sigma_{S/L}$:

$$\cos\theta = \frac{\sigma_S - \sigma_{S/L}}{\sigma_L} \tag{8}$$

Similar contact angles of about 120° (±10°) were measured for drops of water and CMC solution on a layer of polypropylene particles.

Results and Discussion

The addition of either polypropylene (PP) or glass particles reduced the gas holdup in the CMC solution only very slightly. This behavior is quite expected in the slug flow regime because of the wall effect on the rise velocity of the gas slugs (Taylor bubbles). The gas holdup is therefore a poor indicator of the mass transfer characteristics in viscous media (Schumpe and Deckwer, 1987).

Table 2. Rheological Properties of Polypropylene and Glass Suspensions in CMC Solution at 15°C

	Polypropylene, 164 μm		Glass, 50 μm	
Φ_S	n	k Pa · s^n	n	k Pa · s^n
0	0.882	0.111	0.882	0.111
0.02	0.876	0.126	0.884	0.113
0.05	0.859	0.173	0.876	0.129
0.10	0.833	0.280	0.874	0.137
0.20	0.741	1.304	0.832	0.246
0.30	—	—	0.796	0.437

Figure 1 illustrates the effects of the polypropylene volume fraction and the superficial gas velocity on the volumetric mass transfer coefficients in the CMC solution. With increasing polyethylene loading the k_La values drop strongly. The relative effect is about same at various gas velocities. Since this applies also to the other systems studied, the results can be compared in a plot of the relative change of k_La [as compared to $(k_La)_0$ measured in the solid-free liquid] against the solid volume fraction. Such a graph is provided in Figure 2; the bars indicate the maximum variation due to the gas velocity. The relative effect of the polypropylene particles is about same in water (possibly containing traces of CMC) and the CMC solution, in spite of the different flow regimes and differences in $(k_La)_0$ by factors of 4.5 to 6.5.

The effect of the glass spheres, on the other hand, is only moderate. The relative decrease of k_La is similar to that reported by Nguyen-tien et al. (1985) for three-phase fluidized beds of glass spheres (50–1,000 μm) in water:

$$\frac{k_La}{(k_La)_0} = 1 - \frac{\Phi_S}{0.58} \tag{9}$$

At high solid loading, k_La tends to be underestimated. A similar trend has been reported by Nigam and Schumpe (1987).

In the analysis of the very different effects of glass spheres and polypropylene particles on k_La, the flow behavior of the suspensions has to be considered. Table 2 shows that polypropylene particles induce higher effective viscosities than glass spheres at the same solid volume fraction. However, the plot of k_La against the effective viscosity calaculated by Eq. 2 with $C = 2{,}800\ m^{-1}$, Figure 3, reveals that the different flow behavior explains the different mass transfer characteristics only to a minor extent. In the log-log plot the slope is -0.49 in the case of glass spheres; that is, the viscosity effect is similar to that observed in previous studies in slurry bubble columns, Table 1. In the case of polypropylene particles, the slope of -1.16 may not be explained by the influence of effective suspension viscosity alone.

When studying the mass transfer coefficients in suspensions of polymer particles in a hydrocarbon liquid, Öztürk and Schumpe (1987) observed no effect of particle diameter (22–370 μm) and only a moderate viscosity effect, Eq. 7. Therefore, the different behavior of glass and polypropylene suspensions is related to the poor wettability of polypropylene by water.

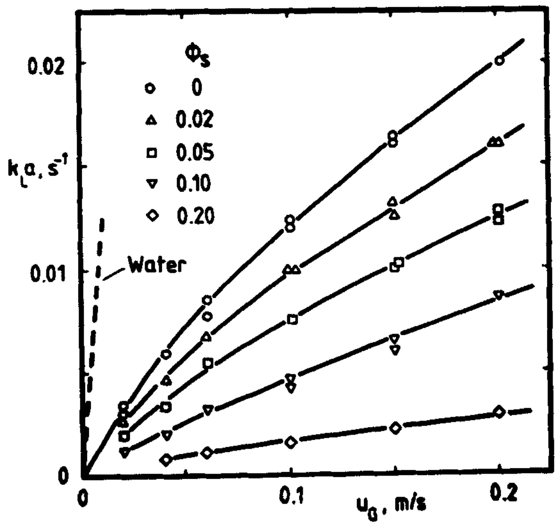

Figure 1. Volumetric mass transfer coefficients in suspensions of polypropylene particles in a CMC solution.

According to the large contact angle, the particles may accumulate at the gas/liquid interface and reduce the area available for mass transfer. This conclusion is supported by the flotation effect observed in polypropylene suspensions; that is, different solid fractions were detected by gravimetric analysis of the samples withdrawn from the bottom and the top of the dispersion. Table 3 shows some results at low polypropylene loading where the effect is most pronounced.

To assess the wettability effect, the results have to be corrected for the influence of effective suspension viscosity as observed in the suspensions of glass spheres in CMC solution. In this system, the k_La values can be empirically correlated by the following equation:

$$k_La = 0.0146\, u_G^{0.71}\, \mu_{\text{eff}}^{-0.49} \tag{10}$$

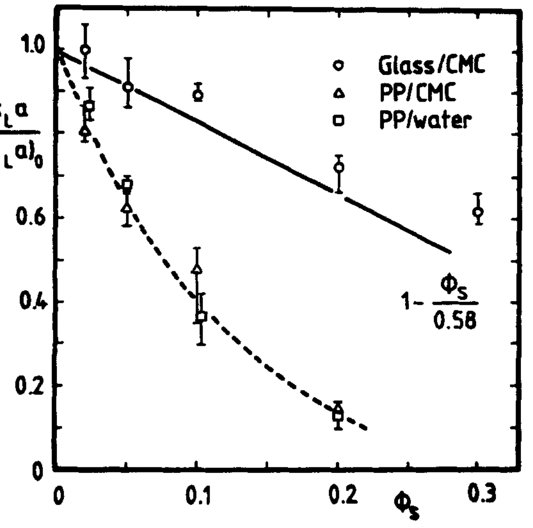

Figure 2. Effects of solid volume fraction on relative decrease of volumetric mass transfer coefficient.

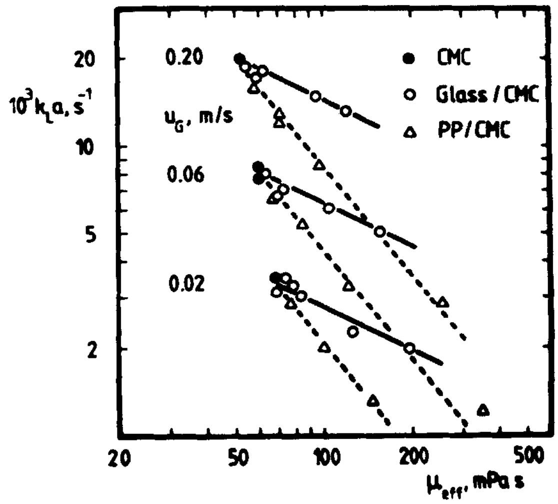

Figure 3. Correlation of k_La with effective slurry viscosity.

Equation 10, obtained by nonlinear regression analysis, describes 39 data points with 3.0% mean error. The ratio of k_La in the PP/CMC system to the predictions of Eq. 10 is interpreted as a measure of the fractional free gas/liquid surface area. Then, the fractional surface coverage is found to conform to the Langmuir adsorption isotherm with the mean solid volume fraction as the concentration measure, Figure 4:

$$k_La/(0.0146\, u_G^{0.71}\, \mu_{\text{eff}}^{-0.49}) = 1 - \frac{9.0\Phi_S}{1 + 9.0\Phi_S} \tag{11}$$

Equation 11 describes 30 k_La values in the PP/CMC system with a mean error of 5.4%. The average solid depletion in the bulk phase can be neglected even at the lowest concentration studied, but the fit might be improved further by considering the axial concentration profile caused by the flotation effect.

It has to be admitted that the interpretation of the wettability effect by a reduction of the area available for mass transfer is tentative, since the liquid-side mass transfer coefficient might be affected as well. A densely packed particle layer at the gas/liquid interface is expected to induce surface rigidity and thus reduce k_L along with the specific interfacial area. On the other hand, it has been suggested (Andrews et al. 1984) that particles being captured at the nose of a bubble and swept to the rear induce surface mobility to small bubbles with a normally rigid surface. Actually, the latter phenomenon might be encountered at the front of a rising bubble, whereas the rear is covered by a dense particle layer. Multilayer accumulation in the bubble wake is quite expected.

To decide on the individual effects on K_L and a, the interfacial areas would have to be measured individually. Godbole et al. (1983) studied the specific interfacial areas in suspensions of

Table 3. Axial Variation of Polypropylene Volume Fraction at a Mean Value of $\Phi_S = 0.02$ in CMC Solution

u_G m/s	Φ_S bottom	Φ_S top
0.020	0.013	0.029
0.200	0.008	0.031

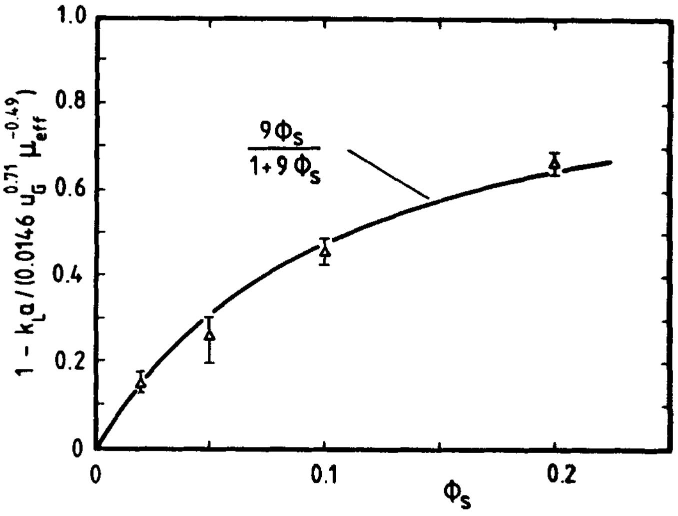

Figure 4. Description of k_La in polypropylene/CMC system in the form of the Langmuir isotherm.

polystyrene particles in sulfite solutions with and without CMC. In both cases the decrease was moderate, in contrast to the findings of this study. However, it may well be that the salt effect causes this discrepancy. Sada et al. (1986) reported that fine aluminum oxide powder significantly increases k_La in a sodium chloride solution but not in water. The effect seems to be caused by a coalescence hindering effect of the solids on small bubbles, which are formed in large numbers in the salt solution but not in water. A similar trend has been detected by Godbole et al. using the dynamic gas disengagement technique to determine the holdup fractions due to small and large bubbles. In sulfite solutions the presence of polystyrene particles increased the fraction of small bubbles, whereas in salt-free suspensions the fraction of small bubbles was reduced. Because of the salt effect, the interfacial areas reported by Godbole et al. can probably not be compared to the present results in salt-free systems.

Conclusions

From the measurements of the volumetric mass transfer coefficients in suspensions of glass spheres and polypropylene particles the following conclusions are drawn:

1. The influence of the effective viscosity on the volumetric mass transfer coefficient is smaller if the viscosity is brought about by suspended solids rather than dissolved polymers. The viscosity measured in a rheometer is therefore an insufficient characterization with respect to the microscopic phenomena affecting gas/liquid mass transfer.

2. Poor wettability of the suspended particles results in very low volumetric mass transfer coefficients in salt-free solutions. The effect can be described in the form of the Langmuir adsorption isotherm. It is suggested that mainly the available mass transfer area is reduced by particle adsorption at the gas-liquid interface.

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Notation

a = specific G/L interfacial area referred to slurry ($G/L/S$) volume, m^{-1}
C = factor in Eq. 2, m^{-1}
k = fluid consistency index, $Pa \cdot s^n$
k_L = liquid-side mass transfer coefficient, $m \cdot s^{-1}$
k_La = volumetric mass transfer coefficient referred to slurry ($G/L/S$) volume, s^{-1}
n = flow behavior index
u_G = superficial gas velocity, $m \cdot s^{-1}$

Greek letters

$\dot{\gamma}$ = shear rate, s^{-1}
ϵ = holdup
μ = viscosity, $Pa \cdot s$
ρ = density, $kg \cdot m^{-3}$
σ = specific surface energy (interfacial tension), $N \cdot m^{-1}$
Φ_S = volume fraction of solids in the gas-free suspension

Indices

eff = effective value in bubble column
G = gas
L = liquid
0 = refers to $\Phi_S = 0$
S = solid

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