Effects of Finely Divided Solids on Mass Transfer between a Gas and an Organic Liquid

Global gas-liquid mass transfer parameters, $k_L a$ and a were determined in an organic liquid in which finely divided solid particles were suspended in a mechanically stirred vessel. The product $k_L a$ and a both decreased linearly with solids loading; both were independent of particle size and particle density. Gas holdup was independent of solids loading.

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SCOPE

Three-phase slurry reactors, in which a gas, a liquid, and a finely-divided solid are contacted, are widely used in industry. Gas-liquid mass transfer often presents a major resistance to the rate of reaction and it can affect product selectivity. If present, this resistance is usually much more important than that of mass transfer from liquid to the outside surface of solid particles. The prediction of gas-liquid mass transfer in these systems is still highly uncertain, partly because most laboratory or pilot plant studies have been conducted with water. Water is safe and cheap, and aqueous systems are of intrinsic interest for some applications. However, aqueous systems often behave substantially differently than organic systems. The latter are of primary interest in the chemical and petroleum industry and much less is known about them.

Interfacial area, a, was determined here by the so-called chemical method (unsteady state absorption with simultaneous chemical reaction in the fast-reaction regime) using the reaction of CO_2 with cyclohexylamine (CHA) in a solution of 90% toluene and 10% isopropanol. The overall mass transfer coefficient, $k_L a$, was determined by the unsteady state desorption of helium from the same liquid into a nitrogen purge stream. The solid properties investigated were particle concentration (0–45 vol.%), size (35–200 μm), density (0.7–4.5 g/mL), and composition (glass, polytetrafluoroethylene, polypropylene). The effect of gas phase mixing upon the calculation of these parameters was also evaluated. Studies were made in a 1 L aerated and mechanically agitated reactor.

CONCLUSIONS AND SIGNIFICANCE

The overall mass transfer coefficient and the interfacial area decreased linearly with inert solids loading. The decrease in $k_L a$ can be attributed to the decrease in a: k_L was independent of solids loading for the conditions of this study. Gas holdup did not vary with inert solids loading, indicating that the decrease in a was due to bubble coalescence.

Both $k_L a$ and a were independent of particle size for particle sizes below 200 μm. Both were also independent of particle density. Stirring speed was shown to be an appropriate basis for comparison of mass transfer parameters. At high solids loadings $k_L a$ and a were lower when the solids were relatively nonwetting. A mechanism for enhanced bubble coalescence was postulated.

The use of an apparent viscosity for prediction of

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mass transfer can be misleading because results differ depending upon whether a viscosity increase is caused by addition of solids or, e.g., by addition of a high-viscosity fluid.

Introduction

Gas-liquid mass transfer often represents a major resistance to the rate of reaction and can affect reaction selectivity. This resistance, if present, is usually much more important than transfer from liquid to the outside surface of solid particles, as shown by a simple geometrical argument. Catalyst particles usually are less than 300 μm in diameter, and a size range of 50–100 μm is common. Bubbles, however, range in size from 1 mm in mechanically stirred vessels to larger than 10 cm in some bubble columns. Even with a solids holdup one-tenth of the gas holdup, the interfacial area available for mass transfer from the liquid to the outside catalyst surface is typically 100 times or more greater than the interfacial area available for transfer from the gas to the liquid.

The calculation of relevant mass transfer parameters for these reactors is still highly uncertain. Frequently, a three-phase slurry reactor is modeled as a two-phase system, gas and slurry, in which the solid-liquid mixture is treated as a homogeneous phase. If gas-liquid mass transfer could be adequately predicted based upon a liquid with the same hydrodynamic characteristics as the slurry, then the three-phase problem would be removed. But the extent to which this assumption is valid has not been fully tested.

This assumption is clearly inadequate under one set of circumstances. If the solid particles are catalytic, mass transfer can be enhanced if the effective diffusion length from the gas-liquid interface to the particle surface is reduced. In terms of film theory, the effective diffusion length can be reduced by penetration into the liquid film of catalyst particles, an effect most noticeable with particles smaller than the film thickness. Thus Pal et al. (1982) have demonstrated enhanced absorption of oxygen into sodium sulfide solutions in which 1 and 4 μm carbon particles were suspended. Very little enhancement was observed for 60–85 μm particles, which exceeded the film thickness of approximately 20 μm. Catalyst particles are most commonly larger than 50 μm or so to facilitate separation from the liquid, but fine particles might be used deliberately upon occasion, and they may be formed by catalyst attrition. The added complication of this effect is not addressed in this work.

Catalytic properties of the particles aside, their effect upon gas-liquid mass transfer, other than through changing the bulk hydrodynamics of the pseudoliquid slurry, has not yet been fully tested. Without this knowledge underdesign of slurry reactors is possible. In a pilot plant bubble column reactor at Sasol in South Africa, which employed a paraffinic wax for the Fischer-Tropsch reaction at 3.0 MPa pressure and 200–300°C, it has been reported that increasing catalyst loading eventually reduced gas holdup and conversion. The observed rate eventually changed from a kinetically controlled regime to a mass transfer-controlled regime. Similar adverse results have been reported by Kurten and Zehner (1979) for interfacial area: increased solids loading resulted in a reduction of the overall bubble surface area available for mass transfer in a bubble column reactor in which air was sparged through an aqueous sulfite solution.

Other studies indicate that the assumption of a pseudoliquid is an oversimplification. Joosten et al. (1977) reported a decrease in the mass transfer coefficient in a stirred vessel with increased solids loading, at high particle loadings. Reduced to a relative viscosity basis, however, the effect varied with the composition and density of the solid employed. Godbole et al. (1983) noted that gas holdup in a three-phase bubble column varied with the particle composition. These observations have not yet been placed within a unifying framework.

Aqueous systems often behave substantially differently than organic systems for several reasons. The ubiquitous presence of ions in aqueous systems, either through contamination or present deliberately, can cause the gas bubbles to be virtually noncoalescing and thus bubble sizes can be very small (Reith and Beek, 1970; Farritor and Hughmark, 1980). A double layer of electrolyte forms at the bubble surface and reduces bubble interactions. Hence interfacial areas an order of magnitude larger than in pure liquids can be generated. Both the bubble size distribution and the coalescence characteristics are poorly representative of many systems employing organic liquids.

Aqueous systems are also affected by surfactant-type impurities. They can alter the surface tension of the liquid, and thus the size and coalescence characteristics of bubble swarms, and consequently cause overall mass transfer coefficients and interfacial areas different from those observed in their absence (Davies, 1963). Short chain alcohols in water can also reduce coalescence considerably without changing greatly the measured surface tension (Calderbank, 1958).

Mass transfer is often altered unpredictably for these systems. The mass transfer coefficient, k_La, can experience two opposing effects from the presence of ions or organic solutes. The interfacial area per unit volume, a, will increase, often dramatically, because of a skewing of the bubble distribution toward smaller diameter bubbles. However, the individual liquid phase mass transfer coefficient, k_L, may decrease by as much as 70%, because of the reduction of turbulence at the bubble interface caused by the presence of solutes (Calderbank and Moo-Young, 1961). Whether the product of k_L and a ultimately increases or decreases cannot always be predicted. Although k_La is the parameter used by the designer, the individual values of k_L and a were sought here to provide a more fundamental interpretation of observations. The experiments were conducted in an organic liquid mixture in order to obtain results more characteristic of liquids commonly encountered in industrial practice.

Experimental

Interfacial area

The interfacial area was determined by the so-called chemical method (absorption with simultaneous chemical reaction in the fast-reaction regime). Traditionally, the sulfite oxidation reaction has been used for this purpose. Oxygen is absorbed with reaction into a sodium sulfite solution, the reaction of oxygen and sulfite being homogeneously catalyzed by cobaltous ions

(Co^{+2}). The rate constant can be varied over a thousandfold range by varying the concentration of the catalyst. Several physicochemical criteria, shown in Table 1, are necessary for the chemical method to be implemented.

The sulfite method has been in use since the work of Cooper et al. (1944). Despite its long history, the kinetics are still not very well understood. Contamination of the water, of the homogeneous catalyst, or of the sulfite salt can lead to incorrect and irreproducible results (Linek and Vacek, 1981). The main advantage is the ability to change the rate constant over a wide range. The sulfite method is clearly limited to aqueous solutions. The noncoalescent behavior of these ionic systems has led to the development of other reaction schemes for measuring interfacial area, but all suffer from the problem of an invariant rate constant. The reaction must be chosen carefully to ensure that the rate and other physicochemical constants satisfy the criteria for use. One class of reactions that has emerged is the carbamation of amines.

The reaction used here was that of CO_2 with cyclohexylamine (CHA) in a 90% toluene and 10% isopropanol mixture, a reaction first investigated for this purpose by Sridharan and Sharma (1976). The kinetic expression was subsequently reevaluated by Alvarez-Fuster et al. (1980) and Imaishi et al. (1981). The kinetics, rate constant, and physicochemical constants from Alvarez-Fuster et al. were used in the present study. The reaction and rate expression are as follows:

$$CO_2\,(\text{gas}) + 2\,\text{CHA (liquid)} \longrightarrow \text{CHA} \cdot CO_2 \cdot \text{CHA (liquid)} \qquad (1)$$

$$R_k = k_{12}[CO_2^*]\,[CHA_o]^2 \qquad (2)$$

Several other amine carbamations have been reported in the literature as available for use in organic liquids (Alvarez-Fuster et al., 1981). However, most amine mixtures are noncoalescent; indeed, severe foaming was encountered in preliminary work in the present study in an attempt to use the other amine reactions investigated by Alvarez-Fuster et al. (1980, 1981). The amine system used here was the only one that visually exhibited coalescence similar to that of pure liquids.

Overall mass transfer coefficient, k_La

The mass transfer coefficient was determined by the unsteady state desorption of a sparingly soluble gas (helium) from a helium-saturated liquid into a nitrogen purge stream, similar to the system used by Joosten et al. (1977). The liquid used was the cyclohexylamine in toluene and isopropanol mixture used for determining interfacial area.

Table 1. Physicochemical Criteria Required for Determination of *a* by Absorption with Irreversible Reaction in the Fast Regime

Reaction:	$A(\text{gas}) + zB\,(\text{liquid}) \longrightarrow \text{products}$
	$M = \dfrac{2D_A k_{mn}\,[A^*]^{m-1}\,[B_0]^n}{k_L^2\,(m+1)}$
Criteria to determine a:	
	1. $\sqrt{M} \ll 1 + \dfrac{[B_0]}{z\,[A^*]}\sqrt{\dfrac{D_B}{D_A}}$
	2. $k_g \gg k_L H^* \sqrt{M}$
	3. $M > 3$
then	$R_r a = a[A^*]\sqrt{D_A k_{mn}\,[B_0]^n [A^*]^{m-1}\left(\dfrac{2}{m+1}\right)}$

Apparatus

Both a and k_La were determined using CHA in toluene and isopropanol in identically shaped vessels. The interfacial area was determined in a 1 L stainless steel stirred autoclave (Autoclave Engineers, Inc.) depicted in Figure 1. It had a diameter (d_t) of 7.6 cm and was equipped with both a propeller and six-blade impeller (d_i = 3.2 cm) mounted on the shaft. This configuration was shown to be more effective in keeping solids suspended than a single impeller (Huff and Setterfield, 1982). A four-blade baffle (d_f = 0.75 cm) was used to prevent vortexing. A machined polyethylene plug was seated above the gas-liquid-solid dispersion to minimize dead volume in the reactor. Gas was sparged into the vessel via an inlet tube mounted flush to the bottom (0.10 cm ID). The reactor was maintained at 20°C by a constant-temperature bath.

A glass replica of the 1 L autoclave was used to determine k_La. All dimensions and internals were identical to the stainless steel autoclave. Gas holdup could be measured visually and complete solids suspension was confirmed at every stirring speed and solids loading. An inlet gas flow rate of 35 mL(STP)/s (u_g = 0.75 cm/s) and a liquid plus slurry volume of 400 mL was used throughout this study. Gases were metered with calibrated rotameters and flows were checked by a bubble meter. Stirring speeds ranged from 350 to 1,750 rpm. Solids used in this study are listed in Table 2. Sieved fractions of solids were used in all experiments. The particle size indicated in any k_La or a measurement thus includes a maximum deviation of ±9%.

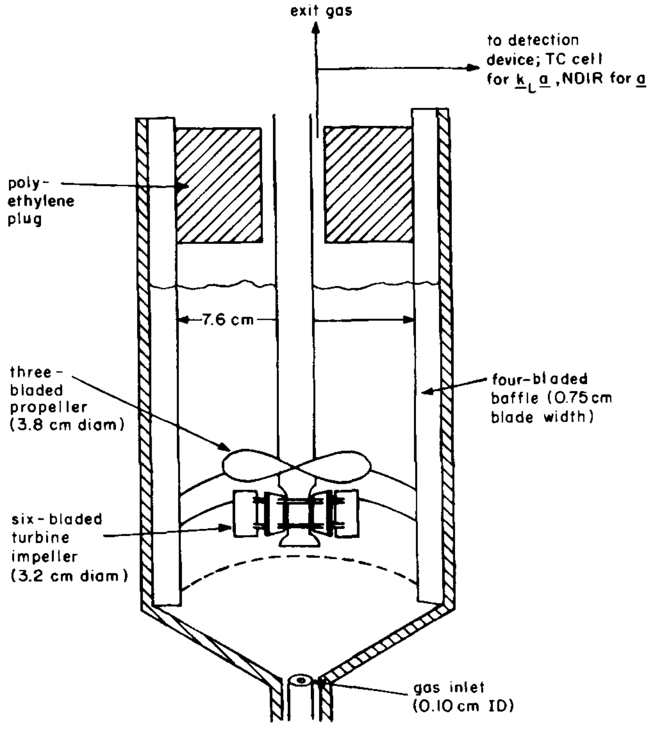

Figure 1. One-liter mechanically stirred vessel for unsteady state determination of k_La and a.

Table 2. Physical Properties of Solids Studied

Particle Composition	Supplier	Designation	Shape	Density g/mL	Size Range micron
Polypropylene	Polysciences	6068, 4342	granular	1.0	30–180
Polytetrafluoroethylene	Polysciences	1344	flat	2.0	350–550
Soda-lime silica glass	Potters Industries	P-004, P-006, P-007, P-008	spherical	2.5	30–220
Barium titanate glass	Potters Industries	H-002, H-003, H-005, H-008	spherical	4.5	30–220
Soda-lime silica glass	Ferro Corp.	MS-M	spherical	2.5	30–180
Silicone–coated soda-lime silica glass	Ferro Corp.	MS-ML-W	spherical	2.5	30–120
Glassy alumina-silica fly ash (fillite)	Fillite, Inc.	200/7	spherical	0.7	30–180

Procedure

The bubble area, a, and the mass transfer coefficient, k_La, were both determined by an unsteady state measurement. For bubble area determination the slurry charge was placed into the reactor, the reactor sealed, and a nitrogen stream introduced to establish a steady state concentration in the reactor, at a pressure approximately 15 kPa above ambient. At the beginning of the measurement, this stream was exchanged with a gas mixture of 6–8% CO_2 in N_2. The CO_2 concentration in the outlet gas was continuously monitored by a nondispersive infrared (NDIR) analyzer and the outlet displayed on a chart recorder. The inlet gas composition was set by combining metered streams of N_2 and CO_2, and the composition verified by gas chromatography.

In the determination of k_La, the liquid was first saturated with helium and then the gas flow and impeller turned off. The vapor space above the liquid was next cleared with a nitrogen purge. The impeller was turned on and a nitrogen flow admitted through the bottom of the reactor. A small fraction of the outlet purge stream was sucked through a calibrated thermal conductivity (TC) cell to determine the helium concentration. A metering piston pump located downstream of the TC cell maintained flow through the cell. As with the determination of a, the outlet concentration was continuously displayed on a high-speed chart recorder.

Values of a and k_La are all reported per volume of slurry on a gas-free basis.

Data Analysis

In order to determine properly the mass transfer parameters, appropriate models for both the gas and liquid phase are required. The liquid was modeled as a continuous stirred tank reactor (CSTR), which was justified by the short mixing times in the vessel (Mehta and Sharma, 1971). The gas phase was modeled as a plug flow reactor (PFR) with recycle, which physically corresponds to surface aeration that may take place in the reactor (Topiwala, 1972). This one-parameter model (R = recycle ratio) thus allowed the complete spectrum of mixing possibilities in the gas phase to be encompassed, from CSTR ($R = \infty$) to PFR ($R = 0$).

The interfacial area was calculated by fitting the outlet concentration curve to the solved mass balance equations for CHA and CO_2. The integrated mass balance equations for this reaction are as follows:

$$\text{Gas:}\quad -(R+1)G\int_{x_i'}^{x_o}\frac{dx}{R_r} = aV \tag{3}$$

$$\text{Liquid:}\quad (1-\epsilon_s)V([\mathrm{CHA}_o]-[\mathrm{CHA}_o]_0) = -2G(R+1)\int_0^t (x_i'-x_o)\,dt \tag{4}$$

$$[\mathrm{CO}_2^*] = H^*P\left(\frac{x}{1+x}\right) \tag{5}$$

$$x_i' = \left(\frac{x_i}{R+1}\right) + \left(\frac{Rx_o}{R+1}\right) \tag{6}$$

The equations were solved using the nitrogen flow rather than the total flow as a basis to take into consideration flow contraction over the length of the agitated vessel. The complete rate expression for the transfer of CO_2 into the liquid is as follows (Jukevar and Sharma, 1977):

$$R_r a = \frac{k_g a([\mathrm{CO}_2^*]-[\mathrm{CO}_{2,\mathrm{eq}}^*])\,[\mathrm{CHA}_o]\,\sqrt{D_{\mathrm{CO}_2}k_{12}}}{k_g + H^*\,[\mathrm{CHA}_o]\,\sqrt{D_{\mathrm{CO}_2}k_{12}}} \tag{7}$$

The appearance of k_g in the numerator and denominator is a consequence of criterion *2* from Table 1 not being completely satisfied. When $k_g \gg H^*\,[\mathrm{CHA}_o]\,\sqrt{D_{\mathrm{CO}_2}k_{12}}$, the denominator becomes dominated by k_g and R_r becomes independent of k_g. In this study k_g at 20°C was taken to be 0.008 kmol/m^{2}s · MPa based upon the work of Sharma and Mashelkar (1968). Gas phase resistance thus accounted for approximately 10% of the total resistance to reaction. The carbamation of cyclohexylamine was also found to be an equilibrium-limited process in this study (Bartos and Satterfield, 1986), not an irreversible one as inferred from Sridharan and Sharma (1976) and Alvarez-Fuster et al. (1980). The effective concentration driving force was thus taken as the CO_2 concentration minus the equilibrium value. The ratio of this driving force, ($[\mathrm{CO}_2^*]$ − $[\mathrm{CO}_2^*]_{\mathrm{eq}}$), to ($[\mathrm{CO}_2^*]$) exceeded 0.55 in all experiments. The presence of a reaction equilibrium thus had an effect upon the rate of transfer of CO_2. The complete expression was retained in the calculations for all data reported here.

The value of the recycle ratio, R, could not be determined independently. Since the conversion of CO_2 was often as great as 80% initially, the calculated value of a was very dependent upon the postulated gas residence time distribution (RTD) as characterized by R. Thus a as calculated could vary by as much as fivefold with the extreme limits of the value of R. Consequently, only relative values of a are reported here. These were determined by assuming that the gas phase RTD remained constant at a fixed stirring speed as solids loading was changed. In this study $R = 0$ (PFR) was used as the basis for comparison of the interfacial areas.

The discrepancy among interfacial areas caused by uncertainty in the gas phase RTD has been addressed by Schumpe and Deckwer (1980) and Midoux et al (1980). They compared the value of a calculated for a particular bubble size distribution with the value of a calculated for a simplification of the gas phase RTD (either PFR [a_{PFR}] or CSTR [a_{CSTR}]). What seems clear is that the values of a calculated for all possible choices of bubble size distributions converge when the calculated values of a_{PFR} and a_{CSTR} converge. This criterion can be used to establish when a particular reaction is suitable for calculating a, independent of any gas phase assumptions.

For this purpose we consider a simplified form of Eq. 7 in which reaction is assumed to be irreversible and gas phase resistance negligible, as follows:

$$R_r a = a[CO_2^*]\,[CHA_o]\,\sqrt{D_{CO_2}k_{12}} \qquad (8)$$

Equation 8 can be substituted into Eq. 3 together with Eqs. 5 and 6 to yield an integrated expression for x_o:

$$St_1 = \frac{a y_i H^* P\,\sqrt{D_{CO_2}k_{12}[CHA_o]^2}}{\left[\dfrac{G y_i}{V}\right]}$$

$$= x_i + x_o + (R+1)\log_e\left[\frac{x_o R + x_i}{x_o(R+1)}\right] \qquad (9)$$

A dimensionless mass Stanton number can be used to characterize the system solution. As formulated above, St_1 is the ratio of the amount of CO_2 transferred into the liquid to the total amount present available for transfer. At low St_1 the solutions to this equation in x_o are indistinguishable for varying values of R. Ranges in St_1 for typical reactions used in determining a are indicated in Table 3 and Figure 2. The physicochemical constants of these reactions satisfy the criteria of Table 1. Figure 2 indicates why the sulfite method remains in use despite these new classes of reactions available for determining a: no a priori knowledge of the gas phase RTD is required in order to determine a.

An attempt was made to lower the reaction rate constant for the CHA carbamation reaction by measuring interfacial areas at 5°C instead of at 20°C for which kinetic data were available. An estimated fourfold reduction in rate constant was effected, based upon the activation energy for similar carbamations (Alvarez-Fuster et al., 1980). Conversion of CO_2 exceeded 80% in all of these experiments, however, still requiring accurate knowledge of the gas phase RTD to calculate a. This result also follows from Figure 2, wherein a fourfold rate constant reduction translates to only a twofold decrease in St_1. This decrease is

Table 3. Comparison of Different Chemical Systems Used to Determine Interfacial Area

	$CO_2 + 2CHA \rightarrow$ $CHA \cdot CO_2 \cdot CHA$	$CO_2 + 2DEA \rightarrow$ $DEA \cdot CO_2 \cdot DEA$	$O_2 + 2SO_3^{-2} \rightarrow$ $2SO_4^{-2}$
Reference	1,2	2	3
Solvent	90% toluene 10% isopropanol	Ethanol	Water
m	1	1	1
n	2	2	1
H^*, kmol/m^{3}MPa	1.0417	0.3788	0.0118
D_A, m^2/s	4×10^{-9}	1.9×10^{-9}	2.4×10^{-9}
k_{1n}, m^{3n}/kmol^{n}s	2,900	840	65–1,628*
$[B_o]$, kmol/m^3	0.25	0.25	0.80
$H^*\sqrt{D_A k_{1n}[B_o]^n}$	89×10^{-6}	12×10^{-6}	$0.2–4 \times 10^{-6}$
VP/G, m$^3 \cdot$ s $\cdot$ MPa/mol	280	280	280
a, m^{-1}	120–900	120–900	120–900
St_1	3–23	0.4–3	0.006–0.5

$$St_1 = \frac{aVPH^*\,\sqrt{D_A k_{1n}\,[B_o]^n}}{G}$$

References:
1 Alvarez-Fuster et al. (1980)
2 Sridharan and Sharma (1976)
3 de Waal and Okeson (1966)
CHA = cyclohexylamine
DEA = diethanolamine
$CHA \cdot CO_2 \cdot CHA$ = carbamate of CHA
$DEA \cdot CO_2 \cdot DEA$ = carbamate of DEA
*k_{11} for the sulfite oxidation is k'_{11} [Co^{+2}] and thus varies with [Co^{+2}]

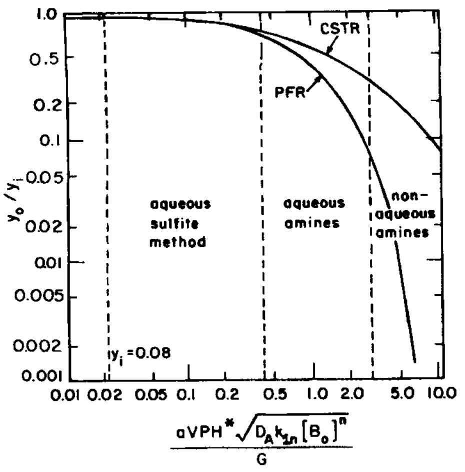

Figure 2. Degree of convergence of calculated interfacial area for two different gas phase RTD's depends upon the chosen reaction.

insufficient to be within the range where a_{PFR} and a_{CSTR} substantially converge.

The overall mass transfer coefficient, $k_L a$, was calculated from a mass balance upon helium in the liquid and in the gas phase. The pertinent equations are as follows:

$$\text{Gas:} \qquad \epsilon_g V \frac{dC^*_{g,avg}}{dt} = k_L a V(C_L - C_i) - QC_{g,o} \qquad (10)$$

$$\text{Liquid:} \qquad V(1 - \epsilon_s)\frac{dC_L}{dt} = -k_L a V(C_L - C_i) \qquad (11)$$

$$C_i = C^*_{g,avg} H \qquad (12)$$

$$C^*_{g,avg} = C_{g,o}\left(\frac{R + 1/2}{R + 1}\right) \qquad (13)$$

$$C_g = 0 \qquad \text{at} \quad t = 0 \qquad (14)$$

$$C_L = C_{L,sat} \qquad \text{at} \quad t = 0 \qquad (15)$$

The concentration of helium in the reactor, C^*_g, was modeled as a linear increase from the inlet to outlet value. The average concentration, $C^*_{g,avg}$, was thus the integrated average over the length of the reactor.

The resulting coupled differential equations yielded a solution for the outlet helium mole fraction that could be approximated by a decaying exponential at long times. The logarithm was thus taken of the outlet helium concentration, the slope of the linear region being approximately equal to $k_L a/(1 - \epsilon_s)$. This measurement was relatively insensitive to R. Variation of only 10% between $R = 0$ and $R = \infty$ was calculated for any given $k_L a$ measurement. Values of $k_L a$ could thus be determined independent of any gas phase assumption.

Results

Carbamation studies

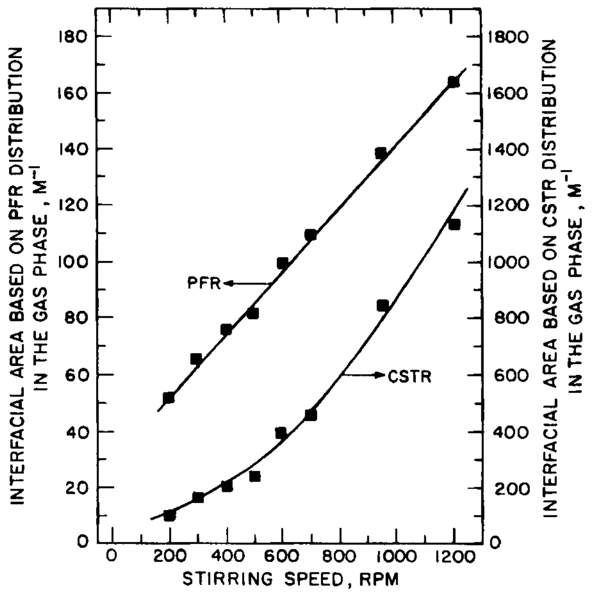

Figure 3. Interfacial area, *a*, varies linearly with stirring speed at low values of *R*; no solids present. Calculated value of *a* depends upon assumed gas RTD.

Experiments were first conducted without inert solids present to establish the variation of a and $k_L a$ with stirring speed, Figures 3 and 4. Both varied linearly with stirring speed over the range encountered in this study, assuming $R = 0$. This linear relationship has also been reported by Mehta and Sharma (1971) and Sridhar and Potter (1982). When CSTR behavior of the gas phase was assumed ($R = \infty$), the calculated interfacial areas varied nonlinearly, showing sharper increases at higher stirring speeds.

For each of the solids, the effect of increasing solids loading upon a and $k_L a$ was determined by progressively removing a quantity of liquid and adding an equal volume of solids, so that the slurry volume was held constant, Figures 5 and 6. A linear decrease in both a and $k_L a$ with volume fraction of inert solids

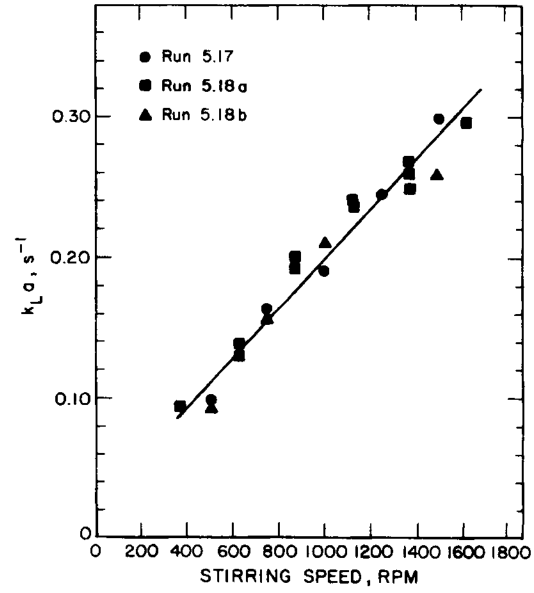

Figure 4. Overall mass transfer coefficient varies linearly with stirring speed; no solids present.

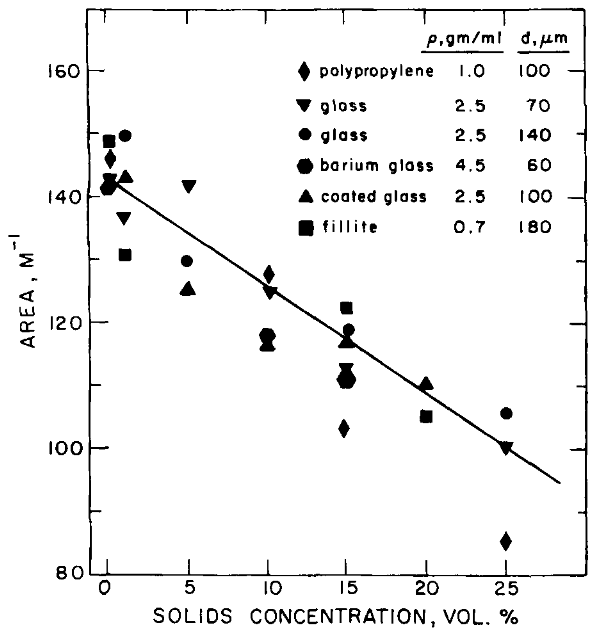

Figure 5. Interfacial area decreases with increased solids concentration; 950 rpm, R = 0 (PFR) assumption.

was observed at all stirring speeds encountered in this study. Gas holdup did not, however, vary with inert solids addition for a fixed stirring speed.

The decrease in a and k_La was independent of particle size over the range of sizes examined in this study. This can be observed by comparing the values of a and k_La for soda-lime glass in Figures 5 and 6. This result was also demonstrated by Ledakowicz et al. (1983), but only for k_La. The decrease in both a and k_La was also independent of particle density. The hollow glass spheres used in this study (fillite) were compositionally similar to the solid glass beads, but had a density almost four times less. The effect of particle density was thus able to be tested free from the effects of particle composition.

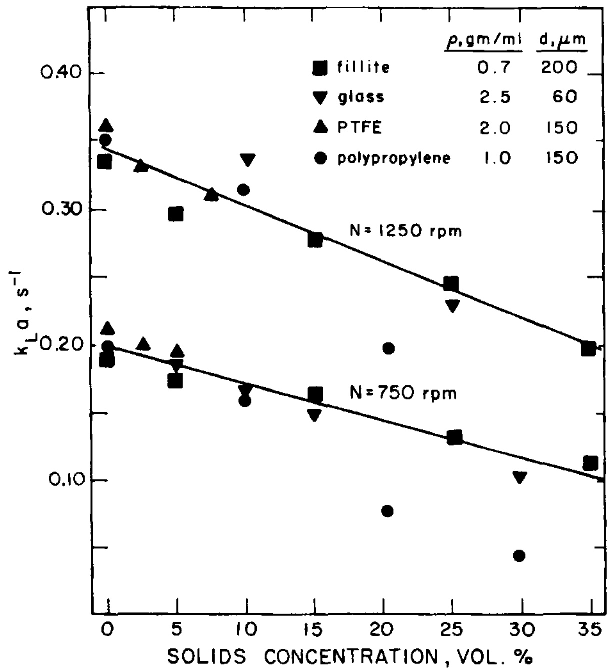

Figure 6. Overall mass transfer coefficient is dependent upon particle composition at high volume fractions of solids.

This independence of both a and k_La from particle density also indicates that stirring speed is a suitable basis for comparison among gas-liquid-solid systems in mechanically stirred vessels. Constant power is often used as the basis for comparison in stirred vessels (Joosten et al., 1977); however, in this study the plots of k_La and a vs. volume fraction solids would not have remained colinear for varying particle density had they been reduced to a constant power basis.

The amount of decrease of a and k_La with increased solids loading also varied moderately with particle composition. At high solids loadings, k_La and a decreased more in the presence of polypropylene than any of the glasses, even though the density of the polypropylene is between the extremes of the glasses. The polypropylene particles are granular, while the glasses are spherical, but this possible effect is discounted since the decrease in k_La is independent of particle size. This effect was also reported by Joosten et al. for k_La measurements, although attributed to density effects in their work.

Discussion

Measurements were performed to determine k_La and a in identical vessels using identical slurries. This procedure should thus allow direct calculation of k_L, based upon the ratio of k_La and a. However, imprecise knowledge of the gas phase RTD did not allow a to be calculated exactly. The values indicated in the figures are based upon $R = 0$. If R is assumed constant at a fixed stirring speed, however, the relative effect of particle loading upon k_L can be ascertained. Figure 7 indicates the variation in k_L with solids loading at 950 rpm. This is the value of k_L for helium, since the k_La experiments were conducted with helium desorption. The value of a in the absorption with reaction exper-

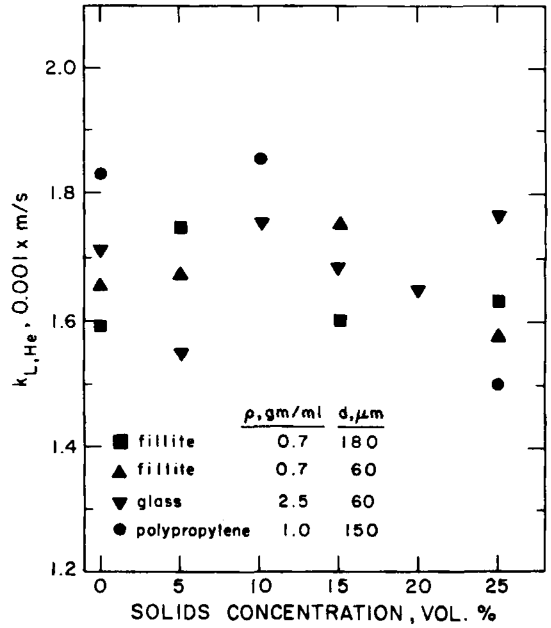

Figure 7. k_L is independent of solids loading; 950 rpm.

iment was assumed to be the same as in the k_La measurement. Sharma and Mashelkar (1968) demonstrated that a was independent of gas composition, justifying this assumption.

No variation in k_L with solids loading was observed, indicating that the decrease in k_La can be attributed entirely to a decrease in a. Since the gas holdup did not change with inert solids loading, the decrease in a must correspond to the presence of larger bubbles in the stirred vessel. This result is consistent with the work of Calderbank and Moo-Young (1961). They identified two bubble classes, rigid (small) or elastic (large) bubbles. They observed that k_L is constant within each bubble class, is smaller for rigid bubbles, and varies linearly with bubble size in the transition region between classes. If the addition of solids were causing bubble coalescence and concomitant increase in bubble diameter, but only within one class of bubbles, both observations in this study would be explained. The value of a would decrease while that of k_L would remain constant.

No successful theoretical framework has been proposed to encompass mass transfer in three-phase slurry reactors. Joosten et al. (1977) attempted to correlate variations in k_La due to increased solids loading in a mechanically agitated vessel with apparent viscosity, the bulk property of the slurry that changes the most. However, while this correlation allowed them to explain differences in particle size upon k_La, it allowed no simplification for particle density or composition differences.

The results of this study indicate that such a simplification may be deceptive. Theories for mass transfer propose that k_L is proportional to diffusivity raised to a power between ½ and 1. Diffusivity is in turn inversely proportional to viscosity through the Wilke-Chang equation. This inverse correspondence between k_L and viscosity, while valid for changes in viscosity caused by the addition of thickening agents, is not valid for changes in apparent viscosity resulting from the addition of inert solids. The fact that k_L in this study was constant serves to clarify the difference between macroscopically and microscopically measured fluid properties. Over the length scale important for diffusion (and hence mass transfer), no effect of solids loading upon mass transfer (k_L) would be anticipated.

Additionally, experiments measuring the change in mass transfer parameters due to increases in viscosity yield differing results depending upon whether the viscosity increase is caused by the addition of solids or by the addition of a high-viscosity fluid. Sharma and Mashelkar (1968) and Abdel-aal et al. (1966) demonstrated an increase in a with increased viscosity for a glycerol and water mixture in a bubble column. Godbole et al. (1983) and Gollakota and Guin (1984), however, reported that a decreased with increased viscosity caused by increased solids loading. Clearly, the mechanism for bubble coalescence and breakup depends upon how the viscosity increase is brought about.

Godbole et al. have attributed the changes observed in a with increased solids loading for different solid compositions to wetting properties of the solids. This was done for an aqueous sulfite solution in a bubble column. However, in the present study all particles used were completely wet by the organic solution. This suggests that another mechanism must be operating to cause the bubble diameters to increase with inert solids loading, which leads to decreased interfacial area.

Bubble diameter is determined by the extent of both bubble breakup and subsequent bubble coalescence. The orifice Reynold's number ($N_{Re,O} = 4Q\rho_g/\pi d_o \mu_g$) is the key parameter characterizing the amount of kinetic energy in the gas available for bubble breakup at the exit from the orifice (Bhavaraju et al., 1978). For the high $N_{Re,O}$ used in this study, they have shown that bubble breakup is independent of the properties of the liquid. Consequently, a marked effect upon bubble breakup is not expected by increased solids loading. An increase in bubble coalescence due to increased solids loading is thus hypothesized as the cause of the enlarged bubble diameters.

Perhaps a cage effect is occurring. As bubbles move toward each other the concentration of solids immediately surrounding the bubble pair could increase. The resistance this cage would provide could increase bubble contact time and enhance coalescence probability. The cage of particles around colliding bubbles would provide the major mechanism for bubble coalescence to which increased bubble diameter is attributed. Wetting differences would provide a secondary mechanism. The presence of solid, nonwetting particles could induce bubble coalescence via a bridging mechanism. As two bubbles approach, particles in the film between them or attached partially to one bubble or another could at some point contact both bubbles. The lowered surface tension at the bubble and particle interfaces would provide a mechanism for increasing bubble contact time and would thus enhance coalescence probability. This additional mechanism would explain why polypropylene particles exhibited a greater rate of bubble increase (and hence area decrease) at higher solids loading.

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Notation

a = measured interfacial area per volume of slurry, m^2/m^3 solid + liquid
a_{CSTR} = calculated interfacial area assuming CSTR behavior in the gas phase, m^{-1}
a_{PFR} = calculated interfacial area assuming PFR behavior in the gas phase, m^{-1}
A = gas phase species in reaction (usually CO_2)
$[A^*]$ = saturation concentration of A in liquid, $kmol/m^3$
B = liquid phase species in reaction (usually CHA)
$[B_o]$ = bulk concentration of B, $kmol/m^3$
CHA = cyclohexylamine
$[CHA_o]$ = bulk concentration of CHA, $kmol/m^3$
$[CHA_o]_0$ = bulk concentration of CHA at $t = 0$, $kmol/m^3$
$[CO_2^*]$ = saturation concentration of CO_2 in liquid, $kmol/m^3$
$[CO_2^*]_{eq}$ = concentration of CO_2 in equilibrium with amine, $kmol/m^3$
C = concentration of solute in bulk, $kmol/m^3$
$C_{g,o}$ = concentration of helium gas leaving the reactor, $kmol/m^3$
C_g^* = concentration of helium gas inside the reactor, $kmol/m^3$
$C_{g,avg}^*$ = average concentration of helium gas inside the reactor, $kmol/m^3$
C_i = concentration of solute at the interface, $kmol/m^3$
C_L = concentration of helium in liquid, $kmol/m^3$
$C_{L,sat}$ = helium saturation concentration in the liquid, $kmol/m^3$
d_f, d_i, d_o, d_t = diameter of baffle, impeller, orifice, tank, m
$D_A, D_B, D_{CHA}, D_{CO_2}$ = diffusivity of A, B, CHA, CO_2, helium, nitrogen in the liquid, m^2/s^2

G = molar flow rate of inerts (usually N_2), kmol/s

H = Ostwald coefficient for helium, mL dissolved gas/mL liquid

H^*, H^*_H = Henry's law constant for CO_2 or O_2, H_2, kmol solute/MPa · m^3 liquid

k_g = gas phase mass transfer coefficient, kmol/m^2 s · MPa

k_L = liquid phase mass transfer coefficient, m/s

$k_{L,H}$ = liquid phase k_L for hydrogen, m/s

k_La = overall mass transfer coefficient, s^{-1}

k_{mn} = rate constant for irreversible reaction: mth order in $[A^*]$, nth order in $[B_o]$, $m^{3m+3n-3}$/kmol^{m+n-1} · s

k_{12} = rate constant for irreversible reaction: first-order in $[CO_2^*]$, second-order in $[CHA_o]$, m^6/kmol^2 · s

m = order of reaction in gas phase component

M = Hatta number = $2D_Ak_{mn}[A^*]^{m-1}[B_o]^n/[(m+1)k_L^2]$

n = order of reaction in liquid phase component

N_m = mass flux, kmol/m^2 · s

$N_{Re,O}$ = orifice Reynold's number = $4Q\rho_g/\pi d_o\mu_g$

p = partial pressure of solute in bulk, MPa

p_i = partial pressure of solute at the interface, MPa

p_H = partial pressure of hydrogen in the reactor, MPa

P = total pressure in the reactor, MPa

Q = purge or reaction gas flow rate, m^3/s

R = recycle ratio = flow of recycle/flow of fresh feed

R_k = kinetic reaction rate of CO_2 and CHA, kmol/m^3 · s

R_r = rate of transfer of A or CO_2 into the liquid, kmol/m^2 · s

STP = standard temperature and pressure, 0.101 MPa, 20°C for gas flow rates and physicochemical properties, unless specified

S_v = space velocity of inlet H_2 and CO, kmol/m^3 · s

St_m = Stanton number = $aVG^{-1}[D_Ak_{mn}[B_o]^n(H^*P)^{m+1}]^{1/2}$

t = time, s

T = temperature, K

u_g = superficial gas velocity = Qh/V, m/s

V = volume of ungassed slurry, m^3

x_i = moles of A inlet feed/moles inert inlet feed

x_i' = moles of A inlet plus recycle/moles inert inlet plus recycle

x_o = moles of A outlet/moles of inert outlet

X = conversion

y_i = mole fraction of A in inlet feed

y_o = mole fraction of A in outlet

z = stoichiometric coefficient relating $[A^*]$ to $(B_o]$

Greek letters

ϵ_g = gas holdup = volume gas/volume ungassed slurry

ϵ_s = solids holdup = volume solids/volume ungassed slurry

μ_g = gas viscosity, kg/m · s

ρ_g = gas density, kg/m^3

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