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Manuscript received October 17, 1978; revision received January 19, and accepted February 5, 1979.

Limits of the Chemical Method for the Determination of Physical Mass Transfer Parameters in Mechanically Agitated Gas-Liquid Reactors

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Interfacial parameters a and k_La in gas-liquid stirred tanks are generally determined in assuming the liquid phase perfectly mixed, which is most often realistic, and the gas phase either in piston flow (Cooper et al., 1944; Karwat, 1959; Yoshida et al., 1960; Liu et al., 1972) or perfectly mixed (Westerterp et al., 1963; Calderbank, 1958; Figueiredo and Calderbank, 1978; Sridharan, 1975). A comparison of the data obtained for both gas flows is sometimes proposed (Mehta and Sharma, 1971; Yagi and Yoshida, 1977). When the gas is dispersed into liquids that we term clean, the coalescence and redispersion due to bubble interaction either inside the dispersion or with the cavities behind the stirrer blades (Van't Riet and Smith, 1973) assure a perfect mixing of the gas phase. On the contrary, for liquids that we term polluted by the presence of dissolved electrolytes or surface active agents that diminish or nearly totally inhibit the coalescence, the piston flow model may not represent conveniently the behavior of the gas, even though the bubbles may be considered independent in a first approximation.

The aim of this communication is to propose a flow model for gas dispersion into liquids inhibiting coalescence that seems more realistic than the piston flow model. Then criteria will be deduced to insure, when the real behavior of the gas phase is ignored, the independence within 10% relatively to this behavior of the mass transfer parameter data measured in a laboratory scale well-stirred tank by the chemical method. First, the model is used to represent the behavior of the dispersion of not shrinking bubbles, that is, absorption of diluted gas. Then, by analogy with the work of Linek and Mayrhoferova (1969), the model is applied to the case of the dispersion of shrinking bubbles, that is, absorption of pure gas.

THEORY: CHARACTERISTIC DISTRIBUTIONS OF THE DISPERSION

The calculation scheme of the two considered cases is presented in Figure 1. Assumptions are either specific or common for both types of dispersion.

1. The bubbles originated by the distributor do not loose their identity up to the moment they leave the reactor or up to their complete dissolution inside the liquid bulk.
2. Each bubble is perfectly mixed except for instantaneous chemical regime.
3. Mass transfer resistance is located in the liquid phase, and the true liquid side mass transfer coefficient only depends on the bubble diameter δ_o as follows:

$$k_L = \overline{xk_L}\delta_o{}^{\mu} \qquad (1)$$

The most frequent value proposed in literature is $\mu = 0.5$ (Levich, 1962; Akita and Yoshida, 1974).

4. For each bubble, the liquid phase composition is invariable; that is, the liquid evolution time is sufficiently slow to be neglected when compared to the residence time of a bubble inside the dispersion.

The assumptions for the dispersion of the nonshrinking bubbles are:

1. The distribution function $f(\delta_o)$ of the size of the bubbles is invariable in the dispersion and is represented by the Bayens (1967) distribution

$$f(\delta_o) = K\delta_o{}^2 \exp(-k^2\delta_o{}^2) \qquad (2)$$

K and k are empirical constants. This distribution has been successfully used for gas-liquid dispersions (Padmanabhan and Gal-Or, 1968).

2. The reduced residence time of each bubble depends on the magnitude of its diameter as follows:

$$\theta_o = t_{\delta_o}/\tau_G = \lambda\delta_o{}^{-\nu} \qquad (3)$$

The bubble diameter fraction δ_o, $\delta_o + d\delta_o$ in the dispersion occupies the gas volume fraction dV_o/V_o, and the corresponding volumetric flow rate is

$$\frac{dQ_o}{Q_o} = \frac{dV_o}{\theta_o V_o} = \frac{\delta_o{}^{\nu+3}f(\delta_o)\,d\delta_o}{\lambda\displaystyle\int_0^{\infty} \delta_o{}^3 f(\delta_o)\,d\delta_o} \qquad (4)$$

Normation of Equation (4) leads to

$$\lambda = I_\nu/k^\nu = \frac{1}{2k^\nu}\int_0^{\infty} y^{\nu/2+2}\exp(-y)\,dy \qquad (5)$$

and if we consider the relations (2), (3), (4), and (5), the outlet fraction of gas flow rate dQ_o/Q_o of age comprised between θ_o and $\theta_o + d\theta_o$ is

$$E(\theta_o) = \frac{1}{\nu} I_\nu{}^{6/\nu}\theta_o{}^{-(2+6/\nu)}\exp[-(I_\nu/\theta_o)^{2/\nu}] \qquad (6)$$

Representative theoretical curves are shown in Figure 2. As the probability for the bubble to leave or to stay inside the dispersion depends on the competition between the drag force and the buoyancy force acting on it, this normally leads to $1 \leq \nu \leq 2$. It may be observed in Figure 2 that the distributions obtained for $1 \leq \nu \leq 2$ are

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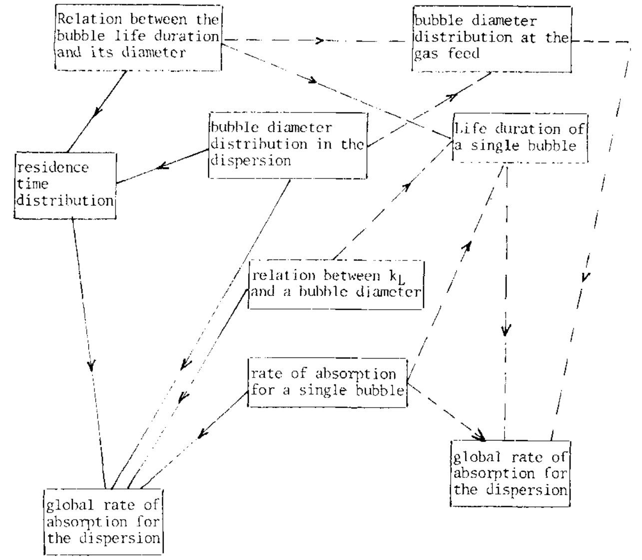

Figure 1. Calculation scheme of the rate of absorption in the dispersion. ——— nonshrinking bubbles, - - - - - shrinking bubbles.

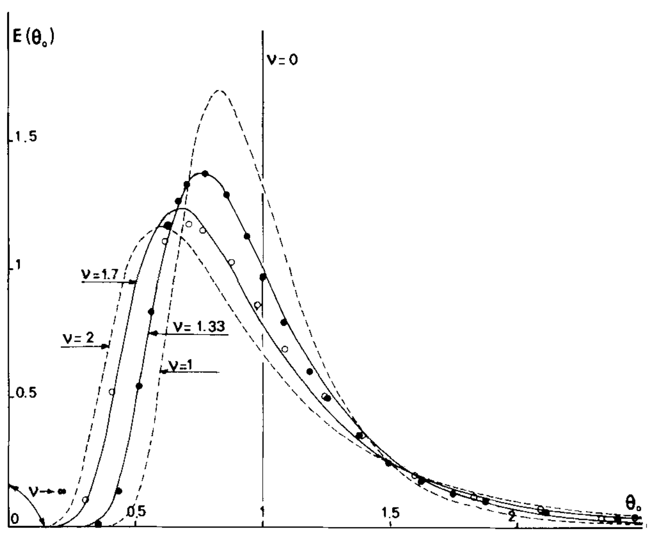

Figure 2. Residence time distribution of the independent bubbles. Comparison with the data of Gal-Or and Resnick (1966): ● u_S = 0.24 cm/s, N = 7.30 rev/s, ○ u_S = 1.4 cm/s, N = 7.30 rev/s.

quite different from the delta function for the piston flow and the exponential function for the perfectly mixed flow. Note that the distribution model may represent the piston flow when $\nu \rightarrow 0$ and a short-circuit behavior for ν sufficiently high. For example, the Gal-Or and Resnick (1966) experimental data for a gas dispersion in agitated sulfite solutions have been correctly fitted with $1.33 \leq \nu \leq 1.7$.

The assumptions for the dispersion of shrinking bubbles are:

1. The gas phase is satured in liquid vapor at the working temperature after its introduction into the reactor. The partial pressure inside the bubble is constant, and thus the initial solute concentration γ_o in the gas feed may be considered constant.
2. The bubble travels the length H of its trajectory with a continuously decreasing velocity

$$u = \frac{H}{\lambda \tau_G} \delta^\nu \tag{7}$$

The mass balance in gas solute for the bubble is

$$-\gamma_o \frac{dV_b}{dt} = \pi d^2 \overline{\Phi}_o$$

with the initial condition $\delta = \delta_o$ for $t = 0$. This leads, after integration, to

$$\delta = \delta_o - \frac{\theta}{3\overline{\theta}_o} \tag{8}$$

Both Equations (7) and (8) provide the exit reduced diameter δ_s of the bubble having an initial diameter δ_o:

$$\begin{aligned} \delta_s/\delta_o &= [1 - (\delta_{co}/\delta_o)^{1+\nu-\mu}]^{1/(1+\nu-\mu)} && \text{if} \quad \delta_o > \delta_{co} \\ \delta_s/\delta_o &= 0 && \text{if} \quad \delta_o < \delta_{co} \end{aligned} \tag{9}$$

$$\delta_{co} = \left[\frac{I_\nu(1-C)(1+\nu-\mu)}{3k^\nu \theta_o} \right]^{1/(1+\nu-\mu)} \tag{10}$$

In the previous relationships, δ is the bubble diameter reduced by the bubble Sauter diameter $\overline{d}_o$ in a reference dispersion that would be obtained if the gas was not consumed, and the reduced time $\overline{\theta}_o = \overline{\tau}_o/\tau_G$ is the ratio between the depletion characteristic time $\overline{\tau}_o = (\overline{d}_o\gamma_o/6\overline{\phi}_o)$ for a bubble having a diameter $\overline{d}_o$ at the gas feed and the gas residence time τ_G in the reference dispersion.

Practically, the distribution function of the size of the bubbles $f(\delta_o)$ defined by Equation (2) is issued from the distribution at the gas feed $g(\delta_o)$ defined by Equation (4):

$$g(\delta_o)\,d\delta_o = \frac{dQ_o}{Q_o} = \frac{k^{6+\nu}}{I_\nu} (\delta_o)^{5+\nu} \exp(-k^2\delta_o^2)\,d\delta_o \tag{11}$$

Moreover, it is assumed that $g(\delta_o)$ is the same in the absence or presence of absorption, which means that the local turbulence conditions in the neighborhood of the stirrer are nearly the same in both cases.

RESULTS CONCERNING NONSHRINKING DISPERSIONS

The previous assumptions together with the classical relationships of the different absorption rates depending on the chemical reaction regimes (Danckwerts, 1970; Laurent and Charpentier, 1975; Charpentier, 1978) lead to the theoretical mean reduced values Γ_S of the gaseous reactant in the gas exit stream and to absorption efficiency E_A for a gas-liquid dispersion, where a_o is the specific interfacial area and $\overline{k}_L$ is the mean true liquid-side mass transfer coefficient defined for a bubble diameter $\overline{d}_o$. Thus, with this value of E_A, apparent values a_{app} and $(k_La)_{\text{app}}$ may be calculated in assuming that the gas phase is perfectly micromixed and then compared with a_o and $\overline{k}_La_o$. For example, in the case of a gas absorption accompanied by a rapid pseudo first-order reaction, the reduced exit concentration for a bubble of initial diameter δ_o will be

$$\Gamma = \exp\left[-k\frac{\theta}{\overline{\theta}_o}\left(\frac{\theta}{I_\nu}\right)^{1/\nu}\right] \tag{12}$$

Then, the exit solute concentration of bubbles in the dispersion will be

$$\Gamma_S = \int_o^\infty \Gamma \cdot E(\theta_o)\,d\theta_o = \frac{1}{\nu} I_\nu^{6/\nu} \int_o^\infty$$

$$\theta^{-(2+6/_\nu)} \exp\left[-k\frac{\theta}{\overline{\theta}_o}\left(\frac{\theta}{I_\nu}\right)^{1/\nu} - \left(\frac{\theta}{I_\nu}\right)^{2/\nu}\right] d\theta \tag{13}$$

If the gas phase is assumed perfectly micromixed, the mass balance is written

$$Q\gamma_o(1 - \Gamma_S) = a_{\text{app}} v_L \bar{\phi}_o \Gamma_S \tag{14}$$

and a comparison between a_{app} and the geometrical area a_o gives

$$\frac{a_{\text{app}}}{a_o} = \frac{\bar{d}_o \gamma_o}{6\bar{\phi}_o \tau_G}\left(\frac{1}{\Gamma_S} - 1\right) = \bar{\theta}_o\left(\frac{1}{\Gamma_S} - 1\right) \tag{15}$$

The variations of $\Gamma_S = 1 - E_A$ and a_{app}/a_o with the reduced time $\bar{\theta}_o = \bar{\tau}_o/\tau_G$ in the case of a bubble distribution in the dispersion predicted by Equation (2) together with $\nu = 1$ and $\nu = 2$ and in the case of a uniform dispersion ($\delta_o = 1$) either in piston flow (RP) or perfectly mixed (PM) are presented in Figure 3. Note that it must be distinguished between the state of perfect mixing that corresponds to $E(\theta_o) = \exp(-\theta_o)$ for the independent bubbles and the state of perfect micromixing defined for a uniform concentration in the gas phase.

It is observed that if all the possible mixing states for the dispersion are comprised between the proposed model and the perfectly mixed flow, the estimated value a_{app} will approximate the true value a_o within 10% if the conditions $\bar{\theta}_o \geqq 2.60$ or $E_A \leqq 0.30$ are fulfilled. This means that less than 30% of the gaseous reactant must be absorbed if the influence of the mixing state on the estimated value of the transfer parameter can be ignored. Limiting values of E_A and $\bar{\theta}_o$ for the different chemical regimes usually employed to determine the interfacial parameters in gas-liquid dispersions and leading to $[(k_L a)_{\text{app}}/\bar{k}_L a_o] = 1 \pm 0.1$ and $a_{\text{app}}/a_o = 1 \pm 0.1$ are presented in Table 1.

Though these results may be considered only like sufficient conditions, they state precisely the limits of the chemical method. So in the slow chemical regime (used to determine $k_L a$), it is easy to satisfy the condition $\bar{\theta}_o > 3.3$. Let us consider, for example, the sodium sulfite system in the presence of Co^{++} ions as a catalyst with the currently used experimental conditions $C_B{}^o =$ 0.2 kgmole/m^3, $\bar{\phi}_o = 8.27 \times 10^{-9}$ kgmole/m^2·s, $\gamma_o =$ 8.32×10^{-3} kgmole/m^3, $[Co^{++}] = 10^{-6}$ kgmole/m^3, and $\bar{d}_o = 10^{-3}$ m. This gives $\bar{\tau}_o = 168$ s and then $\tau_G <$ 51 s to satisfy $\bar{\theta}_o = \bar{\tau}_o/\tau_G > 3.3$. Such a gas residence time has been used in practice in industrial size equipment (Cooper et al., 1944).

On the contrary, the same gas-liquid reaction with the conditions of rapid pseudo second-order regime in oxygen (to determine a), that is, $C_B{}^o = 0.8$ kgmole/m^3, $[Co^{++}]$ $= 3.56 \times 10^{-4}$ kgmole/m^3, $\bar{\phi}_o = 1.56 \times 10^{-7}$ kgmole/m^2·s, cannot be used easily. Indeed, it is calculated from the condition $\bar{\theta}_o > 3.7$ proposed in Table 1 that $\bar{\tau}_o =$ 8.9 s and $\tau_G < 2.4$ s. Such a small gas residence time limits the applicability of this chemical method to the small scale units. This may explain why interfacial areas have been measured in tanks the volume of which are not bigger than 1 m^3, with gas superficial velocity as high as 0.047 m^3/m^2·s (Reith, 1968).

RESULTS CONCERNING GAS SHRINKAGE

Some advantages may be obtained in determining mass transfer by the absorption of a pure gas, such as the disappearance of the variations of solute concentration inside the gas phase. However, the values measured are closely connected with the operating conditions, especially with the initial specific absorption rate $\bar{\phi}_o$, because of the progressive gas shrinkage. Indeed, the measured interfacial parameters cannot be generalized except when the absorption rate is small enough so that a and $k_L a$ may be assimilated to the reference a_o and $\bar{k}_L a_o$ values corresponding to the dispersion of not shrinking bubbles that would be obtained with the same entering gas flow rate, the same liquid holdup, and the same stirring conditions. Thus, like for the case of not shrinking dispersion, it is now possible to deliver limiting criteria so that the measured interfacial parameters approximate the reference values within 10%. This leads to a superior limit of the absorption efficiency $E_A = 1 - Q_S/Q_o$ This is presented here for the slow and the rapid pseudo m-n^{th}-order chemical reaction regimes. Indeed, from the relationships (9) and (11), the exit volumetric gas flow rate Q_S and the gas volume V may be analytically determined and then compared with the similar values obtained in the case of not shrinking dispersion.

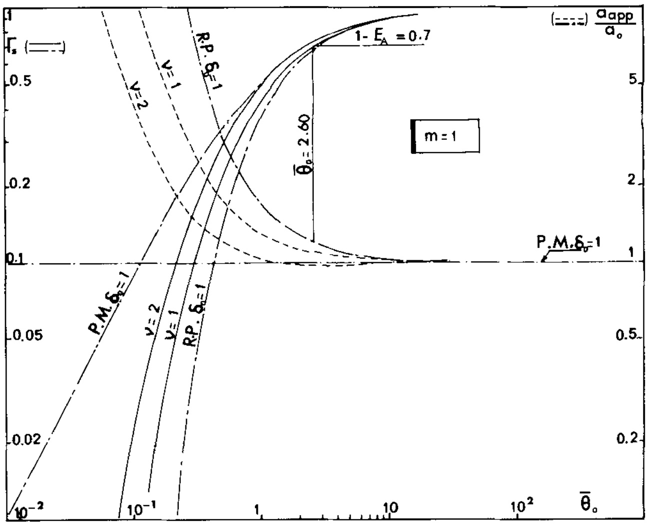

Figure 3. Variation of $\Gamma_S = 1 - E_A$ and a_{app}/a_0 with $\bar{\theta}_0$ for a rapid pseudo first-order chemical reaction.

The fraction δ_o, $\delta_o + \Delta\delta_o$ of the gas feed corresponds to a volume ΔV and to an interfacial area ΔA inside the dispersion in which the life duration or the residence time of the bubble $\theta(\delta_o)$ is given by Equations (8) and (9). Between θ and $\theta + d\theta$ a mass balance on the differential element of the reactor occupied by the fraction δ_o, $\delta_o + \Delta\delta_o$ is written:

$$\frac{d(\gamma_o \Delta Q)}{d(\Delta V)} = \bar{\phi}_o \frac{d(\Delta A)}{d(\Delta V)} \tag{16}$$

By definition $\dfrac{d(\Delta A)}{d(\Delta V)} = \dfrac{6}{\bar{d}_o \delta}$; thus

$$d(\Delta V) = \bar{\tau}_o \delta d(\Delta Q) \tag{17}$$

In steady state regime, there is no accumulation of the bubbles in the different element of the dispersion, and

$$\Delta Q = (\delta/\delta_o)^3 \Delta Q_o \tag{18}$$

The combination of the Equations (11), (17), and (18) leads to

$$\frac{Q_s}{Q_o} = \frac{k^{6+\nu}}{I_\nu}\int_{\delta_{co}}^{\infty} \left[1 - \left(\frac{\delta_{co}}{\delta_o}\right)^{1+\nu-\mu}\right]^{3/(1+\nu-\mu)} g(\delta_o) d\delta_o \tag{19}$$

$$\frac{V}{V_o} = \frac{3}{4-\mu} \cdot \frac{\overline{\theta}_o}{1-C} \left[\int_o^\infty (\delta_o)^{1-\mu} g(\delta_o)\, d\delta_o - \int_{\delta_{co}}^\infty (\delta_o)^{1-\mu} \left[1 - \left(\frac{\delta_{co}}{\delta_o} \right)^{1+\nu-\mu} \right]^{(4-\mu)/(1+\nu-\mu)} g(\delta_o)\, d\delta_o \right] \quad 20)$$

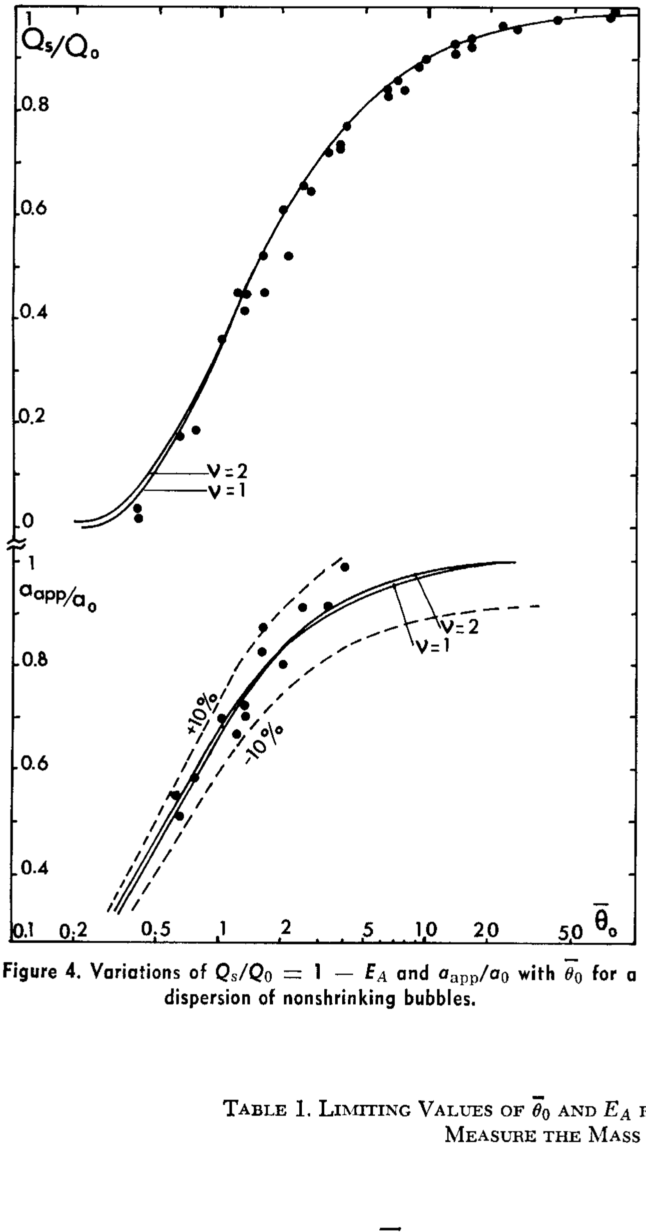

Figure 4. Variations of $Q_s/Q_0 = 1 - E_A$ and a_{app}/a_0 with $\overline{\theta}_0$ for a dispersion of nonshrinking bubbles.

Then a mass balance for the gas solute in the reactor and a comparison with the reference values for the case of no absorption leads to

$$\frac{a_{app}}{a_o} = \frac{(k_L a)_{app}}{\overline{k}_L a_o} = \frac{\overline{\theta}_o}{1-C}\left(1 - \frac{Q_s}{Q_o}\right) \quad (21)$$

Variations of Q_s/Q_o and a_{app}/a_o with $\overline{\theta}_o$ for a rapid pseudo m-n^{th} order are shown in Figure 4. The experimental data of Linek and Mayrhoferova (1969) concerning the absorption of air or pure oxygen into sulfite solutions in a standard stirred tank are also reported, and a good fit is observed. These results together with the complementary one presented by Midoux (1978) afford the following limiting conditions:

$$a_{app} \simeq a_o \text{ within } 10\% \text{ if } \overline{v}_o \geqq 3.2 \text{ and } E_A \leqq 0.29 \quad (22)$$

$$(k_L a)_{app} \simeq \overline{k}_L a_o \text{ within } 10\% \text{ if } \overline{\theta}_o \geqq 4.6 \text{ and } E_A \leqq 0.20$$

In fact, the domain of application is relatively confined because the use of pure gas generally entails high values of the absorption rate $\overline{\phi}_o$ and thus small values of $\overline{\theta}_o$, even with laboratory scale equipment. However, the domain of the experiments may be widened if the exit flow rate Q_s is measurable and if the influence of the coalescence phenomena may be neglected. This last assumption seems reasonable because pure gas bubbles shrink quickly during their stay in the reactor and then have less tendency to coalesce. Thus, for $Q_s/Q_o \geqq 0.05$, the following relationship could be used as a first approximation:

$$\frac{a_o}{a_{app}} = \frac{\overline{k}_L a_o}{(k_L a)_{app}} = \frac{3[1-(Q_s/Q_o)]^{1/3}}{1-(Q_s/Q_o)} \quad (23)$$

This approximation enlarges the range of the small values $\overline{\theta}_o$ by a factor of about 10 and in some cases allows for the measurement of significative values of the mass transfer parameters for absorption efficiency close to unity. For example, when applied to the data of Linek and Mayrhoferova, the fit was within 9%, which is comparable to the reproducibility of the experiments (Midoux, 1978).

Table 1. Limiting Values of $\overline{\theta}_0$ and E_A for the Various Chemical Regimes Used to Measure the Mass Transfer Parameters

Regime	$\overline{\phi}_0$	Parameter to determine	Order m	Minimum value of $\overline{\theta}_0$	Maximum value of E_A
Physical absorption or slow chemical	$\overline{k}_L \frac{\gamma_0}{He}$	$k_L a$		3.3	0.25
Intermediary pseudo 1-n^{th}-order chemical	$(\overline{k}_L^2 + D_L k_{1n}(C_B^0)^n)^{1/2} \frac{\gamma_0}{He}$	a and $k_L a$	1	4.0	0.20
Rapid pseudo m-n^{th}-order chemical	$\left(\frac{2}{m+1} D_L k_{mn}(C_B^0)^n\right)^{1/2} \left(\frac{\gamma_0}{He}\right)^{\frac{m+1}{2}}$	a	0 ½ 1 2 2	1.35 1.80 2.60 3.70 4.80	0.48 0.41 0.30 0.21 0.16
Instantaneous chemical	$\overline{k}_L \frac{D_{BL}}{D_L} \frac{C_B^0}{z}$	$k_L a$		3.3	0.27
Instantaneous chemical at the interface	$k_G p$	$k_G a$		$\overline{\theta}_D > 20$	0.55

CONCLUSIONS

A model that is the antithesis of the perfect coalescent and thus perfectly mixed dispersion is proposed to describe a noncoalescent gas-liquid dispersion of shrinking (pure gas) and not shrinking (dilute solute) bubbles. This has been done in generalizing the behavior of a single bubble to the dispersion with the help of an original residence time distribution model (Equation 6). This has led to:

1. Present the limiting sufficient criteria to set the validity and the accuracy of the mass transfer parameters determined by the chemical method. The authors think that these criteria can be considered as an important laboratory tool.
2. Extend the model proposed by Linek and Mavrhoferova (1969) for the absorption of pure gas in which uniform initial gas bubble distribution was assumed. It is probable that this new model will be helpful in the modeling of the reactors used for hydrogenation, nitration, and chlorination with pure gas.
3. Show the limits of the chemical method for the determination of interfacial area with the use of a rapid pseudo m-n^{th} order. Indeed, the absorption rates of the employed chemical systems (Danckwerts, 1970; Laurent and Charpentier, 1975) are too high and following the criteria of Table 1 likely do not allow to carry out experiments in industrial scale equipment (several tens of cubic meters). This means that the scale-up by the use of this technique seems rather uncertain.

NOTATION

a, a_o, a_{app} = interfacial area per unit liquid volume, geometrical value for a dispersion of nonshrinking bubbles, apparent value measured by the chemical method (L^{-1})
$C_B{}^o$ = concentration of reactant in liquid bulk (kgmole $\cdot L^{-3}$)
C = reduced concentration of the free dissolved gas in liquid $(-)$
d = diameter for a bubble (L)
$\overline{d}_o$ = Sauter diameter for a dispersion of nonshrinking bubbles (L)
D_{BL}, D_G, D_L = diffusion coefficient for the liquid reactant, for solute in the gas phase and in the liquid phase $(L^2 \cdot T^{-1})$
E_A = gas absorption efficiency $(-)$
$E(\theta_o)$ = residence time distribution $(-)$
$f(\delta_o)$ = bubble reduced diameter distribution function $(-)$
$g(\delta_o)$ = bubble reduced diameter distribution function at the gas feed $(-)$
H = length of the trajectory of a bubble (L)
He = Henry's law constant $(-)$
I_ν = gamma function of argument $(\nu/2 + 3)$ $(-)$
k = $8/3\sqrt{\pi}$ $(-)$
k_{ln}, k_{mn} = pseudo l-n^{th}, pseudo m-n^{th} order kinetic constant $(L^3 \cdot \text{kgmole}^{-1})^{m+n-1} \cdot T^{-1}$
k_G, k_L = true gas side, liquid side transfer coefficient $(\text{kgmole} \cdot L^{-2} \cdot T^{-1} \cdot \text{pressure}^{-1})$, $(L \cdot T^{-1})$
$\overline{k}_L$ = k_L value for a bubble of diameter $\overline{d}_o$ $(L \cdot T^{-1})$
$k_La, \overline{k}_La_o, (\overline{k}_La)_{\text{app}}$ = liquid overall mass transfer coefficient per unit liquid volume, real mean value for a dispersion of nonshrinking bubbles, apparent value measured by chemical method (T^{-1})
K = $4k^3/\sqrt{\pi}$ $(-)$
m, n = order of reaction with respect to the gaseous, liquid reactant $(-)$
N = rotational speed of agitator (T^{-1})
P = partial pressure of soluble gas in bulk of gas $(M \cdot L^{-1} \cdot T^{-2})$
Q, Q_o, Q_s = volumetric gas flow rate, inlet, outlet conditions $(L^3 \cdot T^{-1})$
t = time (T)
t_{δ_o} = residence time or life duration of a bubble of diameter δ_o in the dispersion (T)
u = bubble velocity $(L \cdot T^{-1})$
u_s = superficial gas velocity $(L \cdot T^{-1})$
V, V_o = volume occupied by the gas phase in the dispersion, reference volume for a dispersion of nonshrinking bubbles (L^3)
V_b = volume for a bubble (L^3)
V_L = volume of liquid (L^3)
z = number of moles of reactant reacting with each mole of dissolved gas $(-)$

Greek Letters

γ_o = inlet solute gas concentration in bulk of gas $(\text{kgmole} \cdot L^{-3})$
Γ = inlet gas concentration reduced by γ_o for a single bubble $(-)$
Γ_s = outlet gas concentration reduced by γ_o $(-)$
$\delta, \delta_o, \delta_{co}, \delta_s$ = bubble diameter reduced by $\overline{d}_o$, value at the distribution, critical value for a shrinking bubble so that its probability to exit is just zero, value at the exit $(-)$
$\theta, \theta_o, \overline{\theta}_o, \overline{\theta}_D$ = reduced time t_δ/τ_G, t_{δ_o}/τ_G, $\overline{\tau}_o/\tau_G$, $\overline{\tau}_D/\tau_G$ $(-)$
λ = constant $(-)$
μ = constant $(-)$
ν = residence time distribution parameter $(-)$
$\overline{\tau}_D$ = characteristic diffusion time, $\overline{d}_o{}^2/4D_G$ (T)
τ_G = gas residence time in dispersion of nonshrinking bubbles (T)
$\overline{\tau}_o$ = depletion characteristic time for a bubble (T)
$\overline{\phi}_o$ = rate of absorption for a bubble of diameter $\overline{d}_o$ where the solute concentration is γ_o $(\text{kgmole} \cdot L^{-2} \cdot T^{-1})$

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Manuscript received August 14, 1978; revision received December 5, and accepted January 11, 1979.

Velocity Profiles of Viscoelastic Fluids at the Inlet of an Annulus

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Most entry flow problems have been analyzed using boundary-layer approximations. Inherent in the analysis is the assumption of a uniform (flat) velocity profile at the inlet plane. In practice, this condition may not be achieved for viscoelastic fluids unless it is artificially generated. For example, Brocklebank and Smith (1970) and Tan and Tiu (1977) both used a flow distributor upstream of the entry to generate a flat profile in a pipe and an annulus, respectively. For many polymer melts and solutions, flow patterns upstream and downstream of the contraction are strongly influenced by the elastic properties of the fluids (Tordella, 1957; Ballenger and White, 1970; Cable and Boger, 1978). Thus, the inlet velocity profile could attain any shape other than flat for viscoelastic fluids, depending upon the fluid characteristics. Furthermore, conflicting experimental results have been reported concerning the effects of elasticity on the entry length and on the excess pressure drop (Sutterby, 1965; Boger and Ramamurthy, 1972; Busby and MacSporran, 1976). The inconsistency could be attributed to the different inlet velocity conditions employed by these workers in determining the entrance length. This paper aims to resolve experimentally the inlet velocity conditions for viscoelastic fluids flowing through an annulus. Two inlet geometries are studied: an abrupt contraction from a large to a small annulus (2:1 contraction ratio) and a smooth entry through a conical section upstream of the contraction. In both cases, no flow distributor is used in the upstream side. The flow approaches the contraction in its fully developed state.

EXPERIMENT RESULTS AND DISCUSSION

The experimental setup and procedure for velocity profile measurements in the annulus (aspect ratio of 0.42) have been presented in detail elsewhere (Tiu and Bhattacharyya, 1974; Tan and Tiu, 1977). The only alteration in the experimental equipment was the removal of the flow straightener, and also the conical entry section for the abrupt entry work, from the upstream annulus. A technique employing streak photography was used for point velocity measurements. The test fluids were dilute aqueous solutions of Separan AP30 and MG500 (partially hydrolyzed polyacrylamide, Dow Chemical).

The viscometric functions τ and N_1 were measured for all test fluids on an R16 Weissenberg rheogoniometer over the shear rate range $4 \leq \dot{\gamma} \leq 1\,112\ s^{-1}$. Power law models were used to fit the viscometric data:

$$\tau = K\dot{\gamma}^{n} \qquad (1)$$

and

$$N_1 = P_{11} - P_{22} = \sigma\dot{\gamma}^{s} \qquad (2)$$

In instances where the flow curve was not linear on a log-log plot over the entire shear rate range, it was approximated with two power law regions. Fluid parameters evaluated at the same shear rates as those encountered in each experiment were used in the data analysis. Under the experimental conditions, values of n varied from 0.34 to 0.51, and s from 0.611 to 0.875. Two relevant dimensionless groups, Reynolds number Re and elasticity number ξ, used in the analysis of data were in the range $2.53 \leq Re \leq 973$ and $0.0076 \leq \xi \leq 1.761$, respectively. The parameter ξ is considered to give a better measure of fluid elasticity for the present purpose than Weissenberg number, Deborah number, relaxation time, or stress ratio. In the

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0001-1541-80-2500-0162-$00.75.