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*The use of the chemical method
for the determination of interfacial areas
in gas-liquid contactors.*

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ABSTRACT

The interfacial area a_{chem} in a gas-liquid contactor as determined by the chemical method deviates from the true geometrical interfacial area a_{geo} , because the overall conversion of the gas phase reactant represents an incorrect average if bubble sizes and residence times are not uniform. The deviations of a_{chem} from a_{geo} become larger the broader the distribution τ_r/d_b and the higher the overall conversion Ω_A of the reactant in the gas phase.

Model calculations, which take into account both the effect of gas phase backmixing as well as the effect of bubble coalescence on the deviation of a_{chem} from a_{geo} , are performed for a mechanically agitated gas-liquid reactor and a bubble column at practical micro- and macro-mixing conditions. For a gas-liquid model reaction, which is first order in the gas phase reactant, it is found that:

1. For a mechanically agitated reactor the error in a_{chem} will always be smaller than 10% if Ω_A is lower than 0.99.
2. For a bubble column the error in a_{chem} will be smaller than 20% for most practical applications if Ω_A is lower than 0.99.

Gas-liquid model reaction systems with absorption of CO_2 in alkanolamine solutions are recommended for the determination of interfacial areas in gas-liquid contactors.



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1. INTRODUCTION

Since its introduction by Westerterp et al(1963) the chemical method has been widely used for the determination of mass transfer parameters in gas-liquid contactors. Both the interfacial area and the volumetric gas and liquid phase mass transfer coefficients, which are important parameters for the design of gas-liquid contactors, can be determined by the chemical method. The major drawback of the chemical method is its restriction to specific gas-liquid systems and their particular physico-chemical properties. Therefore, in recent years numerous alternative physical methods have been developed for the determination of interfacial areas.

All these physical methods are based on local determinations of the interfacial area a , which have to be integrated in order to obtain the overall value. Some of these physical methods determine the values for the local interfacial areas by means of optical techniques based on light scattering and light reflection, see i.e. Calderbank(1958) and Sridhar and Potter(1978). Other methods determine bubble size distributions either by means of photography or with optical and conductivity probes, see Reith and Beek(1968), Deckwer et al(1978), Buchholtz et al(1979) and Schumpe and Deckwer(1982). The interfacial area is then evaluated from the Sauter mean diameter d_s and the gas hold-up ϵ_G according to:

$$a = \frac{6 \epsilon_G}{d_s} \quad (1)$$

However, these physical methods suffer systematically from restrictions in the maximum detectable interfacial areas, geometrical limitations, maldistribution of the bubbles, bubble identification problems and an underestimation of the value of d_s for non-spherical bubbles. Besides that, it is doubtful whether the hydrodynamics of the dispersion are unaffected by the use of probes. Therefore, in our view the chemical method is still the best available method for the determination of interfacial areas in gas-liquid contactors, because if it is applied carefully an overall value for the effective interfacial area is directly obtained.

The reaction between oxygen and aqueous sodium sulphite solutions catalyzed by cobaltous ions Co^{2+} has been widely used as the standard model system for the chemical method. However, there is still disagreement about the reaction kinetics and especially about the reaction order in oxygen. This is probably caused by the sensitivity of the reaction towards small impurities in the water, the catalyst or the sulphite salt, see the review of Linek and Vacek(1981). The main advantage of this model system is the possibility to change the reaction rate constant over a wide range by changing the Co^{2+} catalyst concentration. However, it is restricted to aqueous solutions; moreover, the non-coalescing behaviour of this ionic system also limits its use, see Bartos and Satterfield(1986).

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The reaction between CO_2 and aqueous alkanolamine solutions was first introduced by Danckwerts and Sharma(1966) as an alternative model system for the determination of mass transfer parameters. Later Sridharan and Sharma(1976) showed that the reaction between CO_2 and alkanolamines in organic and viscous solutions can also be used for the same purpose. The reaction rate can be varied by choosing the amine type. In recent years alkanolamines have been used to determine mass transfer parameters in various reactor types, see a.o. Mehta and Sharma(1971), Midoux et al(1984), Oyevaar et al(1988) and Versteeg(1988).

Advantages of the reaction between CO_2 and alkanolamines are:

1. the ability to meet the different regimes of the chemical method by choosing different amines and different concentrations of these amines.
2. the possibility to work with both aqueous and organic and viscous solutions as well.
3. the certainty that the reaction order in CO_2 is equal to one.

The main disadvantage of this alternative model system is the rather high solubility of CO_2 compared to other gases, which generally results in high CO_2 conversions.

Schumpe and Deckwer(1980) showed that the combination of high conversions of the reactant in the gas phase and of non-uniform bubble sizes in gas-liquid dispersions can lead to an underestimation of the interfacial area. This is a direct result from the use of an overall conversion over the reactor to calculate the interfacial area, while the conversion within a single bubble depends non-linearly on the specific area of that bubble. Besides that, the bubbles may have different residence times τ_b . These two phenomena, the use of an overall conversion and the different residence times of the bubbles, lead to deviations of the chemically determined interfacial area a_{chem} from the true geometric interfacial area a_{geo} ; the deviations become larger the broader the distribution of τ_b/d_b and the higher the conversion of the reactant in the gas phase, see Schumpe and Deckwer(1980).

In order to calculate $a_{\text{chem}}/a_{\text{geo}}$ as a function of the overall conversion of the reactant in the gas phase and the bubble size distribution we will modify the method of Schumpe and Deckwer(1980). Model calculations will be given for both mechanically agitated reactors and bubble columns. For the mechanically agitated reactor it will be assumed that the bubble size distribution is represented by the distribution of Bayens(1967), while for the bubble column the bubble size distribution will be described by a log-normal distribution as proposed by Akita and Yoshida(1974).

In extension to Schumpe and Deckwer(1980), who assumed plug flow behaviour for the gas phase, a constant residence time τ_b for all bubbles, a complete segregation of the gas phase and no interaction between the bubbles, we will take into account the effect of gas phase backmixing as well as the effect of bubble coalescence on the deviation of a_{chem} from a_{geo} . In this study we present calculation results for a series of extreme macromixing and intermediate micromixing conditions of the gas phase:

1. The gas bubbles do not interact, remain completely segregated and all bubbles have the same residence time τ_b . We will call this the plug flow case.

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2. The gas bubbles do not interact, remain completely segregated and the residence times of the individual gas bubbles are distributed according to the distribution found in a completely mixed tank. We will call this the complete mixing case.
3. The gas bubbles do interact by means of coalescence and breakup processes. We will consider the two extreme cases of the individual bubbles having all the same residence time as in plug flow or all having a RTD as in a completely mixed tank. We will call this the intermediate micromixing case. The micromixing of the gas phase will be simulated by the model of interaction by exchange with the mean (IEM model).

Results will be given for zero, first and second order reactions in the gas phase reactant. It will be shown that, for practical conditions and a first order reaction for the gas phase reactant, which holds for the reaction between CO₂ and alkanolamines, micro- and macro-mixing will reduce the deviation of a_{chem} from a_{poo} substantially in comparison to the results for the extreme plug flow conditions of Schumpe and Deckwer(1980). All our model calculations are performed for non-shrinking bubbles and for absorption of a diluted gas phase reactant.

2. THEORY

2.1. Chemical method.

The chemical method is based on the theory of chemically enhanced absorption of a gas phase reactant A into a liquid in which an irreversible reaction takes place with a reactant B, see Sharma and Danckwerts(1970) and Westerterp et al(1984). The general equation for the chemically enhanced mole flux J_A of a component A from the gas into the liquid phase, as derived by Danckwerts(1970) using the penetration theory, is

$$J_A = \frac{k_L \sqrt{1 + Ha^2} \left(m c_{AG} - \frac{c_{AL}}{1 + Ha^2} \right)}{1 + \frac{m k_L \sqrt{1 + Ha^2}}{k_G}} \quad (2)$$

The Hatta number, Ha, equals

$$Ha = \frac{\sqrt{\frac{2}{n+1} k_{sp} c_{RL}^p (m c_{AG})^{n-1} D_A}}{k_L} \quad (3)$$

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if the chemical reaction rate in the liquid is given by $R_c = k_{n,p} (c_{B,L})^p (c_{A,L})^n$. In case the reaction is fast enough to consume A already completely in the film or if the bulk volume is much greater than the film volume, the bulk concentration of component A in the liquid $c_{A,L}$ equals zero.

Together with the fact that in most gas-liquid reactors and for systems with moderate reaction rates and low gas solubilities no gas phase mass transfer limitation occurs, Eq. (2) becomes

$$J_A = k_L m c_{A,G} \sqrt{1 + Ha^2} \quad (4)$$

With no depletion of component B in the liquid phase near the interface and $Ha > 2$ the pseudo n-th order mole flux J_A becomes equal to

$$J_A = K_n c_{A,G}^{(n+1)/2} \quad (5)$$

with

$$K_n = \left[\frac{2}{n+1} k_{n,p} c_{B,L}^p D_A m^{(n+1)} \right]^{1/2} \quad (6)$$

Knowing K_n and the residence time distribution (RTD) of the gas phase the interfacial area in a gas-liquid contactor can be obtained by measuring the overall conversion of the gas phase reactant, because the absorption rate ϕ_A equals $J_A a V_R$. Values of K_n are usually determined separately in a gas-liquid contactor with a known interfacial area, i.e. a stirred cell or a wetted wall reactor. The RTD of the gas phase is normally chosen on the base of data from literature.

2.2. Absorption from a single bubble.

Schampe and Deckwer (1980) considered the absorption of a reactant A from a single bubble into a liquid in which a fast reaction occurs of the n-th order in A and for which the mole flux J_A can be described by Eq. (5). After integration of the mass balance for a single bubble with the assumptions of constant pressure, of constant bubble size and of isothermal conditions, these authors obtained relations for the conversion ζ_A ; these are presented in Table 1. In these relations ζ_A is given for reaction orders equal to 0, 1 and 2 respectively as a function of the Stanton number St_n and the fraction y_o of A in the bubble at the inlet of the contactor.

The conversion ζ_A in a single bubble according to these relations is plotted in Fig. 1 for all three reaction orders. The value of y_o is taken to be equal to 0.21, which is the oxygen fraction in air. It

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Table 1. Relations for the conversion of a reactant A in the gas phase of a single bubble with a fast reaction occurring in the liquid phase.

n	K_n $(N/m^2)^{1/2(1-n)} \text{ m/s}$	St_n	ζ_A
0	$\sqrt{2 m k_{0,p} c_{BL}^p D_A}$	$K_0 \frac{1}{\sqrt{P}} \frac{6 \tau_b}{d_b}$	$1 - \frac{(2\sqrt{y_0} - St_0)^2}{4 y_0}$ $St_0 \leq 2\sqrt{y_0}$
1	$m \sqrt{k_{1,p} c_{BL}^p D_A}$	$K_1 \frac{6 \tau_b}{d_b}$	$1 - e^{-St_1}$
2	$m \sqrt{\frac{2}{3} m k_{2,p} c_{BL}^p D_A}$	$K_2 \sqrt{P} \frac{6 \tau_b}{d_b}$	$1 - \frac{4}{y_0 (St_2 + \frac{2}{\sqrt{y_0}})^2}$

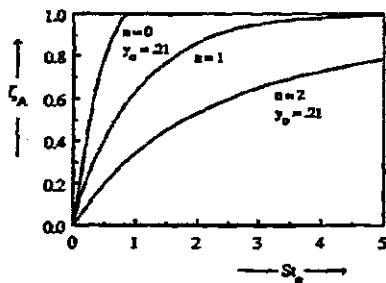


Figure 1: Conversion of reactant A in the gas phase of a single bubble vs. the Stanton number.

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can be seen that ζ_A depends non-linearly on St_n and thus also non-linearly on the interfacial area a , which is proportional to $1/d_b$, see Eq. (1). Only for low conversions ζ_A the dependence on the interfacial area a can be taken as being linear. However, for higher conversions ζ_A one must be alert that ζ_A depends non-linearly on the interfacial area a . In the case of different bubble sizes, as present in a gas-liquid dispersion, this non-linear dependence can give rise to considerable errors in the interfacial areas as calculated from the overall conversion of the gas phase reactant, see Schumpe and Deckwer(1980).

2.3. Absorption from a dispersion.

The bubble sizes in a gas-liquid dispersion are usually not uniform, but have a certain size distribution which depends on the operating conditions, the reactor geometry and the physico-chemical properties of the gas and the liquid phase. In order to calculate the effect of the bubble size distribution on the deviation of a_{chem} from a_{geo} it has to be known. For the mechanically agitated reactor we assumed that the bubble size distribution is represented by the distribution of Bayens(1967)

$$E\left(\frac{d_b}{d_s}\right) = K \frac{1}{d_s} \left[\frac{d_b}{d_s} \right]^2 \exp \left\{ -k^2 \left[\frac{d_b}{d_s} \right]^2 \right\} \quad (7)$$

with

$$k = \frac{8}{3\sqrt{\pi}} \quad \text{and} \quad K = \frac{4k^3}{\sqrt{\pi}} \quad (7a)$$

This distribution has been successfully used by Padmanabhan and Gal-Or(1968) and by Midoux et al(1980). For the bubble column the bubble diameters were assumed to follow a log-normal distribution

$$E(d_b) = \frac{1}{d_b \sigma_{\ln} \sqrt{2\pi}} \exp \left\{ -\frac{(\ln d_b - \ln d_{mb})^2}{2 \sigma_{\ln}^2} \right\} \quad (8)$$

which was proposed by Akita and Yoshida(1974) and used by Schumpe and Deckwer(1980) for their calculations. The two bubble size distribution functions are drawn in Figs 2 and 3 for a constant Sauter diameter of $d_s = 3$ mm. According to experimentally determined data of Akita and

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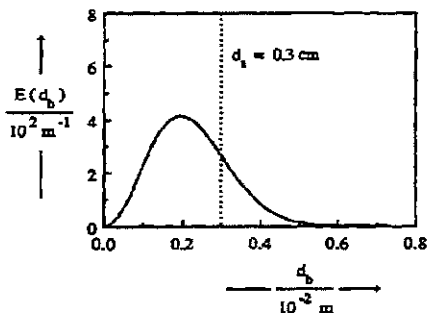


Figure 2: Rayleigh distribution with $d_p = 0.3$ cm.

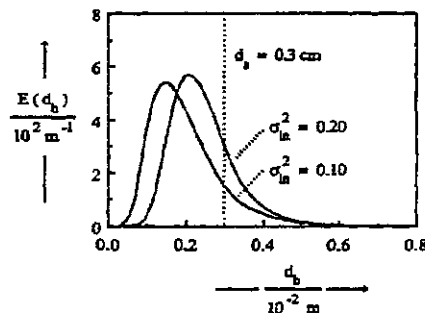


Figure 3: Log-normal distribution with $d_p = 0.3$ cm.

Yoshida(1974) variances σ_{\ln}^2 equal to 0.10 and 0.20 are realistic values for a log-normal distribution of bubble sizes in a bubble column.

Together with the assumption of complete segregation of the gas phase and thus no interaction between the bubbles, these distributions can be used for the calculation of the overall conversion Ω_A of the gas phase reactant A in a gas-liquid contactor from

$$\Omega_A = \frac{\int_0^{\infty} E(d_b) \zeta_A(d_b) d_b^3 dd_b}{\int_0^{\infty} E(d_b) d_b^3 dd_b} \quad (9)$$

The conversion of reactant A in a single bubble $\zeta_A(d_b)$ for Eq. (9) can be obtained from the relations as given in Table 1 if the absorption rate constant K_A and the residence time of the bubble τ_b are known.

In an absorption experiment under these conditions an overall conversion Ω_A equal to the one as calculated from Eq. (9) will be determined. The same values for K_A and τ_b will also be used with the relations of Table 1 in order to evaluate the Stanton number $St_{n,chem}$ and the effective interfacial area a_{chem} from the experimentally determined overall conversion Ω_A . However, the relations between the overall conversion and the Stanton numbers as given in Table 1 are only valid for an ideally micromixed gas phase and will therefore lead to deviations of a_{chem} from a_{geo} . The assumed bubble diameter distributions can also be used to calculate the true geometrical values for $St_{n,geo}$ and a_{geo} from the Sauter mean bubble diameter. The values obtained for a_{chem} and a_{geo} can be compared and used to calculate the effects of the overall gas phase conversion and a bubble size distribution on the deviation of a_{chem} from a_{geo} under segregated conditions.

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This deviation then represents the maximum error in the determination of the interfacial area by means of the chemical method. Any interaction between the bubbles will average the concentration of the gas phase reactant among the bubbles and will therefore lead to smaller errors. In the next part of this study we will generalize this calculation model and evaluate the effects of both backmixing of the gas phase and coalescence of the bubbles on the deviations of a_{chem} from a_{geo} considerably.

3. MODEL CALCULATIONS

3.1. The plug flow case.

3.1.1. Calculation backgrounds.

Schumpe and Deckwer(1980) showed that the error in a_{chem} can be as large as 50% for fast gas-liquid reactions and high conversions of the reactant originally present in the gas phase. These authors assumed plug flow behaviour for the gas phase with a constant residence time τ_b for all bubbles and used the log-normal distribution as given in Eq. (8) to calculate $a_{\text{chem}}/a_{\text{geo}}$ as a function of τ_b . In their calculations they varied the variance σ_{\ln}^2 and assumed the mean bubble diameter d_{mb} to be constant. As a result of this assumption in their calculations the Sauter mean diameter d_s and thus a_{geo} varied with σ_{\ln}^2 . In our view it is better to keep d_s constant in order to study the influence of σ_{\ln}^2 on $a_{\text{chem}}/a_{\text{geo}}$, because only for this condition a_{geo} is constant for each Sauter diameter d_s . This will be done in the calculations that are presented in the next part of this study. The mean bubble diameter d_{mb} can then be calculated from the following relation as derived by Akita and Yoshida(1974) for the log-normal distribution function

$$\frac{d_s}{d_{\text{mb}}} = e^{2.5\sigma_{\ln}^2} \quad (10)$$

3.1.2. Calculation results.

Results on $a_{\text{chem}}/a_{\text{geo}}$, as calculated according to the aforementioned relations, under the assumption of plug flow behaviour for the gas phase with a constant residence time τ_b for all bubbles are given as a function of $(1 - \Omega_A)$ in Fig. 4. The results are obtained for a first order reaction and a log-normal distribution with $d_s = 3$ mm and $\sigma_{\ln}^2 = 0.10$ or 0.20. It can be seen that errors in a_{chem} larger than 20% occur only at overall conversions Ω_A larger than 0.90 and that for $\Omega_A < 0.99$ the errors in a_{chem} will be always smaller than 35%. Errors in the range of 50% as reported by Schumpe and Deckwer(1980) can only be obtained at extremely high overall conversions Ω_A above 0.99.

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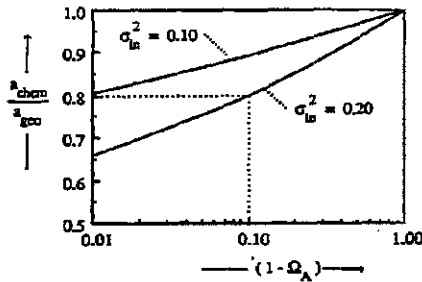


Figure 4: Ratio a_{chem}/a_{geo} of a log-normal distribution with $d_s = 3$ mm vs. $(1 - \Omega_A)$ for a 1-order reaction and plug flow of the gas phase.

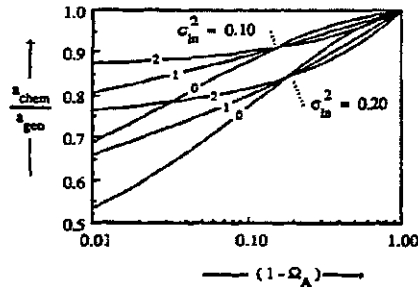


Figure 5: Ratio a_{chem}/a_{geo} of a log-normal distribution vs. $(1 - \Omega_A)$ for 0, 1 and 2-order reactions and plug flow of the gas phase.

Plotting the results in the form of Fig. 4 revealed also that for a log-normal distribution as well as for a Baysens distribution the ratio a_{chem}/a_{geo} for zero, first and second order reactions is only a function of the overall conversion Ω_A and independent of the Sauter mean diameter d_s and the gas inlet fraction y_g . This offers the possibility to generalize the results on a_{chem}/a_{geo} independent from d_s and y_g in order to study the effects of bubble size distribution and overall conversion Ω_A on the deviation of a_{chem} from a_{geo} more closely.

Results as calculated on a_{chem}/a_{geo} for all three reaction orders are plotted versus $(1 - \Omega_A)$ in Fig. 5 for a log-normal distribution with $\sigma_{in}^2 = 0.10$ and 0.20 . It can be seen that for an overall conversion Ω_A above 0.85 the deviation of a_{chem} from a_{geo} decreases with increasing reaction order.

3.2. The complete mixing case.

3.2.1. Calculation backgrounds.

The assumptions of plug flow behaviour for the gas phase and of a constant residence time τ_b for all bubbles is certainly not realistic for a mechanically agitated gas-liquid reactor. The scarce literature data on the RTD of the gas phase for this reactor indicate that, above the critical agitation rate N_0 for a fully developed dispersion, the RTD of the gas phase is in between that of one and two completely mixed tank reactors in series, see Hanhart et al(1963) and Gal-Or and Resnick(1966). Therefore, it is justified as a first approximation to assume that the RTD of the gas phase in a mechanically agitated reactor is equal to that of a completely mixed tank reactor and can be described by the distribution function

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$$E(t) = \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right) \quad (11)$$

If we furthermore assume that the bubbles of one particular diameter d_b have the same RTD as the gas phase, we can calculate the overall conversion for each class of bubbles with diameter d_b from

$$\zeta_A(d_b) = \int_0^{\infty} E(t) \zeta_A(d_b, t) dt \quad (12)$$

For a zero and first order reaction Eq. (12) can be solved analytically, which results for a zero order reaction in

$$\zeta_A(d_b) = \frac{St_0}{\sqrt{y_0}} + \frac{St_0^2}{2y_0} \left(\exp\left(-\frac{2\sqrt{y_0}}{St_0}\right) - 1 \right) \quad (13)$$

and for a first order reaction in the well known relation

$$\zeta_A(d_b) = \frac{St_1}{1 + St_1} \quad (14)$$

For a second order reaction Eq. (12) can only be solved numerically. The conversion $\zeta_A(d_b)$ for a class of bubbles with a RTD of a completely mixed tank reactor according to these relations is plotted in Fig. 6 for all three reaction orders. After substitution of $\zeta_A(d_b)$ in Eq. (9) the overall conversion Ω_A over the whole reactor of the gas phase reactant A can be calculated. Especially for a second order reaction these calculations demand long computation times.

The relations between $St_{n, \text{chem}}$ and Ω_A for a completely mixed gas phase, which is perfectly mixed on a microscale, are different from the relations for plug flow as given in Table 1, because the driving force for mass transfer from the gas to the liquid phase is different. The following general relation between $St_{n, \text{chem}}$ and Ω_A holds for a completely mixed gas phase, which is perfectly mixed on a microscale, and is used for the evaluation of absorption experiments

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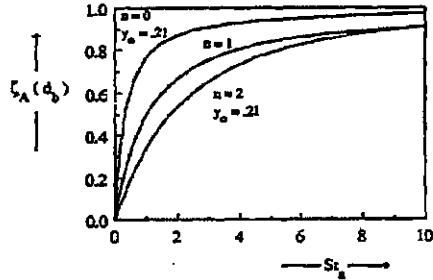


Figure 6: Conversion of a reactant A in a class of bubbles with a RTD of a completely mixed tank reactor vs. the Stanton number.

$$St_{n, \text{chem}} = \frac{\Omega_A}{(1 - \Omega_A)^{(n+1)/2} y_0^{(n-1)/2}} \quad (15)$$

These values for $St_{n, \text{chem}}$ are then substituted in the relations for the Stanton numbers in Table 1 in order to evaluate the effective interfacial area a_{chem} .

For a completely mixed and segregated gas phase with only one uniform bubble diameter d_b the overall conversion Ω_A , as calculated from Eq. (9), is equal to the experimentally determined conversion of the gas phase reactant. Only under these conditions a_{chem} equals a_{geo} at all overall conversions Ω_A . However, any non-uniformity in the bubble sizes will cause a_{chem} to deviate from a_{geo} , because the conversion $\zeta_A(d_b)$ in a class of bubbles with diameter d_b depends non-linearly on the interfacial area of the bubble, see Fig. 6.

3.2.2. Calculation results.

We calculated $a_{\text{chem}}/a_{\text{geo}}$ for the two extreme RTD's of plug flow and of complete mixing under segregated conditions; the results are plotted in Fig. 7 for a Bayens distribution and for all three reaction orders. It can be concluded from Fig. 7 that for a completely mixed gas phase and a first order reaction the deviation of a_{chem} from a_{geo} will always be smaller than 0.90 for $\Omega_A < 0.99$. However, for a zero and second order reaction the deviations of a_{chem} from a_{geo} become considerably larger than for plug flow behaviour of the gas phase. For these two reaction orders the errors in a_{chem} become larger than 50% for overall conversions Ω_A larger than 0.85.

In the case of a zero order reaction these large errors are caused by the presence of bubbles with $St_0 > 2 y_0^{0.5}$, see Table 1, which are depleted of gas phase reactant and do not contribute anymore to the mass transfer from the gas to the liquid phase. This leads to an underestimation of the true interfacial area in the dispersion, because a_{chem} is evaluated with the assumption that all bubbles

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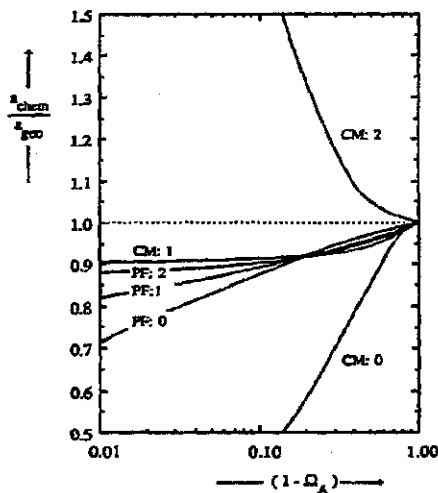


Figure 7: Ratio a_{chem}/a_{geo} of a Bayens distribution vs. $(1 - \Omega_A)$ for 0, 1 and 2-order reactions and complete mixing (CM) or plug flow (PF) of the gas phase.

contribute to the mass transfer until the gas phase is completely depleted of reactant.

The cascade model of N completely mixed tank reactors in series can be used to describe intermediate macromixing behaviour of the gas phase in between plug flow and complete mixing. Some results for intermediate macromixing of the gas phase and a first order reaction are given in the Appendix. As expected these results are in between the results for the two extreme RTD's and do not alter the conclusions, which can be drawn from Fig. 7.

The main conclusion now is that the error in a_{chem} , as determined by the chemical method, is affected considerably by the macromixing behaviour of the gas phase. For a zero and second order reaction and a completely mixed gas phase the error in a_{chem} is a strong function of the overall conversion Ω_A . Examples of gas-liquid model reaction systems with a zero and second order with respect to the gas phase reactant are the absorption of oxygen in aqueous dithionite and aqueous sulphite solutions respectively, see Jhaveri and Sharma(1968) and Linek and Vacek(1980). We see that in a mechanically agitated gas-liquid reactor with a completely mixed gas phase the accuracy for these systems is always within 10% if the overall conversion Ω_A is kept below 0.40 and 0.60 respectively, whatever the real micromixing behaviour of the gas phase will be. The use of these systems at higher conversion levels leads to extremely large errors in the determination of the interfacial area.

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As mentioned before the major disadvantage of the reaction between CO_2 and alkanolamine solutions is the rather high solubility of CO_2 , which can lead to high conversions of CO_2 . However, for the particular case of a mechanically agitated gas-liquid reactor and a first order reaction, which is the case for the reaction between CO_2 and alkanolamines, it can be concluded that the error in a_{chem} will always be smaller than 10% for overall conversions Ω_A smaller than 0.99, provided the gas phase and each class of bubbles are completely mixed, whatever the real micromixing behaviour of the gas phase will be. This means that the gas-liquid model reaction systems with absorption of CO_2 in alkanolamine systems can be used with a good accuracy for the determination of interfacial areas by the chemical method in mechanically agitated gas-liquid reactors.

3.3. The intermediate micromixing case.

3.3.1. Calculation backgrounds.

Up till now we considered only the influence of the macromixing behaviour of the gas phase on the error in a_{chem} , while we assumed the gas phase to be completely segregated and thus no interaction between the gas bubbles. Therefore, we calculated the maximum error in a_{chem} if micromixing effects are totally neglected. However, especially in bubble columns with long residence times for the bubbles and in mechanically agitated gas-liquid reactors with high degrees of turbulence the gas bubbles are likely to interact. The gas bubbles are subjected to complex coalescence and breakup processes on a microscale, which are unfortunately not very well understood. Qualitatively it can be argued that such interactions between the bubbles will level out the concentration differences of the gas phase reactant in the bubbles and will therefore lead to a smaller error in a_{chem} .

In order to get an idea of the magnitude of the effect of bubble coalescence and breakup upon the deviation of a_{chem} from a_{geo} we adopted the well known micromixing model of interaction by exchange with the mean (IEM model), see Villiermaux(1981) and Westerterp et al(1984). Villiermaux(1981) calculated that the IEM model compares very well to the random coalescence model(RCM) in which a fluid is considered to contain only aggregates. These aggregates coalesce with each other and after each coalescence, the two aggregates immediately split again into two new aggregates having the average composition of the two original aggregates. The whole process can be described by the coalescence frequency ω , the number of coalescences per unit of time. This parameter has a clear physical meaning in a gas-liquid dispersion. However, this RCM requires complicated numerical techniques.

We therefore used the IEM model, which is easier to compute and compares very well to the RCM as the characteristic micromixing parameter of the IEM model t_m equals $4/\omega$, see Villiermaux(1981). In the IEM model a single agglomerate, which exchanges mass with the average content of the rest of the reactor, is followed from its birth at the reactor feed inlet. The average

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content is derived from the RTD for the reactor and from the concentration in typical agglomerates with different residence times.

The IEM model can be used to simulate the effects of bubble coalescence and breakup if the gas bubbles are considered as the agglomerates. For reasons of simplicity the IEM model will only be considered for a first order reaction with respect to the gas phase reactant. The mass balance for the concentration of reactant A in a single bubble with diameter d_b then equals

$$\frac{d c_A(d_b, t)}{d t} = \frac{c_{A, av} - c_A(d_b, t)}{t_m} - \frac{6}{d_b} K_1 c_A(d_b, t) \quad (16)$$

in which t_m is the time constant for mass exchange between the bubble and the rest of the reactor, and $c_{A, av}$ the average concentration of A in the gas phase.

For a completely mixed gas phase, in which each class of bubbles with diameter d_b has the same RTD as the gas phase, the average concentration $c_{A, av}$ can be calculated from

$$c_{A, av}(d_b) = \int_0^{\infty} c_A(d_b, t) \frac{1}{t} \exp\left(-\frac{t}{\tau}\right) d t \quad (17)$$

and

$$c_{A, av} = \frac{\int_0^{\infty} E(d_b) c_{A, av}(d_b) d_b^3 d d_b}{\int_0^{\infty} E(d_b) d_b^3 d d_b} \quad (18)$$

For plug flow behaviour of the gas phase the bubble only exchanges mass with the average content of the bubbles with the same residence time and the concentration $c_{A, av}(t)$ can be obtained from

$$c_{A, av}(t) = \frac{\int_0^{\infty} E(d_b) c_A(d_b, t) d_b^3 d d_b}{\int_0^{\infty} E(d_b) d_b^3 d d_b} \quad (19)$$

Both sets Eqs (16)-(17)-(18) and Eqs (16)-(19) require an iteration procedure in order to be solved. The resulting average concentration $c_{A, av}$ can be used to calculate the overall conversion Ω_A , which

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can be substituted in Eq. (15) and the relations of Table 1 in order to obtain a_{chem} . The solutions of Eqs (16) and (17) for complete mixing and plug flow of the gas phase are presented in Table 2.

Table 2. Relations for the fraction of reactant A in a single bubble and for the average content of reactant A for the IEM model with a fast reaction occurring in the liquid.

Complete mixing:

$$y_{A,av}(d_b) = \frac{y_{A,av}}{1 + St_1^* t_m} \frac{\frac{1}{t_m} + St_1^* \tau}{1 + \frac{\tau}{t_m} + St_1^* \tau} + \frac{y_A(d_b, t=0)}{1 + \frac{1}{t_m} + St_1^* \tau} \quad (20)$$

$$y_{A,av} = \frac{\int_0^{\infty} E(d_b) y_{A,av}(d_b) d_b^3 d d_b}{\int_0^{\infty} E(d_b) d_b^3 d d_b} \quad (21)$$

Plug flow:

$$y_A(d_b, t) = \frac{y_{A,av}(t)}{1 + St_1^* t_m} \left\{ 1 - \exp^{-\left(\frac{1}{t_m} + St_1^*\right)t} \right\} + y_A(d_b, t=0) \exp^{-\left(\frac{1}{t_m} + St_1^*\right)t} \quad (22)$$

$$y_{A,av}(t) = \frac{\int_0^{\infty} E(d_b) y_A(d_b, t) d_b^3 d d_b}{\int_0^{\infty} E(d_b) d_b^3 d d_b} \quad (23)$$

with $St_1^* = \frac{St_1}{\tau_b}$

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3.3.2. Calculation results.

Literature data on coalescence frequencies of gas bubbles in gas-liquid contactors are very scarce. For a mechanically agitated gas-liquid reactor Hassan and Robinson(1980) and Reith and Beek(1970) reported coalescence frequencies ranging from 1 to 15 s⁻¹; the magnitude depending both on the operating conditions, like superficial gas velocity and agitation rate, and on the liquid phase properties. We calculated with the IEM model the effect of coalescence on the deviation of a_{chem}/a_{geo} for a completely mixed gas phase in a mechanically agitated reactor. The results are plotted in Fig. 8 for a Bayens distribution with a Sauter mean bubble diameter d_s of 3 mm and for values of t_m equal to 0.25, 1 and 4 s, which correspond to coalescence frequencies of 16, 4 and 1 s⁻¹ respectively. The line representing a completely mixed gas phase under segregated conditions is also plotted in Fig. 8. It can be seen that as expected coalescence of the gas bubbles reduces the deviation of a_{chem} from a_{geo} . At the lowest time constant for mass exchange t_m the error in a_{chem} becomes smaller than 5% for overall conversions Ω_A lower than 0.99. The calculations also show a slight influence of the assumed Sauter mean bubble diameter d_s on the deviation of a_{chem} from a_{geo} .

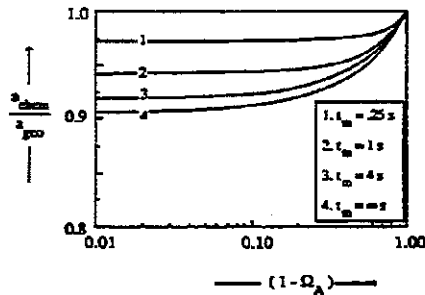


Figure 8: Ratio a_{chem}/a_{geo} of a Bayens distribution with $d_s = 3$ mm vs. $(1 - \Omega_A)$ for a 1-order reaction and complete mixing of the gas phase as calculated according to the IEM model.

To our knowledge no quantitative data on the coalescence frequencies of gas bubbles in a bubble column are available. However, from the papers of Calderbank(1967) and Deckwer et al(1978) it can be qualitatively calculated that the coalescence frequencies of gas bubbles in a bubble column are in the range of 0.5 to 5 s⁻¹. Calculation results for a log-normal distribution in a bubble column with a Sauter mean bubble diameter d_s of 5 mm with $\sigma_m^2 = 0.10$ and 0.20 and for values of t_m equal to 1 and 4 s are plotted in Figs 9a and 9b respectively. The line representing plug flow behaviour of the gas phase under segregated conditions is given also. It can be seen that for these micromixing conditions the error in a_{chem} reduces considerably and is always smaller than 25% for overall conversions Ω_A smaller than 0.99. Also these calculations show a slight dependence of the

results on d_p .

These calculations with the IEM model indicate that, if bubble coalescence and breakup in a dispersion of a gas-liquid contactor are taken into account the deviation of a_{chem} from a_{geo} , as compared to segregated conditions, becomes smaller. If realistic coalescence frequencies are considered the error in a_{chem} may reduce a factor 3. For a mechanically agitated reactor and a first order reaction with respect to the gas phase this means that the error in a_{chem} becomes smaller than 5%. For a bubble column and a first order reaction the calculations indicate that for most practical conditions the error in a_{chem} is smaller than 20%, if the overall conversion of the gas phase reactant Ω_A is kept below 0.99. The gas-liquid model reaction systems with absorption of CO_2 in alkanolamine systems can therefore also be used with a rather good accuracy for the determination of interfacial areas by the chemical method in bubble column reactors.

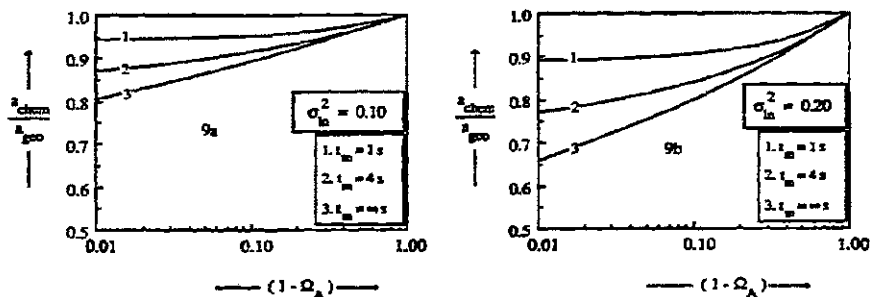


Figure 9: Ratio $a_{\text{chem}}/a_{\text{geo}}$ of a log-normal distribution with $d_p = 5 \text{ cm}$ vs. $(1 - \Omega_A)$ for a 1-order reaction and plug flow of the gas phase as calculated according to the IEM model.

4. DISCUSSION AND CONCLUSIONS

In this study it is shown that due to the use of an overall conversion Ω_A for the gas phase reactant the evaluation of a_{chem} from absorption experiments may lead to serious errors, because the overall conversion Ω_A represents an incorrect average if the bubble sizes and residence times are not uniform, see Schumpe and Deckwer(1980). These authors considered only plug flow behaviour for the gas phase under completely segregated conditions, while we studied for practical conditions both the effect of gas phase backmixing as well as the effect of bubble coalescence and breakup on the deviation of a_{chem} from a_{geo} . In several case studies we performed model calculations for both mechanically agitated gas-liquid reactors and bubble columns.

For a completely mixed gas phase in a mechanically agitated reactor it has been calculated that:

1. For a first order reaction with respect to the gas phase reactant and segregated conditions the

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error in a_{chem} will always be smaller than 10% if the overall conversion Ω_A is lower than 0.99.

2. For a *zero and second order reaction* with respect to the gas phase reactant and *segregated conditions* the errors in a_{chem} become larger than 50% for overall conversions Ω_A larger than 0.85 and the errors in a_{chem} will be smaller than 10% only for $\Omega_A < 0.40$ and 0.60 respectively.
3. If *bubble coalescence and breakup* are taken into account, calculations for a *first order reaction* according to the IEM model show that the error in a_{chem} , as compared to segregated conditions, reduces and becomes a factor 2-3 smaller.

Therefore, it can be concluded that gas-liquid model reaction systems, which are zero and second order in the gas phase reactant, result only in an accurate value for the interfacial area in a mechanically agitated gas-liquid reactor if the overall conversion Ω_A is low. Model reaction systems, which are first order in the gas phase reactant, can be used very well for the determination of interfacial areas in a mechanically agitated reactor, provided the RTD of the gas phase is known. As already aforementioned the literature data on the RTD of the gas phase in this reactor are scarce. Hassam and Robinson(1980) and Oyevaar et al(1988) - see also Chapter 2 - showed that for CO_2 model reaction systems, which are first order in CO_2 and for which the overall conversions Ω_A is lower than 0.80, the assumption of a completely mixed gas phase leads to accurate values for the interfacial areas.

For plug flow behaviour of the gas phase in a bubble column it has been calculated that:

1. For a *first order reaction and segregated conditions* the error in a_{chem} will always be smaller than 35% if the overall conversion Ω_A is lower than 0.99.
2. For *segregated conditions* the deviation of a_{chem} from a_{geo} decreases with increasing reaction order for an overall conversion Ω_A above 0.85.
3. If *bubble coalescence and breakup* are taken into account, qualitative calculations for a *first order reaction* according to the IEM model indicate that the error in a_{chem} , as compared to segregated conditions, reduces and becomes smaller than 20% for overall conversions $\Omega_A < 0.99$.

These calculations demonstrate that the interfacial areas in a bubble column can be determined by the chemical method with a rather good accuracy even for overall conversions Ω_A up to 0.99, provided the gas-liquid model reaction used is first order in the gas phase reactant. The limits with respect to the overall conversion Ω_A , as presented by Schumpe and Deckwer(1980) for a bubble column, are extended to higher values for Ω_A , if bubble coalescence and breakup are taken into account. It should be kept in mind that in the calculations for the bubble column we considered the RTD of the gas phase to be plug flow. This will be the case at low superficial gas velocities in the bubbly flow regime and also in columns with a small diameter, see Shah et al(1982). Deviations from plug flow will occur in the churn turbulent regime at higher superficial gas velocities and in columns with larger diameters due to liquid circulation and to different rising velocities of the

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bubbles.

It can be concluded that, provided the RTD of the gas phase is known, gas-liquid model reaction systems with absorption of CO_2 in alkanolamine solutions can be used for the determination of accurate values for the interfacial areas in gas-liquid contactors, despite the high solubility of CO_2 compared to other gases, which generally results in high CO_2 conversions. Taking into account the advantages of the reaction between CO_2 and alkanolamines compared to the traditional reaction between O_2 and sodium sulphite as aforementioned, the use of CO_2 -alkanolamine systems for the determination of interfacial areas by the chemical method is therefore recommended.

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NOTATION

a	specific interfacial area, m^2/m^3 dispersion
c	concentration, mol/m^3
d	diameter, m
d_b	Sauter mean bubble diameter, m
d_{mb}	mean bubble diameter, m
D_A	diffusivity of reactant A in the liquid phase, m^2/s
$E(d_b)$	bubble diameter distribution function
$E(t)$	residence time distribution
$E_N(t)$	residence time distribution of a cascade
Ha	Hatta number, Eq. (3)
J	mole flux, $\text{mol}/\text{m}^2 \text{ s}$
k	mass transfer coefficient, m/s
$k_{n,p}$	reaction rate constant for a reaction of the order (n,p), $\text{m}^3(\text{p}+n-1)/\text{mol}(\text{p}+n-1) \text{ s}$
K_n	absorption rate constant, $(N/\text{m})^{1/2} (1-\alpha) \text{ m/s}$
m	distribution coefficient, $c_1 = m c_2$
N	number of completely mixed tank reactors
N_0	critical agitation rate, 1/s
P	pressure, Pa
R_c	chemical reaction rate, $\text{mol}/\text{m}^3 \text{ s}$
St_n	Stanton number for a n-th order reaction
t	time, s
τ_m	time constant for mass exchange (IEM model), s
v	superficial velocity based on the empty cross-sectional area of the vessel, m/s
V	volume, m^3
y	molar fraction reactant in the gas phase

Greek symbols

ϵ	hold-up
ϕ	flow rate, mol/s
σ_{ln}^2	variance log-normal distribution
τ	residence time, s

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τ_N	residence time in one tank reactor of cascade, s
ξ	conversion
ω	coalescence frequency, 1/s
Ω	overall conversion gas-liquid contactor

Subscripts

A	reactant originally in the gas phase
av	average content
b	bubble
B	reactant originally in the liquid phase
chem	chemical
G	gas
geo	geometric
L	liquid
n	reaction rate order for reactant A in the liquid phase
o	original
p	reaction rate order for reactant B in the liquid phase
R	reactor

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Appendix

The distribution function of the cascade model with N completely mixed tank reactors in series equals

$$E_N(t) = \frac{N^N t^{(N-1)}}{\tau_N^N (N-1)!} \exp\left(-N \frac{t}{\tau_N}\right) \quad (a1)$$

and can be used in Eq. (12) to calculate the conversion of the gas phase reactant for each class of bubbles $\zeta_A(d_b)$. For a first order reaction Eq. (12) can be solved analytically and results in the well known relation

$$\zeta_A(d_b) = 1 - \left[\frac{1}{1 + St_{1,N} \tau_N} \right]^N \quad (a2)$$

$St_{1,chem}$ can be calculated from

$$St_{1,chem} = N \left[\frac{1}{(1 - \Omega_A)^{1/N}} - 1 \right] \quad (a3)$$

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The limits of the cascade model represent plug flow behaviour for $N \rightarrow \infty$ and complete mixing for $N = 1$. Results on $a_{\text{chem}}/a_{\text{geo}}$ for these two extreme RTD's were already shown in Fig. 6 and are plotted again in Fig. a1 together with results for a cascade of 2 and 5 completely mixed tank reactors in series for a first order reaction. As expected it can be seen that the lines, which represent the intermediate macromixing behaviour, lie in between the lines for the two extreme RTD's.

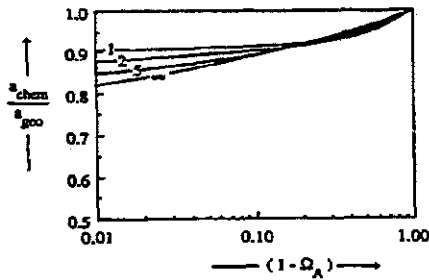


Figure a1: Ratio $a_{\text{chem}}/a_{\text{geo}}$ of a Bayens distribution vs. $(1 - \Omega_A)$ for a 1-order reaction and intermediate macromixing behaviour.

Levensloop

Levensloop

Martin Oyeveaar werd op 24 januari 1961 in Broek op Langedijk geboren. Na lagere scholen in Broek op Langedijk en Creil bezocht hij de Christelijke Scholengemeenschap in Emmeloord, alwaar hij in mei 1979 het Atheneum-B diploma behaalde. Aansluitend startte hij met de studie Chemische Technologie aan de Universiteit Twente. In september 1984 studeerde hij af bij de vakgroep Proceskunde en Industriële Processen (afstudeerdocent Prof. dr. ir. K. R. Westerterp) op een studie naar het gebruik van de gas vast-vast trickle flow reaktor voor de methanolsynthese.

In oktober 1984 begon hij in dienst van de S.O.N. aan het promotie onderzoek naar de invloed van de druk op de stofoverdrachtsparameters in gas-vloeistof reactoren.

In november 1988 is hij in dienst getreden bij General Electric Plastics.