MASS TRANSFER IN BUBBLE COLUMN CONTACTORS

by

VICTOR RUDOLPH

Submitted in fulfilment of the requirements for the
degree of Master of Science in Engineering.

July 1974

SYNOPSIS

Gas holdup and overall volumetric mass transfer coefficients in bubble column contactors have been investigated for water and aqueous electrolyte solutions. Two methods were used to obtain experimental data on volumetric mass transfer coefficients: the steady state oxidation technique and a transient method. The former technique was found to be unsuitable for absorption measurements because chemical enhancement of mass transfer, due to simultaneous absorption and fast reaction, caused erroneously high mass transfer coefficients to be evaluated. In the transient experiments the effect of superficial gas velocity, concentration of electrolytes in solution, bubble column diameter and gas inlet orifice diameter on the gas holdup and the mass transfer rate, were investigated.

The experimental data for gas holdup and overall mass transfer coefficients obtained both in this study and from the literature have been correlated by dimensionless equations.

The author wishes to express his appreciation and gratitude to Assoc. Prof. H.O. Buhr and Dr. J.W. de Kock for their encouragement and guidance throughout this study.

The generous financial assistance of the National Institute for Metallurgy during the course of this investigation is also gratefully acknowledged.

TABLE OF CONTENTS

NOMENCLATURE

ENGLISH SYMBOLS

A	total gas liquid interfacial area, L^2
a	specific gas liquid interfacial area, L
a	cross sectional area of gas bubble column, L^2
a,b	constants, dim.
Bo	Bond number $= gD^2\rho/\gamma$, dim.
c	concentration of dissolved species, ML^{-3}
c,d	constants
D_L	diffusion coefficient of oxygen in liquid, L^2T^{-1}
D	bubble column diameter, L
dp	average bubble diameter, L
E	chemical enhancement factor, dim.
Fr	Froude number $= U_G/\sqrt{gD}$, dim.
G	gas flow rate, $ML^{-2}T^{-1}$
Ga	Galileo number $= gD^3/\nu^2$, dim.
g	gravitational constant, LT^{-2}
H	Henry's constant, T^2L^{-2}
I	ionic strength of solution, dim.
K	kS^y, constant
K_L	volumetric liquid phase mass transfer coefficient, LT^{-1}
k	sulphite reaction rate constant, $L^3M^{-1}T^{-1}$
k,L,n	constants
n	sulphite reaction order with respect to oxygen, dim.
p	partial pressure of oxygen, $ML^{-1}T^{-2}$
R	rate of oxygen transfer per unit area, $ML^{-2}T^{-1}$
S	sulphite concentration in the liquid phase, ML^{-3}
Sc	Schmidt number $= \nu/\rho$, dim.
Sh	Sherwood number $= K_LD/D_L$, dim.
t	bubbling time, T
U_G	superficial gas velocity in total column cross section, LT^{-1}
z	liquid height, L

GREEK SYMBOLS

γ	surface tension, MT^{-2}
ε	gas holdup fraction, dim.
μ	ionic strength of solution, dim.
ν	kinematic viscosity, L^2T^{-1}
ρ	liquid density, ML^{-3}
Σ	sum of

SUBSCRIPTS

calc	calculated value
expt	experimental value
F	aerated
f	final
I	at the phase interface
i	species i or initial
L	liquid phase
O	in water
x	at a distance x from the phase interface
(x+dx)	at a distance (x+dx) from the phase interface

SUPERSCRIPTS

*	equilibrium

CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1.1 INTRODUCTION

In spite of its wide industrial applications as a gas-liquid reactor and fermentor, adequate design criteria for a gas bubble column are not currently available. The design of such a contactor as a reactor will depend largely upon the rate of mass transfer of the reactants to the reaction site and the rate of chemical reaction and, as a fermentor, on the rate at which oxygen dissolves in the fermentation broth. Since the principles behind the operation of such a contactor have not yet been fully investigated, systematic design of a unit operation, incorporating this method of gas liquid contacting is not possible at present.

1.2 BACKGROUND TO THIS INVESTIGATION

The leaching of base metals by ferric chloride involves the reduction of the Iron III ion to Iron II. Regeneration of the leach medium for recirculation and further leaching is economically advantageous in this process. One method of accomplishing the regeneration is by oxidation of the spent liquor by aeration of the ferrous chloride solution and direct reaction with dissolved oxygen. The extreme corrosiveness of the iron chlorides to common materials, and the entrainment of solid particles in the liquor during the leaching process preclude the use of commercially available aeration equipment for this oxidation. A convenient method for regeneration is the batchwise oxidation of spent leach liquor in a bubble column reactor. In such a system, oxygen or air is injected at the base of a column of liquid and bubbles up through it. The oxidation reaction is accomplished by oxygen which continuously dissolves in the liquid. Clearly, the rate of such dissolution is of importance in this system, and it is the influence of parameters affecting the rate of gas absorption which form the basis of this investigation.

1.3 THEORY

A detailed treatment of the outline which follows may be found in the texts of Dankwerts [1] and Astarita [2].

The rate of mass transfer of a gas dissolving in a liquid without chemical reaction is given by:

$$R = K_L a \ (c^* - c_0) \tag{1.1}$$

Where absorption is accompanied by reaction, the mass transfer Equation (1.1) may be modified as:

$$R = EK_L a \ (c^* - c_0) \tag{1.2}$$

where E is the chemical enhancement factor due to chemical reaction. The enhancement factor can be evaluated, as explained by Dankwerts [1] and Astarita [2], using one of the many models for mass transfer, e.g. the "two film" model, surface renewal models, "still surface" models, provided that the chemical reaction is well defined.

It is necessary to distinguish between processes occurring in the diffusion film near the phase interface, and those occurring in the bulk of the liquid. Reaction occurring in the diffusion film directly affects the coefficient of mass transfer K_L, since the reaction site is now closer to the phase interface and the reacting species effectively have a thinner film through which to diffuse before reacting. Reaction in the liquid bulk also affects the rate of mass transfer in that it determines one of the boundary conditions, c_0, which control the transport and reaction of material in the film. Mass transfer with rapid accompanying reaction and purely physically controlled mass transfer are schematically represented in Figure 1.1 by the concentration gradients in the mass transfer films.

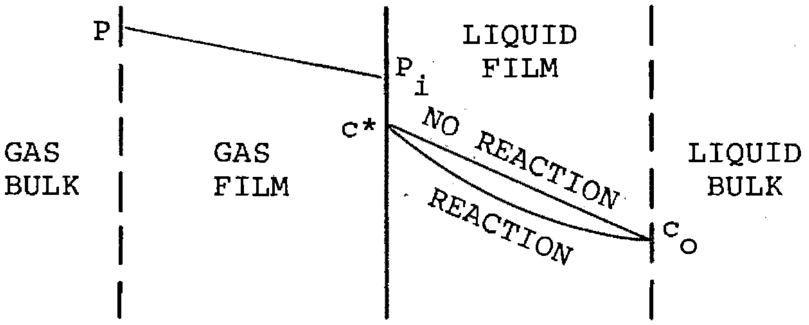


Figure 1.1 Schematic representation of mass transfer with and without accompanying rapid chemical reaction

The interfacial concentration c* is in equilibrium with the interfacial partial pressure, p_i. The rate of mass transfer into the liquid at the phase interface is proportional to the slope of the concentration profile at that point, which is considerably greater for absorption accompanied by fast chemical reaction.

The degree to which chemical reaction affects the absorption process depends on the rate of reaction

(a) When the reaction is very slow, the absorption rate is unaffected and the process becomes equivalent to that of pure physical absorption. In a continuing batch process the whole liquid bulk would become and remain saturated with unreacted gas, and the rate of uptake of gas would equal its rate of reaction in the liquid.

(b) For slow chemical reactions there is still no appreciable reaction of the dissolved gas during its transport through the diffusion film and unsteady state mass transfer would again be the same as for physical absorption. The reaction may be too fast for the bulk of the liquid to ever become totally saturated with dissolved gas however. In both these cases, the chemical enhancement factor, E, is very close to unity and may be neglected.

(c) When the reaction is fast an appreciable amount of gas reacts during its transport through the diffusion film. Consequently chemical enhancement of mass transfer will occur, i.e. the value of the enhancement factor E will be appreciably greater than one. Naturally, in this case the bulk concentration of dissolved gas will be very small.

(d) The catalysed sulphite oxidation reaction is a special case of fast reaction, wherein the reaction is sufficiently fast to maintain a very low bulk concentration of dissolved oxygen, but still slow enough not to cause appreciable chemical enhancement. The sulphite reaction is more fully discussed in section 1.42.

1.4 LITERATURE SURVEY

1.41 Introduction

In general two methods have been used to obtain data on mass transfer in bubble columns.

(a) The sulphite oxidation method of Cooper, Fernstrom and Miller [3] is the most popular and is widely used in evaluating the performance of spargers [3,4], fermentors [5,6,7], packed columns [1,8,9] and gas-liquid reactors [10,11,12]. The method has also been widely applied to the measurement of interfacial areas in gas liquid dispersions [13,14,15,16].

(b) The direct method for evaluating mass transfer coefficients obtains results from the rate of absorption of a sparingly soluble gas into a liquid previously depleted of that gas. Though less elegant than the steady state technique, the transient method has the advantage that chemical reaction cannot influence the rate of mass transfer of the diffusing gas.

1.42 The Sulphite Method

1.421 Introduction. The overall mass transfer coefficient, K_La, is evaluated in the steady state method from the rate of depletion of sulphite by reaction in the column, from

$$-\ (1 - \varepsilon)\ \frac{dc}{dt} = K_L a\ (c^* - c_0) \qquad (1.3)$$

In order to solve this expression for K_La using the sulphite method, two conditions must be fulfilled.

(i) The bulk concentration of dissolved gas, c_0, must be negligibly small. If this is not the case the driving force for mass transfer is not known.

(ii) There must be negligible reaction in the diffusion film otherwise mass transfer will be chemically enhanced, and an erroneously high mass transfer coefficient will be obtained. The order of the reaction with respect to sulphite must obviously be zero, or, as the oxidation proceeds, the reaction rate will decrease. Under these circumstances it will be impossible to maintain conditions under which both the above requirements are simultaneously fulfilled for an appreciable period of time.

The catalysed oxidation of sodium sulphite has been widely considered as satisfying the above conditions [5,6, 10,11,12,17], although there has been disagreement over the interpretation of data obtained by this method (discussed in section 1.423). Notwithstanding these differences of opinion, the method is still the most widely used for the evaluation of mass transfer rates in bubble column and stirred tank contactors.

1.422 Kinetics of the Sulphite oxidation reaction. The sulphite oxidation reaction, because of its wide use in absorption experiments, has been the subject of a great deal of research. The oxidation of sodium or potassium sulphite is normally very slow, but the reaction can be catalysed by many substances. Copper and cobalt are the most commonly used catalysts in the application of the sulphite reaction to mass transfer studies, but the reaction is also sensitive to traces of iron, cesium and manganese, which increase the reaction rate, and to organic compounds such as ethanol, glycerol and mannitol which inhibit the reaction [4,16,18,19].

The reaction is very complex and the kinetics are still uncertain.

Some investigators have found that the reaction is second order in oxygen concentration [5,20,21,22], but others have obtained first order kinetics [1,19,23,24]. Astarita [1] considers the reaction to be zero order in oxygen for sulphite concentrations of less than 0,06 M, first order up to 0,25 M and second order at higher concentrations. Sawiki and Baron [25] have found that the rate controlling step is different when the reaction is carried out under heterogeneous or homogeneous conditions. They conclude the heterogeneous oxidation is second order in oxygen pressure at the interface and state that unless the reaction is carried out in the fast reaction regime, the experimental data will yield the erroneous result of first order kinetics in oxygen. Reith [13] has also found second order kinetics in oxygen and suggests that confusion may have arisen because the reaction was sometimes studied under unfavourable conditions for reaction rate measurements. In most experimental systems there is no way of determining mass transfer rates and reaction rates separately. It is generally agreed that the reaction is zero order with respect to sulphite concentration over a wide range [1,5,13, 17,26].

Baron and O'Hern [26] have investigated the effectiveness of Cu^{++} as a catalyst in sulphite oxidation. They point out that cupric ions in sulphite solutions are reduced, to an unknown extent, to cuprous ions and that while the former are strongly catalytic, the latter are mildly inhibiting to the oxidation reaction. In addition they state that an "unknown fraction of the copper present in the reaction mixture may be either precipitated or associated and thus have little effect on the reaction rate". The variations in the reported reaction rate constants, when copper is used as a catalyst, may be a consequence of any or all of these factors.

The majority of investigators nevertheless have found that the oxidation rate is independent of copper concentration in the range of about 10^{-3} to 10^{-5} M [5,17,19,26,27], and, except in the most recent work, copper has been used almost exclusively in absorption experiments.

Cobalt on the other hand is the more powerful and consistent catalyst and has been extensively used and investigated by workers attempting to use the chemical method to obtain interfacial areas in stirred tank and bubble column contactors. This method requires high reaction rates and large chemical enhancement factors [1,13,16,28]. The use of cobalt as a catalyst in absorption experiments has been limited because the sulphite oxidation rate is sensitive to cobalt concentration. This means that the correct catalyst concentration must be used to obtain a reaction rate which fulfills the two conditions (i.e. no reaction in the diffusion film and very low bulk concentration of oxygen) for the steady state determination of K_La [5,13]. In spite of this difficulty, however, cobalt is probably preferable to copper as a catalyst since its action is more reproducible.

A serious difficulty in sulphite oxidation rate experiments is the extreme sensitivity of the reaction to a large variety of trace impurities [16,18,19]. Reaction rates reported in the literature cannot thus be generally applied. The large variation of reaction rates even in apparently identical situations, may in turn explain the inconsistency of mass transfer data reported by various investigators. If the reaction, in a steady state absorption experiment proceeds too slowly, the bulk concentration of dissolved oxygen will not be negligible and the value of K_La will be erroneously low. On the other hand if the reaction rate is too fast, enhancement will cause an erroneously high mass transfer coefficient to be obtained.

1.423 Reported results by the sulphite method. Although much data on mass transfer rates, obtained by the sulphite method, have been reported in the literature, and the technique is regarded as standard procedure for testing the rate of oxygen absorption in gas liquid contactors, there is still disagreement as to the merits of the method. For example, some investigators have found good agreement between mass transfer coefficients obtained by the sulphite and transient methods [10,11,29,30]. Others have found that the sulphite technique results in high values of K_La in comparison with the unsteady state method [4,31,32].

It has been suggested that much of the conflict arises from misinterpretation of results due to misunderstanding the complicated chemistry of the sulphite reaction or because experiments were carried out under conditions where the reaction rate was such that the two conditions for simple interpretation of mass transfer results were not fulfilled [1,2,7,15].

Another difficulty is that much of the work reported in the literature cannot be easily compared because of the gross differences in the equipment used to obtain data.

In summary various investigators have reported in the literature that:

(1) the copper catalysed sulphite oxidation reaction fulfils the requirements for the steady state evaluation of mass transfer coefficients [5,10].

(2) the resistance to mass transfer in the gas phase is negligible in comparison with that in the liquid phase and that the overall volumetric mass transfer coefficient, K_La, is therefore equivalent, in this system, to the liquid phase mass transfer coefficient, k_La [5,10,17,33].

(3) when a single gas injection orifice is used, the diameter of the orifice has no significance in determining the mass transfer coefficient [17].

(4) the overall mass transfer coefficient is not affected by the height of the column, provided that this is sufficient

to exclude end effects [17]. Urza and Jackson [12] have investigated deep tank aeration using the sulphite and transient techniques. Their results indicate that tall columns, (up to 55 feet) have a potential for reducing operating costs and increasing oxygen utilization efficiencies.

(5) the significance of column diameter is uncertain. Yoshida and Akita [17] have found a slight dependence of absorption rate on column diameter, but this effect was not observed by Shulman and Molstad [48].

(6) bubbling causes sufficient agitation to maintain a uniform liquid concentration throughout the bubble column i.e. the liquid phase is perfectly mixed [13,17,34].

Several investigators have reported on the efficiencies of stirred tank contactors [3,5,6,10,13,29,33,34,35], and much of their work has been summarized by Sideman et al [36]. The general weakness of most of this work is that the results obtained are limited to the particular equipment used and operating ranges investigated.

1.43 The Transient Method

The overall mass transfer coefficient is found by the transient method from the rate of oxygen absorption into a deoxygenated liquid according to the integrated form of equation 1.3:

$$K_La = [(1 - \varepsilon)/t] \ \ln[\frac{c^* - c_i}{c^* - c_f}] \qquad (1.4)$$

The transient method has not been used by many researchers because of its inherent susceptibility to end errors. These arise because of the short periods (less than 1 min) over which the experiments must be conducted before the liquid in the bubble column is very nearly saturated with oxygen. The disturbances caused by the initiation of bubble flow before the column settles down are not representative of the steady state operating conditions, but form an appreciable part of the entire absorption experiment. A more serious disadvantage is that the liquid in the column is nearly saturated with absorbed gas at the end of the experiment and that the determination of the final oxygen concentration c_f must be very accurate, since it is almost equal to the equilibrium oxygen concentration c*, in order to obtain reliable values of K_La.

In spite of these difficulties, Koetsier et al [29] have shown the technique to be both reliable and reproducible. Landberg et al [37], Carpini and Roxburg [31] and others [4,38] are of the opinion that the transient method is the only reliable means of measuring mass transfer rates, and that steady state methods (including the sulphite method) are prone to chemical enhancement and generally produce erroneously high results. Reith [13], on the other hand, concludes that the transient method is inaccurate and that the sulphite oxidation method, provided its requirements are understood and complied with, provides a precise and simple alternative.

Akita and Yoshida [39] have made extensive use of the transient method to investigate the effects of liquid physical properties on gas holdup and volumetric mass transfer coefficients in bubble columns as discussed in section 1.45. Zieminski and co-workers [40,41,42,43,44] have used the method to investigate the effect of a wide range of electrolytes and organic surfactants on bubble dispersions. Their work is summarized in section 1.44.

1.44 Hydrodynamic conditions in bubble columns.

1.441 Introduction: The hydrodynamic conditions in a bubble column will obviously play an important part in determining mass transfer rates, since both the surface area available for mass transfer (governed by the bubble breakup and coalescence rate), and the mass transfer coefficient per unit area (affected by the "thickness" of the mass transfer film) are largely controlled by the degree of turbulence in the column.

Although the situation in a bubble column is so complex that it seems unlikely that any quantitative model will ever be obtained [45], some investigators have made interesting observations in this field.

1.442 Bubble size: Valentin [34] has surveyed the literature dealing with the mechanics of single bubble generation at submerged orifices, but single bubble data are not applicable to bubble swarms such as are considered here. For continuous bubble generation at a single orifice, three regions are apparent [34,36,46]:

(i) At low gas flow rates the bubble diameter does not vary much with gas rate and bubble size depends principally on the orifice diameter.

(ii) As the gas rate is increased, bubble diameter increases with orifice gas velocity while the frequency of bubble generation remains approximately constant.

(iii) At high gas flow rates bubbles of a single size are no longer produced. The large toroidal bubbles which are formed rapidly break up into smaller bubbles. In general though, initial bubble sizes are not characteristic of bubbles rising in the major portion of the column. The average bubble size in the column depends on the coalescence and breakup rates, which are in turn a function of the turbulence caused in the liquid by the injection of the gas [30,36,44,46]. As bubble columns are generally operated at fairly high gas rates, in those bubble columns served by single orifices, the size of the injection orifice will not, therefore, be an important determinant of either the surface area available for mass transfer or the overall mass transfer coefficient.

1.443 Gas Holdup: Many workers have reported on the parameters affecting gas holdup in bubble column contactors

[13,17,39,47,48,49,50,51]. This is of importance because of the close relationship between gas holdup and interfacial area for mass transfer. Much of the work reported on bubble columns involves gas distribution by porous plate spargers [48,49,52,53,54], and while there appears to be no difference in behaviour at high gas velocities whether single orifices, multiple orifices or porous spargers are used for gas injection, at low gas rates holdup is far greater using a porous sparger than for gas orifices [10, 11,36,48]. An interesting observation made by some workers using porous distributors is that a local maximum in gas holdup occurs at a relatively low gas rate [48,52,54], possibly corresponding to a transition from laminar to turbulent bubble flow. This phenomenon is not observed when gas is injected through a single nozzle (see Figure 1.2).

It has been found that holdup is independent of column diameter for columns larger than 10 cm, but that wall effects, causing higher gas holdups, are noticeable in smaller columns [17,49,50]. Reith [13] has shown that gas holdup and bubble size distribution is constant throughout the major portion of the column with variations occurring near the gas inlet and at the top of the column in the bubble breakage zone.

A full qualitative description of the flow regimes in bubble columns as the gas velocity increases has been given by Shulman and Molstad [48]. Nicklin [55,56] has proposed a model of the behaviour of bubble swarms rising in a liquid, assuming no circulation. Towell et al [47] and Reith [13] have shown, however, that in large diameter (>150 mm) bubble columns, turbulent eddies of scale roughly equal to the column diameter occur, with systematic large scale circulation patterns superimposed on these random eddies. This is consistent with data which indicates that axial dispersion is higher in wide columns [36]. Using this information, Reith [13] has attempted a semi-quantitative analysis of bubble flow based on Nicklin's discription, but this model is still too idealized to be of any real value.

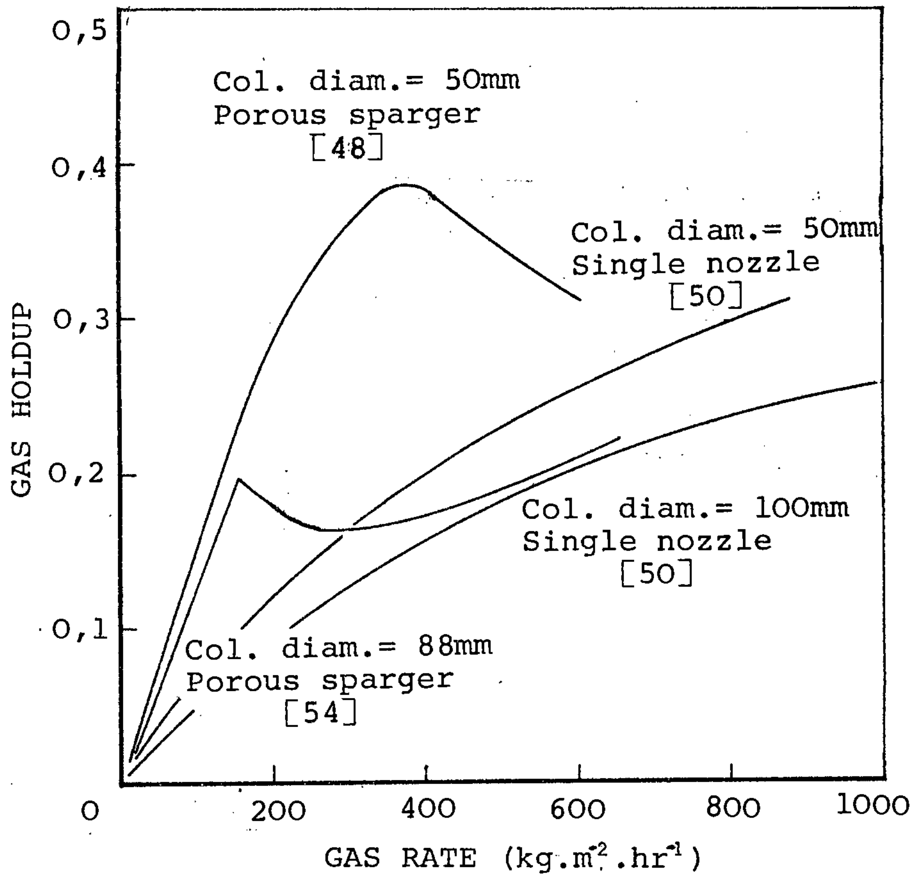


Figure 1,2 Comparison of gas holdup in columns with single nozzles and porous spargers

1.45 The effect of electrolytes on gas holdup and mass transfer

1.451 Introduction: It has long been known that ions in solution have a substantial effect on the coalescence of gas bubbles. In bubble columns this means that a sufficiently high electrolyte concentration results in an increased gas-liquid interfacial area and this possibly provides a means for increasing the mass transfer rate. Until recently, however, no systematic investigations of interfacial area and bubble coalescence phenomena in ionic solutions have been reported.

1.452 Reported Results: Marucci and coworkers [57,58] and Koide et al [30] have investigated the effect of inorganic salts in solution on the average bubble size in bubble column contactors. They found that the average size of the gas bubbles in bubble columns is determined by the coalescence and breakup rates of the bubbles. As electrolyte concentration in solution is increased, the average bubble size diminishes until a minimum bubble size is reached, beyond which any further increase in electrolyte concentration has no further effect on the average bubble diameter. This minimum size is independent of the ionic species in solution although the limiting concentration varies with different salts [30,57].

It is thought that electrolytes hinder coalescence by forming electrical repulsive forces on the bubble surfaces [13,30,40,44,57]. Although qualitative descriptions of these phenomena have been put forward [40,57] no quantitative model has yet been proposed.

Zieminski and Whittemore [40] have shown that the overall mass transfer coefficient per unit volume is much higher in electrolyte solutions than in water, because of the increased interfacial area for mass transfer. They observed that polyvalent ions had a more pronounced effect on the interfacial area for mass transfer than monovalent ions, and found that ionic strength of solution, a parameter which includes both the concentration and valence of the ions in solution, could be successfully used to correlate the effects of a wide range of salts on the surface area of dispersion.

Robinson and Wilke [6] investigating mass transfer in agitated contactors containing electrolyte solutions also found a proportional increase in mass transfer with ionic strength, up to a limiting ionic strength of about 0,4, beyond which no further increase in mass transfer rate was observed.

Lessard and Zieminski [44] have investigated the effect of electrolytes on bubble coalescence in aqueous solutions by contacting two bubbles and observing the percentage of coalescing pairs. They demonstrated that there is a transition concentration at which spontaneous coalescence is noticeably reduced. This transition corresponded to an ionic strength of about 0,18. They deduced from their data that coalescence is probably determined by a charge-viscosity interrelation but were unable to quantify the description with the limited data available. These findings suggest, in contradiction to those of Robinson [6] and Zieminski [40], that the rate of mass transfer should be approximately constant up to the transition concentration, at which point the absorption rate should suddenly increase, because of the rapid reduction in interbubble coalescence and consequent increase in interfacial area, and then remain constant again, at the higher level, as the ionic strength is further increased.

There is evidence that the presence of ions in solution also has a small effect on the mass transfer coefficient per unit area, K_L. Akita and Yoshida [24] working with an unagitated bubble bed have found that K_L increases with the square root of bubble diameter. Zieminski and Whittemore [40] found a small but definite decrease in K_L as ionic strength was increased and attributed this to the decreasing bubble size as electrolyte concentration was raised. Calderbank and Moo-Young [33,59] using an agitated contactor showed that K_L increased linearly with bubble diameter for bubbles of intermediate size, but is approximately constant with bubble diameter for large and small bubbles. Work by Lessard and Zieminski [44] on mass transfer from rising acetylene bubbles showed that K_L increased with ionic strength for constant bubble diameter although it decreased with increasing bubble radius. The increase in mass transfer coefficient in ionic solutions was attributed to increased surface mobility of the bubbles. No explanation for the decrease in mass transfer coefficient with increasing radius was offered.

1.453 Surface Active Agents: Most commercial process liquids contain surface active agents which may drastically affect mass transfer rates. It has been generally concluded that the addition of surface active agents to a system reduces the interphase mass transfer per unit area in most cases [34]. Two mechanisms have been proposed to explain this reduction:

(i) a physical barrier of surfactant is built up on the interface which blocks mass transfer and

(ii) a hydrodynamic mechanism which postulates that surface active agents radically alter they hydrodynamic flow situation [34,60].

Static systems, which eliminate hydrodynamic effects, have been used to investigate the barrier mechanism. These studies have shown that some surface active agents retard mass transfer [41,42], some have no effect, while others enhance the absorption rate [42,60]. This increase in mass transfer coefficient is always associated with increased interfacial mobility, probably caused by the Marangoni effect [61] (local variations in the interfacial tension causing movement of the interface). The mechanisms cannot be easily studied in flow situations because their effects become confounded.

Depression of the mass transfer coefficient per unit area does not necessarily mean that the overall absorption rate is decreased. Indeed, the contrary is most often the case because of the large increase in interfacial area for mass transfer caused by decreased bubble coalescence. Since the effect of surface active agents on the overall mass transfer rate depends not only on the surfactant present and its concentration but also on the gas dispersing system, it seems unlikely that a single correlation for the prediction of mass transfer in gas liquid dispersions containing surface active agents will be obtained.

1.45 Correlations for mass transfer

In a bubble column there exists a wide size distribution of bubbles, varying bubble residence times and unknown hydrodynamic conditions. Consequently, any general correlation for mass transfer must, at this stage, be an empirical expression based on dimensionless groups.

Correlations of the form used for single rigid spheres have been proposed [34,50],

$$Sh = c_1 + c_2 \, Re^m Sc^n \qquad (1.5)$$

but found to be of limited value. Hughmark [50] has proposed a modification of this expression which can be used for both single bubbles and bubble swarms:

$$Sh = 2 + c_1 [Re^{0,484} Sc^{0,339} \left[\frac{d_p g^{1/3}}{D}\right]^{0,072}]^{c_2} \qquad (1.6)$$

where $c_1 = 0{,}061$ and $c_2 = 1{,}61$ for single bubbles and $c_1 = 0{,}0187$ and $c_2 = 1{,}61$ for bubble swarms. The velocity parameter in the dimensionless groups is represented by the slip velocity between the bubbles and the liquid, and the length parameter is the mean bubble diameter.

Valentin [34], putting expressions derived by Calderbank and Moo-Young [59] in terms of common dimensionless groups, proposes correlations of the form:

$$Sh = 0{,}31\ Re^{2/3}\ Sc^{1/3}\ Fr^{-1/3}\ \frac{\Delta\rho}{\rho}^{1/2} \qquad (1.7)$$

$$Sh = 0{,}42\ Re^{2/3}\ Sc^{1/2}\ Fr^{-1/3} \qquad (1.8)$$

Equation 1.7 is a general correlation for liquid phase mass transfer coefficients in gas-liquid (as well as liquid-liquid and solid-liquid) dispersions while the latter equation applies to froths with large gas bubbles which do not behave like rigid spheres as small ones do.

It may be noted that correlations for mass transfer coefficients involving bubble diameter and rising or slip velocities would be difficult to apply in practice since these parameters are generally not available in a design situation.

Akita and Yoshida [39] have recently proposed dimensionless correlations for gas holdup and overall volumetric mass transfer coefficients:

$$\varepsilon/(1-\varepsilon)^4 = 0{,}20\ (Bo)^{1/8}\ (Ga)^{1/12}(Fr)^1 \qquad (1.9)$$

$$Sh\ aD = \frac{K_L aD^2}{D_L} = 0{,}6\ (Sc)^{0{,}5}(Bo)^{0{,}62}(Ga)^{0{,}31}\varepsilon^{1{,}1} \qquad (1.10)$$

The length parameter used in their dimensionless groups is column diameter. The correlations were tested in 77 mm, 150 mm, 300 mm and 600 mm columns. Deviations observed in the 77 mm column were attributed to wall effects. The dependence of mass transfer on column diameter for columns larger than 600 mm is uncertain and the authors note that this trend is unlikely to be maintained for columns of much larger diameter. They recommend that estimates based on 600 mm column should be used in these cases. Akita and Yoshida [39] also found that gas holdups were notably higher in electrolyte solutions than in non-ionic solutions and suggest that holdup estimates obtained from their equation be increased by 25% for solutions containing electrolytes.

1.47 Summary

Two methods for measuring mass transfer coefficients in bubble columns are available. Of these the sulphite method has been used most widely, but with questionable success. The complexity of the sulphite oxidation reaction makes interpretation of mass transfer data difficult and conflicting conclusions have been reached using this method. The transient method is probably more reliable but is prone to experimental error especially at high gas rates.

Although the hydrodynamic conditions in the column play an important role in mass transfer, no quantitative model is available and their influence must be determined empirically. Gas holdup is greater when porous spargers rather than orifices are used for gas injection and are thus more efficient, but the difference becomes less important at high gas rates. The pore size in spargers or the orifice size in nozzle injection do not influence the hydrodynamic conditions in the column and there is thus nothing to be gained by the use of fine rather than coarse spargers, or small rather than large orifices. Bubble size is determined largely by the coalescence and breakup rates of the bubbles in the columns.

Electrolytes in solution increase mass transfer in bubble columns by increasing interfacial area of contact between the two phases, but have little effect on the mass transfer coefficient, K_L. Beyond a limiting concentration salts have little further effect on bubble size.

Dimensionless correlations for mass transfer and gas holdup in unagitated bubble beds, involving column geometry and liquid phase physical properties have recently been put forward, but are not applicable to electrolyte solutions.

1.5 SCOPE OF THIS INVESTIGATION

Available data on the mass transfer characteristics of bubble column contactors under various conditions are scanty and leave one major unresolved problem: the influence of solutes, particularly inorganic electrolytes on the behaviour of the system. Dimensionless correlations for gas holdup and mass transfer coefficients in bubble columns, involving the physical and geometric parameters of the system have recently been published [39], but are not applicable to ionic solutions. There is, furthermore, some disagreement in the literature as to the relative significance of various parameters, viz. gas inlet orifice diameter and column diameter.

This investigation therefore set out

(a) to obtain a correlation for the overall mass transfer coefficient per unit volume in bubble column contactors, taking into account the effects of dissolved inorganic electrolytes and their concentration in solution and,

(b) to check the published correlations with regard to the significance of the injection orifice diameter and column diameter.

The hydrodynamic situation existing in a bubble column is dependent to some extent on the method of introduction of the gas at the base of the column and consequently this investigation was limited to single gas injection orifices. Where possible the findings of other investigators reported in the literature have been used to extend the conclusions to other means of gas injection.

Initially, the method for obtaining the mass transfer data chosen for this investigation was the sulphite oxidation technique, but this method proved to be unsatisfactory and was abandoned when results were found to be unreproducible and it became clear that chemical reaction was causing enhancement of mass transfer. The alternative unsteady state (transient) method was adopted and the bulk of the conclusions reached in this study are based on results obtained by this method.

CHAPTER 2

EXPERIMENTAL EQUIPMENT AND TECHNIQUES

2.1 EXPERIMENTAL EQUIPMENT

One of the major features of a bubble column for gas-liquid contacting is its extreme simplicity. In spite of this, however, a major difficulty encountered while reviewing the literature was that much of the reported data were specific to the apparatus and operating conditions employed. The experimental apparatus for this investigation consequently, was designed to facilitate comparison with data from the literature as much as possible.

Essentially the same equipment was used to obtain mass transfer data for both the steady state and the transient method. The equipment arrangement is shown in Figure 2.1.

The sulphite oxidation experiments were carried out in a 93 mm diameter, 2 m tall column which was made of clear perspex to enable observation of the bubble swarm and facilitate gas holdup measurements. Gas injection was through a single, interchangeable, upward facing nozzle situated 90 mm above the base of the column. Samples for analysis could be removed from sample ports at three different levels, 100 mm, 640 mm and 1,10 m above the base of the column.

Two further columns of diameter 144 mm and 293 mm were used in the unsteady state runs. The 144 mm clear perspex column had a single sample port 640 mm from the base. The largest column which was made of opaque PVC had a sample port 750 mm from the base.

The gas source was pressurized air, reduced to a constant pressure of 200 kPa by a pressure reducing valve, and controlled and measured by rotameters calibrated at the inlet air pressure. The air was passed through a cylinder filled with absorbent paper towels to remove any traces of entrained oil,

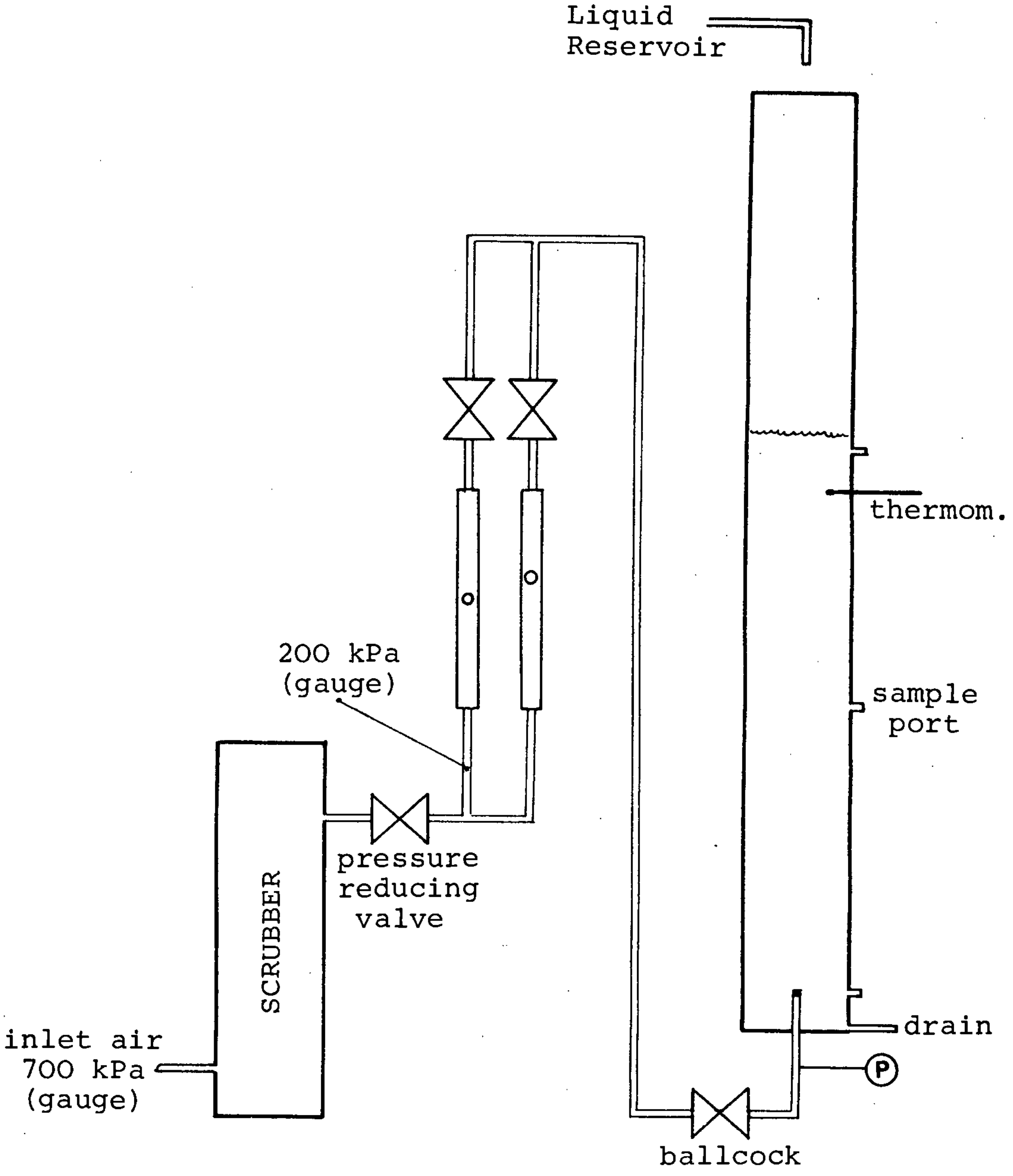


Figure 2.1 Equipment design for steady state and transient experiments.

before being injected into the column. A ball cock at the base of the column allowed the gas flow to be started almost instantaneously at the preset rate.

2.2 EXPERIMENTAL METHODS

2.21 Gas Holdup

The average gas holdup, defined by

$$\varepsilon = \frac{z_F - z_L}{z_F} \qquad (2.1)$$

where z_L is the liquid height and z_F the aerated height, was obtained by direct measurement of the height of the liquid in the column with and without aeration. Because the surface of the liquid was often very turbulent during bubbling, the aerated liquid height was difficult to measure accurately and the holdup measurements presented were obtained from the average of a number of aerated liquid heights estimated by eye. The height was measured from the top of the gas injection nozzle, i.e. 9 cm above the base of the column to the surface of the liquid. The layer of liquid below the nozzle contained almost no bubbles except at the very highest gas flow rates, when small bubbles were carried by turbulent eddies into this section of the column.

No hysterysis was observed on increasing or decreasing the gas flow rate though gas holdup increased gradually in electrolyte solutions as bubbling continued. This was due to the formation of a semi-stable foam on the electrolyte solutions especially sodium sulphite, after prolonged bubbling. This foam was more readily formed the more concentrated the electrolyte solution and is possibly due to the decrease in coalescence between bubbles in electrolyte solutions (see section 1.44).

2.22 Steady State technique

The overall mass transfer coefficient is determined in the steady state method from the decline in sulphite

2.23 The transient method

Using the transient method an overall mass transfer coefficient may be obtained from data on the rate of absorption of oxygen into a previously stripped liquid by the integrated form of Equation 2.2:

$$K_L a = \frac{(1 - \varepsilon)}{t} \ln \frac{c^* - c_i}{c^* - c_f} \qquad (2.3)$$

In a typical physical absorption run, the column was charged with liquid and air flow adjusted to the required rate. Gas holdup at this rate was then measured and the air flow shut off, using the ball cock at the base of the column. Oxygen was stripped from the liquid in the column by sparging with nitrogen for about 5 minutes. A sample was then run out through one of the sampling ports for analysis of the initial oxygen concentration, c_i, for the run. Air flow was initiated and air bubbled up through the liquid in the column for a measured period of time, usually 30 s to 40 s, depending on the gas flow rate. The samples taken at this stage were analysed for the final dissolved oxygen concentration, c_f. The dissolved oxygen at saturation, c^*, was similarly determined by bubbling air through the column for a further period of about 30 minutes.

All samples were withdrawn from the column into 250 mℓ flasks which had been previously flushed with nitrogen. The flasks were completely filled with liquid and tightly stoppered to prevent any further absorption of oxygen before analysis. A few very small air bubbles were sometimes entrained with the sample liquid into the flask but their contribution to the dissolved oxygen concentration was considered to be negligible. The oxygen concentrations in the samples were determined chemically by the Winkler method [63]. A Beckman Fieldlab Oxygen Analyser was tried, but found to be too inaccurate and unreliable for this analysis.

CHAPTER 3

EXPERIMENTAL RESULTS

3.1 GAS HOLDUP

Tabulated gas holdup data may be found in Table A-1 of Appendix A. A comparison of gas holdup results in sodium sulphite solutions of various concentrations with curves presented in the literature is given in Figure 3.1. The data at ionic strengths 0,45 and 1,5 agree well with those obtained by Yoshida and Akita [17] and Braulick et al [11] respectively. Braulick has found that the addition of acid to sulphite solutions results in a noticeable decrease in foaminess and this observation may explain the disparity between the results shown at an ionic strength of 2,4 obtained by Reith [13], who adjusted the pH of the sulphite solution, and the present work, where the pH was not adjusted.

Figure 3.2 shows the variation in volumetric gas holdup with gas rate in water and various ionic solutions. Gas holdup increases with gas rate but is apparently independent of ionic strength, for ionic strengths greater than about 0,1. Concentrated ionic solutions have voidages some 40% greater than water under the same conditions, whereas in dilute solutions voidages are equivalent or only slightly higher than in water. The disparity between the voidages obtained in sodium sulphite solutions, and those measured in sodium sulphate and potassium chloride solutions may be accounted for by the difference in foam head in these cases. In the steady state experiments, where foam formation was particularly marked, the bubbling time, typically about 30 minutes, was long enough for a large head of semi-stable foam to be formed, whereas in the transient runs, which lasted less than 1 minute each, hardly any foam head was built up.

Figures 3.3 and 3.4 clearly show that neither column

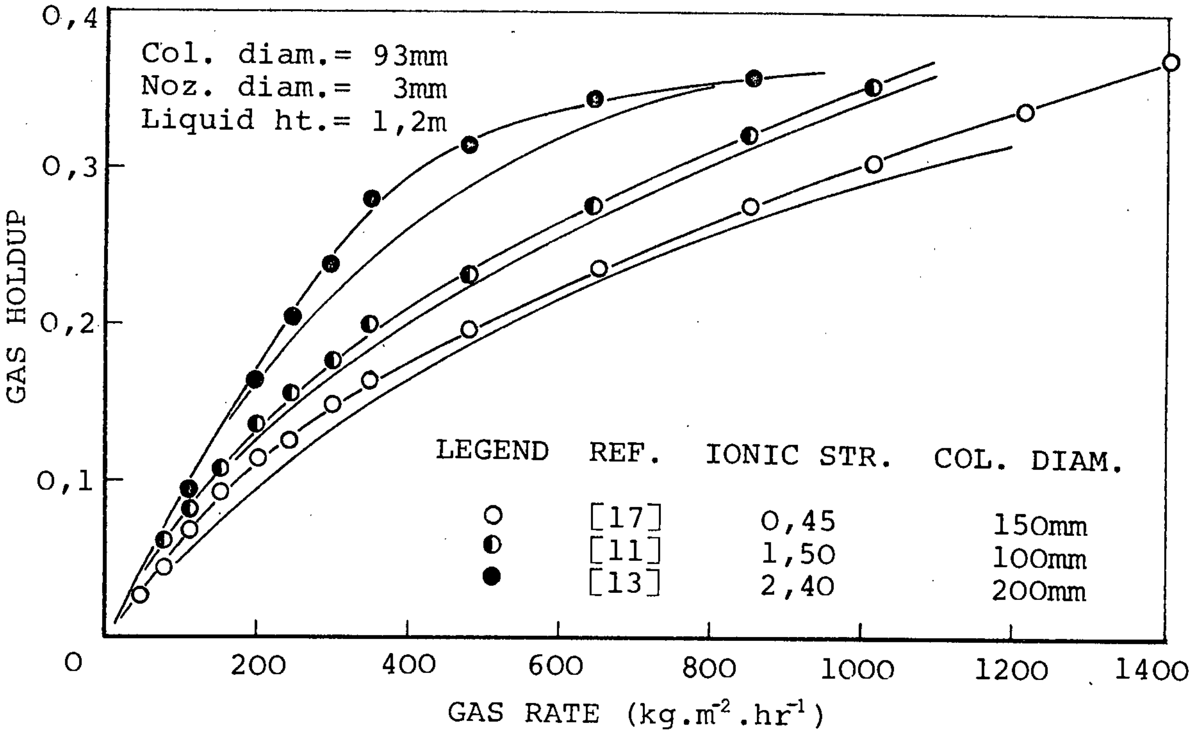


Figure 3.1 Gas holdup in sodium sulphite solutions.

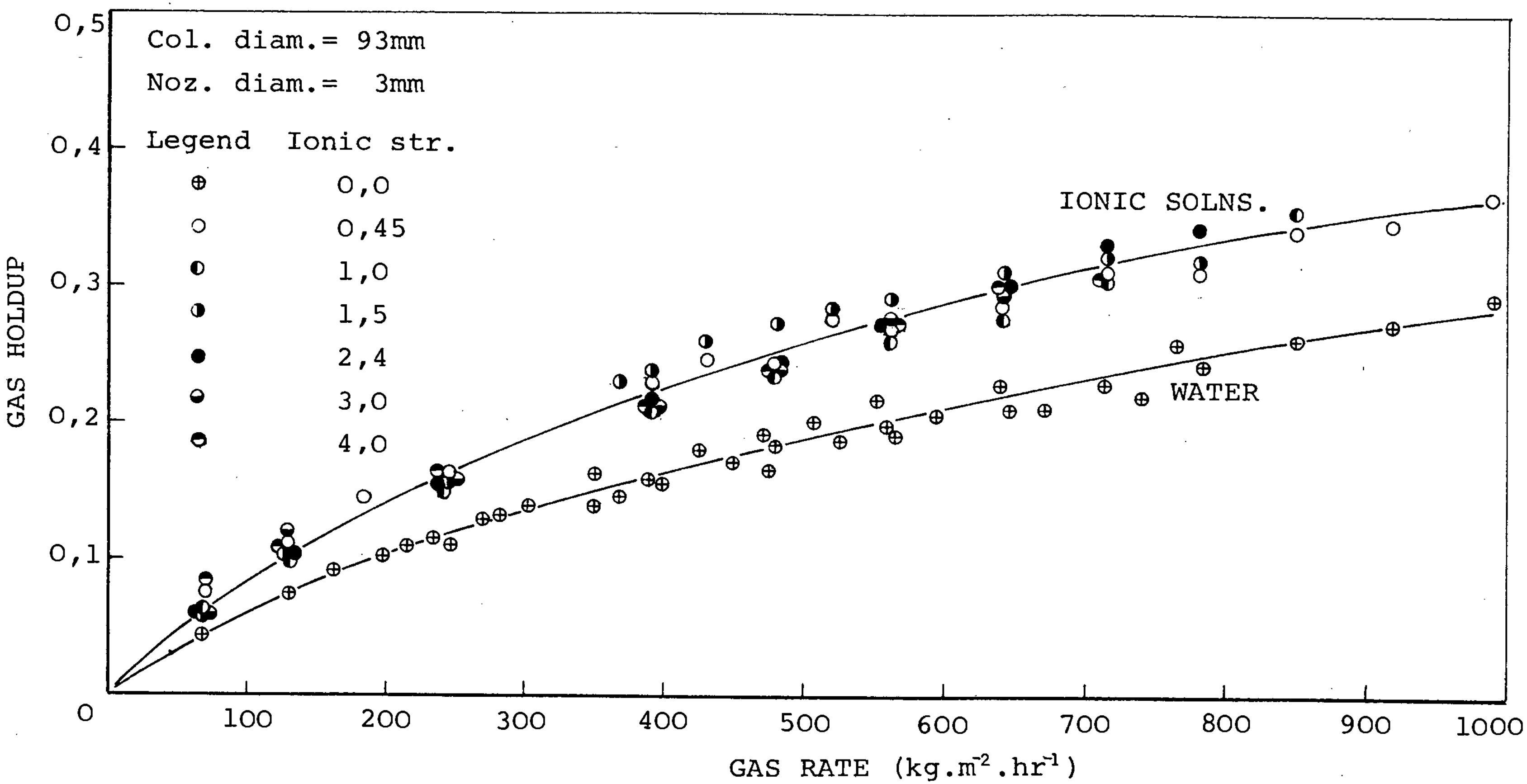
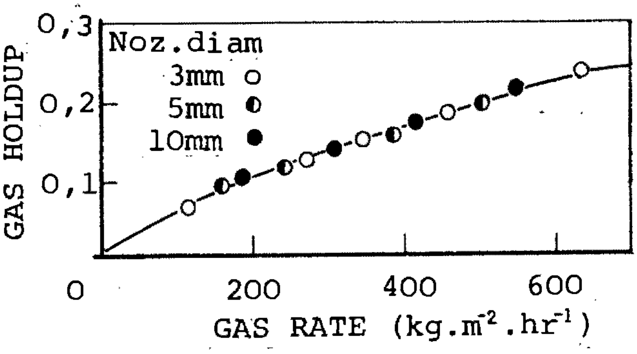


Figure 3.2 Volumetric gas holdup in water and ionic solutions.

diameter nor gas injection orifice diameter were found to have any effect on gas holdup. Yoshida and Akita [17, 39, 46] have made similar observations.



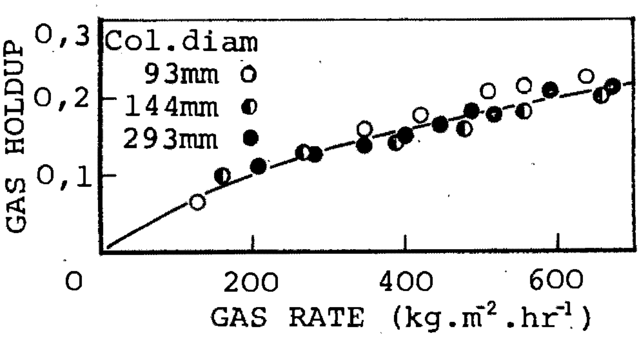


Figure 3.3 Effect of nozzle diameter on gas holdup in water.

Figure 3.4 Effect of column diameter on gas holdup in water.

3.2 VOLUMETRIC MASS TRANSFER COEFFICIENTS

3.21 The sulphite method

The method first employed for the investigation of overall mass transfer coefficients was the sulphite oxidation method. The steady state technique was chosen, in spite of reported controversy over the interpretation of data obtained by this method, for the following reasons:

(1) The sulphite method is widely employed as the standard procedure in testing oxygen absorption [5,6,8,12, 13,16,17,24,64].

(2) The rate of mass transfer could be accurately determined. A single mass transfer coefficient is found, in the steady state method from the linear decline in sulphite concentration with time. By obtaining many points on this line, any random analytical errors in the individual sulphite analysis could be eliminated, and the rate of sulphite oxidation, given by the slope of the line, accurately determined. By conducting the experiment over a suitable period of time any start-up effects could be recognized and disregarded.

(3) The results of some experiments could be compared with curves given in the literature.

(4) The degree of longitudinal mixing in the liquid phase would not affect the driving potential and hence the calculated values of K_La.

(5) The sulphite analysis is convenient and accurate.

For correct evaluation of volumetric mass transfer coefficients from the sulphite method, two conditions must be fulfilled. The reaction must maintain the bulk concentration of oxygen at a negligibly low level and there must be negligible reaction in the diffusion film. If the former condition is not fulfilled, the mass transfer coefficient evaluated will be erroneously low. Lack of compliance with the second condition will result in enhancement of mass transfer and thus lead to incorrectly high mass transfer coefficients.

3.211 Results obtained by the sulphite method: Tabulated results of mass transfer coefficients, obtained by the sulphite method are presented in Appendix A, Table A-2. A sample calculation of K_La from typical data is given in Appendix B. Much of the data are of repetitative nature and many of the points presented in the following graphs represent the average of a number of experimental determinations.

Figure 3.5 shows the overall volumetric mass transfer coefficients obtained at various gas rates for sodium sulphite solutions of different concentrations. In Figure 3.6 the present results are compared with curves presented in the literature. The curves for ionic strengths 0,45; 1,5 and 2,4 were checked for reproducibility after an interval of about 2 months. Only the curve at the lowest ionic strength could not be perfectly reproduced. Figure 3.5 shows that the overall mass transfer coefficient increases linearly with gas rate for all the ionic strengths tested,

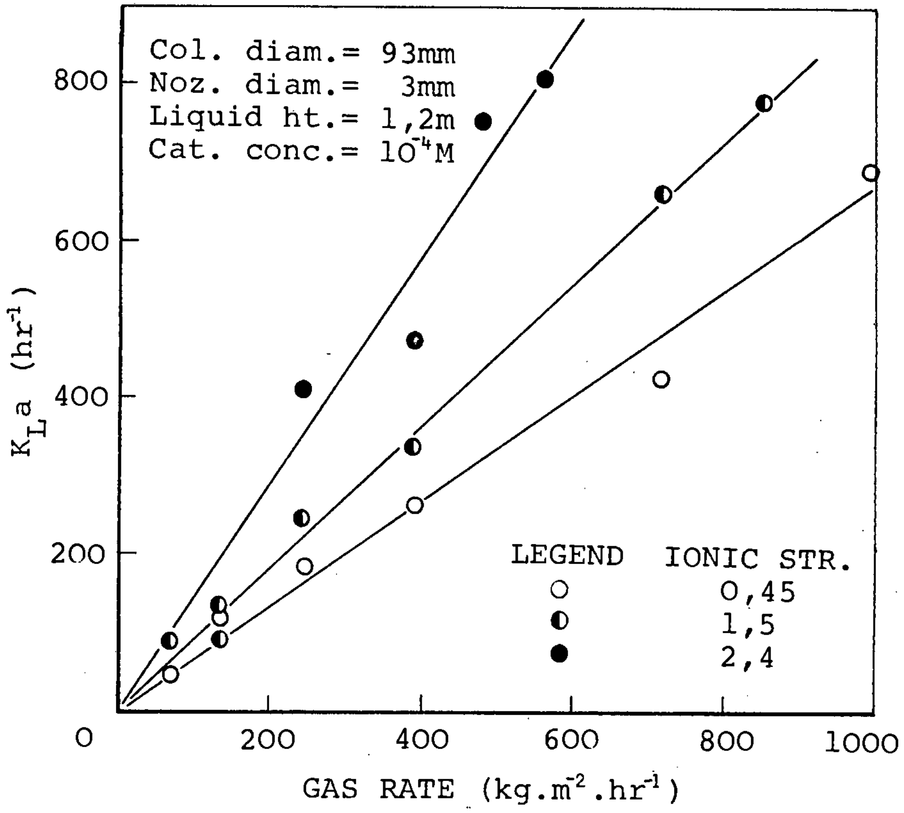


Figure 3.5 Mass transfer coefficients in sodium sulphite solutions.

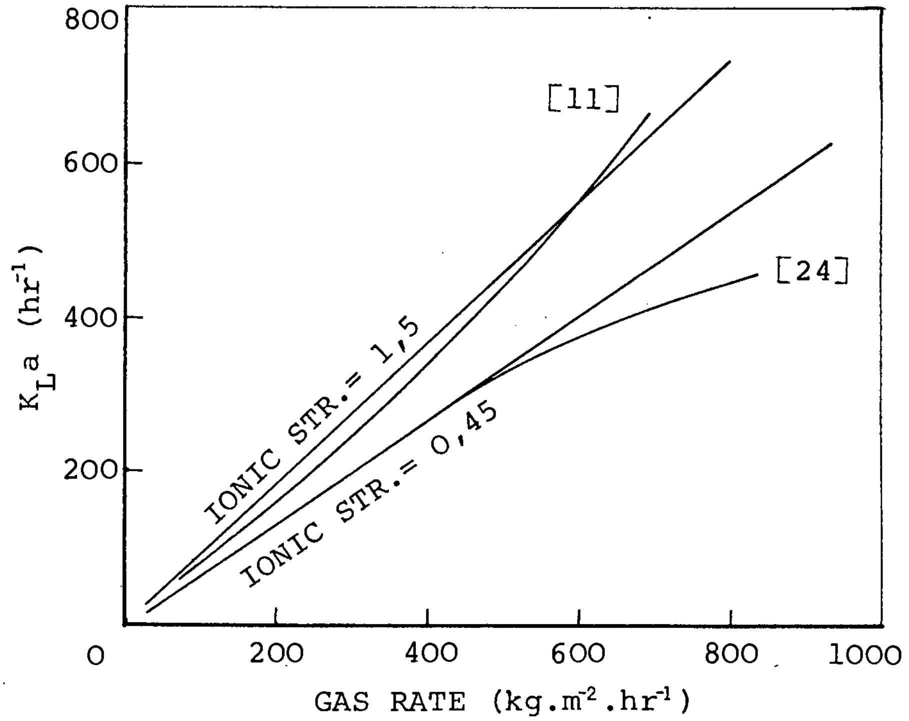


Figure 3.6 Comparison of mass transfer coefficients by the sulphite method with curves from the literature.

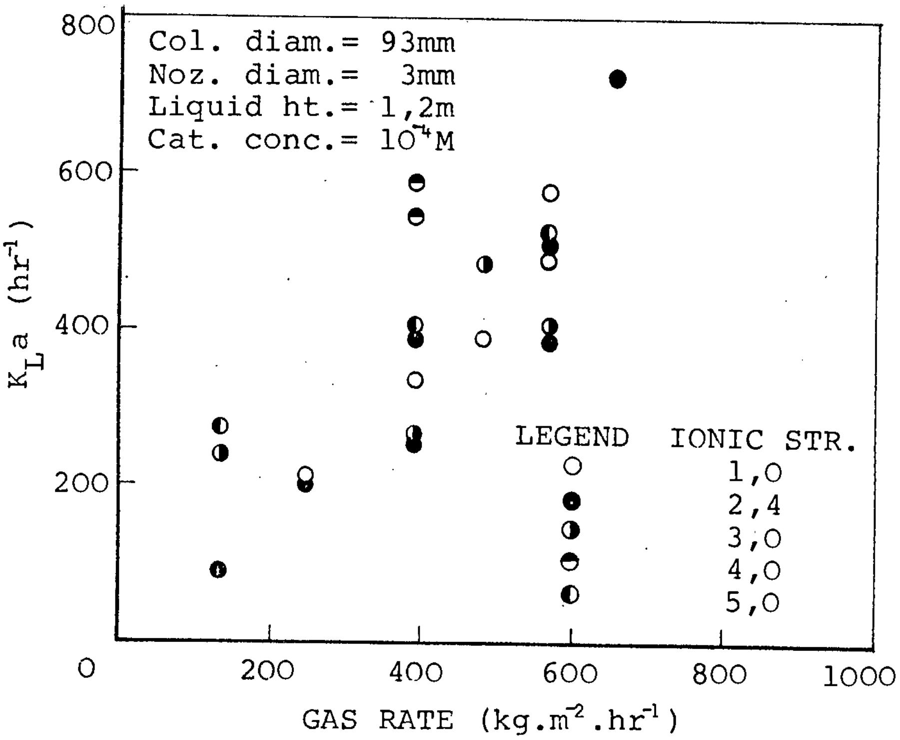


Figure 3.7 Mass transfer coefficients in Na_2SO_4/KCl solutions.

and that there is a proportional increase in K_La with sulphite concentration at any gas rate, for ionic strengths 0,45; 1,5 and 2,4. Only the measurements at ionic strength 3,0, which show a greater scatter than the other results, do not follow this trend. A possible explanation is that interference in the absorption process or the sulphite oxidation reaction was occurring because the sulphite concentration was close to saturation. Since sodium sulphite was thus apparently limited by solubility to ionic strengths of less than 3,0, a mixture of salts was used to extend the results to higher electrolyte concentrations.

3.212 Mixtures of sulphite and potassium chloride: Experiments at ionic strengths 2,4; 4,0 and 5,0 using a mixture of Na_2SO_3 and KCl were accordingly performed with the results shown in Figure 3.7. The runs at ionic strength 2,4 did not agree with the results for sulphite alone at the same ionic strength. The other two sets of results also did not follow the trend with ionic strength exhibited by the sulphite runs. Two possible reasons could be advanced for these discrepancies, viz. the pure sulphite results were too high or the mass transfer coefficients evaluated in the mixed electrolyte experiments were too low. If there was some dependence of the sulphite oxidation rate on sulphite concentration, then enhancement of mass transfer could have caused erroneously high mass transfer coefficients to have been evaluated in those experiments where high sulphite concentrations were used, i.e. in the pure sulphite experiments. On the other hand it was also possible that the KCl in solution was interfering with absorption in the experiments using mixed electrolytes, for example, by affecting the sulphite oxidation in such a way that the reaction was not proceeding quickly enough to maintain a negligible bulk oxygen concentration. Refer to section 1.42 for the requirements which must be complied with in steady state absorption experiments.

In order to test the former possibility, experiments at an ionic strength of 2,4 were performed, using a mixture of 0,1 M Na_2SO_3 and 0,7 M Na_2SO_4. This eliminated any effect foreign ions might have had on the absorption process. Sulphate ions were always present in steady state mass transfer experiments, since the process involves the oxidation of sulphite to sulphate ions, and could not therefore be the cause of any interference. Figure 3.8 shows the result of this test: sulphite only and the sulphite-sulphate mixture behaved identically with regard to oxygen absorption. Sulphite concentration therefore had no effect on mass transfer of oxygen in the range employed in these experiments.

The other possible reason for the discrepancy between the pure sulphite and the mixed electrolyte (Na_2SO_3 - KCl) experiments, namely that the foreign ions in solution were interfering with absorption or reaction, was also tested. The mass transfer coefficients per unit volume over the range of gas rates were obtained for an ionic strength of 1,0 using a sodium sulphite-potassium chloride mixture. These data, presented in Figure 3.7, followed the trend exhibited by the pure sulphite experiments indicating that there was no interference by the KCl. The results for mixed electrolytes at ionic strength 2,4, however, also shown on Figure 3.7, were much lower than those obtained for sulphite only or for the sulphate-sulphite mixture. The conclusion drawn from these results was that KCl, at least at high concentrations, interferes in some way with the steady state absorption of oxygen into sodium sulphite solutions. The sulphite method cannot thus be used to obtain results at high ionic strengths, due to the relative insolubility of sodium sulphite alone, and possible interference with absorption if a foreign electrolyte is used to boost the ionic strength. The transient method was thus adopted to extend the investigation to high ionic strengths.

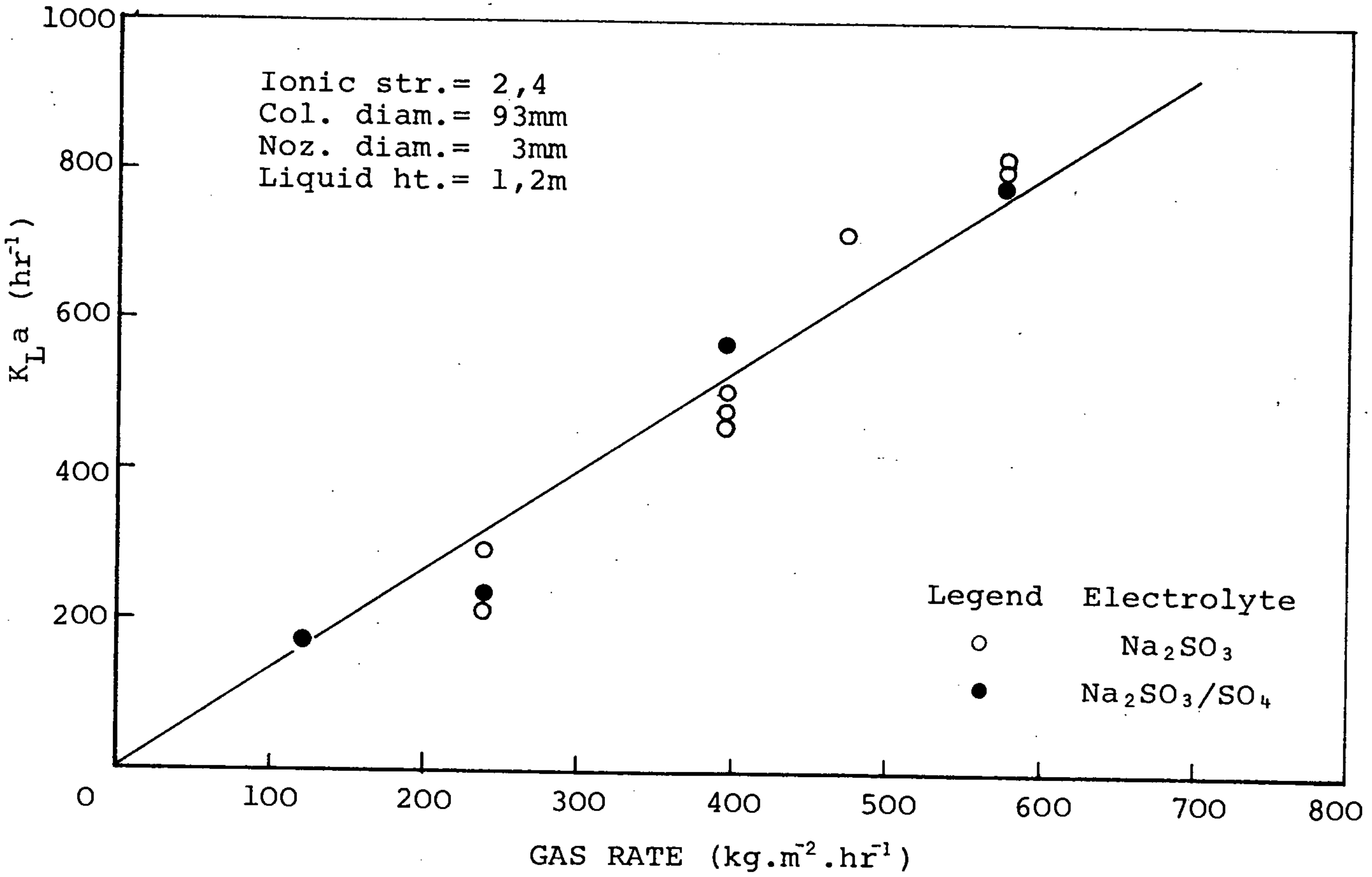
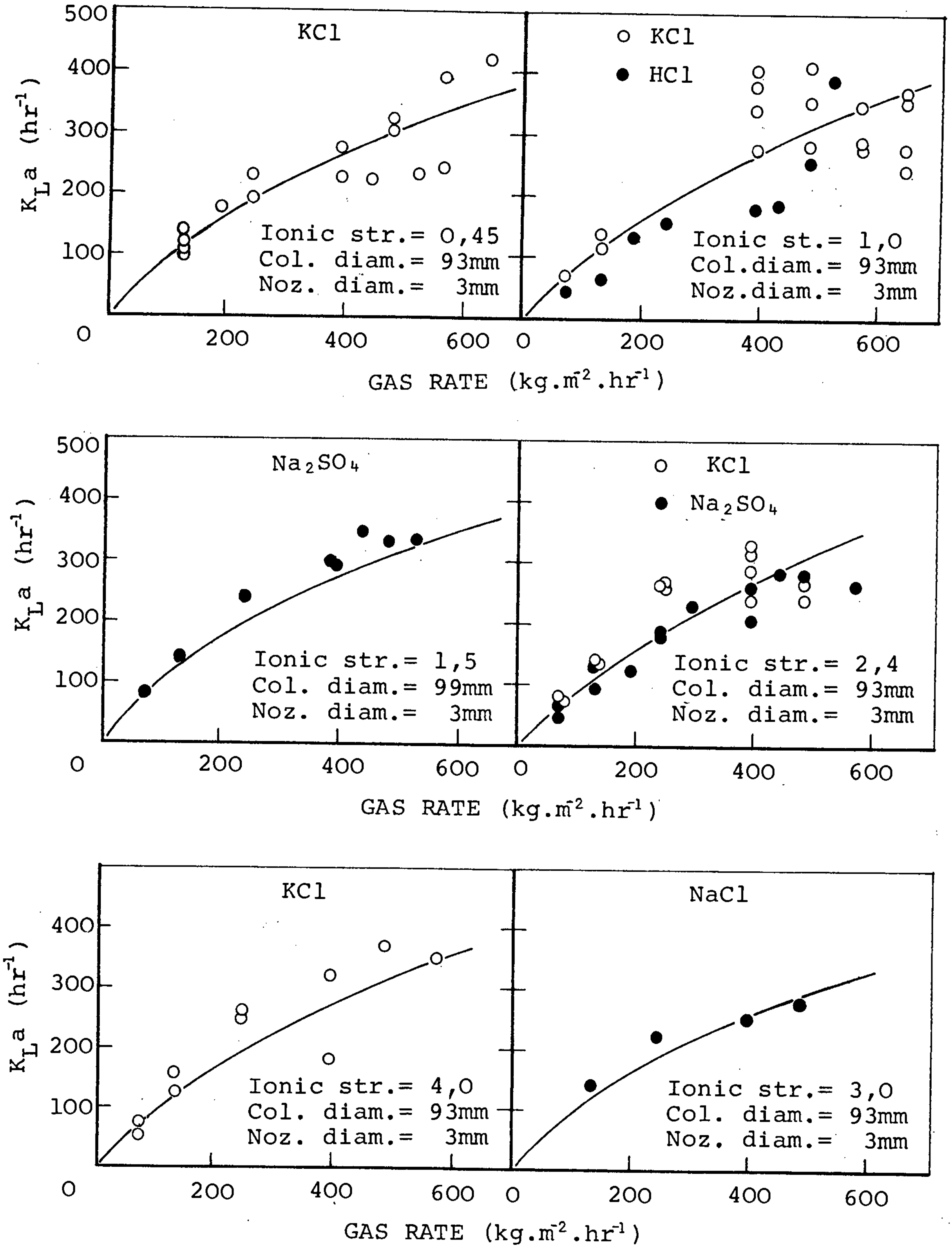


Figure 3.8 The effect of sulphite concentration on the overall mass transfer coefficient.

3.213 Comparison of steady state and transient results:

As a first step a number of mass transfer determinations at low ionic strengths using the transient method were performed to compare with data already obtained from the sulphite technique. These results which are presented in Figures 3.9 to 3.15, are more fully discussed in section 3.3. The important point in this connection is that the mass transfer coefficients obtained by using the transient method were substantially lower than those obtained, at the same conditions, using the steady state technique. The transient results, although they showed a great deal more scatter, especially at high gas rates, cast doubt on the validity of the data obtained by the sulphite method. Although the steady state technique increases the accuracy of mass transfer rate determinations, as explained in section 3.21, the method relies for the valid evaluation of the mass transfer coefficients, on the chemical reaction fulfilling two conditions namely, being fast enough to maintain negligible bulk oxygen concentration in the liquid and slow enough to prevent appreciable reaction in the mass transfer film. Thus enhancement of mass transfer, due to the simultaneous absorption and fast reaction in the steady state experiments (see section 1.3) was thought to be one possible explanation for the discrepancy between data obtained by the sulphite oxidation technique and the transient method. Another possibility was that sulphite was being hydrolysed and sulphur dioxide being evolved and carried out in the exit gas stream. The mass transfer coefficients obtained from the rate of sulphite depletion in the bubble column would thus be erroneously high, since sulphite was being lost not only by reaction but also by evolution of sulphur dioxide. The air stream leaving the column was therefore analysed but found to contain virtually no sulphur dioxide. Details of the analytical method and the exact results are given in Appendix C. As this explanation for the difference between the mass transfer coefficients obtained in the steady state and



Figures 3.9-3.15 Mass transfer in ionic solutions by the transient method.

transient experiments proved to be unfounded, the possibility of chemical enhancement of mass transfer in the sulphite experiments was examined.

3.214 Enhancement: Chemical enhancement of mass transfer occurs when a substantial portion of the diffusing molecules react in the mass transfer film. In this case, for negligible reaction in the diffusion film, the amount of oxygen reacting inside the film must be very much less than the amount being transported through it. If the mass transfer film has a thickness δ then

$$\delta \times r\{[O_2]\} << K_L c^* \qquad (3.1)$$

but, by the film theory of mass transfer [1]:

$$\delta = D_L/K_L \qquad (3.2)$$

The sulphite oxidation is second order in oxygen (see section 1.422)

$$\therefore \quad r\{[O_2]\} = k_2[c]^2 < k_2[c^*]^2 \qquad (3.3)$$

Thus

$$K_L{}^2 >> D_L k_2 c^* \qquad (3.4)$$

for negligible reaction in the film,

$$\text{i.e. } K_L a >> a\sqrt{D_L k_2 c^*} \qquad (3.5)$$

$$\text{or} \quad a << \sqrt{D_L k_2 c^*}/K_L a \qquad (3.6)$$

This condition is difficult to apply without a detailed study of the sulphite reaction rate, which cannot simply be obtained from the literature, as explained in section 1.422, and a knowledge of the interfacial area for mass transfer.

However, the condition may be indirectly applied to give a clue as to whether enhancement is taking place or not.

Since K_La increases as the gas rate increases, because of greater gas holdup and turbulence in the bubble column, the condition becomes more difficult to comply with at higher gas rates. As the gas rate is increased, the number of bubbles increases and a greater proportion of the liquid is contained in the mass transfer film, and therefore a larger proportion of the reaction is taking place inside the film. The possibility or magnitude of enhancement may reasonably be expected therefore to be greater at high gas rates. Thus if enhancement of mass transfer is the reason behind the discrepancy in mass transfer coefficients obtained by the two methods used, the difference between the steady state and the transient data should be greater the higher the gas rate. This is the case with the present data indicating that enhancement may have been taking place.

Another possible method of testing for chemical enhancement in the sulphite system has been presented by Philips and Johnson [5]. If the absorption of oxygen were purely physically controlled, that is, without any chemical enhancement of mass transfer, the ordinary mass transfer equation

$$R = K_Lac^* \qquad (3.7)$$

would hold, and the rate of oxygen absorption would be proportional to the equilibrium oxygen concentration, c^*, in the liquid. On the other hand, Philips and Johnson have shown that if all reaction were to take place in the mass transfer film, the oxygen transfer rate would be proportional to the 1,5 exponent of the equilibrium oxygen concentration. The derivation is presented in Appendix D. Since the presence of ions in solution affects the solubility of oxygen, this can be applied to the sulphite experiments to determine whether enhancement, which implies reaction in the mass transfer film, is taking place. The power dependence of absorption rate R, on the equilibrium driving force c*, is given by the slope of a plot of R against c* on logarithmic coordinates. If the slope of such a plot is greater than 1,0, then enhancement of mass transfer is appreciable since significant reaction is taking place in the mass transfer film. On the other hand if the slope is very close to 1,0 then the absorption is physically controlled and the sulphite oxidation reaction is not interfering with the rate of oxygen mass transfer. The slope would be less than 1,0 only when there is an appreciable amount of oxygen in the bulk of the liquid, i.e. $c_0 > 0$. In this case mass transfer is described by the equation

$$R = K_L a(c^* - c_0) \sim K_L a(c^*)^n \qquad (3.8)$$

where $n < 1$.

The result of such an analysis, given in Figures 3.16 to 3.18 is not conclusive. The slope of the lines in Figures 3.16 to 3.18 give the power dependence of mass transfer rate on the equilibrium oxygen concentration. At high gas rates, the slope is close to 1,5, indicating that enhancement was almost certainly taking place. At a gas rate of about 400 $kg.m^{-2}.hr^{-1}$, which is approximately in the middle of the range investigated, the rate of mass transfer is proportional to about the 1st power of the oxygen concentration, showing no enhancement. When the gas flow was very low, however, the slope of the plot becomes less than 1,0 indicating that the bulk concentration of dissolved oxygen was not negligible in these experiments.

While this evidence alone cannot be regarded as convincing due to the small range in the transfer driving forces investigated, it nevertheless correlates well with the qualitative picture given above and together with the wide scatter, uncertain influence of foreign ions and lack of reproducibility of data at ionic strength 0,45 and in

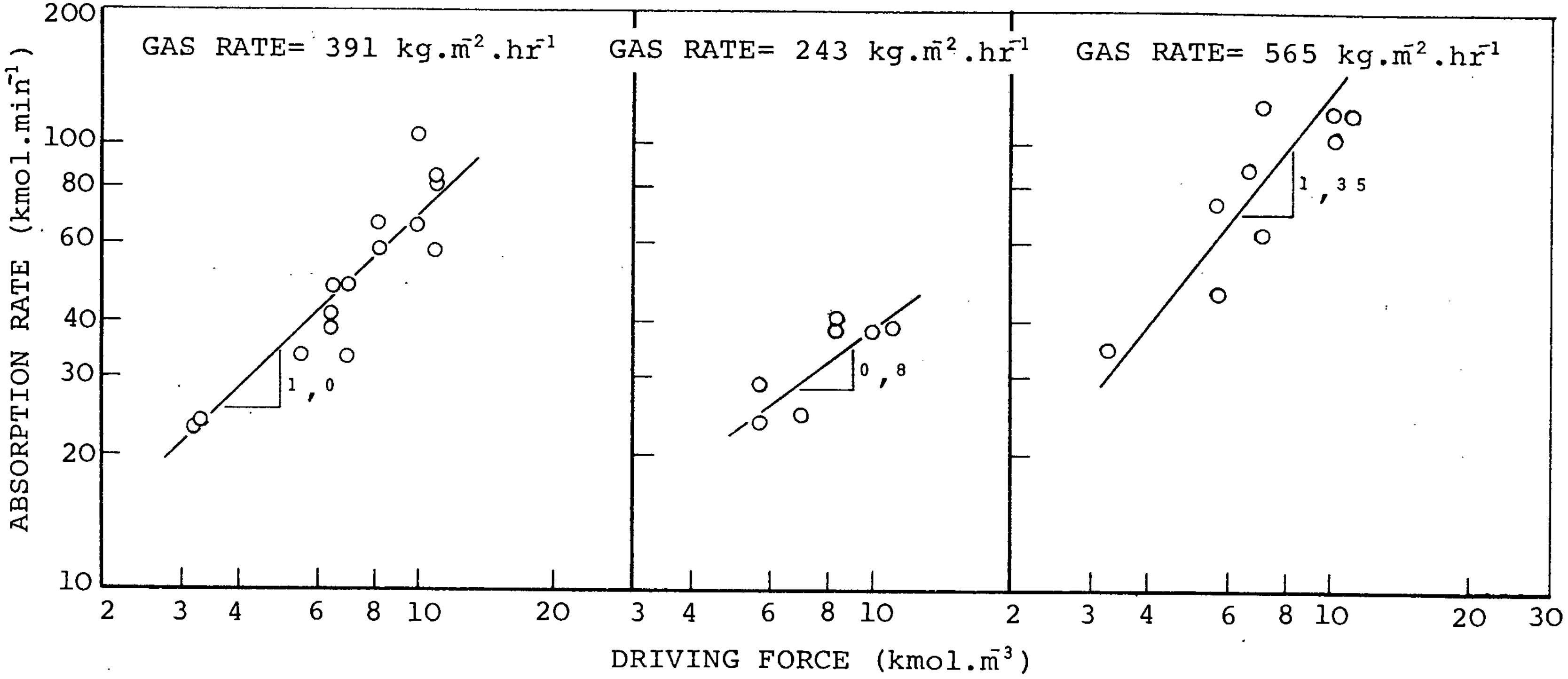


Figure 3.16-3.18 The effect of equilibrium driving force on mass transfer rates.

the mixed electrolyte experiments by the steady state method, as well as disagreement with data obtained at the same conditions by the transient method, provides sufficient reason to discount the sulphite technique as a valid method for obtaining mass transfer data in this investigation.

The demonstrated problems with the sulphite method does not imply that previous investigations using the sulphite method are based on false premises, since in many it has been clearly demonstrated that enhancement was not taking place. It is apparent from the literature dealing with the kinetics of the sulphite reaction, that the reaction rate varies widely between experiments. However, it is equally clear that results obtained from the sulphite method should be regarded with some doubt where it has not been specifically demonstrated that the two conditions for valid interpretation have been complied with.

Since it is evident that enhancement was a distinct possibility in the sulphite results presented here, the transient method was adopted and it is on data obtained by this method that the majority of conclusions regarding mass transfer have been based.

3.3 THE TRANSIENT METHOD

In the transient method the rate of oxygen absorption into a liquid previously stripped of oxygen is obtained from dissolved oxygen measurements before bubbling begins, c_i, and after a short period of gas flow, c_f. The volumetric mass transfer coefficient may then be calculated from the rate of mass transfer of oxygen by the equation

$$K_L a = \frac{1 - \varepsilon}{t} \ln \frac{c^* - c_i}{c^* - c_f} \qquad (1.4)$$

Since the air could be bubbled through the liquid in the column for only a short period of time in these experiments, before the liquid was nearly saturated with oxygen, end effects, especially at the commencement of bubbling could be expected. When gas flow was initiated a large slug of gas rose up through the liquid with apparently well developed turbulent bubbling following in its wake. Longer gas-liquid contacting times would reduce the magnitude of the error caused by the changing hydrodynamic conditions when air flow was initiated, since the start-up period would then be a smaller proportion of the total bubbling time. The bubbling period could not be extended too long though, because then the final measured oxygen concentration, c_f, would be very close to the saturation concentration c^*, and any small analytical error in determining c_f would be greatly magnified in the mass transfer coefficient.

Experiments were conducted to find the best bubbling time to eliminate start-up errors as far as possible, while maintaining an easily measurable difference between the final concentration and the saturation concentration of dissolved oxygen. The variation in the calculated values of K_La with bubbling time caused by these errors, is shown in Figure 3.19. For short bubbling periods, where start-up errors may be expected to be greatest, because initial bubbling instabilities form a significant proportion of the total experiment, erroneously high estimates of K_La were obtained. There is a large amount of scatter in the overall mass transfer coefficients obtained from experiments where the total bubbling time was greater than about 40 s probably because of small analytical errors in dissolved oxygen concentration which are magnified in the calculation of K_La. Bubbling periods of 30 to 40 seconds where both start-up errors and the effect of small analytical errors on the overall mass transfer coefficients were considered smallest, were thus chosen for the experiments. Even for these fairly short bubbling times there was a large scatter in the calculated mass transfer coefficients, especially at high gas rates, where high mass transfer rates resulted in smaller differences between c_f and c^*, and where mass transfer coefficients were therefore more sensitive to small analytical errors in c_f.

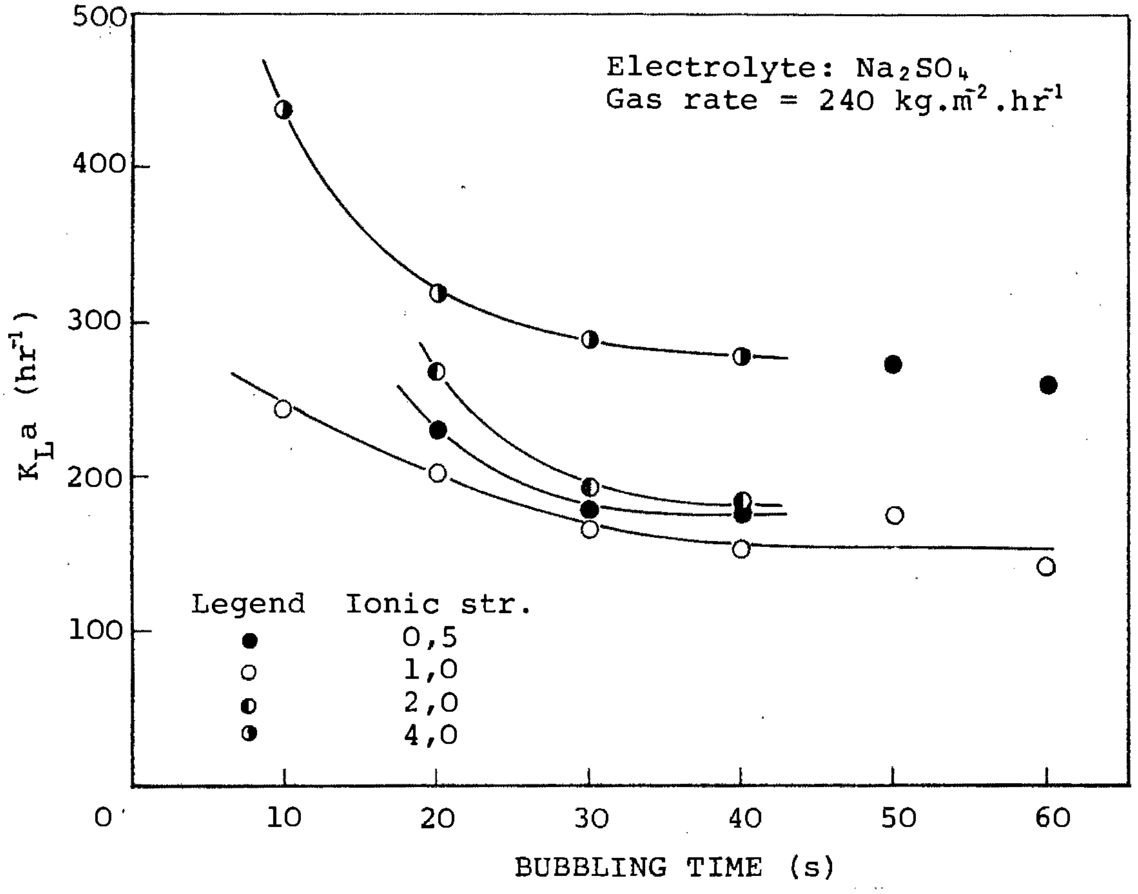
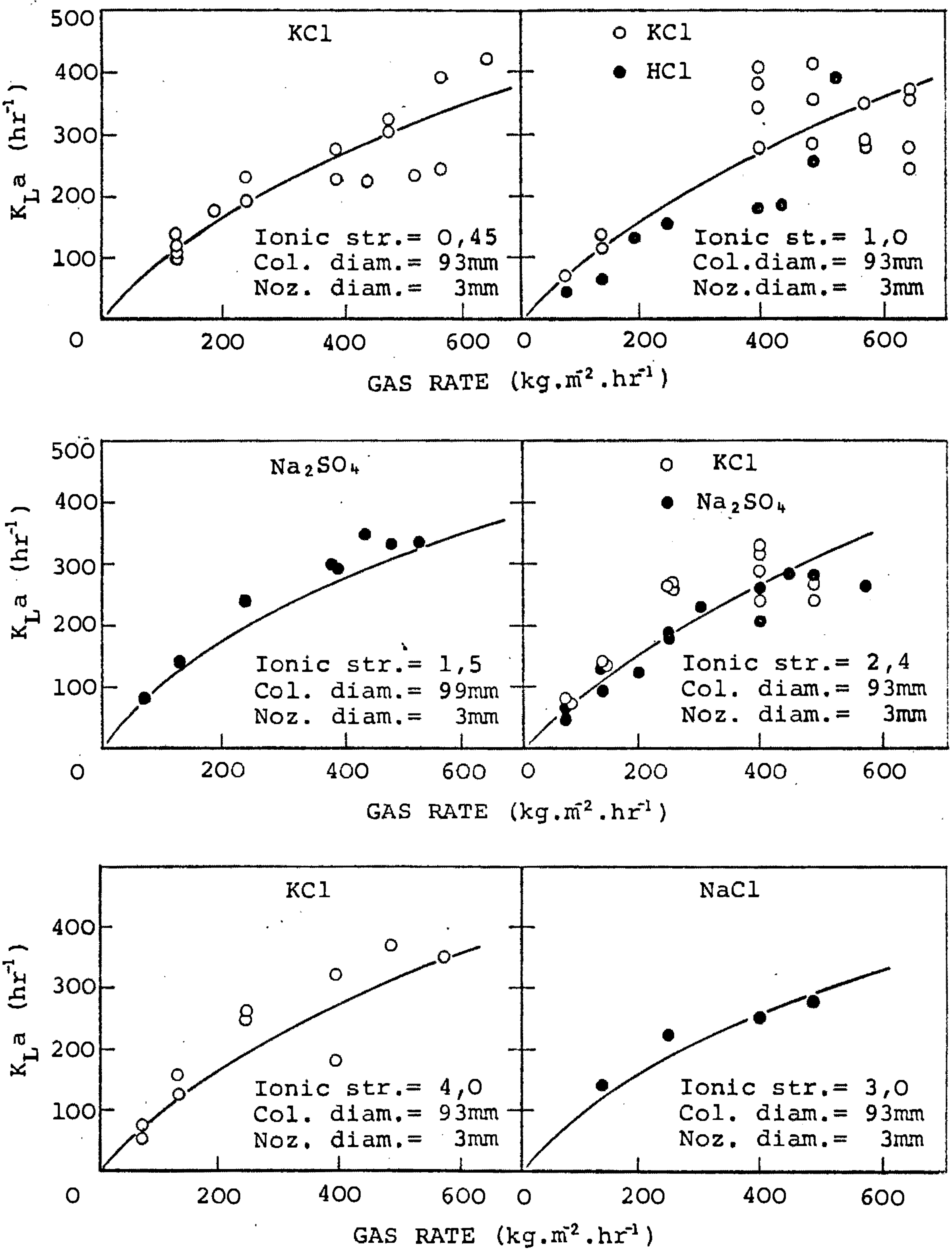


Figure 3.19 Significance of end errors in the transient method

3.31 The effect of gas rate

The tabulated results of mass transfer coefficients obtained in the transient experiments are presented in Appendix A, Tables A-3 and A-4.

The variation of overall volumetric mass transfer coefficients at various ionic strengths is shown in Figures 3.9 to 3.15 (pg 46). The curve shown on each graph, included to facilitate comparison between the figures, is the variation of K_La with gas rate predicted by an equation to be discussed in section 4.2. The mass transfer coefficients were found to increase with gas rate in much the same manner as gas holdup (cf. Figure 3.2), rather than linearly, as in the steady state experiments. Gas rate influences the overall



Figures 3.9-3.15 Mass transfer in ionic solutions by the transient method.

mass transfer coefficient by influencing the hydrodynamic situation in the column; the more turbulent conditions at high gas velocities cause an increase in K_L by decreasing the width of the mass transfer film [1], and an increase in interfacial area for mass transfer, as evidenced by the increased gas holdup in the column at high gas rates.

3.32 The Effect of Ionic Strength

In the steady state experiments using sodium sulphite alone, the mass transfer coefficient was found to increase with ionic strength at any particular gas rate. This trend was not due to greater enhancement of mass transfer at higher sulphite concentrations, since a mixture of sodium sulphate and sodium sulphite which contained a low sulphite concentration gave the same results as sodium sulphite alone at the same overall ionic strength. The only difference between the various steady state experiments in sulphite solutions was the sulphite concentration. The greater mass transfer rates in the more concentrated solutions were thus attributed to greater electrostatic interference between the bubbles the higher the ionic strength of the solution, resulting in greater interfacial area for mass transfer. Literature available on the subject confirmed that this was probably the case; Zieminski and Whittemore [40], Robinson and Wilke [6], Marucci [57,58] and Koide et al [30] had all noticed similar trends with increasing electrolyte concentration.

Figure 3.20, which is a comparison of the average mass transfer results obtained by the transient method for various ionic strengths of solution, shows no discernible trend of the overall mass transfer coefficients with ionic strength of solution. Although mass transfer in the range investigated was considerably higher in electrolyte solutions than in distilled water, all the mass transfer data obtained using ionic solutions appeared to be roughly equal at the same gas rate and independent of ionic strength. Measurements of

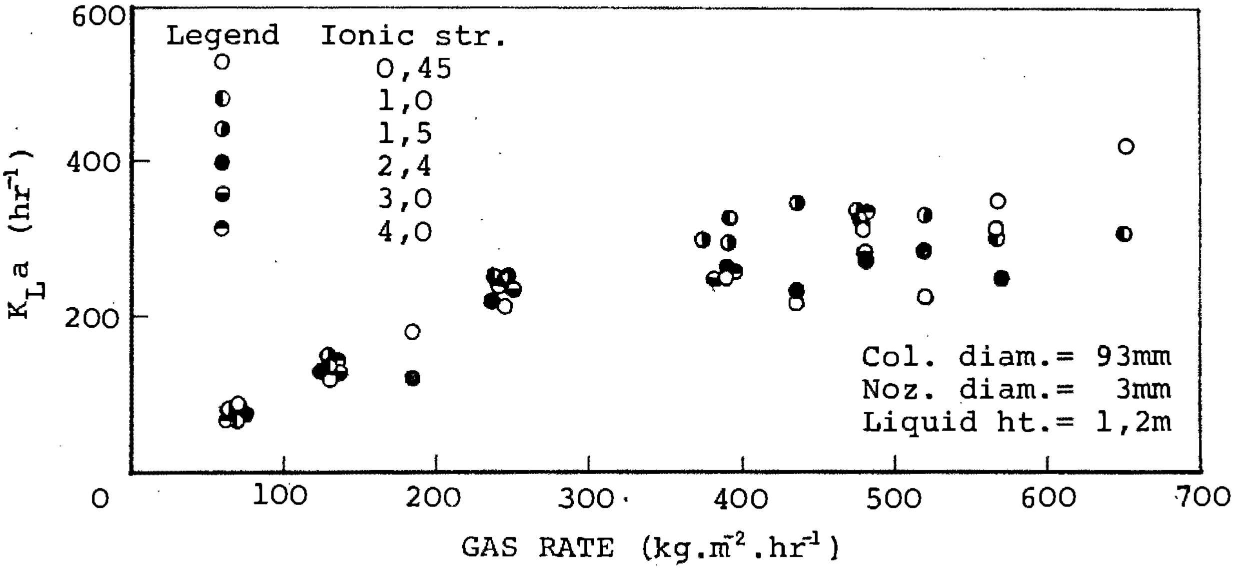


Figure 3.20 Comparison of mass transfer in ionic solutions by the transient method.

mass transfer rates at two gas velocities, 243 kg.m^{-2}.hr^{-1} and 478 kg.m^{-2}.hr^{-1}, over a spectrum of ionic strengths were thus made to obtain the dependence of K_La on ionic strength. The results of these measurements are shown in Figures 3.21 to 3.23.

Mass transfer rates in solutions with ionic strengths of less than 0,1 were found to be equal to those in water at the same conditions and apparently unaffected by the presence of electrolyte. At an ionic strength of 0,1 the mass transfer coefficients increased markedly and thereafter remained at the higher level irrespective of further increase in electrolyte concentration. The proportional increase in overall mass transfer coefficients with ionic strength of solution, observed in the sulphite experiments was not observed in the transient results.

The presence of such a sharp transition may be deduced from the coalescence behaviour reported by Lessard and Zieminski [44] who found that bubble coalescence decreased

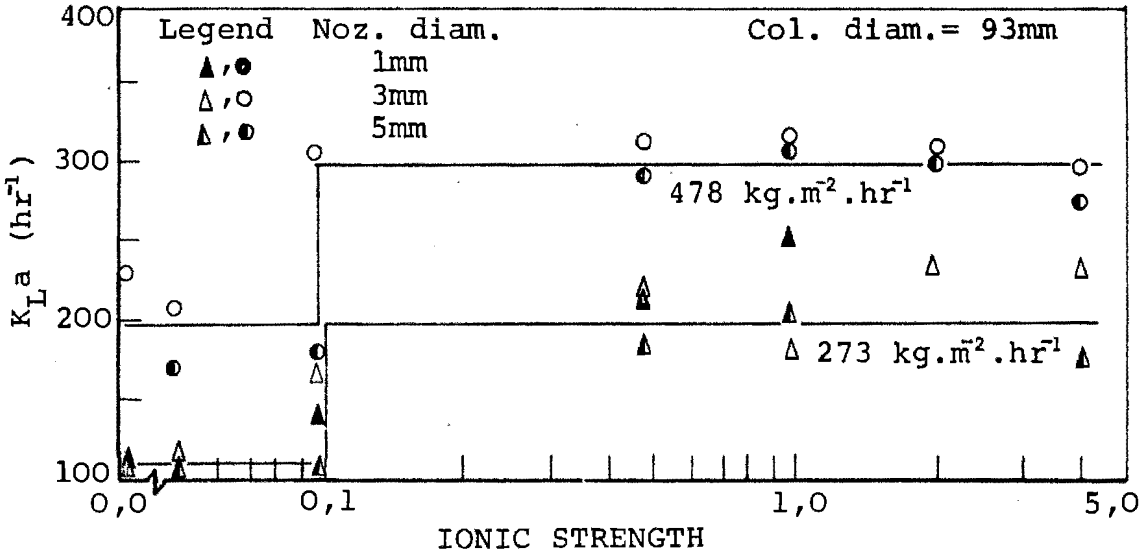


Figure 3.21 The effect of ionic strength on the overall volumetric mass transfer coefficient : 93mm Column.

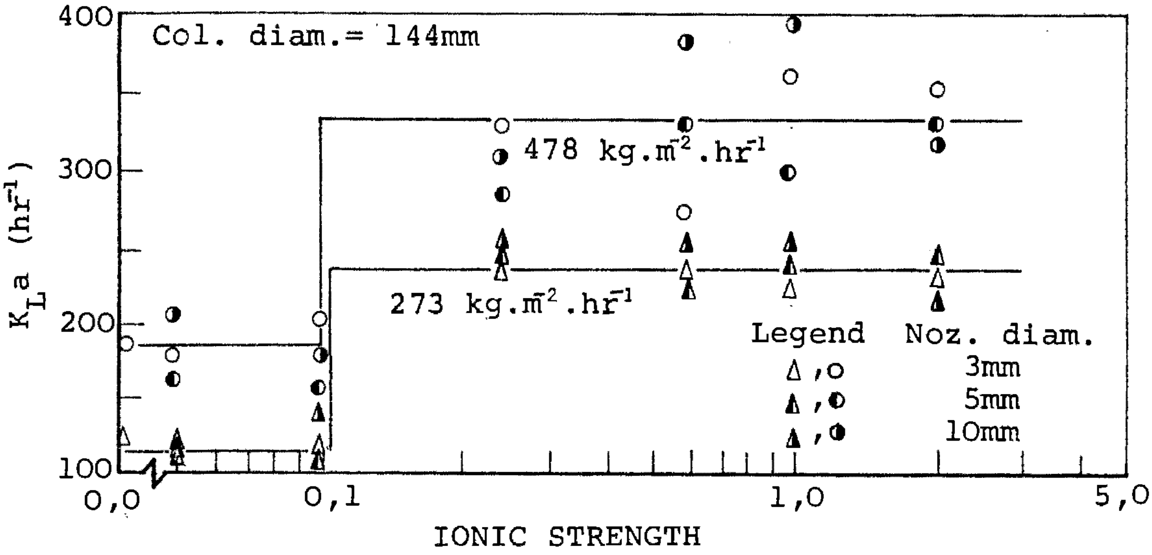


Figure 3.22 The effect of ionic strength on the overall volumetric mass transfer coefficient : 144mm Column.

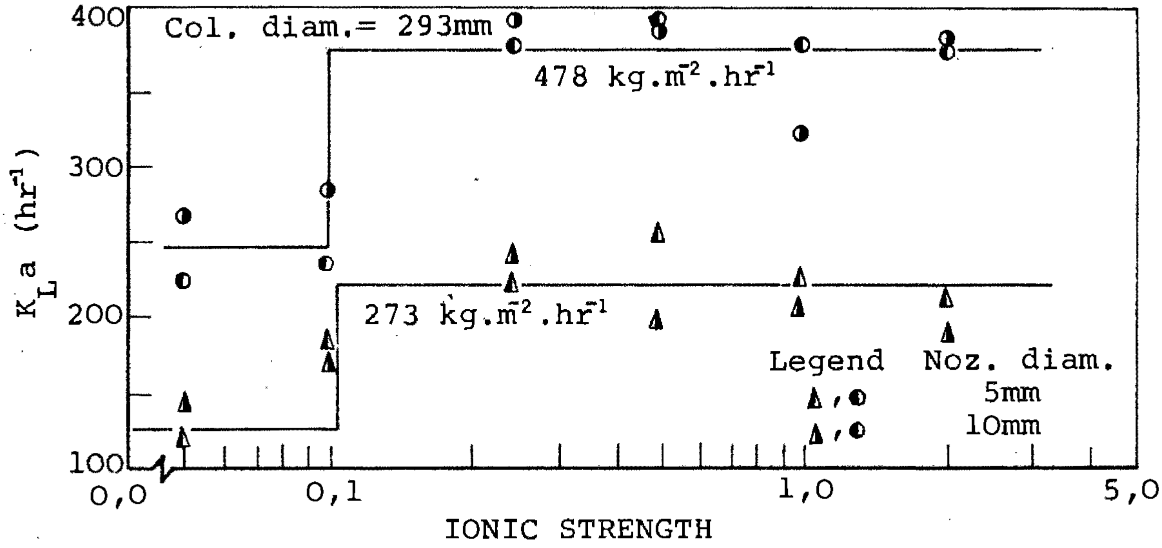


Figure 3.23 The effect of ionic strength on the overall volumetric mass transfer coefficient : 293mm Column.

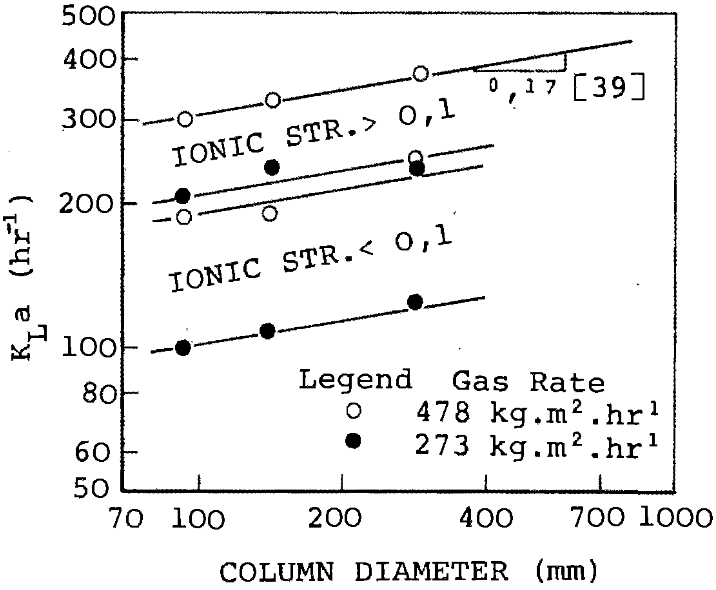


Figure 3.24 The effect of column diameter on the mass transfer rate.

rapidly and markedly at an ionic strength of about 0,18. Such a decrease in bubble coalescence would result in a higher interfacial area for mass transfer in a bubble column contactor at ionic strengths beyond the transition point.

3.33 The Effect of Gas Orifice Diameter

Figures 3.21 to 3.23 show that injection orifice diameter, over the ten-fold range investigated, has no effect on the overall volumetric mass transfer coefficient. This conclusion agrees with the observations of Yoshida and Akita [17,39] and Shulman and Molstad [48], and confirms the opinions of a number of investigators [13,36,40,41,42, 43,44,46] that, except at low gas flow rates, the ultimate bubble size is determined by the coalescence and breakup rates of the bubbles in the column. These rates are a function of the physical properties of the fluids and the level of turbulence in the column, and depend only to a very limited extent on the method of gas injection.

3.34 The Effect of Column Diameter

Yoshida and Akita [17], using the sulphite oxidation method have obtained a dependence of overall volumetric mass transfer coefficients on column diameter to the 0,17 exponent. Three different column diameters were investigated here and a definite dependence of mass transfer rate on column diameter was obtained. The scatter in the data, presented on Figures 3.21 to 3.23, makes it difficult to quantify the effect accurately, but the results confirm that there is a small increase in K_La with column diameter. Figure 3.24 shows that the dependence obtained by Yoshida [17] satisfactorily fits the present data.

3.35 Acid solutions

Ionic strengths of much greater than 4,0 using inorganic salts could not be easily investigated, because of interference by the salts in the dissolved oxygen analysis. Since the addition of an acid, such as HCl, could provide a

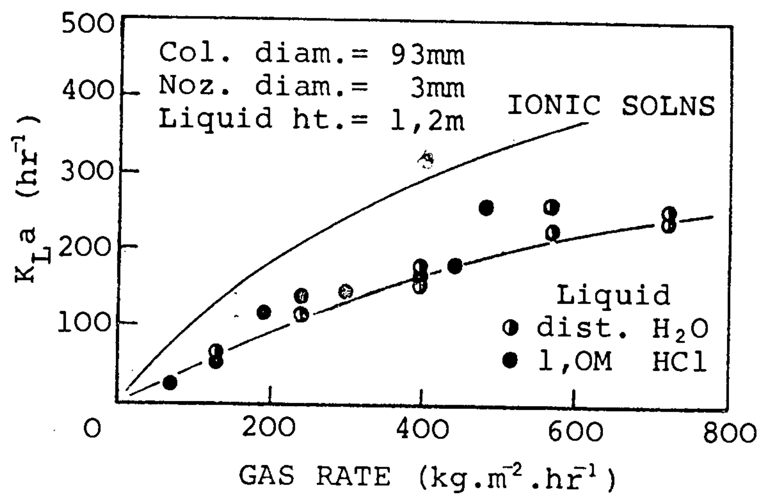


Figure 3.16 Mass transfer coefficients in 1,0M HCl solutions.

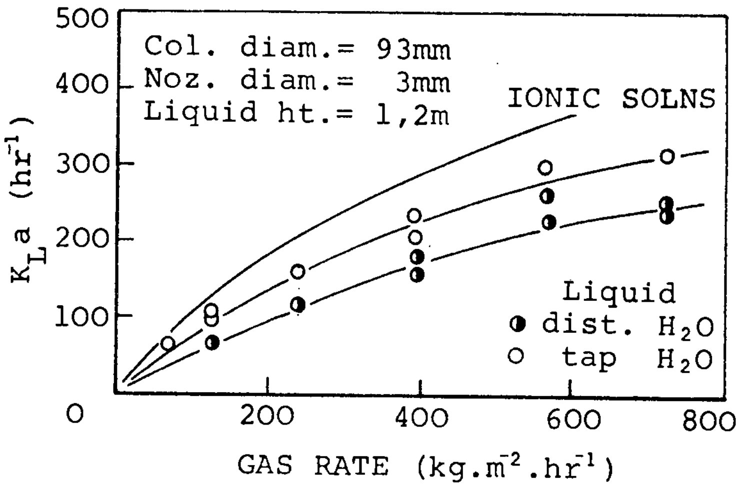


Figure 3.17 Mass transfer coefficients in tap water.

convenient method for increasing the total ionic strength of solution, a number of experiments with 1 M HCl were performed. Although gas holdup in these solutions, shown in Figure 3.25, was slightly higher than in water, but lower than in electrolyte solutions of the same ionic strength, the overall mass transfer coefficients were found to be equivalent to those in water at the same gas rate, as shown in Figure 3.26. Since HCl had no effect on the mass transfer rate, it could not be used to obtain results at high ionic strengths which would be applicable to inorganic salt solutions. The behaviour of HCl suggests that acids in general may behave anomalously, but the effect was not investigated further and no explanation for these observations is attempted here.

3.36 Mass transfer in Tap Water

Municipal mains water was found to give a very much higher mass transfer coefficient than distilled water at the same gas flow rate, as demonstrated in Figure 3.27. This result is similar to that reported by Urza and Jackson [12] who found that K_La in tap water was slightly higher than in dilute sodium sulphite solutions (ionic strength of 0,08), under similar conditions at low gas flow rates. The reason for these unexpectedly high mass transfer coefficients in tap water is likely to be associated with the higher drag coefficients, demonstrated by Haberman and Morton [65], for bubbles rising in tap water than in distilled water, although the exact relationship is not clear. Gas holdup in distilled and tap water was found to be identical at the same gas flow rate.

CHAPTER 4

CORRELATION OF RESULTS

4.1 HOLDUP CORRELATIONS

4.11 Gas holdup in common liquids

Akita and Yoshida [39] have shown by dimensional analysis that

$$f_1(\varepsilon) = f_2(\mathrm{Bo},\mathrm{Ga},\mathrm{Fr}) \qquad (4.1)$$

where

$$\mathrm{Bo} = gD^2\rho/\gamma \quad \text{the Bond number} \qquad (4.2)$$

$$\mathrm{Ga} = gD^3/\nu^2 \quad \text{the Galileo number} \qquad (4.3)$$

$$\mathrm{Fr} = U_G/\sqrt{gD} \quad \text{the Froude number} \qquad (4.4)$$

From experimentally measured voidages in water, glycol and methanol mixtures they empirically determined that a function of gas holdup was directly proportional to the superficial gas velocity,

$$\frac{\varepsilon}{(1-\varepsilon)^4} \propto U_G \qquad (4.5)$$

and thus attempted to correlate their data by the expression

$$\frac{\varepsilon}{(1-\varepsilon)^4} = c(\mathrm{Bo})^a(\mathrm{Ga})^b(\mathrm{Fr})^{1,0} \qquad (4.6)$$

The constants a, b and c were determined by a graphical procedure [39] using the fact that gas holdup is independent of column diameter. The final expression obtained was [39]:

$$\frac{\varepsilon}{(1-\varepsilon)^4} = 0{,}20(\mathrm{Bo})^{1/8}(\mathrm{Ga})^{1/12}(\mathrm{Fr})^{1,0} \qquad (4.7)$$

In Figure 4.1 gas voidage fractions predicted by Equation 4.7 are compared with holdup data in water obtained in the present investigation and with a curve presented by Hughmark [50]. The latter is an average of a large number of holdup data published in the literature. The present results agree well with the predicted values at low gas rates, but at higher gas velocities the experimental data obtained in this study and the averages given by Hughmark [50], are higher than predicted from Equation 4.7.

A re-evaluation of the constant and exponents of Equation 4.6 to get a better fit of all the data available was thus attempted. The method used was the Nelder and Mead simplex sequential search [66] for constants to minimize the sum of the squares of the differences between the predicted and experimentally determined voidages. Whereas Akita and Yoshida had constrained the exponent on $(1 - \varepsilon)$ to get direct proportionality with the Froude number, the computational method employed in this study required no such constraints. The exponents on $(1 - \varepsilon)$, Bo and Ga, and the constant c, were allowed to vary independently. The power on the Froude number was constrained as a function of the exponents on the Bond and Galileo numbers because of the requirement that gas holdup should be independent of column diameter. Equation 4.1 expressed in general terms is

$$\frac{\varepsilon}{(1 - \varepsilon)^n} = c\ \mathrm{Bo}^a\ \mathrm{Ga}^b\ \mathrm{Fr}^d \qquad (4.8)$$

The exponent of column diameter, which must be zero, may be obtained by expansion of Equation 4.8

$$2a + 3b - \tfrac{1}{2}d = 0 \qquad (4.9)$$

Hence the value of d is fixed by a and b:

$$d = 4a + 6b \qquad (4.10)$$

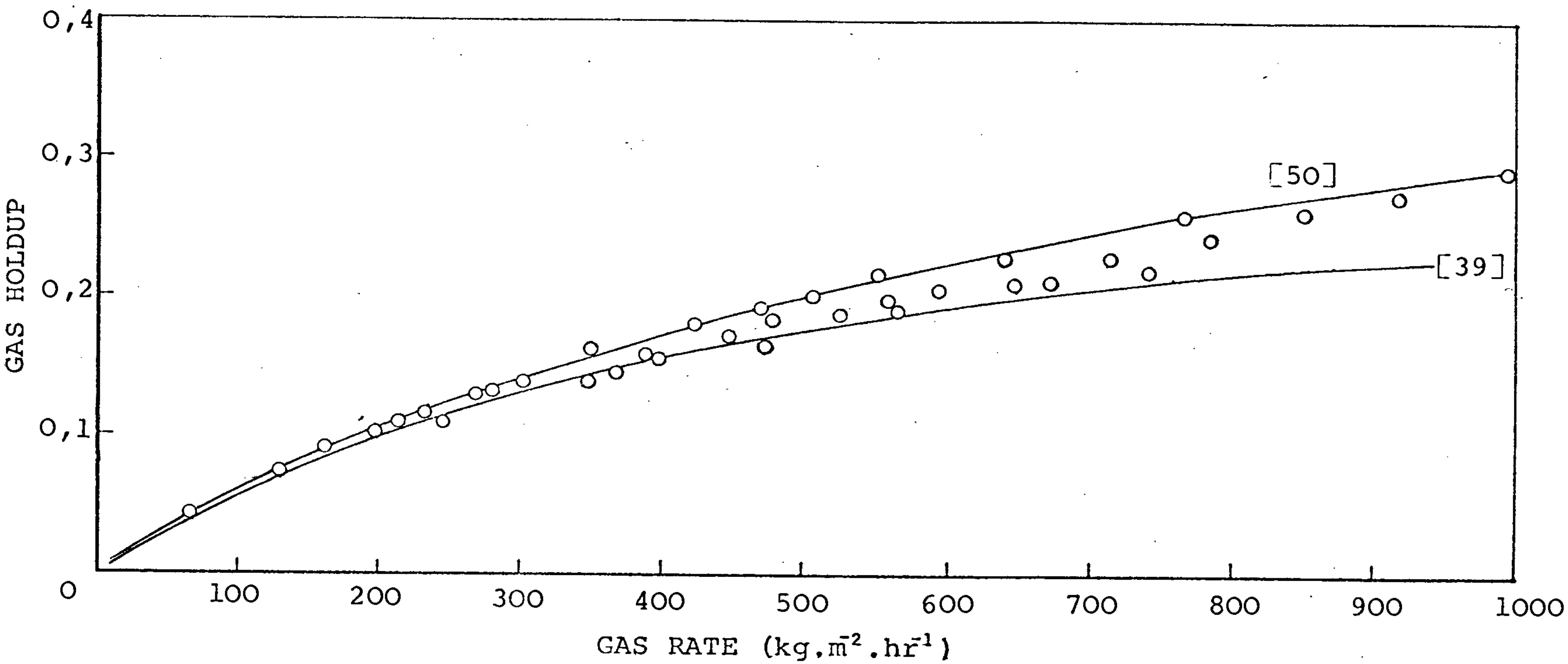


Figure 4.1 Comparison of experimental and predicted gas holdup in water.

The results of Akita and Yoshida on the effect of liquid physical properties on gas holdup, kindly supplied by Professor Yoshida [67], as well as holdup data obtained in this study, were used in evaluating the constants in Equation 4.8. The best fit of this data was obtained for the following expression:

$$\frac{\varepsilon}{(1-\varepsilon)^{0{,}893}} = 0{,}141(\mathrm{Bo})^{0{,}088}(\mathrm{Ga})^{0{,}059}(\mathrm{Fr})^{0{,}707} \qquad (4.11)$$

Since Equation 4.11 would have to be solved for gas holdup by a trial and error procedure, a simplified form of the expression in which the exponent on (1 - ε) was made equal to unity was tested. The correlation thus obtained

$$\frac{\varepsilon}{(1-\varepsilon)} = 0{,}139\ (\mathrm{Bo})^{0{,}078}(\mathrm{Ga})^{0{,}061}(\mathrm{Fr})^{0{,}678} \qquad (4.12)$$

could be conveniently simplified with almost no loss in accuracy to:

$$\frac{\varepsilon}{(1-\varepsilon)} = 0{,}14\ (\mathrm{Bo})^{0{,}08}\ (\mathrm{Ga})^{0{,}06}\ (\mathrm{Fr})^{0{,}68} \qquad (4.13)$$

The standard deviations of the correlations are summarized in Table 4-1. In Figure 4.2 the experimental results for gas holdup in water obtained in this investigation are compared with curves predicted by the various correlations. Equation 4.13 predicts voidages slightly lower than the averages obtained by Hughmark [50], but higher than those predicted by Equation 4.7.

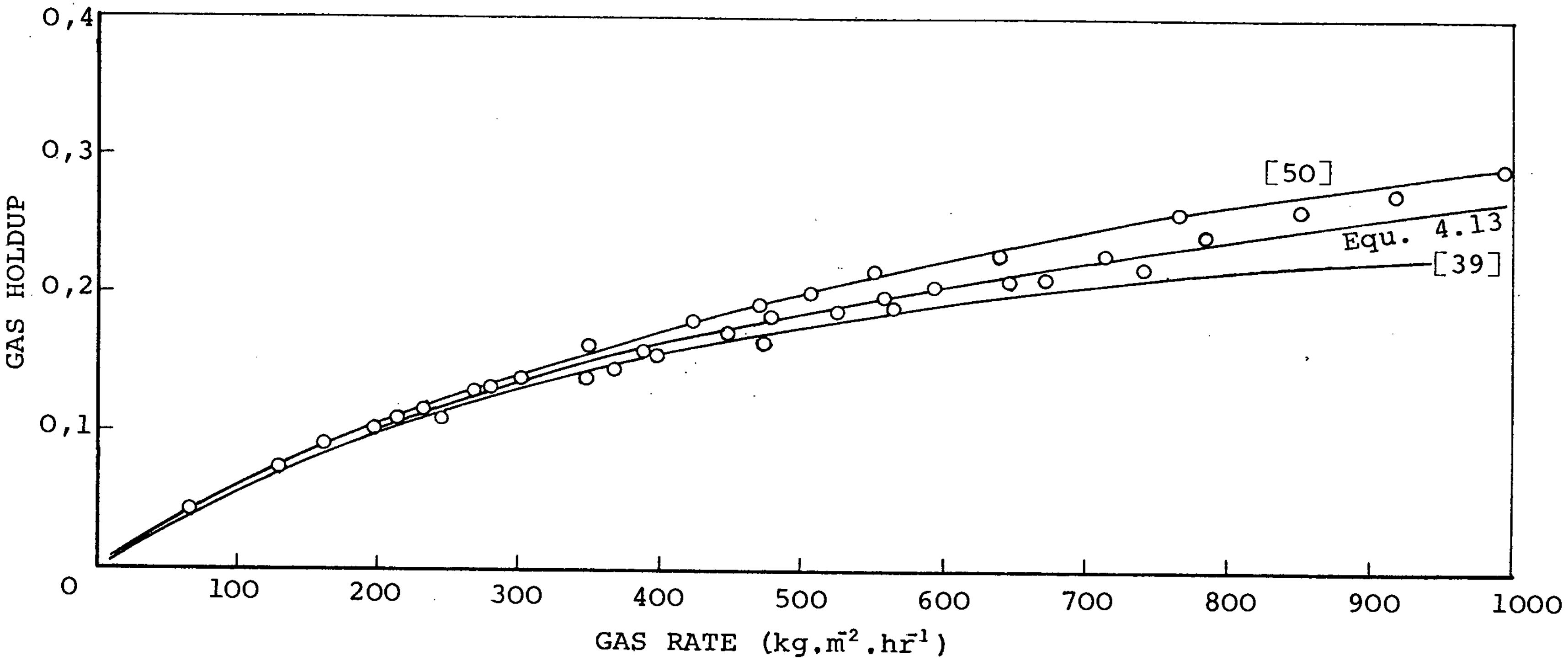


Figure 4.2 Prediction of gas holdup in water.

TABLE 4-1

COMPARISON OF GAS HOLDUP CORRELATIONS

Equation	Standard deviation		
	all data	ref.[67] only	present data
4.7	0,0187	0,0165	0,0223
4.11	0,0152	0,0165	0,0122
4.12	0,0156	0,0168	0,0136
4.13	0,0156	0,0165	0,0138

4.12 Gas Holdup in Electrolyte solutions

Voidages in inorganic salt solutions, shown in Figure 4.2, are higher than in water under the same conditions. Since the physical properties of the liquid phase do not vary appreciably with electrolyte concentration, as shown in Table 4-2, it is proposed, for the sake of simplicity, to use a multiple of Equation 4.13 for the correlation of gas holdup fractions in salt solutions. The new constant was found by regression analysis to be 0,20.

Gas holdup in inorganic salt solutions, with ionic strength greater than 0,1, may thus be predicted from the expression

$$\frac{\varepsilon}{(1 - \varepsilon)} = 0{,}20\ (Bo)^{0{,}8}\ (Ga)^{0{,}6}\ (Fr)^{0{,}68} \qquad (4.14)$$

Experimental data are compared with voidage fractions predicted by Equation 4.14 in Figure 4.3 which shows that Equation 4.14 is a satisfactory correlation of the experimental data. Liquid physical properties corresponding roughly to an ionic strength of 1,0 have been used in drawing up the curve given in this figure.

TABLE 4-2

PHYSICAL PROPERTIES OF Na SO SOLUTIONS

IONIC STR. μ	TEMP. $^{\circ}C$	DENSITY $10^{3}kg.m^{-3}$	SURFACE TENS. 10^{-2} $N.m^{-1}$	VISCOSITY 10^{-3} $N.s.m^{-2}$	DIFFUSIVITY 10^{-9} $m^{2}.s^{-1}$	REF.
0	20	0,998	7,28	1,005	2,20	[39]
0,45	20	1,016	7,39	1,105	1,91	[39]
1,00	20	1,040	7,30	1,200	1,80	
2,40	20	1,088	6,24	1,452	1,60	[13]

4.2 APPLICATION OF GAS HOLDUP CORRELATIONS

Gas holdup may be predicted by Equation 4.13 for common liquids not containing electrolytes in solution or of ionic strength less than 0,1, and by Equation 4.14 for aqueous salt solutions with ionic strength of greater than 0,1. These expressions may be generally applied to bubble column contactors with the following restrictions

(a) gas injection is by single nozzle,
(b) the liquid in the column is not contaminated by surface active agents,
(c) the bubble column diameter is sufficiently large to exclude wall effects, and
(d) gas holdup does not vary appreciably with liquid depth.

4.21 Multiple gas orifices and porous spargers

Porous spargers and multiple gas injection orifices result in increased gas holdup at low gas flow rates by providing a more uniform gas dispersion as described in section 1.443, and voidages predicted by the correlations presented will be low in these cases. At high gas rates, holdup is largely independent of the method of gas injection and depends mainly on the coalescence and breakup rates of the bubbles in the column. Multiple orifices, where the number of orifices is small, are reported to give similar voidages as single orifices [11,46,47,50,51] and holdup predictions by the voidage correlations presented above many thus also be applicable to columns where gas injection is through several orifices.

4.22 Surface Active Agents

Surface active agents affect the hydrodynamic situation in bubble column contactors by altering bubble shapes and rising velocities. The effect of a surfactant depends on its chemical nature, its concentration and to some extent on the average size of the bubbles in the column [34].

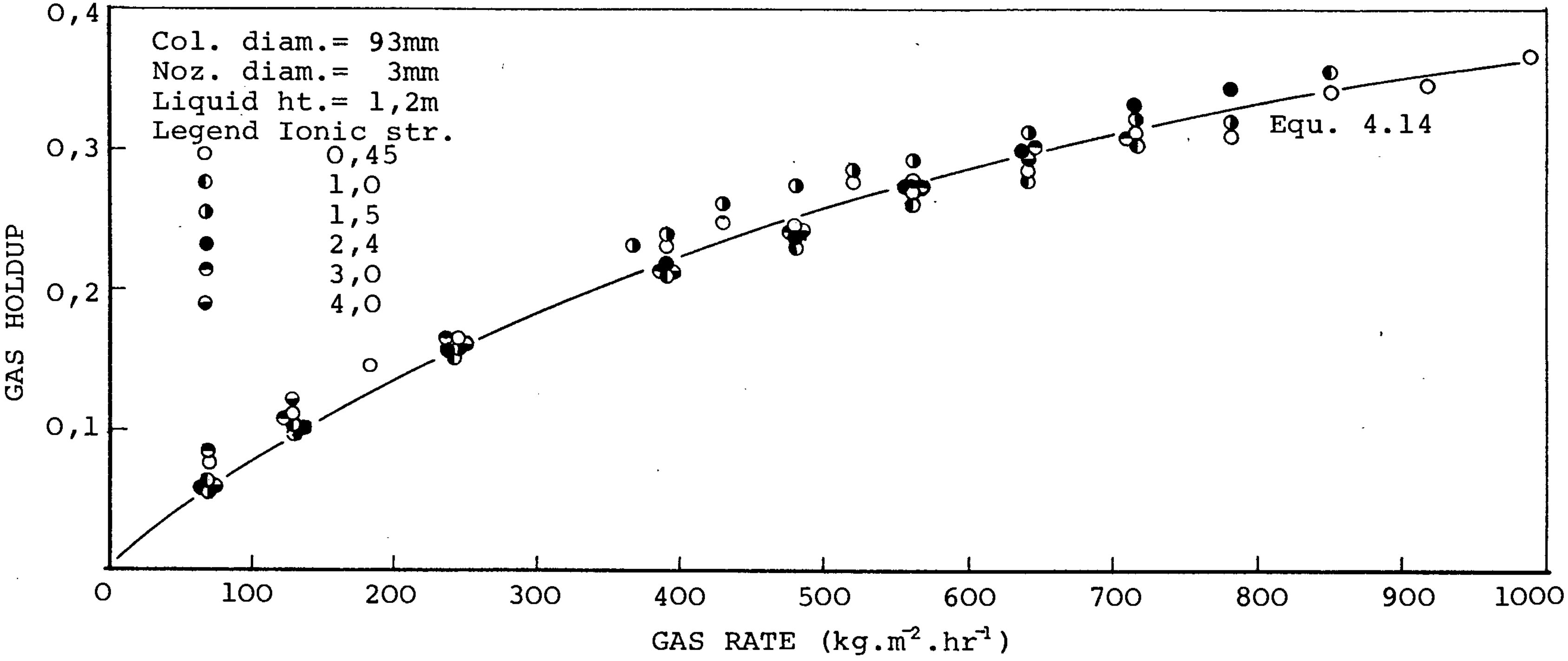


Figure 4.3 Gas holdup in ionic solutions.

No investigation of these effects has been carried out here, but it is clear from the literature, briefly reviewed in section 1.453, that surface active agents have an appreciable effect on gas holdup.

4.23 Column Diameter

For bubble columns of diameter less than about 90 mm, wall effects result in increased gas holdup [17,49,50]. The gas voidage fraction in small columns will thus be higher than predicted by the gas holdup correlations. In columns of diameter greater than 90 mm where wall effects are negligible, the diameter of the column does not influence gas holdup.

4.24 Local variations in gas holdup

In situations where mass transfer rates are very high, there may be an appreciable decrease in bubble volume and hence voidage fraction as the bubbles rise and the gas contained in them dissolves in the liquid. The voidage correlations given above may predict incorrectly high gas holdup fractions in such circumstances. In the present experiments, the change in bubble volume due to mass transfer was very small (less than 1%, as shown in Appendix C), because the dissolving gas, oxygen, was only very sparingly soluble.

The correlations presented above for gas holdup do not apply to shallow liquid pools, such as bubble plates or columns less than about 1 m tall. In the vicinity of gas injection, which forms an appreciable portion of such shallow beds, bubble size and flow conditions are determined by the gas injection device, rather than by coalescence behaviour. A survey of the literature dealing with froth formation and gas holdup in shallow liquid pools has been presented by Valentin [34].

4.3 MASS TRANSFER CORRELATION

The following dimensionless expression for the prediction of overall volumetric mass transfer coefficients in bubble columns has been proposed by Akita and Yoshida [39] for common liquids not containing electrolytes or surface active agents;

$$K_L a = c\, D_L^{0,5} \nu^{-0,12} (\gamma/\rho)^{-0,62} D^{0,17} g^{0,93} \varepsilon^{1,1} \qquad (4.15)$$

This may be expressed in terms of dimensionless groups as [39]

$$\mathrm{Sh}\ aD = c\ \mathrm{Sc}^{0,5}\ \mathrm{Bo}^{0,62}\ \mathrm{Ga}^{0,31}\ \varepsilon^{1,1} \qquad (4.16)$$

where

$\mathrm{Sh} = K_L D/D_L$ the Sherwood number (4.17)

$\mathrm{Sc} = \nu_L/D_L$ the Schmidt number (4.18)

This expression (4.16) has been tested in this investigation for water and aqueous electrolyte solutions of various ionic strengths over a wide range of gas rates. The constant, c, was found by regression analysis on the experimental data to equal 0,8, in comparison with 0,6 proposed by Akita and Yoshida [39]. The same expression (4.6) applies to both water and aqueous electrolyte solutions. The greater mass transfer rates observed in ionic solutions are wholly accounted for by the greater gas voidages in these solutions.

The experimentally determined values of the overall volumetric mass transfer coefficients in water and electrolyte solutions of ionic strength less than 0,1 are compared, in Figure 4.4, with values predicted by the expression

$$\mathrm{Sh}\ aD = 0,8\ \mathrm{Sc}^{0,5}\ \mathrm{Bo}^{0,62}\ \mathrm{Ga}^{0,31}\ \varepsilon^{1,1} \qquad (4.19)$$

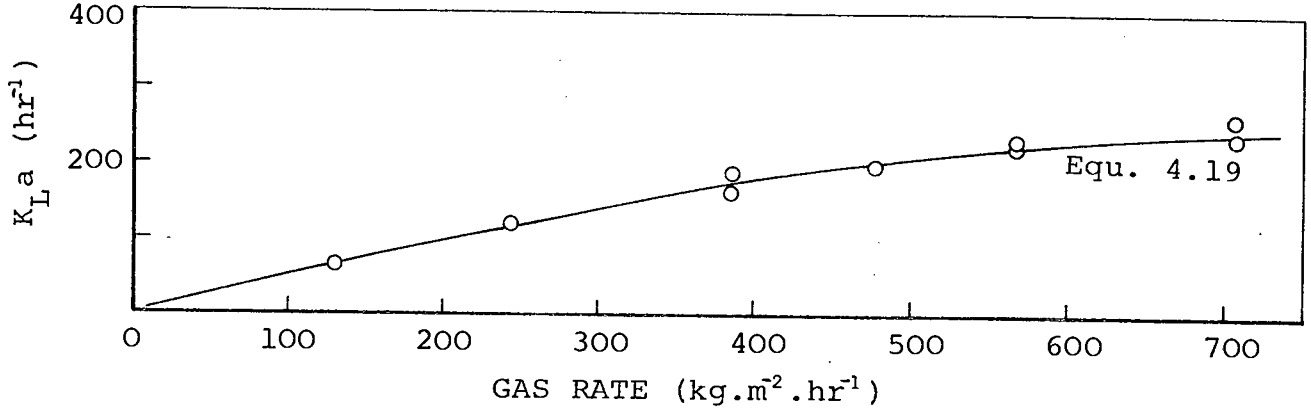


Figure 4.4 Mass transfer coefficients in water and dilute electrolyte solutions.

In Figure 4.5 a similar comparison is made between average mass transfer coefficients in concentrated electrolyte solutions and results predicted by Equation 4.19. Once again approximate physical properties, corresponding to an ionic strength of about 1,0 have been used to obtain a single predicted curve. The wide scatter in the experimentally measured mass transfer coefficients is principally due to the inaccuracies inherent in the transient method, as discussed in section 1.43. The standard deviation of all the mass transfer coefficients determined experimentally from the values predicted by Equation 4.19, using gas holdup estimates obtained by Equations 4.13 or 4.14, is about 50 hr^{-1} for concentrated electrolyte solutions and slightly less for dilute solutions and water. The high standard deviation may be attributed to the wide scatter in the measured values of K_La rather than to poor correlation. Expression 4.19 is a satisfactory fit of the mass transfer data, as can be seen on Figures 4.4 and 4.5.

4.4 APPLICATION OF THE MASS TRANSFER CORRELATION

Overall volumetric mass transfer coefficients in bubble columns may be predicted for both common liquids and solutions of inorganic salts by a single equation, 4.13. This correlation may be generally applied to a wide variety of systems with the following restrictions:

(a) In columns of diameter greater than 600 mm in diameter, the dependence of mass transfer rate on column size has not been verified, and for design purposes, the values predicted for a 600 mm column will provide conservative estimates of the overall mass transfer coefficients [39].

(b) The correlation does not apply to liquids containing surface active agents, except when these do not affect mass transfer. The conditions under which surfactants do not affect gas absorption have been outlined by Meijboom and Vogtländer [68].

(c) The mass transfer Equation 4.19 may also apply to columns served by porous spargers or multiple orifices. Akita and Yoshida [39] have verified that mass transfer coefficients may be successfully predicted by Equation 4.19 at very low gas rates in columns where gas injection is by porous spargers, provided that the measured voidage fraction is used. (The voidage correlations, 4.13 and 4.14 do not apply to columns where gas injection is by porous sparger.) It has not yet been shown whether the mass transfer correlation may be successfully used to predict mass transfer coefficients in columns served by porous spargers or multiple gas orifices at moderate and high gas rates.

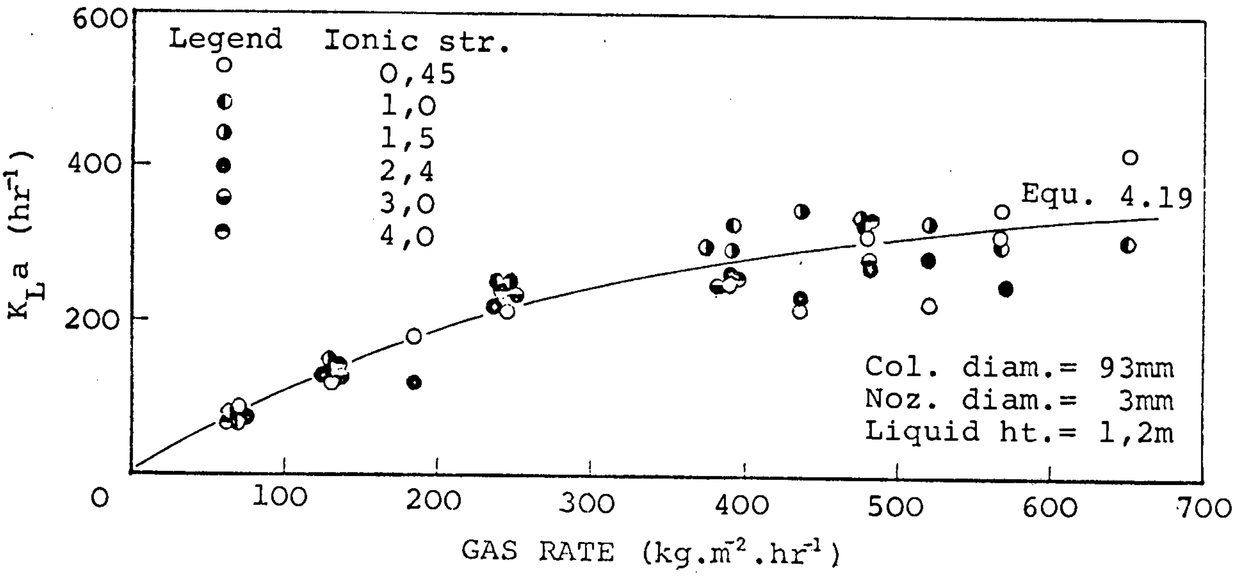


Figure 4.5 Mass transfer coefficients in concentrated electrolyte solutions.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

(a) Gas holdup in bubble column contactors may be predicted from the expressions:

$$\frac{\varepsilon}{1-\varepsilon} = 0{,}14\ Bo^{0{,}08}\ Ga^{0{,}06}\ Fr^{0{,}68} \qquad (4.13)$$

for common liquids not containing electrolytes or surface active agents and,

$$\frac{\varepsilon}{1-\varepsilon} = 0{,}20\ Bo^{0{,}08}\ Ga^{0{,}06}\ Fr^{0{,}68} \qquad (4.14)$$

for aqueous electrolyte solutions of ionic strength greater than 0,1.

(b) The catalysed sulphite oxidation reaction is not a reliable means of determining mass transfer coefficients in spite of its wide application for this purpose. The method is liable to yield erroneously high mass transfer coefficients because of chemical enhancement caused by the simultaneous absorption and fast reaction of oxygen in the liquid. Results obtained by this method should be viewed with some doubt unless it has been unambiguously demonstrated that chemical enhancement of mass transfer is not taking place.

(c) Absorption measurements obtained by the transient method have confirmed that

(i) When a single nozzle is used for gas injection in bubble columns, the orifice size has no influence on either gas holdup or the rate of mass transfer in the column;

(ii) The overall mass transfer coefficient in bubble columns is proportional to the 0,17 exponent of the column diameter as found by Akita and Yoshida [39] using the sulphite oxidation technique;

(iii) The method of van Krevelen and Hoftijzer [67] for the prediction of gas solubilities in electrolyte solutions is inaccurate.

(d) A slight modification to the correlation for K_La put forward by Akita and Yoshida [39] has been proposed. The same correlation

$$Sh\ aD = 0{,}80\ Sc^{0{,}5}\ Bo^{0{,}62}\ Ga^{0{,}31}\ \varepsilon^{1{,}1} \qquad (4.19)$$

may be used to predict overall mass transfer coefficients in both common liquids and aqueous electrolyte solutions.

While the present study has clarified the effect of inorganic salts on the gas holdup and mass transfer rates in bubble column contactors, a limitation in the practical application of these results is the largely undefined effect of surface active contaminants on the behaviour of bubble columns. Some investigations have been done along these lines (briefly summarized in section 1.453) but most of the results obtained are specific to the experimental apparatus used in the particular investigation. Further research is required in order to fully elucidate the effects surface active agents have on mass transfer and gas holdup in bubble columns and provide a means for predicting volumetric mass transfer coefficients in liquids containing surfactants.

The use of porous gas spargers rather than single nozzles for gas injection into bubble columns could provide a possible means of increasing mass transfer rates at low gas velocities by providing a more uniform bubble dispersion and hence greater interfacial area for mass transfer. An investigation of the mass transfer and gas holdup characteristics of columns served by porous gas spargers, especially at low gas flow rates, possibly leading to some means of predicting these parameters, would provide an experimental basis for the choice of gas distributor in any practical application.

The effect of acids on mass transfer and gas holdup appears to be anomalous from the limited experimental evidence available and merits further experimental investigation to define the behaviour.

REFERENCES

1. Dankwerts, P.V., "Gas Liquid Reactions", Chem.Engng Series, McGraw Hill, N.Y., (1970).

2. Astarita, G., "Mass Transfer with Chemical Reaction", Elsevier Pub. Co., Netherlands, (1967).

3. Cooper, C.M., Fernstrom, G.A. and Miller, S.A., "Performance of gas liquid contactors", Ind.Engng Chem., 36, 504, (1944).

4. McWhirter, J.R., "Fundamental aspects of surface aerator performance and design", 20th Purdue Ind. Waste Treat. Conf., (1965).

5. Philips, D.H. and Johnson, M.J., "Oxygen transfer in agitated vessels", Ind. Engng Chem., 51, 1, 83, (1959).

6. Robinson, C.W. and Wilke, C.R., "Oxygen volumetric mass transfer coefficients in agitated Basal salt solutions simulating fermentation media", Proc. IV IFS: Ferment. Technol. Today, 73, (1972).

7. Schultz, J.S. and Gaden, E.L., "Sulphite oxidation as a measure of aeration effectiveness", Ind. Engng Chem., 48, 2209, (1956).

8. Onda, K., Taklucki, H. and Malda, Y., "The absorption of oxygen in sodium sulphite solutions in a packed column", Chem. Engng Sci., 27, 2, 449, (1972).

9. Mashelkar, B., and Sharma, M.M., "Mass transfer in bubble and packed bubble columns", Trans. Instn Chem. Engrs., 48, T162, (1970).

10. Yoshida, F., Ikeda, A., Imakawa, S., and Muria, Y., "Oxygen absorption rates in stirred gas-liquid contactors", Ind. Engng Chem., 52, 5, 435, (1960).

11. Braulick, W.J., Fair, J.R. and Lerner, B.J., "Mass transfer in a sparged contactor: Part 1, physical mechanisms and controlling parameters", A.I.Ch.E.J., 11, 1, 73, (1965).

12. Urza, I., and Jackson, M., "Pressure aeration in a 55-foot bubble column", A.I.Ch.E. 74th National Meeting, N. Orleans, (1973).

13. Reith, T., "Physical Aspects of Bubble Dispersions in Liquids", Thesis, Delft Tech.U., Delftsche Uitgevers Maatschappij N.V., (1968).

14. Reith, T., "Interfacial area and scaling up of gas-liquid contactors", Br. Chem. Engng, 15, 12, 1559, (1970).

15. Reith, T. and Beek, N.J., Paper presented at the 4th Europ. Sym. on Chem. React. Engng, Brussels, (1968).

16. Westerterp, K.R., van Dierendonck, L.L. and de Kraa, J.A., "Interfacial areas in gas-liquid contactors', Chem. Engng Sci., 18, 157, (1963).

17. Yoshida, F. and Akita, K., "Performance of gas bubble columns: volumetric liquid-phase mass transfer coefficient and gas holdup", A.I.Ch.E.J., 11, 1, 9, (1965).

18. Linek, V., and Tvrdik, J., "Kinetics of sulphite oxidation systems", Biotech. and Bioengng, 13, 3, 353, (1971).

19. De Waal, K.J.A. and Okeson, J.C., "The oxidation of aqueous sodium sulphite solutions", Chem. Engng Sci., 21, 559, (1966).

20. Alper, E., "The kinetics of oxidation of sodium sulphite solutions", Trans. Instn Chem. Engrs., 51, 159, (1973).

21. Pasnik-Bronikowska, W., "Attempts to determine the liquid film coefficient for physical absorption and effective interfacial area in a sieve plate column by the chemical method", Chem. Engng Sci., 24, 1139, (1969).

22. Reith, T., and Beek, W.J., "The oxidation of aqueous sodium sulphite solutions", Chem. Engng Sci., 28, 1331, (1973).

23. Linek, V., and Mayrhoferova, J., "The kinetics of aqueous sodium sulphite solutions", Chem. Engng Sci., 25, 5, 787, (1970).

24. Yagi, S. and Inone, H., "The absorption of oxygen into sodium sulphite solutions", Chem. Engng Sci., 17, 411, (1962).

25. Sawiki, J.E. and Baron, C.H., "On the kinetics of sulphite oxidation in heterogeneous systems", Chem. Engng J., 5, 153, (1973).

26. Baron, C.H. and O'Hern, H.A., "Reaction kinetics of sodium sulphite oxidation by the rapid mixing method", Chem. Engng Sci., 21, 397, (1966).

27. Fuller, E.C. and Christ, R.H., "The rate of oxidation of sulphite ions by oxygen", J. Am. Chem. Soc., 63, 1644, (1941).

28. Linek, V. and Mayrhoferova, J., "A chemical method for the determination of surface area. The influence of absorption rate on the holdup and interfacial area in a heterogeneous gas-liquid system", Chem. Engng Sci., 24, 481, (1969).

29. Koetsier, W.T., Thoenes, D. and Frankena, J.F., "Mass transfer in closed stirred gas-liquid contactor", Chem. Engng J., 5, 61, (1973).

30. Koide, K., Hayashi, T., Noro, M., Takemura, Y., Kawamata, N. and Kobuta, H., "Bubbles generated from porous plate in pure liquid and aqueous solutions of inorganic electrolytes", J. Chem. Engng Japan, 5, 3, 236, (1972).

31. Carpini, R.E. and Roxburg, J.M., "Studies on fermentation aeration", Can.J. Chem. Engng, 36, 73, (1958).

32. Wise, W.S., "The aeration of culture media: A comparison of the sulphite and polarographic methods", J.Soc. Chem. Ind., London, Suppl.1, S40, (1950).

33. Calderbank, P.H., "Physical rate processes in Industrial Fermentation - Part II", Trans. Instn Chem. Engng (London), 37, 173, (1959).

34. Valentin, F.H.H., "Absorption in Gas-Liquid dispersions", E.F. Spon Ltd., London, (1967).

35. Friedman, A.M. and Lightfoot, E.N., "Oxygen absorption in agitated tanks", Ind. Engng Chem., 49, 1227, (1957).

36. Sideman, S., Hortacsu, O., and Fulton, J.W., "Mass transfer in gas-liquid contacting systems", Ind. Engng Chem., 58, 7, 32, (1966).

37. Landberg, G.G., Graulick, B.P. and Kipple, W.H., "Experimental problems associated with the testing of surface aeration equipment", Water Research, 3, 6, (1969).

38. Morgan, P.F. and Bewtra, J.K., "Air diffuser efficiencies", Wat. Pollut. Control Fed.J., 32, 1047, (1960).

39. Akita, K. and Yoshida, F., "Gas holdup and volumetric mass transfer coefficient in bubble columns", Ind. Engng Chem. Process Des. Dev., 12, 1, 76, (1973).

40. Zieminski, S.A. and Whittemore, R.C., "Behaviour of gas bubbles in aqueous electrolyte solutions", Chem. Engng Sci., 26, 509, (1971).

41. Zieminski, S.A., Caron, M.M. and Blackmore, R.B., "Behaviour of air bubbles in dilute aqueous solutions", Ind. Engng Chem. Fundam., 6, 2, 233, (1967).

42. Zieminski, S.A. and Lessard, R.R., "Effects of chemical additives on the performance of an air water contactor", Ind. Engng Chem. Fundam., 8, 69, (1969).

43. Zieminski, S.A. and Raymond, D., "Experimental study of the behavour of single bubbles", Chem. Engng Sci., 23, 17, (1968).

44. Lessard, R.R. and Zieminski, S.A., "Bubble coalescence and gas transfer in aqueous electrolyte solutions", Ind. Engng Chem. Fundam., 10, 2, 260, (1971).

45. Levich, V.G., "Physicochemical Hydrodynamics", Prentice-Hall Inc., p 466, (1962).

46. Akita, K. and Yoshida, F., "Bubble size, interfacial area and liquid phase mass transfer coefficient in bubble columns", Ind. Engng Chem. Process Des. Dev., 13, 1, 84, (1974).

47. Towell, G.D., Strand, C.P., and Ackerman, G.H., A.I.Ch.R. Inst. Chem. Engrs. Symp. series, (London), No.10, 10, (1965).

48. Shulman, H.L. and Molstand, M.C., "Gas-bubble columns for gas-liquid contacting", Ind. Engng Chem., 42, 6, 1058, (1950).

49. Fair, J.R., Lambright, A.M. and Anderson, V.W., "Heat transfer and gas holdup in a sparged reactor", Ind. Engng Chem. Process Des. Dev., 1, 33, (1962).

50. Hughmark, G.A., "Holdup and mass transfer in bubble columns", Ind. Engng Chem. Process Des. Dev., 6, 2, 218, (1967).

51. Hobbs, S.Y. and Pratt, C.F., "Modifications in bubbly flow on anti-foam addition", A.I.Ch.E.J., 20, 1, 179, (1974).

52. Datta, R.L., Napier, D.H. and Newitt, D.M., "The properties and behaviour of gas bubbles formed at a circular orifice", Trans. Instn Chem. Engrs., 28, 14, (1950).

53. Bridge, A.G., Lapidus, L. and Eglin,J.C. "The mechanics of verticle gas-liquid fluidized systems 1: Counter-current flow", A.I.Ch.E.J., 10, 819, (1964).

54. Verschoor, H., "Some aspects of the motion of a swarm of gas bubbles rising through a verticle column of liquid", Trans. Instn Chem. Engrs., 28, 52, (1950).

55. Nicklin, D.J., "Two Phase bubble flow", Chem. Engng Sci., 17, 693, (1962).

56. Nicklin, D.J., Wilkes, J.O. and Davidson, J.F., "Two phase flow in verticle tubes", Trans. Instn Chem. Engrs., 40, 61, (1962).

57. Marucci, G. and Nicodema, L., "Coalescence of gas bubbles in aqueous solutions of inorganic electrolytes", Chem. Engng Sci., 22, 1257, (1967).

58. Marucci, G., "A theory of coalescence", Chem. Engng Sci., 24, 975, (1969).

59. Calderbank, P.H. and Moo-Young, M.B., "The continuous phase heat and mass transfer properties of dispersions", Chem. Engng Sci., 16, 39, (1961).

60. Burnett, J.C. and Himmelblau, D.M., "The effect of surface active agents on interphase mass transfer", A.I.Ch.E.J., 16, 185, (1970).

61. Sternling, C.V. and Scriven, L.E., "Interfacial turbulence: Hydrodynamic instability and the Marrangoni effect", A.I.Ch.E.J., 5, 514, (1959).

62. Vogel, A.I., "A textbook of Quantitative Inorganic Analysis", 3rd Ed., Longmans, London, (1966).

63. "Standard methods for the examination of water and wastewater", 12th Ed., American Pub. Health Assoc. Inc., (1965).

64. Brian, P.L.T., Vivian, J.E. and Mayr, S.T., "Cellular convection in desorbing surface tension - lowering solutes from water", Ind. Engng Chem. Fundam., 10, 75, (1971).

65. Haberman, and Morton, David W. Tayor Model Basin Report 802, (1953) in Perry, J.H., ed., "Chemical Engineers' Handbook", 4th Ed., McGraw Hill, N.Y., (1963).

66. Nelder, J.A. and Mead, R., "A simplex method for function minimization", Compt. J., 7, 308, (1965).

67. Yoshida, F., Private communication.

68. Meijboom, F.W. and Vogtlander, J.G., "The influence of surface active agents on the mass transfer from gas bubbles in a liquid", Chem. Engng Sci., 29, 857, (1974).

69. Van Krevelen, D.W. and Hoftijzer, P.J., Chimie et Industrie: Numero Speciale du XXle Congres International de Chimie Industrielle, Bruxelles, Sept. 1948, p.168 in Dankwerts, P.V. op.cit.

70. International Critical Tables, lst Ed., 3, 256, (1928).

71. Cape Town City Council, private communication.

APPENDIX A

GAS HOLDUP RESULTS

TABLE A-1.1

GAS HOLDUP IN SODIUM SULPHITE SOLUTIONS

GAS RATE	IONIC STRENGTH		
$kg.m^{-2}.hr^{-1}$	0,45	1,5	2,4
70	0,045	0,060	-
110	0,069	0,081	0,094
129	0,085	0,104	-
186	0,114	0,135	0,164
243	0,125	0,154	0,203
300	0,149	0,176	0,240
348	0,163	0,200	0,280
478	0,197	0,232	0,315
640	0,236	0,275	0,345
847	0,276	0,330	0,358
1021	0,301	0,353	
1201	0,340		
1400	0,320		

TABLE A-1.2

GAS HOLDUP IN WATER

COLUMN DIAM: 93mm		COLUMN DIAMETER: 144mm				COL DIAM: 293mm	
Gas Rate	Noz Diam	Gas Rate	Noz Diam			Gas Rate	Noz Diam
kg.m^{-2}.hr^{-1}	3 mm	kg.m^{-2}.hr^{-1}	3 mm	5 mm	10 mm	kg.m^{-2}.hr^{-1}	5 mm
129	0,072	162	0,090	0,090	0,100	107	0,108
243	0,109	198	0,104	0,102	0,106	278	0,133
391	0,145	270	0,130	0,132	0,130	348	0,140
478	0,158	351	0,155	0,158	0,157	449	0,172
565	0,186	423	0,178	0,179	0,178	524	0,184
640	0,204	504	0,195	0,208	0,208	562	0,196
716	0,225	549	0,216	0,220	0,220	594	0,207
847	0,260	639	0,236	0,232	0,234	669	0,213
989	0,291	766	0,245	0,256	0,251	738	0,218

TABLE A-1.3

GAS HOLDUP IN ELECTROLYTE SOLUTIONS

GAS RATE	IONIC STRENGTH						
kg.m^{-2}.hr^{-1}	0,0	0,45	1,0	1,5	2,4	3,0	4,0
70	0,045	0,076	0,055	0,060	0,060	0,060	0,083
129	0,072	0,113	0,090	0,105	0,101	0,101	0,119
186	0,100	0,146			0,133		
243	0,109	0,165	0,151	0,165	0,159	0,146	0,172
391	0,145	0,216	0,207	0,240	0,213	0,201	0,218
435	0,171	0,250		0,260	0,255		
478	0,158	0,240	0,234	0,275	0,240	0,234	0,240
521	0,185	0,270		0,284			
565	0,186	0,279	0,260	0,291	0,275	0,275	0,260
640	0,204	0,284	0,275	0,315	0,306	0,297	0,297
716	0,225	0,315	0,297	0,323	0,311	0,315	
782	0,240	0,319	0,315		0,343		
847	0,260	0,339	0,327				

TABLE A-2

RESULTS OF STEADY STATE ABSORPTION EXPERIMENTS

Column Diameter = 93 mm Nozzle diameter = 3 mm

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_3	KCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	^oC	hr^{-1}
01	0,45	70	0,05	0,15	-	20	46
02	0,45	129	0,08	0,15	-	20*	105
03	0,45	243	0,13	0,15	-	20*	185
04	0,45	391	0,13	0,15	-	20*	262
05	0,45	716	0,25	0,15	-	20*	425
06	0,45	989	0,30	0,15	-	20*	696
07	1,5	70	0,06	0,5	-	20	92
08	1,5	129	0,10	0,5	-	15	99
09	1,5	129	0,10	0,5	-	16	130
10	1,5	243	0,15	0,5	-	16	248
11	1,5	391	0,21	0,5	-	15	336
12	1,5	716	0,30	0,5	-	18	655
13	1,5	847	0,33	0,5	-	17	785
14	2,4	243	0,13	0,8	-	21	407
15	2,4	391	0,34	0,8	-	23	472
16	2,4	478	0,37	0,8	-	18	758
17	2,4	565	0,28	0,8	-	22	809

* assumed

TABLE A-2 Cont.

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_3	KCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	^oC	hr^{-1}
18	5,0	129	0,11	0,5	3,5	19	271
19	5,0	391	0,23	0,5	3,5	19	406
20	5,0	565	0,27	0,5	3,5	18	533
21	4,0	391	0,35	0,8	1,6	19	596
22	4,0	391	0,35	0,8	1,6	21	544
23	1,0	243	0,17	0,15	0,55	20	215
24	1,0	391	0,24	0,15	0,55	21	341
25	1,0	478	0,30	0,15	0,55	19	394
26	1,0	565	0,29	0,15	0,55	21	579
27	1,0	565	0,30	0,15	0,55	22	494
28	1,0	391	0,21	0,15	H_2SO_4	18	-
29	1,0	565	0,24	0,15	H_2SO_4	21	-
30	3,0	129	0,13	0,5	1,5	21	242
31	3,0	391	0,21	0,5	1,5	19	268
32	3,0	478	0,34	0,5	1,5	21	494
33	3,0	565	0,29	0,5	1,5	20	404
34	2,4	129	0,12	0,15	1,95	17	76
35	2,4	243	0,17	0,15	1,95	19	206
36	2,4	391	0,20	0,15	1,95	20	398

TABLE A-2 Cont.

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_4	KCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	^oC	hr^{-1}
37	2,4	391	0,20	0,15	1,95	19	268
38	2,4	565	0,27	0,15	1,95	18	523
39	2,4	565	0,27	0,15	1,95	20	387
40	2,4	640	0,36	0,15	1,95	18	736
41	2,4	243	0,21	0,8	-	22	234
42	2,4	243	0,21	0,8	-	18	241
43	2,4	391	0,29	0,8	-	22	513
44	2,4	391	0,29	0,8	-	20	497
45	2,4	565	0,34	0,8	-	20	795
46	0,45	129	0,09	0,15	-	22	137
47	0,45	243	0,15	0,15	-	22	252
48	0,45	243	0,13	0,15	-	22	290
49	0,45	391	0,17	0,15	-	20	381
50	0,45	391	0,17	0,15	-	24	388
51	0,45	478	0,20	0,15	-	24	469
52	0,45	565	0,22	0,15	-	23	512
53	0,45	565	0,22	0,15	-	18	516
54	0,45	640	0,23	0,15	-	21	596

TABLE A-2 Cont.

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_4	KCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	^oC	hr^{-1}
55	3,0	243	0,19	1,0	-	20*	331
56	3,0	391	0,30	1,0	-	20*	341
57	3,0	478	0,35	1,0	-	25	697
58	3,0	165	0,35	1,0	-	24	645
59	1,5	129	0,11	0,5	-	20	114
60	1,5	243	0,17	0,5	-	22	278
61	1,5	391	0,22	0,5	-	23	402
62	1,5	565	0,26	0,5	-	23	540

* assumed

TABLE A-3

RESULTS OF TRANSIENT EXPERIMENTS: VARIATION OF GAS RATE

Column Diameter = 93 mm　　　　Nozzle Diameter = 3 mm

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_4	KCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	^oC	hr^{-1}
001	0,0	129	0,072	-	-	19	75
002	0,0	243	0,109	-	-	19	125
003	0,0	391	0,15	-	-	19	162
004	0,0	391	0,15	-	-	19	184
005	0,0	565	0,19	-	-	19	268
006	0,0	565	0,19	-	-	19	235
007	0,0	716	0,23	-	-	19	251
008	0,0	716	0,23	-	-	17	253
009	tap water	70	0,045	-	-	19	69
010	tap water	129	0,072	-	-	19	105
011	tap water	129	0,072	-	-	19	102
012	tap water	243	0,109	-	-	19	153
013	tap water	243	0,109	-	-	19	162
014	tap water	391	0,15	-	-	19	207
015	tap water	391	0,15	-	-	19	238

TABLE A-3 Cont.

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_4	KCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	^oC	hr^{-1}
016	tap water	565	0,19	-	-	19	378
017	tap water	565	0,19	-	-	19	298
018	tap water	716	0,23	-	-	19	322
019	0,45	129	0,11	-	0,45	20	97
020	0,45	129	0,11	-	0,45	20	127
021	0,45	129	0,11	-	0,45	20	112
022	0,45	129	0,11	-	0,45	20	147
023	0,45	186	0,15	-	0,45	20	178
024	0,45	243	0,17	-	0,45	20	237
025	0,45	243	0,17	-	0,45	20	191
026	0,45	391	0,22	-	0,45	20	229
027	0,45	391	0,22	-	0,45	20	275
028	0,45	435	0,25	-	0,45	20	225
029	0,45	478	0,24	-	0,45	20	305
030	0,45	478	0,24	-	0,45	20	324
031	0,45	521	0,27	-	0,45	20	230
032	0,45	565	0,28	-	0,45	20	393
033	0,45	565	0,28	-	0,45	20	242
034	0,45	640	0,28	-	0,45	20	427

TABLE A-3 Cont.

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_4	KCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	^oC	hr^{-1}
035	1,0	70	0,055	-	1,0	20	67
036	1,0	129	0,109	-	1,0	20	138
037	1,0	129	0,09	-	1,0	20	116
038	1,0	391	0,21	-	1,0	20	278
039	1,0	391	0,21	-	1,0	20	404
040	1,0	391	0,21	-	1,0	20	385
041	1,0	391	0,21	-	1,0	20	345
042	1,0	478	0,23	-	1,0	20	284
043	1,0	478	0,23	-	1,0	20	357
044	1,0	478	0,23	-	1,0	20	275
045	1,0	478	0,23	-	1,0	20	423
046	1,0	478	0,23	-	1,0	20	392
047	1,0	565	0,26	-	1,0	20	349
048	1,0	565	0,26	-	1,0	20	282
049	1,0	565	0,26	-	1,0	20	279
050	1,0	640	0,28	-	1,0	20	281
051	1,0	640	0,28	-	1,0	20	361
052	1,0	640	0,28	-	1,0	20	370
053	1,0	640	0,28	-	1,0	20	238

TABLE A-3 Cont.

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	HCl	KCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	^oC	hr^{-1}
054	1,0	70	0,054	1,0	-	21	33
055	1,0	129	0,086	1,0	-	21	58
056	1,0	186	0,11	1,0	-	21	132
057	1,0	243	0,13	1,0	-	21	157
058	1,0	380	0,15	1,0	-	21	159
059	1,0	391	0,18	1,0	-	21	169
060	1,0	435	0,20	1,0	-	21	182
061	1,0	478	0,21	1,0	-	21	262
062	1,0	521	0,22	1,0	-	21	396
RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_4	KCl	TEMP	K_La
063	1,5	70	0,06	0,5	-	22	86
064	1,5	129	0,11	0,5	-	22	148
065	1,5	243	0,17	0,5	-	22	246
066	1,5	380	0,23	0,5	-	22	300
067	1,5	391	0,24	0,5	-	22	294
068	1,5	435	0,26	0,5	-	22	352
069	1,5	478	0,28	0,5	-	22	333
070	1,5	521	0,28	0,5	-	22	333

TABLE A-3 Cont.

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_4	KCl	TEMP	K_La
	μ	kg.m^{-2}.hr^{-1}	ε	kmol.m^{-3}	kmol.m^{-3}	^{o}C	hr^{-1}
071	2,4	70	0,06	–	2,4	20	77
072	2,4	70	0,06	–	2,4	20	82
073	2,4	129	0,10	–	2,4	20	147
074	2,4	129	0,10	–	2,4	20	143
075	2,4	243	0,16	–	2,4	20	255
076	2,4	243	0,16	–	2,4	20	267
077	2,4	243	0,16	–	2,4	20	277
078	2,4	391	0,21	–	2,4	20	244
079	2,4	391	0,21	–	2,4	20	290
080	2,4	391	0,21	–	2,4	20	337
081	2,4	391	0,21	–	2,4	20	326
082	2,4	478	0,24	–	2,4	20	237
083	2,4	478	0,24	–	2,4	20	279
084	2,4	478	0,24	–	2,4	20	424
085	2,4	70	0,07	0,8	–	22	64
086	2,4	70	0,06	0,8	–	21	48
087	2,4	129	0,11	0,8	–	22	128
088	2,4	129	0,09	0,8	–	21	97
089	2,4	186	0,13	0,8	–	21	123

TABLE A-3 Cont.

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_4	KCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	^{o}C	hr^{-1}
090	2,4	243	0,17	0,8	-	22	180
091	2,4	243	0,17	0,8	-	21	190
092	2,4	295	0,20	0,8	-	21	234
093	2,4	391	0,23	0,8	-	22	206
094	2,4	391	0,24	0,8	-	21	262
095	2,4	435	0,27	0,8	-	21	289
096	2,4	478	0,28	0,8	-	21	283
097	2,4	565	0,29	0,8	-	22	262
098	4,0	70	0,08	-	4,0	19	55
099	4,0	70	0,08	-	4,0	19	78
100	4,0	129	0,12	-	4,0	19	134
101	4,0	129	0,12	-	4,0	19	159
102	4,0	243	0,17	-	4,0	19	262
103	4,0	243	0,17	-	4,0	19	254
104	4,0	391	0,22	-	4,0	19	182
105	4,0	391	0,22	-	4,0	19	326
106	4,0	478	0,24	-	4,0	19	375
107	4,0	565	0,26	-	4,0	19	353

TABLE A-3 Cont.

RUN NO.	IONIC STR	GAS RATE	VOIDAGE	Na_2SO_4	NaCl	TEMP	K_La
	μ	$kg.m^{-2}.hr^{-1}$	ε	$kmol.m^{-3}$	$kmol.m^{-3}$	°C	hr^{-1}
108	3,0	129	0,10	-	3,0	21	143
109	3,0	243	0,15	-	3,0	21	231
110	3,0	391	0,20	-	3,0	21	255
111	3,0	478	0,23	-	3,0	21	279

TABLE A-4

RESULTS OF TRANSIENT EXPERIMENTS: VARIATION OF IONIC STRENGTH

TABLE A-4.1

Column diameter = 93 mm

Nozzle diameter = 3 mm

Gas rate = 243 kg.m^{-2}.hr^{-1}

RUN NO.	IONIC STR μ	Na_2SO_4 kmol.m^{-3}	TEMP ^oC	K_La hr^{-1}
112	4,0	1,33	23	282
113	4,0	1,33	23	184
114	4,0	1,33	23	231
115	2,0	0,67	22	271
116	2,0	0,67	22	273
117	2,0	0,67	22	216
118	1,0	0,33	21	201
119	1,0	0,33	21	178
120	1,0	0,33	21	173
121	0,5	0,17	20	263
122	0,5	0,17	20	176
123	0,5	0,17	20	212
124	0,1	0,033	22	186
125	0,1	0,033	22	164
126	0,1	0,033	22	150
127	0,05	0,017	23	118
128	0,05	0,017	23	132
129	0,05	0,017	23	114

TABLE A-4.2

Column diameter = 93 mm

Nozzle diameter = 5 mm

Gas rate = 478 kg.m^{-2}.hr^{-1}

RUN NO.	IONIC STR μ	Na_2SO_4 kmol.m^{-3}	TEMP ^oC	K_La hr^{-1}
130	4,0	1,33	23	321
131	4,0	1,33	23	288
132	4,0	1,33	23	277
133	2,0	0,67	23	344
134	2,0	0,67	23	272
135	1,0	0,33	21	319
136	1,0	0,33	21	356
137	1,0	0,33	21	282
135	0,5	0,17	22	384
139	0,5	0,17	22	288
140	0,5	0,17	22	273
141	0,1	0,033	21	229
142	0,1	0,033	21	318
143	0,1	0,033	21	395
144	0,05	0,017	23	193
145	0,05	0,017	23	227
146	0,05	0,017	23	228

TABLE A-4.3

Gas rate = 243 kg.m^{-2}.hr^{-1}
Column diameter = 93 mm
Orifice diameter = 5 mm

RUN NO.	IONIC STR μ	Na_2SO_4 kmol.m^{-3}	TEMP ^oC	K_La hr^{-1}
147	2,0	0,67	23	174
148	2,0	0,67	23	169
149	1,0	0,33	22	212
150	1,0	0,33	22	198
159	0,5	0,017	22	199
152	0,5	0,017	22	160
153	0,1	0,033	24	97
154	0,1	0,033	24	95
155	0,05	0,017	21	97
156	0,05	0,017	21	96
157	0,0	-	23	102

TABLE A-4.4

Gas rate = 478 kg.m^{-2}.hr^{-1}
Column diameter = 93 mm
Orifice diameter = 5 mm

RUN NO.	IONIC STR μ	Na_2SO_4 kmol.m^{-3}	TEMP ^oC	K_La hr^{-1}
158	2,0	0,67	23	278
159	2,0	0,67	23	268
160	1,0	0,33	22	322
161	1,0	0,33	22	307
162	0,5	0,017	22	309
163	0,5	0,017	22	284
164	0,1	0,033	24	165
165	0,1	0,033	24	175
166	0,05	0,017	21	165
167	0,05	0,017	21	183
168	0,0	-	23	236

TABLE A-4.5

Gas rate = 243 kg.m^{-2}.hr^{-1}
Column diameter = 93 mm
Orifice diameter = 5 mm

RUN NO.	IONIC STR μ	Na_2SO_4 kmol.m^{-3}	TEMP ^oC	K_La hr^{-1}
169	2,0	0,67	22	305
170	2,0	0,67	22	295
171	1,0	0,33	23	255
172	1,0	0,33	23	251
173	0,5	0,017	23	242
174	0,5	0,017	23	198
175	0,1	0,033	22	139
176	0,1	0,033	22	145
177	0,05	0,017	22	101
178	0,05	0,017	22	106
179	0,0	-	22	97
180	0,0	-	22	103

TABLE A-4.6

Gas rate = 243 $kg.m^{-2}.hr^{-1}$
Column diameter = 144 mm
Nozzle diameter = 3 mm

RUN NO.	IONIC STR μ	Na_2SO_4 $kmol.m^{-3}$	TEMP ^oC	K_La hr^{-1}
181	2,0	0,67	23	255
182	2,0	0,67	23	233
183	1,0	0,33	23	270
184	1,0	0,33	23	246
185	0,5	0,17	23	251
186	0,5	0,17	23	211
187	0,25	0,085	22	280
188	0,25	0,085	22	240
189	0,1	0,033	24	125
190	0,1	0,033	24	125
191	0,05	0,017	23	116
192	0,05	0,017	23	111
193	0,0	-	22	129
194	0,0	-	22	122

TABLE A-4.7

Gas rate = 478 $kg.m^{-2}.hr^{-1}$
Column diameter = 144 mm
Nozzle diameter = 3 mm

RUN NO.	IONIC STR μ	Na_2SO_4 $kmol.m^{-3}$	TEMP ^oC	K_La hr^{-1}
195	2,0	0,67	23	340
196	2,0	0,67	23	369
197	1,0	0,33	23	403
198	1,0	0,33	23	327
199	0,5	0,17	23	292
200	0,5	0,17	23	267
201	0,25	0,085	22	375
202	0,25	0,085	22	299
203	0,1	0,033	24	193
204	0,1	0,033	24	229
205	0,05	0,017	23	172
206	0,05	0,017	23	188
207	0,0	-	22	194
208	0,0	-	22	188

TABLE A-4.12

Column diameter = 293 mm
Nozzle diameter = 10 mm
Gas rate = 243 $kg.m^{-2}.hr^{-1}$

RUN NO.	IONIC STR μ	Na_2SO_4 $kmol.m^{-3}$	TEMP °C	K_La hr^{-1}
356	2,0	0,67	21	180
257	2,0	0,67	21	175
258	1,0	0,33	22	224
259	1,0	0,33	22	198
260	0,5	0,17	22	190
261	0,5	0,17	22	203
262	0,25	0,08	22	240
263	0,25	0,08	22	240
264	0,1	0,033	22	160
265	0,1	0,033	22	180
266	0,05	0,017	22	120
267	0,05	0,017	22	114

TABLE A-4.13

Column diameter = 293 mm
Nozzle diameter = 10 mm
Gas rate = 478 $kg.m^{-2}.hr^{-1}$

RUN NO.	IONIC STR μ	Na_2SO_4 $kmol.m^{-3}$	TEMP °C	K_La hr^{-1}
268	2,0	0,67	21	332
269	2,0	0,67	21	413
270	1,0	0,33	22	331
271	1,0	0,33	22	295
272	0,5	0,17	22	394
272	0,25	0,08	22	396
274	0,25	0,08	22	398
275	0,1	0,033	22	272
276	0,1	0,033	22	268
277	0,05	0,017	22	244
278	0,05	0,017	22	261

TABLE A-4.14

Column diameter = 293 mm
Nozzle diameter = 5 mm
Gas rate = 243 $kg.m^{-2}.hr^{-1}$

RUN NO.	IONIC STR μ	Na_2SO_4 $kmol.m^{-3}$	TEMP °C	K_La hr^{-1}
279	2,0	0,67	22	211
280	2,0	0,67	22	220
281	1,0	0,33	22	286
282	1,0	0,33	22	200
283	0,5	0,17	22	270
284	0,5	0,17	22	235
285	0,25	0,08	22	239
286	0,25	0,08	22	213
287	0,10	0,033	22	200
288	0,10	0,033	22	150
289	0,05	0,017	22	130
290	0,05	0,017	22	160

TABLE A-4.15

Column diameter = 293 mm
Nozzle diameter = 5 mm
Gas rate = 478 $kg.m^{-2}.hr^{-1}$

RUN NO.	IONIC STR μ	Na_2SO_4 $kmol.m^{-3}$	TEMP °C	K_La hr^{-1}
291	2,0	0,67	22	427
292	2,0	0,67	22	327
293	1,0	0,33	22	371
294	1,0	0,33	22	372
295	0,5	0,17	22	404
296	0,5	0,17	22	399
297	0,25	0,08	22	347
298	0,25	0,08	22	399
299	0,10	0,033	22	230
300	0,10	0,033	22	220
301	0,05	0,017	22	240
302	0,05	0,017	22	200

APPENDIX B

SAMPLE CALCULATIONS

B.1 SAMPLE CALCULATION OF THE OVERALL MASS TRANSFER COEFFICIENT BY THE STEADY STATE METHOD

The overall mass transfer coefficient is obtained in the steady state method, from the equation:

$$-(1-\varepsilon)\frac{dc}{dt} = 2K_L aHp \qquad (2.2)$$

The factor 2 is necessary in equation (2.2) if c is expressed in sulphite molarity because one mole of oxygen is sufficient to oxidize two moles of sulphite. As an example, for the gas rate 129 $kg.m^{-2}.hr^{-1}$, the drop in sulphite concentration with time, presented in Table B-1, and shown on Figure B.1, is

$$\frac{dc}{dt} = 9{,}6 \times 10^{-4}\ kmol.min^{-1}.m^{-3}$$

Average oxygen pressure in the bubbles:

Pressure at the top of the column, P_t = 100 kPa

Pressure at the base of the column, P_b = 100 kPa + 1,2 m water

= 111 kPa

The oxygen consumed by the reaction, may be obtained by mass balance:

Rate of O_2 entering column = 129 $kg.m^{-2}.hr^{-1}$ x 0,21 x (π x 93^2 x 10^{-6} x 0,25)m^2

= 0,1836 $kg.hr^{-1}$

Rate of sulphite depletion = 9,6 x 10^{-4} $kmol.min^{-1}.m^{-3}$

.: Rate of oxygen depletion = 9,6 x 10^{-4} $kmol.min^{-1}m^{-3}$ x (π x 93^2x10^{-6} x 0,25 x 1,2)m^3 x 32 $kg.kmol^{-1}$ x 0,5 kmol O_2. kmol SO_3 = - 1

= 0,0075 $kg.hr^{-1}$

.: Change on O_2 pressure from bottom to top of column

$$= \frac{0,0075}{0,1836} \sim 4\%$$

Oxygen pressure at bottom of column:

$$= 111 \text{ kPa} \times 0,21 = 23,31 \text{ kPa}$$

Oxygen pressure at top of column:

$$= 100 \text{ kPa} \times 0,21 \times 0,96 = 20,16 \text{ kPa}$$

Log mean pressure of oxygen in the rising bubbles is thus

$$\frac{23,32 - 20,16}{\ln(23,32/20,16)} = 21,70 \text{ kPa}$$

(cf. arithmetic mean: 21,74 kPa).

As an illustration, in this example, Henry's constant, H, is calculated by van Krevelen's method [1]; in general the experimentally determined Henry's constant was used in preference to the calculated value.

In van Krevelen's method, Henry's constant is corrected for the presence of electrolytes in solution by the equation:

$$\log_{10}(H/H_0) = - kI \qquad (B.1)$$

where I is the ionic strength of solution defined by

$$I = \tfrac{1}{2} \Sigma c_i z_i^2 \qquad (B.2)$$

c_i is the concentration of species i and z_i the valence of the ion. It is assumed that $SO_4^=$ ions and $SO_3^=$ ions in solution have the same effect on oxygen solubility at the same concentration. The constant k in Equation B.1 is then given by the sum of the effects of the ions present in solution and the dissolving gas.

$$k = 0{,}141$$

for oxygen dissolving in sodium sulphate solution at 20°C [1].

In this experiment, the concentration of sodium sulphite was 0,15 M

.: $c_{Na^+} = 0{,}3 \text{ M}$ and $c_{SO_3^=} = 0{,}15 \text{ M}$

.: $I = \frac{1}{2}\left[(93 \times 1^2) + (0{,}15 \times 2^2)\right]$

$= 0{,}45$

The solubility of oxygen in water at 20°C, H_0, is 13,943 $\text{kmol.m}^{-3}.\text{kPa}^{1}$ [70]

.: $\log_{10}(13{,}493/H) = 0{,}141 \times 0{,}45$

.: $H = 12{,}04 \times 10^{-6} \text{ kmol.m}^{-3}.\text{kPa}^{-1}$

(cf. experimentally determined $H = 11{,}61 \times 10^{-6}\text{kmols.m}^{-3}\text{kPa}^{-1}$)

The gas holdup was determined from

$$\varepsilon = \frac{z_F - z_L}{z_F} \qquad (2.1)$$

The column was filled with liquid to a height of 1,2 m i.e. $z_L = 1{,}2$ m.

The height of aerated liquid was determined by eye

$$z_F = 1{,}306 \text{ m}$$

.: $\varepsilon = 0{,}081$

Substituting into Equation 2.2

$$(1 - 0{,}018) \times 9{,}6 \times 10^{-4} \times 60 = 2 \times 11{,}61 \times 10^{-6} \times 21{,}7 \times K_La$$

.: $K_La = 105 \text{ hr}^{-1}$

TABLE B-1.1

DECLINE IN SULPHITE CONCENTRATION WITH TIME

Gas rate = 70 $kg.m^{-2}.hr^{-1}$ Gas holdup = 0,05

Catalyst conc. = 10^{-4}M Column diameter = 93 mm

Temperature = 20,5°C Nozzle diameter = 3 mm

time min	sample port	conc.Na_2SO_3 $kmols.m^{-3}$
0	bottom	0,126
11	middle	0,125
16	top	0,122
20	bottom	0,121
25	middle	0,118
35	top	0,118
45	bottom	0,104
55	middle	0,104
60	top	0,102

TABLE B-1.2

Gas rate = 129 $kg.m^{-2}.hr^{-1}$ Gas holdup = 0,08

Catalyst conc. = 10^{-4}M Column diameter = 93 mm

Temperature = 20,5°C Nozzle diameter = 3mm

time min	sample port	conc.Na_2SO_3 $kmols.m^{-3}$
0	-	0,128
5	top	0,126
10	middle	0,123
15	bottom	0,118
20	top	0,114
30	middle	0,105
35	bottom	0,101
50	middle	0,084

B.2 SAMPLE CALCULATION OF THE OVERALL MASS TRANSFER COEFFICIENT BY THE TRANSIENT METHOD

In the transient method the overall volumetric mass transfer coefficient is obtained from the expression

$$K_La = \frac{(1 - \varepsilon)}{t} \ln \frac{c^* - c_i}{c^* - c_f} \qquad (2.3)$$

as outlined in section 2.1.

For run 001,

$$\varepsilon = \frac{z_F - z_L}{z_F} = 0{,}067$$

Initial oxygen concentration, after stripping with nitrogen for about 5 min, $c_i = 0{,}04$ ppm.

Oxgyen concentration after 60 s bubbling,

$$c_f = 7{,}07 \text{ ppm.}$$

Saturation oxygen concentration, determined after 20 min bubbling,

$$c^* = 9{,}60 \text{ ppm}$$

$$\therefore \quad K_La = \frac{(1 - 0{,}067)}{60} \times 3600 \times \ln \frac{9{,}60 - 0{,}04}{9{,}60 - 7{,}07}$$

$$= 75 \text{ hr}^{-1}.$$

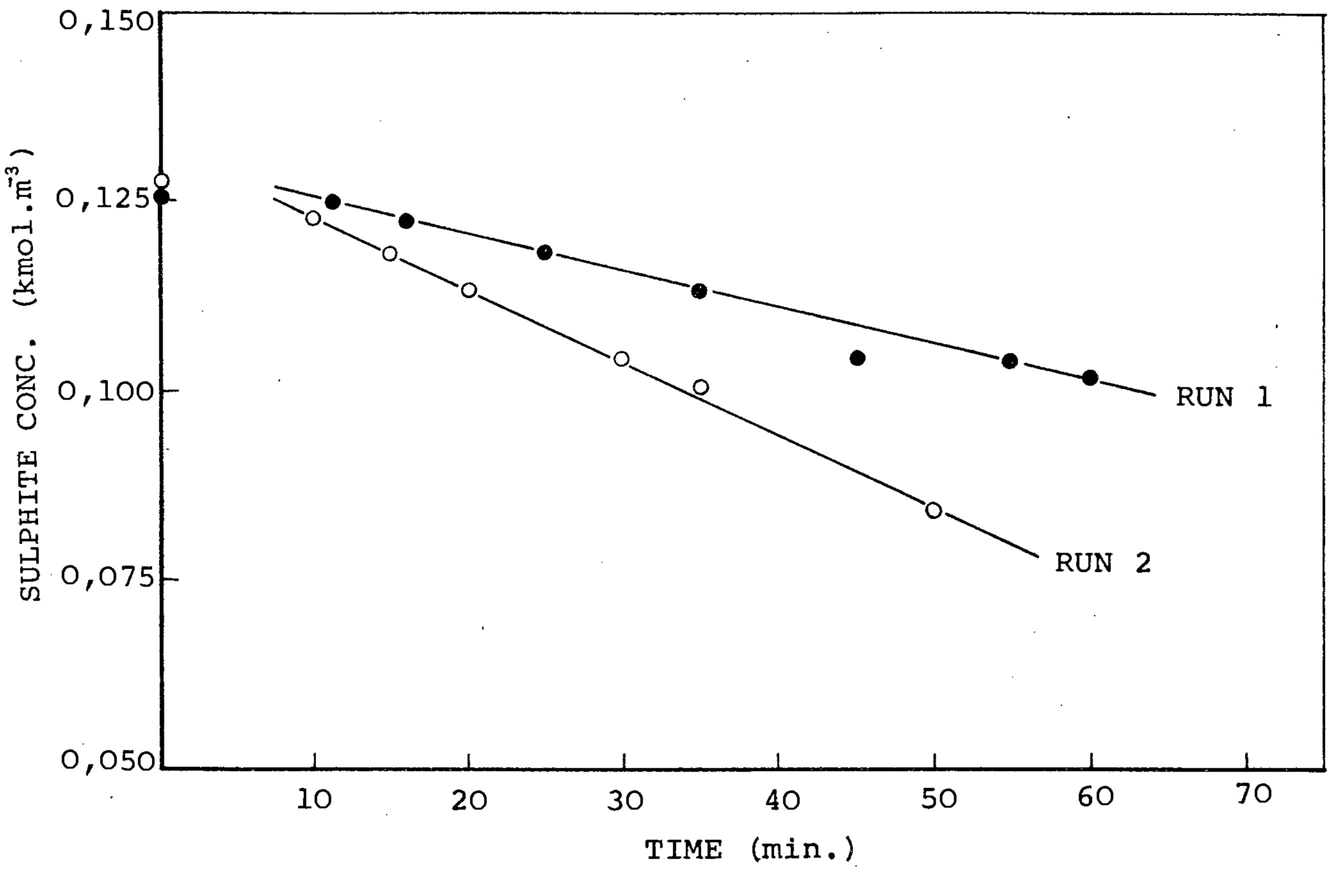


Figure B.1 Decline of sulphite concentration in the steady state mass transfer experiments.

APPENDIX C

LOSS OF SO_2 BY HYDROLOSIS OF Na_2SO_3

The exit air stream from a 0,5 M Na_2SO_3 solution including copper catalyst, as in a normal oxygen absorption experiment was analysed for SO_2 by drawing a quantity of the air stream through a gas wash bottle containing 3% H_2O_2 solution. Any SO_2 present in the air would be oxidized to H_2SO_4 by the H_2O_2, and the increase in acid concentration could be determined by titration with KOH [71].

Volume of air drawn through the wash bottle = 150 ℓ
Titre of 0,1 M KOH = 2,95 mℓ
Blank titre = 2,20 mℓ

.: 150 ℓ of air contain 0,075 mmol of SO_2

.: Concentration of SO_2 in the stream = $0{,}5 \times 10^{-6}\text{kmol.m}^{-3}$

$= 0{,}5 \times 10^{-6}/1{,}205 = 0{,}415 \times 10^{-6}\text{kmol.kg}^{-1}$

If the cross sectional area of the column is a, for an air rate of 847 $\text{kg.m}^{-2}.\text{hr}^{-1}$ for example, the sulphite loss by hydrolosis is

$$847 \times 0{,}415 \times 10^{-6} \times a = 0{,}351a \times 10^{-6}\text{kmol.hr}^{-1}$$

The rate of decline of sulphite by reaction at this gas rate, determined in run 13 (Table B-1) is

$$2{,}5 \times 10^{-2}\text{kmol.m}^{-3}.\text{min}^{-1}$$

.: Rate of decline of sulphite by reaction

$$= 2{,}5 \times 10^{-2} \times 60 \times (\text{vol. of liquid in column})$$

$$= 2{,}5 \times 10^{-2} \times 60 \times 1{,}2 \times a$$

$= 1{,}8a\ \text{kmol.hr}^{-1}$

$\therefore$ Sulphite loss by hydrolosis

$\sim$ 0,02% of the total sulphite decline

APPENDIX D

ENHANCEMENT IN SODIUM SULPHITE MASS TRANSFER EXPERIMENTS

When mass transfer is accompanied by rapid chemical reaction, the rate of mass transfer is entirely determined by the chemical reaction rate in the liquid boundary layer and is unaffected by the liquid phase mass transfer coefficient. The following derivation, first presented by Phillips and Johnson [5], demonstrates that when the reaction zone is entirely within the stagnant phase mass transfer film, the rate of mass transfer is proportional to the 1,5 exponent of the equilibrium oxygen solubility.

The rate of sulphite oxidation follows the following equation:

$$- \frac{dc}{dt} = kS^{y} \ C^{n} \qquad (D.1)$$

All the oxygen is consumed in the stagnant liquid film; its concentration at the interface (in equilibrium with the gas phase) is c*, and remains constant. The sulphite concentration, S, in the liquid phase is constant throughout the liquid phase. Steady state conditions are maintained.

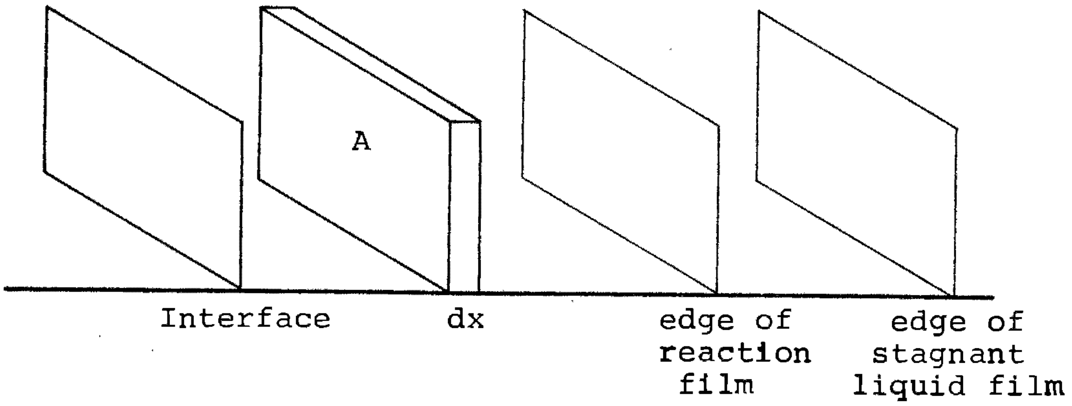


Figure E.1 Representation of absorbtion into an element of liquid, with accompanying fast chemical reaction.

The amount of oxygen entering the volume A dx in Figure D.1 is

$$AR_x = - AD_L \frac{dc}{dx} \qquad (D.2)$$

The amount of oxygen leaving this volume per unit time is

$$AR_{x+dx} = - AD_L \left[\frac{dc}{dx} + \frac{d^2c}{dx^2}\, dx\right]$$

The amount entering minus the amount leaving is equal to the amount of oxygen consumed in the volume

$$- AD_L \frac{dc}{dx} + AD_L \frac{dc}{dx} + AD_L \frac{d^2c}{dx^2}\, dx = Kc^n\, A\, dx \qquad (D.3)$$

or

$$\frac{d^2c}{dx^2} = \frac{Kc^n}{D_L} \qquad (D.4)$$

multiplying both sides by $2 \frac{dc}{dx}$

$$2 \frac{dc}{dx} \frac{d^2c}{dx^2} = \frac{2Kc^n}{D_L} \frac{dc}{dx} \qquad (D.5)$$

but

$$2 \frac{dc}{dx} \frac{d^2c}{dx^2} = \frac{d}{dx} \frac{dc^2}{dx} \qquad (D.6)$$

$$\therefore \quad \frac{d}{dx} \frac{dc^2}{dx} = \frac{2Kc^n}{D_L} \frac{dc}{dx} \qquad (D.7)$$

upon integrating,

$$\frac{dc}{dx}^2 = \frac{2Kc^{n+1}}{(n+1)D_L} + L \qquad (D.8)$$

or

$$\frac{dc}{dx} = \left[\frac{2Kc^{n+1}}{(n+1)D_L} + L \right]^{\frac{1}{2}} \tag{D.9}$$

Since $\frac{dc}{dx}$ and c approach zero at large values of x, L must equal zero. The rate of absorption is

$$AR_I = AD_L \left.\frac{dc}{dx}\right|_{x=0} \tag{D.10}$$

or

$$AR_I = AD_L \left[\frac{2K(c^*)^{n+1}}{(n+1)D_L} \right]^{\frac{1}{2}} \tag{D.11}$$

Therefore, when the reaction film is completely contained within the stagnant liquid mass transfer film, the oxygen transfer rate is

$$AR_I = A \left[\frac{2KD_L}{n+1} \right]^{n+1} (S)^{y/2} (c^*)^{n+1/2} \tag{D.12}$$

Since the sulphite oxidation reaction is second order in oxygen concentration at the interface [5,20,21,22], the mass transfer rate is proportional to the 1,5 exponent of the equilibrium oxygen solubility.

APPENDIX E

SOLUBILITY OF OXYGEN IN ELECTROLYTE SOLUTIONS

The method of van Krevelen and Hoftijzer [69] is widely used for the estimation of the solubilities of gases in solutions of electrolytes. The method relates the solubility in solution to that in water by the expression

$$\log (H_0/H) = kI \qquad (B.1)$$

where H_0 is the solubility (Henry's constant) in pure water, I is the ionic strength of the solution and k is a constant depending on the gas being dissolved and the ionic species in solution. Ionic strength of solution is defined by

$$I = \tfrac{1}{2} \Sigma (c_i z_i^2) \qquad (B.2)$$

where c_i is the concentration of species i in solution and z_i its valence. In mixed electrolytes, expression B.1 becomes

$$\log (H_0/H) = k_1 I_1 + k_2 I_2 + \ldots. \qquad (E.1)$$

although there seems to be no experimental evidence to confirm the validity of this expression [1].

The solubility of oxygen in sodium sulphate solutions was estimated by de Waal and Okeson [19] using the method of van Krevelen [69]. Dankwerts [1] has pointed out that the results may be suspect, because the oxygen solubilities as estimated by van Krevelen's method change very little with temperature. Linek and Mayeroferova [23] have found that van Krevelen's method for the determination of solubilities, again of oxygen in sodium sulphate solutions, predicted substantially lower results than were experimentally determined.

In view of these uncertainties in the accuracy of van Krevelen's method, the equilibrium concentration of dissolved oxygen was measured in sodium sulphate and potassium chloride solutions at a number of ionic strengths. The solutions were saturated with oxygen by bubbling air through them at a rate of about 500 $kg.m^{-2}.hr^{-1}$ for about a half hour. Samples withdrawn from the column after bubbling were analysed for dissolved oxygen by the Winkler method [63].

Figure E.1 shows that van Krevelen's method predicted lower oxygen solubilities in Na_2SO_4 solutions than were experimentally found, in solutions more concentrated than about 0,3 M, and higher solubilities in dilute solutions. The predicted results for KCl solutions are very close to the experimentally determined values.

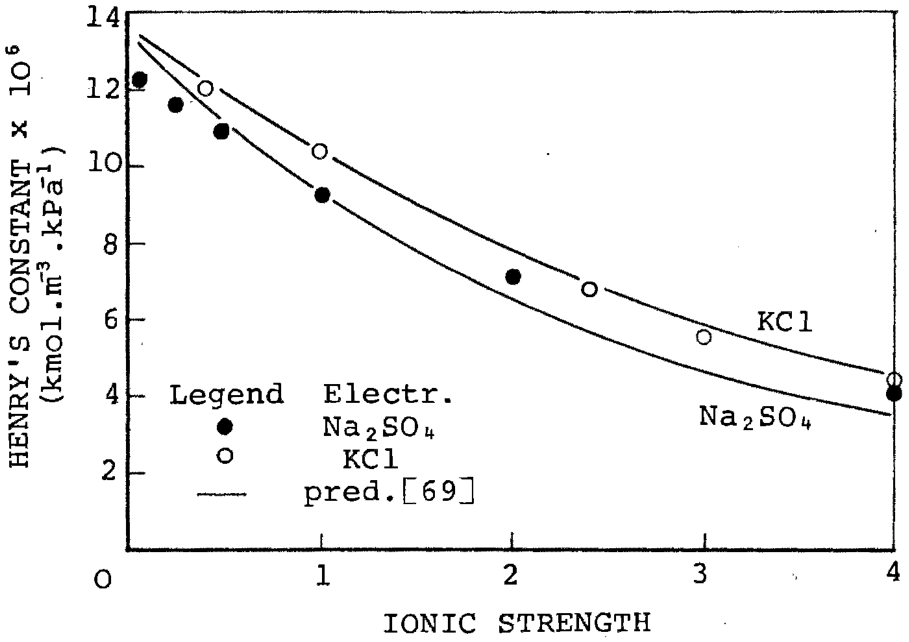


Figure E.1 Solubility of oxygen in electrolyte solutions.

TABLE E-1.1

SOLUBILITY OF O_2 IN Na_2SO_4 SOLUTIONS

temperature = 23°C

Ionic Str. μ	$H_{expt} \times 10^{-4}$ $kmols.m^{-3}.atm^{-1}$	$H_{calc} \times 10^{-4}$ $kmols.m^{-3}.atm^{-1}$	difference %
0,05	12,18	13,00	7
0,25	11,75	12,16	3
0,50	11,07	11,18	1
1,0	9,54	9,77	2
2,0	7,24	6,75	-7
4,0	4,14	3,45	-16

TABLE E-1.2

SOLUBILITY OF O_2 IN KCl SOLUTIONS

temperature = 21°C

Ionic Str.	$H_{expt} \times 10^{-4}$	$H_{calc} \times 10^{-4}$	difference
0,45	12,07	12,15	-
1,0	10,27	10,40	1
2,4	6,81	6,99	3
3,0	5,62	5,90	5
4,0	4,39	4,44	1