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March 1970

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MASS TRANSFER COEFFICIENTS AND INTERFACIAL AREA FOR GAS
ABSORPTION BY AGITATED AQUEOUS ELECTROLYTE SOLUTIONS

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ABSTRACT

The oxygen mass transfer characteristics of several aqueous electrolyte solutions of varying ionic strength are reported for a wide range of agitation-aeration intensity in a 2.5 litre fully-baffled stirred tank.

Unsteady-state oxygen probe response methods are described which permit measurement of the overall liquid phase physical mass transfer coefficient with minimum experimental complexity. Mathematical analysis of and computer solution for probe response are outlined.

A new simultaneous measurement technique involving concurrent chemical absorption of carbon dioxide and desorption of oxygen is proposed for separately evaluating the liquid-film coefficient and the specific interfacial area. Preliminary experimental results are given.

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INTRODUCTION

The performance capability of a particular absorber-reactor design has generally been characterized by the overall volumetric mass transfer coefficient, $K_L a$, for a given gas-liquid system. Scale-up is usually based on correlations of various kinds to predict $K_L a$ for a specified reactor. Most commonly, $K_L a$ has been assumed to be a function of agitation power per unit liquid volume (P_G/V_L) in addition to superficial gas velocity (v_S), and the liquid phase viscosity, density, interfacial tension, and diffusion coefficient (3,25). However, no completely general correlation has been developed, particularly for those cases in which $K_L a$ is strongly influenced by physicochemical factors which are functions of ionic composition. Furthermore, the liquid phase mass transfer coefficient, k_L , and the interfacial area per unit volume of liquid, (a), have fundamentally different dependences upon the physicochemical factors, and the behavior of the combined parameter $K_L a$ may be inadequate for predicting the behavior of a new system from the known behavior of a system having several different physicochemical characteristics.

This paper describes the variation of the overall volumetric coefficient of mass transfer for oxygen with P_G/V_L and v_S in one stirred tank absorber-reactor for aqueous electrolytic solutions of varying composition and ionic strength.

The range of power input has been extended beyond those of previous workers to include the higher power levels characteristic of processes for the production of biomass or single-cell protein from hydrocarbon substrates.

Utilizing a new technique for separately evaluating the behavior of the liquid phase mass transfer coefficient (k_L) and the interfacial area per unit volume of liquid (a), preliminary results from one system show that at high power input levels, k_L decreases with increasing P_G/V_L , which is in contrast with the results of others at lower agitation levels or in nonelectrolytic liquids.

MEASUREMENT OF $K_L a$

The value of $K_L a$ at a given agitation rate can be determined from an unsteady-state mass transfer experiment using a semibatch stirred tank (SBST) operating mode.

Material balance differential equations describing the absorption process can be written for both the gas and liquid phases (1). To obtain an analytical solution of these coupled equations, it is necessary to make several assumptions or simplifying approximations. First, we assume that the dispersed gas phase is well mixed. Hanhart et al. (2) found that at impeller rotational speeds greater than a certain minimum level (calculated to be 15.8 rev/sec for our particular tank), the residence time distribution of a dispersed gas closely resembled that of one perfectly mixed volume. Consequently, the mass transfer rate achieved in actual

practice (where the individual bubbles may have compositions varying between feed composition and that in equilibrium with the liquid) is the same as if all the bubbles had the same composition equal to the cup-mixed oxygen mole fraction in the outlet gas. Thus, for a gaseous component species k obeying Henry's law

$$C_k^* = C_k^*(y_{k2}, H, P_T, t) = P_T y_{k2}(t)/H \quad (1)$$

We also assume that the dispersed gas holdup h is not a function of gas composition for similar gases sparged at the same rate. To simplify the mathematics, we restrict our system to one in which the component transfer rate is small with respect to the total gas rate, i.e., $Q_1 \cong Q_2$, which is usually the case for sparingly soluble gases such as oxygen. We also postulate that the gas-phase component accumulation term $h dy_2/dt$ in the gas-phase material balance is negligibly small compared to the input, output, and transfer rate terms; this condition may be approached experimentally with sparingly soluble gases at high ratios of gas flow rate to liquid volume. Finally, we take the liquid phase as being perfectly mixed.

Where the gaseous component undergoes no liquid-phase reaction, using the preceding assumptions and approximations the unsteady-state desorption behavior of the batch liquid phase which results from a step change in inlet gas composition from air to an oxygen-free gas is described by an equation analogous to one given by Galderbank (3), namely

$$C_B = C_0 \exp(-\beta t) \quad (2)$$

$$\text{where } C_0 \equiv (P_T/H)(y_1)_0 \quad (3)$$

$$\text{and } \beta \equiv Q_1 H K_L a / [Q_1 H + 23.7(10^3) V_L P_T K_L a] \quad (4)$$

C_0 is the saturation concentration in equilibrium with the oxygen-containing gas initially in contact with the batch liquid before the step change to deoxygenated inlet gas is made.

The use of Eq. (2) for the evaluation of $K_L a$ indirectly through the aeration-agitation parameter β , requires a means of accurately analysing the oxygen concentration and its rate of change with time.

Dissolved Oxygen Probe Characteristics

The measurement of a rapidly changing dissolved oxygen content in an aqueous phase is most accurately done in situ, and can be accomplished using an electrode system at the cathode of which molecular oxygen is reduced. Clark et al. (4) conceived the oxygen probe, where the electrodes are separated from the aqueous solution by a semipermeable membrane which permits only the passage of gas. The membrane is the controlling resistance to oxygen flux and therefore the probe output is negligibly affected by agitation intensity above a threshold level. The amount of gaseous component transported across the membrane is dependent upon its partial pressure in the bulk external phase.

It is assumed that the inner membrane surface fits tightly against the cathode where the oxygen is instantaneously removed by electrolysis; the oxygen tension at the inner membrane surface therefore approaches zero. The probe then measures the partial

pressure p_k of oxygen, the so-called "oxygen tension" of the solution. It must be emphasized that the probe does not directly measure oxygen concentration; it measures HC_k .

The electric current produced by the probe is directly related to the molar flux of oxygen through the membrane surface at the cathode.

Probe Transient Response: Desorption

When the oxygen tension is changing rapidly with time, the diffusional lag in the membrane results in appreciable deviation from the steady-state linear relationship between oxygen tension and oxygen probe reading. We allow for this response lag by assuming that the transport of oxygen is solely in the direction normal to the membrane surface, and further that the oxygen diffusion coefficient in the membrane, D_M , is a constant independent of concentration and position, the latter implying that the membrane material is isotropic. These approximations allow us to solve Fick's Second Law of Diffusion for unidirectional transport with constant diffusivity by the method of Laplace transformation (5), inverting the transform by contour integration (5,6). The solution is

$$E_t = E_0 \left\{ \tau^{1/2} \exp(-\beta t) / \sin \tau^{1/2} - 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \pi^2 D_M t / L^2) / (1 - n^2 \pi^2 / \tau) \right\} \quad (5)$$

$$\text{where } \tau \equiv \beta L^2 / D_M \quad (6)$$

E_0 is the initial probe voltage corresponding to the dissolved oxygen concentration C_0 (Eq. 4), and L is the thickness of the membrane.

Theoretical desorption response curves for various values of the parameter β are given on Fig. (1). Transient oxygen absorption behavior is given by an expression similar in form to Eq. (5), such behavior also having been described by Heineken (13).

To use Eq. (5) to compute $K_L a$ from transient response data, it is necessary to calculate the best value of β which fits several pairs of data points (E_t, t) to the theoretical E_t vs t equation. $K_L a$ is obtained from the best-fit value of β by means of rearranging Eq. (4).

Computer Evaluation of β

β is evaluated for each experimental run by the nonlinear least squares procedure of Beals (7) designated LSQVMT. The chi-squared function

$$\text{CHISQ}(X) = \sum_{i=1}^n [\text{YDATA}(i) - F(\beta, D_M/L^2, t)]^2 [\text{WEIGHT}(i)]$$

is minimized with respect to one or both of the parameters β and D_M/L^2 by programme VARMIT (8). VARMIT is an iterative gradient method which uses a variable metric and is a modified version of the method of Davidon (9); VARMIT computes local minima of differentiable functions containing up to 40 variable parameters. In this work all data were given equal weight; $\text{WEIGHT}(i) = 1$ throughout.

Although we had originally assumed D_M to be a constant, in polymeric materials its value in fact depends upon the concentration

gradients in all three coordinate directions; in transient response runs, the instantaneous values of the concentration gradients depend upon the value of β . Therefore, one expects the effective value of D_M to vary slightly from run to run, and as the E_t vs t response is somewhat sensitive to the value of D_M/L^2 chosen, a better value of β was obtained by allowing the fitting programme to vary both parameters.

CONCURRENT MEASUREMENT OF k_L AND a

For the absorption of sparingly soluble gases wherein the major resistance to mass transfer resides in the liquid phase, it can be shown that (10)

$$k_L \cong K_L = K_L a/a \quad (7)$$

where the coefficients k_L and K_L are defined for the case of mass transfer without chemical reaction.

At high concentrations of the liquid-phase reactant, or with added catalyst in some cases, as shown by Danckwerts (11), absorption can be accompanied by a fast, pseudo-first order reaction in the liquid phase. Under these conditions, the rate of absorption per unit interfacial area becomes independent of k_L being dependent only upon the chemical reaction rate. Therefore, by choice of a suitable system, the interfacial area (a) may be evaluated directly. By reducing the liquid-phase reactant concentration to a sufficiently low level, the chemical reaction merely

increases the driving force, and $K_L a$ corresponds to the value for purely physical absorption. Some investigators have employed these principles to separately evaluate (a) and k_L by conducting an absorption at two different concentration conditions. However, this approach is valid only if the interfacial area and k_L are independent of the change in liquid-phase reactant concentration.

To obtain a consistent value of k_L from Eq. (7), $K_L a$ and (a) must be determined concurrently in the same gas-liquid system. A suitable system for this purpose is the desorption of oxygen from an aqueous solution of potassium hydroxide into a nitrogen-carbon dioxide dispersed gas phase. The alkaline solution is initially equilibrated with oxygen from air, then a step change in the inlet gas composition is made by switching to the dilute carbon dioxide stream at the same flow rate. Unsteady-state oxygen desorption is used in the manner previously described to evaluate an overall volumetric coefficient $K_{L4} a$. A quasi-steady state rate of carbon dioxide absorption with pseudo-first order chemical reaction is established, and from this rate we obtain a value of the specific interfacial area (a_3) . The key feature of this technique is that all the mass transfer parameters are measured simultaneously under identical hydrodynamic and physicochemical conditions.

We first relate the liquid phase coefficient in the absence of reaction for carbon dioxide (subscript 3) to that for oxygen (subscript 4) according to the random surface renewal model (11)

$$k_{L3} = k_{L4} (D_{L3}/D_{L4})^{1/2} \quad (8)$$

We further assume that the effective interfacial area for physical desorption and chemical absorption are the same

$$a_3 = a_4 = a \quad (9)$$

This assumption seems to be reasonable for the case of a highly-agitated stirred tank; there are no stagnant zones where the age distribution of surface elements has a different effect upon chemical and physical absorption. Using Danckwerts' solution of the transient diffusion equation for the random surface renewal model in the presence of a pseudo first-order reaction (11,12) in the transition between the slow and fast reaction regimes, combined with Eqs. (8) and (9), algebraic manipulation gives an expression for the specific area

$$a = \left\{ \left[(R_{V3}^r / C_3^*)^2 - (K_{L4} a)^2 (D_{L3} / D_{L4}) \right] / D_{L3} k_2 [\text{OH}^-]_B \right\}^{1/2} \quad (10)$$

where R_{V3}^r is the rate of chemical absorption of carbon dioxide, and k_2 is the second-order kinetic rate constant for the reaction between carbon dioxide and hydroxyl ion.

Having determined $K_{L4} a$ and the concomitant specific area (a), the liquid phase mass transfer coefficient for oxygen in the absence of reaction, k_{L4} , is obtained by the procedure described by Eq. (7).

EXPERIMENTAL

Systems Studied

For oxygen transfer from air, the physical absorption characteristics of the following aqueous solutions were studied:

(i) 0.125, 0.250, 0.375, 0.50 M sodium sulphate with $4(10^{-3})$ M cupric sulphate; (ii) an electrolyte solution used by Champagant (14) as a source of basal mineral salts in the production of biomass from hydrocarbon substrate, designated here as medium A-1 and consisting of 1.6 g K_2HPO_4 , 0.48 g $MgSO_4 \cdot 7H_2O$, 4.6 g NH_4Cl , and 0.02 g $NaCl$ per litre of distilled water; and (iii) distilled water.

The mass transfer of oxygen from air with chemical reaction was studied in SBST mode with the sulphite oxidation system used by Cooper, Fernstrom, and Miller (15). Initial sulphite ion concentration was 0.5 M, and the reaction was catalysed by cupric ion, $4(10^{-3})$ M.

The quasi steady-state absorption of carbon dioxide from a 0.1 CO_2 :0.9 N_2 gas stream was studied by reaction with 0.06 M potassium hydroxide. The mode is designated quasi steady state as the concentrations of both the hydroxide and reaction product carbonate ion were not strictly invariable, causing the absorption rate to change slightly during the course of a run.

Apparatus

A schematic flow diagram of the apparatus is given on Fig. 2.

The stirred tank absorber-reactor was constructed from 6-in. I.D. Pyrex pipe; in all runs the depth of gas-free liquid equalled the diameter, giving a working volume of 2.5 litres. The internals corresponded to the recommended "standard" dimension ratios (16); the four equally spaced baffles were $0.1 D_T$ in width, while the single 6-blade, turbine-type impeller had a diameter of $1/3 D_T$ and was located one impeller diameter above the bottom. Inlet gas was admitted through a single $1/8$ -in. diameter bevelled orifice located in the centre of the bottom head plate.

The impeller rotational speed was measured by a tachometer generator-indicating meter system. Agitation power input to the dispersion was measured directly by an in-line torque meter located between the impeller and drive motor shafts.

The inlet gas was preheated to the operating temperature of 30°C and humidified before entering the stirred tank which was maintained at atmospheric pressure.

In the carbon dioxide absorption-reaction experiments, the stirred tank was equipped with pH electrodes. The hydroxide ion concentration in the reactor was controlled by the addition of small amounts of concentrated potassium hydroxide solution; the addition rate (about 20 ml/min) was regulated by a pH indicator-controller meter.

Analytical

The oxygen probes were galvanometric type (self-generating) described by Johnson, Borkowski, and Engblom (17), and were obtained from J. Borkowski. The membrane material was Teflon, 0.002 in. thick. The probe transient response was recorded on a high-speed (30 inch/min), 0-10 mV strip chart recorder having a full-scale response time of 0.25 second.

The carbon dioxide content of the gas stream was determined chromatographically.

Sulphite ion concentration was determined by reaction with excess iodine, followed by back-titration with sodium thiosulphate (18). Hydroxide and carbonate ion concentrations were determined by titration with HCl, using a pH meter, to end points of 8.30 and 3.70 pH.

Range of Parameters

The parameters affecting both $K_L a$ and (a) were varied over the following ranges: impeller rotational speed, 400 to 2200 rpm; power input to the dispersion per unit volume of clear liquid, 40 to 22,400 ft-lb_f/min-ft³, 0.0012 to 0.68 hp/ft³ or 0.16 to 90.8 hp/1000 gal.; inlet gas rate 0.5 to 2.0 VVM or superficial gas velocity 0.00375 to 0.0150 ft/sec.

RESULTS

$K_L a$ for Oxygen Transfer

In all solutions studied, $K_L a$ for oxygen transfer was found to correlate well with the term $(P_G/V_L)^n$ where n is dependent upon

the nature of the solution. An example of the behavior of the different systems at one particular aeration rate determined by transient or steady-state absorption runs is given on Fig. 3, where some data points are omitted for clarity. The power input is expressed in units of $\text{ft-lb}_f/\text{min-ft}^3$ to facilitate direct comparison with previous work, e.g. (15). Oxygen solubility at the interface in sulphite solution was taken to be the same as that in sulphate solution of identical ionic strength, estimated by the method of van Krevelen and Hoftijzer (19). For the sulphite oxidation result, the appropriate coefficient is $K_L^R a$, determined in the presence of chemical reaction. The reaction regime is intermediate between the diffusional and fast-reaction regimes, such that K_L^R for sulphite is somewhat greater than K_L for sulphate. Similar plots were obtained for the other three aeration rates used in the study, leading to the conclusion that the $K_L a - (P_G/V_L)^n$ relationship is linear over the larger part of the power-input range. Deviation from linearity occurs at both the low and high power-input ends of the range. From cross plots of the data obtained at different aeration rates, $K_L a$ was found also to correlate linearly with $(v_S)^m$ over the range of aeration rates used. Furthermore, over the power range where the $K_L a$ dependency on $(P_G/V_L)^n$ was linear, there appears to be no effect of v_S upon n . The variation of the exponents n and m with solution composition are given in Table 1, where the total ionic strength is defined as

$$\Gamma_T = \frac{1}{2} \sum_i z_i^2 C_i \quad (11)$$

with C_i expressed as gmole/litre.

Table 1. Variation of Agitation and Aeration Exponents with Solution Composition

Solution	Total electrolyte concentration (gmole/litre)	Γ_T (g-ion/litre)	n	m
$\text{Na}_2\text{SO}_3 + \text{CuSO}_4^a$	0.504	1.51	0.90	0.38
$\text{Na}_2\text{SO}_4 + \text{CuSO}_4^a$	0.504	1.51	0.90	0.39
	0.379	1.13	0.90	0.39
	0.254	0.758	0.90	0.39
	0.129	0.383	0.90	0.39
Medium A-1	0.100	0.136	0.71	0.43
KOH	0.062	0.062	0.55	(b)
Distilled water	0.000	0.000	0.40	0.35

^a) $4(10^{-3}) \text{ M CuSO}_4$.

^b) Not determined.

The data of Table 1 indicate that for sodium sulphate solutions of concentration above 0.125 M (chosen to simulate sulphite solutions typically used) the effect of agitation and aeration upon $K_L a$ is independent of electrolyte concentration. However, a separate experiment at a fixed agitation-aeration condition showed that $K_L a$ was strongly dependent upon electrolyte concentration at molarities below 0.08, as shown on Fig. (4).

Table 1 also shows that n decreases with decreasing concentration of electrolyte regardless of its chemical nature. As shown on Fig. (5) n correlates well with total ionic strength, and from the form of the relationship it appears that

$$n = 0.40 + 2.38 \Gamma_T, 0 \leq \Gamma_T < 0.21 \quad (12a)$$

$$n = 0.90, \quad \Gamma_T \geq 0.21 \quad (12b)$$

Attempts to correlate $K_L a$ or $K_L^r a$ with impeller rotational speed and aeration rate gave poor results for each system tested, with the exception of physical absorption in 0.125 M sodium sulphate. The slopes of $K_L a$ vs N plots for a given solution were different for each aeration rate, indicating that $K_L a$ dependency upon N was not separable from its dependency upon v_g . For 0.125 M sulphate, $K_L a$ was linearly related to N and independent of aeration rate in the range $900 \leq N \leq 2000$.

We find that the aeration rate exponent varies only slightly with solution ionic strength; $0.35 \leq m \leq 0.43$.

k_L and (a) for Oxygen Transfer

The results of the simultaneous oxygen desorption-carbon dioxide absorption runs in potassium hydroxide solution are given on Fig. (6) for one gas sparging rate. Diffusivities were estimated from the data of Ratcliff and Holdcroft (20) and the Wilke-Chang correlation (21), while k_2 was calculated from the data of Pinsent et al. (22) in applying Eq. (10).

Figure (6) shows data points and correlating lines for $K_{L4}a$, (a), and k_{L4} . Individual k_{L4} points were calculated from the corresponding paired values of $K_{L4}a$ and (a). The line representing the overall average behavior of k_{L4} was computed from the least-squares lines for $K_{L4}a$ and (a). The results clearly show that for mass transfer of oxygen without reaction the individual parameters k_{L4} and (a) have distinctly different dependencies upon the agitation power. There is a definite trend of decreasing k_{L4} with increasing P_G/V_L for the mass transfer from the relatively small bubbles in the electrolyte solution. Work is in progress to measure the effect of gas rate upon the three mass transfer parameters which should lead to a more complete understanding of their behavior; meanwhile we tentatively conclude for the bubble size distribution obtained in dilute KOH solution at $P_G/V_L > 10^3$ that

$$a \propto (P_G/V_L)^{0.89} \quad (13)$$

and

$$k_L \propto (P_G/V_L)^{-0.34} \quad (14)$$

We have calculated that the temperature rise at the interface due to the heats of solution and reaction for carbon dioxide is negligible (less than 0.01°C), the gas phase fractional resistance to the overall mass transfer process is insignificant (less than 1.6%), and there is no appreciable effect of backmixing from the vapor space above the free liquid surface (less than 1%).

DISCUSSION

Physical Absorption: $K_L a$

Although the density, viscosity, and interfacial surface tension of electrolyte solutions vary with both the nature and concentration of the solute, the values of these three physicochemical parameters differ from those of water by less than 15 percent for the solutions tested. Therefore, the increase in n shown on Fig. (5) cannot be attributed to these factors to any significant degree. It is known that the addition of small quantities of solutes to water may appreciably decrease the bubble size, even though other physicochemical properties remain essentially constant (23,24). In the case of electrolyte solutions, this phenomenon has been attributed to electrical effects at the gas-liquid interface; repulsive forces generated by the surface potentials hinder bubble coalescence, and the average equilibrium bubble size is therefore smaller. Visual observation indicated that upon addition of increasing amounts of ionic solute, the average bubble diameter decreased and the dispersed gas fractional holdup increased. We conclude, therefore, that the variation of n primarily reflects variation in (a). This conclusion is in qualitative agreement with the work of Marrucci and Nicodemo (24) on the effect of electrolyte concentration on nitrogen bubble diameters in a bubble column.

Calderbank (25) used an optical light-scattering technique to measure (a) for air dispersions in pure liquids at 15°C in stirred tanks having geometric ratios identical to the absorber used

here, and found (a) varies as $(P_G/V_L)^{0.4} (v_S)^{0.5}$. He also determined the variation of $K_L a$ for oxygen absorption (3), and from the combined results showed that k_L for a given bubble size range was independent of both aeration and agitation rates (for $330 \leq P_G/V_L \leq 3300$ in a 5-litre tank); hence, for water, $K_L a$ varied as $(P_G/V_L)^{0.4} (v_S)^{0.5}$. Our results over a wider power range are in agreement with Calderbank's power exponent, but we find the aeration exponent to be 0.35.

Chemical Reaction: $K_L^r a$ and a

Cooper et al. (15) measured $K_G^r a$ at 20°C by means of sulphite oxidation using vaned disc impellers to disperse the gas at $P_G/V_L < 3600$. Converting their data to $K_L^r a$ values at 30°C, and correcting for the fact that they based their calculated values on the logarithmic mean gas mole fraction rather than on the exit gas mole fraction, our sulphite oxidation $K_L^r a$ values agree remarkably well with theirs up to the same power level regardless of the fact that our geometric ratios are quite dissimilar. However, over the greater power range tested here, our overall results do not agree with their conclusion that $K_L^r a$ varies as $(P_G/V_L)^{0.95} (v_S)^{0.67}$, the main difference being in the aeration exponent.

In Fig. (5), $K_L a$ for oxygen absorption in sulphate and $K_L^r a$ for absorption with reaction in sulphite solution of identical ionic strength exhibit the same dependency upon power input in the range $300 \leq P_G/V_L \leq 4000$, and Table 1 shows that the dependency upon aeration rate is nearly the same in both cases. $K_L^r a/K_L a$ is greater

than 1.0, as predicted by the theory of mass transfer in the diffusional-to-fast intermediate reaction regime assuming that the value of (a) is the same in both solutions for a given agitation-aeration intensity. The decline in $K_L a$ in sulphate at high power levels may be due to a decrease in K_L as a minimum bubble diameter is approached; K_L^r , of course, depends as well on the kinetics of the reaction and is less dependent on the hydrodynamics.

Westerterp et al. (26) investigated the behavior of copper-catalysed sulphite oxidation (0.79 M) at 30°C, using superficial air velocities at least double the maximum used in our work. $K_L^r a$ in their system varied as $(N-N_0)D_I$, being completely independent of aeration rate when $N > N_0$, an observation unique to their work and that of Friedman and Lightfoot (27). Westerterp et al. conclude that $K_L^r a$ or (a) in stirred tanks depends on aeration rate only if the experiments are done at very low rpm ($N < N_0$) where agitation rate has no effect, or if the log mean partial pressure driving force is used instead of the exit gas partial pressure. However, Westerterp's criterion indicates that $N_0 = 950$ rpm for the stirred tank used in this work, and we find a measurable dependency of $K_L a$ or $K_L^r a$ upon v_s at $N > N_0$ for all solutions tested, except 0.125 M sodium sulphate which, coincidentally, was the only one that had characteristics that could be well correlated with N as well as P_G/V_L . It appears, then, that mass transfer is only independent of gas sparging rate at relatively high superficial velocities, greater than those normally used in submerged fermentation processes, for example.

Mass transfer coefficients obtained by the sulphite oxidation method are normally measured at ionic strengths greater than 1.5. Therefore, application of the results to fermentations in media of lower ionic strength may not be valid. Also, during the course of batch fermentations consumption of mineral components may lead to significantly lower values of $K_L a$.

The interfacial area per unit volume measured by dilute carbon dioxide absorption in hydroxide is much greater than the values obtained by other workers at lower agitation levels, in nonelectrolytic solutions, or with pure reactive gases. Calderbank (25) reported a maximum integral (a) of about 1.1 cm^{-1} for air-pure liquid systems; Yoshida and Miura (28), at $60 < N < 400$, measured (a) by carbon dioxide desorption-reaction with hydroxide in the fast reaction regime at 20°C and reported a maximum (a) of 0.8 cm^{-1} .

Liquid Film Coefficient: k_L

As previously discussed, Calderbank (25) found for relatively large bubbles ($d_b > 0.2 \text{ cm}$) dispersed in nonelectrolytic liquids that k_L was independent of agitation rate.

Yoshida and Miura combined their CO_2 -hydroxide solution results for interfacial area (a) (28) with values of $K_L a$ measured in an air-water system (23) to calculate the variation of k_L without reaction, and found for $d_b > 0.15 \text{ cm}$ that the Nusselt number for mass transfer could be correlated with the Reynolds and Schmidt numbers, so that k_L varies as $(N D_I)^{0.6} / d_b^{0.4}$, predicting that k_L

increases with increasing agitation. However, this method does not ensure (1) that the (a) in the physical absorption runs in water is the same as the (a) in the chemical reaction runs since (a) increases with increasing ionic strength, and (2) that the average d_b is the same in both types of liquids since d_b decreases with increasing electrolyte concentration. Therefore the dispersed bubbles may have been subjected to significantly different hydrodynamic regimes.

CONCLUSIONS

The effect of agitation upon $K_L a$ or $K_L^r a$ appears best described in terms of the power input per unit volume concept. The relationship between the overall volumetric transfer coefficients in solutions of electrolytes and P_G/V_L is strongly dependent upon the ionic strength of the solution in the range $0 \leq \Gamma_T \leq 0.2$. Preliminary results indicate that the ionic strength predominantly affects the interfacial area per unit volume (a) , which increases with increasing Γ_T . However, as the average bubble diameter decreases with increasing (a) , the hydrodynamics at the gas-liquid interface may therefore be affected, and the ionic strength may have a secondary influence upon k_L .

The simultaneous desorption-absorption technique described in this paper provides a convenient means of separately evaluating k_L and (a) under consistent interfacial area and hydrodynamic conditions. It should be possible to extend the use of this technique to any normally nonreactive electrolyte solution by

replacing a portion of the original electrolyte with hydroxide while keeping the total ionic strength constant, thereby separately evaluating the effect of ionic strength upon k_L (without reaction) and (a).

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SYMBOLS USED

- a = gas-liquid interfacial area per unit volume of liquid
 (cm^{-1})
- C = liquid-phase concentration (gmole/cm^3)
- d_b = Sauter mean bubble diameter (cm)
- D_I = impeller diameter (cm)
- D_{Lk} = liquid-phase diffusivity of species k (cm^2/sec)
- D_M = effective diffusivity of oxygen in probe membrane (cm^2/sec)
- D_T = internal diameter of tank (cm)
- E = potential difference across external resistor in oxygen
 probe circuit (volt)
- h = dispersed gas molar holdup in the liquid phase
 $(\text{gmole free gas}/\text{cm}^3 \text{ gas-free liquid})$
- H = Henry's law coefficient ($\text{atm-cm}^3/\text{gmole}$)
- k_2 = second-order reaction velocity constant ($\text{cm}^3/\text{gmole-sec}$)
- k_L = liquid phase coefficient for mass transfer without
 reaction (cm/sec)
- k_L^r = effective liquid phase mass transfer coefficient with
 chemical reaction (cm/sec)
- K_L = overall mass transfer coefficient without reaction based
 on liquid-phase concentration-difference driving force
 (cm/sec)
- K_L^r = effective overall mass transfer coefficient with chemical
 reaction based on liquid-phase concentration-difference
 driving force (cm/sec)

- K_G^r = overall mass transfer coefficient with reaction based on gas-phase partial-pressure-difference driving force (gmole/cm²-atm-sec)
- K_L^a = overall volumetric mass transfer coefficient without reaction based on liquid-phase concentration-difference driving force (sec⁻¹)
- K_L^r = effective overall volumetric coefficient for mass transfer with chemical reaction (sec⁻¹)
- L = thickness of oxygen probe membrane (cm)
- m = exponent of v_S (dimensionless)
- n = exponent of P_G/V_L (dimensionless)
- N = impeller rotational speed (rev/min)
- N_0 = critical impeller rotational speed (rev/min)
- p = partial pressure of gaseous component (atm)
- P_G = power input to gas-liquid dispersion (ft-lb_f/min)
- P_T = total pressure in absorber-reactor vapour space (atm)
- Q = volumetric gas flow rate at 60°F, 1 atm (cm³/sec)
- R_V^r = rate of absorption with reaction of gaseous component per unit liquid volume (gmole/cm³-sec)
- t = time (sec)
- v_S = superficial gas velocity in stirred tank (ft/sec)
- V_L = volume of gas-free liquid (cm³; ft³ with P_G)
- VVM = volume of gas/volume of liquid-min at 60°F, 1 atm.

- y = mole fraction in gas phase
- z = electric charge carried by ionic species

Greek Letters

- β = aeration-agitation parameter, defined by Eq. (4) (sec^{-1})
- Γ = ionic strength defined by Eq. (11) (g-ion/litre)
- τ = rate ratio parameter, defined by Eq. (6) (dimensionless)

Superscripts

- * = liquid-phase property in physical equilibrium with bulk gas-phase property

Subscripts

- 0 = initial condition
- 1 = refers to inlet stream
- 2 = refers to outlet stream
- 3 = denotes oxygen
- 4 = denotes carbon dioxide
- B = bulk phase (cup-mixed) property
- i = value at gas-liquid interface; ionic species
- k = absorbing component
- L = property or condition of gas-free liquid
- M = value in polymeric membrane
- t = unsteady-state condition
- T = property of total phase or system
- V = denotes value per unit volume of gas-free liquid

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FIGURE CAPTIONS

- Fig. 1. Oxygen probe theoretical transient response to step change in inlet gas composition: desorption.
- Fig. 2. Schematic flow diagram of apparatus.
- Fig. 3. Comparison of overall volumetric mass transfer coefficients for oxygen. Superficial gas velocity 0.015 ft/sec.
- Fig. 4. Effect of sulphate concentration on overall volumetric mass transfer coefficient for oxygen.
- Fig. 5. Effect of ionic strength on agitation power per unit liquid volume exponent.
- Fig. 6. Oxygen mass transfer parameters in 0.06 M potassium hydroxide solution. Superficial gas velocity 0.015 ft/sec.

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Fig. 1

Fig.2 Schematic flow diagram of apparatus

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Fig. 3

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Fig. 4

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Fig. 5

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Fig. 6

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