Simultaneous Measurement of Interfacial Area and Mass Transfer Coefficients for a Well–Mixed Gas Dispersion in Aqueous Electrolyte Solutions

A new measuring technique involving concurrent chemical absorption of carbon dioxide and desorption of oxygen is developed for simultaneously evaluating the liquid-phase mass transfer coefficient k_L and the specific area a of sparingly-soluble gas dispersions in stirred tanks containing an aqueous solution of inorganic electrolytes. The method ensures that k_L and a are evaluated under consistent hydrodynamic conditions.

Results from three different nonviscous systems show that at high agitation power, such that the average bubble diameter is between 0.2 and 2 mm, k_L decreases with increasing power input and is dependent on the bubble diameter. This behavior is in contrast to the results of others at lower agitation levels or in nonelectrolytic liquids, but in general agreement with previous results for bubbles of the same diameter range produced in viscous, nonelectrolytic solutions.

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SCOPE

In the absence of a sufficiently fast chemical reaction in the liquid phase, the gas absorption rate capability of a particular stirred tank design customarily has been characterized by the overall volumetric mass transfer coefficient K_La. It would seem preferable, however, to be able to predict K_La from separate correlations for its constituent parameters K_L and a since their values are predominantly dependent upon distinctly different physico-chemical parameters of the system. In previous studies k_L has been shown both theoretically (Higbie, 1935; Danckwerts, 1951) and experimentally (Calderbank and Moo-Young, 1961) to be dependent primarily upon liquid-phase diffusivity and viscosity. On the other hand, a is dependent primarily upon interfacial tension for pure liquids or nonelectrolyte solutions (Calderbank, 1958) or upon ionic strength in solutions of inorganic electrolytes exhibiting Newtonian rheological behavior (Robinson and Wilke, 1971).

Direct measurement of k_L in stirred tank gas dispersions is not possible. However, given separate evaluations of K_La and a for sparingly soluble gases wherein the major resistance to mass transfer resides in the liquid phase, the liquid-phase mass transfer coefficient k_L may be computed from

$$k_L \approx K_L = K_La/a \tag{1}$$

This procedure, of course, only gives meaningful results if both K_La and a are determined under identical physico-chemical and hydrodynamic conditions such that the dispersion characteristics (average bubble diameter, bubble size distribution, and gas holdup) are constant.

No general correlations for either k_L or a applicable to stirred tank gas dispersions in aqueous electrolyte solutions have yet been developed. The purpose of the present study was to develop and to conduct preliminary experimental tests of a new technique by means of which k_L and a could be simultaneously evaluated under consistent physico-chemical and hydrodynamic conditions in aqueous electrolyte solutions having a wide variation in both composition and ionic strength.

Experimentally, the new technique involves unsteady state desorption of oxygen from an aqueous electrolyte solution containing a controlled, low concentration of hydroxyl ion accompanied by concurrent, pseudo steady state absorption with chemical reaction of carbon dioxide from the sparged gas. The oxygen desorption rate is measured by a dissolved oxygen probe, the response of which, after correction for the diffusional lag in its membrane, is used to evaluate the overall volumetric coefficient for oxygen transfer K_La. The rate of absorption with reaction of carbon dioxide is used to evaluate a, the corresponding value of k_L being calculated by combining the two results. The results may be used to predict k_L for other sparingly-soluble gases.

CONCLUSIONS AND SIGNIFICANCE

A preliminary test of the new technique was conducted in three different aqueous solutions of ionic solutes, at one gas sparging rate but over a wide range of impeller agitation power input. The results lead to the conclusion that k_L and a have diametrically opposite dependencies upon P/V; k_L decreases with increasing P/V (concomitantly with decreasing average bubble diameter), while a

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increases with increasing P/V. The decrease in k_L with decreasing d_b may be attributed to change in bubble hydrodynamic regimes from the deformable, circulating bubbles of large diameter to the rigid, spherical bubbles of small diameter.

Sideman, Hortacsu, and Fulton (1966), based on works such as those of Calderbank (1958), and Calderbank and Moo-Young (1961) which indicate that k_L is independent of P/V or nearly so, suggested that for all practical purposes K_La depends only on the variation of a with agitation rate and superficial gas velocity. It is concluded from the results of this present study that such is not the case in electrolyte solutions of ionic strength ranging from 0.10 $\leqq \Gamma_T \leqq$ 0.40 agitated over the power range 800 to (1.5) $(10)^4$ W/m^3. These results have significant implications for the design and operation of stirred tank or other gas absorption processes wherein the liquid phase consists solely or predominantly of an aqueous electrolyte solution: aerobic fermentations (including hydrocarbon fermentations), carbonation in the Solvay process, biological or wet air oxidation (Zimmermann process) treatment of organic-bearing brackish wastes, etc.

A definitive study of the effect of ionic strength upon gas holdup, average bubble diameter, and the liquid-phase mass transfer coefficient was not part of this present work. However, the results of the three systems examined suggest that it would be profitable to fully define the ionic strength effect on these three parameters and on the specific interfacial area in stirred tanks, applying the concurrent measurement technique to solutions of ionic strength range $0.05 \leqq \Gamma_T \leqq 1.0$. The results of such a separate study could lead to even better predictions for K_La in electrolyte solutions based on the separate behavior of K_L and a than those presently available which were, for the most part, obtained from investigations of gas dispersions in pure liquid phases or solutions of nonelectrolytes.

PREVIOUS WORK

Calderbank (1958, 1959) and Calderbank and Moo-Young (1961), using an optical method, measured the specific interfacial area of gases dispersed by turbine impellers in liquid phases of zero or negligible ionic strength (for example, water, aqueous solutions of glycol or glycerol, or organic solvents) and combined the results with K_La values which were determined in the same systems in order to evaluate k_L from Equation (1). Calderbank and Moo-Young (1961) presented generalized correlations applicable to pure liquids or solutions of nonionic solutes in which k_L was shown to be independent of the agitation power input, being solely dependent upon the physical properties of the phases according to:

small bubbles:

$$N_{Sh} = k_L d_b/D_L = 2.0 + 0.31\,[d_b^3(\rho_L - \rho_G)g/\mu_L D_L]^{1/3} \tag{2}$$

large bubbles

$$N_{Sh} = 0.42\,(N_{Sc})^{1/2}\,(N_{Gr})^{1/3} \tag{3}$$

where d_b is the average bubble diameter and D_L is liquid phase solute (dissolved gas) diffusivity. Small and large bubbles were defined as having average diameters less than or greater than 2.5 mm, respectively (Calderbank, 1958, 1959); in practice, the small bubble diameters were apparently generally less than 1 mm (Calderbank and Moo-Young, 1961). For small bubbles, $3(10^{-5}) \leqq k_L < 5(10^{-4})$ m/s, while for large bubbles $5(10^{-4}) \leqq k_L \leqq 11(10^{-4})$ m/s (Calderbank, 1959). Equations (2) and (3) both show k_L to be independent of d_b.

For the nonelectrolyte solutions or pure liquids tested, Calderbank (1958) found that, unlike k_L, the specific interfacial area a was dependent on the agitation power being correlated by

$$a = A_0(P/V)^{0.4}\,(v_S/v_t)^{0.5}\,\rho_c^{0.2}\,\sigma^{-0.6} \tag{4}$$

in the range $260 \leqq P/V \leqq 2600$ W/m^3. For air dispersions in pure, nonelectrolytic liquids at 15°C, the maximum integral average value of a reported was about 110 m^{-1}. The overall results of these studies led to the conclusion that the change in k_La with changing P/V solely was due to changes in a, k_L remaining constant as long as the average bubble diameter distinctly remained in either the small or the large category over the range of the agitation power applied.

For carbon dioxide absorption in viscous aqueous solutions of glycerol, Calderbank and Moo-Young (1961) demonstrated the existence of a transitional bubble regime intermediate between those of small and large bubbles. In this transitional regime, characterized by $0.5 \leqq d_b \leqq 2.5$ mm, k_L decreased with decreasing d_b. Hence, in general, as P/V is increased k_L may be anticipated to remain constant until d_b decreases to a value of about 2.5 mm, then to decrease more-or-less in direct proportion to d_b until d_b reaches about 0.5 mm, and then to assume a smaller, constant value as d_b is further decreased with increasing P/V.

Yoshida and Miura (1963) measured a in stirred tanks from the rate of CO_2 absorption with chemical reaction using sodium hydroxide solutions. At the relatively low impeller rotational speeds used (ranging from 1 to 6.67 rev/s) the specific area varied from about 10 to 100 m^{-1}. They combined their results for a with the K_La results of Yoshida, Ikeda, Imakawa, and Miura (1960) for oxygen absorption in water to calculate from Equation (1) the variation of k_L for mass transfer without chemical reaction. These results showed that k_L increased with agitation rate (N) according to

$$k_L = A_1(N\,D_I)^{0.8}(d_b)^{-0.4} = A_2N(D_I)^{0.2} \tag{5}$$

a result contrary to those of Calderbank and Moo-Young (1961), and, as will be shown, the results of this present study which were obtained at higher agitation rates (10 to 35 rev/s). It is known that the addition of electrolytes to water significantly decreases the rate of bubble coalescence, resulting in lower values of d_b and somewhat higher values of H_G, the net effect being that the specific area can be appreciably greater. Therefore, it is possible that the specific interfacial areas in the two different works of Yoshida et al. (1960, 1963) at equivalent agitation conditions were not identical as assumed in order to compute k_L.

Westerterp, van Dierendonck, and deKraa (1963) using the cupric ion catalyzed sulfite oxidation method (Γ_T = 2.38), which they inferred occurred in the fast-reaction regime, developed on empirical correlation in which a varied directly with N, D_I, and the square root of the tank diameter. The general validity of these results may be open to question as it subsequently has been shown that cupric ion catalyzed sulfite oxidation does not generally occur in the fast reaction regime (DeWaal and Okeson, 1966; Srivastava, McMillan, and Harris, 1968). Also, sulfite oxidation results are not generally applicable to other electrolyte solutions of lower ionic strength; recent work shows that K_La and, most likely, a are independent of ionic strength in solutions where $\Gamma_T > 0.40$ mol/liter (Robinson and Wilke, 1973).

Reith (1968) investigated the behavior of air dispersions in both water and sodium sulfite solutions, measuring a by photographic or chemical absorption methods, respectively. Interfacial areas in the sulfite solution (800 mol/m^3) varied from about 350 to 2200 m^{-1} over an agitation range of 10 to 22.5 rev/s, being some 1.5 to 3 times greater than the corresponding a in water. In a slow reaction rate sulfite oxidation system, Reith also found k_L to be constant at $4(10^{-4})$ m/s regardless of the agitation and gas sparging rates. This particular value of k_L is somewhat surprising in that it corresponds more closely to large bubble behavior than to the small bubble regime which would be anticipated to be the case in such an electrolyte solution.

Lee and Meyrick (1970) investigated the interfacial area in air-aqueous electrolyte solution dispersions in a stirred tank by means of the light transmission method. Their solutions consisted of sodium chloride or sodium sulfate ranging in concentration from 50 to 500 and 50 to 250 mol/m^3, respectively; impeller rotational speed was varied over the range 5 to 10 rev/s. They found that the specific interfacial area at constant N increased with increasing solute concentration and that the effect of solute concentration became more pronounced as the impeller rotational speed was increased. At the same solute concentration, solutions of sodium sulfate had greater values of a than did solutions of sodium chloride subjected to identical agitation-aeration conditions. The interfacial areas for the electrolyte solutions varied from 20 to 550 m^{-1} over the range of solute concentrations investigated. Interfacial areas in water were only about 20 to 50 m^{-1}, agreeing in magnitude with the results of Calderbank (1958) in water or nonelectrolyte solutions. The up to ten-fold increase in interfacial area in the electrolyte solutions was shown by Lee and Meyrick to be due to both a decrease in average bubble size and an increase in gas dispersion holdup; in water, d_b ranged from 2 to 9 mm, whereas in 250 mol/m^3 sodium sulfate the range was 0.7 to 1.6 mm.

MASS TRANSFER MODELS

Overall Coefficient (K_La)

K_La for oxygen transfer may be most conveniently evaluated by using an unsteady state process wherein oxygen is desorbed from a batch liquid. We used a membrane-covered dissolved oxygen probe of the galvanometric type (Johnson, Borkowski, and Engblom, 1964) to follow the change of dissolved oxygen tension (the partial pressure of oxygen that would be in physical equilibrium with the liquid phase concentration) during the transient desorption period. Oxygen desorption results from making a step change in sparge gas composition from air to an oxygen-free CO_2-N_2 mixture. In this case and where both the gas dispersion and the liquid can be considered to be well mixed, the transient response of the probe in terms of its external voltage drop E (across a precision resistor in the external circuit as shown on Figure 1) has been shown to be (Robinson and Wilke, 1973)

$$E_t = E_0 \{[\tau^{0.5} \exp(-\beta t)/\sin(\tau^{0.5})] - 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2\pi^2 D_M t/L^2)/[1-(n^2\pi^2/\tau]\} \tag{6}$$

where D_M is the diffusivity of oxygen in the membrane, L is the thickness of the membrane, and E_0 is the initial probe voltage (solution saturated with air). The parameter β is given by

$$\beta = Q_1 H K_La/[Q_1 H + 22.4\ (10^{-3})\ V P_T K_La] \tag{7}$$

and is a constant for a given run (Q_1, H, P_T, V and K_La all constant). Equation (6) incorporates a necessary correction for the diffusional response lag of the membrane through the parameter τ which is defined as

$$\tau = \beta L^2/D_M \tag{8}$$

D_M/L^2 for a particular probe may be evaluated from separate experiments utilizing a step change in dissolved oxygen tension (Aiba, Minoru, and Huang, 1968).

In application of the theory to experimental data, a nonlinear least squares fitting computer program of Beals (1966) was used to determine the best value of β for each run from the experimental data (E_t, t) minimizing the chi-squared function with respect to both the parameters β and D_M/L^2. Once β is evaluated, K_La is obtained from a simple rearrangement of Equation (7).

A more extensive discussion of the development of transient desorption model, Equation (6), its use in computing K_La values, and the correlation of K_La with agitation power, sparge gas superficial velocity and solution ionic strength have been reported elsewhere (Robinson and Wilke, 1973) where it is also shown that the unsteady state model and method yields results which generally are in excellent agreement with those obtained from continuous-flow, steady state runs wherein probe response lag is not a factor.

Specific Interfacial Area (a)

Whenever gas absorption is accompanied by chemical reaction, the presence of the chemical reaction may affect the overall absorption rate capability of the system in several ways, the exact effect being dependent upon the relative magnitudes of the reaction rate and the physical transfer rate capability of the system. Astarita (1967) and Danckwerts and Sharma (1966) have identified several distinct cases. One of these, the fast-reaction regime, has particular utility for measuring a. In this regime, the reaction rate is sufficiently fast such that an appreciable amount of the absorbing gas component is reacted during the lifetime of the liquid surface elements.

The criterion to be met for the absorption-reaction process to occur in the fast-reaction regime is (Danckwerts and Sharma, 1964)

$$(D_L k_2 B_B)^{0.5} \geqq 5\, k_L \tag{9}$$

where B represents the concentration of the nonvolatile liquid-phase reactant. For sparingly soluble gas absorption, B in the liquid surface elements is nearly the same as the concentration in the bulk liquid which in turn can be nearly constant over the gas-liquid contact period. In these circumstances, the bimolecular reaction becomes in effect a pseudo first-order one, that is, k_2B_B = constant $= k_1$.

According to Danckwerts and Sharma (1964) the criterion for such pseudo first-order behavior is

$$(D_L k_2 B_B)^{0.5} \leqq \frac{1}{2} k_L (1 + B_B/ZC^*) \tag{10}$$

Danckwerts (1951) solved the transient diffusion equation with boundary conditions applicable to the random surface renewal model for the case of a pseudo first-order, irreversible reaction in the liquid phase. For carbon dioxide, denoted by subscript 3, the result is

$$R_3^r = a_3 C_3^* \left(k_{L3}^2 + D_{L3} k_2 B_B\right)^{0.5} \tag{11}$$

where a_3 is the specific interfacial area effective for the transfer of carbon dioxide.

Equation (11) forms the basis of the new technique for the simultaneous evaluation of k_L and a. When both the dispersed gas and the liquid phases are well mixed (Hanhart, Kramers, and Westerterp, 1963)

$$C^* = P_T y_2 / H \tag{12}$$

in Equation (11). y_2 is the mole fraction of the reactive component in the exit gas.

Under fast-reaction conditions such that $k_L^2 << D_L\ k_2\ B_B$, Equation (11) shows that the volumetric absorption rate is independent of the liquid-phase coefficient k_L and hydrodynamically depends solely upon the specific interfacial area. This provides a useful tool for separately evaluating the interfacial area for mass transfer but gives no information about k_L under the same hydrodynamic condition and absorbing solution physicochemical properties.

Simultaneous Evaluation of k_L and a

The application of Equation (11) to the simultaneous evaluation of k_L and a under consistent hydrodynamic conditions requires the use of an experimental system in which the absorption with reaction proceeds as a pseudo first-order reaction at a rate which is somewhat less than or equal to that required to meet the fast-reaction criterion. In effect, as may be seen from examination of Equations (9) and (10), this means that there is a restricted range of values of the ratio $k_L/k_2\ D_L\ B_B$ for practical application of the method. The reaction between dissolved carbon dioxide and hydroxyl ion in solutions of strong alkalies has appropriate values of the aforementioned ratio in the temperature range of 15° to 40°C.

The kinetics of the reaction of carbon dioxide in aqueous alkaline solutions has been studied by a number of workers (Himmelblau and Babb, 1958; Sharma and Danckwerts, 1963; Pearson, Pinsent, and Roughton, 1954 and 1956). The temperature dependency of the reaction velocity constant for the reaction between dissolved carbon dioxide and hydroxyl ion has been well established (Pinsent et al., 1956), but its dependency upon the total ionic strength of the aqueous phase and upon the nature of any nonreacting ionic species present has been studied in only a limited number of systems (Sharma and Danckwerts, 1963b; Pinsent et al., 1956).

In aqueous solutions of sodium or potassium hydroxide, whenever $[OH^-] > 10$ mol/m³, the overall reaction is essentially irreversible and may be considered as being

$$CO_2 + 2OH^- \rightarrow CO_3^= + H_2O \tag{13}$$

Experimentally, we transiently desorb oxygen from a batch aqueous solution containing KOH (a small amount of concentrated KOH solution is continuously added on pH control to maintain constant hydroxide concentration, that is, constant k_1) into an oxygen-free, carbon-dioxide-bearing sparge gas. The sparge gas is dilute in carbon dioxide (10% CO_2 to 90% N_2) to avoid the excessive degree of bubble shrinkage that would result from the use of pure CO_2 and to adhere to the assumptions implicit in Equation (6).

The use of Equation (11) to determine a_3 requires separate knowledge of the value of k_{L3}. Concurrent desorption of oxygen, denoted by subscript 4, gives a value of $K_{L4}a_4$ from the computer fitting of Equation (6). Assuming that the penetration or the random surface renewal models describe the process of desorption or absorption over the entire range of bubble sizes, for identical interfacial hydrodynamic conditions, that is, identical rates of surface renewal for both the desorption and the absorption-with-reaction processes, it follows that

$$k_{L3} = k_{L4}(D_{L3}/D_{L4})^{0.5} \tag{14}$$

If we further assume that the effective interfacial area for physical mass transfer of oxygen is the same as that for the absorption-with-reaction of carbon dioxide, then $a_3 = a_4 = a$. In the case of mass transfer with chemical reaction, the effective specific interfacial area a_3 depends not only upon the average bubble size and the liquid-phase hydrodynamics, but also upon the reaction time, that is, the time required for the reaction to proceed to a considerable extent. In the fast-reaction regime, the volumetric absorption rate per unit surface area can be independent of the rate of surface renewal or the age of the surface element; absorption into the surface element may continue until all the liquid-phase reactive component has been completely consumed and the liquid surface element reaches a state of physical equilibrium (saturation) with the gaseous component. Therefore, an as-yet-unrenewed surface element can be effective for mass transfer for a considerably longer period than it would be if there were no reaction within it. Such indeed is known to be the case in packed-tower absorbers where stagnant liquid zones can exist at the ends of packing elements.

Recently, Joosten and Danckwerts (1973) using various column packings found $\kappa > 1.0$, where κ is the ratio of the volumetric coefficients for mass transfer with and without chemical reaction: $\kappa = k_L a^r / k_L a$. Further, they inferred that the ratio of the effective areas for mass transfer a^r/a deviated somewhat more from unity than did κ; however, κ tended towards unity as the liquid rate increased and at the highest liquid rates used, κ was only about 1.3 to 1.4, depending on the type of packing. The applicability of their results to stirred tank gas dispersions is not known, but in highly agitated dispersions the area ratio would likely not exceed and might possibly be less than that found in their packed tower study.

Combining Equations (14) and (11), rearranging, using the sparingly-soluble gas approximation that $k_{L4} \approx K_{L4}$, and solving for the specific interfacial area, we obtain

$$a = \{[(R_3^r/C_3^*)^2 - (K_{L4}a)^2\ (D_{L3}/D_{L4})]/D_{L3}k_2B_B\}^{0.5} \tag{15}$$

The volumetric rate of carbon dioxide absorption-with-reaction R_3^r is obtained from gas-phase analyses.

From the concurrent but separate evaluation of $K_{L4}a$ and a, the liquid phase mass transfer coefficient for oxygen is calculated following Equation (1).

For a given solution of constant initial composition, reproducibility tests of the transient method showed that probable errors in $K_{L4}a$ and a_3 measurements averaged 5.1 and 3.8%, respectively, in the agitation range 11.67 to 23.33 rev/s; these increased to 7.9 and 6.2%, respectively, for agitation rates above 25.0 rev/s.

METHODS AND APPARATUS

Apparatus

A schematic flow diagram of the entire system is given on Figure 1. The apparatus was the same as that used in the prior work concerned with evaluating K_La in nonreactive

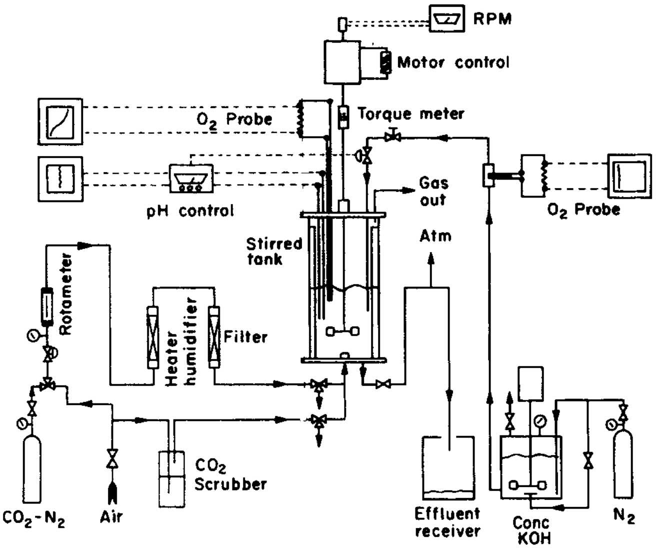

Fig. 1. Schematic flow diagram of apparatus.

systems (Robinson and Wilke, 1973). Complete details are also available elsewhere (Robinson and Wilke, 1971), and therefore only the most pertinent points will be discussed here.

The stirred tank was constructed of 0.1524 m I.D. Pyrex pipe; the clear liquid volume used in all runs was 2.5 (10^{-3}) m^3. The tank was fully baffled and was equipped with a single, 6-blade turbine impeller of 5.08 cm diameter. Standard geometry was used throughout (Aiba et al., 1965).

The temperature of the tank contents was maintained at 30 ± 0.3°C; both the CO$_2$-N$_2$ sparge gas and the concentrated KOH solution used for pH control were preheated to 30°C. The sparge gas was also humidified to near saturation at 30°C and filtered before it entered the inlet gas piping manifold and was admitted to the tank through a 3.17 mm (⅛-in.) diameter bevelled orifice fitting located directly under the impeller axial center line. The head space pressure was local atmospheric in all runs. Air sparged to the tank prior to initiating a desorption run was scrubbed of carbon dioxide.

The pH of the reactor liquid phase was held constant at the initial pH ± 0.02. However, liquid analysis showed that in all runs the concentration of hydroxide ion decreased slowly with time. The insensitivity of the pH electrodes was presumably due to the inherent difficulty in accurately measuring pH's greater than 11 with general-purpose glass electrodes and to the fact that the response of the glass electrode is influenced by large concentrations of other ions in solutions of high alkalinity. The liquid effluent left the reactor from the bottom by gravity flow through a nonsyphoning loop at a rate equal to that of the concentrated KOH addition (thereby holding the liquid volume in the tank constant) and was directed to a collection vessel.

Methods

The volume fraction of gas in the dispersion H_G was determined manometrically from the decrease in differential hydrostatic pressure between two pressure tap points resulting from the gassing of the clear liquid. The pressure differential was measured by a manometer inclined 15° from the horizontal, using hexadecane (S.G. = 0.775) as the manometer fluid. Tests on the apparatus showed that in a nongassed liquid, the manometer differential increased with increasing impeller rotational speed just as it would in a gas-liquid dispersion wherein the gas holdup increases. Therefore, the manometer data was corrected for the effect of these dynamic pressure differences. The dynamic manometer differential in gas-free liquid was measured and correlated with the square of the impeller rotational speed. Aiba (1958) has shown that the fluid tangential velocity at any point in a stirred tank is proportional to the impeller tip speed ND_I. The correction was found to be linear in N^2 from 8.33 to 26.6 rev/s, and ranged from about 6% to 25% of the total manometer displacement for rotational speeds ranging from 8.33 to 35 rev/s. Some previous investigators also measured gas holdup by manometric techniques, for example, Calderbank (1958) and Yoshida and Miura (1963). No mention of a dynamic pressure contribution was made in these works, but it is difficult to see how their manometers were free from this source of interference.

For the relatively small bubbles produced by the fluid shearing forces in the agitated electrolyte solutions, the bubble shape was assumed to be spherical. For such bubbles the average bubble diameter may then be calculated from

$$d_b = 6H_G/a(1 - H_G) \qquad (16)$$

The manometer correction method assumes that the dynamic pressure differential at any given agitation rate is the same in the gas-liquid dispersion as in the gas-free liquid. This assumption introduces an element of uncertainty in holdup values and the bubble average diameters computed therefrom.

Initially, the test solution containing 10 to 100 mol/m^3 potassium hydroxide was sparged with air and was at a fully-oxygenated state, the dilute carbon dioxide-nitrogen mixture (0.10 mole fraction CO$_2$) being vented to atmosphere at the inlet gas manifold. To start the run, the gas streams were switched at the inlet manifold.

Samples of the reactor liquid and vapor-space gas (the latter from 1 in. above the surface of the dispersion) were taken at suitable intervals for analysis; at least three sets of such samples were taken per run. The carbon dioxide content of the gaseous streams was determined chromatographically using a 80/100 mesh "Poropak Q" column with thermal conductivity detection. The hydroxide and carbonate concentrations of the liquid phase were determined by titration with standard HCl to endpoints of 8.30 and 3.70 pH using a pH meter. Duplicate titrations were done on each sample, the average result being used in the subsequent calculations. The titrations were corrected where necessary for blank titrations made on the hydroxide and carbonate-free solutions.

Oxygen and carbon dioxide solubilities for the electrolyte solutions were calculated from their solubilities in pure water at 30°C (*Handbook of Chemistry and Physics*, 1962), using the method of van Krevelen and Hoftijzer (1948). For the mixed electrolyte solutions, the method was modified incorporating the mixing rule suggested by Danckwerts and Sharma (1966).

The aqueous phase dissolved gas diffusivities were estimated from the data of Ratcliff and Holdcroft (1963) for carbon dioxide and the Wilke-Chang correlation (1955). For oxygen, the reference diffusivity was taken as 2.41 (10^{-9}) m^2/s at 25°C (Vivian and King, 1964).

The second-order reaction velocity constant for the reaction described by Equation (13) is dependent upon the species of hydroxyl base, the species of nonreactive electrolyte(s) present, and upon the solution ionic strength Γ_T effects which have not been fully evaluated to date. A reasonable estimate of the value of k_2 can be obtained by interpolation of the data of Pinsent et al. (1956) and Nijsing, Hendriksz, and Kramers (1959), such that for the solutions used in this work

$$k_2 = 12.4\,(10^3)\exp(0.392\,\Gamma_T) \qquad (17)$$

For the highest ionic strength solution examined, having an average Γ_T of 0.418 mol/liter, Equation (17) shows that k_2 has a value 17.8% greater than at infinite dilution.

The rate of admission of concentrated KOH on pH control was not sufficient to achieve carbonate ion reaction product steady state. Carbonate concentration increased slowly with time, but this did not significantly affect Γ_T during the transient oxygen desorption period, as this comprised only the first 10 to 20% of the total run time. The continuous decrease in hydroxide ion concentration mentioned previously, however, did result in a slight increase in the exit gas carbon dioxide content, amounting to about a 10% increase. As neither the

TABLE 1. INTERFACIAL AREA, LIQUID-PHASE OXYGEN MASS TRANSFER COEFFICIENT, GAS HOLDUP, AND AVERAGE BUBBLE DIAMETER IN KOH — K_2CO_3

		Concentrations							
N rev/s	P/V W/m^3	OH^- mol/m^3 $\times 10^{-3}$	$CO_3^=$ mol/m^3 $\times 10^{-3}$	Γ_T mol/m^3 $\times 10^{-3}$	Exit gas CO_2 $y_{3,2}$	Specific area a, m^{-1}	k_{L4} m/s $\times 10^2$	Gas holdup, H_G	Bubble avg. diam, d_b m $\times 10^2$
13.33	780	0.0827	0.0057	0.0998	0.02230	118	0.0443	0.0453	0.231
15.00	1,030	0.0862	0.0063	0.1051	0.00988	310	0.0271	0.0573	0.111
16.67	1,355	0.0758	0.0071	0.0971	0.00586	523	0.0180	0.0693	0.0796
18.33	1,920	0.0828	0.0036	0.0936	0.00472	607	0.0148	0.0800	0.0791
20.00	2,480	0.0798	0.0061	0.0981	0.00399	834	0.0200	0.0990	0.0690
21.67	3,260	0.0650	0.0091	0.0923	0.00350	1,050	0.0156	0.107	0.0609
23.33	4,240	0.0830	0.0042	0.0956	0.00250	1,650	0.0105	0.116	0.0422
26.67	6,740	0.0189	0.0241	0.0912	0.00439	1,900	0.0133	0.140	0.0441
28.33	7,930	0.0136	0.0267	0.0937	0.00478	1,680	0.0150	0.144	0.0514
33.33	12,630	0.0211	0.0257	0.0982	0.00219	3,210	0.0098	0.181	0.0340
			Avg.	0.0965					

TABLE 2. CONCURRENT OXYGEN DESORPTION, CARBON DIOXIDE ABSORPTION-WITH-REACTION: COMPARISON OF STEADY STATE AND UNSTEADY STATE/PSEUDO STEADY STATE METHODS WITH KOH — K_2CO_3

N rev/s	$K_{L4}a$ (s^{-1}) (a)	$K_{L4}a$ (s^{-1}) (b)	a (m^{-1}) (a)	a (m^{-1}) (b)	k_{L4} (m/s $\times$ 10^2) (a)	k_{L4} (m/s $\times$ 10^2) (b)
15.00	0.0717	0.0820	314	310	0.0228	0.0271
16.67	0.0907	0.0944	475	523	0.0191	0.0180
21.67	0.167	0.164	1,160	1,050	0.0144	0.0156
26.67	0.248	0.253	1,810	1,900	0.0137	0.0133

(a) Continuous flow steady state method.
(b) Unsteady state O_2 desorption, pseudo steady state CO_2 absorption-with-reaction.

gaseous or the liquid phase concentration were truely invariant, the mode of operation is denoted as pseudo steady state. Area values reported for each run are averages of the computed point values which varied slightly with time due to the variations in y_2, k_2 and H_3.

Range of Investigation

The operating parameters were varied over the following ranges: impeller rotational speed, 6.67 to 35 rev/sec; power input to the dispersion per unit volume of clear liquid, 320 to 13,800 W/m^3. Sparge gas rate was 8.33 (10^{-5}) m^3/s giving a superficial velocity of 4.57 mm/s in all runs.

RESULTS AND DISCUSSION

The method was first tested experimentally in dilute solutions (average $\Gamma_T = 0.0965$ mol/liter) of potassium hydroxide and potassium carbonate, the latter being produced by the reaction with carbon dioxide. Measured values of a and H_G and the calculated values of k_{L4} and d_b are given in Table 1. 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 per unit volume. There is definite trend of decreasing k_{L4} with increasing P/V in the electrolyte solution. The decrease in k_{L4} with increasing P/V accompanies a decrease in average bubble diameter from 2.3 to 0.34 mm as shown in Table 1.

At 2,600 W/m^3, the specific interfacial area in the KOH-K_2CO_3 solution is about 900 m^{-1}, about an order of magnitude greater than previous results at the same P/V in water (Calderbank, 1958) or under conditions of relatively low agitation rate (Yoshida and Miura, 1963). At the maximum agitation rate of 33.33 rev/s, a was 3210 m^{-1}. The substantial increase in a which was found in this and in the other electrolyte solutions is in general agreement with the observations of Lee and Meyrick (1970) and Reith (1968).

A few continuous-flow steady state runs were made with KOH-K_2CO_3 solutions of average Γ_T equal to 0.0886 in order to evaluate $K_{L4}a$, a, and k_{L4} in steady state. The results are compared to those obtained from transient oxygen desorption with pseudo steady state carbon dioxide absorption-with-reaction runs in 0.0965 Γ_T (average) KOH-K_2CO_3 at the same agitation rates in Table 2. Generally good agreement was obtained, confirming the validity of the transient method.

In a separate series of continuous-flow, steady state experiments, the dependency of $K_{L4}a$ upon agitation and aeration conditions was determined for an air-sparged KCl solution of concentration 220 mol/m^3. The results (Robinson and Wilke, 1973) showed that for this specific system

$$K_{L4}a = 3.89\ (10^{-3})\ (P/V)^{0.74}\ (v_S)^{0.36} \qquad (18)$$

over the entire agitation range $160 \leqq P/V \leqq 12{,}600$ W/m^3.

KCl solutions are, of course, essentially nonreactive to carbon dioxide. Therefore, in order to be able to determine the k_{L4} behavior in this type of solution, a reactive (with respect to carbon dioxide) analog solution was prepared by reducing the concentration of KCl to 135 mol/m^3 and adjusting the initial KOH and K_2CO_3 concentrations such that, on the average, the initial ionic strength of the reactive solution was 0.221 mol/liter as compared to 0.22 mol/liter for the unreactive KCl. This consistency of ionic strength ensured that $K_{L4}a$ differences between the nonreactive and the reactive (with carbon dioxide) KCl solutions would be slight; significantly different $K_{L4}a$ dependencies upon P/V can result from small changes in the ionic strength in the vicinity of 0.22 mol/liter (Robinson and Wilke, 1973). $K_{L4}a$ values determined from the transient desorption model, Equation (6), with concurrent measured values of a and k_{L4} are given on Figure 2. Values of H_G and d_b are shown on Figure 3.

The transiently-determined $K_{L4}a$ correlation with P/V (solid line) shown on Figure 2 for the reactive solution is in close agreement with the $K_{L4}a$ correlation Equation (18) for 220 mol/m^3 KCl determined from steady state experiments and given as the dashed line on Figure 2. The transiently-determined values are somewhat greater at the low end of the power range and slightly lower at the high end. The close agreement between the two sys-

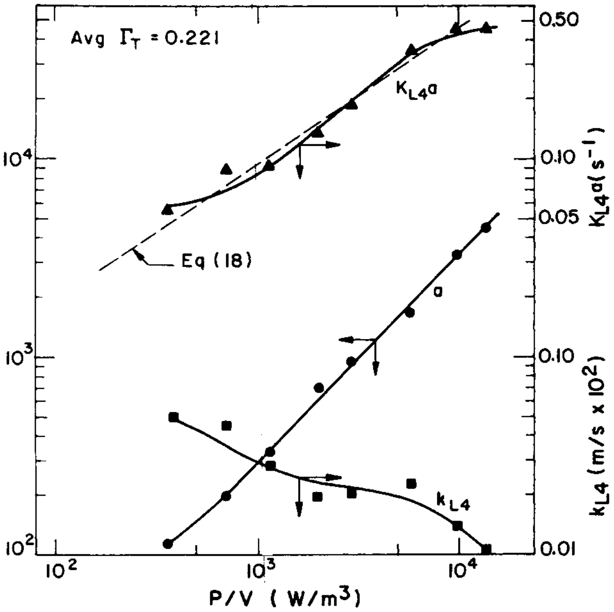

Fig. 2. Oxygen mass transfer coefficients and specific interfacial area in KCl (135 mol/m³) + KOH − K_2CO_3 solution.

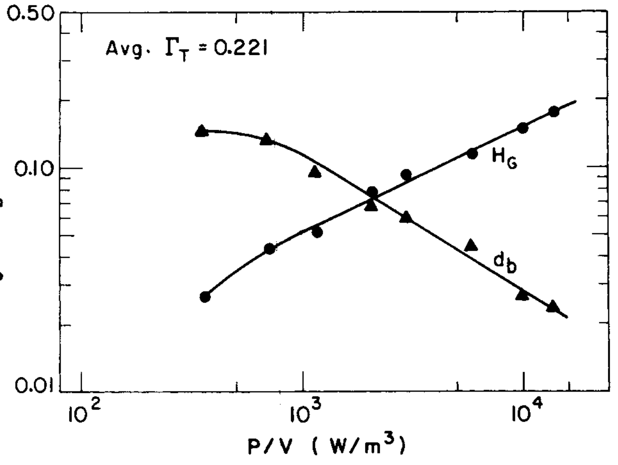

Fig. 3. Gas fractional holdup, and average bubble diameter in KCl (135 mol/m³) + KOH − K_2CO_3 solution.

tems suggests that the addition of a relatively small concentration of KOH and K_2CO_3 to achieve carbon dioxide reaction in an otherwise nonreactive solution has an insignificant effect on the oxygen mass transfer capability, as long as the total ionic strength is unchanged.

The individual k_{L4} points shown on Figure 2 were calculated from the corresponding paired values of $K_{L4}a$ and a using Equation (1). The line representing the overall behavior of k_{L4} was computed from the least-squares fitted lines for $K_{L4}a$ and a. Here, too, it is evident that k_{L4} decreases with increasing P/V. The rate of decrease in k_{L4} does not appear to be uniform over the entire power range investigated; the k_{L4} data points on Figure 2 suggest that there may be a plateau-like region in the range $2000 \leqq P/V \leqq 6400$ over which k_{L4} is independent of P/V. Again, values of a obtained in this solution are considerably greater than those previously reported for nonelectrolytes in stirred tanks.

The average bubble diameter decreases concurrently with k_{L4} as shown on Figure 3, going from 1.42 to 0.23 mm. Individual data points and the correlating line representing the overall behavior of d_b were located by a similar procedure to that discussed in reference to Figure 2.

Finally, we studied the mass transfer characteristics of Na_2SO_4 (110 mol/m³)-KOH-K_2CO_3 solutions of average Γ_T of 0.418 mol/liter. This solution is a carbon dioxide reaction analog of a solution of Na_2SO_4 (125 mol/m³)-$CuSO_4$ (4 mol/m³) of $\Gamma_T = 0.391$, the $K_{L4}a$ behavior of which previously had been investigated by both steady state and unsteady state methods (Robinson and Wilke, 1973).

$K_{L4}a$ values obtained in the CO_2-reactive and the unreactive Na_2SO_4 solutions were in close agreement, again suggesting that the presence of small concentrations of alkaline species has a negligible effect on the overall transfer characteristics as long as Γ_T is held constant. Results for k_{L4}, a, H_G, and d_b obtained by the concurrent desorption-absorption with reaction method are given in Table 3. k_{L4} remains nearly constant as P/V increases from 330 to 1150 W/m³, and then markedly decreases with increasing P/V in an apparently uniform manner as does d_b. The specific interfacial area in Na_2SO_4 + KOH − K_2CO_3 (average $\Gamma_T = 0.418$), is about 10% greater than that in KCl + KOH − K_2CO_3 (average $\Gamma_T = 0.221$).

k_L-d_b Relationship

The average gas bubble diameters in the three electrolyte solutions studied range from 2.3 to 0.24 mm as the power input was increased from 715 to 12,700 W/m³. This size range is in general agreement with the results of Lee and Meyrick (1970) in a stirred tank containing electrolyte solutions. The bubble average diameter found here is considerably smaller (about one-fifth to one-tenth) than that for bubbles mechanically dispersed in water or organic liquids (Calderbank, 1958, Lee and Meyrick, 1970), the size difference becoming more pronounced as P/V is increased. On the other hand, over the agitation range studied, H_G in the electrolyte solutions used ranged from 0.024 to 0.181 compared to 0.021 to 0.0853 for water. The fact that the bubble size decreases more than the holdup is increased with increasing ionic strength results in a being significantly greater in electrolyte solutions than in water at the same P/V and v_S, as shown by Equation (16).

The decrease in d_b (with concomitant increase in a) most likely is the result of a reduction in bubble coalescence rates caused by the presence of ionic solutes. Similar behavior has been found in bubble columns (Marrucci and Nicodemo, 1967; Zieminski and Whittemore, 1971; Lessard and Zieminski, 1971). In pure liquids having interfacial surface tensions less than that of water, or in

TABLE 3. INTERFACIAL AREA, LIQUID-PHASE OXYGEN MASS TRANSFER COEFFICIENT, GAS HOLDUP AND AVERAGE BUBBLE DIAMETER IN Na_2SO_4 + KOH − K_2CO_3 (AVG. $\Gamma_T = 0.418$)

N rev/s	P/V W/m³	Specific area (a), m⁻¹	k_{L4} m/s × 10²	Gas holdup, H_G	Bubble avg. diam., (d_b) m × 10²
11.67	331	138	0.0259	0.0240	0.104
15.00	875	185	0.0483	0.0427	0.138
16.67	1,135	304	0.0318	0.0534	0.105
20.00	2,160	749	0.0212	0.0853	0.0684
21.67	2,690	891	0.0183	0.0906	0.0611
23 33	3,470	1,310	0.0164	0.104	0.0476
25.00	4,120	2,150	0.0119	0.112	0.0313
28.33	6,120	2,080	0.0126	0.128	0.0369
31.67	8,075	2,740	0.0138	0.147	0.0322
35.00	10,840	3,750	0.0101	0.171	0.0274

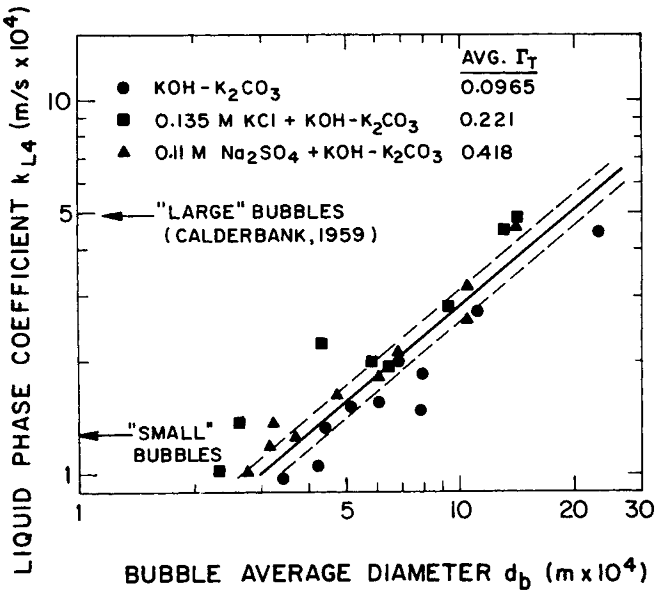

Fig. 4. Effect of bubble average diameter on liquid-phase mass transfer coefficient.

viscous aqueous solutions (for example, glycerol-water mixtures) values of a are significantly greater than the specific area obtained in pure water under otherwise identical conditions. In these cases, the increase in a can be correlated directly with the differences in interfacial tension and/or density and viscosity (Calderbank and Moo-Young, 1961). In relatively dilute aqueous solutions of electrolytes such as those used in this present work, the interfacial tensions, and solution viscosities and densities do not vary appreciably from their values in pure water, and the large increase in specific interfacial area cannot, therefore, be attributed to these factors to any significant degree.

As shown on Figure 4, k_{L4} decreases uniformly with decreasing d_b from 2.31 to 0.231 mm. Such behavior has not been previously reported for bubble dispersions in mechanically-agitated electrolyte solutions but is consistent with prior results for bubbles of the same general size range for dispersions and for single bubbles in viscous, Newtonian, nonelectrolytic aqueous solutions (Calderbank and Moo-Young, 1961). The results of the present study of k_{L4} behavior in nonviscous aqueous solutions of electrolytes are in general agreement with the work of Calderbank and Moo-Young in the same average bubble size range characteristic of the transitional regime. However, in Calderbank and Moo-Young's systems, k_L was proportional to $(d_b)^{1.04}$ in the transitional regime, whereas our results indicated that k_L is proportional to $(d_b)^{0.813}$ for relatively nonviscous, electrolyte solutions.

The results of this and previous studies strongly suggest that the decrease in k_{L4} over the range $2.5 \geqq d_b \geqq 0.2$mm is due solely to the change in bubble-liquid interfacial motion characteristics; the interfacial relative motion and the subsequent mass transfer behavior is dependent on the bubble size for the most part, there being, perhaps, only a relatively minor effect due to the nature of the solution (for example, viscosity) in which the bubble is produced. In electrolyte solutions, the average bubble size is significantly affected by ionic strength.

Values of k_L for other sparingly soluble gases may be calculated from the reported k_{L4} values allowing for diffusivity differences according to Equation (14).

Unlike pure liquids or solutions of nonelectrolytes where a was found to have a common dependency upon P/V as shown by Equation (4) (Calderbank, 1958), we found that for solutions of electrolytes the dependency of a upon P/V increased somewhat with increasing ionic strength. For KOH-K_2CO_3 (avg. $\Gamma_T = 0.0965$), a varied as $(P/V)^{0.89}$; in KCl-KOH-K_2CO_3 (avg. $\Gamma_T = 0.221$), a was proportional to $(P/V)^{1.06}$ and for Na_2SO_4-KOH-K_2CO_3 (avg. $\Gamma_T = 0.418$), a was dependent upon $(P/V)^{1.01}$ over most of the agitation range. Similar behavior has also been found for correlation of K_La with P/V in electrolyte solutions (Robinson and Wilke, 1973).

Effect of Varying Ionic Strength on Results

The concurrent oxygen desorption, carbon dioxide chemical absorption technique as applied here results in a pseudo steady state process wherein the carbonate ion concentration and hence the ionic strength increases with time. The percentage increase in Γ_T during a particular run depends upon the rate of carbon dioxide absorption-with-reaction, the rate of addition of concentrated KOH for pH control (which depends on the molarity of this feed stream), and upon the ionic strength contribution of any non-reactive salts present. The increase in Γ_T is greatest in the KOH − K_2CO_3 solution as these two components are the only electrolytes present which contribute ionic strength. On the other hand, in the Na_2SO_4 + KOH − K_2CO_3 solutions, the greatest contribution to Γ_T comes from the sodium sulfate, and the conversion of hydroxide to carbonate has much less effect on the time variance in ionic strength.

The increase in carbonate ion concentration during a run is most pronounced in the initial time portion. In practice, oxygen desorption data for the evaluation of $K_{L4}a$ were taken over a 50- to 90-second time period following the step change in inlet gas composition, the actual time interval depending upon the rate of oxygen desorption. Carbon dioxide absorption-with-reaction instantaneous point data for the evaluation of a were taken after an elapsed run time of 3 to 6 min., the actual sampling time interval varying with the rate of carbon dioxide chemical absorption, smaller time intervals being used at the higher agitation rates.

Because of the transient increase in ionic strength, the physicochemical properties of the aqueous phase at the time of $K_{L4}a$ measurement and at the time of measuring a were not strictly identical. As a, in general, increases with increasing ionic strength, the values of k_{L4} computed from Equation (1) which assumes time constancy of a, are, therefore, possibly somewhat low. In the case of the KOH-K_2CO_3 solution, the maximum increase in Γ_T during a run period was about 30%, whereas in the Na_2SO_4-KOH-K_2CO_3 solution the maximum increase in Γ_T was 15%. Comparing values of a for constant P/V in solutions of different ionic strengths over the range examined, it is considered that the time variation during a run results in an error in the value of k_{L4} computed from Equation (1) amounting to less than 5% over the entire agitation range.

In applying our new concurrent oxygen desorption, carbon dioxide absorption-with-reaction technique for the simultaneous evaluation of k_{L4} and a, it is implicitly assumed that the gas-phase mass transfer resistance is negligible, that the temperature rise at the interface (resulting from the heats of absorption and reaction of carbon dioxide) is insignificant such that interfacial physical properties may be evaluated at the bulk solution temperature, and that surface aeration (reinclusion of head space gas into the dispersion) is negligible. All the foregoing assumptions were found to be valid for the systems tested (Robinson and Wilke, 1971).

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NOTATION

a = gas-liquid interfacial area per unit liquid volume, m^{-1}
A_0, A_1, A_2 = proportionality constants
B = concentration of liquid-phase nonvolatile reactant, mol/m^3
C = concentration of dissolved gas, mol/m^3
d_b = gas bubble average diameter ($\sum_i n_i d_i^3/\sum_i n_i d_i^2$), m or mm
D_I = impeller diameter, m
D_L = diffusivity in liquid phase, m^2/s
D_M = effective diffusivity of oxygen in probe membrane, m^2/s
E = potential difference across external resistor in oxygen probe circuit, volt
g = gravitational acceleration, m/s^2
H = Henry's law coefficient, $N \cdot m/mol$
H_G = fractional gas holdup, volume of dispersed gas per volume of gas-liquid dispersion, dimensionless
k_1 = pseudo first-order reaction velocity constant, s^{-1}
k_2 = second-order reaction velocity constant, $m^3/mol \cdot s$
k_L = liquid-phase mass transfer coefficient in nonreactive system, m/s
K_L = overall mass transfer coefficient based on liquid-phase concentration difference driving force for absorption without reaction, m/s
K_La = overall volumetric mass transfer coefficient based on liquid-phase concentration difference driving force for absorption without reaction, s^{-1}
L = thickness of oxygen probe membrane, m
n = interger in a mathematical series, dimensionless
N = impeller rotational speed, rev/s
N_{Gr} = Grashof number, $d_b^3 \rho_L \Delta\rho g/\mu_L^2$, dimensionless
N_{Sc} = Schmidt number, $\mu_L/\rho_L D_L$, dimensionless
N_{Sh} = Sherwood number, $k_L\, d_b/D_L$, dimensionless
P = agitation power input to gassed liquid, W/m^3
P_T = total pressure in absorber-reactor vapour space, N/m^2
Q = volumetric gas flow rate (0°C, 1.013 (10^5) N/m^2), m^3/s
R = liquid-phase absorption rate of gaseous component, $mol/m^3 \cdot s$
t = time, s
v_S = gas superficial velocity based on empty tank cross-sectional area, m/s
v_t = terminal velocity of bubble rise, m/s
V = volume of gas-free liquid, m^3
y = mole fraction of component in gas phase, dimensionless
z = electric charge carried by ionic species
Z = reaction stoichiometric coefficient, dimensionless

Greek Letters

β = aeration-agitation parameter defined by Equation (7), s^{-1}
Γ = ionic strength, $\Gamma = \frac{1}{2} \sum_j Z_j^2 C_j$, mol/liter
μ = viscosity, $N \cdot s/m^2$
ρ = density, kg/m^3
σ = interfacial surface tension, kg/s^2
τ = rate ratio parameter defined by Equation (8), dimensionless

Subscripts

0 = initial condition
1 = inlet stream
2 = exit stream
3 = carbon dioxide species
4 = oxygen species
B = bulk phase; cup-mixed property
c = continuous phase property
j = ionic species
t = unsteady state condition

Superscripts

r = property determined in and affected by a chemically-reacting system
$*$ = hypothetical gas-phase property in physical equilibrium with bulk liquid-phase property, or viceversa

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Comparison of Parametric Pumping with Conventional Adsorption

A continuous thermal parametric pumping system is compared to a conventional adsorption system with thermal regeneration. Well-defined mathematical models are used to find the operating conditions which maximize the separation and throughput of each system.

Under practical operating conditions, the model equations indicate parametric pumping can process a larger volume feed stream at equivalent separations than conventional adsorption for the solute/adsorbent system studied. At equilibrium conditions equivalent results are obtained but parametric pumping requires more energy.

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SCOPE

Parametric pumping is a periodic separation technique which represents an alternative to conventional adsorption processes. This concept requires a solute/adsorbent system in which some controllable thermodynamic variable affects the solute equilibrium distribution between the fluid and solid phases. Significant separations were reported using a periodic temperature change coupled with a periodic flow in a packed bed of adsorbent (Wilhelm et al., 1968). A quantitative comparison of a parametric pumping process and a conventional adsorption process for a specific solute/adsorbent equilibria is presented here.

Model equations for the two processes are used which assume realistic, finite mass transfer between the fluid and solid phases. The optimum operating conditions for the two processes are determined using a numerical solution of the model equations. The maximum separations and throughputs for each process are compared under the assumption that the physical equipment is the same in both cases.