

OXYGEN TRANSFER IN AERATED SYSTEMS
CONTAINING ONE AND TWO LIQUID PHASES

by

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INTRODUCTION

Microorganisms can be effectively used to produce pharmaceuticals, chemicals, and single cell protein, or to oxidize municipal and industrial wastes. In every case, biological reactors are part of the process used to obtain the products or treat the waste. The biological oxidation is often carried out aerobically and substantial quantities of oxygen need to be supplied to the organisms. These reaction systems contain several phases, and oxygen must be transported from a gas phase to the organisms which are dispersed in an aqueous phase. Optimal process design cannot be accomplished without having some knowledge about the mechanisms and pathways of oxygen transport within the multiphase system. Information about relative oxygen transfer rates and efficiencies that can be achieved with various types of equipment is equally important in the design process. Vessels that can be used include mechanically stirred tanks, towers with or without recirculation, and large outdoor ponds. Air or oxygen is pumped into the vessels and diffused by sparging devices, mechanical mixing, static mixers, or any combination of such equipment.

In this thesis, models that describe oxygen transport in biological oxidation systems have been developed from a macroscopic equation of change for multiphase systems. One model has been used to study oxygen transport in hydrocarbon fermentations in an effort to determine the relative importance of possible transfer pathways. The effects of extracellular products, microorganisms, and a second liquid phase on oxygen transfer have been investigated. Another model is presented to describe oxygen transport phenomena in towers in which

concentration gradients exist. Oxygen transfer coefficients were found for an oxygen-water system in a tower containing static mixers and operated at gas flow rates suitable for wastewater treatment. Both the models and the experimental results can be useful to engineers designing similar biological reaction processes. It is hoped that the work presented in this report will encourage the use of rigorously derived macroscopic equations of change for modeling mass transport in multiphase systems.

The thesis is divided into three chapters. References and figures have been placed at the end of each chapter. The first chapter contains a review of work reported in the literature that deals with oxygen transfer in systems containing two liquid phases. Mass transfer in general is also briefly discussed. In Chapter Two, the model simulations and experimental results for systems containing two liquid phases are presented, and Chapter Three contains the modeling and experimental results for tower systems containing one liquid phase.

CHAPTER ONE

OXYGEN TRANSFER IN AERATED SYSTEMS CONTAINING TWO LIQUID PHASES - A REVIEW

INTRODUCTION

The recent interest in the production of single cell protein by growing microorganisms on various water-insoluble hydrocarbon substrates has resulted in several investigations of the nature of oxygen transfer in aerated systems with two liquid phases. The presence of a non-aqueous liquid phase may have a significant effect on the rate of oxygen transfer from the gas phase to the organisms. In the design of an industrial hydrocarbon fermentation process, this effect needs to be considered quantitatively in order to achieve optimal operating conditions and to determine the most economical reactor type. In as much as an important part of the production cost of single cell protein by hydrocarbon fermentation is the cost of supplying the organisms with oxygen⁽¹⁾, a small improvement in oxygen transfer efficiency may significantly reduce the production cost. A discussion of mass transport in multiphase systems follows, and then investigations that deal with oxygen transfer in systems with two liquid phases are reviewed.

MASS TRANSPORT IN MULTIPHASE SYSTEMS

In a hydrocarbon fermentation reactor, four phases are present: gas (usually air), a liquid hydrocarbon, an aqueous solution, and microorganisms. Oxygen may be transported from the gas directly to any of the other phases, and transport may also occur between the liquid phases or between cells and either liquid. Thus, the addition of a second liquid phase to the three phases that normally constitute a fermentation system doubles the number of interfaces across which mass may be transferred. This is pictorially shown in Figure 1. Modeling the oxygen transport in a four phase system is considerably more complex than in a three phase system.

Whitaker has derived macroscopic equations of change for multiphase

systems, and has demonstrated the application to mass transfer in a tower system⁽²⁾. Using the modification suggested by Gray⁽³⁾, the mass balance for a multiphase system is:

$$\frac{\partial C}{\partial t} + v \cdot \nabla C = \nabla \cdot (D \cdot \nabla C) + \sum_i K_{i1} a_i (C_i^1 - C) + P + \sigma \quad (1)$$

where C , v , D , K_a , P and σ are the time averaged values of the volume averaged instantaneous quantities. The assumptions made in the derivation of equation (1) are that no phase changes occur; the fluid is incompressible; the time averaged, volume averaged, volume fraction of the given phase is time independent; and the species of interest forms a dilute solution. These assumptions are valid for fermentation systems where oxygen is the species, except for the gas phase in tall tanks or towers, where compression is significant. For a well mixed system, the concentration gradients are zero, and Equation (1) reduces to

$$\frac{\partial C}{\partial t} = \sum_i K_{i1} a_i (C_i^1 - C) + P + \sigma \quad (2)$$

In a fermentation system, the oxygen usage rate of the cells may be limited by the rate of biological reaction, oxygen transport across the cell membrane, or oxygen transport to the cell surface. Several investigators have found that the oxygen uptake rate of cells in hydrocarbon fermentations is not limited by oxygen transport to the cell surface for oxygen concentrations ranging from 7% to 17% of the air saturated value^(4,20). It is generally desirable to operate a fermentor with the dissolved oxygen concentration at the minimum value which will allow the maximum rate of biological reaction to be achieved. When the oxygen transfer resistance to the cell is negligible, the cell can be treated as a reacting species. The production term P is then replaced by the negative value of the volumetric oxygen uptake rate of the cells. The

source term σ arises when the macroscopic equation is time averaged. No method has been presented for handling this term, and it shall be neglected. Equation (2) now becomes

$$\frac{\partial C}{\partial t} = \sum_i K_i a_i (C_i^i - C) - QX \quad (3)$$

Most investigators have chosen to treat systems with two liquid phases as if there was only one liquid phase by assuming oxygen equilibrium between the liquids or by neglecting mass transfer to the dispersed phase. Mimura et al. found that when the hydrocarbon volume fraction of the liquid phase is 2% or less, the liquid mixture can be treated as one phase⁽⁵⁾. The dispersed liquid phase can influence oxygen transfer by absorbing oxygen or supplying it to other phases, or by influencing the fluid mechanics of the continuous phase, thereby influencing the mass transfer coefficients and interfacial areas of the continuous phase. Suspended solid particles have been found to both increase and decrease the oxygen transfer rate when compared with rates in gas-liquid systems without the particles^(6,7,8,12). Thus for a hydrocarbon volume fraction of 1% the effect on the aqueous phase fluid movement may be significant. In all work reviewed in the following paragraphs the liquid mixture is treated as one phase, with the exception of the investigations of Matsumura and coworkers⁽⁹⁾.

It may be useful at this point to consider the significance of the mass transfer coefficient K and the interfacial area term a in more detail. Investigators have not been uniform in their definitions of either term and one must be careful in comparing values of Ka . The diffusion flux of a species across the interface between two phases is specified by Whitaker⁽²⁾ and Gray⁽³⁾ as

$$N = \epsilon K (C_i^i - C) \quad (4)$$

where ϵ and C refer to the same phase and K has units of

$$\frac{\text{total system volume}}{\text{interfacial area} \cdot \text{time}}$$

Other authors^(10,21,22) have described the species diffusion flux by

$$N = K'(C^i - C) \quad (5)$$

where K' has units of

$$\frac{\text{referenced phase volume}}{\text{interfacial area} \cdot \text{time}}$$

Equations (4) and (5) are based on the assumption that the diffusion rate is proportional to the driving force $(C^i - C)$. The value of K or K' depends on which phase concentration is referenced. The total interfacial area between two phases is expressed by $A = Va$ where a is the interfacial area per unit volume of some phase or mixture; V is the volume of that phase or mixture. If we define a as interfacial area per unit of total system volume and a' as interfacial area per unit of referenced phase volume, then

$$Ka = K'a'$$

Equation (1) was derived using the definitions for K and a given above. Most investigators, however, use a volumetric mass transfer coefficient defined as $K'a'$ is above. In the work reviewed in the following paragraphs, the definitions of K and a vary, but they are compared as dimensionless ratios. A review of methods used to determine volumetric oxygen transfer coefficient values has been presented by Liu⁽⁸⁾.

EFFECT OF HYDROCARBON PHASE ON OXYGEN TRANSPORT IN AIR-WATER-HYDROCARBON SYSTEMS

Mimura and coworkers studied oxygen transfer in closed shaking flasks containing air, sodium sulfite solution, and kerosene by following the change in the gas phase oxygen partial pressure⁽¹¹⁾. They found that

K_a/H increased exponentially with the volume fraction of kerosene, when the total volume of the liquid mixture was held constant, for $0 \leq \phi \leq 0.85$. They considered H to be an average of the Henry's law constants for the aqueous solution and kerosene. When the value of H was calculated as $H = (1-\phi)H_w + \phi H_h$ they found that K_a decreased and then increased, suggesting that the presence of hydrocarbon does affect the volumetric oxygen transfer coefficient as they defined it. These results are compared with the results of others in Figure 2.

Yoshida and coworkers determined values of K_a in both an agitated vessel and in a bubble column for aqueous dispersions of kerosene, a liquid paraffin, toluene, oleic acid, and powdered polyvinylchloride⁽¹²⁾. The bubble column was operated continuously. The oxygen concentration in the feed and exit streams were measured to find the oxygen uptake rate of each liquid mixture. They assumed the oil and water phases were always in equilibrium so that the liquid mixture could be treated as a single phase. Yamane et al. further discussed the validity of this assumption, showing that indeed small oil droplets will very rapidly come into oxygen equilibrium when placed in an aqueous liquid⁽¹³⁾. The dynamic method for determining K_a ⁽⁸⁾, which involves recording the oxygen concentration in the liquid following a step change in the gas phase oxygen concentration, was used in batchwise experiments for the PVC-in-water system. They found that K_a decreased with increasing oil fraction for the kerosene, paraffin and PVC powder dispersions, but that K_a decreased slightly, then increased with increasing oil fraction for the toluene and oleic acid dispersions (see Figure 2).

Yoshida et al. pointed out that the spreading coefficient, $S = \gamma_{wg} - (\gamma_{hg} + \gamma_{wh})$, is negative for the kerosene and paraffin-water mixtures, but positive for the toluene and oleic acid-water mixtures. They suggested that when the spreading coefficient is positive, the dispersed phase may act like

a surface active agent, and increase the interfacial area while decreasing K . At low oil fractions, the effect on K may dominate. They showed that the surfactant Tween 85 has an effect on oxygen transfer similar to that of toluene and oleic acid. Gas hold-up values for the toluene and oleic acid systems showed trends similar to the K_a values, indicating that the increase in K_a may have been at least partially due to an increase in interfacial area. Gas hold-up in the kerosene and paraffin-in-water systems varied little with oil fraction, indicating that the decrease in K_a was likely due to a decrease in K . The authors suggested that this apparent decrease in K may have been caused by oil drops partially covering the gas bubble surfaces. The diffusion or convection rate of oxygen through these oil drops would be expected to be slower than through the continuous phase. The PVC powder had a greater effect on K_a than did the oil drops, perhaps due to the inability of oxygen to be transported through the solid or a more pronounced effect on the fluid motion of the continuous phase.

Coty and coworkers used the sodium sulfite oxidation method⁽⁸⁾ to study the oxygen uptake rate of mixtures containing hexadecane and a mineral salts medium in which the oil phase was continuous⁽¹⁴⁾. They found that the oxygen transfer rates from air to mixtures containing 50% and 66% oil in air lift reactors were much larger than to the medium without oil. However, if the solubility of oxygen in the hexadecane is assumed to be six times greater than that in the medium⁽⁹⁾, it is calculated on the basis of a weighted average of these solubilities, and the oxygen concentration in both liquids is assumed to be zero, then K_a values for the pure medium and the 50% oil mixture are about the same, while those for the 66% oil mixture are about twice the K_a values for the pure medium. The results of Mimura et al.⁽¹¹⁾ indicate

that K_a decreases in value with increasing oil fraction until $\phi = 0.40$, then K_a increases as ϕ increases (Figure 2). Coty et al.⁽¹⁴⁾ found that phase inversion may be occurring at $\phi = 0.40$. If so, it appears that an increase in the dispersed phase volume fraction causes a decrease in the volumetric oxygen transfer coefficient to the liquid mixture, regardless of which liquid phase is dispersed.

Mimura and coworkers measured K_a by the dynamic method⁽⁸⁾ for a hydrocarbon fermentation broth in a stirred tank, containing a cell concentration of 3.1 g/l⁽⁵⁾. In the calculation of K_a , they apparently used the Henry's law constant for pure water. K_a increased slightly, then decreased as ϕ was increased from 0 to 0.06 (Figure 2). However, the oil phase may not have been in equilibrium with the aqueous broth during the relatively rapid changes in concentrations which occur in these dynamic experiments. These workers found that their dynamic method was suitable only for $\phi < 0.02$.

In only one investigation has the oxygen transfer between liquid phases been considered. Matsumura and coworkers, with appropriate modeling, determined volumetric oxygen transfer coefficients for transport between gas and water phases and water and hydrocarbon phases in an air-water-hydrocarbon system⁽⁹⁾. They measured the gas phase oxygen partial pressure change in a closed agitated vessel with a draft tube as oxygen was absorbed by the liquid mixture. The hydrocarbon was a mixture of n-paraffins, mainly n-pentadecane. The partial pressure data was then fitted with the solution to the model equations and correlations were developed. They assumed the pathway of oxygen transport was from air to water to oil, and that the oil phase was in equilibrium with the water phase oxygen concentration present at the oil-water interface. They also determined the

oxygen partition coefficient as a function of temperature for the n-paraffin and water mixture. The correlations they obtained are

$$C_w = 3.3 \times 10^{-3} C_h \exp \left(\frac{10^3}{230+T} \right) + 5.0 \times 10^{-6}$$

for $25^\circ\text{C} \leq T \leq 40^\circ\text{C}$, and

$$(K_a)_{wg} = \left[1.75 \times 10^{-2} \exp(0.115\phi) - 0.8 \times 10^{-3} \exp(-46.9\phi) \right] R V_s^{1/3}$$

$$(K_a)_{wh} = \frac{1}{1 + H_{wh} \left(\frac{1}{\phi} - 1 \right)} (K_a)_{wg}$$

Relative values of $(K_a)_{wg}$ found by Matsumura et al. are compared with the results of other authors in Figure 2.

The disagreement between the results of Matsumura et al. and the other investigators may be attributed to the implicit or explicit assumption of the other investigators that the hydrocarbon and aqueous phases were in oxygen equilibrium and that an average Henry's law constant could be used in calculating values of the volumetric oxygen transfer coefficient. The data reported by Matsumura et al. indicates that the increase in $(K_a)_{wg}$ and $(K_a)_{wh}$ as ϕ increased gave a combined effect which would appear as a decrease in K_a if the liquid mixture was treated as one phase. However, Yoshida et al.⁽¹²⁾ and Yamane et al.⁽¹³⁾ presented good evidence that in a continuous operation where the residence time of the contacting device is of the order of several minutes, the liquid phases are indeed in equilibrium. Their results for the PVC dispersion add further evidence that $(K_a)_{wg}$ decreases with increasing oil fraction for non-spreading oils, if

the oil droplets have an effect when in dispersion that is similar to solid particles. Thus, there is room and need for considerably more investigation in the area of oxygen transfer in systems with two liquid phases.

EFFECT OF CELL CONCENTRATION ON OXYGEN TRANSPORT IN HYDROCARBON FERMENTATIONS

In a hydrocarbon fermentation broth, not only are aqueous and oil phases present, but also respiring cells; their presence has a pronounced effect on the oxygen transport phenomena. Several investigators have studied oxygen transport in hydrocarbon fermentations, and have found volumetric oxygen transfer coefficients. Both the dynamic and mass balance methods⁽⁸⁾ were used, giving different results.

Mimura and coworkers used both methods in stirred tank batch cultivations in which the media initially contained 1% n-hexadecane by volume⁽⁵⁾. K_a values found by the dynamic method showed a decrease as the fermentation progressed and cell concentration increased. However, K_a values found by making a gas phase oxygen balance increased slightly as the growth progressed. They calculated that as much as 90% of the oxygen consumption was from a source other than oxygen dissolved in the bulk of the broth. They also found that when the hexadecane had been exhausted in the fermentation, the value of K_a returned to the value found at the beginning of the batch cultivation. This lead the investigators to postulate that as growth increased, cells formed flocs with oil droplets and accumulated at the gas-liquid interface. This decreased the interfacial area available for oxygen transfer to the liquid and as well enabled the cells to take up oxygen directly from the gas or from the surface film. It is well established that during hydrocarbon fermentations cells adsorb to the surface of the oil drops⁽¹⁵⁾ and it appears that the interfacial tension between aqueous and

hydrocarbon phases decreases as fermentation proceeds⁽¹⁶⁾. The decrease in the interfacial tension may cause the spreading coefficient to become positive, allowing the oil to form a film at the gas-liquid interface, as suggested by Yoshida et al.⁽¹²⁾. The surface tension values found by Nakahara during batch fermentation of *Candida lipolytica* on n-hexadecane indicates that the spreading coefficient changes value from negative to positive and reaches a large positive value as growth proceeds⁽¹⁶⁾. The cells would then be attracted to the hydrocarbon film at the interface. The occurrence of this phenomena, however, is not well established.

Prokop and coworkers found results similar to those found by Mimura et al.⁽⁵⁾ for a batch cultivation in a stirred draft tube fermentor with an initial hydrocarbon volume fraction of 5%⁽¹⁷⁾. The oil was a mixture of n-alkanes. They used an oxygen balance on the gas phase to determine the oxygen uptake of the broth and a weighted mean Henry's law constant to determine K_a values with the dynamic method. Hatch and coworkers found that the volumetric oxygen transfer coefficient values were larger for a hydrocarbon fermentation than for a glucose fermentation in a bench scale airlift fermentor, but less in a pilot plant fermentor⁽¹⁸⁾. They indicated the results in the pilot plant may have been misleading because of the addition of antifoam to the hydrocarbon broth necessitated by excess foaming. The fermentors were operated continuously and the hydrocarbon content was 10% of the liquid volume. K_a values were determined by using a mass balance on the gas phase and with the assumption that oxygen equilibrium existed between the liquid phases. Thus there is good evidence that the oxygen uptake rate by the broth in a hydrocarbon fermentation is enhanced by the presence of the oil, and that cells may obtain oxygen directly from the

gas phase or from a surface film. This enhancement effect may be similar to that discussed by Tsao et al. for non-hydrocarbon fermentations⁽¹⁹⁾.

In studying oxygen transport in fermentation systems, the dynamic and the gas phase oxygen balance methods have been used. In fermentations with one liquid phase, both methods should give similar results for values of the volumetric oxygen transfer coefficient. During dynamic experiments in a well mixed system the following relation applies:

$$\frac{dC_w}{dt} = Ka(C_w^g - C_w) - QX \quad (6)$$

Ka reflects the rate at which oxygen dissolves in the liquid. Ka is found with the gas balance method by using the relation

$$\frac{r}{V} = Ka(C_w^g - C_w) \quad (7)$$

where r is the total rate of loss of oxygen from the gas phase. Now if all of the oxygen transported from the gas phase across the gas-liquid interface becomes dissolved in the bulk of the liquid before being consumed, the Ka in Equation (7) is equivalent to that in Equation (6). However, if cells are removing oxygen directly from the gas phase or from an interfacial film, Equation (7) should be written

$$\frac{r}{V} = Ka(C_w^g - C_w) + \alpha QX \quad (8)$$

where α is the fraction of oxygen consumed by the cells that is obtained at the gas-liquid interface. Then the Ka in Equation (8) should be equivalent to that in Equation (6). Thus, if r and QX are known and Ka is determined by the dynamic method, α can be found. A study of the variation of α with cell and oil concentrations may be of value in developing an understanding of the oxygen uptake and transport phenomena in hydrocarbon fermentations.

CONCLUSIONS

It is not certain at this time what the effect of the presence of a second liquid phase has on the rate of oxygen transfer across the interfaces that are present in a hydrocarbon fermentation. Indeed, it is not well established what interfaces actually exist. It is suggested that in further studies of hydrocarbon systems where the oil fraction is greater than 2%, the hydrocarbon phase should be treated as a distinct phase in the system. This greatly complicates the modeling, but it is necessary in order to arrive at an understanding of the oxygen transport phenomena. In addition, methods need to be developed to facilitate the study of the effects cells have on the oxygen transport when they adsorb to the hydrocarbon phase, and to what extent gas-oil interfaces are formed. Much work lies ahead for investigators desiring to unravel the mysteries of oxygen transport in these complex systems.

Nomenclature

a	interfacial area per unit volume
C	concentration per unit volume
C_i	concentration in i phase, g mole/liter
C_i^i	concentration that would be in equilibrium with i phase concentration
D	dispersion coefficient
H	average Henry's law constant
H_i	Henry's law constant for i phase
H_{ij}	partition coefficient between i and j phases
K	overall mass transfer coefficient
K_i	overall mass transfer coefficient for transport from or to i phase
$(Ka)_{ij}$	volumetric mass transfer coefficient for transport between i and j phases, based on concentration in i phase, sec^{-1}
N	oxygen diffusion flux at phase interface
P	production by reaction
Q	specific oxygen uptake rate of organisms
r	oxygen transfer rate
R	rotation speed of impellar, rps
S	spreading coefficient
t	time
T	temperature, absolute or $^{\circ}\text{C}$
v	velocity
v_s	superficial velocity
V	volume
X	cell concentration per unit volume
ϵ	fraction of total system volume occupied by a given phase
γ_{ij}	interfacial tension between i and j phases
σ	source term

ϕ volume fraction of hydrocarbon in liquid mixture

SUBSCRIPTS AND SUPERSSCRIPTS

g gas phase

w water or aqueous phase

h hydrocarbon phase

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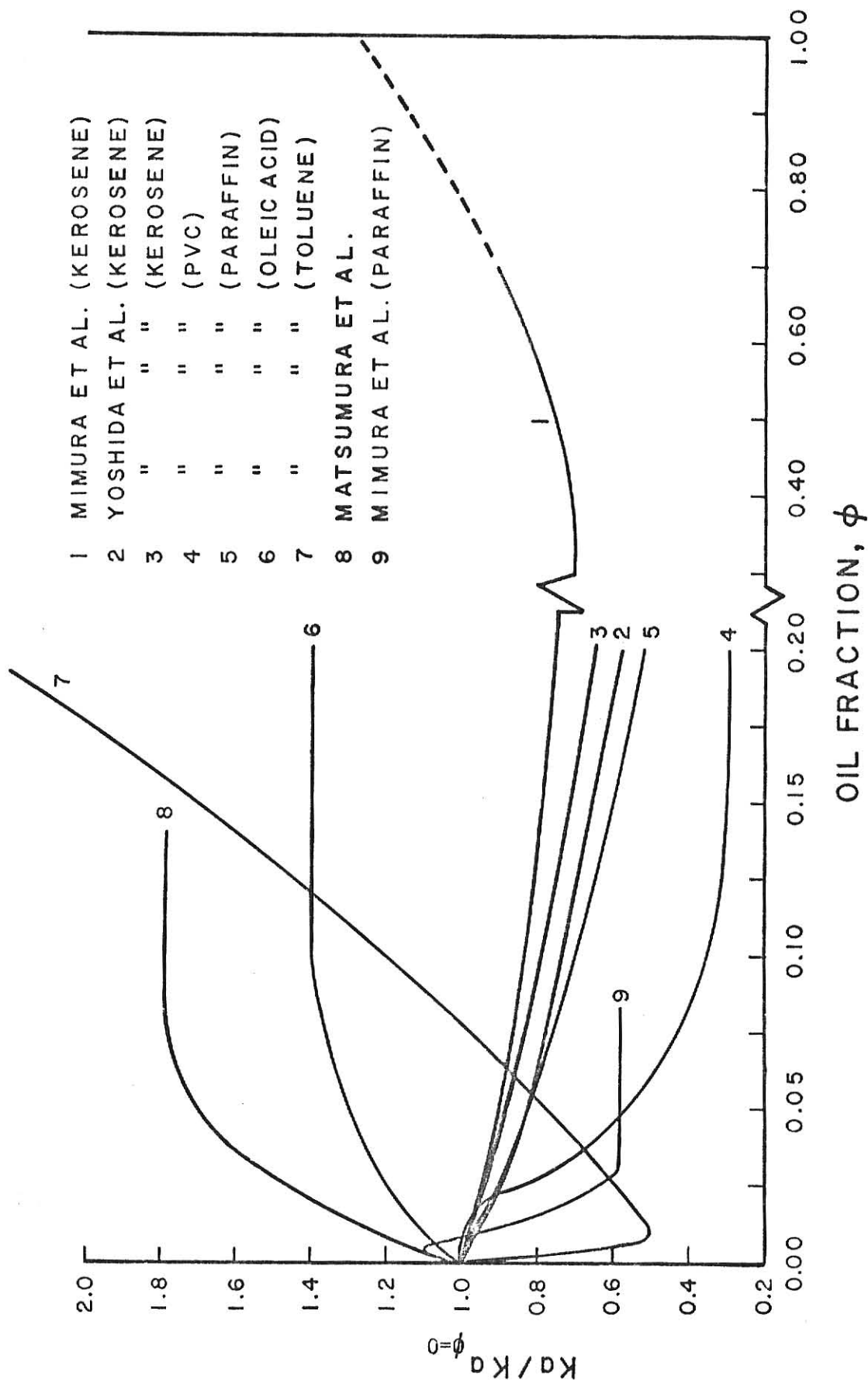


Figure 2. Effect of Oil on the Volumetric Oxygen Transfer Coefficient in Air - Water - Oil Systems

CHAPTER TWO

OXYGEN TRANSFER IN AERATED SYSTEMS CONTAINING TWO LIQUID PHASES - THEORETICAL AND EXPERIMENTAL RESULTS

INTRODUCTION

In hydrocarbon fermentations two liquid phases are present, and oxygen can be transported from the gas phase to either liquid phase, or it can be transported across the interfaces between the two liquids. Little is known about the relative rates of transport between each pair of phases during fermentation conditions. The effects of extracellular products and respiring cells on these transport rates are also not well understood. One difficulty in analyzing oxygen transport phenomena in hydrocarbon fermentations is the complexity of the pathways by which the oxygen species can move. In this paper a dynamic model is presented that accounts for the presence of all phases and important species. Oxygen transfer coefficients have been evaluated for mass transfer between the gas and aqueous phases using the model, but evaluating the coefficients for transfer between the gas and hydrocarbon and the aqueous and hydrocarbon phases was not found to be possible.

THEORETICAL ANALYSIS

The macroscopic equation of change for multi-phase systems derived by Whitaker⁽¹⁾ and modified by Gray⁽²⁾ is the starting point for developing a description of oxygen transport in aerated systems containing two liquid phases. For a small, well mixed vessel, the oxygen concentration in each liquid phase can be represented by the following simplification of the macroscopic equation of change:

$$\frac{dC_i}{dt} = \sum_j K_{ij} a_{ij} (C_i^j - C_i) + R_i \quad (1)$$

The source term arising from time averaging has been neglected⁽¹⁾. It is not yet known whether this term has significant values in the systems discussed in this work. All the quantities in equation (1) are volume averaged and time averaged⁽¹⁾. It should be noted that equation (1) is not valid in systems where concentration gradients occur, such as in towers. For these systems, the dispersion and convection terms that appear in the general form of the macroscopic mass balance cannot be neglected⁽¹⁾.

Since the solubility of oxygen in water and hydrocarbons is very small, the oxygen concentration or partial pressure changes little in the gas phase as it passes through a small absorption vessel. Thus the concentration of oxygen in a liquid phase that would be in equilibrium with the gas phase is assumed to be constant. For a system in which oxygen is consumed during microbiological growth processes, equation (1) applied to a liquid phase becomes

$$\frac{dC_i}{dt} = \sum_j K_{ij} a_{ij} (C_i^j - C_i) - QX \quad (2)$$

The organisms are treated as a reacting species, rather than as a separate phase. This is valid if the growth process is limited by the biological reaction rate

or by diffusion within flocs of cells, rather than by oxygen transport to the cell or floc surfaces. If equation (2) is multiplied by the Henry's Law constant, H_i , which relates the oxygen partial pressure to the concentration, the following is obtained:

$$\frac{dP_i}{dt} = \sum_j K_{ij} a_{ij} (P_j - P_i) - Q H_i X \quad (3)$$

P_i is the oxygen partial pressure in the i phase.

Equation (3) will now be applied to the aqueous and hydrocarbon phases of a hydrocarbon fermentation broth. Since interfaces between any combination of the gas and the two liquid phases can exist, oxygen transfer across each of these interfaces must be allowed. For the aqueous phase, equation (3) becomes

$$\frac{dP_w}{dt} = K_{wg} a_{wg} (P_g - P_w) + K_{wh} a_{wh} (P_h - P_w) - Q H_w X \quad (4)$$

If it is assumed that organisms are not removing oxygen directly from the hydrocarbon phase, then

$$\frac{dP_h}{dt} = K_{hg} a_{hg} (P_g - P_h) + K_{hw} a_{hw} (P_w - P_h) \quad (5)$$

Since the partial pressure of oxygen in the aqueous phase can be measured with rapidly responding oxygen sensors, it is desirable to simultaneously solve equations (4) and (5) for P_w as a function of the volumetric oxygen transfer coefficients, P_g , and $Q H_w X$. The respiration rate term is related to steady-state partial pressures by equation (4) as follows:

$$Q H_w X = K_{wg} a_{wg} (P_g - P_{ws}) + K_{wh} a_{wh} (P_{hs} - P_{ws}) \quad (6)$$

If the volumetric oxygen transfer coefficients are assumed to be constant, then equations (4), (5), and (6) can be combined to obtain

$$\frac{d^2Y}{dt^2} + B \frac{dY}{dt} + CY = 0 \quad (7)$$

where $Y = (P_w - P_{ws}) / (P_{wo} - P_{ws})$

$$B = K1 + K2 + K3 + K4$$

$$C = K1K3 + K1K4 + K2K3$$

and $K1 = K_{wg} a_{wg}$

$$K2 = K_{wh} a_{wh}$$

$$K3 = K_{hg} a_{hg}$$

$$K4 = K_{hw} a_{hw}$$

Two boundary conditions are needed in order to find Y as a function of the parameters (volumetric coefficients) and time. The initial condition

$$Y = 1 \text{ at } t = 0$$

is useful, but the final condition

$$Y = 0 \text{ at } t = \infty$$

adds no useful information because the solutions to equation (7) are negative exponential functions and Y becomes zero as t becomes infinite. A second constraint can be found for the case where the transient partial pressure in the aqueous phase is the response to a step change in the gas phase oxygen partial pressure. If the steady state form of equation (5) is combined with equation (6),

$$\frac{Q_H X_w}{P_g - P_{ws}} = K1 + \frac{K2K3}{K3 + K4}$$

Also, if the system is assumed to be at steady state prior to the step change in the gas phase oxygen partial pressure, and the respiration rate and the values of the volumetric oxygen transfer coefficients have the same value before and after the step change, then

$$\frac{Q_H X}{P_g' - P_{wo}} = \frac{Q_H X}{P_g - P_{ws}} = K1 + \frac{K2K3}{K3 + K4}$$

where P_g' is the gas phase oxygen partial pressure prior to the step change. Therefore,

$$P_g' - P_g = P_{wo} - P_{ws} \quad (8)$$

By combining equations (4) and (6) and using the above result, the following initial condition is obtained:

$$\frac{dY}{dt} = -K1 \quad \text{at } t = 0$$

The above condition and the condition that

$$Y = 1 \text{ at } t = 0$$

can now be used to solve equation (7), giving the following solutions:

for $B^2 > 4C$,

$$Y = \left(\frac{K1 + m_1}{n} \right) \exp(m_2 t) - \left(\frac{K1 + m_2}{n} \right) \exp(m_1 t)$$

where $n = \sqrt{B^2 - 4C}$

$$m_1 = -\frac{1}{2}(B-n)$$

$$m_2 = -\frac{1}{2}(B+n)$$

and for $B^2 = 4C$,

$$Y = [1 + (\frac{1}{2}B - K1)t] \exp(-\frac{1}{2}Bt)$$

It can be shown that

$$B^2 - 4C = (K1 + K2 - K3 - K4)^2 + 4K2K4$$

Therefore, m_1 and m_2 are real and negative for all positive values of the oxygen transfer coefficients. Notice that if $K2 = K3 = K4 = 0$

$$Y = \exp(-K1t)$$

The above expression describes the response of the aqueous phase to a step change in the gas phase oxygen partial pressure when only one liquid phase is present, or when the dispersed liquid phase does not absorb or desorb oxygen.

The coefficients $K2$ and $K4$ are not independent, and are related by

$$V_w K_2 (C_w^h - C_w) = -V_h K_4 (C_h^w - C_h)$$

or $K_2 = \beta K_4$ where

$$\beta = \left(\frac{1-\phi}{\phi} \right) \left(\frac{H_h}{H_w} \right)$$

Thus, for systems in which β is fixed, the rate at which oxygen is transported to or from the aqueous phase is a function of K_1 , K_2 , and K_3 .

The oxygen partial pressure in the hydrocarbon phase can also be expressed as a function of the volumetric coefficients and time. If equation (5) is applied to an aerated system when it is at steady state, both before and after a step change in the gas phase partial pressure occurs, the following relation is obtained:

$$K_3 (P_g' - P_g) + K_4 (P_{wo} - P_{ws}) = (K_3 + K_4) (P_{ho} - P_{hs})$$

Combining this equation with equation (8) gives

$$P_{wo} - P_{ws} = P_{ho} - P_{hs} \quad (9)$$

Using equation (9), equation (5) can then be rewritten in the following general dimensionless form:

$$\frac{dZ}{dt} + (K_3 + K_4)Z = K_4 Y \quad (10)$$

where $Z = \frac{P_h - P_{hs}}{P_{ho} - P_{hs}}$. Equation (10) can be solved using the appropriate

expression for Y and the following initial conditions:

$$Z = 1 \text{ at } t = 0$$

$$\frac{dZ}{dt} = -K_3 \text{ at } t = 0$$

The solutions are for $B^2 > 4C$,

$$Z = \left(\frac{K3+m_1}{n}\right) \exp(m_2 t) - \left(\frac{K3+m_2}{n}\right) \exp(m_1 t)$$

and for $B^2 = 4C$,

$$Z = [1 + (\frac{1}{2}B - K3)t] \exp(-\frac{1}{2}Bt)$$

These expressions are analogous to those for Y, with K3 replacing K1.

SYSTEM SIMULATION

In order to determine the effects system parameters ϕ , K_1 , K_2 , and K_3 have on the response of the oxygen partial pressure in the aqueous phase to a step change in the gas phase partial pressure, the appropriate solutions to equation (7) were plotted as functions of time, using a CALCOM plotter, for a range of values of the parameters. These plots are shown in figures 1 through 12. It is apparent that the effect of the value of a given parameter is more pronounced at higher oil fractions, and that the effect of K_3 is greater than that of K_2 . It is also observed that for a value of K_3 between 0.25 and 1.0 min^{-1} , the direction of oxygen transfer across the oil-aqueous interface reverses direction. For the value of K_3 at which reversal occurs, both liquid phases are in equilibrium with each other, as each phase absorbs (or desorbs) oxygen from (or to) the gas phase at just the necessary rate to maintain this equilibrium. Therefore, the value of K_2 near this point would have little effect on the aqueous phase response.

EXPERIMENTAL METHODS AND MATERIALS

The solutions to equation (7) were used to estimate values of K_1 , K_2 , and K_3 in several dispersions containing aqueous and liquid hydrocarbon phases. The gassed systems were allowed to reach steady state, then the oxygen concentration in the gas phase was rapidly changed to a new value. An oxygen sensor (Beckman 39553 Oxygen Sensor, used with a Beckman Fieldlab Oxygen Analyzer and a Bausch and Lomb strip chart recorder) was placed in the dispersion or broth, and the oxygen partial pressure was recorded. It was assumed that the bulk partial pressure in the aqueous phase was being followed, as the oil was the dispersed liquid phase in all experiments. Hydrocarbon volume fractions in the liquid ranged from zero to twelve percent.

Two vessels were used. One was a small, air-lift absorption column three inches in diameter with a two inch diameter draft tube. The liquid volume was maintained at 0.6 liters and the oxygen sensor probe was located at the bottom of the vessel. The circulation rate was very rapid, as the gas flow rate used was 12 liters/min, and the time for complete mixing to occur after introducing a small amount of dye into the vessel was of the order of one second. The feed gas and the dispersion were maintained at 30°C, and the feed gas was saturated with water at this temperature. A 6 mm inside diameter pipe with no diffuser was used to feed the gas into the vessel.

The second vessel was a small, circular plexiglass container, closed at both ends, with a water jacket around the circular surface. A magnetic stirrer was used to mix the liquid, which was maintained at a constant volume of 0.1 liters. The gas entered this stirred tank through a 1 mm hole in the center of the bottom of the vessel. The liquid was maintained at 30°C by circulating water through the jacket, but the gas temperature was not controlled. The

oxygen probe was inserted through the side of the vessel at a slight angle to the horizon to prevent air bubbles from adhering to the probe tip. The gas flow rate to the stirred vessel was maintained at 0.36 liters/min. A three-way valve was placed in the gas line of both experimental vessels near the feed point, enabling a step change in feed gas composition to be made between air and 99% pure oxygen. In the air-lift experiments, the step change was made from oxygen to air; in the stirred tank, from air to oxygen.

Three liquid dispersions were used in the oxygen transfer experiments: distilled water and n-hexadecane; a culture broth containing respiring cells and n-hexadecane; and the same culture broth with cells removed. Technical grade n-hexadecane was used in the air-lift systems, and 99% pure n-hexadecane was used in the stirred vessel systems (both manufactured by The Humphrey Chemical Co.). The broth used in the air-lift device contained 32 grams of Candida lipolytica per liter of medium, grown at 30°C and a pH of 5.0. The broth used in the stirred vessel contained 9.0 grams of Candida intermedia per liter of medium, grown at 30°C and a pH of 3.5. After cultivating the organisms, the residual oil was removed from the broth by cooling the mixture, centrifuging it, and filtering out the solid alkane. Some cells which adhered to the oil were lost, but the concentrations reported above were determined by dry weight measurement after separating out the oil. Hexadecane was then added to the broth during the course of the experiments to give the desired volume fraction.

The oxygen partial pressure change with time in the aqueous phase, resulting from the step change in the gas phase composition, was recorded. This data was then fitted with the appropriate solution to the model equation (7) using the least squares portion of Bard's⁽³⁾ parameter estimation computer program. Since there was a response lag of about seven seconds in the aqueous

phase partial pressure, the time at which the response commenced was estimated, as well as the three volumetric oxygen transfer coefficients, for each experiment. For both the simulations and the parameter estimations, the value of $H_h/H_w = 0.1545$, reported by Matsumura et al.⁽⁴⁾ for 30°C, was used.

RESULTS AND DISCUSSION

For the case when $\phi=0$, the partial pressure response in the aqueous phase should decrease exponentially with time, and so a plot of the logarithm of the partial pressure versus time should be a straight line with a slope of $-K_1$. The actual data showed a deviation from this theoretical expectation during an initial time period of the order of thirty seconds. The data from the experiments in which hydrocarbon was present in the system was therefore disregarded for this initial time period. The point at which $t=0$ as used in the parameter estimation procedures was either found by extrapolating the straight line to $Y=1$ for the cases in which $\phi=0$, and using the same result for cases in which $\phi \neq 0$, but for which the aqueous phase and vessel were the same; or it was found by treating the initial time as a fourth parameter and estimating it numerically. The values of K_1 and the initial time as estimated by both methods were found to be similar. The estimated values of K_2 and K_3 were not similar, however, and in fact were not related to ϕ or to the composition of the aqueous phase, but were found to be highly dependent on the starting values supplied to the numerical procedure. The standard deviations of K_2 and K_3 were as much as several orders of magnitude larger than the estimated values. It is not clear why such difficulty was encountered in estimating values of K_2 and K_3 . Of course, if the oxygen partial pressure in the hydrocarbon phase could be monitored, the estimations would be considerably easier to obtain.

In other experiments⁽⁵⁾ carried out at Kansas State University in a ten liter air-lift absorption tower, a fat soluble dye was added to a gassed water and n-hexadecane dispersion and it was plainly observed that oil

drops and air bubbles adhered to each other. Therefore, gas to oil oxygen transfer could be significant. It has also been observed during the experimental work reported in this paper, and in other reports⁽⁶⁾, that micro-organisms adhere to the oil drops in hydrocarbon fermentations. The Candida lipolytica appeared to cover much of the surface of the oil drops when the cell concentration was 32 grams/liter. The expected values of K_2 , then, in an aerated system containing broth with cells removed would be larger than with cells present. The true values of K_2 and K_3 could be indicators of the relative amount of interfacial area that existed in the several systems studied.

Values of K_1 can be found experimentally by graphically estimating the initial slopes of the response curves as well as by numerical estimation. Figures 13 and 14 show the relative values of K_1 (compared to the pure water system) plotted as a function of oil fraction and aqueous phase composition. These values were found graphically, but results from the numerical estimation are similar. These results indicate that the oil phase has a very significant effect on oxygen transport between the gas and the aqueous phases. The values of K_1 when a very small amount of hydrocarbon is present are considerably smaller than when no oil is present, while increases in hydrocarbon fraction above 0.03 have a much less pronounced effect. This could be due to a decrease in the degree of mixing (or surface renewal rate) in the aqueous phase, or to a decrease in interfacial area, or both. Certainly if gas bubbles and oil drops adhere to each other, interfacial area between the gas and aqueous phases is reduced. In order to examine the effect of spherical drops on the fluid dynamics of the aqueous phase, values of K_1 were determined in the air-lift absorber containing distilled water and glass beads with a diameter of about

50 μm . Relative values are shown in Figure 15 as a function of bead volume fraction of the solid-liquid mixture. The results do not parallel those for the hydrocarbon containing systems, and the effect of the glass beads on values of K_L are not as large. It visually appeared that the presence of the oil actually caused a decrease in the air bubble size. The most likely explanation for the decrease of K_L with ϕ , then, is that the oil and gas phases adhere, and that the limit in amount of oil that will adhere with the gas bubbles is reached about when $\phi = 0.03$.

From Figures 13 and 14 it is also noted that the values of K_L for the systems containing fermentation broth without cells are lower than those for the water-hydrocarbon system, but that the presence of cells increases K_L to values equal to or greater than those for the water-hydrocarbon system. The larger difference in values among the three systems in the air-lift absorber, compared to the stirred vessel, occurred possibly because the cell concentration of the Candida lipolytica was more than three times larger than the same of Candida intermedia. Apparently the extracellular products act as surface active agents at the gas-aqueous phase interface. The surface tension of the aqueous phase has been observed by others⁽⁷⁾ to decrease as the cell concentration increases in batch hydrocarbon cultivations. The surface tension of the aqueous phase of the Candida lipolytica broth was found by the ring method to be 72% of the value for distilled water, and it was observed that the gas bubbles in the gassed broths were smaller than those in the gassed water. Surface active agents obstruct the transport of oxygen across the interface, and also decrease the turbulence or mixing near the interface⁽⁸⁾. It seems likely, therefore that the lower values of K_L found in the broth without cells results from a large reduction

in the oxygen transfer coefficient K_{wg} , even though the interfacial area a_{wg} is greater than that for the pure water system.

The explanation of the fact that larger values of K_l were obtained in broth containing the cells is not as apparent. Both Mimura and coworkers⁽⁹⁾ and Prokop et. al.⁽¹⁰⁾ found using a dynamic method that K_l decreased as cell concentration increased in batch cultivations where a hydrocarbon was the substrate. Mimura et. al.⁽⁹⁾ postulated that cells were congregating at the gas-liquid interfaces, preventing much of the oxygen from being transported to the bulk of the aqueous phase. The results reported in this work, however, do not support this postulation. Perhaps the biological reaction (respiration) enhances the absorption⁽¹¹⁾. Greenhalgh and coworkers⁽¹²⁾ found that in a non-hydrocarbon fermentation E. coli had an effect on oxygen transport similar to that found in the work reported here. They reviewed the work of other authors who investigated the effect of cells on the fluid dynamics of the liquid, and the effect of respiration on the gas absorption rate.

CONCLUSIONS

The dynamic model described in this paper has been found very useful for determining values of the volumetric oxygen transfer coefficient for transport between the gas and aqueous phases in aerated systems containing two liquid phases, provided the systems are well mixed. Experimental results indicate that the value of this coefficient is less in aerated hydrocarbon and aqueous phase dispersions than it is in dispersions containing no hydrocarbon. The extracellular products in the aqueous phase of a hydrocarbon fermentation broth appear to inhibit interfacial oxygen transfer between the gas and aqueous phases, while the presence of respiring cells appears to enhance transfer between these phases.

Efforts to evaluate the volumetric oxygen transfer coefficients for transport between the gas and hydrocarbon phases, and between the aqueous and hydrocarbon phases were not successful. The reason is not clear, but the dynamic model may yet be useful for estimating these coefficients.

NOMENCLATURE

a_{ij}	interfacial area between the i and j phases
C_i	oxygen concentration in the i phase
C_i^j	oxygen concentration in the i phase that would be in equilibrium with the j phase
H_i	Henry's Law constant for oxygen in the i phase
K_{ij}	overall mass transfer coefficient for oxygen transport between the i and j phases
P_i	oxygen partial pressure in the i phase
Q	specific oxygen consumption rate of organisms (based on unit mass of organisms)
R_i	production of oxygen by biological reaction
t	time
V_i	volume of i phase
X	organism mass concentration in aqueous phase
Y	dimensionless oxygen concentration or partial pressure in the aqueous phase
Z	dimensionless oxygen concentration or partial pressure in the hydrocarbon phase

Superscripts and Subscripts

g	gas phase
h	hydrocarbon phase
w	water or aqueous phase
o	denotes initial condition
s	denotes steady state condition

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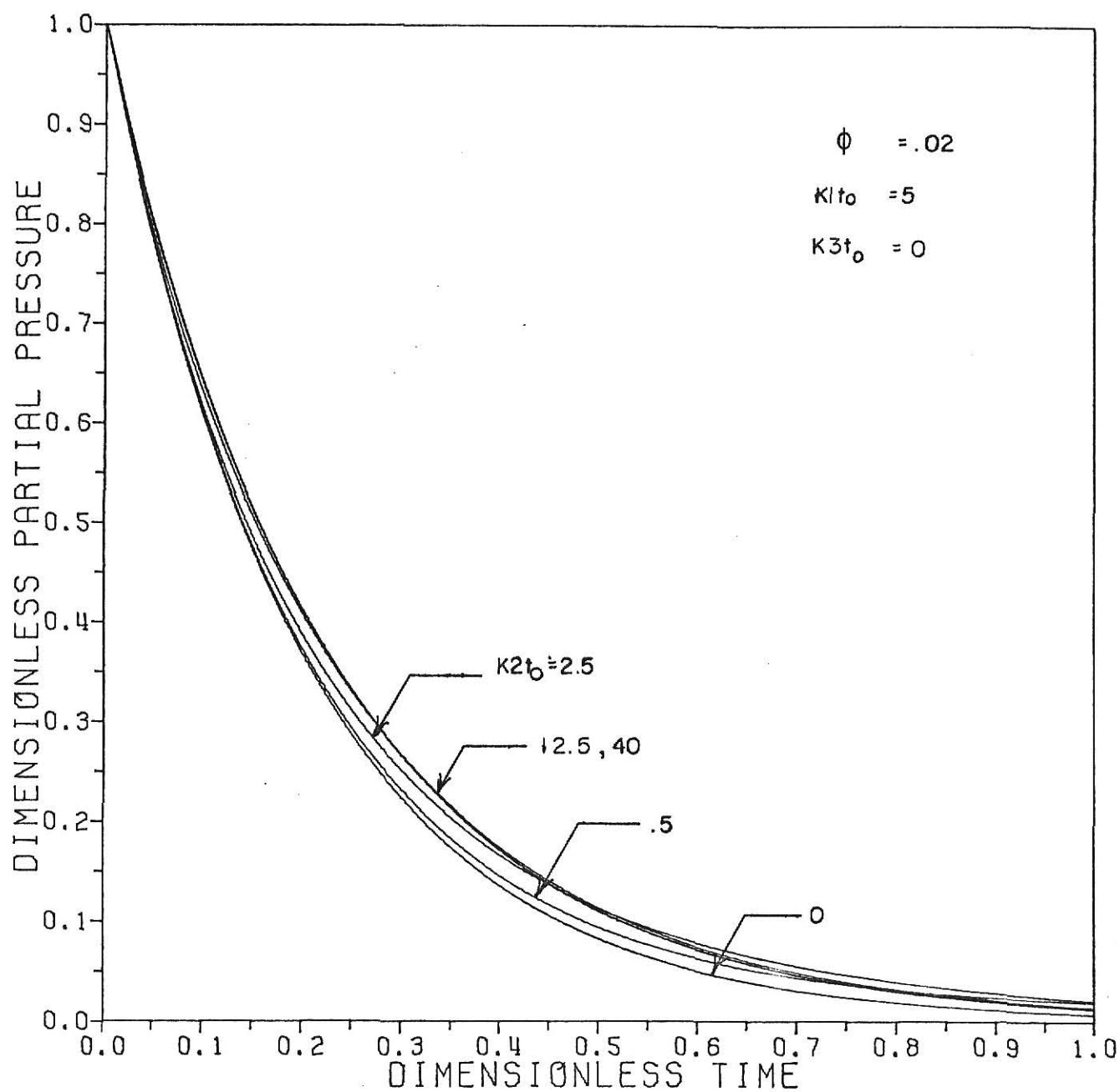


Fig. 1 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

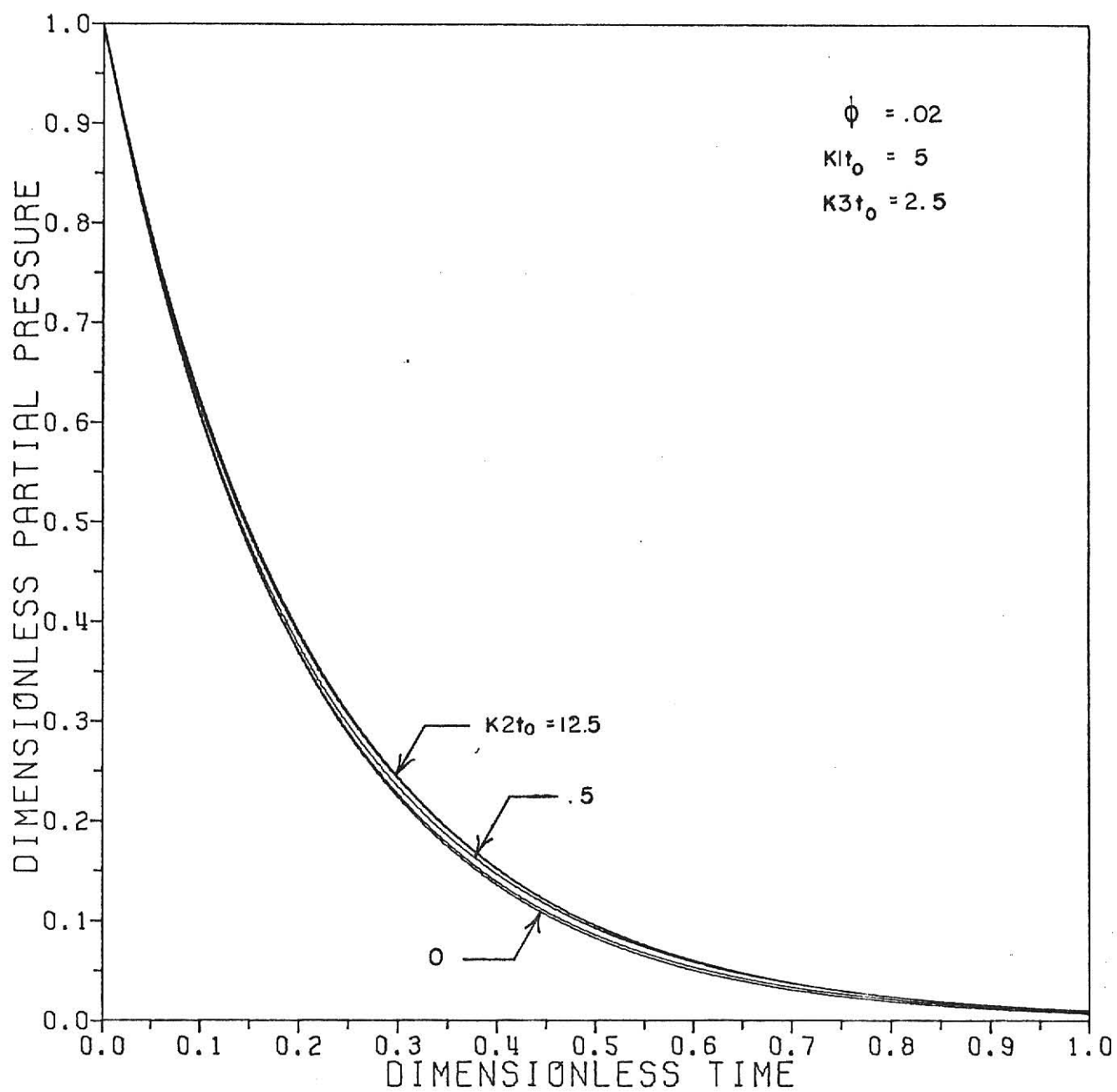


Fig. 2 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

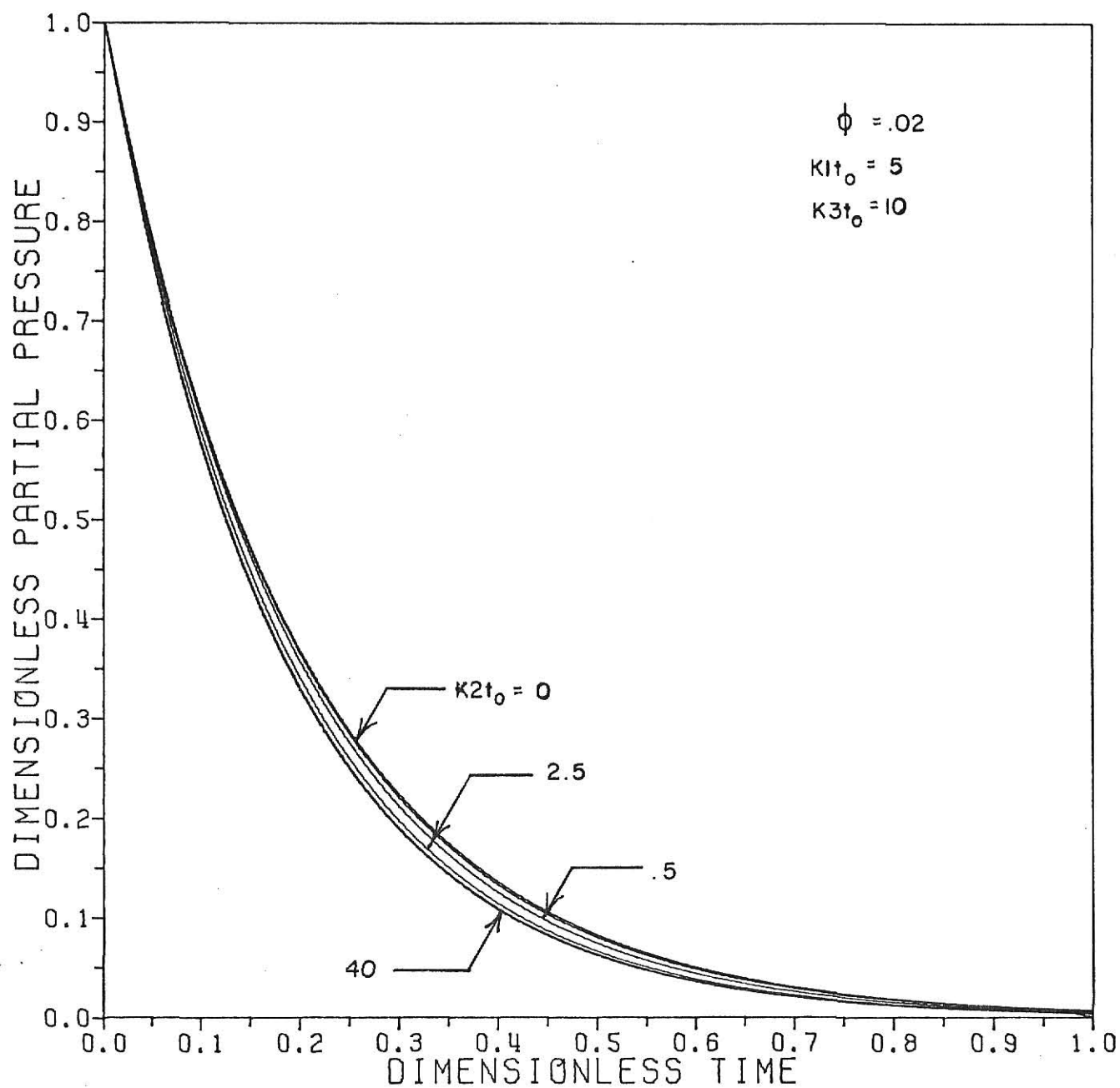


Fig. 3 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

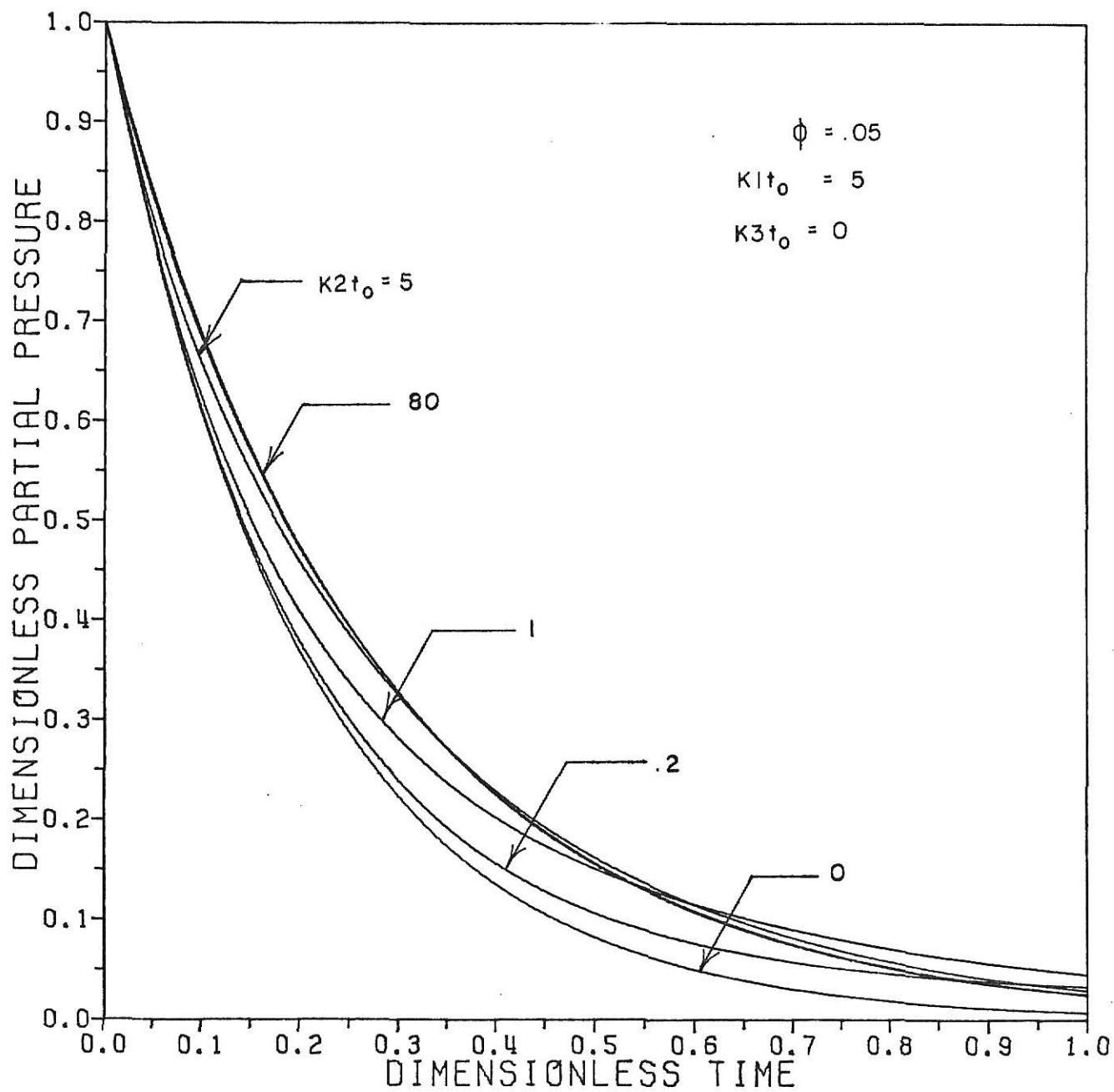


Fig. 4 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

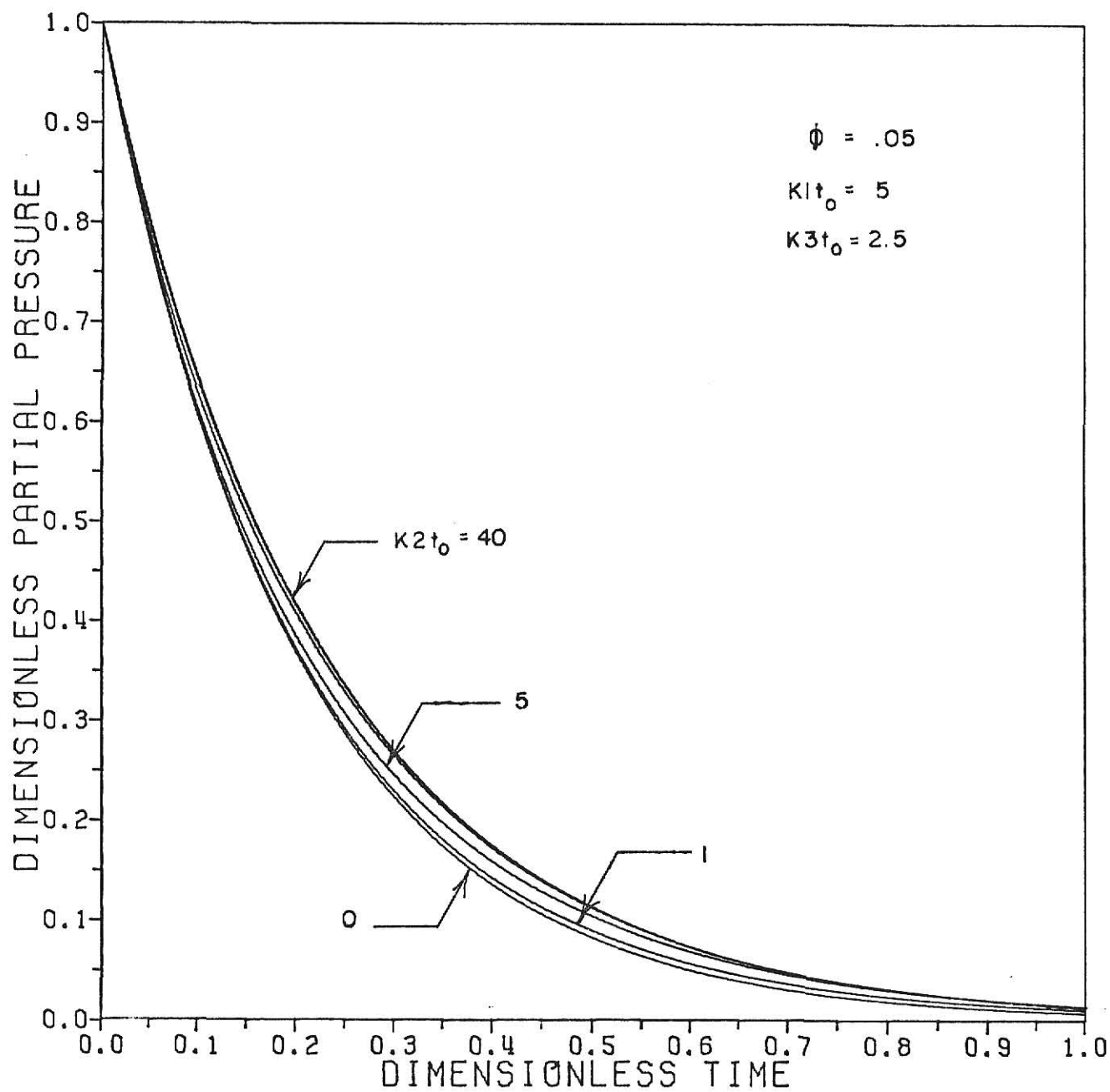


Fig. 5 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$.

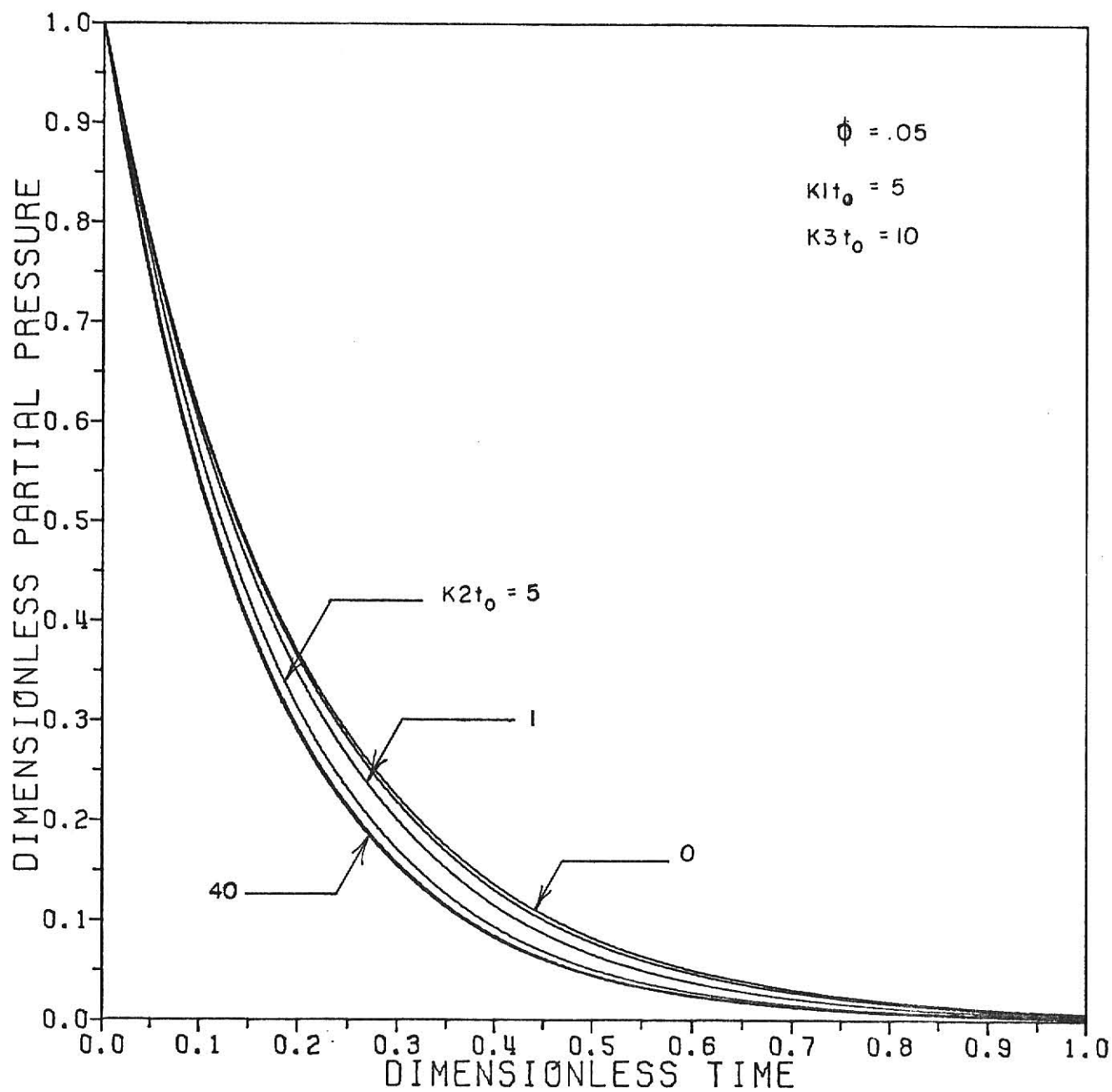


Fig. 6 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

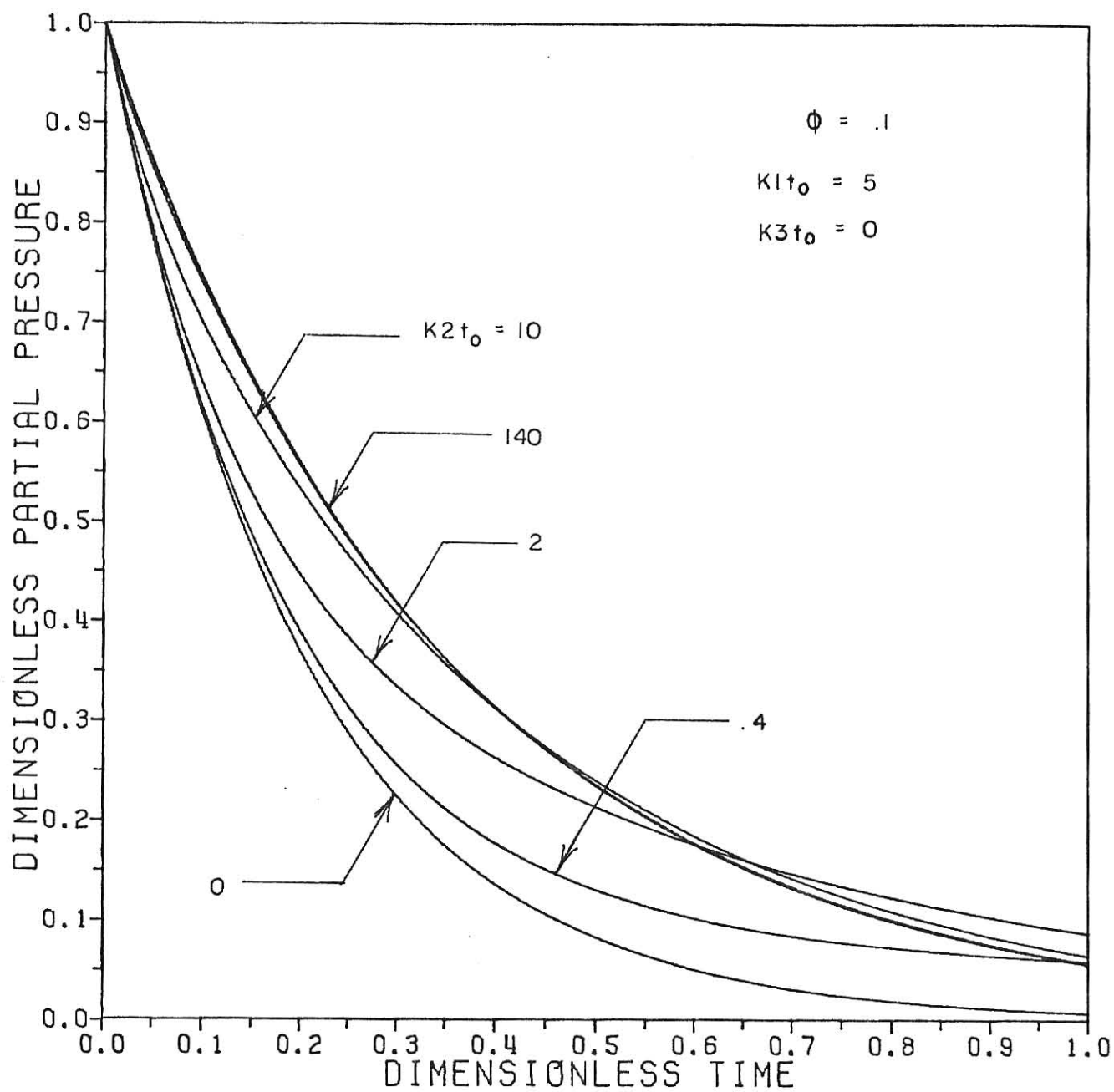


Fig. 7 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

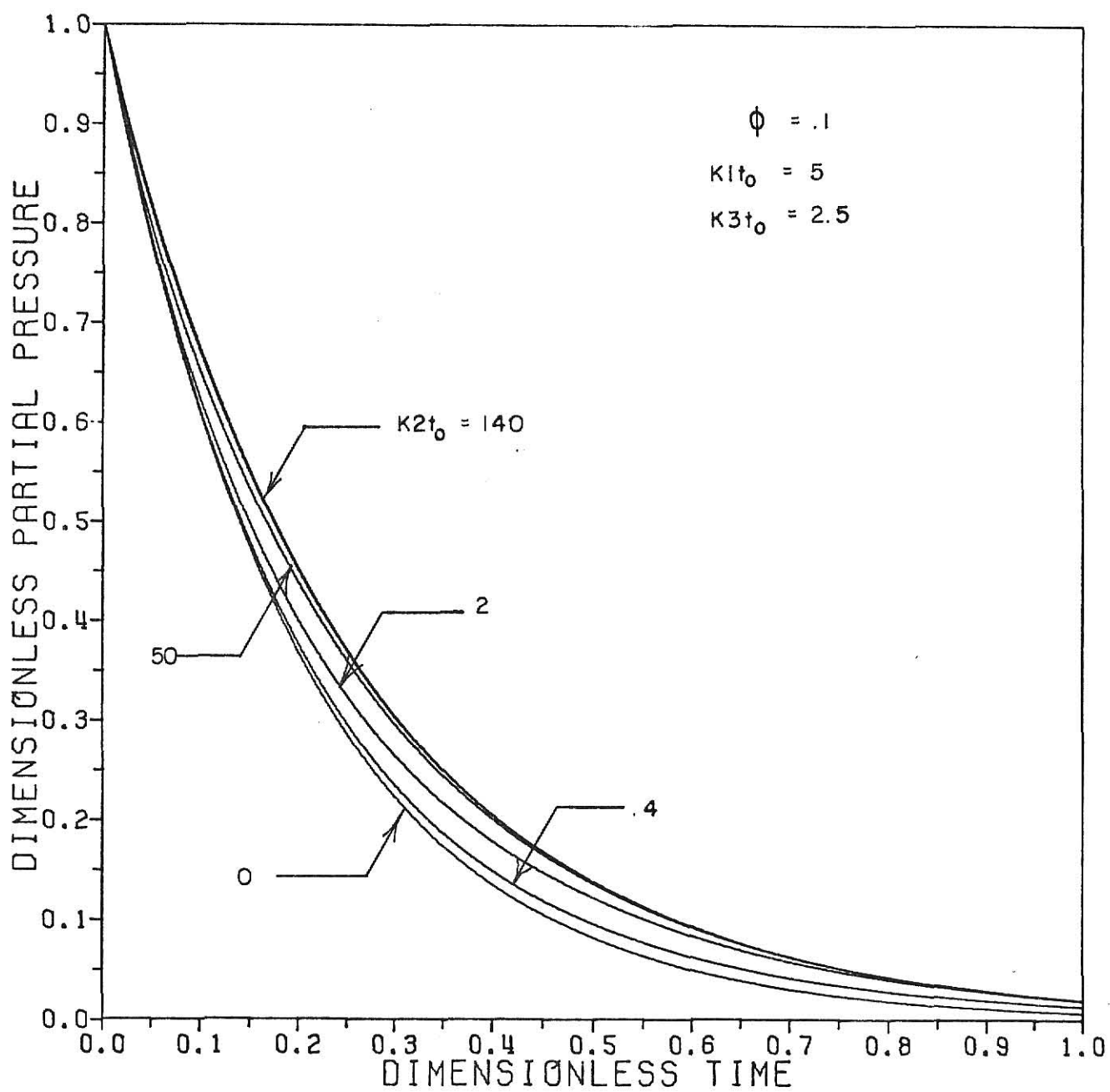


Fig. 8 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

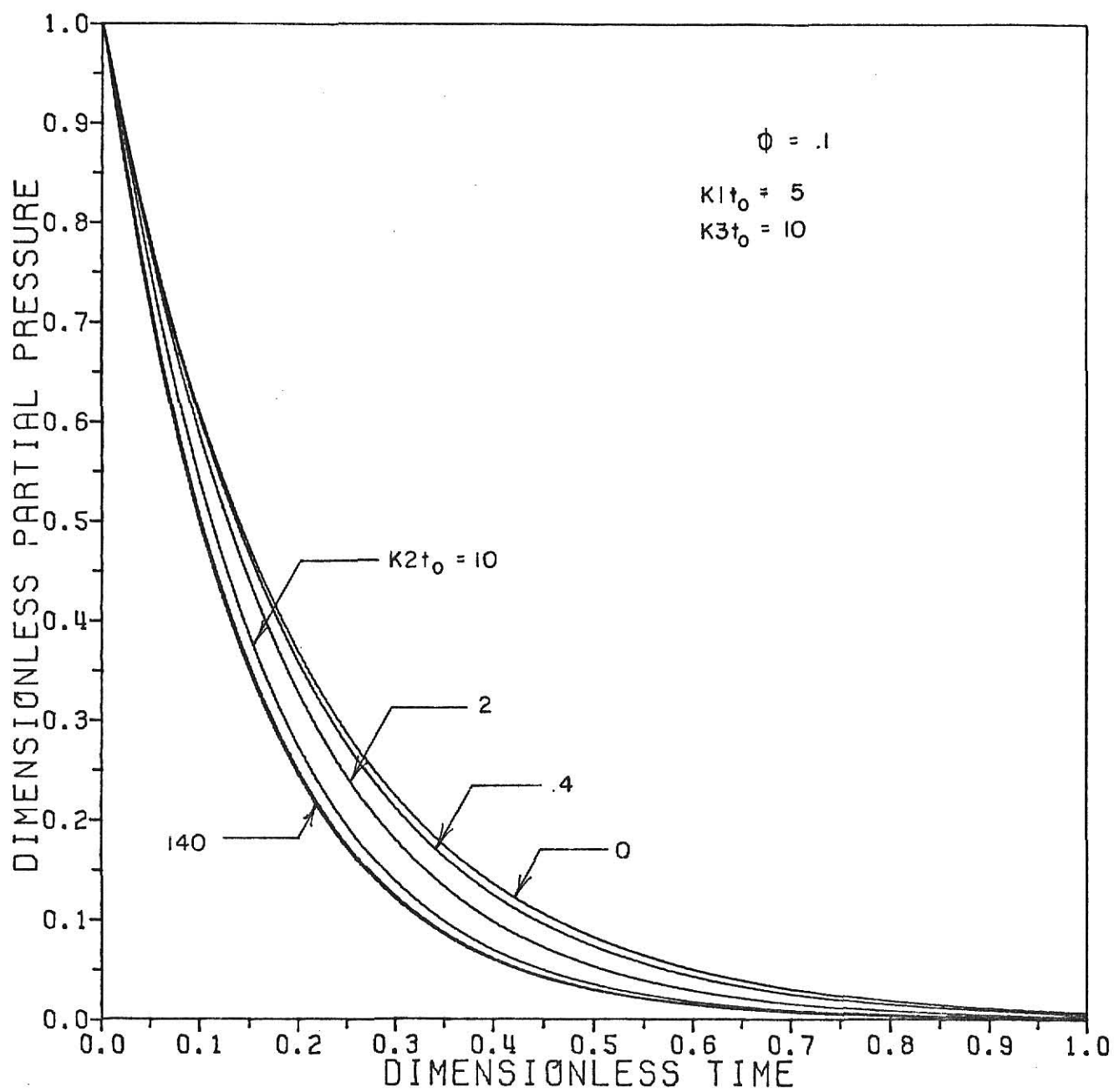


Fig. 9 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

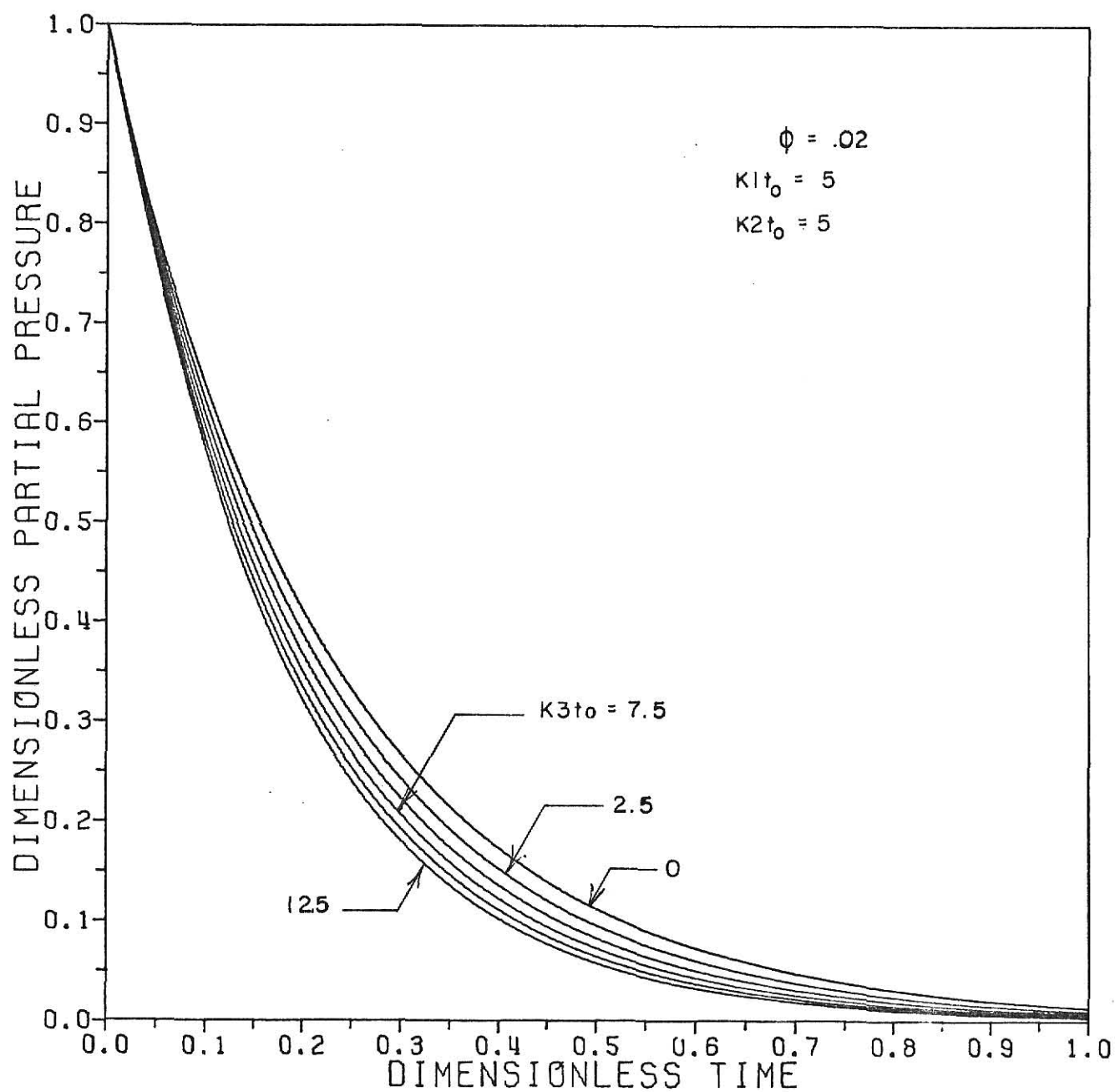


Fig. 10 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

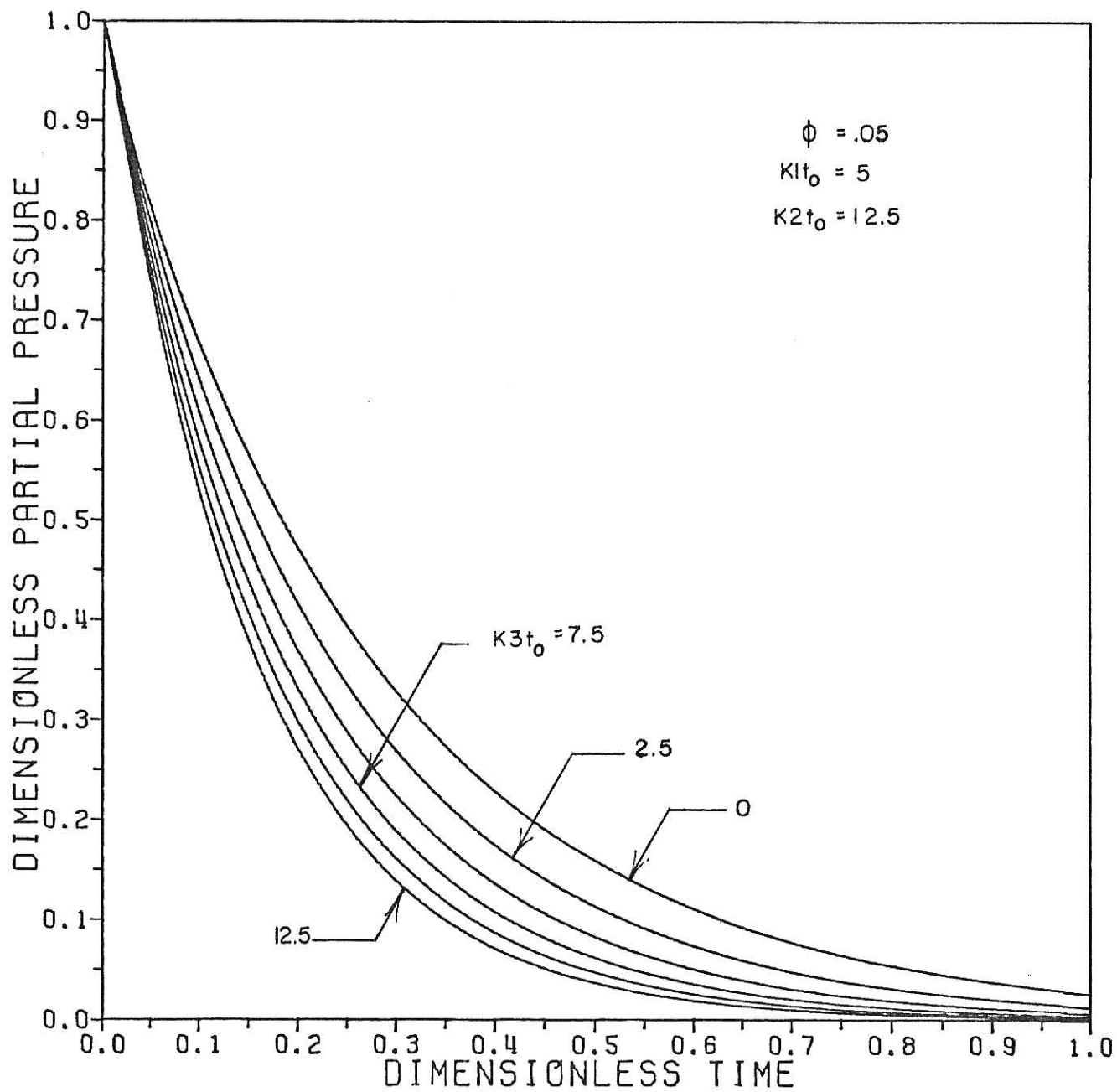


Fig. 11 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

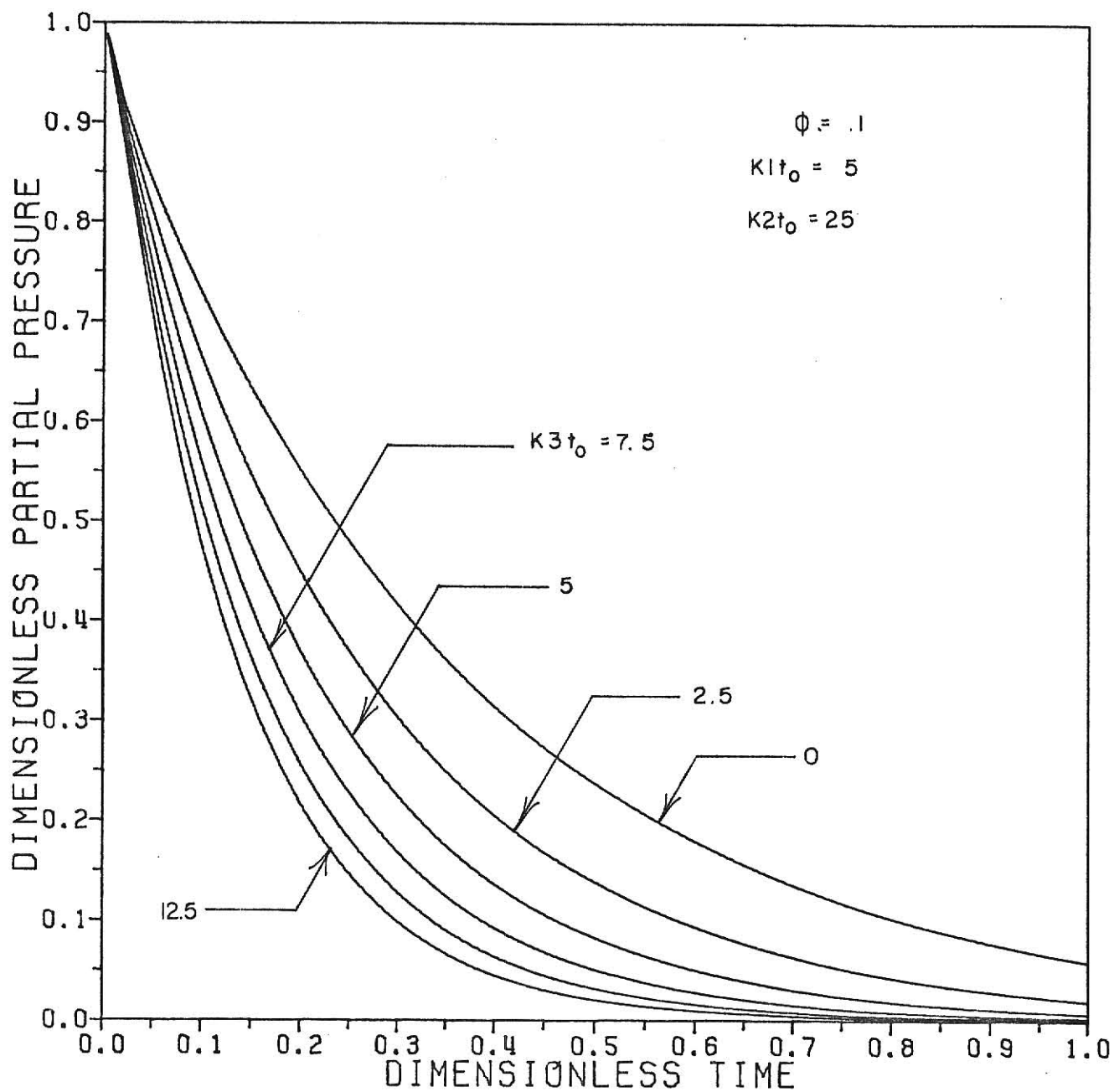


Fig. 12 Response of the aqueous phase partial pressure to a step change in the gas phase partial pressure. $t_0 = 10$ min.

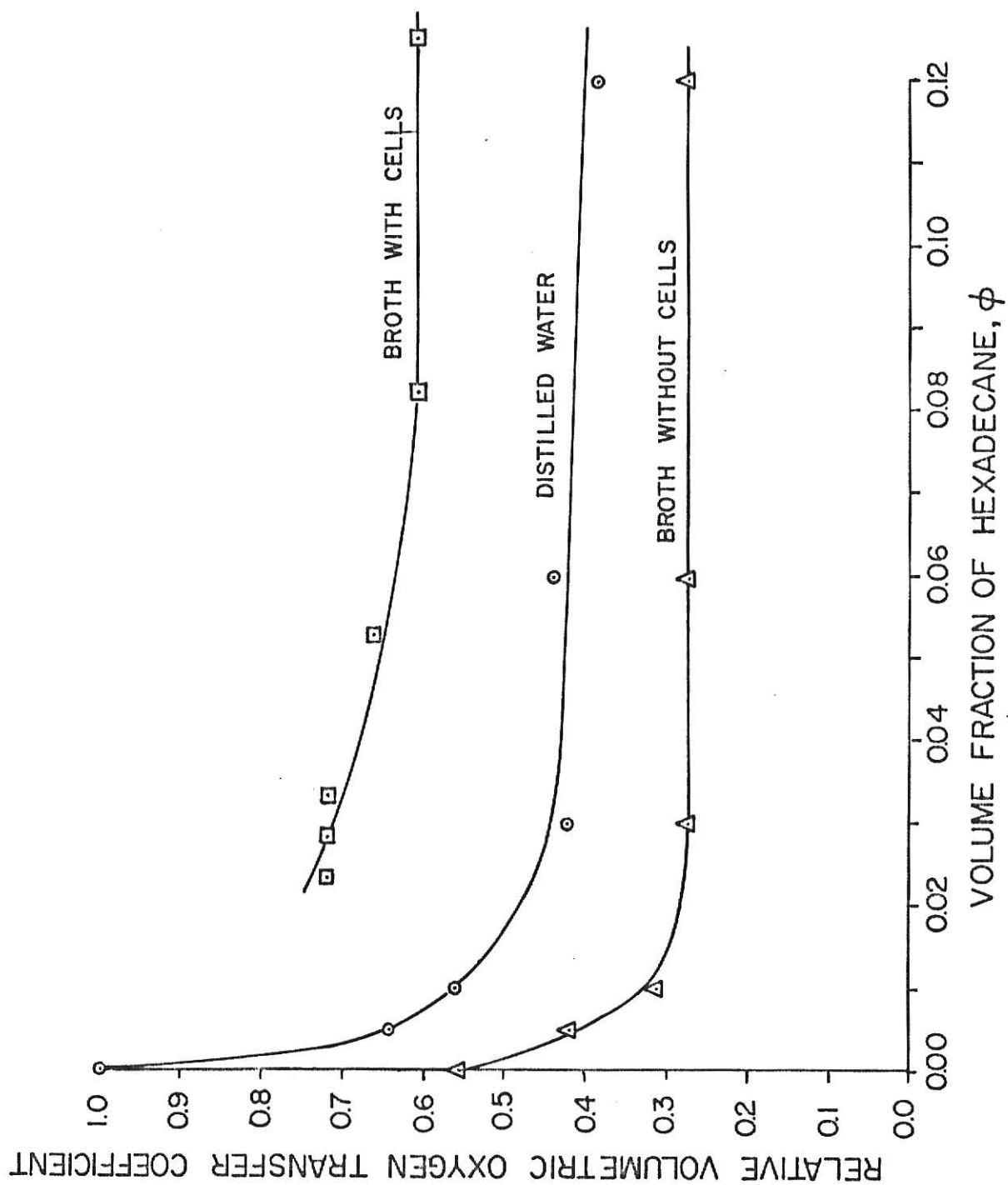


Fig. 13 Oxygen transfer coefficients between gas and aqueous phases in airlift vessel. For distilled water containing no oil, $K_a = 2.63 \text{ min}^{-1}$

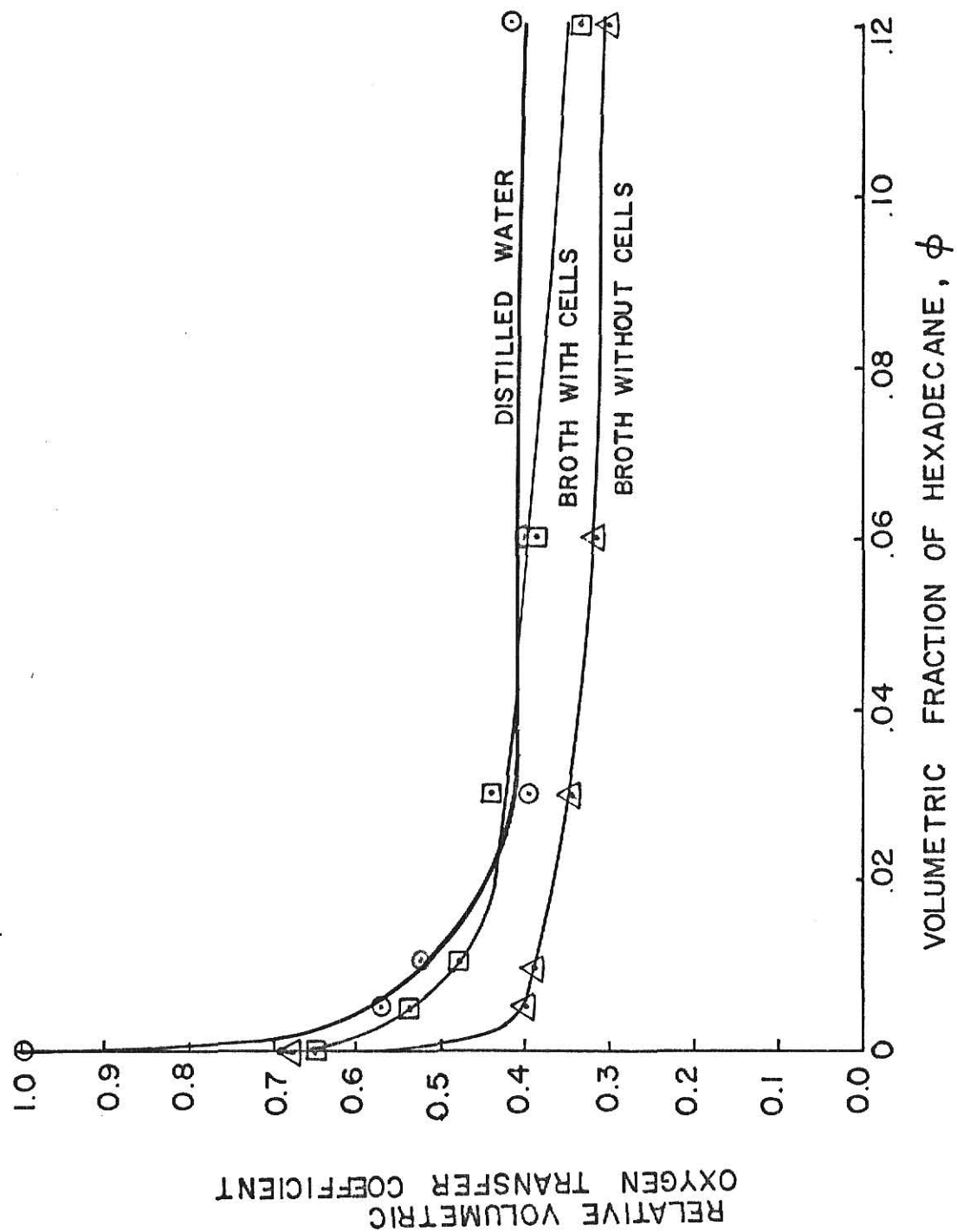


Fig. 14 Oxygen transfer coefficients between gas and aqueous phases in stirred vessel. For distilled water containing no oil, $K_a = 1.16 \text{ min}^{-1}$

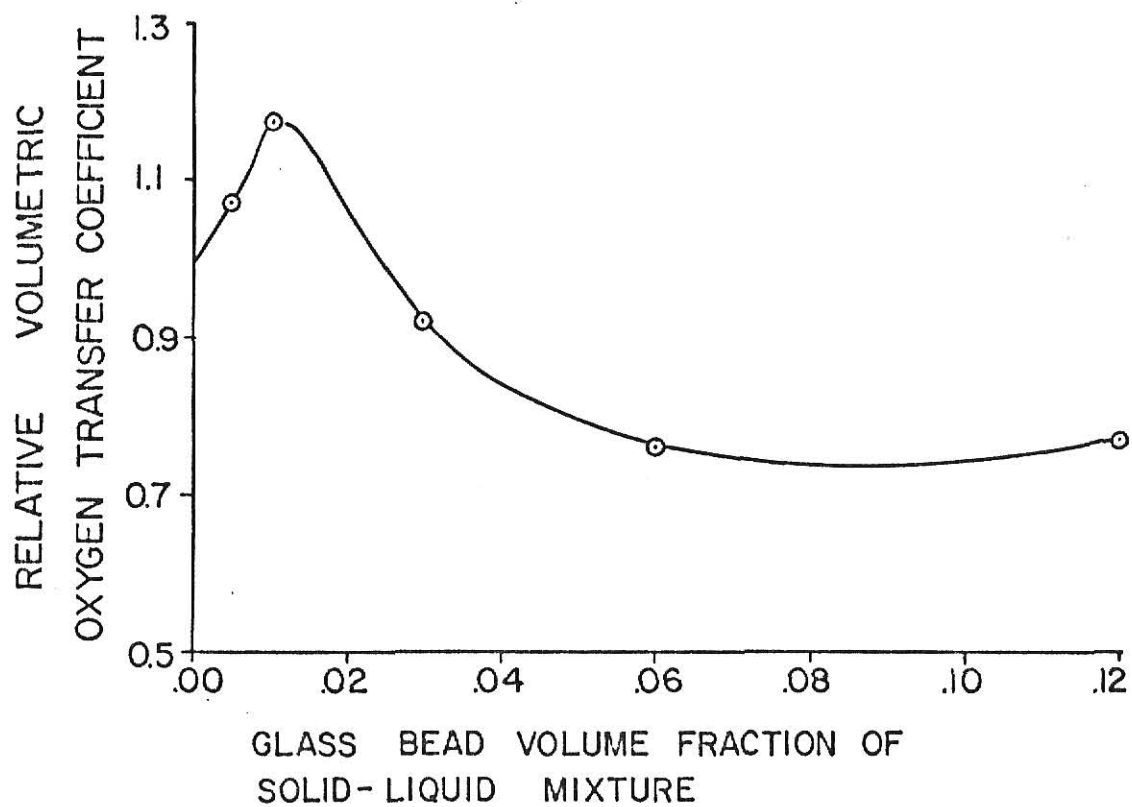


Fig. 15 Volumetric oxygen transfer coefficients for air-water-glass bead system. $K_a = 1.61 \text{ min}^{-1}$ for air-water system.

CHAPTER THREE

OXYGEN TRANSFER AND MIXING IN AN AERATION TOWER CONTAINING STATIC MIXERS

INTRODUCTION

Gas absorption towers can be used for oxidation of activated sludge effluent or biologically active wastewaters^(1,2). Hsu⁽³⁾ reported values for volumetric oxygen transfer coefficients in towers with and without static mixers, using water and oxygen as the liquid and gas phases. Flow rates used were in the range useful for activated sludge treatment. Systems used included a bubble column, a sieve tray column, and a column containing Koch static mixers⁽⁴⁾. His analyses were based on both a plug flow model and a perfect mixing model. However, as he indicated, these systems were most likely not well represented by either model. In the work reported here, dispersion coefficients were experimentally determined in a column nearly identical to that used by Hsu which contained Koch static mixers. Based on a dispersion model, then, volumetric oxygen transfer coefficients were calculated from the data of Hsu.

THEORETICAL ANALYSIS

The macroscopic mass balance for a species in one phase of a multi-phase system is given by (5,6)

$$\frac{\partial C}{\partial t} + v \cdot \nabla C = \nabla \cdot (D \cdot \nabla C) + \sum_i K_i a_i (C_i^* - C) + P + \sigma \quad (1)$$

where all variables except t are the time averaged values of the volume averaged instantaneous quantities. This equation can be nicely applied to a gas absorption tower system. Reasonable assumptions that allow simplification of Equation (1) are that radial mixing in the tower is perfect, that the dispersion coefficient is independent of position, and that resistance to mass transfer occurs only between the bulk of the gas and the liquid phases. The first assumption was visually observed with the aid of a dye tracer to be satisfied in the tower unit studied. The third assumption is always valid in a gas absorption system where only two phases are present, and is generally valid in a biological oxidation system if the oxygen concentration in the aqueous phase is large enough to ensure that the biological reaction rate or the oxygen diffusion rate within cell flocs⁽⁷⁾ limits the rate of oxygen uptake by the organisms. With these assumptions, and the further requirements that the system is at a steady-state and that the source term σ can be neglected⁽⁵⁾, Equation (1) can be reduced to

$$v \frac{dC}{dz} = D \frac{d^2 C}{dz^2} + Ka(C^* - C) + P \quad (2)$$

By substituting $Z = z/L$, $U = (C^* - C)/(C_o^* - C_o)$, and rearranging, Equation (2) becomes

$$\left(\frac{D}{vL}\right) \frac{d^2 U}{dZ^2} - \frac{dU}{dZ} + \left(\frac{KaL}{v}\right) U + \frac{PL}{v(C_o^* - C_o)} = 0 \quad (3)$$

In a biological oxidation system, the production term represents the oxygen uptake rate of microorganisms. If a specific growth rate of the organisms can be described by

$$\mu = \mu_{\max} G$$

where G is a dimensionless function of the concentrations of one or more substrates and of diffusion phenomena within flocs of cells, then

$$P = -\frac{\mu X}{Y} = -\frac{\mu_{\max} G X}{Y}$$

Equation (3) then becomes

$$\left(\frac{D}{vL}\right) \frac{d^2 U}{dZ^2} - \frac{dU}{dZ} + \left(\frac{KaL}{v}\right) U = \left(\frac{\mu_{\max} L}{v}\right) \left[\frac{G_o X_o}{Y(C_o^* - C_o)} \right] W \quad (4)$$

where $W = \frac{XG}{X_o G_o}$. C_o and X_o may be chosen as the feed or exit values, or any other values. Four dimensionless groups appear in Equation (4):

$$N_D = \frac{D}{vL} = \text{Dispersion Number}$$

$$N_A = \frac{KaL}{v} = \text{Absorption Number}$$

$$N_G = \frac{\mu_{\max} L}{v} = \text{Growth Number}$$

$$N_Y = \frac{G_o X_o}{Y(C_o^* - C_o)} = \text{Yield Number}$$

If C_o , G_o , and X_o are chosen to be the feed concentrations, and U and W are functions only of Z , then a system described by Equation (4) is characterized by the above four dimensionless groups and the exit values of U and W . And in some cases W may be assumed independent of Z . For example, if cell growth follows Monod kinetics⁽⁸⁾ and

$$G = \frac{S}{K_s + S}$$

where S is some substrate concentration, then

$$W = \frac{X S (K_S + S_o)}{X_o S_o (K_S + S)},$$

and it could well be that W is approximately constant throughout the reactor. Generally, however, both X and S , and thus W , will be functions of Z , and so expressions relating X and S with Z will be needed to solve Equation (4). Heydweiller ⁽⁹⁾ has modeled the effects of cell sedimentation on cell concentration within an activated sludge tower system. It is well to remind the reader at this point that Equations (2), (3), and (4) are only valid when resistance to oxygen transport to the organisms or flocs is negligible.

Oxygen transfer coefficients are often determined for a particular absorption unit when no reacting species is present; this simplifies comparing oxygen transfer efficiencies ⁽¹⁰⁾ with other types of equipment. For a tower system containing no reacting species, Equation (3) reduces to

$$N_D \frac{d^2 U}{dZ^2} - \frac{dU}{dZ} + N_A U = 0 \quad (5)$$

For the tower systems discussed in this report, Danckwerts' boundary conditions ⁽¹¹⁾ are suitable to use in solving Equation (5). These boundary conditions are

$$U = 1 + N_D \frac{dU}{dZ} \quad \text{at} \quad Z = 0$$

$$\frac{dU}{dZ} = 0 \quad \text{at} \quad Z = 1.$$

The solution to Equation (5) is then ⁽¹²⁾

$$U_e = \frac{4 b \exp(1/2N_D)}{(1+b)^2 \exp(b/2N_D) - (1-b)^2 \exp(-b/2N_D)} \quad (6)$$

where $b = \sqrt{1+4N_A N_D}$. Thus, if values of the dispersion number and the exit dimensionless concentration are known for the steady-state operation of a given tower unit, values of the absorption number can be determined.

Values of the dispersion number can be found for an absorption tower system using a steady-state tracer technique. For a tracer species soluble in the liquid phase, equation (1) applied to the liquid phase can be simplified to

$$N_D \frac{d^2 C}{dZ^2} - \frac{dC}{dZ} = 0 \quad (7)$$

C now represents the tracer concentration in the tower. The solution to equation (7) is

$$C = C_1 \exp(Z/N_D) + C_2$$

where C_1 and C_2 are integration constants. Now if tracer solution is injected at some point along the tower, equation (7) must be solved separately for the sections of the tower above and below the point of injection. An overall mass balance on the tracer within the tower is given by

$$\beta F C_t = (1+\beta) F C_e$$

or
$$C_e = \left(\frac{\beta}{1+\beta}\right) C_t$$

where C_t is the concentration of the tracer in the injected solution, C_e is the tracer concentration in the exit stream of the tower, and β is the tracer solution feed rate divided by the liquid feed rate to the tower.

Below the injection point

$$C = N_D \frac{dC}{dZ} \text{ at } Z=0$$

and C is continuous at the point of injection. Above the point of injection the following constraints apply:

$$C = \left(\frac{\beta}{1+\beta}\right) C_t \quad \text{at } Z = 1$$

$$\frac{dC}{dZ} = 0 \quad \text{at } Z = 1.$$

The solution to Equation (7) for the lower section of the tower is then

$$\frac{C}{C_t} = \left(\frac{\beta}{1+\beta}\right) \exp\left(-\frac{Z-Z_t}{N_D}\right)$$

where Z_t is the height at which tracer is injected. The dispersion number and the dispersion coefficient are then given by

$$N_D = \frac{\ln\left[\frac{C}{C_t} \left(\frac{1+\beta}{\beta}\right)\right]}{Z - Z_t}$$

and

$$D = \frac{vL (Z - Z_t)}{\ln\left[\frac{C}{C_t} \left(\frac{1+\beta}{\beta}\right)\right]}$$

The average liquid velocity in the lower section is given by

$$v = \frac{F}{\epsilon A}$$

where ϵ is the gas hold-up and A is the cross-sectional area of the tower.

Thus, the dispersion number and dispersion coefficient can be calculated

if the tracer concentration is known at a given height in the tower.

EXPERIMENTAL METHODS AND MATERIALS

The mixing experiments were carried out in a three-inch inside diameter glass column containing three Koch static mixers (BY whole element type)⁽⁴⁾. Tap water was fed at the base of the column and exited to a drain from an overflow sidearm. The liquid level was thus maintained at a height of 25 inches from the bottom of the column. The Koch mixers used are 3 inches in diameter and 3 inches long, and were placed 2.5 inches from the bottom. Air was fed at the bottom of the column through a .25 inch inside diameter pipe with no sparger, diffuser, or other device attached. The water flow rate was monitored with a Fischer and Porter Flowrator rotameter, and the air with a Brooks rotameter. Liquid flow rates ranged from .22 to 1.73 liters per minute, and gas flows from .8 to 10 liters per minute.

The steady-state method discussed previously was employed to obtain dispersion information. Either a salt solution (NaCl, 100 g/l) or a dye solution (Durkee green food color, .0625 g/l) was continuously injected into the center of the column at a position 22.5 inches from the bottom, while water and air were continuously being fed to the column. When the tracer concentration reached a steady value, it was measured at a sampling point 8.5 inches from the bottom of the column. The salt solution conductance was measured with a Beckman conductivity cell (model CEL-G1), which was inserted into the column, and a Thomas Serfass conductivity bridge manufactured by Beckman Instruments, Inc. The conductance was correlated with concentration using salt solutions of known concentrations. The dye concentration was determined by the colorimetric method using a Bausch and Lomb Spectronic 20 spectrophotometer. The transmission of the solution was correlated with the concentration. The tracer solution flow rate ranged from 2.3% to 7.0% of the tap water flow rate.

The gas hold-up in the column was determined for various gas and liquid flow rates. By simultaneously terminating the flow of air and water to the column, the volume of water remaining was measured and compared with the liquid volume in the column when the air flow rate was zero.

RESULTS AND DISCUSSION

Values of the gas hold-up, shown in figure 1 , vary nearly linearly with gas flow rate, and are slightly affected by a change in the liquid flow rate. Values obtained for the dispersion coefficient, shown in figure 2 , depend on the liquid flow rate and decrease rapidly at low flow rates. The points plotted in figure 2 are an average of values resulting from the salt tracer and dye tracer experiments. The data points are scattered, and only a weak dependence on gas flow rate is apparent. Values of the ratio of the liquid velocity and the dispersion coefficient are shown in figure 3 . The values of D used to determine v/D are the average for the range of gas flow rates at a given liquid flow rate, represented by the line in figure 2 . It was felt that this ratio of v/D would be more representative of the same ratio in Hsu's (3) column than would values of D from figure 2 be of values of D in Hsu's column.

Peclet numbers (the inverse of the dispersion numbers) were then calculated from the values in figure 3 and the liquid height of Hsu's column (80.4 cm.). With these values of the Peclet number and Hsu's data⁽¹³⁾ for the corresponding dimensionless exit concentrations, the values of the absorption number were calculated from equation (6) using a simple numerical search technique. Values of the volumetric oxygen transfer coefficient were then obtained using Hsu's data⁽³⁾ for gas hold-up values. In figures 4 through 8 are plotted the values of K_a obtained from the perfect mixing, dispersion, and plug flow models. Indeed it is observed that neither the perfect mixing nor the plug flow model adequately describes the system. As the liquid flow rate is increased, the liquid phase approaches plug flow, as shown in figure 8 . It also appears that little improvement in the rate of oxygen transfer from the gas to the

liquid phase would result by using gas flow rates above 8 liters/min. (which is a superficial gas velocity of 2.92 cm./sec.). Liquid flow rates should be greater than 1.4 liters/min. (which is a superficial gas velocity of 0.51 sm./sec.) to maximize the rate of oxygen transfer.

NOMENCLATURE

A	cross-sectional area
a	interfacial area
C	concentration of oxygen or tracer
D	dispersion coefficient
F	liquid feed flow rate
G	dimensionless organism growth function
K	mass transfer coefficient
K_s	saturation constant
L	liquid height in column
N_A	absorption number
N_Y	yield number
N_D	dispersion number (reciprocal of Peclet number)
N_G	growth number (dimensionless maximum specific growth rate)
P	volumetric production rate
S	substrate concentration
t	time
U	dimensionless concentration
v	velocity
W	product of dimensionless organism concentration and dimensionless organism growth function
X	organism concentration
Y	yield, or mass of organisms produced per unit mass of oxygen consumed
Z	dimensionless axial distance
z	axial distance

Greek Letters

β	fraction that injected tracer solution flow rate is of the liquid feed flow rate
ϵ	gas volume fraction or hold-up
μ	specific growth rate of organisms
μ_{\max}	maximum specific growth rate of organisms
σ	source term resulting from time averaging

Superscripts

- i denotes equilibrium condition with the i phase
- * denotes equilibrium condition with the gas phase

Subscripts

- e exit stream value
- i value in common with or with respect to the i phase
- o reference value
- t tracer feed

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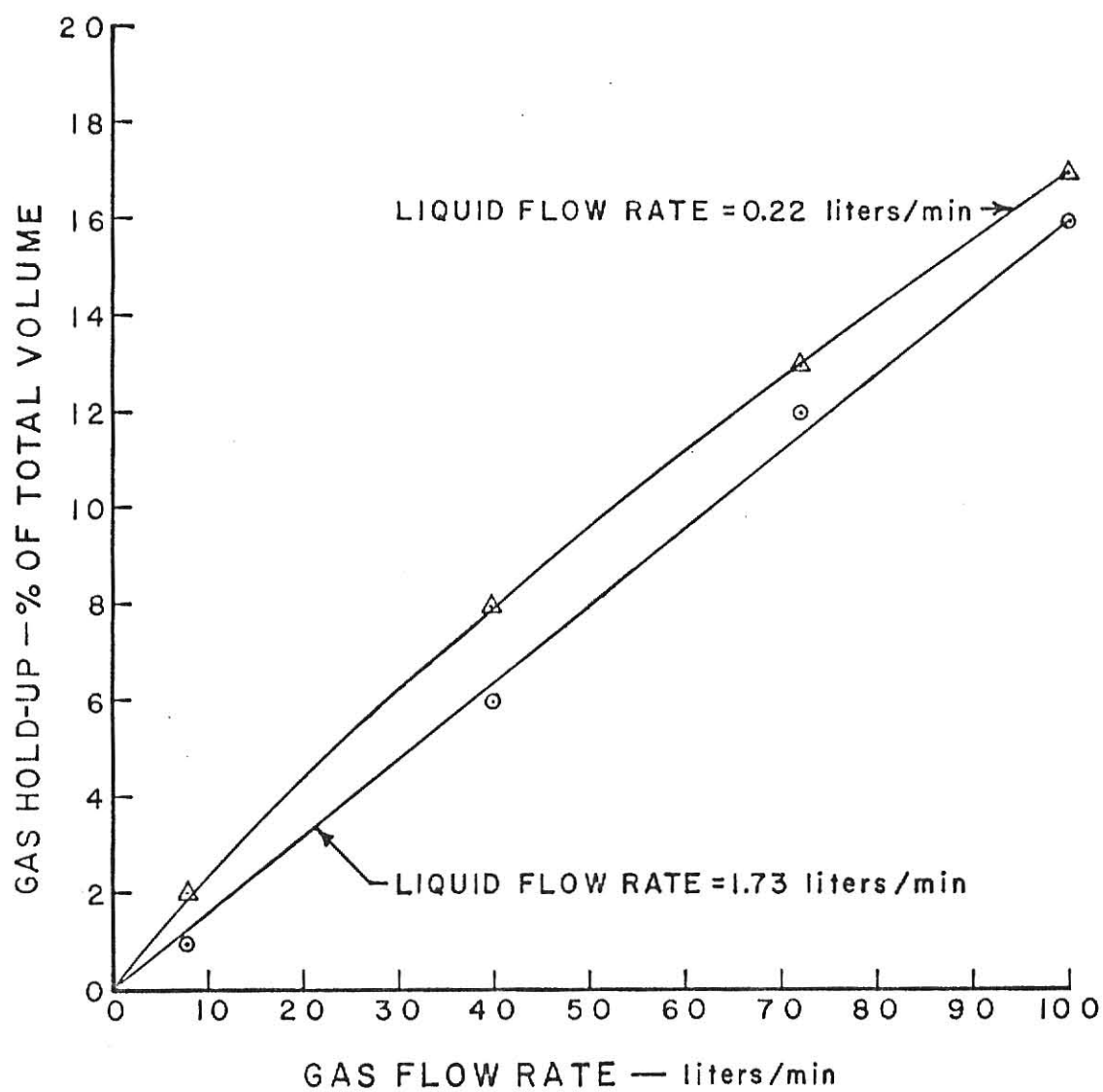


Fig. 1 Gas hold-up in a 7.62 cm diameter column containing Koch static mixers

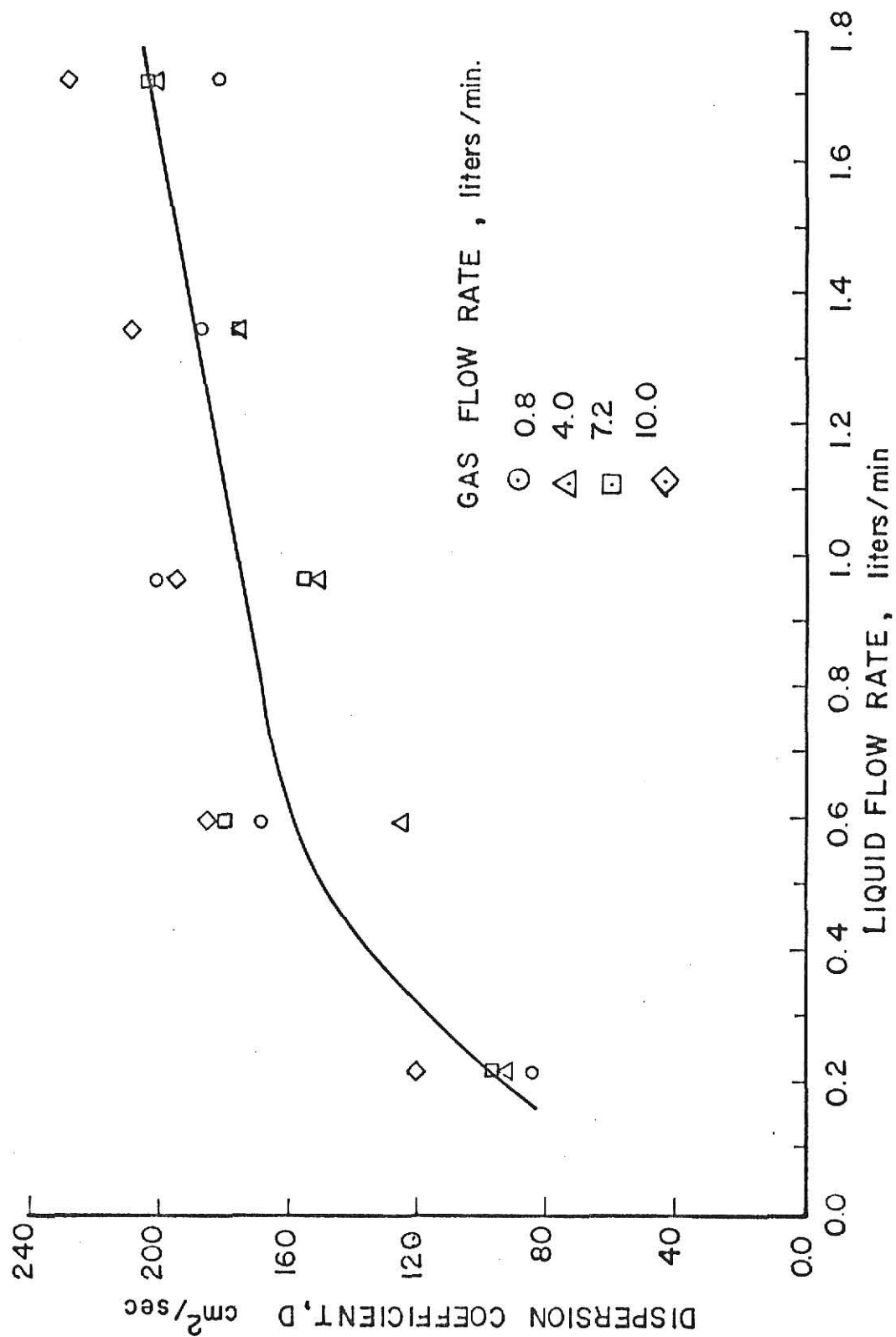


Fig. 2 Dispersion coefficients in a 7.62 cm diameter column containing Koch static mixers

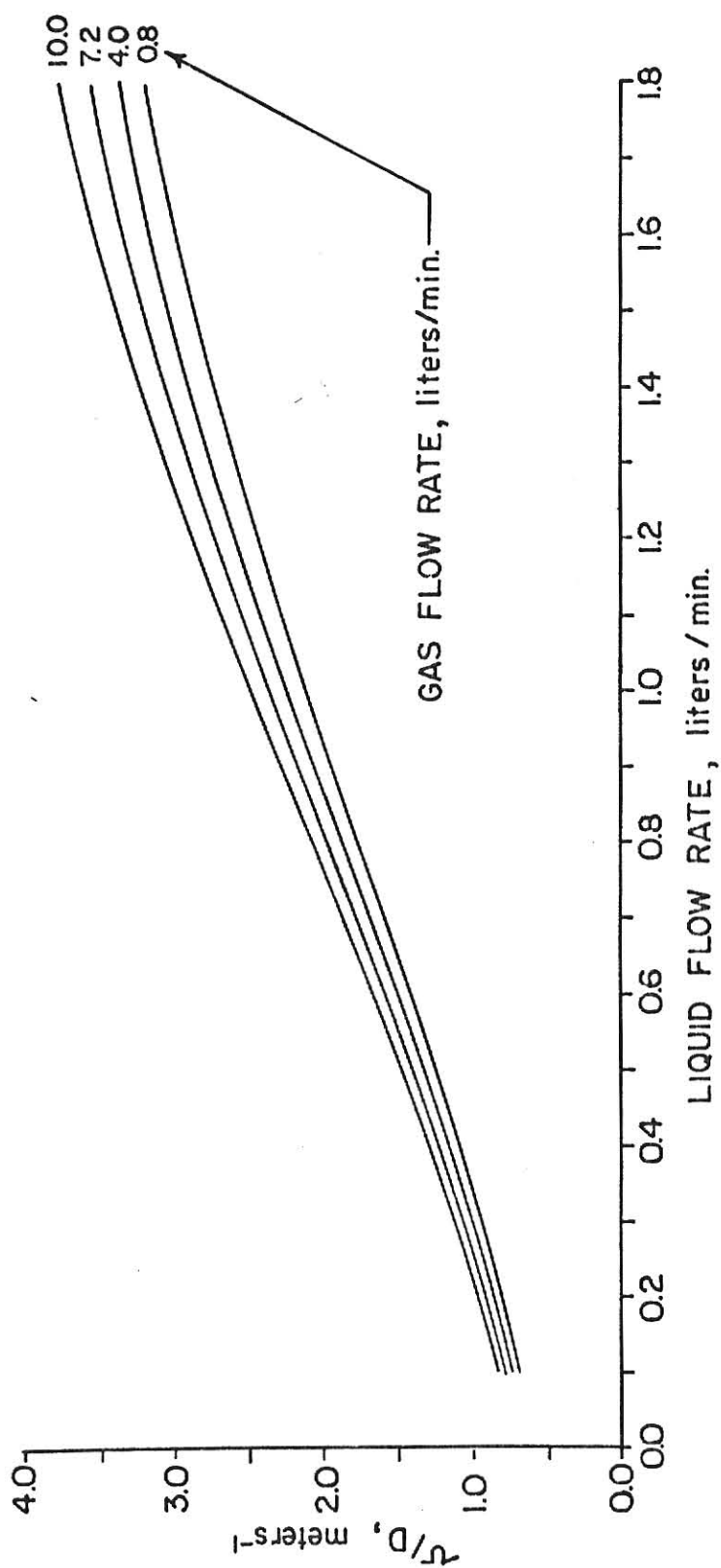


Fig. 3 Effect of the liquid flow rate on the ratio of the liquid velocity and the dispersion coefficient in a 7.62 cm diameter column containing Koch static mixers

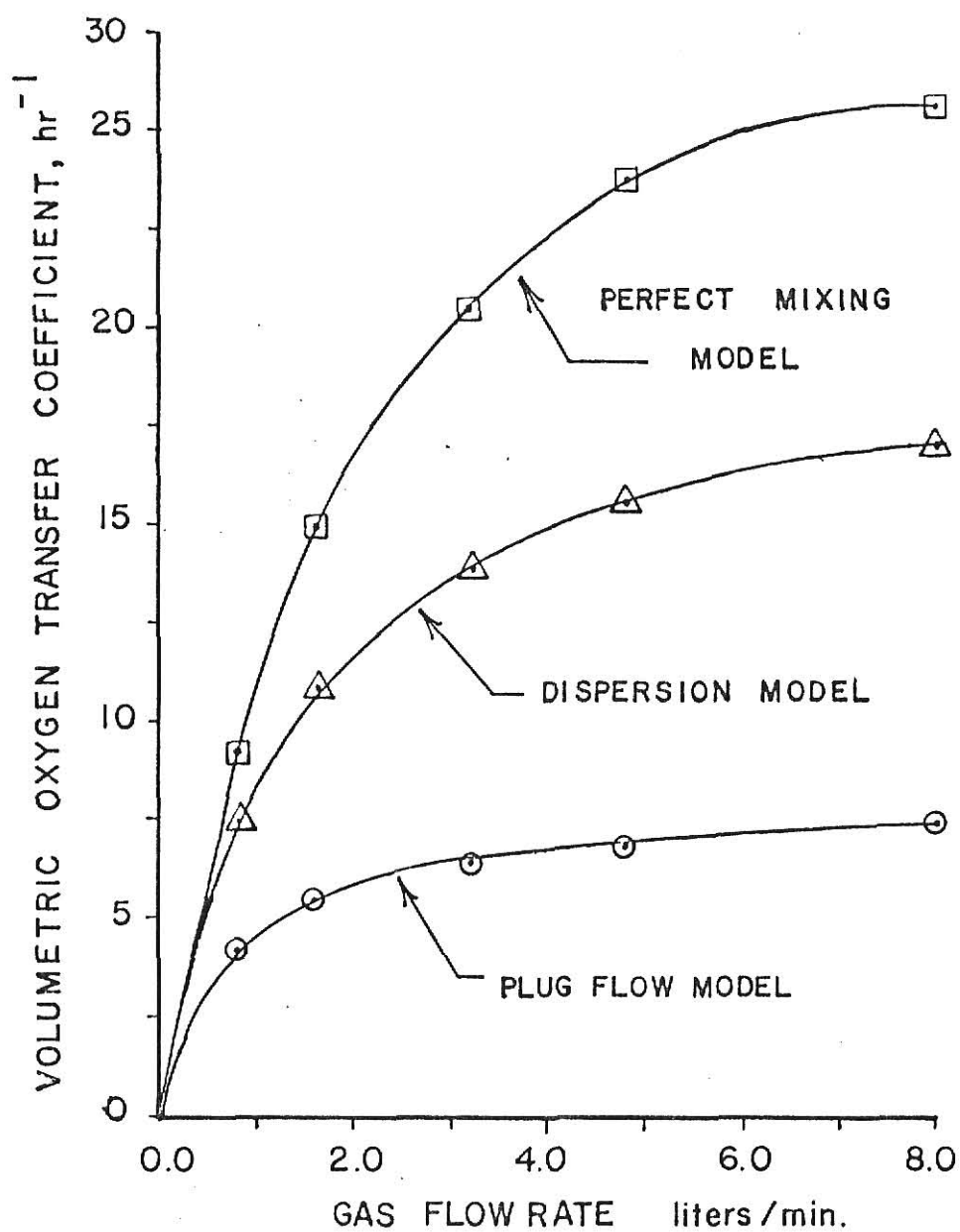


Fig. 4 Oxygen transfer coefficients in a 7.62 cm diameter column containing Koch static mixers with liquid flow = 0.18 liters/min

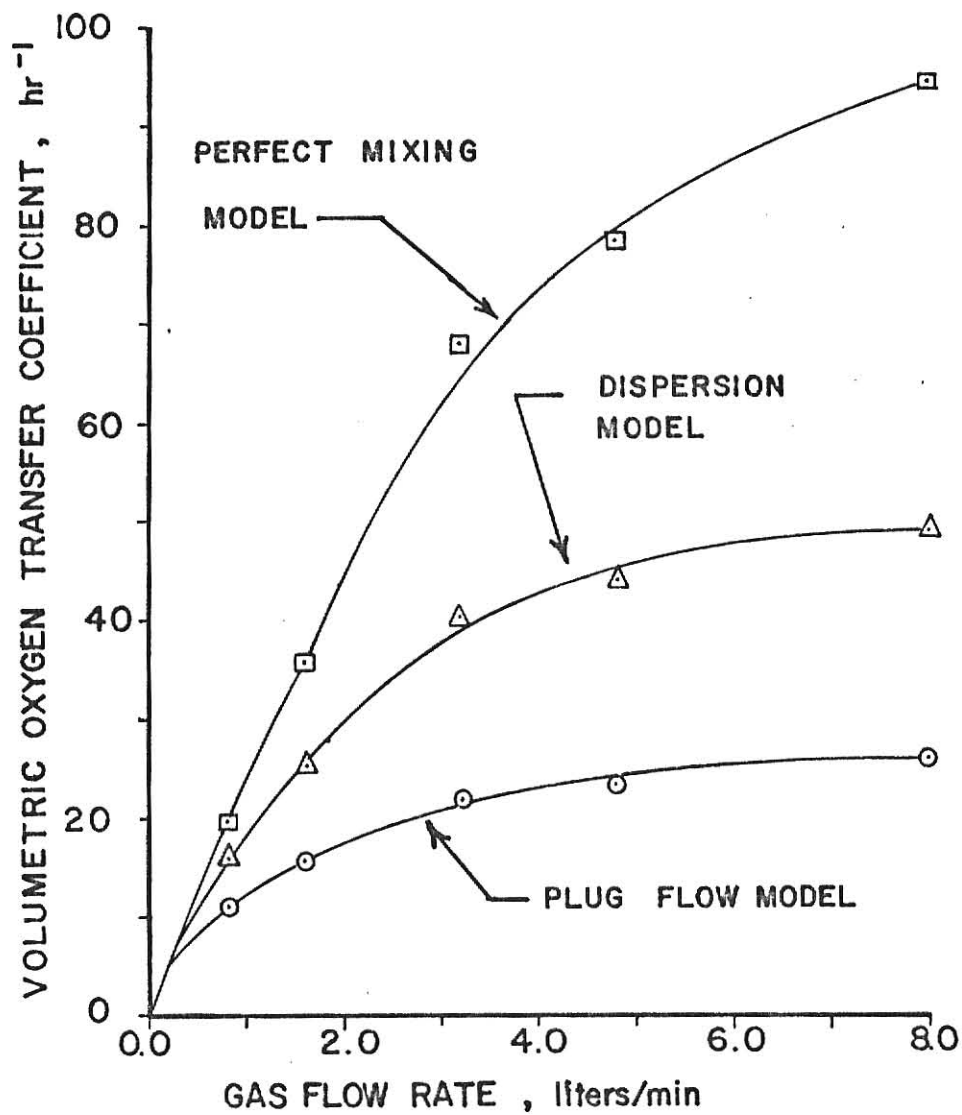


Fig. 5 Oxygen transfer coefficients in a 7.62 cm diameter column containing Koch static mixers with liquid flow rate = 0.64 liters/min

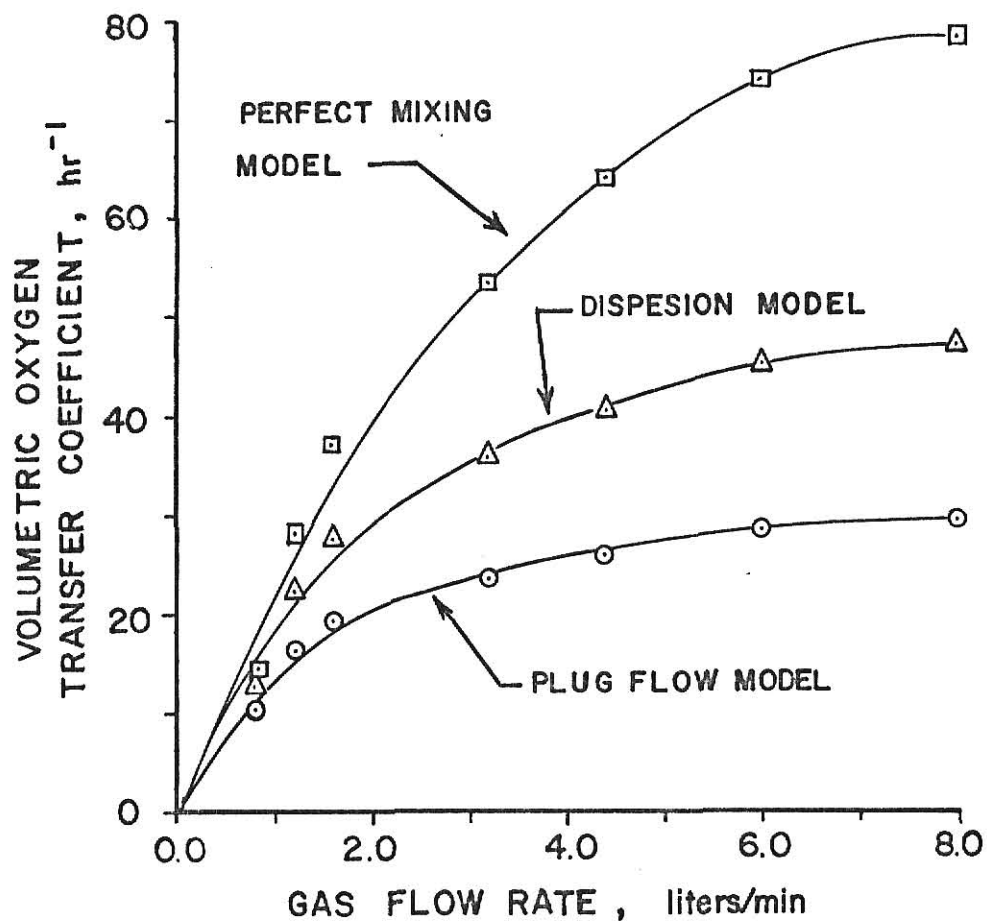


Fig. 6 Oxygen transfer coefficients in a 7.62 cm diameter column containing Koch static mixers with liquid flow rate = 0.93 liters/min

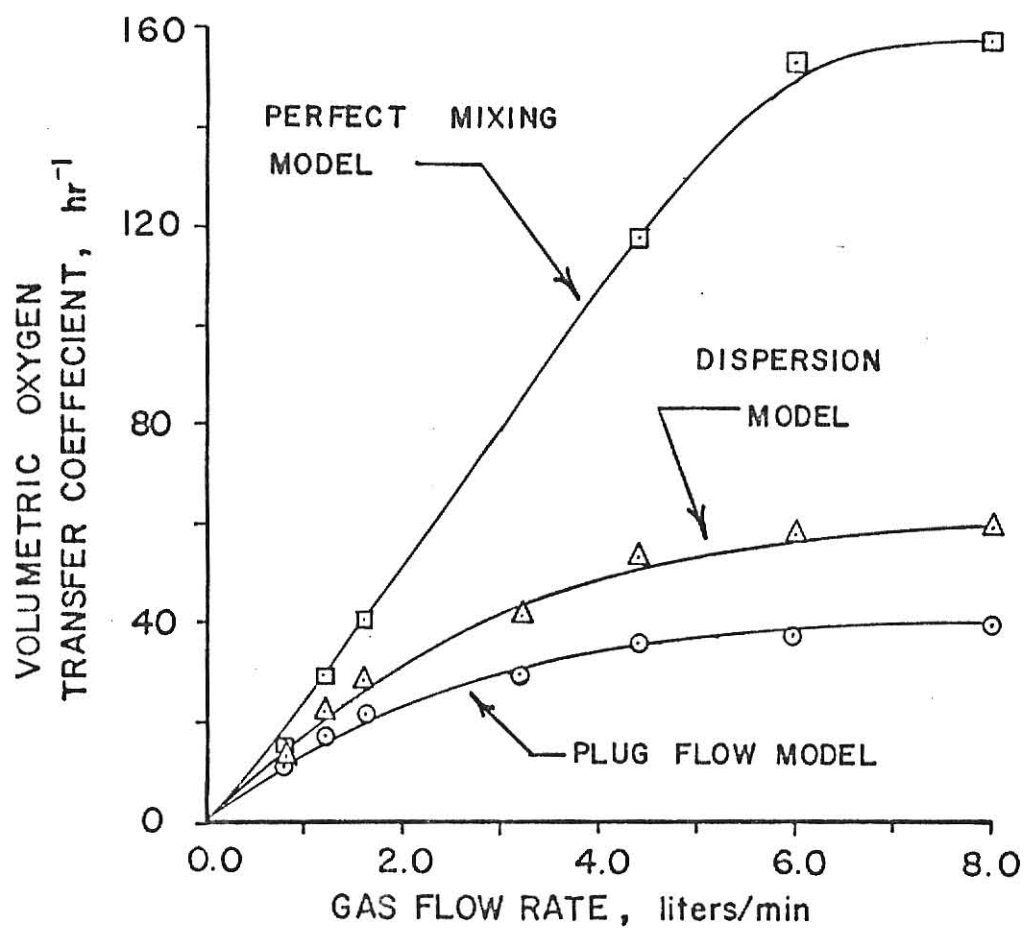


Fig. 7 Oxygen transfer coefficients in a 7.62 cm diameter column containing Koch static mixers with liquid flow rate = 1.30 liters/min

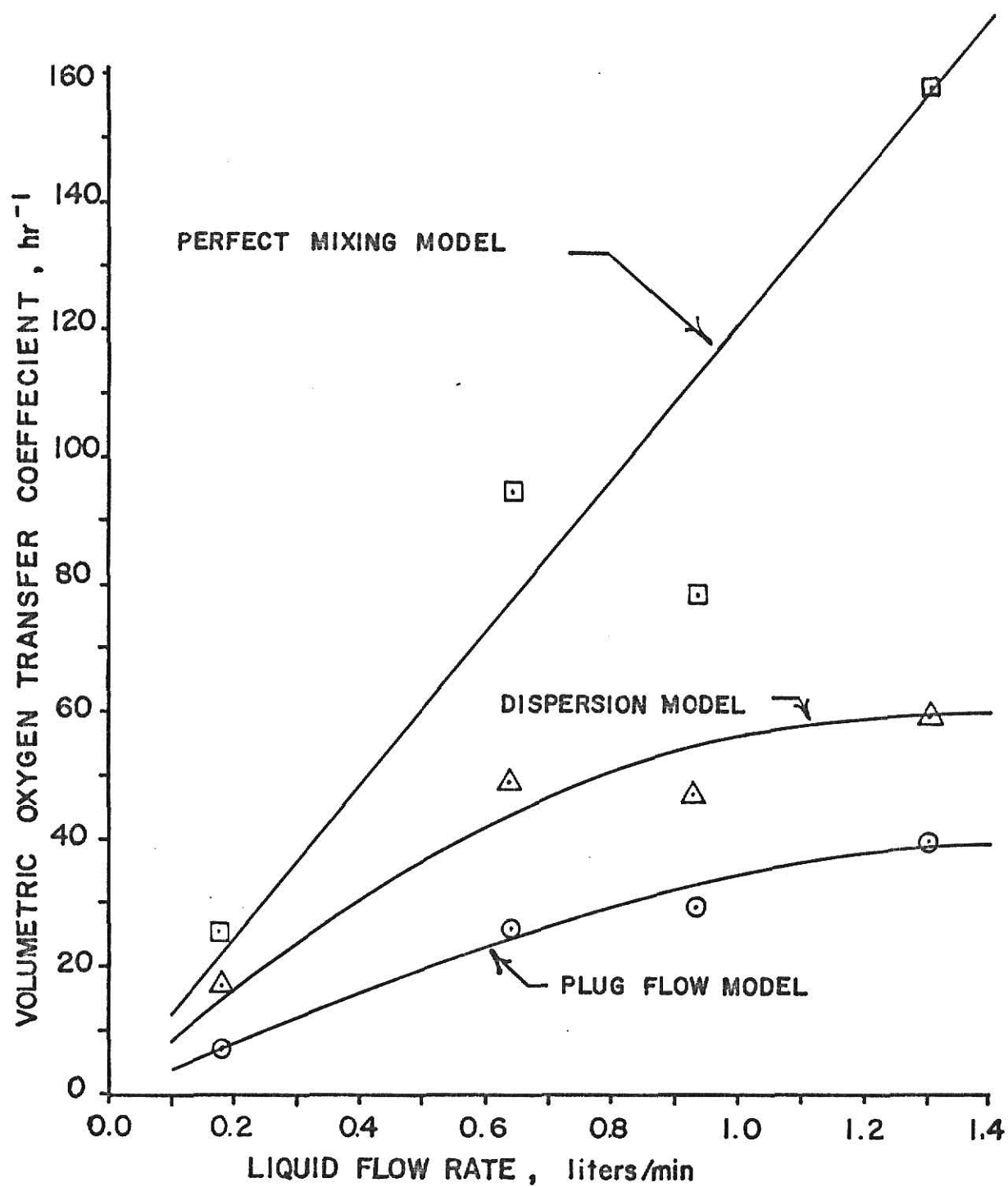


Fig. 8 Oxygen transfer coefficients in a 7.62 cm diameter column containing Koch static mixers with gas flow rate = 8.0 liters/min

OXYGEN TRANSFER IN AERATED SYSTEMS
CONTAINING ONE AND TWO LIQUID PHASES

by

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Oxygen transport phenomena were studied in hydrocarbon fermentation systems and in other systems containing two liquid phases. A dynamic model describing oxygen transfer is derived, and simulations of the aqueous phase oxygen partial pressure response to a step change in the gas phase partial pressure are presented. Values of the volumetric oxygen transfer coefficient for transport between the gas and aqueous phases were estimated from experimental data, and they were found to decrease as the hydrocarbon volume fraction of the liquid increased. The presence of extracellular products caused a decrease in the values, while the presence of respiring cells caused an increase. Efforts to estimate values of the coefficients for transfer between the gas and hydrocarbon phases and between the aqueous and hydrocarbon phases were unsuccessful.

Oxygen transport was also modeled in towers for systems containing one liquid phase. Dispersion coefficients and volumetric oxygen transfer coefficients were determined for a gas-water system in a tower containing static mixers. The gas flow rates used were in the range suitable for wastewater treatment. It was found that considerable axial mixing occurred in the liquid phase of the system, but that perfect mixing could not be assumed. A dispersion model appeared to adequately describe the system.