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ABSTRACT

This paper reports on the status of (1) preliminary results from the two phase hydrodynamic study and (2) the development of a new measurement technique in the project titled : Fischer-Tropsch Slurry Reactor Modeling.

Hydrodynamic studies were conducted in a hot pressurized bubble column reactor. The hydrodynamic properties in a 10.16-cm diameter bubble column with a 5 x 1-mm perforated-plate gas distributor were studied from atmospheric pressure to 1.36 MPa, and from ambient temperature to 265 °C, using a dual hot-wire probe, with nitrogen as the gas phase and Drakeol-10 oil as the liquid phase. Preliminary data show that the gas holdup in the column increased as temperature increased. The opposite trend is found on the bubble size. The bubble size decreases with increasing pressure and temperature at a constant superficial gas velocity.

An ultrasonic technique is under development for measuring solids concentrations in a three-phase slurry reactor. Preliminary measurements have been made on slurries consisting of water, glass beads, and air bubbles. The data show that both the sound speed and attenuation are well-defined functions of both the solid and gas concentrations in the slurries. A simple model is proposed to correlate the solids concentrations with the measured ultrasonic signals.

OBJECTIVE

The objectives are to study the hydrodynamics in a hot pressurized bubble column reactor that can be used for reliable design of F-T slurry-bubble-column reactors and to develop a new technique for the direct measurement of catalyst concentrations in the slurry-bubble-column reactor. The ultimate goals are to develop a data base which would provide reliable estimates of hydrodynamic parameters relevant to a F-T slurry-bubble-column reactor.

INTRODUCTION

The application of the three-phase slurry-bubble-column reactor system for coal liquefaction processing has recently received considerable attention. Slurry-bubble-column Fischer-Tropsch (F-T) reactors have many advantages over other types of F-T reactors. Among them are low capital/operating costs, good temperature control of the F-T reaction, the ability to utilize a low H_2/CO ratio synthesis gas, low carbon deposition on the catalyst, and small mass-transfer resistances.

Designing and efficiently operating a three-phase slurry reactor requires an understanding of the hydrodynamic parameters and the degree of dispersion of the catalyst in the reactor.

The important hydrodynamic factors in the operation of a slurry-bubble-column reactor are the gas bubble size, gas holdup, and flow regimes. Extensive work on the hydrodynamic measurements in two-phase systems has been reported in the literature and has been reviewed by several authors (1,2); however, the majority of these studies have been limited to the air-water system. Hydrodynamic measurements using molten wax (typical slurry medium) as liquid medium are rather limited (3-6). Different hydrodynamic behavior (e.g., Sauter mean-bubble diameter, gas holdup) was reported in these studies for similar physical properties of wax. As indicated by Bukur et al.(3), different waxes, despite similar physical properties, show dissimilar hydrodynamic behavior. A possible cause for the different hydrodynamic behavior is the flow regime which exists in a particular bubble column. As indicated by Smith et al.(7), at least four flow regimes have been identified: homogeneous bubbling, transition, churn-turbulent, and slug flow (for small diameter columns). A comprehensive flow regime map for a range of F-T slurry reactor conditions remains to be developed. It has become clear that additional experimental data is required on the hydrodynamic behavior of slurry-bubble-column reactor systems that employ operating conditions and liquid-phase media like those in F-T slurry reactors. This information is necessary for reliable design/scaleup of F-T slurry reactors.

One of the important issues that needs to be fully understood in the slurry-bubble-column reactor is the degree of dispersion of the catalyst in the reactor. The distribution of catalyst (solids) concentration down the reactor greatly affects the operation of the slurry-bubble-column reactor. A number of empirical studies have been reported which show that nonuniform distributions of catalyst concentration can result even for small particles and well-agitated (by gas flow) slurry-bubble-column reactors (8-11). While such non-uniform distributions have been shown to occur using cold flow experiments which permit quantification more easily, measurements under reaction conditions are much more difficult. However, without such measurements, it is difficult to fully understand the influence of various reaction, reactor, and catalyst parameters on the catalyst concentration profile in the reactor or to discern the effect of catalyst distribution on the overall conversion, product selectivity, and possible catalyst deactivation. Extensive calculations to predict the effect of nonuniform catalyst distribution on the performance of a slurry-bubble-column reactor under Fischer-Tropsch synthesis have been reported in the literature (12,13). These results suggested that there can be significant non-uniformity of catalyst distribution for small diameter slurry-bubble-column reactors (column diameter < 30 cm). Therefore, the direct measurement of catalyst concentration under reaction conditions must be made. The most obvious methods of making this measurement, such as optical and direct sampling, suffer from either a need to perturb the reaction system or a difficulty of measurement because of high pressure, temperature, or opaqueness of the slurry phase (14,15). Recently, a method involving the measurement of ultrasound transmission has been reported in a slurry-phase stirred tank reactor which offers the possibilities of using the ultrasonic technique for the measurement of solids concentration in a three-phase slurry reactor (16). Since the velocity of sound is significantly different in a liquid (1324 m/sec at 25°C for kerosene) compared to that in a solid (5968 m/sec at 25°C for fused silica), a phase shift and an amplitude change in the sound wave relative to that for the pure liquid can be detected when solid particles are present. Figure 1 shows how the detected sound wave is changed in time and in amplitude when solids are suspended in a liquid. Okamura et al. (16), used a continuous stirred tank reactor to correlate solids concentration to the relative phase shift $[(t_a-t_b)/t_o$ where t_o is the travel time of the sound wave between the transmitter and the receiver]. Thus, the solids concentration in a slurry reactor can be measured by sending an ultrasonic pulse across the slurry and measuring the amplitude and phase shift of that portion of the transmitted pulse received at the opposite side of the reactor. Then, comparing the values with those for known concentrations, the solids concentration is determined from the measured signal. The successful development of this ultrasonic technique permits the direct measurement of catalyst concentration during reaction in a bubble column slurry reactor.

EXPERIMENTAL

A schematic diagram of this slurry-bubble-column reactor is shown on Figure 2. The unit consists of two stainless steel columns, each of which has an internal diameter of 10.16 cm and a height of 244 cm. The wax melt column is utilized to store and melt the wax. The main column in which the hydrodynamic studies were conducted has 12 different axial locations for data collection. Experiments were conducted in batch-mode operation - continuous flow of gas and a stationary liquid. The feed nitrogen was metered with a mass flow meter, passed through a preheater into the gas distributor, and into the main column. The gas distributor was a 5 x 1-mm perforated-plate. The effluent from the reactor was passed through a cold trap, a back-pressure regulator, a wet-test meter, and vented into a hood.

The local gas holdup, bubble diameter, bubble velocity, and bubble size distribution were measured by inserting a dual hot-wire probe horizontally into the column at any of the 12 positions and moving it to the desired radial position. The details of the dual hot-wire probe were described elsewhere (17,18). The local gas holdup was determined from the ratio of the measured signal's time in the gas phase to its total sampling time at the given location. The bubble diameter was calculated from the time lag in the signals from the two sensing tips (the time difference between the bubble encountering the first hot-wire and the second hot-wire), using the known time of duration of the signals and the distance between the sensing tips (19).

The hydrodynamic parameters were measured by the dual hot-wire probe at 30, 50, 71, 111, and 132 cm above the gas distributor in the bubble column. The experiments were conducted at temperatures ranging from 20 °C to 200 °C, at pressures from 0.1 to 1.36 MPa, and at superficial gas velocities of up to 9 cm/sec with the Drakeol-10 oil as the liquid-phase medium and nitrogen as the gas-phase medium.

The details of the experimental setup for the ultrasonic investigation have been reported elsewhere (20). The basic setup consisted of a reactor 10.16 cm in diameter and 60 cm in length. Air bubbles were introduced through a sintered frit at the bottom of the reactor, while the slurry was mechanically agitated by a motor-driven stirrer. The physical location of the stirrer was slightly off the center in the reactor so as not to interfere with the transmitted ultrasonic signals. The air flow was controlled electronically to a maximum of 200 ml/min through a mass flow controller. Glass beads (50 to 180 microns in diameter) were used as the solid in the slurry. The solids concentrations (solid weight/total weight) were varied from 1 wt% to 20 wt%. Ultrasonic measurements were made by using a computer-based TestPro system, manufactured by Infometrics, Inc.

RESULTS

TWO PHASE HYDRODYNAMIC STUDY

Figure 3 shows the effect of temperature on the average gas holdup as a function of superficial gas velocity under a constant reactor pressure of 0.1 MPa. The average gas holdup was found to increase with an increase in superficial gas velocity and temperature. At 20 °C, the average gas holdup increased approximately linearly with increasing superficial gas velocity. It increased from 0.004 at a gas velocity of 0.7 cm/sec to 0.13 at a superficial gas velocity of 6 cm/sec. At a higher reaction temperature of 200 °C, there was a significant increase in the average gas holdup at a given value of the superficial gas velocity. It increased linearly from 0.15 at a superficial gas velocity of 0.7 cm/sec to 0.33 at a superficial gas velocity of 4.4 cm/sec.

Figure 4 illustrates the effect of superficial gas velocity on the average gas holdup for experiments conducted under two different pressures (0.1 vs. 1.36 MPa) with a constant reactor temperature of 200 °C. The average gas holdup was found to increase linearly with increasing superficial gas velocity. It can be seen from the data that the reactor pressure has only a slight effect on the observed average gas holdup. The average gas holdup increases slightly with increasing pressure at a constant temperature.

Figure 5 illustrates the Sauter mean bubble diameters versus the superficial gas velocity at two different temperatures (20 vs. 200 °C) under a constant pressure of 0.1 MPa. The temperature has a significant effect on the Sauter mean bubble diameter. It was approximately 1.5 cm at 20 °C; however, it decreased to approximately 4 mm as the temperature increased to 200 °C. The effect of superficial gas velocity on the Sauter mean bubble diameter can be demonstrated in Figure 3. The Sauter mean bubble diameter profiles in the bubble column were rather uniform at both temperatures. Thus, one can infer that the superficial gas velocity did not have any effect on the Sauter mean bubble diameter.

Figure 6 shows the effect of pressure on the Sauter mean bubble diameter at 200 °C. The results were obtained at the same conditions, except for different pressures. One was obtained at 0.1 MPa, and the other was collected at 1.36 MPa. The bubble size decreased slightly as the pressure was increased, from approximately 4 mm at 0.1 MPa to approximately 3 mm as the pressure increased to 1.36 MPa. It can be clearly seen that pressure did affect the Sauter mean bubble diameter.

ULTRASONIC INVESTIGATION

Figure 7 illustrates the typical data of the ultrasonic signal as affected by 1 wt% of solids (glass beads 80±5 microns). The presence of the solids caused a substantial decrease in the amplitude of the sound wave, as well as a decrease in the transit time (The 1st distinct zero crossing time was determined as the transit time). Figure 8 illustrates the change in amplitude as a function of solids concentration up to 20 wt % (for glass beads 80±5 microns). As can be seen from Figure 8, the average absolute amplitude decreased as the solids concentrations increased from 1 wt% to 20 wt%. The presence of air further decreased the amplitude of the signal. Figure 9 shows the change in the fractional change on transit time $\Delta t/t_o$ ($\Delta t = t_a - t_b$) as a function of solids concentration up to 20 wt % for three different sizes of glass beads–50, 80, and 180 microns. The fractional change on transit time (time ratio) increased as the solids concentration increased, with or without the presence of air (174 ml/min) in the reactor. It is interesting to note that the presence of air did not significantly affect the time ratio. It should be noted that the principal effect of the air bubbles is to improve the suspension of the beads, thereby increasing the attenuation and time ratio over the values obtained with the stirrer alone. Separate tests with air bubbles in the absence of beads confirm that their presence alone causes no effects (20). At solids concentrations above 15 wt% the solids may not be fully dispersed under the current experimental setup and this effect is even more pronounced in the absence of air. This would explain the scattered data in the fractional change on transit time obtained at wt% > 15.

In general, both the amplitude and the fractional change of transit time (or time ratio) were affected by the changing of solids concentrations. It would appear that the time ratio depends mainly on the solids concentration. The size of the solids may not have any effect on the observed fractional change of transit time (or time ratio). This is significant progress in the development of the ultrasonic technique for solids concentration measurement.

DISCUSSION

TWO PHASE HYDRODYNAMIC STUDY

As shown in Figure 3 the average gas holdup increased with increasing superficial gas velocity and with increasing temperature. The effect of temperature is consistent with the results in the literature, i.e., the lower the viscosity of the liquid medium, the higher the gas holdup, since the viscosity of the Drakeol-10 is 44.9 cp at 20 ^{o}C and 1.2 cp at 200 ^{o}C. The trends are in qualitative agreement with results from other studies. Kuo (4) and Shah et al.(2), also reported that the gas holdup increased substantially as the liquid temperature was increased. However, Deckwer et al.(6), reported low gas holdup at higher temperature in a 4.1-cm diameter column, and no change with temperature in a 10-cm diameter column for temperatures greater than 240 ^{o}C. The reason for this discrepancy is unclear; it could be due to the different reactor systems and/or reaction conditions utilized.

It can be seen that the reactor pressure has a slight effect on the observed average gas holdup (Figure 4). Kuo's study (4) also shows similar trends indicating that the effect of pressure on the average gas holdup was insignificant. The slight change in gas holdup with increasing pressure is probably due to the change in bubble size (21) or the scattered experimental data. It has been reported that the bubble size decreases with increasing pressure at a constant superficial gas velocity (21). As can be seen in Figure 6, the bubble size changed from 4 mm to 3 mm as the pressure increased from 0.1 MPa to 1.36 MPa. This would explain the observation of pressure effect on average gas holdup.

The Sauter mean diameter obtained at 200 ^{o}C and 0.1 MPa was about 4 mm (Figure 6). This is consistent with the results in the literature, i.e., Bukur et al.(22), reported diameters of 4 to 5 mm for Mobil wax., Calderbank et al.(23), reported values of 3 to 5 mm under similar reaction conditions. More recently, O'Dowd et al.(25), obtained Sauter diameters in reactor wax using the hot wire probe at 250 ^{o}C and 1.48 MPa. Their values were in the range of 2.7 to 3.9 mm.

ULTRASONIC INVESTIGATION

As can be seen in Figure 8, the amplitude of the transmitted ultrasonic signals decreased as the gas flows and the solids concentrations increased. After the transducer sends an ultrasonic pulse across the slurry reactor, the pulse is partially scattered when it strikes a solid in the slurry. The pulse is partially transmitted through the solid and any air bubbies in the path to the receiver. The amplitude of the transmitted portion of the pulse is measured by the receiver located on the opposite side of the vessel. Therefore, the measured amplitude of the sound wave transmitted through a slurry mixture is expected to be a strong function of the concentration of solids and the presence of gas bubbles. The results illustrated in Figure 9 can be understood by a simple model, in which it is assumed that the presence of particles in the path of the sound wave reduces the transit time because the sound speed in the solid is faster than that in the liquid. If the particles are assumed to be distributed randomly, the time ratio $\Delta t/t_0$ is related to the concentration fraction ω by the equation.

$$\Delta t/t_0 = \alpha\, \omega^{1/3}(1 - v_0/v_1) \qquad (1)$$

Here α is a constant for particles of a given composition and v_0 and v_1 are the sound speeds in the liquid and solid, respectively. A derivation of this equation is reported elsewhere (20). The above equation, which predicts that the time ratio should be independent of the particle size, is approximately the case in experiments presented here for solids well suspended in the liquid phase. However, it is clear that the predicted experimental dependence on solids concentration fraction is not correct, the observed dependence being close to a linear rather than a cube root dependence on ω. This discrepancy is perhaps not surprising, since equation (1) is only expected to be true for $\omega << 1$ and this condition is violated over the range of particle concentrations investigated here. A more complete theory involves a complicated multiple-scattering problem, which currently is under investigation. It should be noted that the simple model predicts that air bubbles in the liquid should increase the transit time, because the speed of sound in air is less than that in the liquid. This increase will be masked by the component of the sound wave corresponding to propagation in the liquid alone. As noted previously, the observed behavior is consistent with this prediction. The results from this study are in qualitative agreement with those previously reported by Okamura et al. (16).

SUMMARY

Reaction conditions had significant effects on the observed hydrodynamics in a hot pressurized bubble column reactor. The average gas holdup increased as the temperature increased. The average gas holdup also increased slightly as the pressure increased. The Sauter mean bubble diameter decreased with increasing temperature and pressure at a constant superficial gas velocity.

Based on the results from the ultrasonic investigation, it can be concluded that the ultrasonic technique has potential application for solids concentration measurements in the slurry-bubble-column reactor.

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DISCLAIMER

REFERENCES

1. S. C. Saxena, D. Patel, D. N. Smith, and J. A. Ruether, Chem. Eng. Comm. 63, 87 (1988).
2. Y. T. Shah, B. K. Kelkar, S.P. Godbole, and W. D. Deckwer, AIChE J. 28, 353 (1982).
3. D. B. Bukur, J. G. Daly, and S. A. Patel, AIChE J. 36, 93 (1990).
4. J. C. Kuo, DOE Final Report, DE-AC22-83PC60019 (1985).
5. E. S. Sanders, E. L. Ledakowicz, and W. D. Decker, Can. J. Chem. Eng. 64, 133 (1986).
6. W. D. Deckwer, Y. Loiisl, A. Zaldi, and M. Ralek, Ind. Eng. Chem. Pro. Des. Dev. 19, 699 (1980).
7. W. J. O'Dowd, D. N. Smith, J. A. Ruether, and S. C. Saxena, AIChE J. 33, 1959 (1987).
8. D. R. Cova, Ind. Eng. Chem. Pro. Des. Dev., **5**, 21 (1966).
9. K. Imafuku, T-Y. Wang, K. Koide, and H. Kubota, J. Chem. Eng. Japan., **1**, 153 (1968).
10. H. Kolbel, M. Molzahn, and H. Hammer, DECHEMA., monograph **68**, 477 (1970).
11. Y. Kato, A. Nishiwaki, T. Fukuda, and S. Tanaka, J. Chem. Eng. Japan., **5**, 112 (1972).
12. W. D. Deckwer, Y. Serpemen, M. Ralek, and B. Schmidt, Ind. Eng. Chem. Pro. Des. Dev., **21**, 231, (1982)
13. W. D. Deckwer, A. Schumpe, and G. Quicker, Chem. Eng. Sci., **39**, 179 (1984)
14. K. Kato, S. Morooka, T. Kago, T. Saruwatari, and S. Z. Yang, J. Chem. Eng. Japan, **18**, 303 (1985)
15. S. L. P. Lee, and H. I. de Lasa, AIChE. J., **33**, 1359 (1987).
16. S. Okamura, S. Uchida, T. Katsumata, and K. Iida, Chem. Eng. Sci., **44**, 196 (1989).
17. Y. Soong, M. F. Zarochak, J. J. Boff, F. W. Harke, and B. G. Blackwell, Proceedings, Liquefaction Contractors' Review Conference, Sept, 22-24, Pittsburgh, PA, P559,(1992).
18. W. Fuchs, and D. N. Smith, Sixth Annual Sym. on Inst. and Control for Fossil Energy Process., 233 (1982).
19. D. N. Smith, W. Fuchs, R. J. Lynn, D. H. Smith, and M. Hess, Am. Chem. Soc., Symp. Ser. 237, 125 (1984).
20. Y. Soong, A. G. Blackwell, R. R. Schehl, M. F. Zarochak, and J. A. Rayne, Proceeding 18th Int. Tech. Confer. on Coal Utilization & Fuel Systems, 161, (1993)
21. P. M. Wilkinson, and L. L. v. Dierendonck, Chem. Eng. Sci., 45, 2309 (1990).
22. D. B. Bukur, J. G. Daly, and S. A. Patel, DOE Final Report, DE-AC22-86PC90012, (1990).
23. P. H. Calderbank, F. Evans, R. Farley, G. Jepson, and A. Poll, Instn. Chem. Engs., 66 (1963).
25. W. J. O'Dowd, D. N. Smith, J. A. Ruether, AIChE J., 33, 1959, (1987).

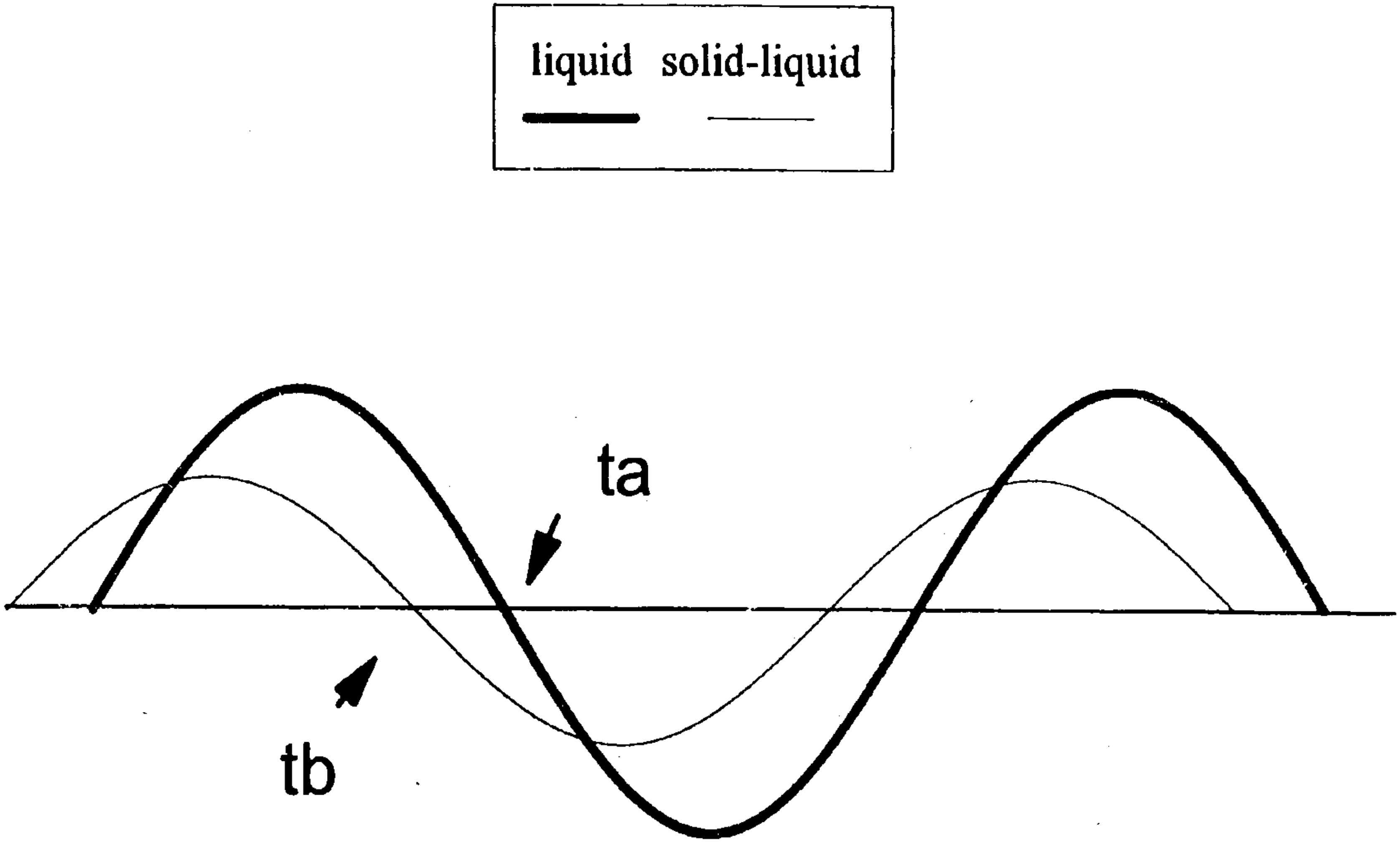

Figure 1. Effects of Solids on the Ultrasonic Signal in Liquid. t_a is the Arbitrary First Distinct Zero Crossing Time in Liquid and t_b is the Arbitrary First Distinct Zero Crossing Time in the Presence of Solid in Liquid.

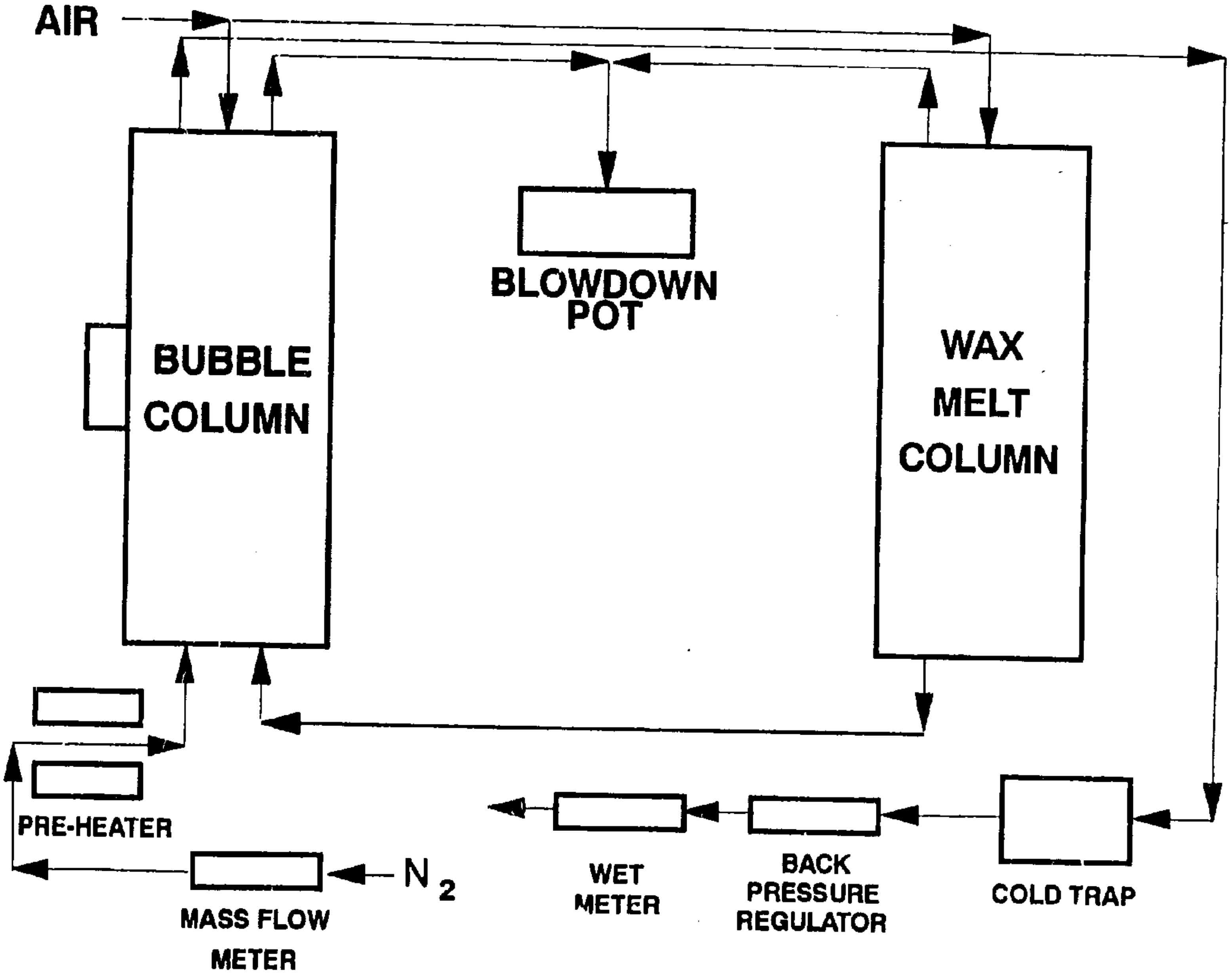

Figure 2. Schematic Diagram of Bubble-Column Reactor

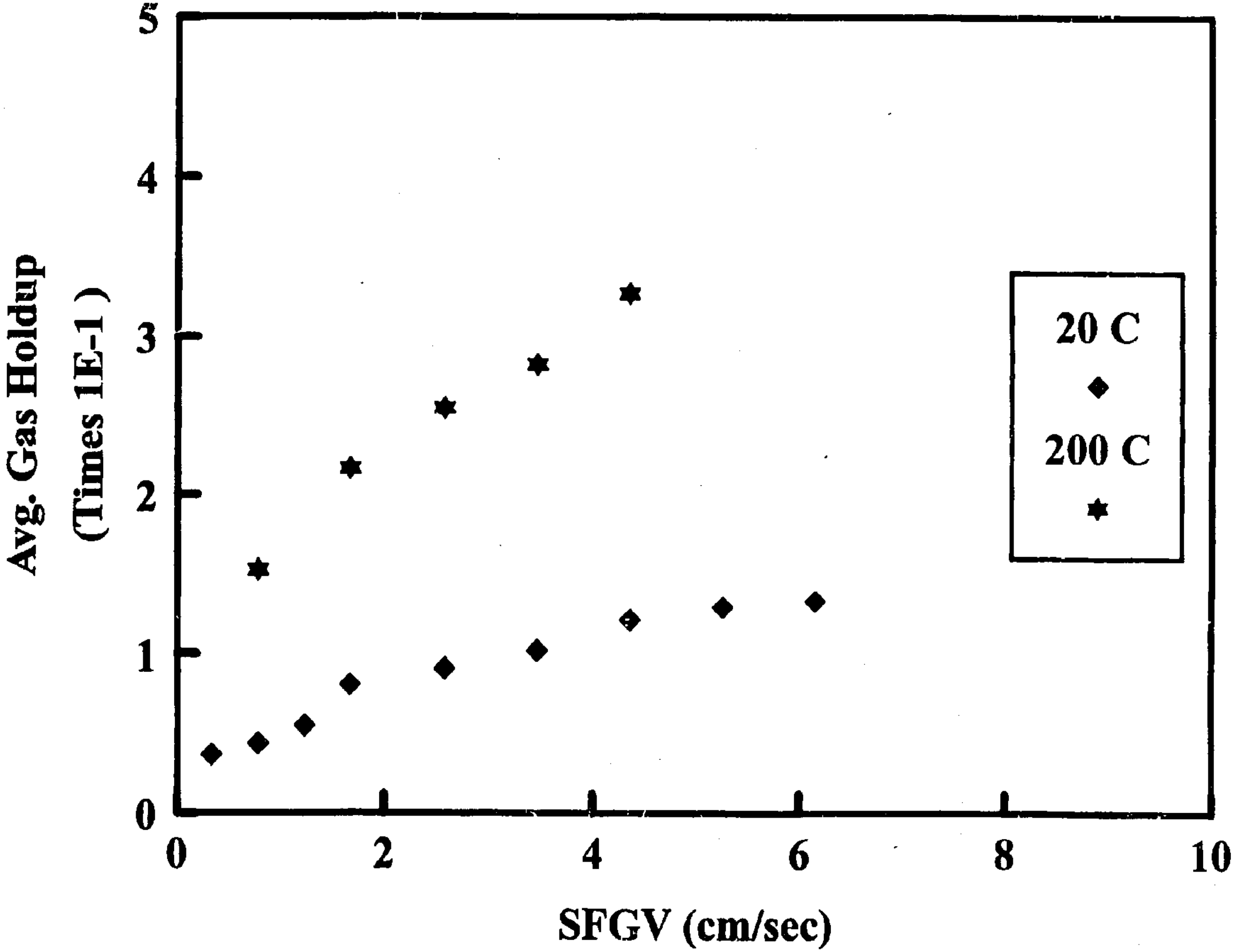

Figure 3. Effects of Temperature and Superficial Gas Velocity on Average Gas Holdup Under a Constant Pressure (0.1 MPa)

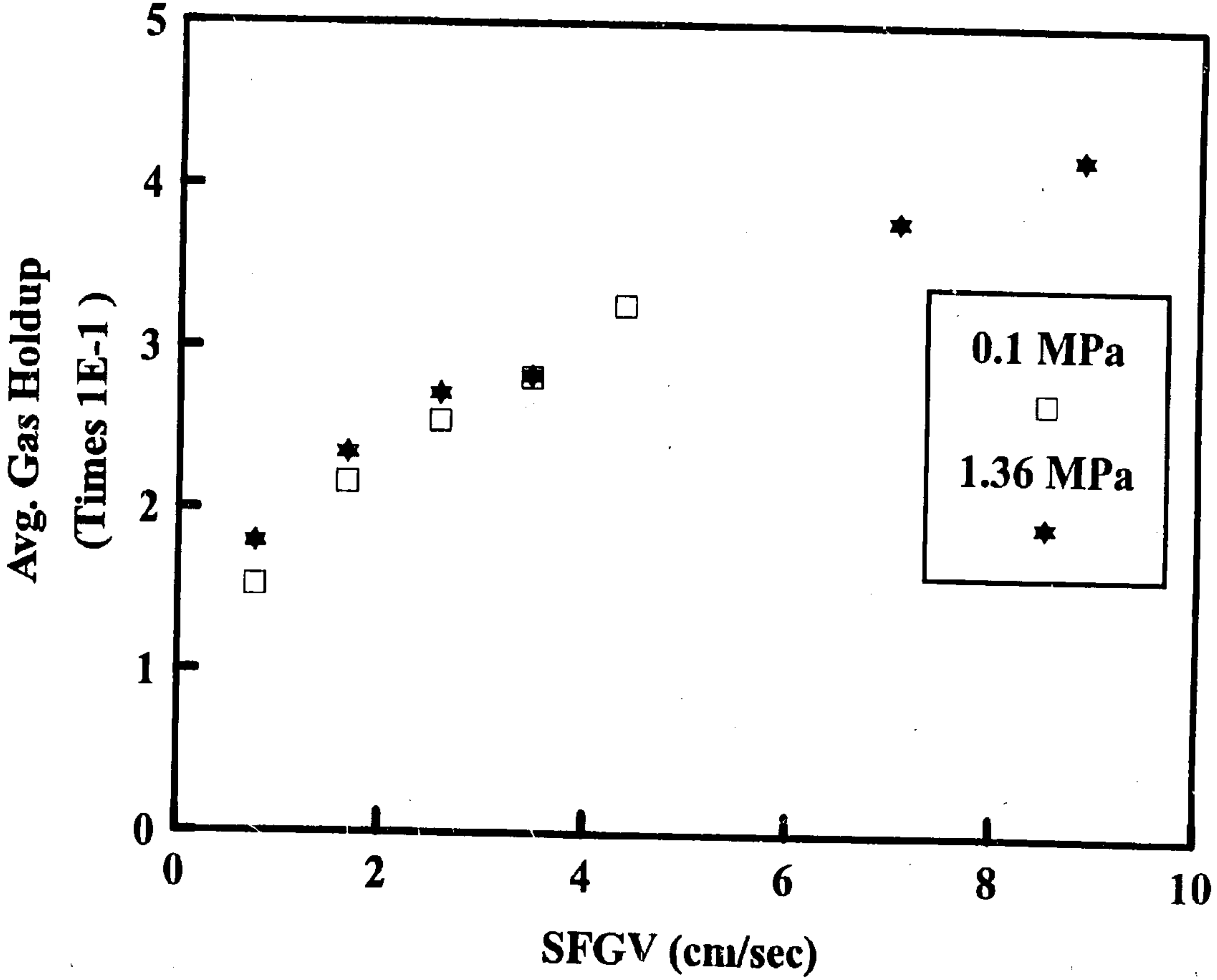

Figure 4. Effect of Pressure on Average Gas Holdup Under a Constant Temperature (200 °C)

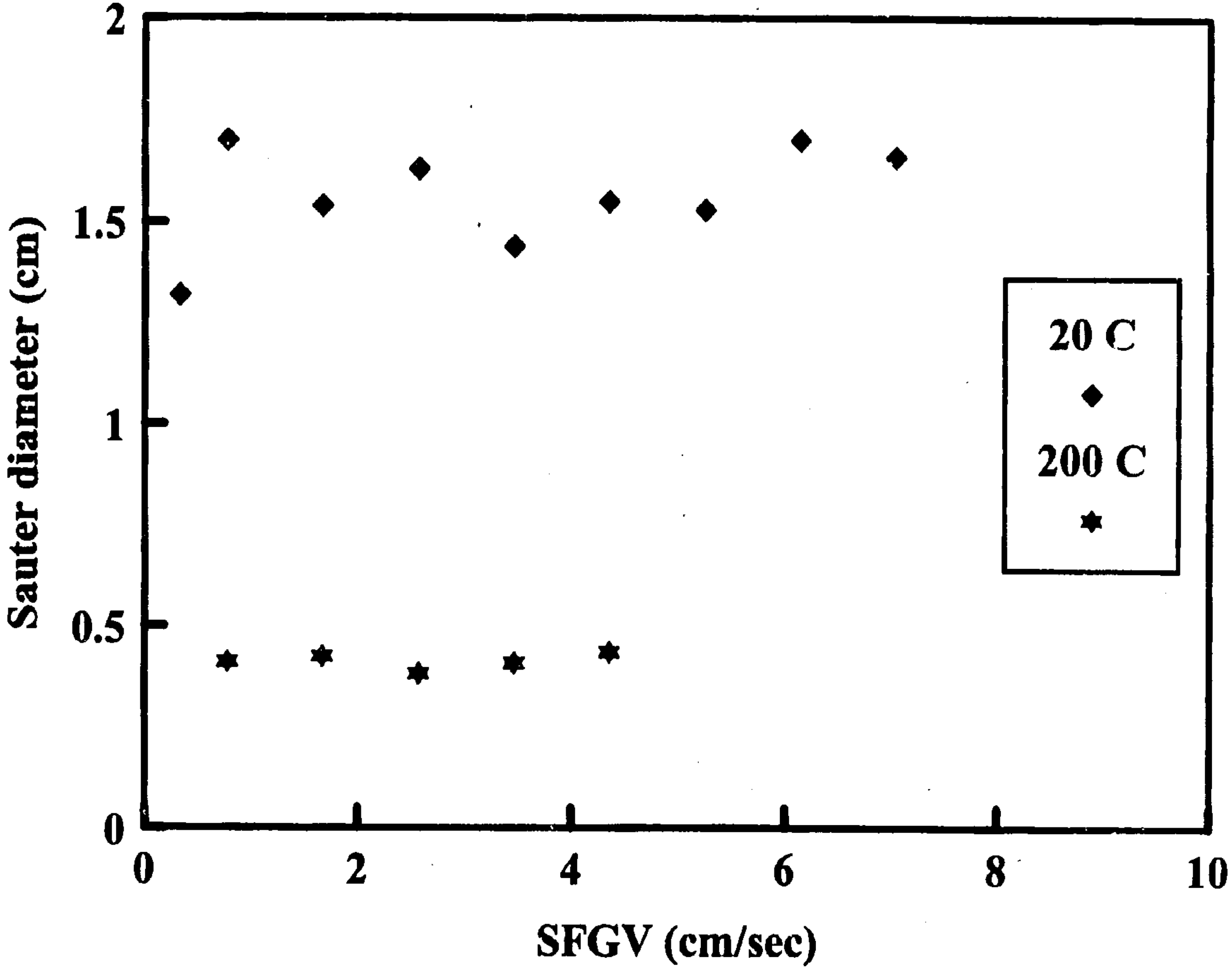

Figure 5. Effects of Temperature on Sauter Mean Bubble Diameter Under a Constant Pressure (0.1 MPa).

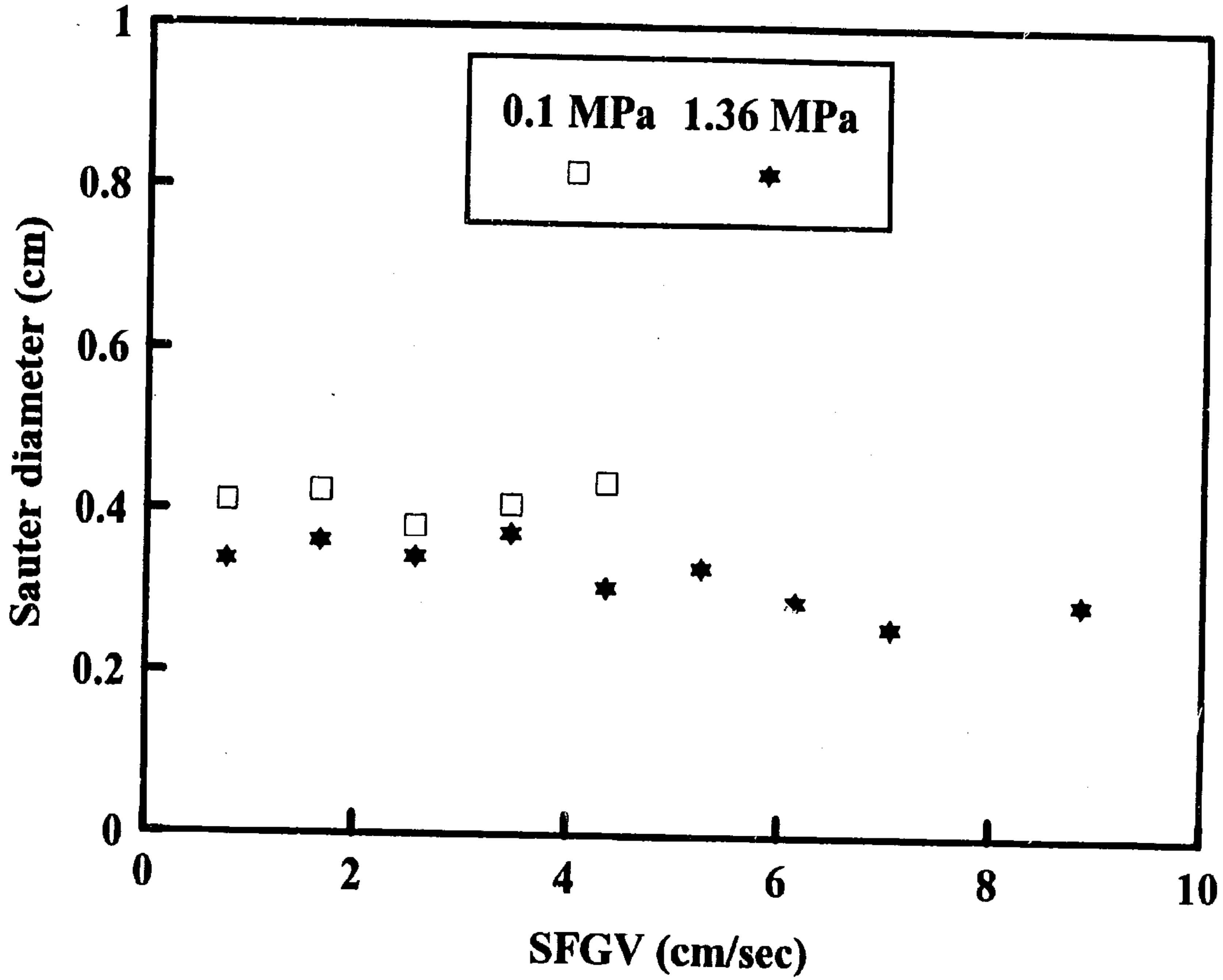

Figure 6. Effects of Pressure on Sauter an Bubble Diameter Under a Constant Temperature (200 °C).

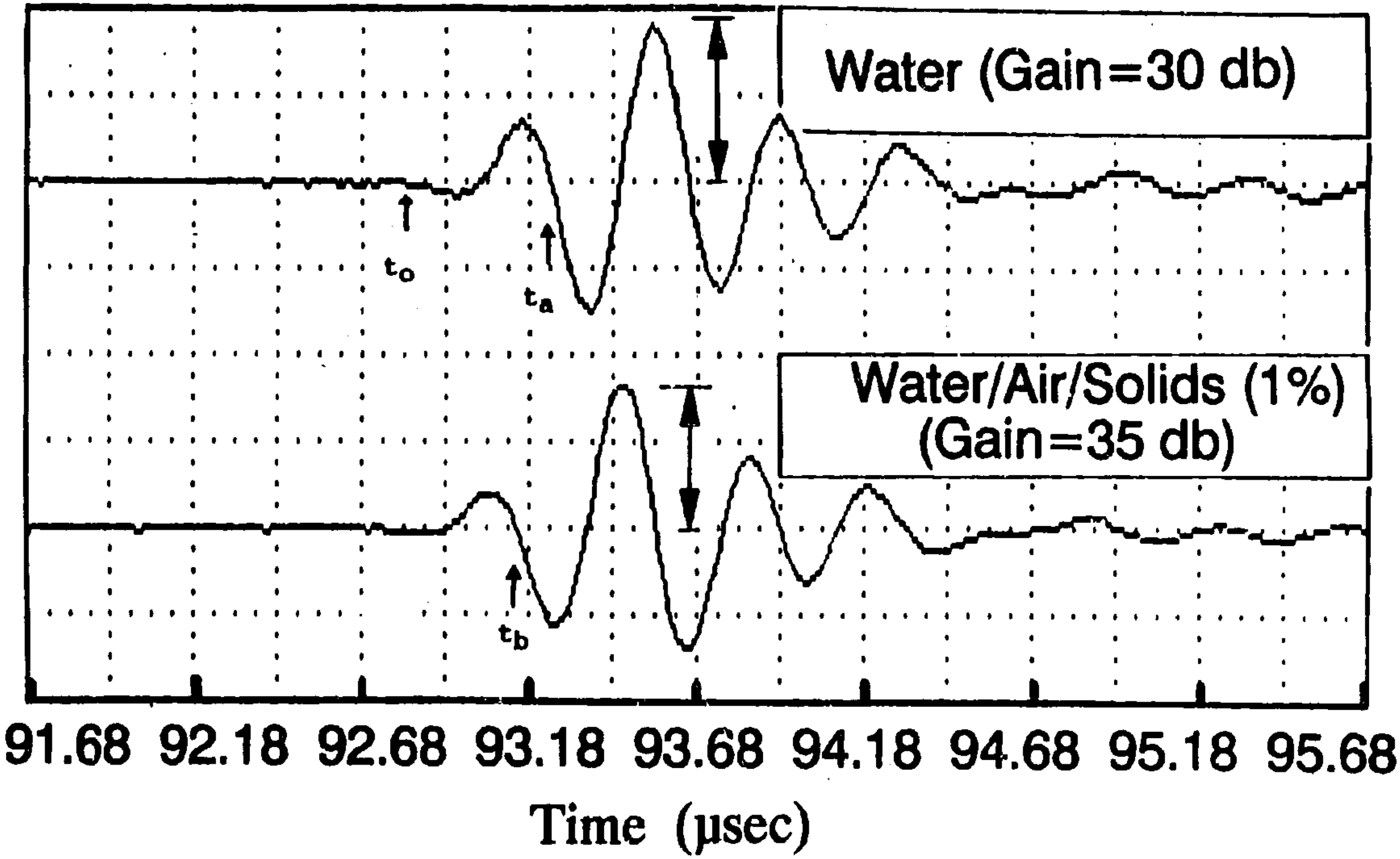

Figure 7. Effect of Solids on the Ultrasonic Signal. The first Distinct Zero Crossing Time was Determined as the Transit Time.

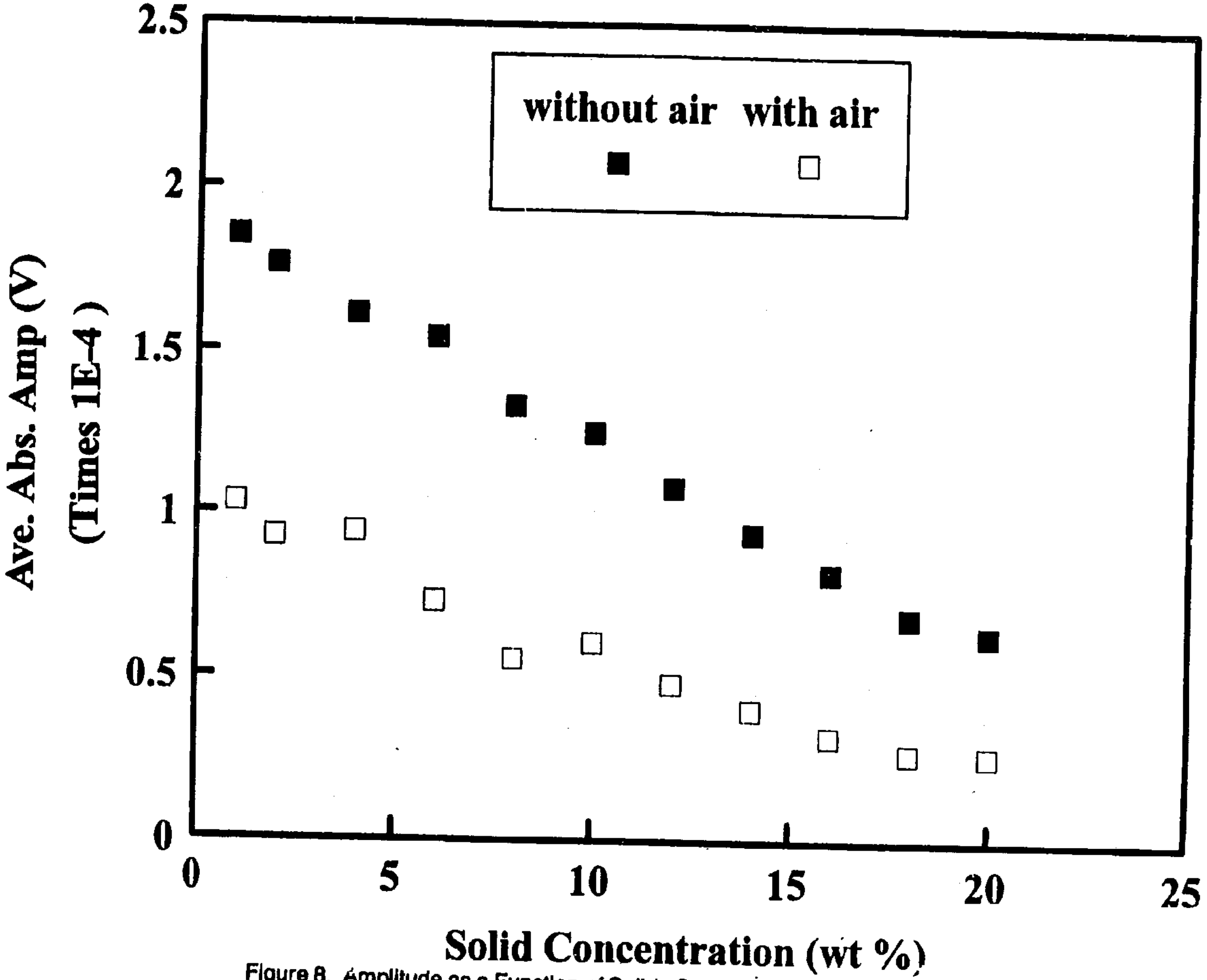

Figure 8. Amplitude as a Function of Solids Concentration (Glass Beads 80 microns; The Air Flow Rate is 174 ml/min.)

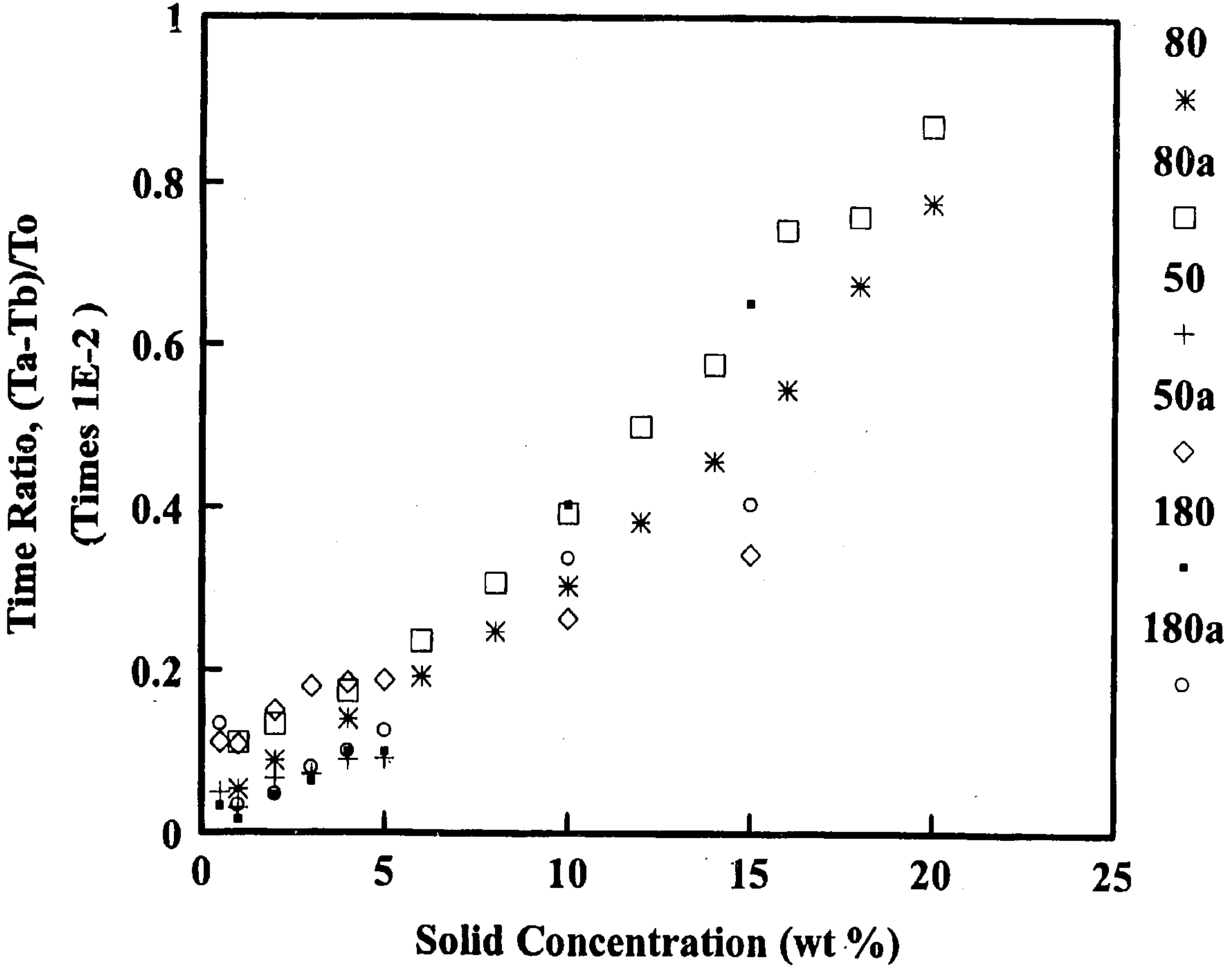

Figure 9. Variation of Time Ratio with Solids Concentration with and without Air Bubble Present (Glass Beads 50, 80 and 180 microns; 50a, 80a, and 180a are with air bubbles).