A STUDY OF THE REACTIONS OF ETHYLENE, CHLORINE AND WATER IN BUBBLE COLUMNS

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AND WATER IN BUBBLE COLUMNS

By

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SCOPE AND CONTENTS:

An investigation of the reactions of ethylene, chlorine and water in
a bubble column reactor, forming ethylene chlorohydrin and ethylene dichloride
has been carried out.

The effect of gas flow rates on the yield of the products was
studied in an unbaffled column reactor.

In the later period of this study, baffles made of perforated plates
were introduced into the column to investigate the effect of reducing the
axial mixing on the product distribution. An improvement in the conversion
and yield of ethylene to ethylene chlorohydrin was observed in the baffled
reactor. The results were compared with an axial dispersion model.

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CHAPTER 1

INTRODUCTION

Of many gas-liquid contactors, bubble column reactors are commonly used in industry. In such a device, gas is passed through a gas disperser and the bubbles so formed react with the liquid during their passage through the column. It usually has no means of agitation other than that caused by the bubbling action. For this reason, it is relatively inexpensive to build and easy to operate.

As most bubble reactors fall into non-ideal flow processes, it is important to study mixing in a bubble reactor in order to be able to design such a reactor.

Ethylene chlorohydrin has been produced by bubbling ethylene and chlorine into water, and it still remains an important process for the synthesis of ethylene glycol although it is rapidly being replaced by direct oxidation of ethylene to ethylene oxide and subsequent reaction with water.

Experiments were carried out in an unbaffled column reactor with the ethylene-chlorine-water system. The effect of gas flow rates was investigated during the experiments. An enhancement factor was obtained from mass transfer with and without chemical reaction, and was compared with Hatta's model.

The effect of reducing the axial mixing on the product distribution and on the yield of the products was studied. The results were compared with an axial dispersion model.

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CHAPTER 2

LITERATURE SURVEY

In this chapter, the existing literature concerning the present work is reviewed. It can be grouped into the following four sections: mass transfer with chemical reaction, bubble column reactors, mixing in a reactor and chemistry of the system.

2-1. Mass transfer with chemical reaction

The theory of simultaneous mass transfer and chemical reaction in the liquid phase has been developed by Hatta[29,30] based on the assumption that the resistance to mass transfer exists only in a thin film adjacent to the gas-liquid interface. This film is assumed to have negligible capacity for holding the dissolved gas as compared with the liquid bulk which is so well mixed that no concentration profile exists in it. The assumption of two such films, one in the liquid and the other in the gas, is the basis of Lewis and Whitman's two-film theory[44] in which the concept of resistances in series is assumed.

An alternate theory, proposed by Higbie[31], is based on the unsteady-state diffusion. Dankwerts[15] modified this theory introducing an age distribution function. In his surface renewal theory, the surface is assumed to be continually replaced by fresh liquid.

In the penetration theory the liquid-phase mass transfer coefficient without reaction varies with the square root of the diffusivity, but in the

two-film theory it is a linear function of the diffusivity.

For mass transfer with a rapid second-order, irreversible reaction, Hatta[29] and Sherwood[51] proposed expressions for liquid-phase mass transfer coefficients based on the film theory and the penetration theory respectively.

For mass transfer with a slow first-order reaction, Hatta[30] and Dankwerts[14] proposed an enhancement factor based on the film theory and the penetration theory respectively.

Astarita[3] reviewed theories of mass transfer accompanied by various orders of reaction for different rates of reaction. He summarized these theories and organized information on such as chemical absorption, heterogeneous catalysis, axial mixing in chemical reactors etc. in a coherent fashion.

Dankwerts[16] surveyed theories involved in gas-liquid reactions and gave methods for designing a gas-liquid contacting reactor. He examined the mechanism of absorption processes, and related chemical and physical quantities such as physical mass transfer coefficient, interfacial area, diffusivity and the rate of reaction to the rate of absorption.

Several theoretical studies on mass transfer from a sphere have been developed recently using boundary layer theory. This theory is based on the fact that there exists, next to the solid body, a very thin layer in which the fluid friction is significant to the flow of the fluid when the fluid flows over a solid body.

LeClair and Hamielec[39,40] solved the equations of continuity for viscous flow through rigid spheres, gas bubbles and infinitely long cylinders using a surface-interaction model. They also developed mass transfer correlations for bubbles as a function of Reynolds number, Sherwood number and Schmidt number.

Ishii and Johnson[33] studied mass transfer with and without reaction from single bubbles. They solved the equation of continuity numerically using the potential flow theory. They suggested that the velocity profile in the liquid could be well described by this theory since the viscosity of the bubble could be negligible as compared with the liquid viscosity.

Johnson et al[35] proposed an equation to calculate the mass transfer coefficient for single rising bubbles in water taking the effect of bubble size into consideration. They also reported the mass transfer coefficients based on the potential flow theory and the penetration theory, and compared them as well as those proposed by other authors[4,9] with the experimental results.

Johnson and Akeheta[1,36] studied mass transfer with a second-order chemical reaction from gas bubbles. They calculated an enhancement factor by a one-dimensional penetration theory and a three-dimensional penetration theory, and concluded that the analysis of absorption rate should be made carefully using the three-dimensional solution for small bubbles or for the liquid of high viscosity.

2-2. Bubble column reactor

Bubble column reactors have been commonly used for mass transfer with chemical reaction because they have some advantages over other devices. Because of the complicated bubble motion, however, it is difficult to analyse a bubble column. In this section, some of the existing work on bubble column reactors is surveyed in order to give a general background to this study.

Much work has been done on bubble mechanisms and Calderbank[8,10] has reviewed mass transfer without chemical reaction in bubble columns for a wide range of bubble diameters.

For small bubbles, the works of many authors agree with one another since the assumption of spherical shape holds for each bubble. But this is not the case for large bubbles.

Calderbank[9] proposed equations to calculate the bubble volume, bubble rise velocity, interfacial area, gas hold up and other properties in a multi-nozzle bubble column for nozzle diameters varying from 1/18 inch to 1/16 inch assuming that the bubble frequency was constant for a gas flow rate greater than 30 cc/sec which includes most of the work done in industry.

The effect of various parameters on the liquid-phase mass transfer coefficient in bubble column reactors has been studied by some authors. Shulman and Molstad[53] reported that two distinctly different regions were found during the investigation of the mass transfer rate. They concluded that the rate of mass transfer was a function of the gas flow rate at low gas rates (streamline region), while it was not at high gas flow rates (turbulent region).

Yoshida and Akita[57] studied the effect of nozzle diameter, column diameter and gas flow rate on the liquid-phase mass transfer coefficient in their sulfite oxidation experiments. These investigations are useful for the scale-up of a single-stage bubble column reactor.

A few studies have been done using commercial-scale bubble column reactors. Fair et al[23] reported that perforated baffles increased the efficienc of the bubble column reactor significantly, and this is one of the major topics considered in this thesis.

Even though some studies have been done on bubble column reactors, it is still difficult to design an industrial-scale bubble column reactor. Fair[21,22] gave a guide for designing such large-scale bubble reactors. He pointed out that the design of the gas distributor was critical for operation in the stream-line region since gas dispersion is brought about mainly by flow through the distributor.

On the other hand, the break-up due to the turbulent flow dominates gas dispersion in the turbulent region. He suggested that gas dispersion, gas hold up, mass transfer, axial mixing of the liquid phase, and the kinetics of the system should be well described in order to be able to design such a reactor.

Recently, Russell and co-workers have reviewed most of the work done in gas-liquid two-phase reactors. They proposed model equations for analysing such reactors and methods for evaluating parameters used in model equations for tank reactors[49] and tubular reactors.

Cichy and Russell[11,12] grouped flow configurations in two-phase tubular reactors into the following regimes:

i) Continuous fluid phases with a well-defined interface, where continuous gas and liquid phases flow simultaneously.

ii) Continuous fluid phases with complex interfaces and fluid interchange, where gas and liquid flows are essentially continuous while a part of one phase enters the other phase in the form of droplets or bubbles.

iii) Alternating discrete fluid phases, where the fluid flow alternates period-ically between principally liquid flow and principally gas flow.

iv) One continuous phase and one dispersed phase, where discrete units of one phase are present in the other phase while the second phase is continuous.

v) Homogeneous two-phase mixtures, where the fluid phases are sufficiently intermixed.

They proposed model equations and evaluated the model parameters for each of the above flow configurations.

2-3. Mixing in a reactor

2-3-1. General

In order to predict the performance of a flow reactor, it is very important to have information on mixing. Until recently, the treatment of chemical flow processes has been limited to the two extreme cases, one in which perfect mixing of the liquid is assumed and the other in which no mixing is assumed to occur.

Most chemical reactors, however, do not fall into either of these two categories, and thus partial mixing must be described. This introduces mathematical complexity.

Many authors have recently characterized these types of flow patterns by means of residence time distribution functions obtained by tracer studies. Bischoff and McCracken[5] summarized three distribution functions and gave methods for the treatment of situations such as dead space and by-passing which often occur in real flow processes.

Levenspiel and Smith[43] first showed that the variance obtained from a distribution function could be conveniently related to the coefficient of axial mixing.

Van der Laan[55], Levenspiel and Bischoff[42], and Himmelblau and Bischoff[32] summarized the relationships between the variance of the distri-

bution functions and the coefficient of axial mixing for various input signals and end conditions.

Many types of models have been proposed to characterize non-ideal flow patterns. Dispersion models are based on the analogy between mixing in an actual flow and a diffusion process.

Levenspiel and Bischoff[42] proposed several dispersion models. The axial dispersion model in which every property is assumed to be constant in the radial direction is the most commonly used model because of its simplicity.

Tanks-in-series models are also commonly applied to non-ideal flow processes. In this model, the actual flow reactor is represented by a series of equal-sized completely-stirred tank reactors.

Macklenburgh[46] proposed general methods for the evaluation of concentration profiles and the design of reactors with back-mixing. He compared the axial dispersion model with the tanks-in-series model, and concluded that the difference in the concentration at the reactor outlet using the axial dispersion model as compared with using the tanks-in-series model was inversely proportional to the square of the number of equivalent stirred tanks.

Levenspiel and Bischoff have also proposed combined models to characterize non-ideal flow patterns more accurately.

2-3-2. Axial mixing in a bubble column reactor

Very little work has been done on axial mixing in bubble column reactors. Argo and Cova[2] investigated the degree of back-mixing as a function of column diameter and gas flow rate using a tracer. They concluded that the coefficient of axial mixing was reduced in a baffled column and that liquid velocity had no significant effect on axial mixing.

Bischoff and Phillips[6] and Ottmers and Rase[48] carried out tracer studies in orifice plate gas-liquid contactors for different arrangements of plates. They both concluded that plate designs with one large hole in the center of the plate or with many small holes tended to perfectly mixed or plug flow conditions respectively.

Koide[38] investigated the flow mechanisms in a bubble column using both perforated plates and porous plates as the distributor. He concluded that the coefficient of the axial mixing would be strongly affected by column diameter, gas velocity relative to liquid velocity, bubble size, and gas hold up. He observed no liquid velocity gradient or gas hold up gradient for a liquid velocity less than 10 cc/sec, which is the major assumption in the axial dispersion model.

Fair[22] pointed out that information on liquid mixing is essential for designing bubble column reactors as it could affect reaction yields and selectivities.

2-4. Chemistry of the system

Numerous processes have been developed for the synthesis of ethylene chlorohydrin. One of the principal uses of ethylene chlorohydrin is in the production of ethylene oxide which in turn is an intermediate in the synthesis of ethylene glycol, though ethylene chlorohydrin was first used industrially to produce indigo.

Wurz first prepared ethylene chlorohydrin in 1859 by reacting ethylene glycol with hydrochloric acid[37].

Carius, in 1863, reported a more direct synthesis[47]; the addition of hypochlorous acid to ethylene. This has become the basic reaction for industrial processes.

In 1921, the first commercial plant using this process was built in the United States. A flow diagram for this plant is given in reference (27). Gomberg[26] pointed out that there would be two main methods of preparing ethylene chlorohydrin:

i) the addition of hypochlorous acid to ethylene.

ii) the action of either sulfur monochloride, or of hydrochloric acid, or of chlorine upon pure ethylene glycol.

He suggested that the first method would be better from a practical point of view.

Hypochlorous acid is most commonly prepared by bringing chlorine into water which gives rise to the following equilibrium:

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl \qquad (2-1)$$
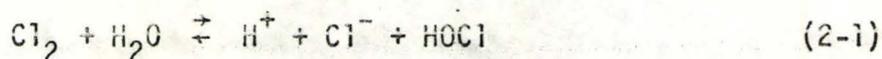
Various procedures have been proposed in order to shift the above equilibrium in favor of hypochlorous acid, and thus in favor of ethylene chlorohydrin formation. Gomberg investigated and summarized the effect of various factors on the equilibrium. Much work has been done with the chlorine-water system to study the equilibrium involved. Spalding[54] proposed that the initial pH values of the absorbent affected the equilibrium. He concluded:

i) pH < 3.0   reversible reaction controlling.

ii) 3.0 < pH < 10.5   forward reaction dominant.

iii) 10.5 < pH < 12.0   the reaction of chlorine with hydroxyl ion occurs simultaneously with the chlorine-water reaction.

iv) 12.0 < pH   the second-order reaction between chlorine and hydroxyl ion controlling.

Brian et al[7] and Spalding investigated the effect of the hydrolysis reaction upon the rate of absorption of chlorine into water. The enhancement factor was very well represented by the penetration theory in their work.

Since World War I, some authors have published papers on the formation of ethylene chlorohydrin. Gomberg first investigated the influence of various factors on the ratio of ethylene consumed in ethylene chlorohydrin formation to that consumed in ethylene dichloride formation. He and Domask and Kobe[17] reported that the production of undesired by-products increased as the concentration of ethylene chlorohydrin increased. Domask and Kobe also suggested that high molar ratios of ethylene to chlorine would be favorable to high yield of ethylene chlorohydrin.

Akehata and Johnson[1] studied the absorption of ethylene in aqueous chlorine solution and reported the results in terms of an enhancement factor, which was compared with Hatta's theory. They described the process by a model based on mass transfer with second-order chemical reaction. They also reported the rates of reaction for ethylene chlorohydrin formation at 0^oC, 5^oC and 10^oC and are the only source of the kinetic data available so far.

For ethylene dichloride formation, Dun and Wood[18,19] reported a rate constant obtained from studies using a wetted tower.

Shilov[52] criticized proposed mechanisms[1,17,26] for ethylene chlorohydrin and ethylene dichloride formation. He pointed out that ethylene chlorohydrin would be formed by direct reaction of chlorine with ethylene in aqueous solution while ethylene dichloride would be formed due to participation of chloride ion.

CHAPTER 3

THEORETICAL CONSIDERATIONS

3-1. Mixing in a reactor

3-1-1. Axial dispersion model

Several methods have been proposed in order to characterize non-ideal flow patterns in reactors[42]. In this section one of the dispersion models, the axial dispersion model, is discussed.

In this model, every property is assumed to be constant in the radial direction. Koide[38] reported that no liquid velocity gradient or gas hold up gradient was observed in the radial direction in his study on bubble mechanisms for a liquid velocity less than 10 cm/sec. He suggests that this result supports the applicability of the axial dispersion model in which the radial diffusion is neglected.

The basic equation for this model is derived from a material balance for each component in the liquid phase.

$$E_L \frac{d^2C}{dz^2} - U \frac{dC}{dz} + N + r = 0 \qquad (3-1)$$

In dimensionless forms, by letting $Z = z/L$ be the fractional length of the reactor measured from the entrance, eq. (3-1) becomes:

$$(E_L/UL) \frac{d^2C}{dZ^2} - \frac{dC}{dZ} + (L/U)(N + r) = 0 \qquad (3-2)$$

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For ethylene chlorohydrin and ethylene dichloride, eq. (3-2) can be written as:

$$(E_L/UL) \frac{d^2C_{ECH}}{dZ^2} - \frac{dC_{ECH}}{dZ} + (L/U) r_{ECH} = 0 \qquad (3-3)$$

$$(E_L/UL) \frac{d^2C_{EDC}}{dZ^2} - \frac{dC_{EDC}}{dZ} + (L/U) r_{EDC} = 0 \qquad (3-4)$$

Here, it should be noticed that the term (E_L/UL) is the inverse of the Peclet number. Eqs. (3-3) and (3-4) could be solved analytically assuming that the formation of ethylene chlorohydrin and of ethylene dichloride are constant along the column. The results are:

$$C_{ECH} = (L/U) r_{ECH} (Z - \exp(Pe.Z)/(Pe.\exp(Pe)) + 1/Pe) \qquad (3-5)$$

$$C_{EDC} = (L/U) r_{EDC} (Z - \exp(Pe.Z)/(Pe.\exp(Pe)) + 1/Pe) \qquad (3-6)$$

3-1-2. Coefficient of axial mixing

The concentration profiles of the products can be predicted by eqs. (3-5) and (3-6), provided that the Peclet number is given. In this section, determination of the coefficient of axial mixing or Peclet number from the distribution function is discussed[41].

The mean residence time, or the first moment of the distribution function about the origin, is calculated as follows:

$$T_m = \int_0^\infty TCdT / \int_0^\infty CdT \qquad (3-7)$$

The second moment of the distribution function about the mean T_m commonly called

the variance, can be calculated in the following way:

$$\sigma_t^2 = \int_0^\infty (T - T_m)^2 \, CdT \Big/ \int_0^\infty CdT \qquad (3\text{-}8)$$

This variance has been related to the coefficient of axial mixing or Peclet number for different types of input signals and end conditions[32,42]. The following correlation was proposed for the conditions involved in this study:

$$\sigma^2 = (\sigma_t/T_m)^2 = 2(E_L/UL) - 2(E_L/UL)^2(1 - \exp(-UL/E_L)) \qquad (3\text{-}9)$$

The coefficient of axial mixing can be calculated using eqs. (3-7), (3-8) and (3-9).

3-2. Enhancement factor

Much work has been done on the effect of chemical reaction upon the rate of mass transfer. Hatta's model[29], proposed for mass transfer with a rapid second-order, irreversible chemical reaction, is discussed here. In this model, a solute gas A is assumed to be absorbed by a solution of a substance B, which combines with A according to the following reaction:

$$A + B \rightarrow AB \qquad (3\text{-}10)$$

As the solution is first brought into contact with the gas, A will dissolve and react immediately with B at the reaction plane. Fig. 3-1 shows a sketch of concentration profiles based on the two-film theory. RS represents the equilibrium
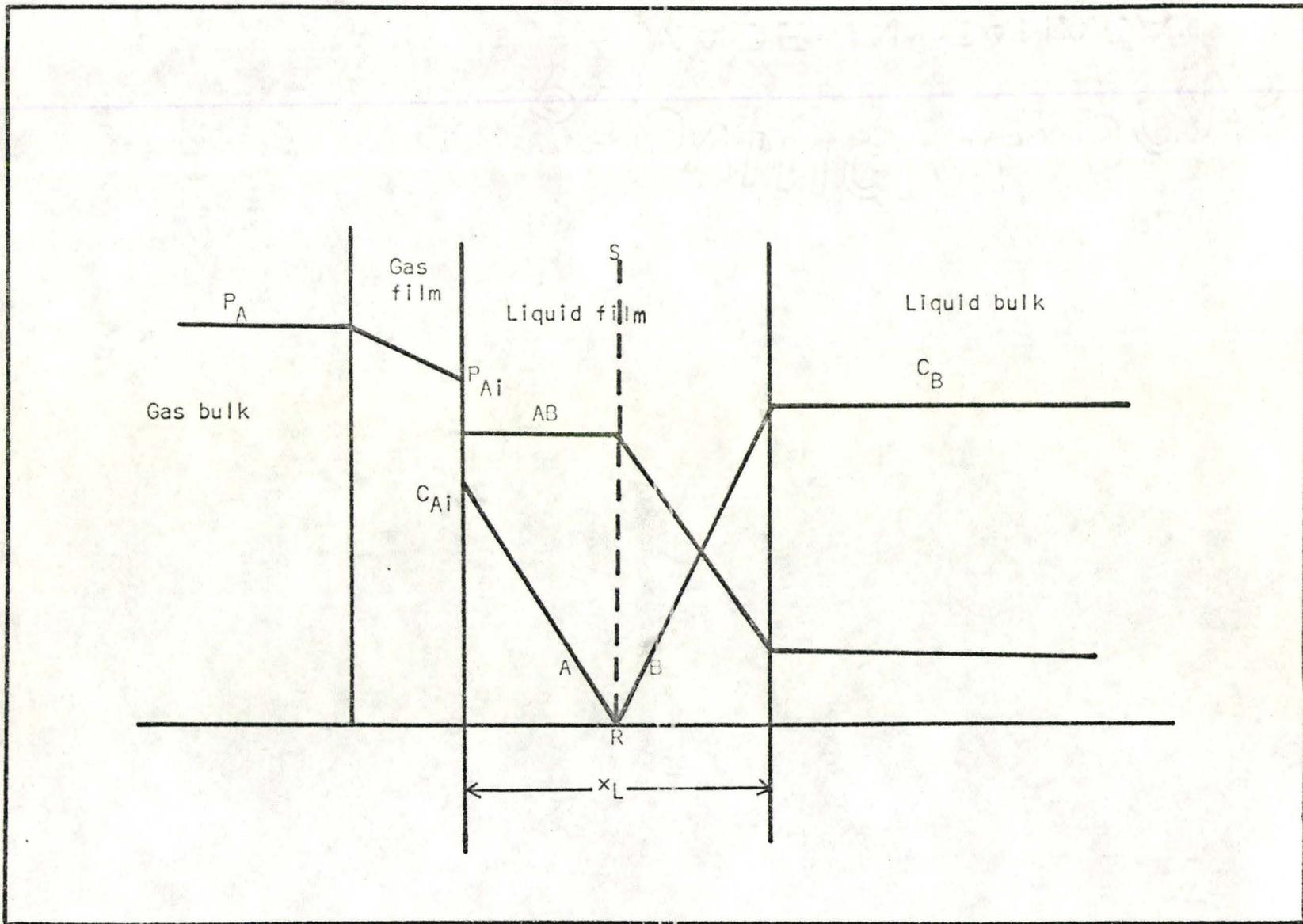
Fig. 3-1   Concentration profiles based on the two film theory

position of the reaction zone, to which A and B diffuse and from which the product AB diffuses toward the main body of the liquid. Other major assumptions are as follows:

i) Henry's law applies to the equilibrium at the interface,

ii) The molal diffusion rates of B and AB are equal,

iii) The solvent concentration is large as compared with the concentrations of A, B and AB.

The result in terms of the liquid-phase mass transfer coefficient is:

$$k_L = (D_A/X_L)(1 + D_B C_B/D_A C_{Ai})$$ (3-11)

On the other hand, the physical mass transfer coefficient can be written by:

$$k_L^o = D_A/X_L$$ (3-12)

In the ethylene-chlorine-water system, ethylene is assumed to diffuse from the interface, and chlorine and hypochlorous acid from the liquid phase. The ionic nature of the reactants is not considered. The enhancement factor, k_L/k_L^o, is calculated for this system as follows:

$$\phi = 1 + D_{Cl}/(D_E C_{Ei})(C_{Cl} + D_{HOCl} C_{HOCl}/D_{Cl})$$ (3-13)

3-3. Chemistry of the system

In this section, reactions involved in the ethylene-chlorine-water system are discussed. Chlorine reacts with water yielding the following equilibrium:

$$Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HOCl \qquad (3-14)$$
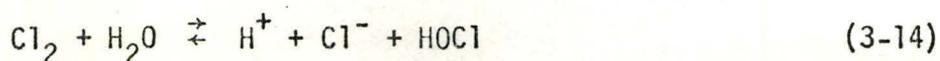
Much work has been done on the above equilibrium, and the equilibrium constant[13] and the rate expressions[45,54] for the hydrolysis were reported.

Ethylene reacts with hypochlorous acid and dissolved chlorine to produce ethylene chlorohydrin and ethylene dichloride respectively:

$$C_2H_4 + HOCl \rightarrow ClC_2H_4OH \qquad (3-15)$$

$$C_2H_4 + Cl_2 \rightarrow ClC_2H_4Cl \qquad (3-16)$$

Several authors[1,37,47] pointed out that reaction (3-15) would be much faster than reaction (3-16). Akehata and Johnson[1] proposed equations to describe the reactions involved in this system:

$$D_E \frac{d^2 C_E}{dX^2} = k_{ECH} C_E C_{HOCl} \qquad (3-17)$$

$$D_{HOCl} \frac{d^2 C_{HOCl}}{dX^2} = k_{ECH} C_E C_{HOCl} - k_{HOCl} (C_{Cl} - C_{HCl}^2 C_{HOCl}/K) \qquad (3-18)$$

$$D_{HCl} \frac{d^2 C_{HCl}}{dX^2} = - k_{HOCl} (C_{Cl} - C_{HCl}^2 C_{HOCl}/K) \qquad (3-19)$$

$$D_{Cl} \frac{d^2 C_{Cl}}{dX^2} = k_{HOCl} (C_{Cl} - C_{HCl}^2 C_{HOCl}/K) \qquad (3-20)$$

They reported the rate constants for reactions (3-15) and (3-16), and concluded that the former was about 100 times larger than the latter.

CHAPTER 4

EXPERIMENTAL

4-1. Apparatus

A schematic diagram of the experimental apparatus used in this study is shown in Fig. 4-1. The bubble column reactor (B), constructed by Yau[56], was made 3 inches I.D., 36 inches long glass tube. It had 7 sampling points (S) and a liquid outlet along the column. They were located 3 inches apart from one another, with the first one 3 inches apart from the top of the nozzles.

The bottom of the reactor was joined to a ⑀ 103/60 ground glass joint. The lower plug of the reactor containing the nozzle cluster was machined to fit the ground glass joint from a 6 inch x 6 inch Teflon cylinder. This plug was drilled to accommodate 55 1/16-inch holes, each of which was fitted with a nozzle; the nozzles were arranged on a 3/8 inch triangular pitch as shown in Fig. 4-2. The liquid outlet was placed at the bottom of the Teflon plug.

The nozzles were made of 1/16 inch O.D., 1/32 inch I.D. Teflon tubing in order to prevent corrosion. Each nozzle was inserted into the hole of the Teflon plug.

Glass beads, 5 mm in diameter, were used to fill the space between nozzles, thus reducing the volume below the point where gases were bubbled to avoid a dead space in this section of the reactor. They also supported the Teflon nozzles.

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B: Bubble column reactor
BF: Baffle
C: Chamber
F: Filter
G: Gas-liquid separator
R: Rotameter
S: Sampling point
T: Tank
W: Water jacket
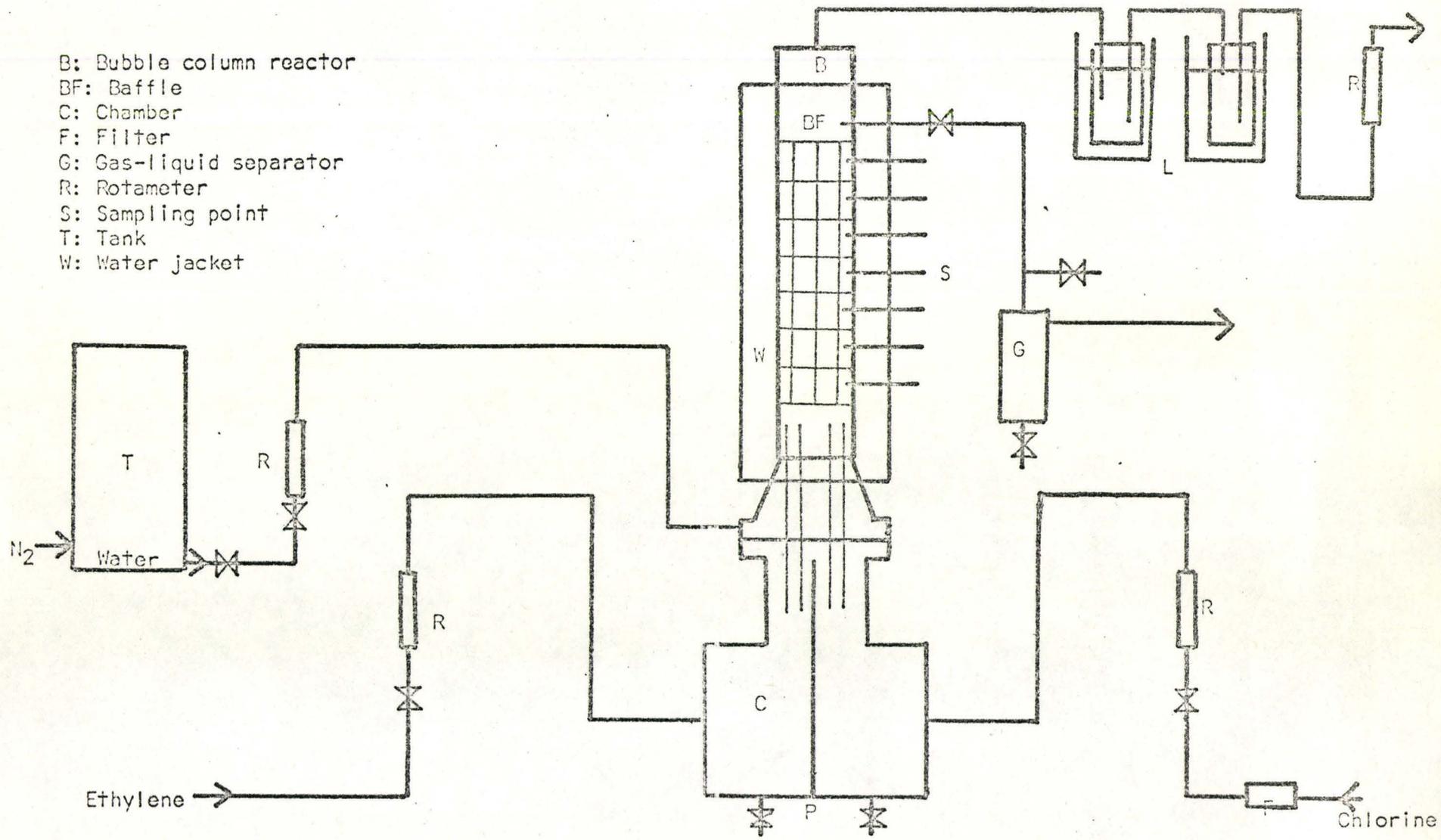
Fig. 4-1   Experimental apparatus
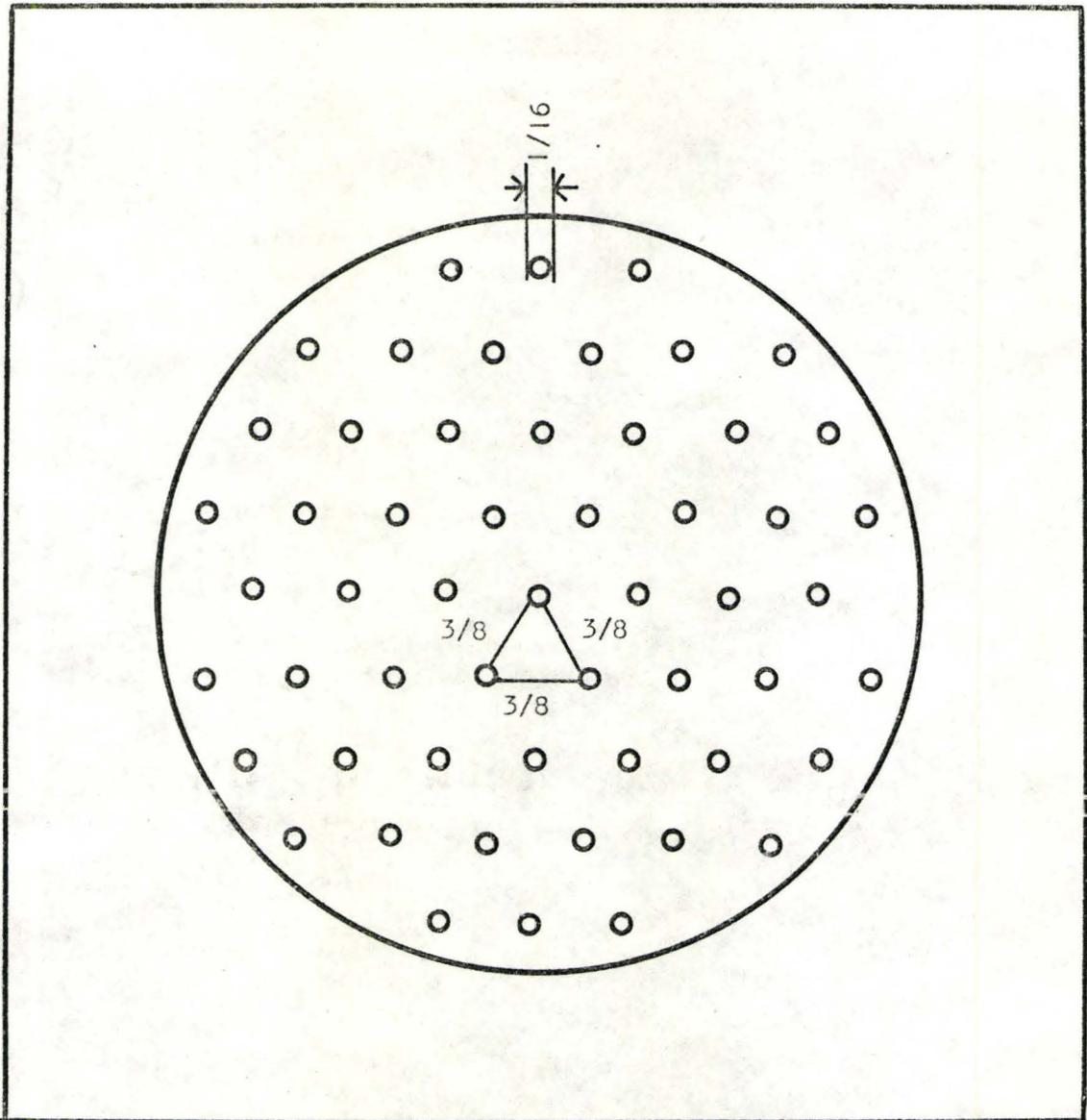
Fig. 4-2 Arrangement of nozzles

The chamber (C), made of acrylic resin, was connected to the plug of the reactor by means of a flanged joint. It had a partition plate (P) in it to avoid mixing of two gases before flowing through the nozzles. The chamber was an 8 inch cube and allowed steady bubble rates at the nozzles.

The bubble column reactor was enclosed in the water jacket (W) made of acrylic resin. During a run with chemical reaction, cooling water was passed through the water jacket to control the reactor temperature.

Ion-exchanged water was stored in the tank (T) made of type 304 stainless steel with a capacity of approximately 80 liters. The pressure of the tank was maintained constant by compressed nitrogen gas.

The material of the chlorine line was Teflon, glass and polyethylene in order to prevent corrosion. The filter (F), packed with silica gel, was used to get rid of moisture included in chlorine from the cylinder.

Ethylene gas of technical grade, minimum 98.0% pure, and chlorine gas of highest purity, minimum 99.5%, were fed from the gas cylinders to the chamber through rotameters (R).

Water was also fed through a rotameter and the flow rates of all the reactants were controlled by needle valves.

The outlet gas passed through dry ice-methanol liquid traps (L) and a rotameter to the atmosphere.

The outlet gas and liquid were separated at the gas-liquid separator (G) which allowed gas to the atmosphere and liquid to the drain, respectively.

Chromel-Alumel thermocouples were located at the liquid inlet, liquid outlet, gas inlet and gas outlet as well as at each sampling point.

In the later part of the study, nests of baffles (BF) having two different free areas were introduced into the bubble column reactor. These

baffles were made of acrylic resin and were composed of eight perforated plates and rod spacers. Both of the plates had holes with 3/8 inch triangular pitch as shown in Fig. 4-3. The first of these had 37 9/32-inch holes that provided a free area representing 32.5% of the total cross-sectional area of the column. The other had 43 1/8-inch holes corresponding to a free area of 7.5%. Each nest of baffles was inserted in the bubble column reactor so that each plate was located just between the sampling points, with the first one just between the top of the nozzles and the first sampling point from the bottom.

For mixing studies, an injection point for the tracer into the column was constructed by a 1/4 inch Swagelok nut with a rubber septum. The injection point was placed at the liquid inlet.

4-2. Operating procedure

4-2-1. Mass transfer with chemical reaction

At first, ethylene gas was fed from the gas cylinder to the bottom of the reactor until air in the reactor was purged. The chlorine was introduced, followed by water.

During the early period of a run, the flow rate of chlorine was kept lower than the desired rate lest it should come out in the gas outlet. When the liquid level was reached at the half of the column height, the flow rate of chlorine was raised up to the desired level.

The operation was continued until the steady-state was reached as indicated by reading of the reactor temperature, the flow rate of gas outlet, and the concentration of hydrochloric acid. It took approximately two hours until
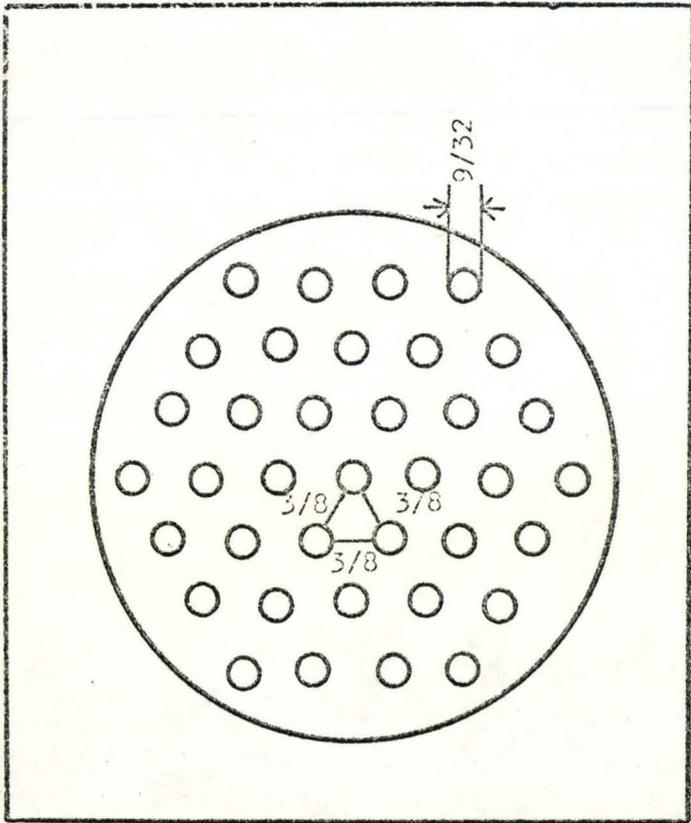
Perforated plate (A)
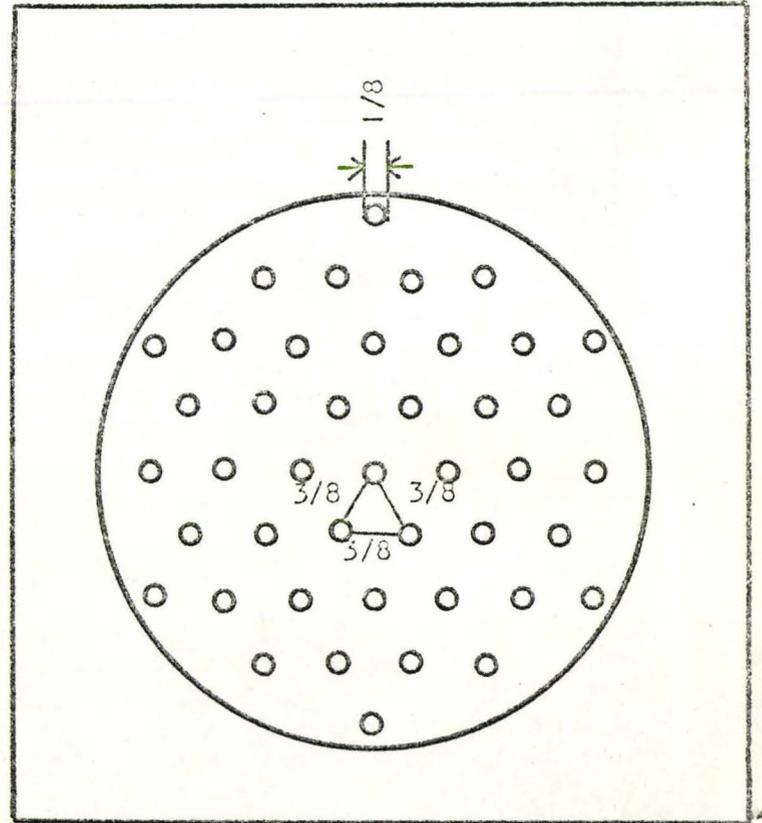
Perforated plate (B)

Fig. 4-3   Arrangements of holes of perforated plates

the steady-state was reached after the liquid level had come to the top of the column. Then, liquid samples were taken from the liquid outlet and three of the 7 sampling points. Temperatures were recorded, the flow rate of the outlet gas was read and the gas phase was analysed for chlorine.

4-2-2. Mass transfer without chemical reaction

The physical absorption rate of ethylene into water was measured. Ethylene and nitrogen were introduced into the bubble column followed by water. The operation was carried out in a similar way to that discussed above.

Water was heated to about $30^{o}C$ before being fed to the bubble column. This was done in order to maintain the same reactor temperature as existed during the chlorine and ethylene reaction runs.

Nitrogen flow rates were maintained at the same levels as those that were used for chlorine in the case of chemical reaction.

From time to time, the gas phase was analysed for ethylene and nitrogen by gas chromatograph. After the steady-state had been indicated by the gas chromatogram, the observed values were recorded.

4-2-3. Mixing studies

The mixing in the reactor was investigated by means of tracer studies. The response for an impulse input was obtained which gave a relationship between the concentration and time, the so-called C-curve[41]. Potassium chloride was chosen as the tracer.

At first, nitrogen gas was introduced into the bubble column, and water followed. After the liquid level had been reached and the flow rates had been

steady, about 10 cc of saturated potassium chloride solution was introduced into the column through the injection point using a hypodermic syringe of a capacity of 10 cc. Simultaneously, a stop watch was started.

A sample was taken every fifth minute from the liquid outlet and was analysed by a conductivity meter. When the concentration at the liquid outlet dropped almost to zero, a run was completed. This required about three hours.

4-2-4. Gas hold up

Gas hold up was measured with and without baffling. The bubble column was operated in the same way as mentioned in 4-2-3. After the steady-state was reached, both the gas and liquid were shut off and the liquid level was read.

4-3. Analysis

4-3-1. Gas chromatography

A Beckman GC-2A gas chromatograph with a thermal conductivity detector was used during this work. Helium was used as the carrier gas. The output signal from the gas chromatograph was recorded by a Servo II laboratory recorder with an automatic disc integrator.

Generally, it is very difficult to analyse a liquid sample which includes water in large amounts because of the strong tailing. For determination of ethylene chlorohydrin, ethylene dichloride and water, a combination of Porapak P and Paraplex G-25 on Teflon was employed in a dual-column system as shown in Fig. 4-4 Porapak P, a cross-linked polystyrene, was used to successfully separate water from ethylene chlorohydrin and ethylene dichloride without any significant tailing,

GSV: Gas sampling valve
IJP: Injection point

HC: Heating coil
PP: Porapak-P column
PT: Paraplex G-25 on Teflon column
SG: Silica gel column
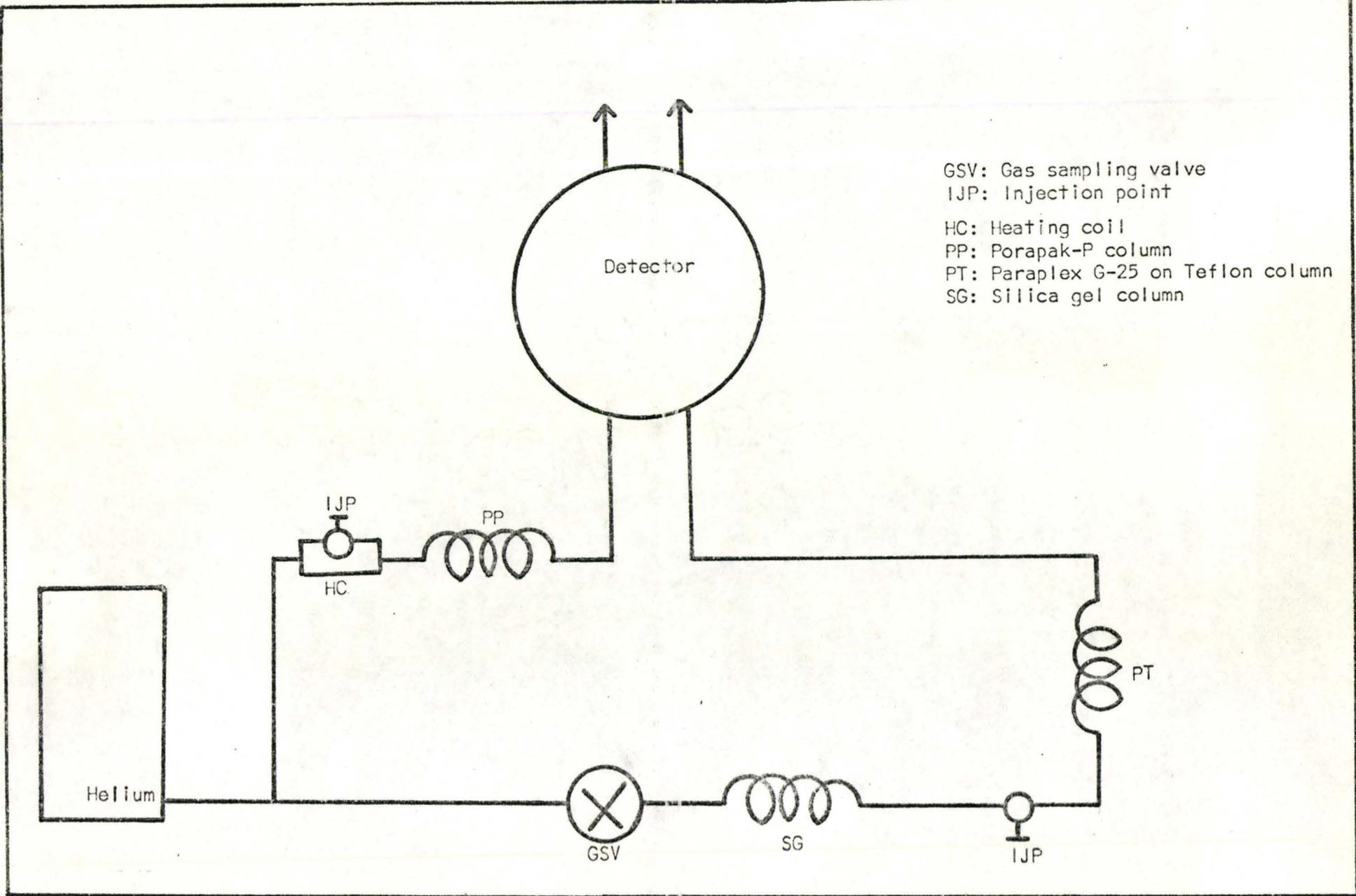
Fig. 4-4 Dual-column system

although the latter two components were not separated. The Paraplex G-25 on Teflon column separated ethylene chlorohydrin from the other two ingredients[1]. An injection point was constructed for the Porapak P column with a 1/4 inch Swagelok nut with a rubber septum. This part was heated by an electric heating tape to 100°C approximately. The operating condition of this system was as follows:

i)   Column length

          Paraplex G-25 on Teflon   150 cm
          Porapak P   55 cm

ii)   Column temperature   130°C

iii)   Helium flow rate   30 cc/min

iv)   Electric current   150 mA

v)   Retention time

          Paraplex G-25 on Teflon

          Water and ethylene dichloride   0.5 min
          Ethylene chlorohydrin   10   min

          Porapak P

          Water   0.5 min
          Ethylene chlorohydrin and
                  ethylene dichloride   10   min

For separation of ethylene and nitrogen, a Porapak P column was successfully employed. The operating condition was as follows:

i)   Column length   50 cm

ii)   Column temperature   25°C

iii)   Helium flow rate   20 cc/min

iv)   Electric current   150 mA

v)   Retention time
            Nitrogen   40 sec
            Ethylene   90 sec

For separation of ethylene and chlorine, a silica gel column was recommended[25]. The operating condition was as follows:

i)   Column length   50 cm

ii)   Column temperature $40^{\circ}C$

iii)   Helium flow rate   30 cc/min

iv)   Electric current   150 mA

v)   Retention rate

            Ethylene   2 min
            Chlorine   4.5 min

4-3-2. Conductivity

A Radiometer conductivity meter, type CDM-2, was used for determination of the concentrations of hydrochloric acid and of potassium chloride.

4-3-3. Titration

A combination of acidimetry and iodometry was adopted for determination of hypochlorous acid and chlorine in the liquid sample.

Scott's procedure[50] was followed except that no hydrochloric acid was added to the sample during this work. The determination depends on the

following reactions:

$$2KI + HOCl \rightarrow KCl + KOH + I_2 \qquad (4-1)$$

$$2KI + Cl_2 \rightarrow 2KCl + I_2 \qquad (4-2)$$
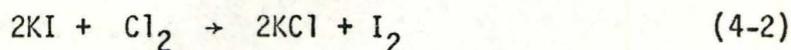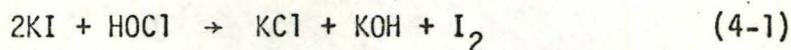
The alkali liberated by hypochlorous acid and the total iodine were determined, and calculations were made for each component.

At first, sufficient potassium iodide was added to complete reactions (4-1) and (4-2). The liberated iodine was titrated with sodium thiosulfate.

$$2 Na_2S_2O_3 + I_2 \rightarrow 2 NaI + Na_2(S_2O_3)_2 \qquad (4-3)$$
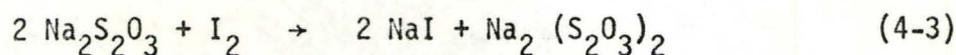
Part of the hydrochloric acid originally present in the sample had been consumed in neutralizing potassium hydroxide produced by reaction (4-1), and the excess hydrochloric acid was titrated with sodium hydroxide using methyl orange as the indicator.

$$NaOH + HCl \rightarrow NaCl + H_2O \qquad (4-4)$$
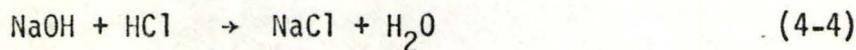
CHAPTER 5

RESULTS AND DISCUSSION

5-1. Mass transfer with chemical reaction

Experiments were carried out with co-current flow in the multi-nozzle bubble column reactor with and without baffles.

5-1-1. Experimental conditions

During this study, the water flow rate was maintained at 40 ml/min. The ethylene flow rate changed between 1550 cc/min and 2700 cc/min at $25^{o}C$ and atmospheric pressure. The flow rate of chlorine ranged from 1070 cc/min to 1600 cc/min at the same conditions. All the flow rates were kept constant during the run. The ethylene to chlorine ratio varied between 1.2 and 1.9.

Inlet gas temperatures were $25^{o}C$ and that of water was $21^{o}C$ during the experiment. Cooling water was kept flowing through the water jacket during the run with chemical reaction, thus controlling the reactor temperature at $30^{o}C$ approximately.

Experimental condtiions are summarized in Tables Al-1A, Al-1B and Al-1C. Experimental results are shown in terms of concentration profiles of the products in Tables Al-2, Al-3 and Al-4. Position 0 means the reactor outlet, 2 means the second sampling point from the top and 4, the 4th and 7, the bottom.

No appreciable temperature profiles along the column were observed during the study, and the reactor temperatures at the middle of the column reactor are given in Table Al-1.

5-1-2. Effect of variation in the gas flow rates

Several effects of gas flow rates were investigated in the unbaffled column reactor.

Fig. 5-1 shows the effect of the chlorine flow rate on the yields of ethylene chlorohydrin and ethylene dichloride. Here, the yield of the products is based on the amount of chlorine fed to the reactor. During this study, the flow rate of chlorine was varied keeping other variables constant. The figure shows that more ethylene dichloride and less ethylene chlorohydrin were produced as the chlorine flow rate increased. It is suggested that the low chlorine flow rate be favored for the formation of ethylene chlorohydrin. This tendency agrees with Domask and Kobe's result[17].

Fig. 5-2 shows the effect of ethylene to chlorine ratio on the yield of ethylene chlorohydrin and of ethylene dichloride. Here, the yield of the products is based on the amount of ethylene fed to the reactor. This figure was obtained by keeping the chlorine flow rate at 1350 cc/min at 25°C and atmospheric pressure. It is found that the yields of the products were strong functions of the ratio. It shows that the highest yield of ethylene chlorohydrin was obtained when the flow rate of ethylene was 2120 cc/min corresponding to an ethylene to chlorine ratio of about 1.6. This ratio, 1.6, would be the optimum for a high yield of ethylene chlorohydrin and a low yield of ethylene dichloride. Domask and Kobe suggest that the ratio of 1.5 be used for the formation of ethylene chlorohydrin.

A set of experiments was done keeping the ratio of ethylene to chlorine at 1.6. The result of this study is given in Fig. 5-3. Neither the yield of ethylene chlorohydrin nor that of ethylene dichloride seems to be a strong function
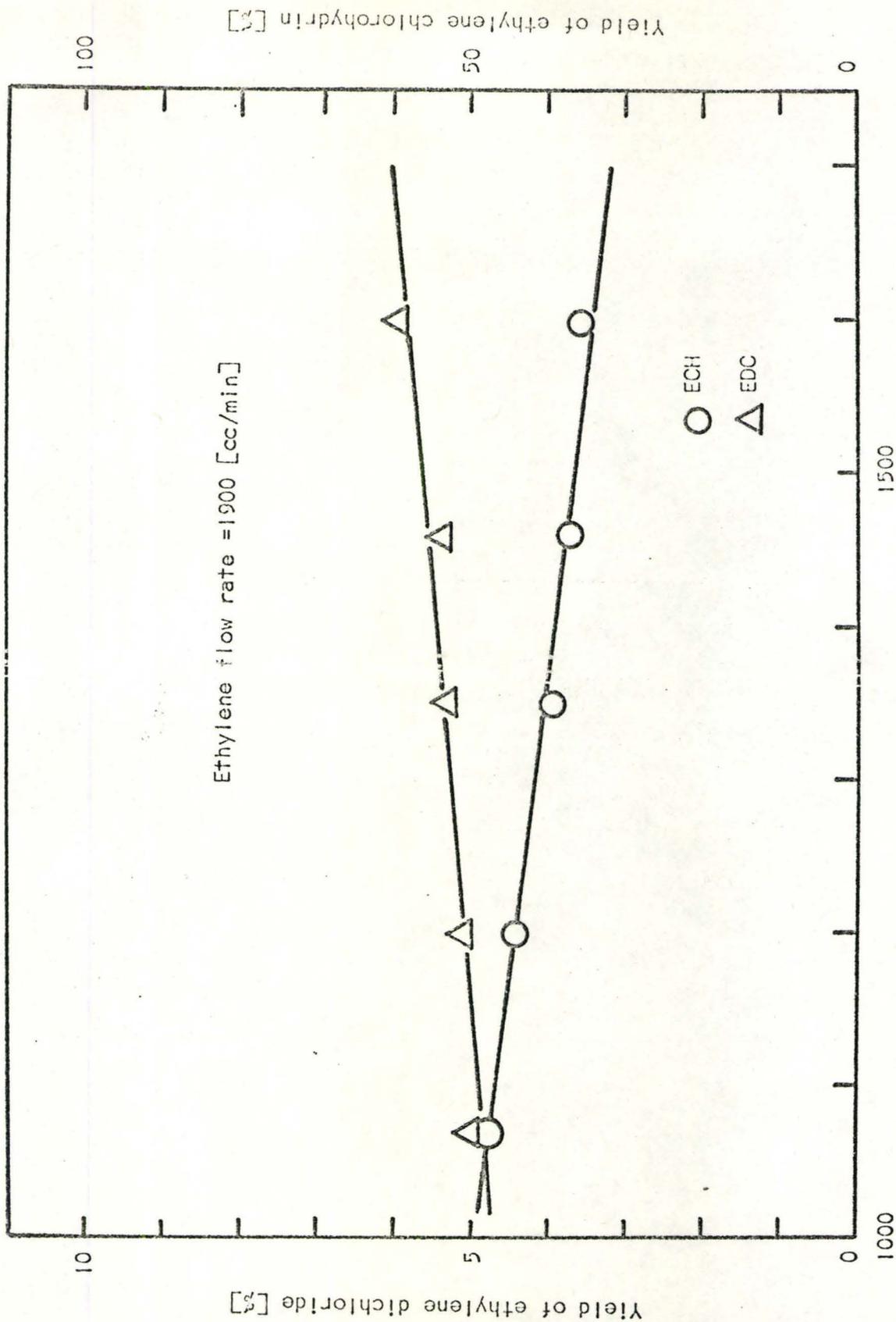
Fig. 5-1   Effect of chlorine flow
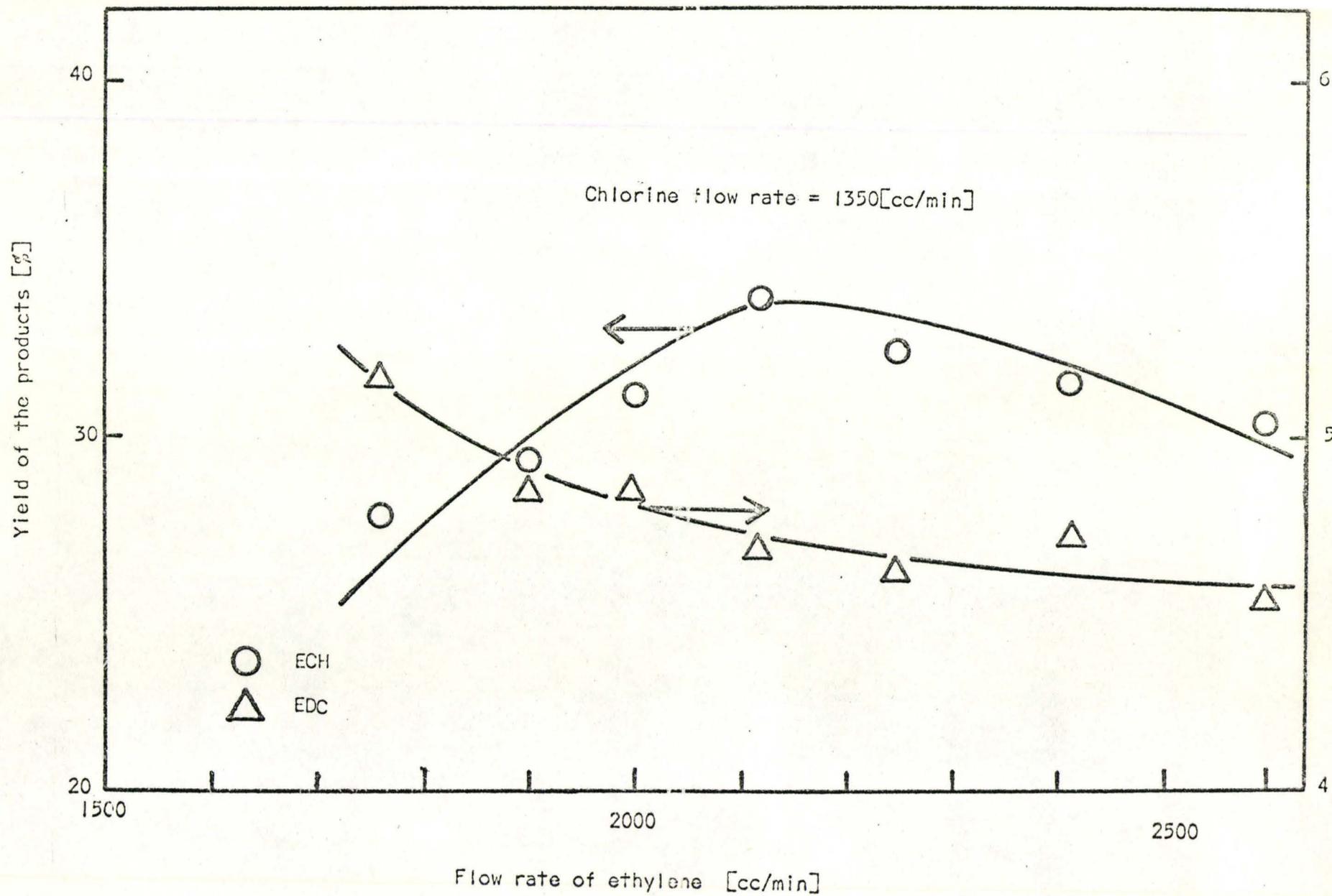
Fig. 5-2   Effect of ethylene flow
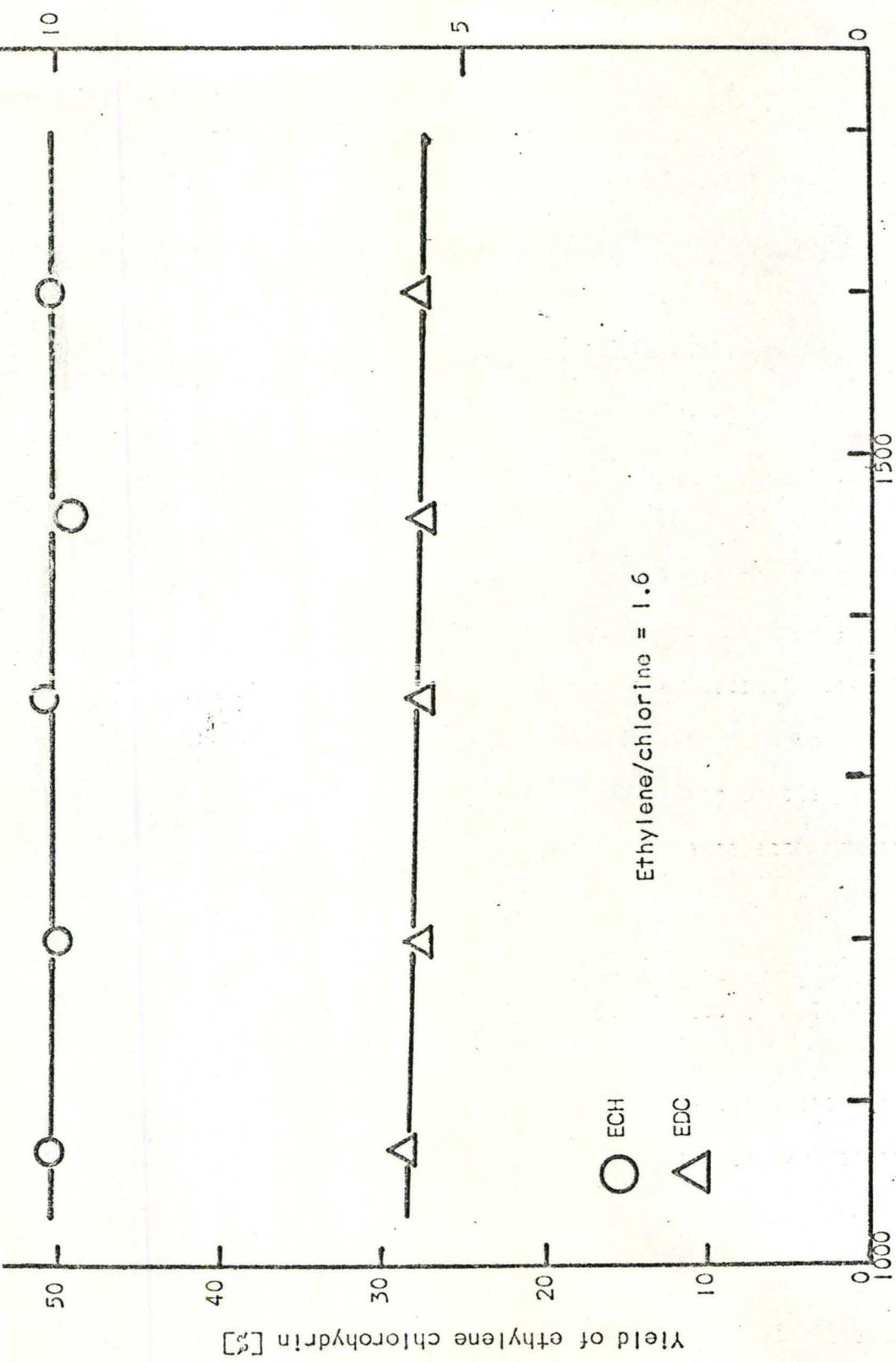
Fig. 5-3   Effect of gas flow rates

of the gas flow rates although Domask and Kobe reported that they obtained more yield of ethylene chlorohydrin at low gas flow rates.

5-1-3. Effect of baffling

Two sets of baffles having different free areas were introduced into the column reactor in the later period of this work. The first (A) had a large free area, 32.5% of the total cross-sectional area of the column, and the other had a small free area, 7.5%.

Figs. 5-4 and 5-5 show the effect of baffling on the yield of ethylene chlorohydrin. The sets of data for Fig. 5-4 were obtained by keeping the flow rate of chlorine at 1350 cc/min. The same effect of the ethylene flow rate on the yield of ethylene chlorohydrin is shown both in the baffled and in the un-baffled reactor. Fig. 5-5 is the result of sets of runs in which the ethylene to chlorine ratio was maintained at 1.6.

Fig. 5-6 shows the effect of baffling on the yield of ethylene dichloride. Fig. 5-7 shows the effect of baffling on the selectivity of ethylene chlorohydrin. Here the selectivity is defined as:

$$C_{ECH}/(C_{ECH} + C_{EDC}) \times 100 \ (\%) \qquad\qquad (5-1)$$

Fig. 5-8 shows the effect of baffling on the conversion of ethylene. The sets of data for Figs. 5-6, 5-7 and 5-8 were obtained by keeping the ratio constant at 1.6.

From these figures, the following conclusions were made:

1) The baffled reactors gave a higher yield of ethylene chlorohydrin and a lower yield of ethylene dichloride than the unbaffled reactor.
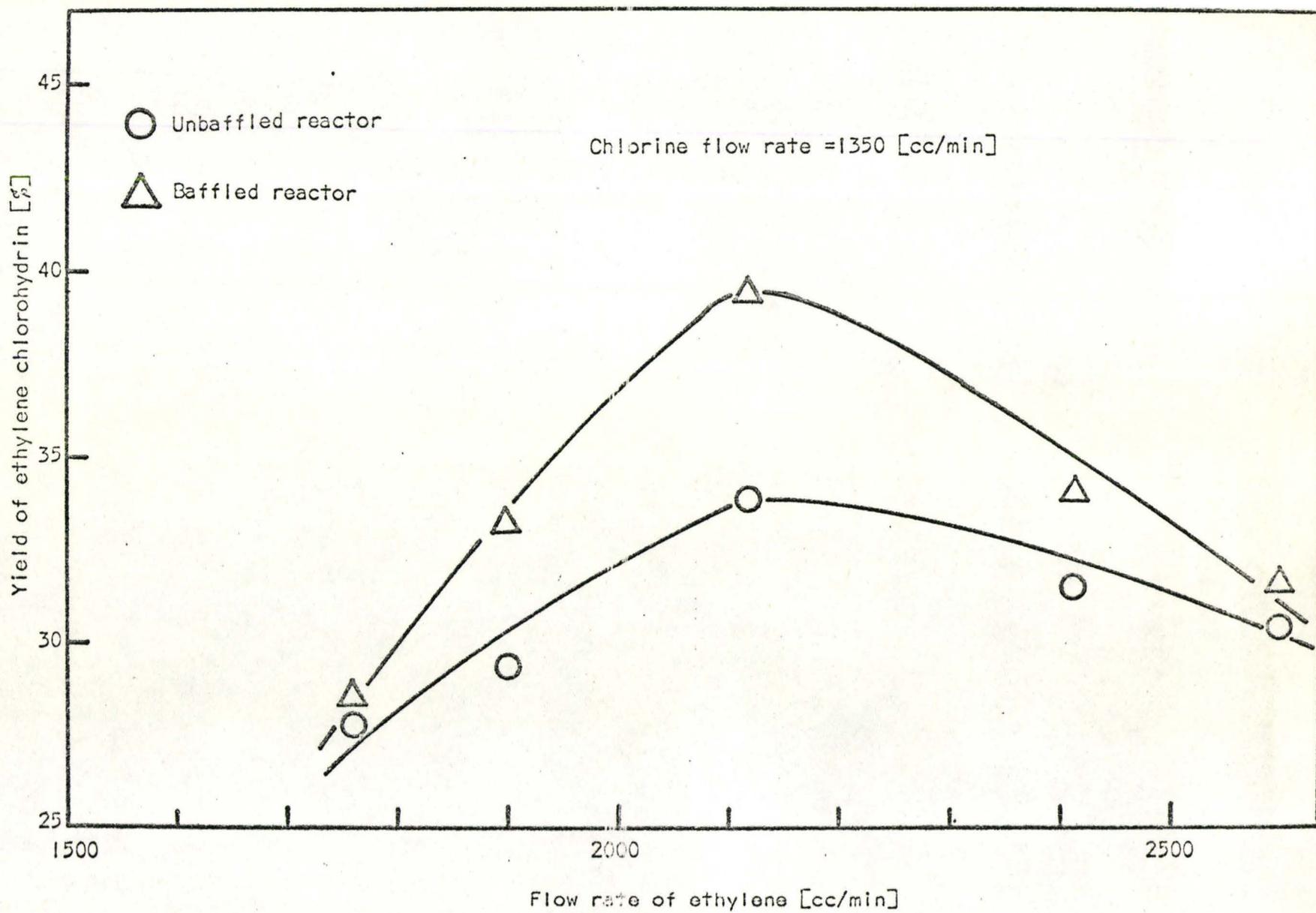
Fig.5-4　Effect of baffling on the yield of ethylene chlorohydrin
(Constant chlorine flow)
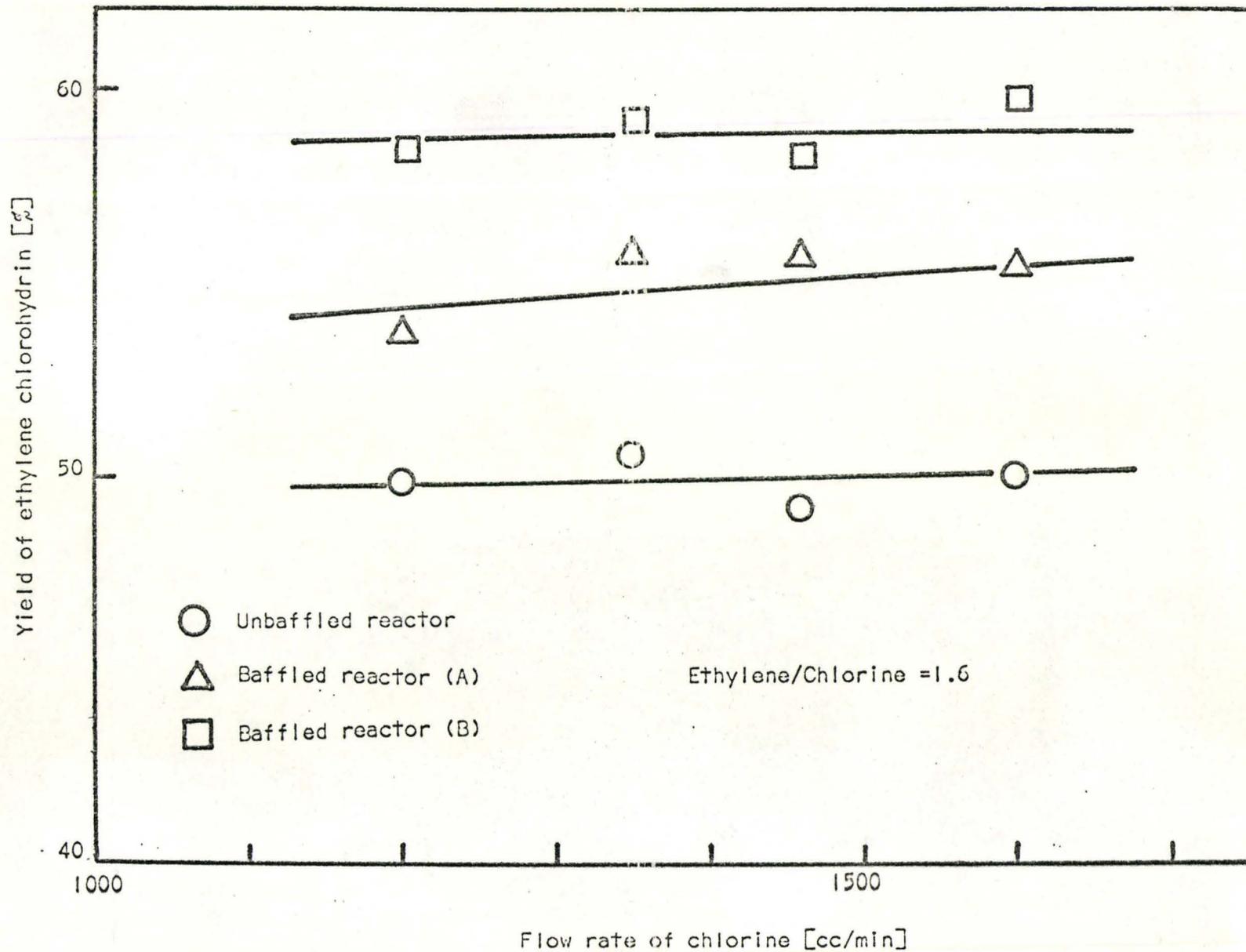
Fig.5-5   Effect of baffling on the yield of ethylene chlorohydrin
(Constant ratio)
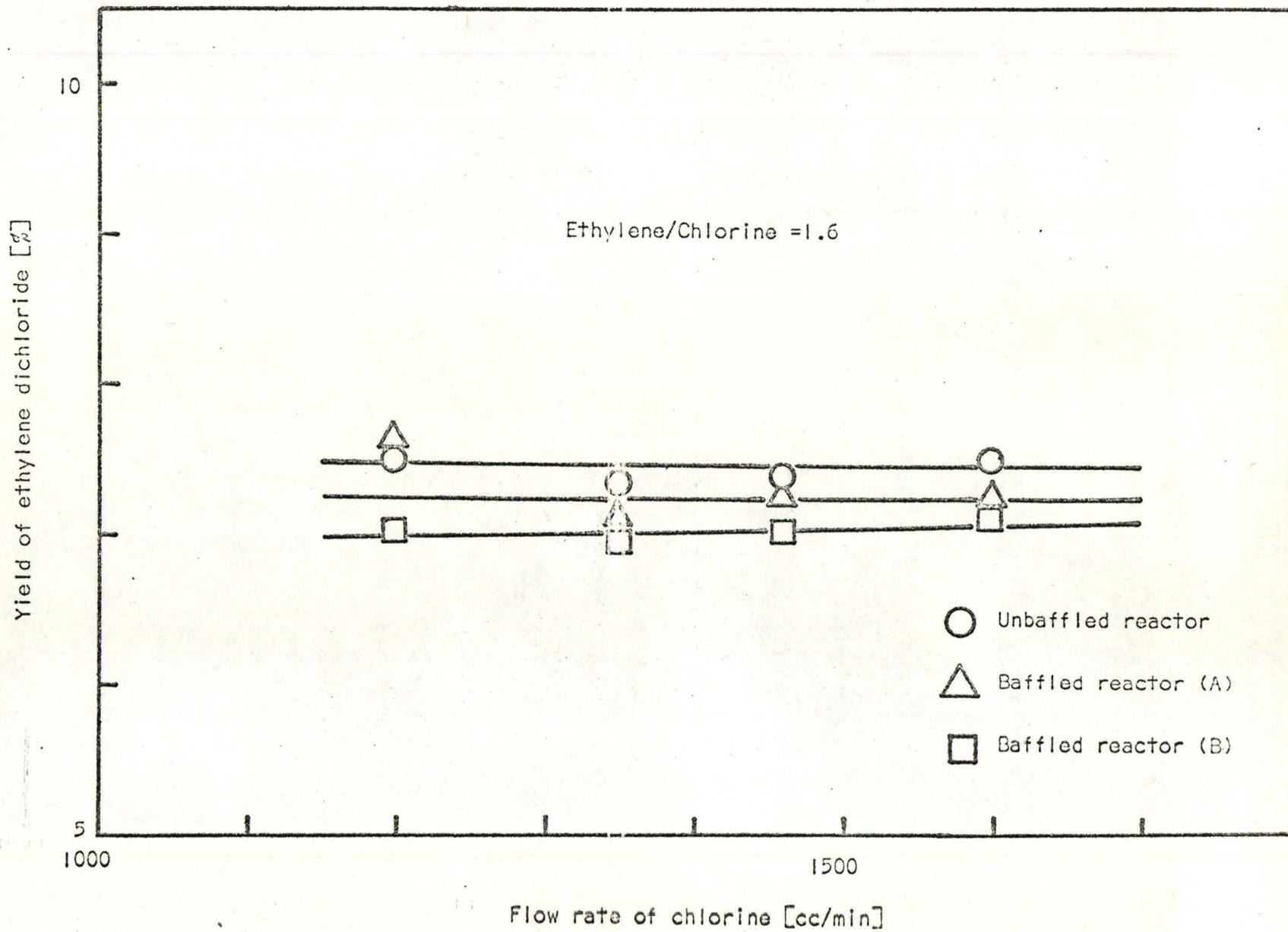
Fig. 5-6   Effect of baffling on the yield of ethylene dichloride

38
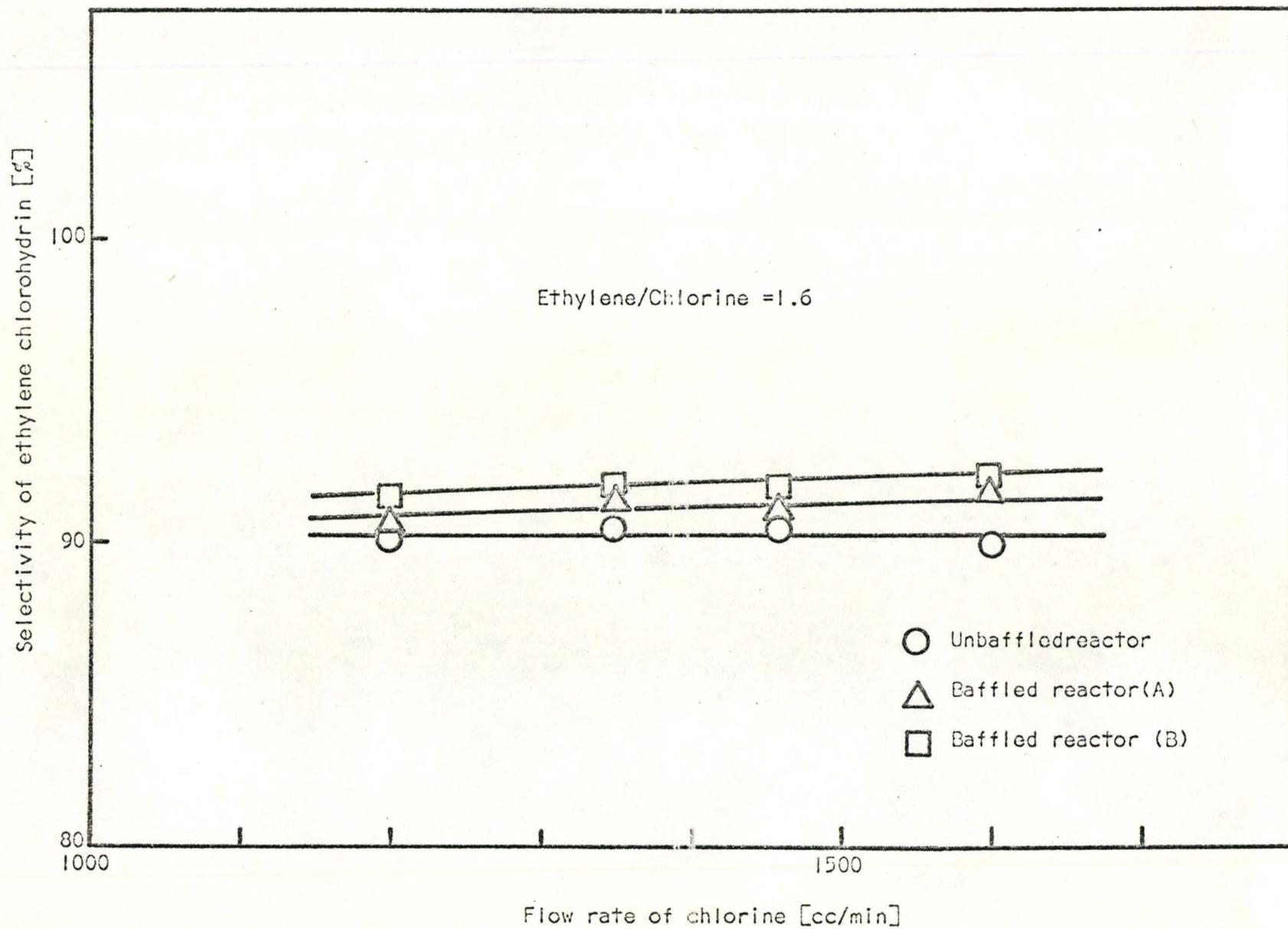
Fig. 5-7   Effect of baffling on the selectivity of ethylene chlorohydrin
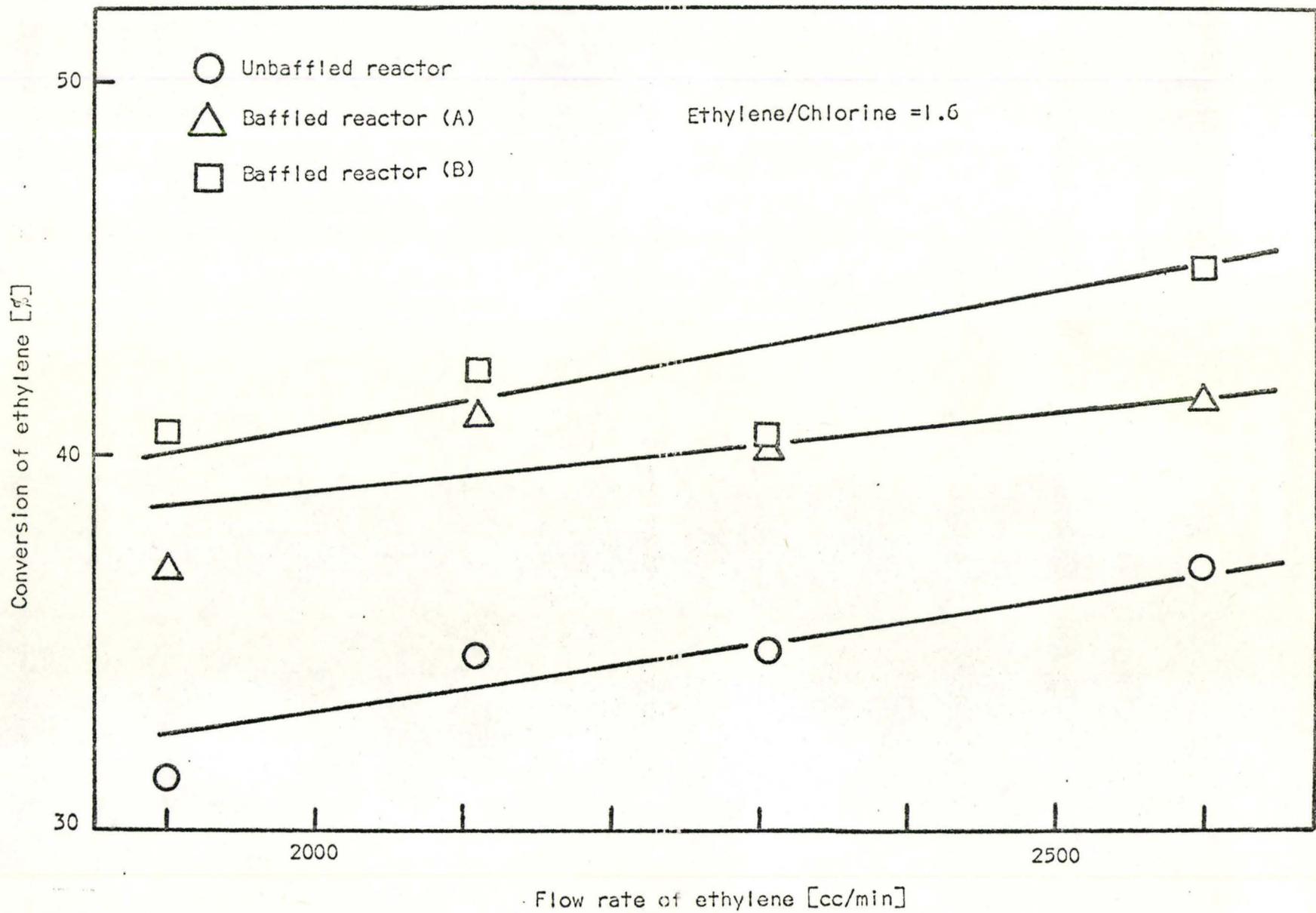
Fig. 5-8   Effect of baffling on the conversion of ethylene

2) The baffled reactor (B) provided more ethylene chlorohydrin and less ethylene dichloride than the baffled reactor (A).

3) The selectivity of ethylene chlorohydrin was increased in the baffled reactors.

4) An improved conversion of ethylene was obtained in the baffled reactors.

The perforated plates in the baffled reactor caused more bubbles to be broken than the broken-up in the unbaffled reactor. Also more bubbles are broken up in the baffled column (B) than in the baffled column (A). Thus, gas hold up and the interfacial area between gas bubbles and the liquid phase are increased. Fig. 5-9 shows the effect of baffling on gas hold up. It was increased about 50% in the baffled column (B). This is one of the reasons for the enhanced conversion of ethylene.

Fig. 5-10 shows that more hydrochloric acid was produced near the reactor outlet in the baffled reactor. When the axial mixing is controlled by baffling, the reaction (3-14) is proceeding as the liquid phase moves up the column. In the lower part of the column, low concentration of hydrochloric acid should affect the equilibrium in favor of hypochlorous acid formation. As the liquid phase moves further up the column, the forward reaction of (3-14) proceeds, thus increasing the hydrochloric acid concentration as indicated by Fig. 5-10. Although it might be suspected that the accumulation of hydrochloric acid tends to restrict the forward reaction, chlorine should have been largely used up before this happens. Hence, it is suggested that the improvement in conversion of ethylene to ethylene chlorohydrin may be related to the control of hydrochloric acid concentration.
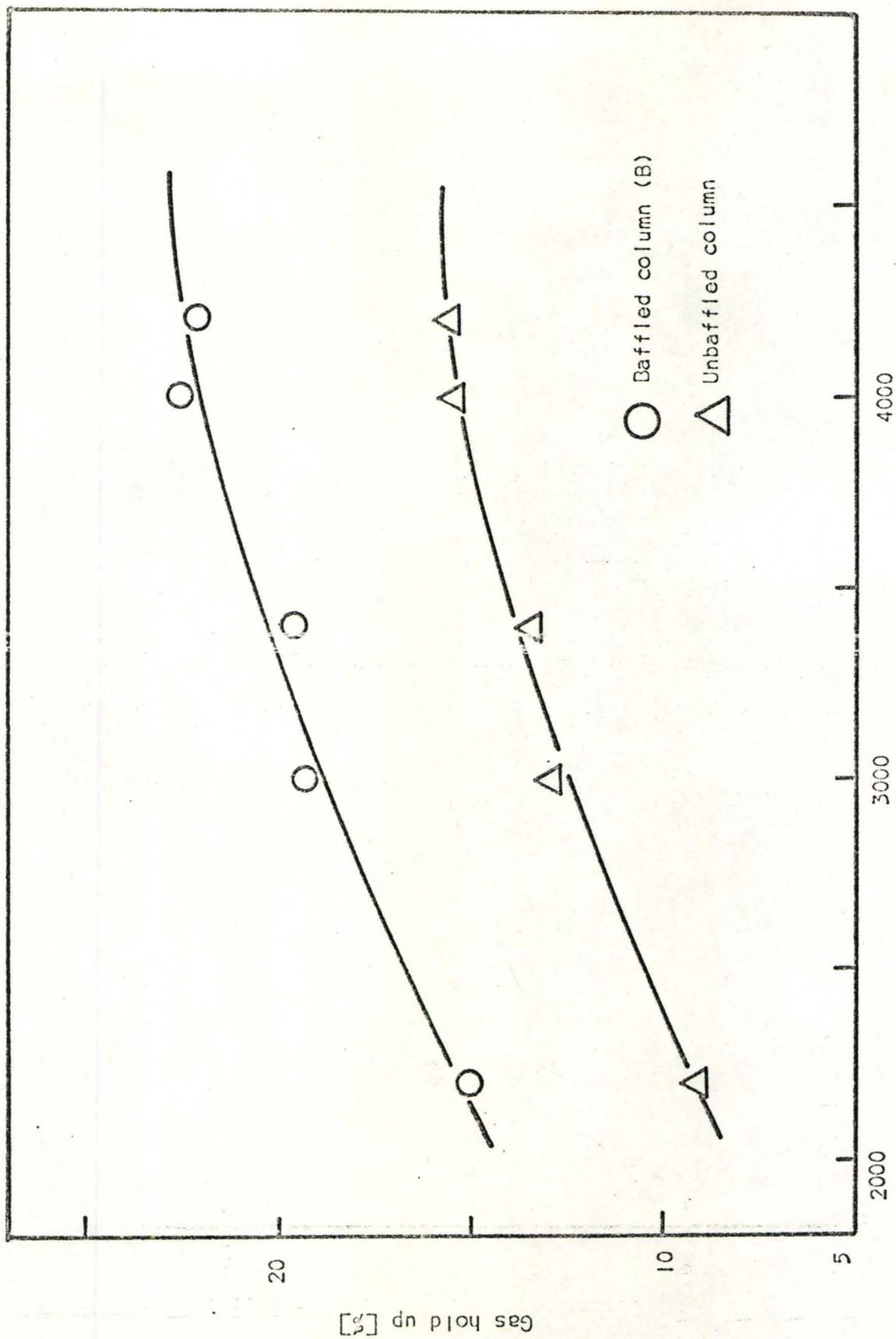
Fig. 5-9   Effect of baffling on gas hold up
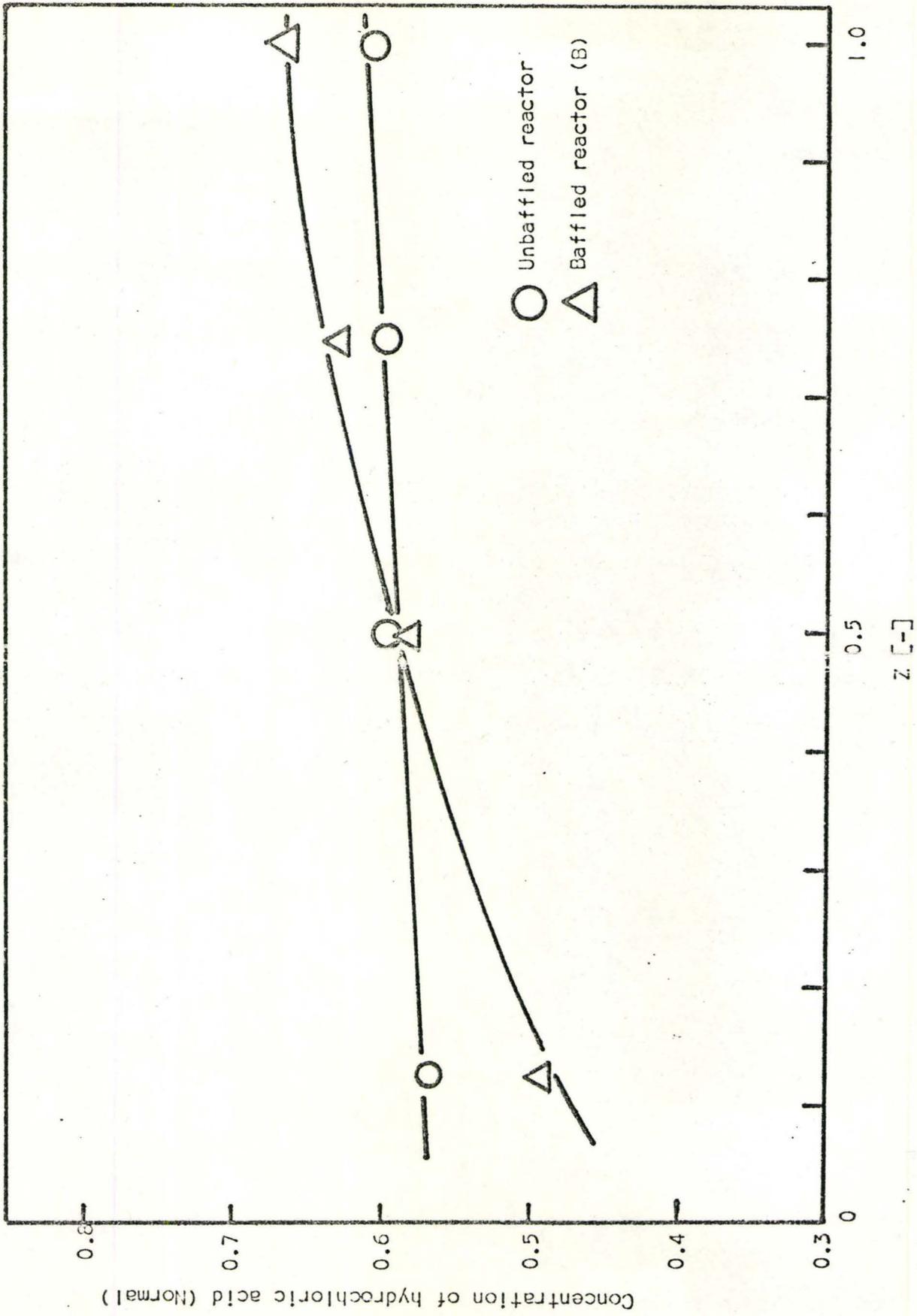
Fig. 5-10 Concentration profiles of hydrochloric acid

Little entrainment of liquid in the outlet gas in the baffled column reactor, and even less entrainment in the baffled reactor (B) was observed. It is because the baffles caused a less violent bubble action.

5-1-4. Material balance

Material balances were checked based on ethylene and chlorine around the apparatus. This gives an indication of the performance in the reactor and the reliability of the analysis carried out. The outlet gas flow rate and the inlet gas flow rates of ethylene and chlorine were measured by using calibrated rotameters. The outlet liquid was analysed for water, ethylene chlorohydrin, hydrochloric acid, ethylene dichloride, hypochlorous acid and chlorine. The gas phase was also analysed by means of the gas chromatograph. However, no chlorine was detected in the outlet gas during the experiments.

The ethylene balance based on the amount of ethylene fed to the reactor involved an imbalance less than ± 8% on molar basis; that for chlorine was less than ± 5%. A result is shown in Table Al-5.

5-1-5. Reproducibility

Several experiments were carried out in order to determine the reproducibility of the results in terms of the product concentration with and without baffling. The results are shown in Table Al-6. Discrepancies were less than ± 5% for both ethylene chlorohydrin and ethylene dichloride concentration.

5-2. Mixing in the reactor

5-2-1. Tracer studies

Tracer studies were carried out in order to investigate the degree of mixing in the baffled column as well as in the unbaffled column. Table Al-7 shows the experimental results, and Fig. 5-11 is a typical result in terms of the C-curves for the unbaffled column, the baffled column (A), and for the baffled column (B). These runs were made with a nitrogen flow rate of 4000 cc/min at room temperature and atmospheric pressure. The flow rate of water was 40 ml/min.

The coefficient of axial mixing was calculated numerically for each run by the method mentioned in 3-1-2.

Fig. 5-12 is the result of tracer studies in terms of the inverse Peclet number in the baffled and unbaffled columns. It shows that back-mixing was appreciably reduced by introducing baffles. As mentioned previously, Argo and Cova[2] reported that back-mixing was reduced in the baffled column. Their conclusion agrees with this result. Fig. 5-12 also shows that the baffled column (B) produced less back-mixing than the baffled column (A). Bischoff and Phillips[6] pointed out that the plate design with one large hole in the center tended to perfect mixing while plates with many small holes tended to plug flow. This result coupled with the fact that the baffle (B) had less free area than the baffle (A) is probably the reason for baffled column (B) providing less back-mixing than the baffled column (A).

The variance was also related to the tanks-in-series model:

$$1/n = \sigma_t^2/T_m^2 \qquad (5-2)$$
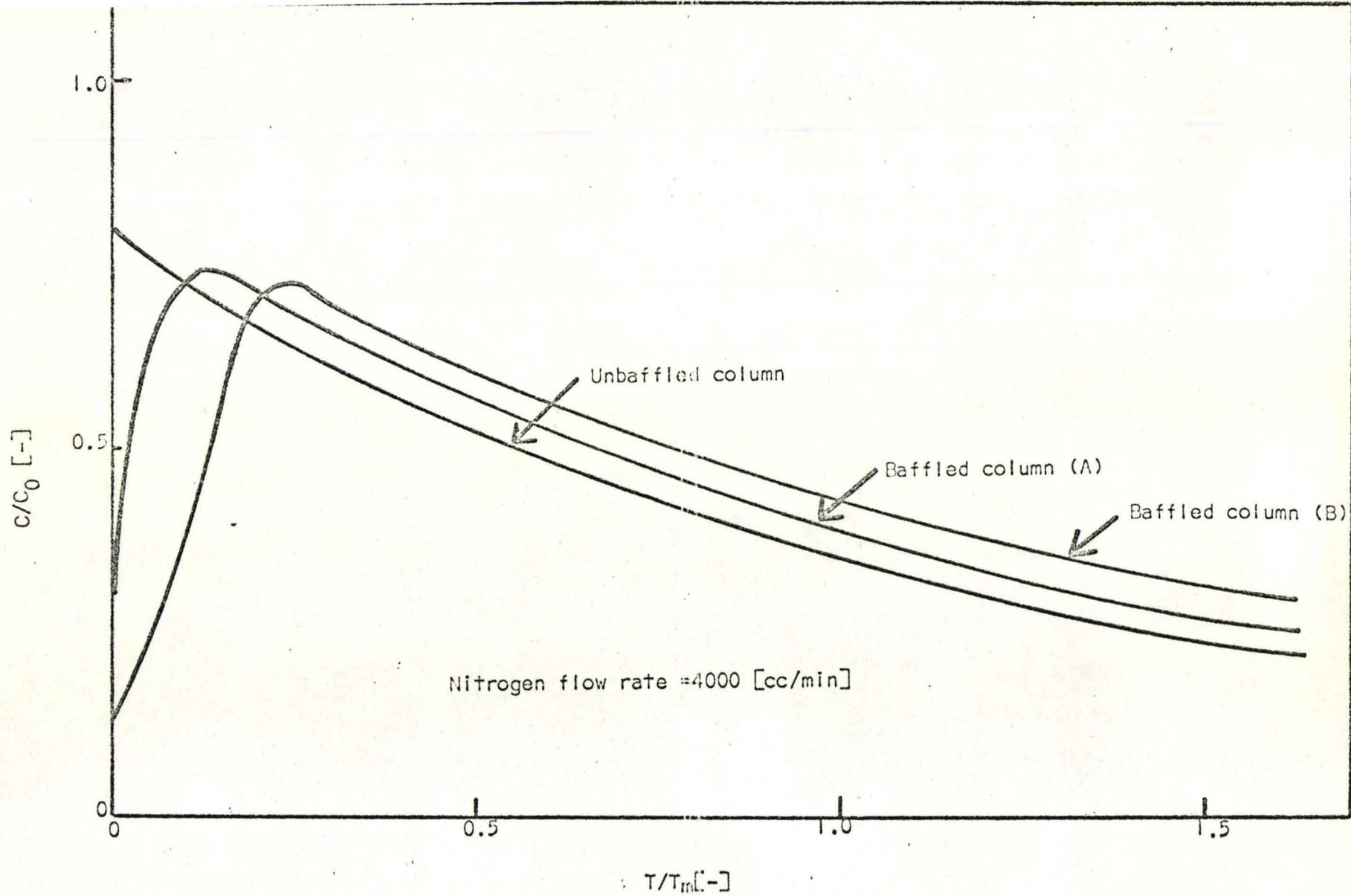
Fig. 5-11   Experimental   C-curves
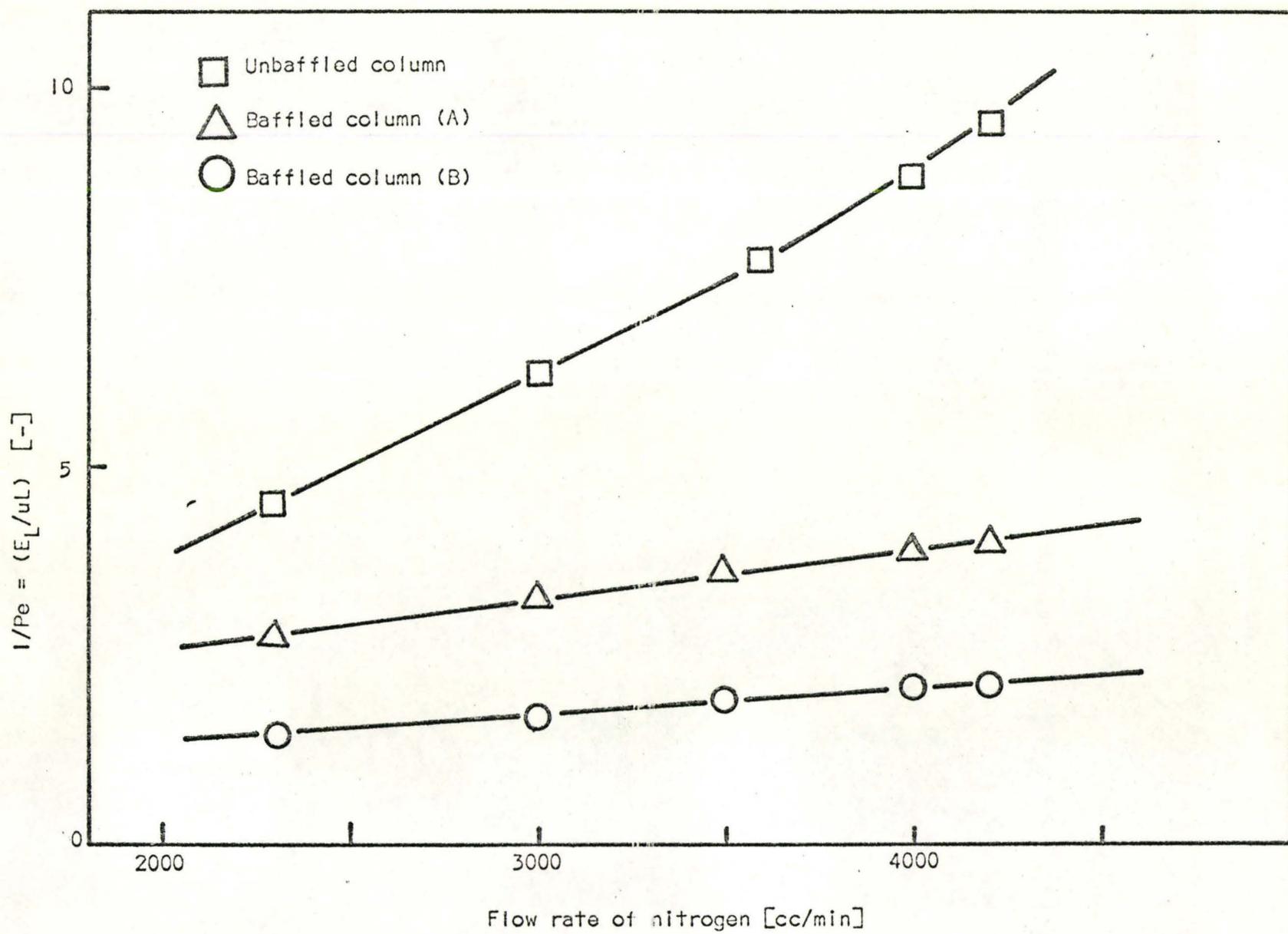
Fig. 5-12   Inverse of Peclet number

Experimental results were also treated by eq. (5-2), which gives the number of equivalent stirred tanks. It is shown in Table Al-8A.

The effect of the liquid flow rate on the coefficient of axial mixing was also investigated. The result is shown in Table Al-8B. As reported by several authors[2,22,38], the liquid flow rate did not affect the coefficient of axial mixing appreciably.

5-2-2. Axial dispersion model

The axial dispersion model, discussed in 3-1-1, was tested for the concentration profiles in the baffled and unbaffled reactors. Experimental values of Peclet number, and the production of ethylene chlorohydrin and of ethylene dichloride were substituted into eqs. (3-5) and (3-6). Predicted concentration profiles of the products were compared with the experimental results in Figs. 5-13, 5-14 and 5-15. Gas flow rates for these runs were 2310 cc/min for ethylene and 1460 cc/min for chlorine. The ethylene to chlorine ratio was 1.6. The term (E_L/UL) was obtained from Fig. 5-12 and substituted into eqs. (3-5) and (3-6).

Fig. 5-13 shows a very good agreement of the equations with the experimental results. It is because the assumption of constant product formation along the column holds well in the unbaffled column reactor due to strong axial mixing. But in the baffled column reactor (A) (Fig. 5-14), the concentration profiles predicted by the equations show less change with position than the experimental results, and this deviation is more pronounced in the baffled reactor (B) (Fig. 5-15).

As shown in Fig. 5-12, back-mixing is appreciably reduced in the baffled columns. It caused more pronounced concentration profiles of the products
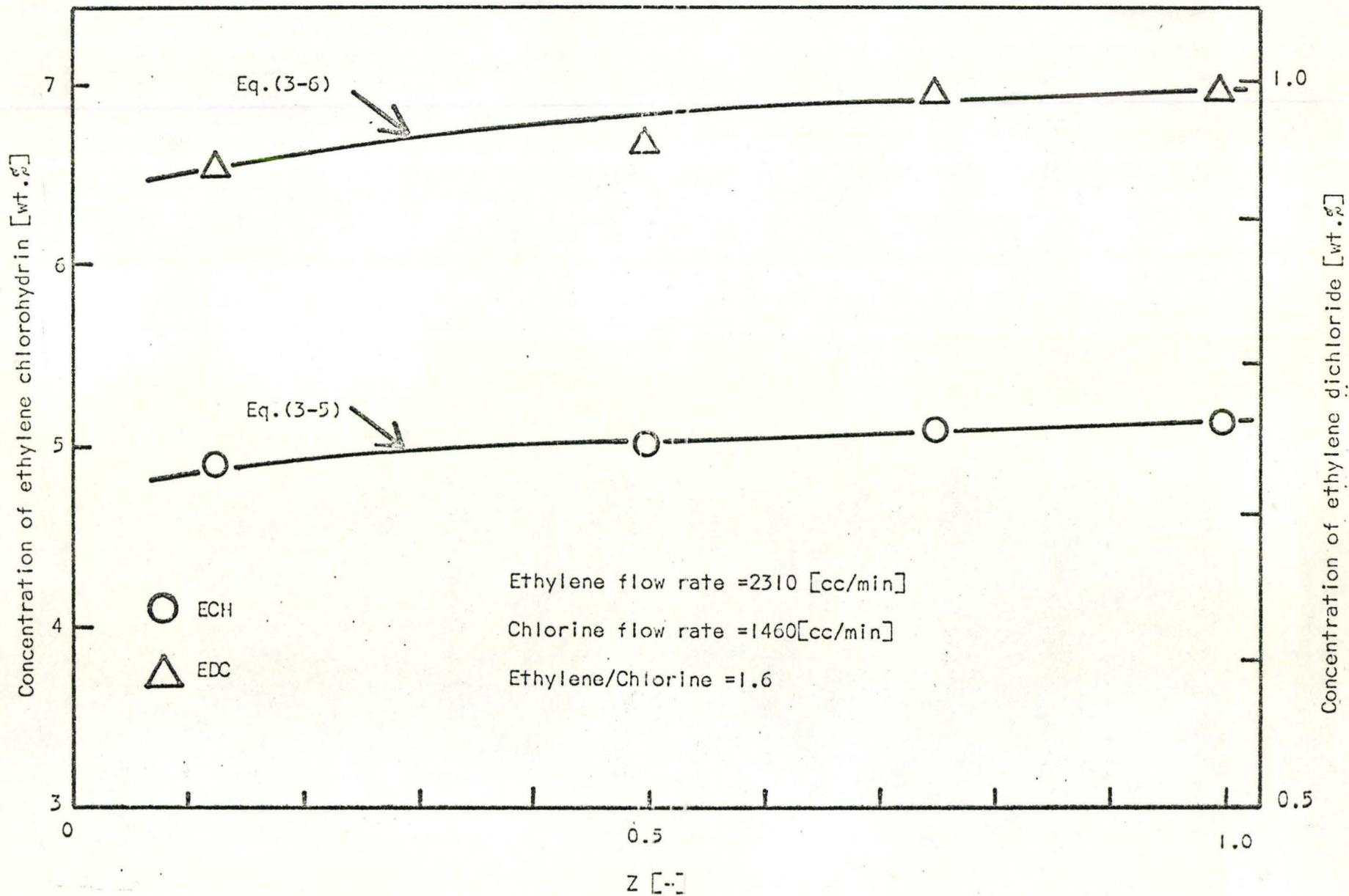
Fig.5-13   Concentration profiles in the unbaffled reactor
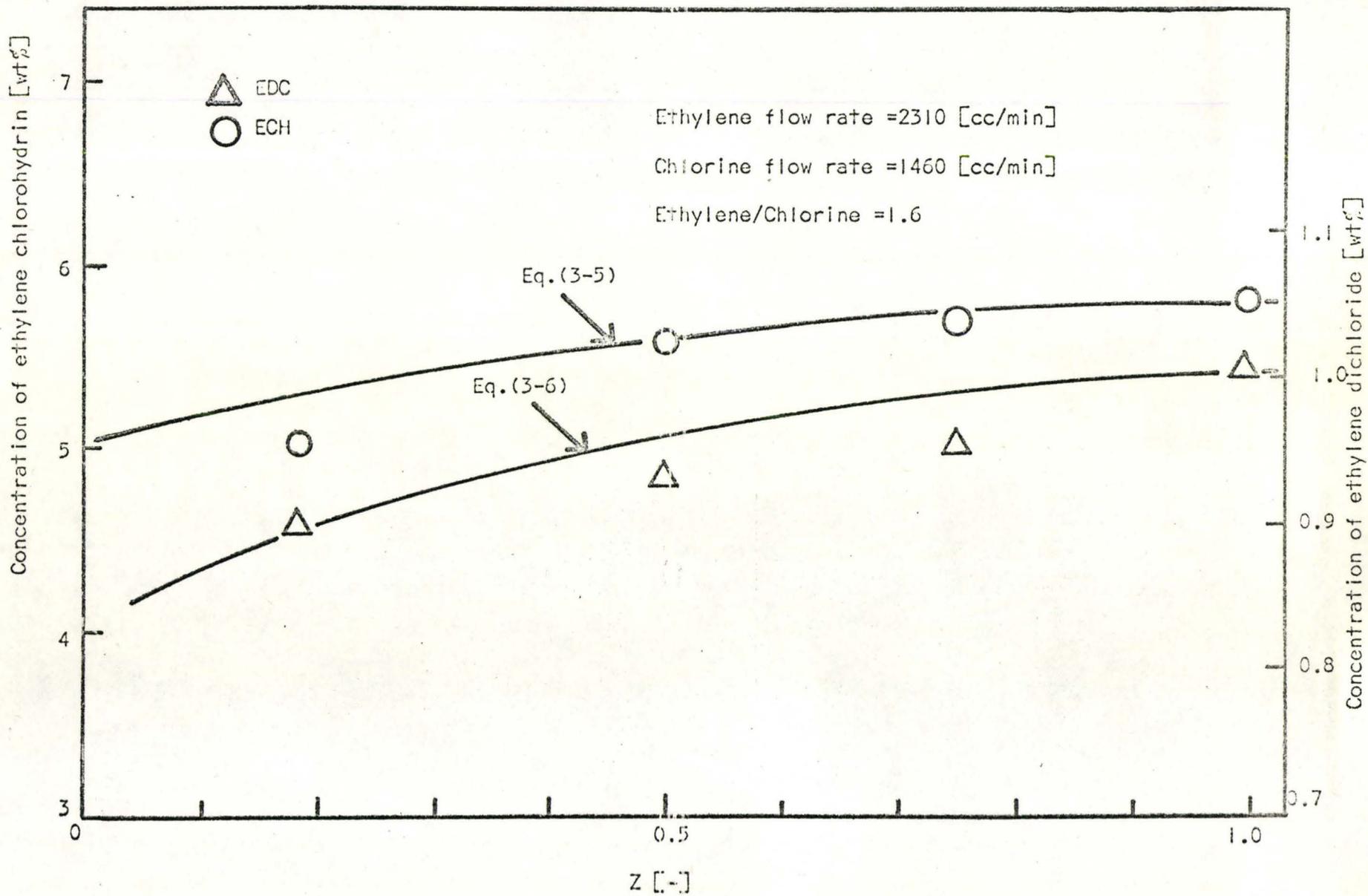
Fig. 5-14   Concentration profiles in the baffled reactor (A)

50
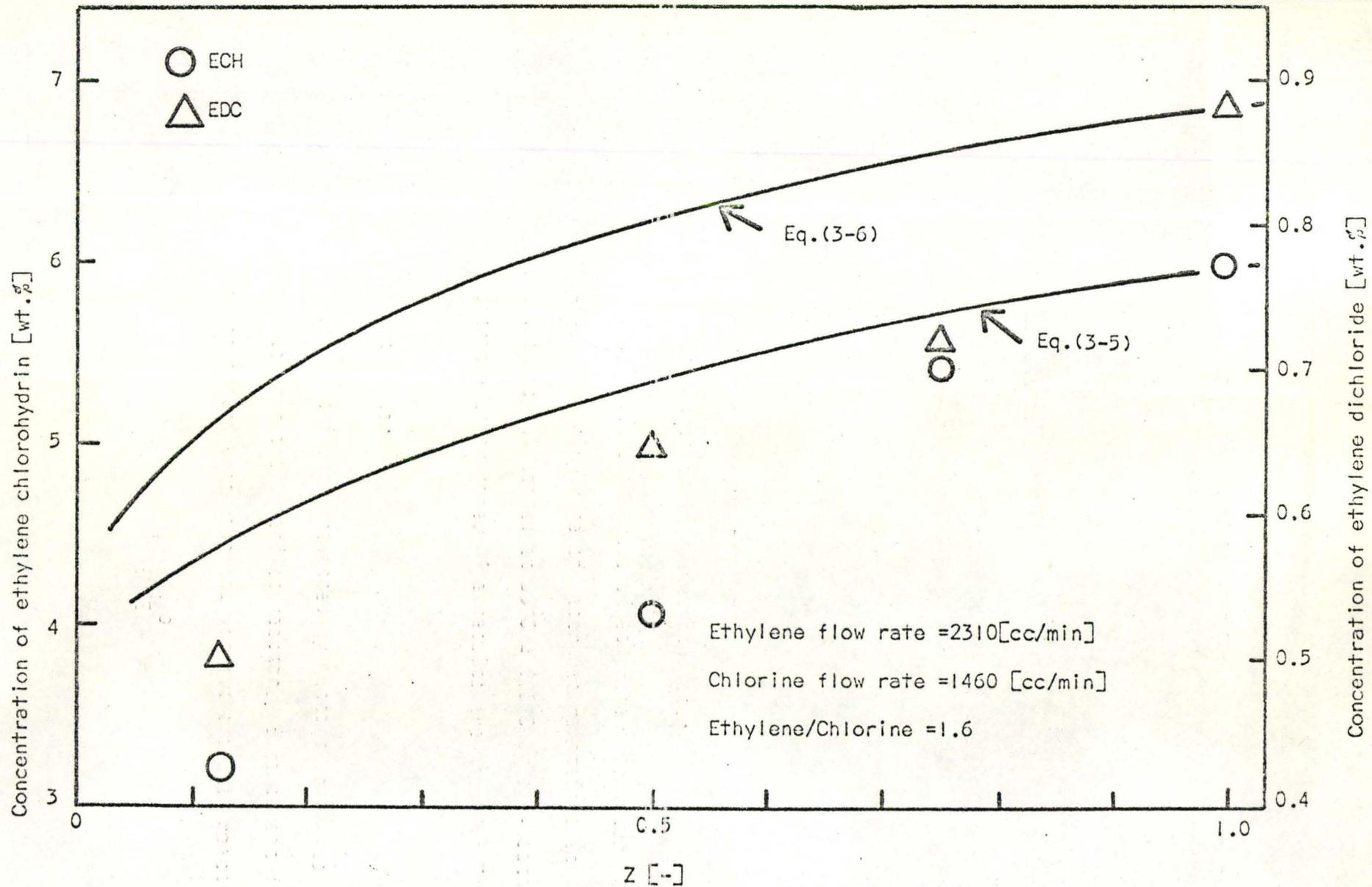
Fig. 5-15   Concentration profiles in the baffled reactor (B)

in the baffled reactors (Figs. 5-14 and 5-15). For that reason, the assumption
of constant formation of the products along the column should be modified under
reduced back-mixing conditions.

5-3. Enhancement factor

The physical absorption rate of ethylene into water was measured.
Nitrogen gas was introduced into the bubble column instead of chlorine in order to
make the same hydrodynamic condition as that existed in the case of chemical
reaction. Results were treated in terms of the enhancement factor and compared
with Hatta's model.

5-3-1. Physical absorption of ethylene into water

The physical absorption rate of ethylene into water was measured as
mentioned in 4-2-2. The flow rate of water was maintained at 40 ml/min. The
reactor temperature was maintained at $30^{\circ}C \pm 0.5^{\circ}C$ by pre-heating water by
means of an electric heating tape. The results are shown in Table A1-9.

5-3-2. Enhancement factor

The enhancement factor predicted by Hatta's model was compared with the
experimental results from the unbaffled reactor. Enhancement factors were obtained
from the absorption experiments with and without chemical reaction:

$$\phi = N_E/N_E^{\ O} \qquad\qquad (5-3)$$

Fig. 5-16 shows a comparison of Hatta's model, eq. (3-13), with the experimental results. Concentrations in eq. (3-13) were obtained from experiments, and diffusivities[7] and the saturated concentration of ethylene[34] were taken from literature. Eq. (3-13) agrees fairly well with the experimental results. Akehata and Johnson[1] reported that the enhancement factor predicted by Hatta's model was higher than their experimental results at lower temperatures while slightly lower at $20^{\circ}C$. They suggested that better agreement with the model would be observed at higher temperatures.
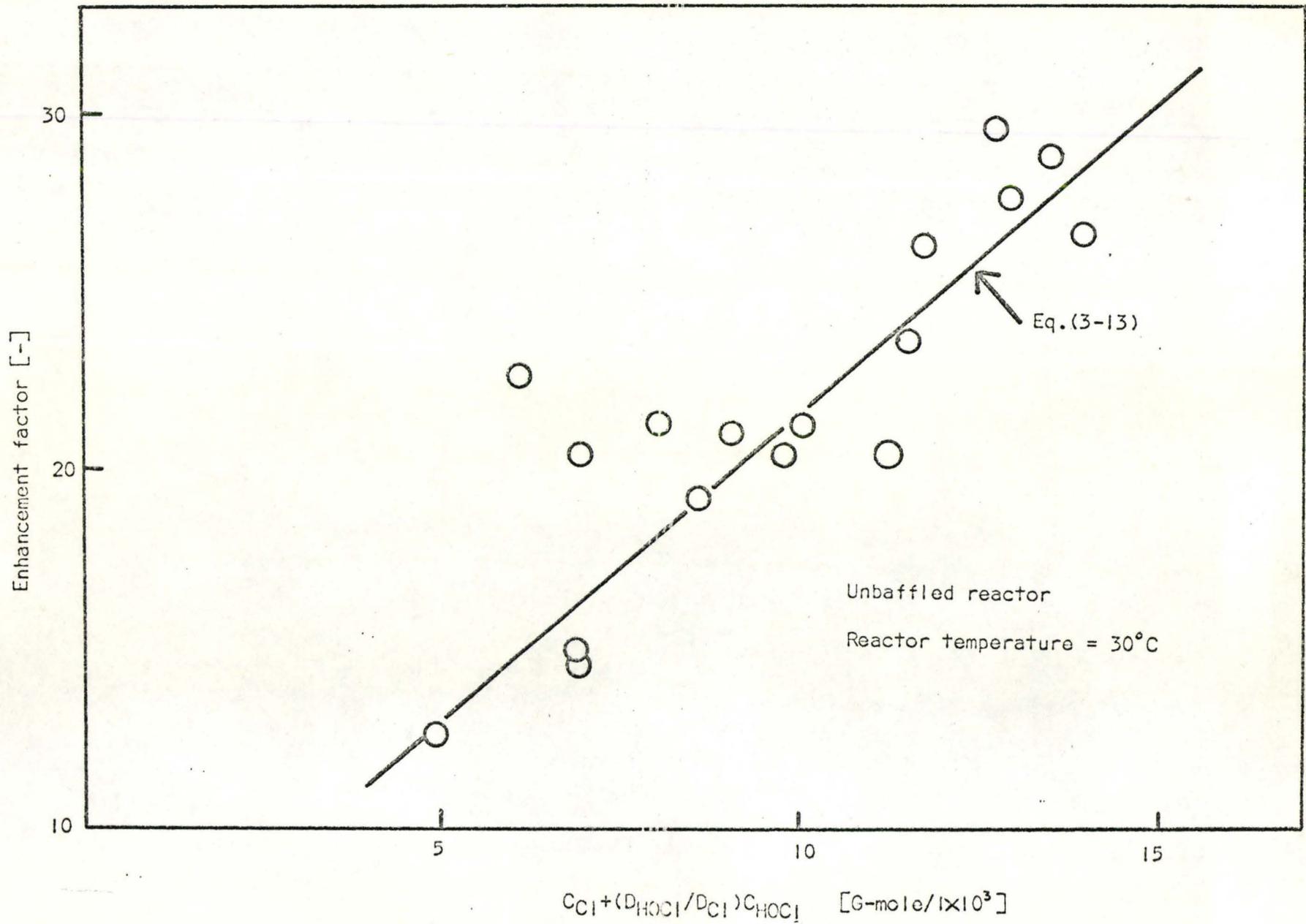
Fig. 5-16   Enhancement factor

The x-axis is labeled $C_{Cl} + (D_{HOCl}/D_{Cl})C_{HOCl}$ [G-mole/l×10³]

The y-axis is labeled Enhancement factor [-]

Eq.(3-13)

Unbaffled reactor

Reactor temperature = 30°C

CHAPTER 6

CONCLUSIONS

Experiments were carried out with the ethylene-chlorine-water system in the multi-nozzle bubble column reactor with and without baffling. The effect of axial mixing on the product distribution was investigated. The following conclusions were obtained:

1) For high yields of ethylene chlorohydrin and low yields of ethylene di-chloride, high molar ratios of ethylene to chlorine were favored.

2) An ethylene to chlorine ratio of about 1.6 was found to be optimum for high production of ethylene chlorohydrin and low production of ethylene dichloride in the apparatus studied.

3) The gas flow rates did not affect the formation of the products when the ethylene to chlorine ratio was constant.

4) The baffled reactor gave higher yields of ethylene chlorohydrin and lower yields of ethylene dichloride than the unbaffled reactor.

5) The baffled reactor with perforated plates having a less free area yielded more ethylene chlorohydrin and less ethylene dichloride than that with plates having a larger free area.

6) An improvement in the conversion of ethylene was observed in the baffled reactors.

7) In the baffled reactors, more appreciable concentration profiles of the products were observed because of reduced back-mixing.

8) The axial dispersion model with the assumption of constant product formation along the column predicted the concentration profiles of the products well when large axial mixing existed.

9) Axial mixing was reduced in the baffled columns.

10) Gas hold up was increased about 50% in the baffled column (B).

11) Hatta's model predicted the enhancement factor fairly well in this system.

CHAPTER 7

RECOMMENDATIONS

In the course of this study, the reaction of chlorine with water has caused serious trouble by corrosion in the experimental apparatus. For the material to construct the apparatus for this system, Teflon, glass and polyethylene are recommended.

It is very difficult to analyse a sample of aqueous solution by gas chromatography since water causes a strong tailing. However, it could be overcome by choosing a suitable column. It is preferable to have a column which separates ethylene chlorohydrin and ethylene dichloride without significant tailing.

For this system, very few kinetic data are available. More work should be done on the reaction rate for production of ethylene chlorohydrin and ethylene dichloride.

In this study, an axial dispersion model was tested, which predicted the concentration profiles of the products well when the liquid-phase axial mixing was large. It is suggested that eq. (3-2) be solved numerically for each component in the liquid-phase in the case of small axial mixing.

Experiments carried out during this study covered the range between 1 and 10 for the inverse of Peclet number. It is suggested that experiments be made under more reduced back-mixing conditions.

The yield of the desired product was increased by baffling during this work. The effect of baffling on the yields of products should be studied

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with other systems.

During the study, no concentration profiles of reactants were obtained. It is suggested that the concentration profiles be developed for the reactants as well as for the products.

NOMENCLATURE

A	area (counted by the integrator) (-)
C	concentration (g-moles/l)
Co	initial concentration of the tracer (g-moles/l)
D	diffusivity (cm^2/sec)
E_L	coefficient of axial mixing in the liquid phase (cm^2/sec)
f	detector response factor (-)
k	rate constant (1/g-mole.sec)
K	equilibrium constant (-)
k_L	liquid-phase mass transfer coefficient (cm/sec)
k_L^o	liquid-phase mass transfer coefficient without chemical reaction (cm/sec)
L	length of the column (cm)
N	chemical absorption rate (g-moles/cm^2.sec)
N^o	physical absorption rate (g-moles/cm^2.sec)
n	number of equivalent stirred tanks (-)
Pe	Peclet number (= UL/E_L) (-)
Q	quantity of a component (g)
r	rate of reaction (g-moles/l.sec)
T	time (min)
T_m	mean residence time (min)
U	linear liquid velocity (cm/sec)
X	distance (cm)
X_L	liquid-film thickness (cm)

z   length measured from the reactor entrance (cm)

Z   dimensionless length (=z/L) (-)

Greek Letters

ρ density (g/cm^3)

σt variance defined by eq. (3-8) (min)

σ variance (= σ_t^2/T_m^2) (-)

ϕ enhancement factor (-)

Subscripts

Cl   chlorine

E   ethylene

ECH   ethylene chlorohydrin

EDC   ethylene dichloride

f   float

HCl   hydrochloric acid

HOCl   hypochlorous acid

i   interface

N_2 nitrogen

WAT   water

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APPENDIX I

TABLES OF THE EXPERIMENTAL RESULTS

Experimental results obtained in this study are summarized in Tables here. They were obtained from mass transfer with and without reaction studies, and from mixing studies carried out in the baffled and unbaffled column.

Table A1-1A

Experimental Conditions in the Unbaffled Reactor

Run No.	Ethylene flow (cc/min)	Chlorine flow (cc/min)	Ethylene to Chlorine ratio	Reactor temperature (^{O}C)
01	1670	1200	1.39	29.3
02	1550	1200	1.29	29.5
03	1800	1460	1.23	29.8
04	2700	1600	1.69	31.0
05	1900	1070	1.77	30.5
06	1900	1200	1.58	31.0
07	1900	1350	1.41	30.2
08	1900	1460	1.29	31.2
09	1900	1600	1.18	31.5
10	1760	1350	1.30	30.2
11	2120	1350	1.58	31.0
12	2410	1350	1.78	31.0
13	2600	1350	1.92	30.3
14	1700	1070	1.58	29.5
15	2310	1460	1.58	29.8
16	2510	1600	1.58	30.1
17	2000	1350	1.48	30.0
18	2250	1350	1.67	29.9

Table A1-1B

Experimental Conditions in the Baffled Reactor (A)

Run No.	Ethylene flow (cc/min)	Chlorine flow (cc/min)	Ethylene to Chlorine ratio	Reactor temperature (°C)
A1	2120	1350	1.58	30.2
A2	2510	1600	1.58	30.5
A3	2310	1460	1.58	29.5
A4	1900	1200	1.58	31.3
A5	1900	1350	1.41	31.0
A6	2410	1350	1.78	31.0
A7	2600	1350	1.92	31.2
A8	1760	1350	1.30	30.3
A9	1900	1070	1.78	31.0
A10	2700	1600	1.69	31.5

Table A1-1C

Experimental Conditions in the Baffled Reactor (B)

Run No.	Ethylene flow (cc/min)	Chlorine flow (cc/min)	Ethylene to Chlorine ratio	Reactor temperature (°C)
B1	2120	1350	1.58	31.5
B2	2310	1460	1.58	31.5
B3	2510	1600	1.58	31.0
B4	1900	1200	1.58	30.8

Table A1-2

Concentration Profiles in the Unbaffled Reactor

Position	Run No.	EDC (wt.%)	ECH (wt.%)	Run No.	EDC (wt.%)	ECH (wt.%)
0		0.49	3.18		0.39	3.32
2		0.47	3.15		0.36	3.10
	1			2		
4		0.45	3.08		0.33	3.05
7		0.49	3.03		0.34	3.12
0		0.62	3.68		0.99	5.68
2		0.59	3.52		0.95	5.48
	3			4		
4		0.58	3.55		0.93	5.29
7		0.53	3.51		0.95	5.25
0		0.47	3.51		0.55	3.81
2		0.40	3.41		0.47	3.79
	5			6		
4		0.39	3.27		0.52	3.47
7		0.40	3.22		0.46	3.46
0		0.65	3.87		0.70	3.84
2		0.63	3.83		0.72	3.56
	7			8		
4		0.65	3.77		0.63	3.53
7		0.46	3.63		0.61	3.34
0		0.85	3.97		0.76	3.30
2		0.78	3.79		0.65	3.33
	9			10		
4		0.70	3.74		0.58	3.26
7		0.71	3.65		0.54	3.04
0		0.93	5.10		0.95	5.21
2		0.92	4.85		0.97	5.00
	11			12		
4		0.66	4.73		0.63	4.89
7		0.88	4.80		0.69	4.80

Table A1-2 (contd)

Position	Run No.	EDC (wt.%)	ECH (wt.%)	Run No.	EDC (wt.%)	ECH (wt.%)
0 2 4 7	13	0.98 0.88 0.84 0.86	5.39 5.38 5.07 4.88	14	0.49 0.52 0.42 0.43	3.88 3.87 3.59 3.78
0 2 4 7	15	0.99 0.99 0.95 0.94	5.10 5.08 5.04 4.96	16	1.00 0.93 0.92 0.90	5.73 5.75 5.69 5.69
0 2 4 7	17	0.80 0.75 0.74 0.67	4.50 4.39 4.35 4.38	18	0.94 0.88 0.89 0.82	5.15 5.13 5.05 4.98

Table A1-3

Concentration Profiles in the Baffled Reactor (A)

Position	Run No.	EDC (wt.%)	ECH (wt.%)	Run No.	EDC (wt.%)	ECH (wt.%)
0 2 4 7	A1	1.08 1.03 1.05 0.95	5.68 5.21 4.77 4.31	A2	0.99 0.82 0.70 0.54	6.61 6.29 6.23 5.90
0 2 4 7	A3	0.93 0.95 0.93 0.90	5.83 5.68 5.56 5.00	A4	0.79 0.75 0.53 0.45	4.52 3.90 3.75 3.39
0 2 4 7	A5	0.69 0.59 0.54 0.49	4.03 3.91 3.63 3.37	A6	0.98 0.96 0.79 0.81	5.55 5.25 4.88 4.62
0 2 4 7	A7	1.00 0.94 0.87 0.75	5.63 5.39 5.07 4.77	A8	0.91 0.85 0.83 0.73	3.45 3.26 3.04 2.76
0 2 4 7	A9	0.56 0.54 0.44 0.42	4.79 4.03 3.93 3.50	A10	0.95 0.91 0.91 0.89	5.94 5.70 5.47 5.26

Table A1-4

Concentration Profiles in the Baffled Reactor (B)

Position	Run No.	EDC (wt.%)	ECH (wt.%)	Run No.	EDC (wt.%)	ECH (wt.%)
0		0.85	5.82		0.88	5.98
2		0.73	5.47		0.70	5.39
	B1			B2		
4		0.70	4.75		0.53	4.95
7		0.55	3.52		0.50	3.18
0		0.92	7.20		0.77	4.86
2		0.82	6.64		0.71	4.77
	B3			B4		
4		0.72	6.07		0.65	4.28
7		0.55	4.62		0.55	3.23

Table A1-5

Material Balance (Run No. 06)

Ethylene balance (in g-mole/min)

Ethylene in   Ethylene out

7.30×10^{-2}

ECH	2.27×10^{-2}
EDC	0.49×10^{-2}
Unreacted	3.90×10^{-2}

6.96×10^{-2}

Imbalance $= (7.30 - 6.96) \times 100/7.30$

$= 4.66 \ (\%)$

Chlorine balance (in g-mole/min)

Chlorine in   Chlorine out

4.88×10^{-2}

ECH	1.15×10^{-2}
EDC	0.49×10^{-2}
HCl	1.24×10^{-2}
HOCl	0.43×10^{-2}
Cl_2	1.24×10^{-3}

4.78×10^{-2}

Imbalance $= (4.88 - 4.78) \times 100/4.88$

$= 2.09 \ (\%)$

Table A1-6

Reproducibility of the Product Concentration

Unbaffled reactor (Run No. 6)

Position	EDC (wt.%)	ECH (wt.%)	EDC (wt.)	ECH (wt.%)
0	0.55	3.81	0.55	3.80
2	0.47	3.79	0.48	3.85
4	0.52	3.47	0.49	3.51
7	0.46	3.46	0.47	3.48

Baffled reactor A (Run No. A1)

0	1.03	5.72	1.08	5.68
2	0.99	5.18	1.03	5.21
4	1.08	4.75	1.05	5.77
7	0.93	4.41	0.95	4.31

Baffled reactor B (Run No. B1)

0	0.85	5.82	0.84	5.86
2	0.73	5.47	0.78	5.53
4	0.70	4.75	0.72	4.77
7	0.55	3.52	0.58	3.49

Table A1-7

Experimental C-Curve

Time (min)	Concentration (g-mole/l) x 10^3		
	Unbaffled Column	Baffled Column (A)	Baffled Column (B)
0	2.68	1.14	0.28
5	3.15	3.07	0.51
10	3.01	3.04	1.03
15	2.80	2.91	1.46
20	2.63	2.76	1.73
25	2.57	2.55	1.97
30	2.40	2.41	1.99
35	2.38	2.27	1.94
40	2.17	2.13	1.89
45	2.06	2.00	1.80
50	1.95	1.88	1.74
55	1.87	1.79	1.69
60	1.78	1.69	1.64
65	1.67	1.61	1.50
70	1.56	1.53	1.34
75	1.47	1.43	1.25
80	1.37	1.33	1.17
85	1.30	1.28	1.10
90	1.23	1.23	1.03
95	1.17	1.17	0.98
100	1.11	1.10	0.91
105	1.05	1.06	0.84
110	1.00	1.02	0.78
115	0.95	0.98	0.73
120	0.90	0.93	0.68
125	0.85	0.89	0.65
130	0.80	0.84	0.60
135	0.77	0.81	0.56
140	0.73	0.78	0.52
145	0.70	0.75	0.48
150	0.66	0.72	0.46
155	0.67	0.69	0.45
160	0.58	0.66	0.43
165	0.55	0.65	0.39
170	0.52	0.63	0.36
175	0.50	0.60	0.30
180	0.48	0.58	0.25

Table A1-8A

Number of Equivalent Stirred Tanks

Nitrogen flow rate (cc/min)	Number of Equivalent Stirred Tanks		
	Unbaffled Column	Baffled Column (A)	Baffled Column (B)
2300	1.1	1.6	2.2
3000	1.1	1.4	2.0
3500	1.1	1.3	1.8
4000	1.0	1.2	1.7
4200	1.0	1.1	1.7

Table A1-8B

Coefficient of Axial Mixing

(cm^2/sec)

Nitrogen flow rate (cc/min)	Water flow rate	
	40 (ml/min)	45 (ml/min)
2300	4.6	4.5
3000	6.3	6.3
3500	7.2	7.3
4000	8.9	8.5
4200	9.4	9.4

Table A1-9

Physical Absorption Rate
(cc/min)

Ethylene flow rate (cc/min)	Nitrogen flow rate (cc/min)			
	1200	1350	1450	1600
1900	54	58	48	38
2120	61	72	94	65
2410	79	84	71	96
2600	175	135	138	160

APPENDIX 2

GAS CHROMATOGRAPHY

A2-1 Calibration of the gas chromatograph

The gas chromatograph used in this work was calibrated using detector response factors[20]. This method is based on the fact that the area of each peak recorded is proportional to the amount of the respective sample component. Usually, the detector response or proportionality factor is not expressed as an absolute quantity but rather is expressed relative to a given standard. This relative detector response factor can be expressed in an equal molar or volume or weight basis for each component. If this factor is known, the concentrations can be calculated directly from the peak areas.

The relative detector response factor is determined in the following way. As mentioned above, the peak area for each component in the sample is proportional to the amount of corresponding component.

$$A = f \, Q \qquad\qquad\qquad (A2-1)$$

If a sample containing a known amount of each component is injected into the gas chromatograph, the detector response factors can be calculated using eq. (A2-1). Any one of the detector response factors could be assigned the value of 100, and all others would be expressed as relative detector response factors.

The calibrations were obtained by using this method. Samples of known concentration were prepared and the response factor for each component was calculated using eq. (A2-1). Water was chosen as the standard and its detector response factor was assigned the value 100.

Attenuation of 200 for water and that of 2 for the combined ethylene chlorohydrin and ethylene dichloride peak were used when the gas chromatograph was operated with the Porapak P column. For the calibration with the Paraplex G-25 on Teflon column, attenuation of 100 for the combined water and ethylene dichloride and that of 2 for ethylene chlorohydrin were used.

The relative detector response factors obtained are given in Table A2-1 and are on a weight basis.

A2-2. Interpretation of the gas chromatogram from the reaction runs

The concentration of each component in the sample is calculated from the peak area obtained from the chromatogram.

From the chromatogram from the Paraplex on Teflon column, the peak area for ethylene chlorohydrin and for other components are obtained. Then the concentration of ethylene chlorohydrin was calculated as follows:

$$C_{ECH} = \frac{(A_{ECH}/f_{ECH}) \times 100}{(A_{WAT}/f_{WAT}) + (A_{ECH}/f_{ECH})} \qquad (A2-2)$$

Using the chromatogram from the Porapak P column, the concentration of ethylene dichloride is calculated in the following way:

$$C_{ECH} = \frac{(A_{ECH}/f_{ECH}) \times 100}{(A_{WAT}/f_{WAT}) + (A_T - A_{ECH})/f_{EDC} + A_{ECH}/f_{ECH}} \qquad (A2-3)$$

Table A2-1

Relative Detector Response Factors

Porapak P Column

ECH (wt.%)	f_{ECH}	ECH (wt.%)	f_{ECH}
2.340	2818	7.398	2890
2.340	2835	4.923	2869
5.963	2851	4.923	2879
5.963	2880	4.923	2889
11.310	2895	7.276	2824
11.310	2890	7.276	2821
7.398	2879		

$$f_{ECH} = 2815$$

Discrepancies $\leq$ 1.57%

Paraplex G-25 on Teflon Column

ECH (wt.%)	f_{ECH}	EDC (wt.%)	f_{EDC}
7.276	5272	0.756	5165
7.276	5287	0.756	5170
7.276	5264	0.756	5156
4.923	5233	0.695	5124
4.923	5309	0.695	5196
4.923	5227	0.695	5163
7.398	5294	1.015	5183
7.398	5281	1.015	5145
5.963	5297	0.839	5125
5.963	5289	0.839	5158
2.340	5281	0.455	5096
2.340	5278	0.455	5140

$$f_{ECH} = 5280 \qquad\qquad f_{EDC} = 5150$$

Discrepancies $\leq$ 1.78%   Discrepancies $\leq$ 2.54%

where
$$A_T = A_{EDC} + A_{ECH} \qquad \text{(A2-4)}$$

Similarly to eq. (A2-3), the concentration of ethylene dichloride is calculated by:

$$C_{EDC} = \frac{(A_{EDC}/f_{EDC}) \times 100}{(A_{WAT}/f_{WAT}) + (A_{EDC}/f_{EDC}) + (A_{ECH}/f_{ECH})} \qquad \text{(A2-5)}$$

From eq. (A2-3), A_{ECH} can be calculated since C_{ECH} is known.

$$A_{ECH} = \frac{C_{ECH} (A_{WAT}/f_{WAT} + A_T/f_{EDC})}{(100/f_{ECH} + C_{ECH}/f_{EDC} - C_{ECH}/f_{ECH})} \qquad \text{(A2-6)}$$

By substituting eq. (A2-6) into eq. (A2-5), the concentration of ethylene dichloride can be given.

Relative response factors of ethylene chlorohydrin were checked using pure water, 0.2 N-HCl solution, 0.5 N-HCl solution, and 1.0 N-HCl solution as the standard. Discrepancies among the relative response factors of ethylene chlorohydrin were less than 1 percent.

A2-3. Interpretation of the gas chromatogram from the physical absorption runs

During the physical absorpiton runs, the gas chromatograph was not calibrated by the method given above since it was difficult to measure the amount of gases accurately.

A physical absorption run was carried out as follows. At first, desired amounts of ethylene and nitrogen were fed to the bubble column. The

outlet gas led to the gas sampling valve of the gas chromatograph. The gas
mixture which had passed through the column was analysed by gas chromatograph
from time to time until the chromatogram showed no change in the composition
of the gas mixture. Then, water was introduced and a physical absorption run
was carried out. After the chromatogram had shown no change in the composition
of the gas from the bubble column, the run was completed.

The physical absorption rate of ethylene into water was calculated
assuming that the absorption rate of nitrogen into water could be neglected.

$$N_E^O = Q_{N_2} \left((A_E/A_{N_2}) - (A_E^O/A^O_{N_2}) \right) \qquad (A2\text{-}7)$$

Here Q_{N_2} is the flow rate of nitrogen. A's are peak areas before the absorption
run, and A^O's are peak areas after the run.

APPENDIX 3

CALIBRATION OF ROTAMETERS

Rotameters used in this study were calibrated at the same operating condition as that existed during the experiments.

The rotameters for measuring the flow rates of inlet ethylene and the outlet gas were calibrated with ethylene by a wet test meter as shown in Fig. A3-1. The rotameter for chlorine was calibrated in the same way with nitrogen gas. The flow rates were converted to those of chlorine by the following equation[34,24]:

$$Q_A/Q_B = \sqrt{(\rho_f - \rho_A)\,\rho_A/\rho_B(\rho_f - \rho_B)} \qquad (A3-1)$$

The rotameter for water was calibrated measuring the water flow at the reactor outlet by a measuring cylinder.

Calibration curves are shown in Figs. A3-2, A3-3, and A3-4.

B: Bubble column

E: Ethylene gas cylinder

N: Nitrogen gas cylinder

R: Rotameter

W: Wet test meter
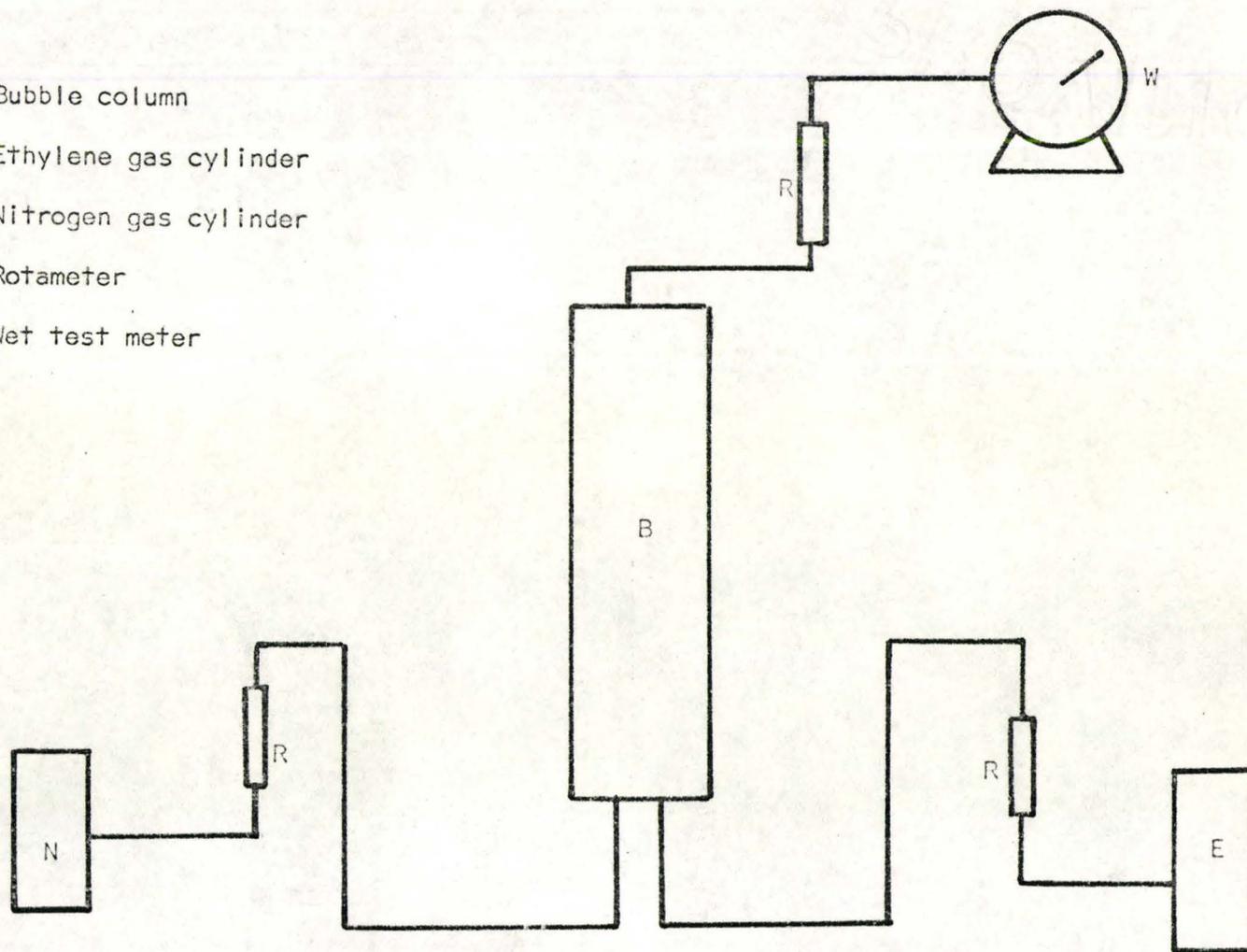
Fig. A3-1   Calibration of rotameters
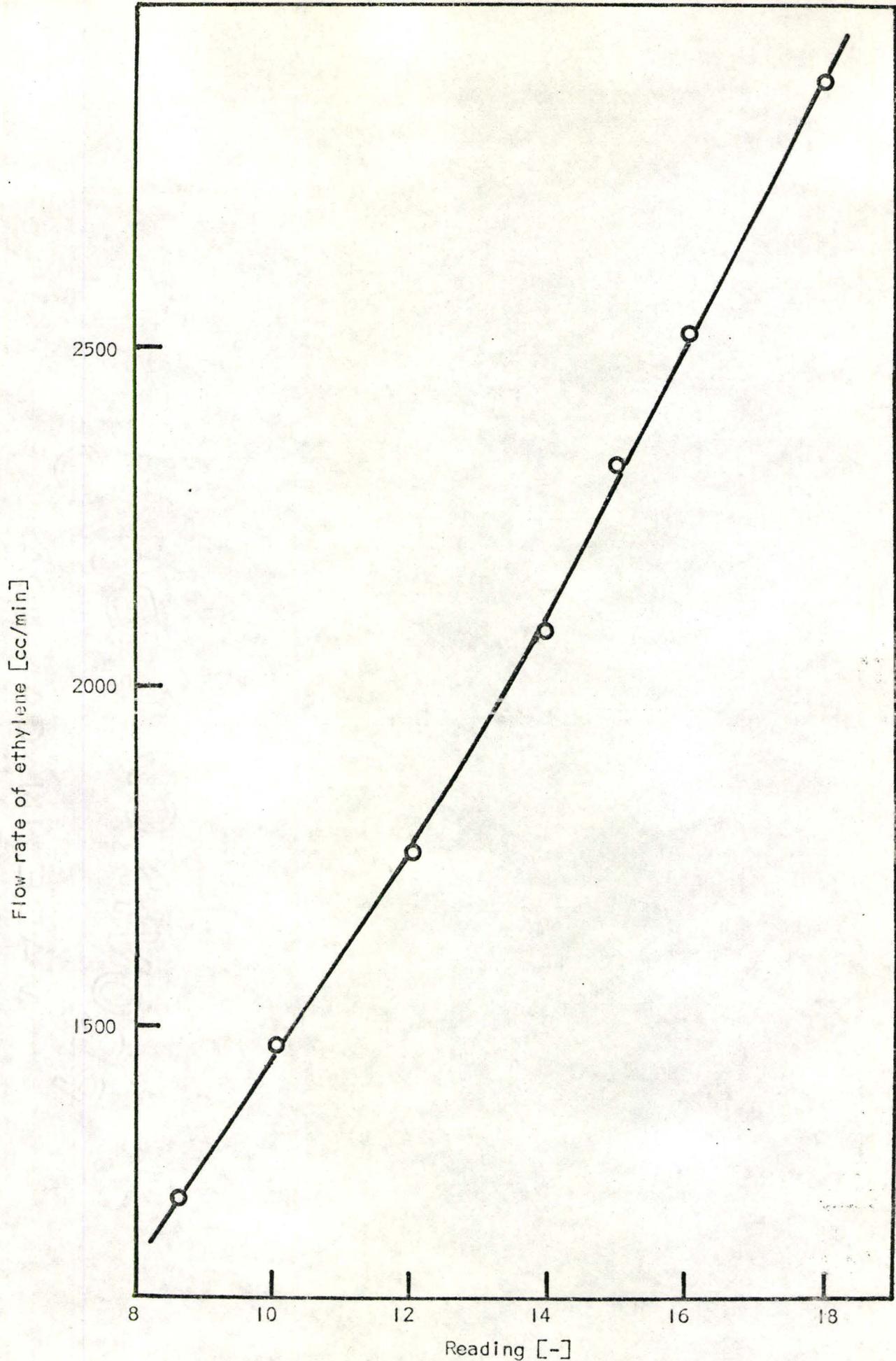
Fig. A3-2   Calibration curve for ethylene flow
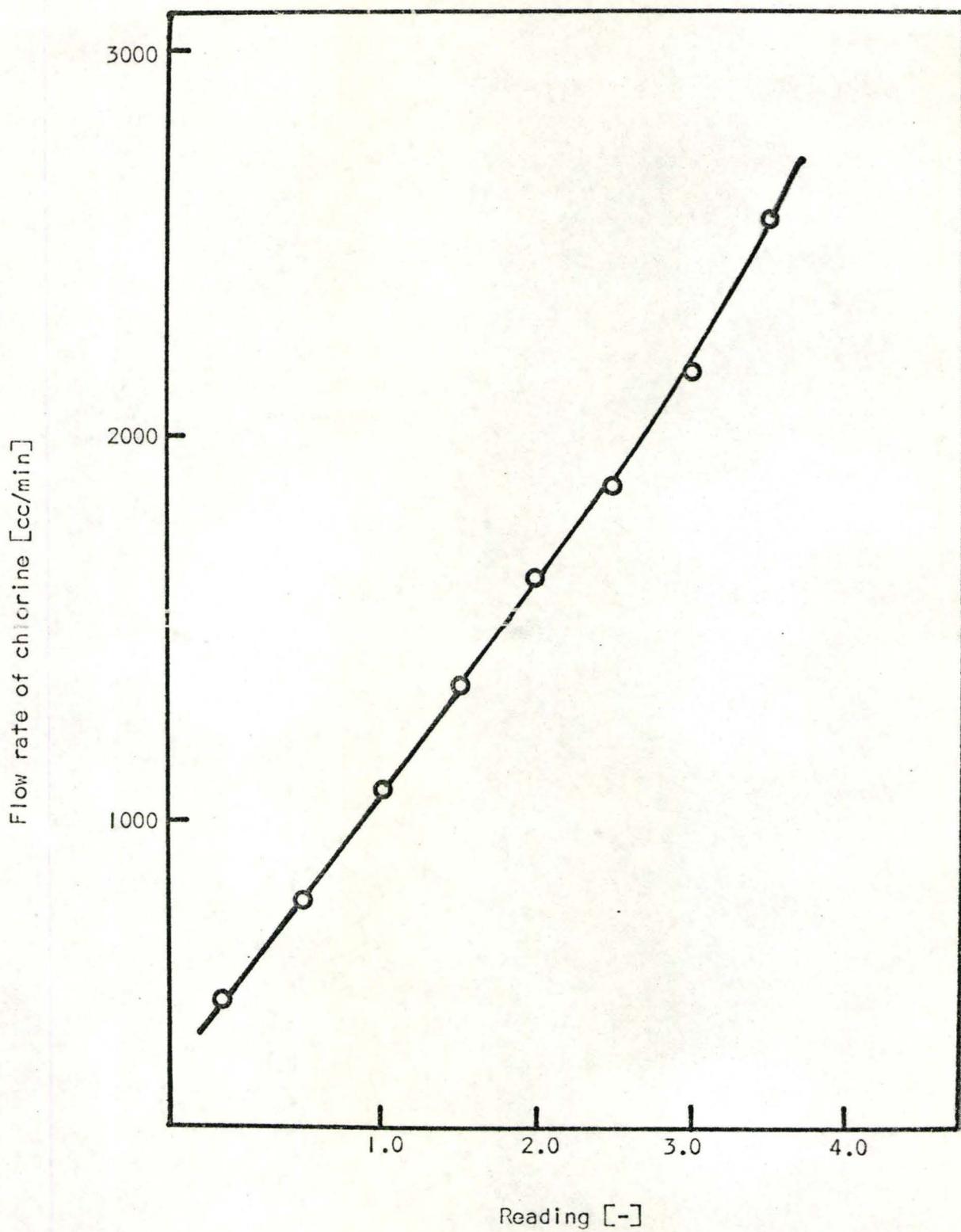
Fig. A3-3   Calibration curve for chlorine flow
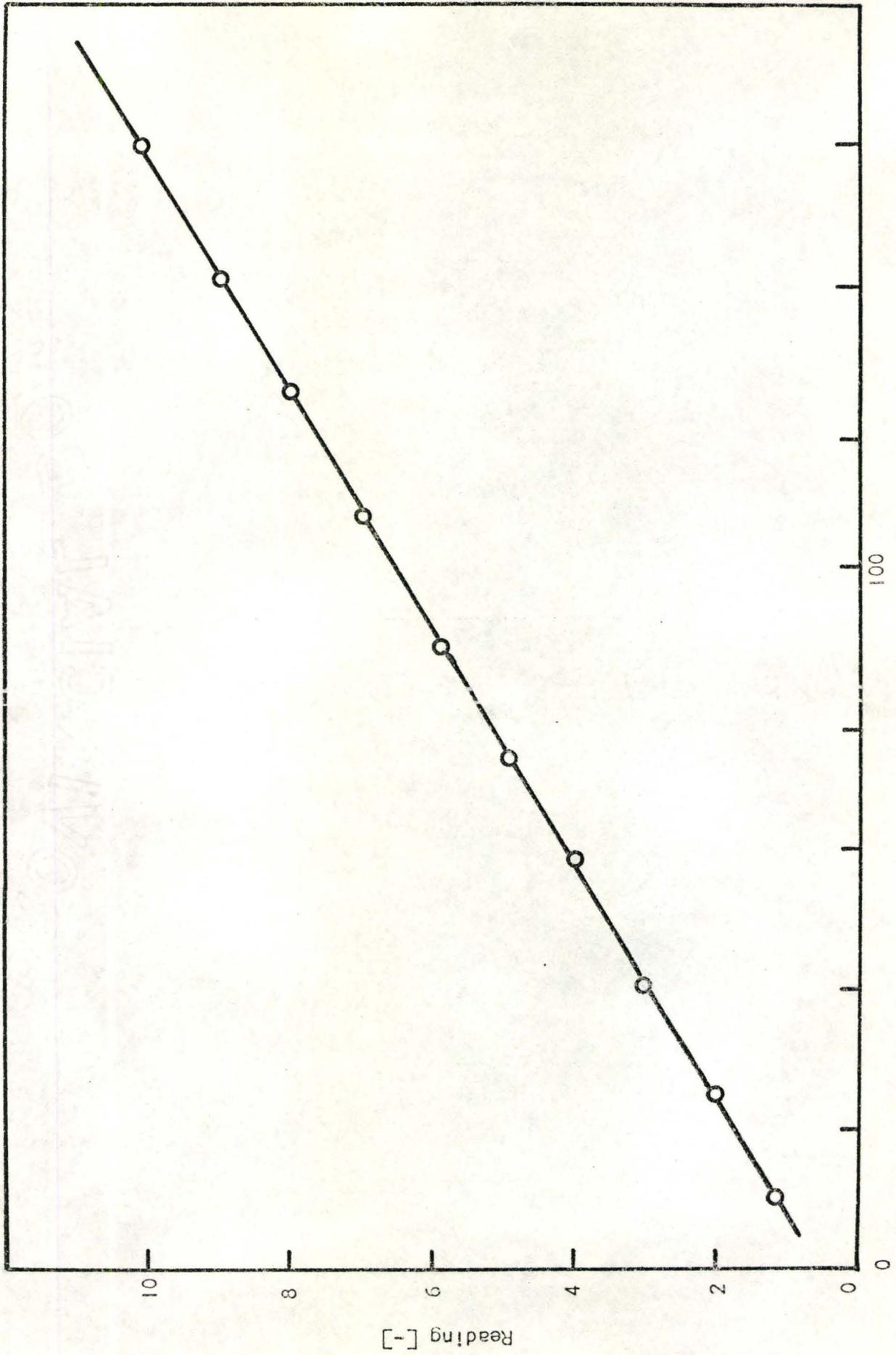
Fig. A3-4   Calibration curve for water flow