

THE UNIVERSITY OF CALGARY

Use of Mixed Amines for CO₂ Removal

by

Pushkar Shahi

A THESIS

**SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE
DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING**

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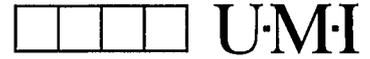
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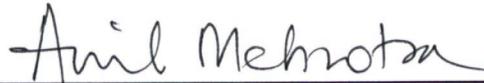
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Abstract

The process of sweetening of gas mixtures has widespread applications. Removal of acid gases like H_2S and CO_2 using alkanolamines has been the most widely used method. The amine process involves absorbing the acid gas in an absorption column and subsequently regenerating the solvent in a stripping column by the application of heat.

Monoethanolamine (MEA) is an excellent solvent in terms of its absorption characteristics while Methyldiethanolamine (MDEA) can be regenerated using less energy. However, in spite of its higher capacity to absorb CO_2 , MDEA has slower mass-transfer rates as compared to MEA due to its slower reaction. Therefore, blending the two amines to obtain their individual advantages is an attractive proposition.

Experimental studies were carried out on a pilot scale unit consisting of an absorber and a stripper. The effect of various process parameters was studied single as well as mixed amines. It was conclusively observed that a mixture of MEA and MDEA has vastly improved absorption characteristics and at the same time consumed less energy during its regeneration. A simple solubility model is presented which predicts the solubility of CO_2 in individual amines and their mixtures. Excellent agreement is observed with existing experimental data and predictions of another rigorous solubility model.

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*Dedicated
To My Family*

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LIST OF SYMBOLS

K	Reaction equilibrium constant
H	Henry's Law constant
R_i	Alkyl group in the alkanolamine
P	Pressure (kPa)
T	Temperature (K)
N	Normal solution
v/v	Volume % solution
w/w	Weight % solution
$wt\%$	Weight % solution
MEA	Monoethanolamine
$MDEA$	Methyldiethanolamine
DEA	Diethanolamine
$[]$	Concentration (kmol/m ³)
α	Loading of CO ₂ (mol CO ₂ /mol amine)
β	Parameter in Reaction 2.15
K_g, K_G	Overall Mass Transfer Coefficient
a	Interfacial Area, m ²
G_M	Molar Mass Velocity, g mol/m ² h or kg mol/m ² h
h	Apparent Packed Height in the Column, m
y	Mole Fraction of Solute in the Gas Stream
P	Parameter defined in Equation 4.2, (mol CO ₂ /mol amine)(1/KJ/h)

- A* Difference in the Loading Values of CO₂ in the Liquid Phase at the Top and Bottom of the Absorption Column, (mol CO₂/mol amine)
- S* Difference in the Loading Values of CO₂ in the Liquid Phase at the Top and Bottom of the Stripping Column, (mol CO₂/mol amine)
- x1* Loading Values of CO₂ at the Top of the Column, (mol CO₂/mol amine)
- x2* Loading Values of CO₂ at the Bottom of the Column, (mol CO₂/mol amine)
- E* Rate of Energy Consumption in the Reboiler, KJ/h

CHAPTER 1

Introduction

Absorption is one of the most important gas purification techniques and is commonly employed in a large number of industrial processes. The process of absorption involves the transfer of a substance from the gaseous to the liquid phase through the phase boundary. The absorbed component may dissolve physically in the solvent liquid or chemically react with it. The absorption of CO_2 from a gaseous mixture using alkanolamine solvents is a typical example of an absorption process where chemical reaction is involved.

Removal of CO_2 from gas streams has widespread applications. Natural gas frequently contains varying amounts of CO_2 and/or H_2S . These acid gases must be separated from the natural gas prior to its transportation and subsequent use. The process of removal of acid gases from gas streams is commonly known as 'sweetening of the gas'. The removal of acid gases from natural gas streams is necessary to reduce pipeline corrosion, avoid pollution in the atmosphere and also increase the heating value of natural gas. With increasing emphasis being placed on environmental pollution control and consequences of "the green-house effect", the problem of acid gas absorption has not only restricted itself to economic advantages, but it has also become a moral obligation to find better methods of minimizing emissions of CO_2 into the atmosphere.

The process of acid gas absorption is also used in synthetic ammonia industries (for hydrogen purification in ammonia synthesis), oil refineries (for the treatment of flue gas and tail gas to meet pollution standards), fertilizer plants (for the removal of acid gases from the feeds streams for ammonia synthesis) and in petrochemical plants (for the removal of acid gases in the feed to polymerization units to avoid catalyst poisoning).

CO₂ is used as a flooding agent for reservoirs in the tertiary recovery of oil. This process is commonly known as enhanced oil recovery (EOR). The use of CO₂ in enhanced oil recovery (EOR) projects necessitates its subsequent removal when it resurfaces with the produced oil. The rate of CO₂ return with produced oil in areas employing EOR changes with time and it is thus essential to devise an absorption process which can be tailored to these changes.

Monoethanolamine (MEA) and diethanolamine (DEA) have been the most widely used alkanolamines for acid gas absorption in the past several decades. Alkanolamines undergo an exothermic chemical reaction with CO₂ to form complexes which vary in their stabilities depending on the amine used. MEA is a primary amine while DEA is a secondary amine. These amines form a stable complex with CO₂ called 'carbamates'. The energy required to reverse this reaction is high. Therefore, the cost of stripping of CO₂ from primary and secondary amines is extremely high (high reboiler heat duties).

In recent years methyldiethanolamine (MDEA), a tertiary amine, is finding

widespread use in the gas industry as an alternative to MEA and DEA in certain specialized gas treating processes. MDEA reacts almost instantaneously with H_2S but relatively slowly with CO_2 (Astarita et al.,1983). Therefore, it is often used for the selective removal of H_2S from gas streams containing both the acid gases. This process of selective removal of H_2S is particularly important when H_2S needs to be converted to elemental sulphur in downstream sulphur recovery units as the presence of CO_2 impairs the conversion efficiency. The heat of reaction of CO_2 with MDEA is relatively low (Kohl and Riesenfeld, 1985). As a result, the energy required to strip CO_2 from a carbonated solution of MDEA is comparatively much less. Thus, MDEA is a better candidate than MEA or DEA in terms of stripping characteristics . Consequently, its use as an alternative to MEA and DEA for bulk removal of CO_2 could be well justified considering the savings in energy. But the low reactivity of MDEA with CO_2 inhibits its use, particularly in producing sweet gases containing very low levels of CO_2 . A brief description of the Amine Process is presented in the next section.

The phenomenon of absorption of two or more gases in a reactive solvent or the absorption of a single gas in a mixture of two or more reactive solvents is often complex. The interactions that might arise vary widely depending on the individual rates of reactions, the equilibrium characteristics of the system, the hydrodynamics of the contact device, and the physical properties of all the components. The rates of absorption of acid gases into alkanolamine solutions are strongly influenced by the rates of chemical reactions taking place in the liquid phase because these reactions have a profound effect

on the liquid phase mass transfer coefficients (Chakravarty et al., 1985).

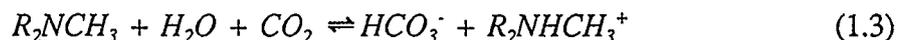
1.1 The Amine Process

The aqueous diethanolamine process belonging to the amine process group, was developed by R.R. Bottoms in 1930 to remove acid gases (CO₂ and H₂S) from high volume, high pressure natural gas streams (Kohl and Riesenfeld, 1985). It became commercially known as the Girbotol process from the early 1930's when a patent was assigned to the Girdler Corporation by R.R. Bottoms. The process is based on the reaction of a weak organic base and a weak acid (CO₂ or H₂S), in a countercurrent absorption tower. Subsequently, regeneration of the absorbent is achieved in a stripping column where the water soluble salt formed in the absorber is thermally decomposed, thus liberating acid gas for further processing or disposal.

When CO₂ is absorbed into aqueous solutions of MEA, the following two overall reactions must be considered (Astarita et al., 1964 ; Danckwerts and McNeil, 1967):



The overall reaction with MDEA can be represented by the reaction given below (Savage et al., 1981), where *R* refers to HOCH₂CH₂ :



The equilibrium of the above reactions is favoured to the right at low temperature

and high pressure and to the left at high temperature and low pressure. For this reason, industrial absorbers are operated at low temperatures (typically 40°C) and at high pressures (typically above 4 MPa.). On the other hand, stripping columns are operated at high temperatures (typically 115-120°C) and low pressures close to atmospheric pressure.

A simplified flow sheet of an industrial amine sweetening unit is shown in Fig. 1.1. The gas mixture or sour gas flows upwards from the bottom of the absorber, counter-currently contacting aqueous amine solution being fed from the top. The acid gases are absorbed by the amine solution and sweetened gas leaves the top of the absorber.

The rich amine solution (loaded with acid gases), from the bottom of the absorber is fed to the top of the stripper. On the way, this rich amine gets heated by passing through a lean-rich heat exchanger where it exchanges heat with the lean amine (stripped of acid gases) leaving the stripper. Upon entry into the stripper, some of the absorbed acid gases are immediately flashed. The carbonated solution then flows downward against a counter-current flow of hot vapours generated in the reboiler. The stripping vapour, which mainly consists of steam, removes most of the remaining acid gases from the rich amine solution.

The overhead mixture passes through a condenser where most of the steam is condensed. The acid gases are separated and the condensate is returned to the top section

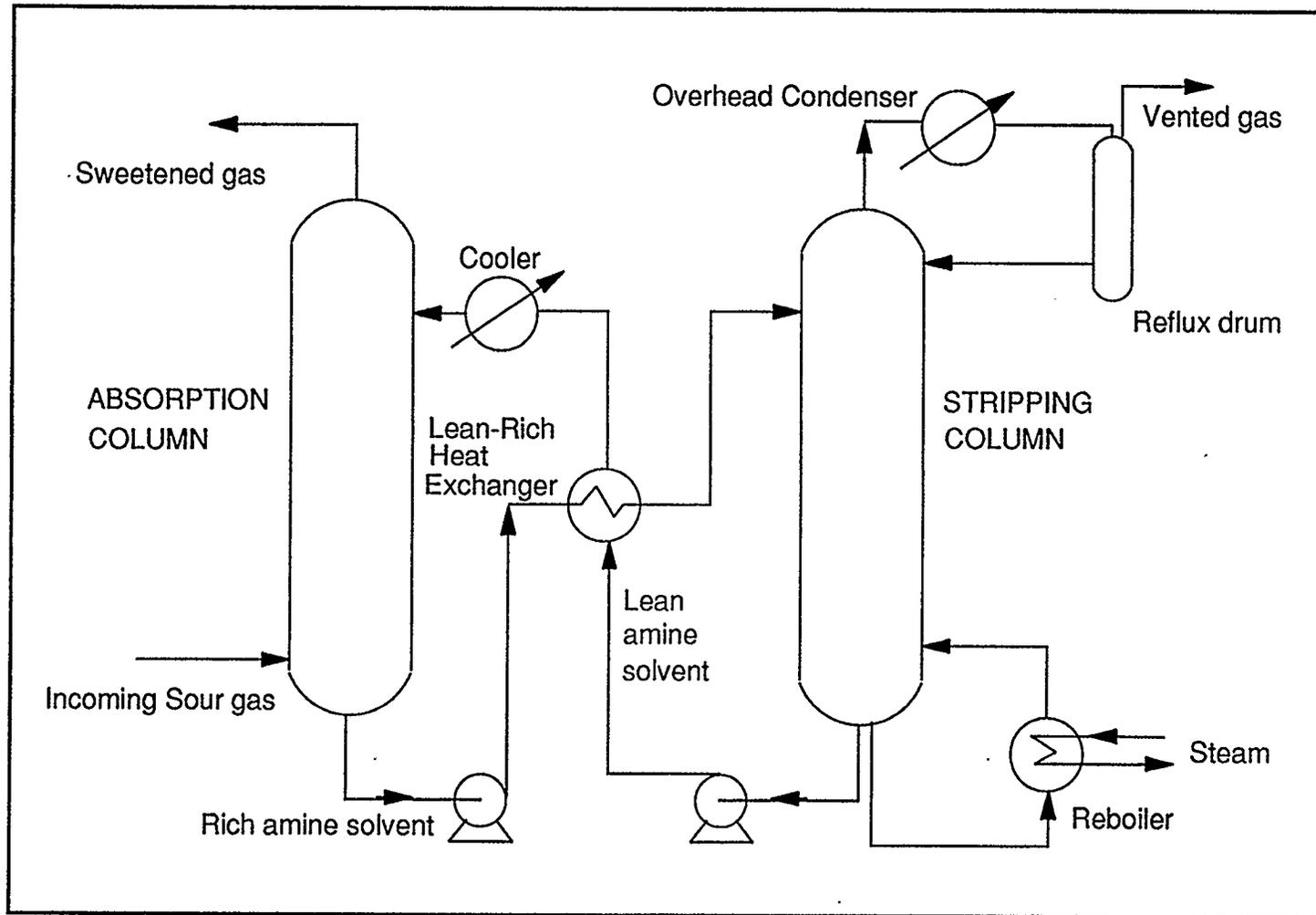


Fig. 1.1 Flow diagram of an industrial amine treating unit

of the stripper as reflux. The lean solution leaving the stripper, as mentioned before, gets cooled down by exchanging heat with the rich amine and is fed again into the absorber.

1.2 Critical Review of the Process

The use of a single amine limits the performance of a plant to a specific use according to the choice of the amine. MEA has excellent absorption characteristics but at the same time it requires high energy input for regeneration. The process of regenerating the solvent requires substantial amounts of energy which adds on to the operating cost of such plants. Over 70% of the total energy requirement of such CO₂ removal units is consumed in solvent regeneration (Chakravarty et al., 1985). MDEA on the other hand, undergoes a slow reaction with CO₂ but requires comparatively less energy for regeneration.

The above mentioned disadvantages associated with the use of single amines encourages one to try and blend them in various proportions and obtain the individual advantages of both. Blending of two amines would introduce another degree of freedom in the system : varying the proportion of each amine in the mixture. This flexibility could be used to tailor the process according to the composition of various gases in the feed gas stream. For instance, primary amine MEA and tertiary amine MDEA could be blended so that the advantages of both could be combined. This would require carrying out extensive experiments on a pilot scale unit using individual amines, MEA and MDEA,

as well as their mixtures in various proportions. A comparison of the heat duty in the reboiler would also be essential to justify the use of mixed amines from the energy savings point of view.

1.3 Scope and Objective of this Study :

- ★ To carry out experimental studies using single as well as mixed amines on a pilot scale unit consisting of an absorber and stripper. Pilot plant data is essential in the scale up of the process for industrial use.
- ★ To carry out an analysis of the data so obtained in terms of mass transfer coefficients which would give an indication of the rate characteristics of the process.
- ★ To carry out a comparative study of the energy requirements involved in the use of single and mixed amines. The objective would also be to determine the optimum heat duty in the process.
- ★ To develop a sufficiently rigorous solubility model which could predict the solubility of CO₂ in single as well as mixed amines. This data is essential because it gives an indication of the absorption characteristics of the solvent.
- ★ To carry out a comparative study with existing data available in the open literature.

CHAPTER 2

Literature Review

2.1 Solvent Selection

This section deals with a comparative study of the advantages and disadvantages of MEA and MDEA and a brief description of their use in industry. Before carrying out a comparative study it would be beneficial to define an 'ideal solvent' for CO₂ removal. Though this definition would vary according to the actual process requirements, a general definition could be, nevertheless, coined. An 'ideal solvent' would be one which had a high capacity for CO₂, high reaction rates with CO₂, low viscosity to allow for better mass transfer through improved diffusivity, low specific heat, low heats of reaction with CO₂, high alkalinity, less corrosive, low vapour pressure to avoid solvent loss through vaporization, resistant to thermal and chemical corrosion, low solubility in hydrocarbons etc.

Low molecular weight of MEA resulting in high solution capacity at moderate concentrations (on a weight basis) and its high alkalinity are some of the advantages of MEA. However, MEA solutions are appreciably more corrosive than solutions of most other amines, particularly if the amine concentration exceeds 20% w/w and the solutions are heavily loaded with acid gas (Kohl and Riesenfeld, 1979). This limits its

use in cases where high partial pressure of the acid gas would permit substantially higher loadings. High vapour pressure of MEA causes significant vaporization losses, especially in low pressure operations.

Because of its low vapour pressure, MDEA can be used in concentrations upto 60% w/w in aqueous solutions without appreciable evaporation losses. At high concentrations the capacity of the solvent to absorb CO_2 increases because of the increased availability of molecules of solvent for chemical reaction. MDEA is highly resistant to thermal and chemical degradation, is essentially non-corrosive, has low specific heat and heats of reactions with CO_2 and is only sparingly soluble in hydrocarbons.

The use of MDEA as a non-selective solvent for removing acid gases, particularly CO_2 from synthesis and natural gases, has been disclosed by BASF, Aktiengesellschaft and described by Meissen and Wegner (1983). At present, MDEA is used mostly for selective absorption of H_2S from gas streams containing both CO_2 and H_2S .

2.2 Solubility Measurements and Models

This section consists of a review of literature data available for the solubility of CO_2 in MEA, MDEA and their mixtures. It also presents a review of existing

solubility models for predicting the solubility of CO₂ in amines.

2.2.1 Experimental Measurement of Solubility

Aqueous ethanolamine solutions are widely used in the gas processing industry for the removal of acid gases (like CO₂, H₂S and COS) particularly in the fields of natural gas processing, bitumen or heavy oil upgrading, coal gasification, ammonia production, refinery gas processing, recovery of CO₂ to be used in enhanced oil recovery projects and in petrochemical plants.

The operating conditions in these units vary in terms of temperature, pressure and acid gas loading. Typically, the temperature varies between 30°C-140°C, partial pressure of acid gas between 100 kPa-4 MPa and acid gas loadings range from 0.001 to 0.1 mole of acid gas per mole of amine. An accurate determination of acid gas solubility in the alkanolamine is necessary for the proper design of related equipment like absorbers and strippers. This is because absorption and stripping are both processes where transfer of solute occurs according to the driving force defined by the deviation from the equilibrium value.

Substantial experimental data are available in the open literature on the solubility of acid gases in ethanolamines. Although these measurements have been made for various acid gas ethanolamine pairs, the present review is restricted to only

those which pertain to CO₂ solubility in MEA, MDEA and their mixtures.

Mason and Dodge (1936) investigated the solubility of CO₂ in the range of MEA concentrations from 0.5 to 12.5 N at temperatures between 0° and 75°C and partial pressures of CO₂ ranging from about 1.33 to 99.67 kPa. Reed and Wood (1941) published a plot showing the solubility of CO₂ in 2.5 N (15.3% w/w) MEA solutions at temperatures of 100°, 120° and 140°C and CO₂ partial pressures from 140 to 350 kPa. Similar data was presented by Reed (1942). Lyudkovskaya and Leibush (1949) studied the solubility of CO₂ in 0.5, 2 and 5 N MEA solutions at temperatures of 25°, 50° and 75°C and partial pressures of CO₂ from 252.5 to 4040 kPa. Muhlbauer and Monaghan (1957) reported data on the solubility of CO₂ in 2.5 N MEA solutions at 25° and 100°C and partial pressures of about .13 to 133 kPa.

Jones et al. (1959) determined the solubility of CO₂ in 2.5 N (15.3% w/w) MEA at temperatures of 40°, 60°, 80°, 100°, 120° and 140°C with partial pressures of CO₂ ranging from .13 to 930 kPa. Until this time there were considerable differences in the reported values for the solubility of CO₂.

Lee et al. (1974) determined the solubility of CO₂ in 2.5, 5.0 N aqueous MEA solutions at 40°C and 100°C and partial pressures of CO₂ between 0.7 to 6965 kPa. An extensive literature review on the experimental determination of CO₂ in MEA was compiled by Lee et al. (1974) which has been updated and presented in Table 2.1.

Table 2.1 : Literature review of MEA Solubility data

Author	Acid Gas	Normality	Temperature (°C)	Partial Pressure
Mason and Dodge (1936)	CO ₂	0.5,2.0,5.0,9.5,12.5	0,25,50,75	0.19 - 14.5 psia
Reed and Wood (1941)	CO ₂	2.5	100,120,140	20 - 250 psia
Lyudkovskaya and Leibush (1949)	CO ₂	0.5,2.0,5.0	25,50,75	36.8 - 588 psia
Adatan	CO ₂	2.5,5.0,7.5,10.0	30,50,70	15 - 500 psia
Muhlbauer and Monaghan (1957)	CO ₂	2.5	25,100	19.3 psia
Jones, Froning and Claytor (1959)	CO ₂	2.5	40,60,80,100,120	< 135 psia
Murzin and Leites (1971)	CO ₂	0.5,1.0,2.0,2.5,3.4	30,40,50,60,70,80	< 13.5 psia
Lee et al. (1974)	CO ₂	2.5,5.0	40,100	0.1 - 1000 psia
Lee at al. (1976)	CO ₂	2.5	80,100	0.7 - 5630 kPa
Nasir et al. (1977)	CO ₂	2.5,5.0	80,100	0.001 - 9.0 kPa
Isaacs et al. (1980)	CO ₂	2.5	100	0.003 - 3.36 kPa

Lee et al. (1976) also determined solubility of mixtures of CO₂ and H₂S in a 2.5 N MEA solution at 40° and 100°C and partial pressures of CO₂ ranging from 0.7 to 563 kPa. Nasir et al. (1977) measured the solubility of CO₂ in 2.5 N, 5.0 N solutions of MEA at 80°C and 100°C and CO₂ partial pressures between 0.001 - 9 kPa.

Isaacs et al. (1980), determined the solubility of CO₂ in a 2.5 N aqueous solution of MEA at 100°C and acid gas partial pressure between 0.003 and 3.36 kPa. Their results were compared to the predictions made by solubility models of Klyamer et al. (1973) and Kent and Eisenberg (1976). Kent and Eisenbergs' model was, at that stage, found to be in better agreement with the experimental data obtained.

Since MDEA as a solvent has mostly been used for selective removal of H₂S from gas mixtures, data is available mostly for CO₂/H₂S/ alkanolamine/water systems. However this study concerns reporting such measurements in CO₂/alkanolamine/water systems exclusively.

Solubility of CO₂ in 1.0, 2.0, and 4.28 N aqueous solutions of methyldiethanolamine was measured by Jou et al. (1982). The temperature and acid gas partial pressures ranged from 25 to 120°C and 0.001 to 6600 kPa respectively. Approximate values of the differential enthalpy of solution of CO₂ in MDEA was calculated based on using a form of the Gibbs-Helmholtz equation. They also correlated the data obtained based on Kent and Eisenberg's model (1976).

Haimour et al. (1984) measured the solubility of CO₂ in MDEA over the temperature range 15-35°C and MDEA concentrations of up to 3.36 N (40% w/w). Austgen et al. (1991) reported experimental measurements of CO₂ solubility in 2.5N MEA solution at 40° and 80°C and in 2.0 and 4.28 N MDEA solutions. Solubility measurements in mixed amine systems (MEA + MDEA) were made at 40° and 80°C over CO₂ partial pressures ranging from 0.05 to approximately 300 kPa.

The available equilibrium data for MDEA are generally acceptable at moderate and high acid gas loading since consistent values do not exist at very low loadings of CO₂. Rochelle (1991, 1992) showed that the available data for acid gas loading in MDEA solutions had an average error of about 10%. Data at low acid gas loading had an average error of 15% compared to only 5% for data at high loading. Standard experimental techniques of measuring solubility, however, are reliable only within moderate ranges of temperature, pressure and acid gas loadings. In such cases, therefore, it is essential to have a credible extrapolation technique to represent data.

2.2.2 Solubility Models

Solubility prediction can either be done by fitting experimental data to various equations or by a rigorous solubility model. The following sub-sections reviews work done on both of these approaches.

2.2.2.1 Correlating Experimental Data

Since solubility data is sometimes not reliable or even unavailable (especially at very low or very high pressures) within certain ranges of process parameters, it is essential to have sound models to compute required data confidently within that range. This problem arises particularly under conditions of high temperature, low pressure and low CO₂ loading. There are various approaches to tackle this problem. Some researchers have taken the approach of fitting experimental data to various equations and establishing correlations for the computation of solubility. Other authors have handled the issue more boldly and developed rigorous models to predict solubility.

The earliest attempt to correlate solubility data was made by Mason and Dodge (1936). The method apparently was more or less a curve fitting approach. The exact procedure of fitting equilibrium constants of the reaction was not described probably due to insufficient knowledge about the reaction kinetics between CO₂ and ethanolamines. Van Krevlen et. al. (1949) later developed a procedure for the prediction of partial pressures of CO₂ and NH₃ over aqueous solutions. They made use of pseudo-equilibrium constants (or "apparent" equilibrium constants) in their calculations which did not contain activity coefficients. In effect, activity coefficients of all species in the system were set equal to unity. These pseudo-equilibrium constants were related to ionic strength of the solution. This approach, however, was unsuccessful in representing the entire range of concentrations.

Danckwerts and McNeil (1967) used the same approach to predict the equilibrium partial pressure of CO_2 over carbonated amine solutions. This model also used pseudo-equilibrium constants which were a function of ionic strength. A major limitation of this model was that ionic strength alone is insufficient to determine the concentration dependence of the pseudo-equilibrium constants.

Atwood et al. (1957) suggested a method for the calculation of equilibria in $\text{H}_2\text{S}/\text{amine}/\text{H}_2\text{O}$ systems, the principal feature of which was the use of a " mean ionic activity coefficient ". In this model the activity coefficients of all ionic species were assumed to be equal, an assumption which is valid only at low ionic strengths or if only one cation and one anion are present in significant amounts. However this is generally not the case for the $\text{CO}_2/\text{H}_2\text{S}/\text{alkanolamine}/\text{H}_2\text{O}$ system or $\text{CO}_2/\text{alkanolamine}/\text{H}_2\text{O}$ system. The single " mean ionic coefficient " was correlated with ionic strength. This model was essentially equivalent to the apparent equilibrium constant approach of Van Krevlen et. al. (1949). Instead of lumping the effects of solvent non-ideality directly into equilibrium constants, they separated non-ideality into an empirical parameter which was used to adjust the equilibrium constant for the effect of ionic strength. This same model was employed by Klyamer and Kolesnikova (1972) for the $\text{CO}_2/\text{amine}/\text{H}_2\text{O}$ system and was later generalized by Klyamer et. al. (1973) for the $\text{CO}_2/\text{H}_2\text{S}/\text{alkanolamine}/\text{H}_2\text{O}$ system. If the activity coefficients in the Klyamer et. al. (1973) model are set equal to unity, the model becomes algebraically equivalent to the Kent and Eisenberg model (1976). Comparisons of both the models have been

made by Lee et. al. (1976) where it was observed that the differences between the predicted and experimental partial pressures were as high as 100%.

Kent and Eisenberg (1976) modified the above approach in correlating equilibrium solubilities for the $\text{CO}_2/\text{H}_2\text{S}/\text{amine}/\text{H}_2\text{O}$ system. They tried to correlate the solubility data using published equilibrium constants without any dependence on ionic strength. However, it was seen that predicted values deviated significantly from experimental values. Instead of using ionic characterization factors for the dependence of the pseudo-equilibrium constants on ionic strength, they used the same value of all but two pseudo-equilibrium constants (those for amine protonation and carbamate reversion) and treated these two as variables to be found by fitting experimental data as functions of temperature.

Although the use of apparent equilibrium constants allows adequate representation of experimental acid gas partial pressures, it has two significant drawbacks. First, the method cannot be extended to solution compositions outside the range over which equilibrium constants are adjusted. Second, speciation which involves the determination of true composition of all liquid phase species, ionic and molecular, requires accurate representation of activity coefficients for use in equations of chemical equilibria. Speciation using apparent equilibria equations should be considered only an approximation to the true liquid phase composition. The capability to calculate accurate values of all liquid phase species is important for design and simulation based upon

rates of mass transfer and chemical reaction (Hermes and Rochelle, 1987 ; Sivasubramanian et al., 1985). In this approach, liquid phase concentrations enter into kinetic expressions, affecting mass transfer at vapour liquid interfaces. In addition, the bulk liquid phase is generally assumed to be in a state of chemical equilibrium. Rigorous models for solubility prediction are considered in the next section.

2.2.2.2 Rigorous Models for Solubility Determination

Rigorous models are often based on a thermodynamic framework where both liquid phase (chemical) equilibria and vapour - liquid (phase) equilibria are taken into consideration. Austgen et al. (1989) provided an extensive literature review and discussion on various models, most of which is reproduced here.

Edwards et al. (1975) developed a molecular thermodynamic framework to calculate vapour-liquid compositions for dilute aqueous solutions of volatile weak electrolytes (sour water systems). They treated chemical equilibria rigorously by employing component activities rather than concentrations. Activity coefficients were represented with a Guggenheim -type equation (1935) by treating long range ion - ion interactions and short - range solute ion - ion, ion - molecule and molecule - molecule interactions. Molecule - molecule parameters of the model, representing binary interactions, were determined by data regression. Ion - ion binary parameters were approximated by using the procedure of Bromley (1972). Molecule - ion parameters

were approximated from ion - ion and molecule -molecule parameters. Because Guggenheims equation is valid only to ionic strengths of 0.1 m , the method was limited to weak electrolyte concentrations of less than 1 or 2 m .

Deshmukh and Mather (1981) used a similar approach to calculate the solubility of H_2S and CO_2 in MEA solutions. They also used Guggenheim's equation to represent activity coefficients. The adjustable binary interaction parameters of the model were fitted on ternary system VLE data of MEA - H_2S - H_2O and MEA - CO_2 - H_2O . They also adjusted the temperature dependence of two equilibrium constants on experimental data. Chakravarty (1985) extended the model of Deshmukh and Mather (1981) to systems of mixed amines. In this model, the interaction parameters in the Debye-Huckel (1923) equation were obtained by fitting to experimental data of the corresponding single amine systems. Due to unavailability of experimental acid gas solubility data for mixed amine systems at that time, the Chakravarty method could not be validated.

Edwards et al. (1978) extended the range of validity of their sour water model to weak electrolyte concentrations of 10-20 m by adopting Pitzer's model (1973) to represent activity coefficients. Pitzer's model is an extension of the Guggenheim equation. It is an improved treatment of the long - range ion - ion electrostatic interactions and short - range ion - ion interactions, although, Edwards extended Pitzer's model to account for short - range ion - molecule and molecule - molecule

interactions.

Buetier and Renon (1978) also used Pitzer's model with the thermodynamic framework of Edwards et al. (1975) to calculate vapour-liquid equilibria (VLE) in sour water systems. These researchers accepted the binary molecule - molecule interaction parameters determined in the earlier work of Edwards and co-workers (1975) or refitted the parameters on binary system data. Molecule -ion parameters were estimated using Debye - McAulay's electrostatic theory (Harned and Owen, 1958).

While Pitzer's Gibbs excess energy model has been shown to be valid to ionic strengths representative of those encountered in industrial uses, its application is generally limited to single - solvent, aqueous systems. The solute - solute binary interaction parameters are unknown functions of solvent composition. The amine - water system is more properly treated as a mixed solvent system of variable composition. Furthermore, Pitzer's model contains a large number of binary and ternary temperature dependent adjustable parameters. Approximating these parameters is difficult for a system with a large number of liquid phase solute species, ionic and molecular, such as in the amine - H_2S - CO_2 - H_2O system (Austgen et al., 1989).

Dingman et al. (1983) developed a VLE model for the diglycolamine - H_2S - CO_2 - H_2O system. The framework of the model was equivalent to the framework used by Edwards et al. (1975). Activity coefficients were developed from a combination of

NRTL theory (Renon and Prausnitz, 1968), Brombley's correlation (1973), the method of Meissner et al. (1972), and the Born theory. The drawback of this approach was that the functional form of the expressions for the activity coefficient correlations was thermodynamically inconsistent.

MacGregor and Mather (1991) modified the Deshmukh-Mather model (1981) by accounting for mixed solvent effects on the system. A comparison of model predictions with experimental data was made for mixed solvent systems consisting of one chemical solvent and one physical solvent.

Several semi-empirical excess Gibbs energy models or activity coefficient models for aqueous electrolyte systems valid for ionic strengths representative of industrial applications have been developed. Among them are the models of Pitzer (1973), Meissner and Tester (1972), Bromley (1973), Cruz and Renon (1978), Ball et al. (1985), Chen et al. (1982), Chen and Evans (1986), and Christensen et al. (1983).

Austgen (1989) developed a rigorous physical-chemical model for providing liquid phase chemical equilibria and vapour-liquid equilibria of acid gas/alkanolamine/water systems. Equilibrium constants for all reactions in the solution, Henry's constant for gases and binary interaction parameters of the Electrolyte-NRTL equation for all important solution species were required as input in this model. Cheng and Rochelle improved upon Austgen's model and the existing database, so that it

could be used to predict acid gas solubility at low acid gas loading in MDEA solutions.

Austgen et al. (1991) extended the model of Chen and co-workers (Chen et al., 1982 ; Chen and Evans, 1986 ; Mock et al., 1986) to include amine mixtures with MDEA with MEA or DEA. This model combines the Debye-Huckel equation accounting for long range electrostatic interactions and the NRTL (Renon and Prausnitz, 1968) equation accounting for short range van der Waals type interactions. With the adjustable parameters fitted to the experimental vapour-liquid-equilibrium (VLE) data, the representation of the data was reported to be good.

2.3 Kinetics of the Alkanolamine-CO₂ Reaction

The absorption of acid gases into blended amines is a gas-liquid mass transfer process accompanied by complex (parallel and reversible) chemical reactions. The rates of absorption are strongly influenced or enhanced by the rates of chemical reaction taking place in the liquid phase. There are mainly two approaches in solving the differential equations describing mass transfer with chemical reaction : numerical solutions and approximate analytical solutions.

Chakravarty et al. (1985) developed a kinetic model for acid gas reaction with mixtures of amines using approximate analytical methods. This model claimed

agreement with numerical calculations to within 5% accuracy. Critchfield and Rochelle (1987) used the DeCoursey (1982) approximate analytical solution to predict the enhancement factor for CO₂ in mixed amines.

Haimour et al. (1984) determined gas absorption rates for CO₂ in MDEA using a laminar liquid jet absorber. It was found that for short contact times (< 0.012 s) there was only a small effect of any reaction between CO₂ and MDEA. Xu et al. (1991) studied the kinetic rate of absorption of CO₂ in a mixed solvent consisting of MMP, sulfolane and water within the temperature range of 15° - 45°C.

Rangwala et al. (1992) determined absorption rates of CO₂ into TEA, MDEA and blends of MEA with MDEA and TEA. The experimental studies were done in a quiescent surface stirred cell reactor. The technique was similar to that described by Laddha and Danckwerts (1981) and Blauwhoff et al. (1984). Second order rate constant for CO₂-MDEA was obtained from single amine data for temperatures in the range of 25-60°C. A modified first order model based on the film theory was used to predict the rate of absorption of CO₂ into a mixed solvent. This model accounted for the variation of amine concentration in the film and assumed a "shuttle" mechanism for rate enhancement. Bulk liquid concentrations of the various species present were obtained from a simplified thermodynamic model. Their simplified model gave amine concentration profiles in the film similar to those calculated numerically by Bosch et al. (1989). The model predictions of absorption rates were shown to be in good

agreement with experimental measurements.

Numerical methods have also been applied to blended amine systems to provide a rigorous solution to the mass transfer differential equations (Bosch et al., 1989 ; Versteeg et al., 1990 ; Glasscock et al., 1991). A comparison of the two methods of solution show that the approximate analytical solution usually has mean deviations of 2-3% from the numerical model (Versteeg 1989 ; Winkleman, 1992).

Zhang et al. (1993) developed a thermodynamic and kinetic model which permit the application of a rigorous non-equilibrium stage model and the Peng-Robinson equation of state for the simulation of acid gas treating with blended amine systems.

2.4 Mechanism and Reactions of Alkanolamines with CO₂

Before describing the reactions involved in the system it would be pertinent to describe the structural formulas of various commonly used alkanolamines (Fig. 2.1). Each alkanolamine has at least one hydroxyl group and one amino group. It can generally be considered that the hydroxyl group serves to reduce the vapour pressure and increase the water solubility while the amino group provides the necessary alkalinity in water solutions to cause the absorption of acid gases. The mechanism of reaction of primary and secondary amines with CO₂ is fairly well understood and was

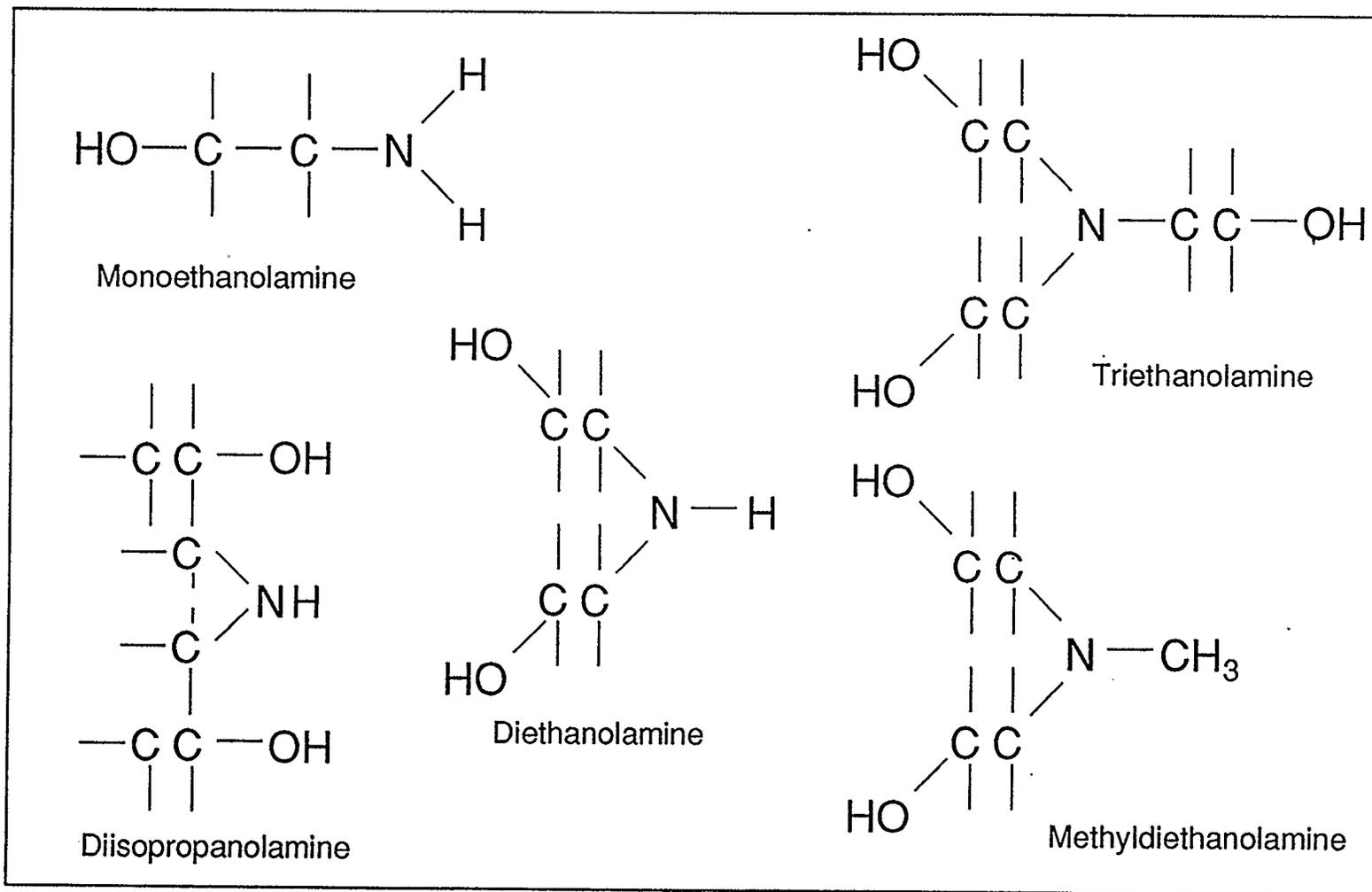
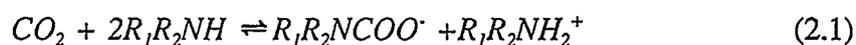


Figure 2.1 : Structural formulas for different alkanolamines

originally presented by Caplow (1968) and reintroduced by Danckwerts (1979). These reaction mechanisms differ in principle due to the difference in their structures. In aqueous solutions of primary and secondary alkanolamines, the following reactions occur with CO_2 (Danckwerts and Sharma, 1966 ; Danckwerts, 1979) :

Carbamate formation :



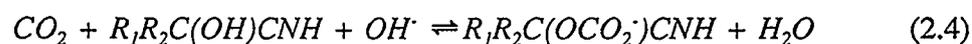
Bicarbonate formation :



Carbonic acid formation :



Alkylcarbonate formation :



where R_1, R_2 represent the alkyl group in a primary or a secondary amine.

It has been stated by Blauwhoff et al. (1984) that tertiary amines do not react with CO_2 according to reaction (2.1), because they lack the free proton, although, they do combine with CO_2 in aqueous solutions by reaction (2.4). They further state that each of the reactions (2.1 - 2.4) for primary and secondary amines and reaction (2.2 - 2.4) for tertiary alkanolamines contributes to the overall reaction rate constant. However, a few assumptions can conveniently be made for the above mentioned

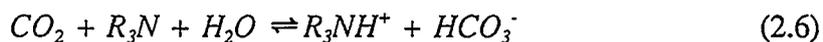
reactions. The formation of carbonic acid by reaction (2.2) proceeds at a very slow rate ($k = 0.026 \text{ s}^{-1}$ at 25°C , Pinsent et al., 1956) and therefore is normally neglected in rate constant calculations. Also, the formation of alkylcarbonate by reaction (2.4) becomes significant only at pH values above 12, which is not reached in the case of MDEA.

The reaction of primary and secondary amines with CO_2 involves the formation of an intermediate, the "zwitterion", as shown in reaction 2.1. The "zwitterion" can be deprotonated by any base (B) present in the solution producing a carbonate ion and a protonated base according to the reaction

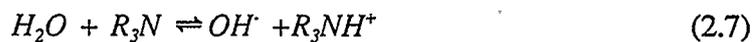


Although the exact mechanism of the reaction between CO_2 and tertiary amines in aqueous solutions is not fully understood, they differ from primary and secondary amines in their inability to form carbamates. The reaction between CO_2 and tertiary amines proceeds at a very slow rate.

Donaldson and Nguyen (1980) proposed a reaction mechanism where it was concluded that the tertiary amines acted as a base catalyst for the hydration reaction of CO_2 according to the reaction :



Savage et al. (1981) assumed that the mechanism for this reaction is given by the following two reactions :

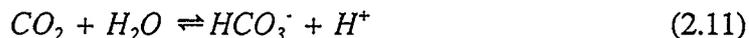


where R_3 represents the alkyl groups in a tertiary alkanolamine.

Barth et al. (1981,1984), Blauwhoff et al. (1984), Yu et al. (1985), Haimour et al. (1981) and Versteeg and van Swaij (1988) were in agreement with this same mechanism. In aqueous solutions the following reactions can also occur (Danckwerts, 1979) :



Jou et al. (1982) suggested that the CO_2 must first react with water to form bicarbonate according to the reaction :

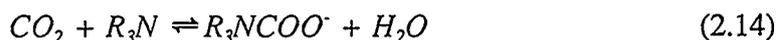


The bicarbonate then reacts with the amine via an acid-base neutralization reaction so that the overall reactions 2.12 and 2.13 occur. They also asserted that the formation of HCO_3^- is slow and controls the rate of reaction of CO_2 .



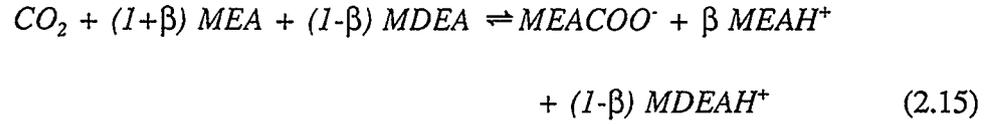


Tertiary amines cannot react with CO₂ directly, although a limited number of authors reported that a reaction occurred at extremely high pH of the solution. Jorgensen and Faurholt (1954) studied the reaction for a tertiary amine, TEA, at a high pH value (pH = 13) and concluded that the formation of monoalkylcarbonate occurred according to the reaction :

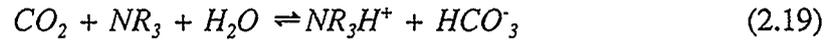
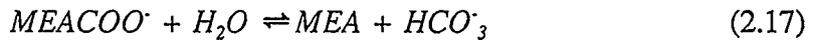
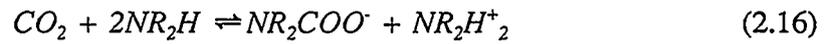


At 298 K, good agreement was found for the above proposed mechanisms for the tertiary amine MDEA. Compared to Sada et al. (1976) and Hikita et al. (1977), however, the observed reaction rates were found to be substantially lower, probably due to small amounts of primary and secondary amine impurities (Versteeg et al., 1988). Versteeg et al. (1988b) also showed that these impurities can have an overruling effect even in very low concentrations on the reaction rate measured experimentally.

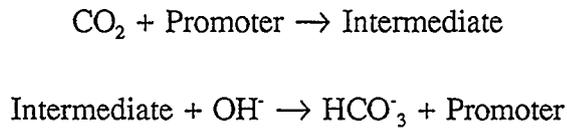
Blends of amines react in a more complex manner with CO₂. The influence of the tertiary amine on the primary or secondary amine reaction rate through the deprotonation of the zwitterion has to be taken into consideration (Bosch et al., 1986b) as in the reaction :



The following set of chemical reactions could best describe the blended amine system of MEA and MDEA.



The enhancement in the rate of mass transfer due to the blending of amines is believed to be due to a "shuttle" mechanism (Astarita et al., 1981). A general mechanism for the "shuttle" effect was proposed in the form:



A schematic representation of the shuttle mechanism is illustrated in Fig. 2.2. Bosch et al. (1989) proposed that in the case of MEA, MDEA blend, the net enhancement factor is not equal to the sum of the enhancement factors of the independent reactions of the amines, but to the product of the enhancement factors for MDEA and the square root of the enhancement factor for MEA.

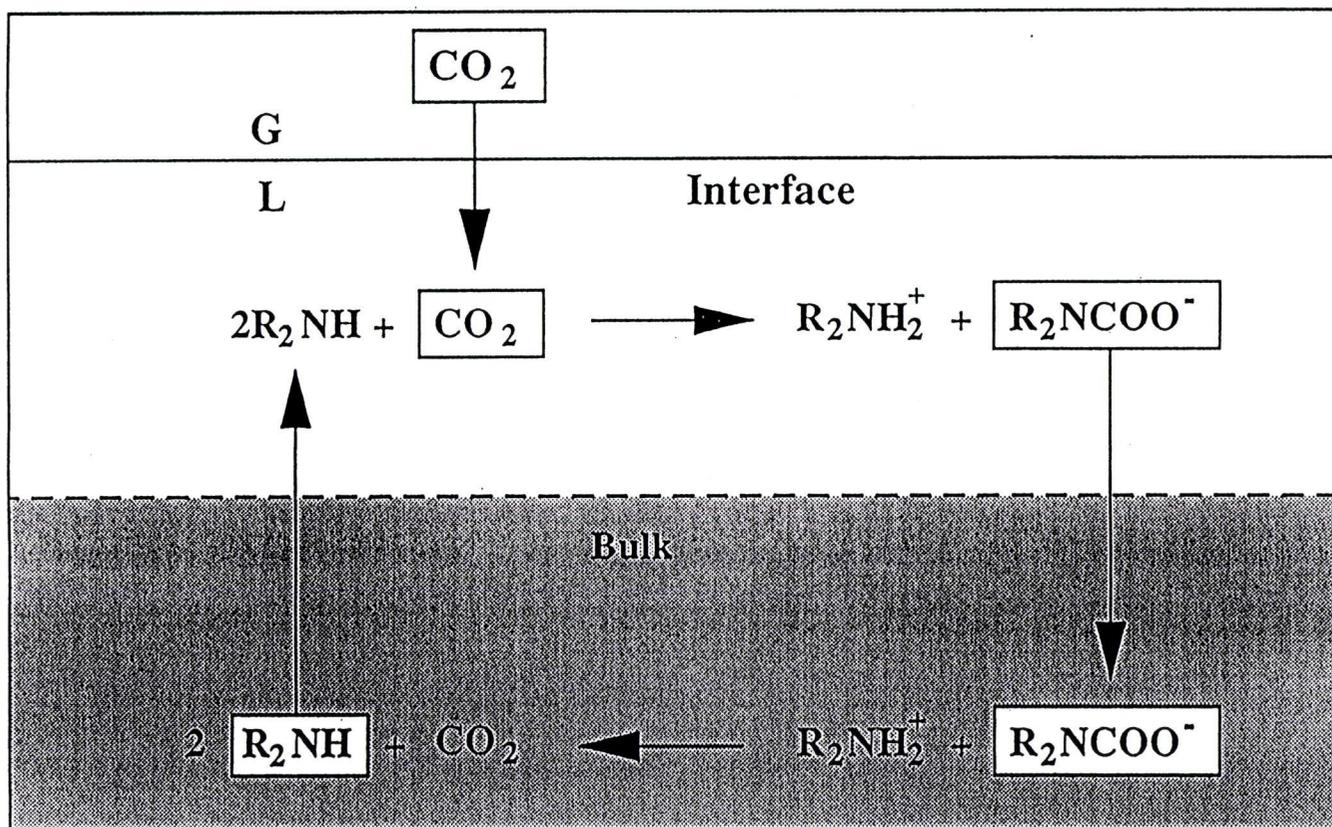


Fig.2.2 Schematic representation of the shuttle mechanism

2.5 Absorption - Stripping columns for CO₂ removal

Numerous methods have been devised to recover CO₂ on an industrial scale, as described by Kohl and Riesenfeld (1979). However, chemical absorption of CO₂ in liquid solutions followed by stripping of the purified gas remains the most popular and commercially viable process. This is done usually accomplished in an integrated absorber-stripper column. An obvious requirement, thus, is that the absorbent must have great capacity to absorb CO₂, must be reaction specific and should also be renewable once the CO₂ is eliminated. Aqueous MEA solutions fulfil these requirements and are thus frequently used in practice (Sharma, 1965). An extensive discussion on the absorption of CO₂ into solutions of alkalis and amines was provided in the review article by Danckwerts and Sharma (1966).

2.5.1 Modelling and Experimentation

A number of attempts have been made by various authors to design and simulate absorbers specific to this process. These methods of design sometimes differ entirely in their approach, which is why an elaborate discussion on the subject is necessary. The universal problem in designing absorbers undergoing absorption with chemical reaction is the lack of reliable information about interfacial areas and mass transfer coefficients in various types of absorption equipment. This problem of designing absorbers and strippers is accentuated when a mixture of solvents is present

and parallel or competing reactions are taking place. In such a case, the interacting reaction kinetics also play a major role in predicting absorption phenomenon.

Bradley and Andre (1972) published a dynamic analysis of CO₂ absorption into an aqueous MEA solution in a packed absorber, assuming plug flow of gas and liquid phases among other simplifying assumptions. Data from steady state experiments were used to empirically correlate the mass transfer rate coefficients and liquid hold up. Their model fairly well predicted the experimental measurements in a laboratory scale column. Suenson et al. (1985) and Marini et al. (1985) performed steady-state and dynamic modelling of an integrated gas absorber-stripper system in pilot-scale packed columns, for CO₂ removal through the hot carbonate diethanolamine promoted process. Rigorous energy balances were, however, not included in the model since heats of reaction and solution were considered negligible. Model predictions and experimental measurements were also compared by the authors.

The process of stripping which forms an integral part of the whole process has surprisingly received little attention by researchers. Considering the fact that almost 80% of the energy input in CO₂ removal units is consumed by the reboiler in a stripper, it certainly deserves more attention. However, little is mentioned in the open literature about modelling and exclusive experimentation on the CO₂ stripping units. Stripping of CO₂ from MEA solutions in a packed column was reported by Weiland et al. (1982) which was an important contribution to clarify modelling aspects of this

process. Pandya (1983) presented a design procedure for adiabatic gas absorption and stripping with chemical reaction in packed towers and illustrated it with sample calculations for CO₂ absorption in MEA.

De Leye and Froment (1986 a,b) presented a rigorous simulation of packed and plate columns for gas absorption with chemical reaction. Calculations for the absorption of CO₂ in an MEA solution were included as an example of the application of the packed column model. Although, this rigorous model consumed more computation time as compared to lesser rigorous models, it definitely gave a better insight into the process. No energy balances were included to account for non-isothermal conditions due to the heat of solution and reaction. Energy balances were considered in the tray column, but the stripping process of CO₂ from MEA was not analyzed.

Cornelissen (1980) presented a calculation model for the simultaneous absorption of H₂S and CO₂ into aqueous alkanolamines in tray and packed columns. The model was set up in terms of Lewis two-film theory with linearized concentration profile in the interfacial liquid film. The resulting set of linear (rather than differential equations which would have been obtained if a linearized concentration profile was not assumed) equations were solved numerically. Several numerical models describing the simultaneous absorption of CO₂ and H₂S in an alkanolamine have been presented in literature (Goettler and Pigford, 1971 ; Cornelisse et al., 1980 ; Haimour and Sandall,

1983 ; Haimour et al., 1987 ; Al-Ghawas and Sandall, 1983 ; Bosch et al., 1989).

Escobillana et al. (1991) presented a simple but sufficiently rigorous model to develop a steady-state simulator of an integrated absorption/desorption plant for CO₂ recovery with aqueous MEA solutions. A packed absorption column and a sieve tray desorption column were considered in this case. The effective interfacial area in the absorption column and the mean equivalent bubble diameter in the stripping column were the two parameters which were adjusted to fit the integrated model to experimental data. The calculation procedure was applied to experimental measurements made by Vanischeni (1977) and Albrecht (1977) on a pilot plant operating at steady-state.

Cox and Weiland (1992) reported absorption rates of CO₂ into DGA - MDEA and DEA - MDEA blends in a pilot scale column containing three sieve trays. Recently, Tontiwachwuthikul et al. (1992) presented experimental concentration and temperature measurements for the absorption of CO₂ from air aqueous solutions of NaOH, MEA and AMP (2-amino-2-methyl-1-propanol) in a packed absorber.

CHAPTER 3

Experiments

3.1 Experimental apparatus

The experimental apparatus consisted of an integrated pilot scale unit consisting of an absorber column, stripper column and associated instrumentation. The entire system was controlled by a Univox Control system supplied by Fisher Control, Inc.. Thus, depending on the requirement, manual or automatic operation of the control valves could be made. Most of the process parameters in the absorber as well as the stripper were obtained in the form of a digital output on the screen of the control system thus enabling continuous visual monitoring.

The description of the apparatus is subdivided into three sections, namely the absorber, the stripper and the control system. Reference to Fig. 3.1 can be made for a better understanding of the flow diagram. The materials in contact with the process fluids were glass (Pyrex QVF, Great Britain), stainless steel (316 and 304 stainless steel), teflon, butyl rubber and PVC.

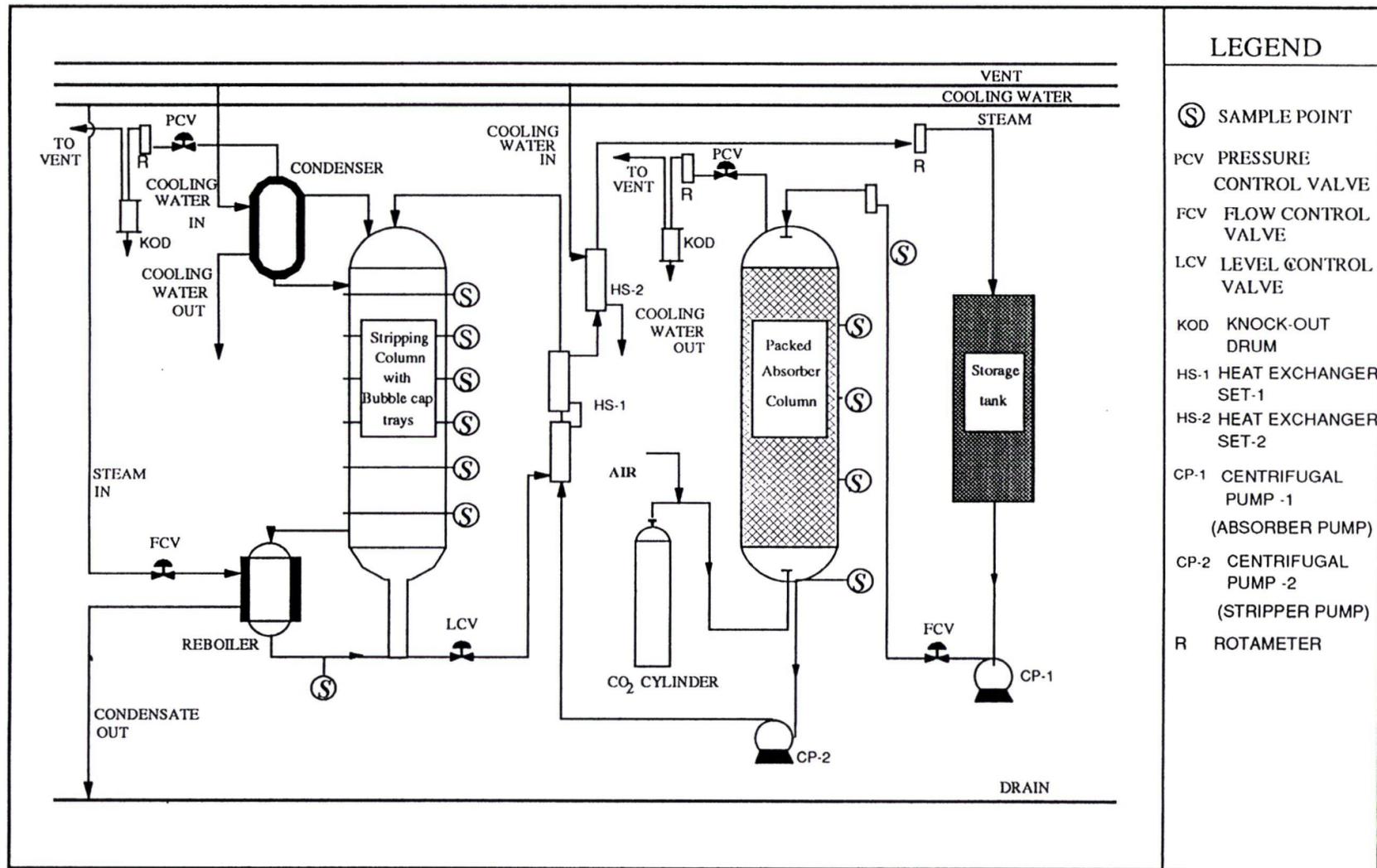


Fig. 3.1 Schematic flowsheet of the apparatus based on the Girbotol process

3.1.1 Absorber column :

Absorption studies were carried out in a 7.62 cm ID, 3.048 m long glass column, packed to height of 2.82 m with glass Raschig rings (0.9525 cm x 0.9825 cm x 0.15875 cm). Reference can be made to Fig. 3.2 for detailed schematic information on the absorber configuration and instrumentation. The packing material was supported on a 0.635 cm mesh stainless steel screen above a 0.1016 m disengagement section. A flange was fitted at every 0.61 m height from the bottom of the column. It held a 0.15875 cm (dia.) thermocouple probe and a 0.3175 cm (dia.) tubing for sampling purposes. The sample tubings were, on an average, 1.0 m in length and were provided with needle valves at the ends. Besides the flanges, sampling points were also provided at the inlet and outlet lines of the circulating amine solution. Thus, CO₂ loadings in the solution could be obtained at various points in the absorber. Above each flange a Teflon redistributor was mounted to prevent liquid channelling down the walls.

The vent line at the top of the absorber was connected directly to a Model 880 Non-Dispersive Infrared Analyzer supplied by Rosemount Analytical Inc., California. Vent gas (or treated gas) before being fed to the analyzer was routed through a knock-out vessel to avoid any carry over of liquid into the analyzer. Flow of exit gas from the absorber could also be estimated by a rotameter installed in the line.

Inlet gas consisting of a mixture of CO₂ and air was passed from the bottom of the absorber to countercurrently contact the downcoming amine solution. Flow rate and concentration of the incoming gas could be varied by tuning the related flow control valves, by remote operation from the control system. Rotameters were included in both the CO₂ and air inlet lines to provide local flow readings. Amine solution being pumped by a centrifugal absorber pump from the recirculating tanks, was passed through a filter to remove any small particles which could clog some of the valves downstream in the line. Flow of amine solution could also be varied with the help of a pneumatic flow control valve (FC-4) installed in the line. A rose head distributor mounted at the top of the column was used to evenly distribute the incoming solvent. Flow readings could be obtained locally from a rotameter or as digital output on the screen.

Level could be controlled in the column with the help of a level control valve which caused the flow of solution into the stripper at a faster rate in case the level overshoot the set point. Pressure in the absorber was displayed by a Bourdon Pressure gauge. Thermocouple probes were installed at various points in the absorber through the aforementioned flanges on the column and their output could be read as a digital output on the control system. The advantage of having a glass column was that the flow patterns and current level of solution in the absorber could be conveniently observed. Thus, the range of flow rates for the liquid and gas could be determined, whereby, proper contact of gas and liquid was ensured. Also, any foaming tendencies

or colouration of the amine could be easily noticed.

The rich amine from the bottom of the column was pumped by another centrifugal pump to the top of the stripping column. This pump had a control valve upstream which opened or closed to maintain the set-point level in the absorber.

3.1.2 Stripping column :

The stripping column employed in this study was a plate tower integrated with a vertical thermosiphon tube and shell reboiler, and a gravity return horizontal U-tube type baffled condenser. Reference can be made to Fig. 3.3 for a detailed schematic diagram of the stripping column configuration and instrumentation. The unit differed from a conventional distillation column, principally in the location of the feed (which was to the top tray) and in the overhead product drawoff arrangement. There were six bubble-cap trays, each 0.1524 m in dia. and placed 0.3048 m apart with five bubble-caps per tray. Copper-Constantan thermocouples and a 0.3175 m sample tap were mounted on each tray and at the column bottom. Thermocouples were also mounted on the feed, bottoms, vent vapour, cooling water and steam lines. 0.254 m (10") rotameters were mounted in the feed, cooling water and vent lines.

The entire column was well insulated to avoid heat loss. Liquid from the stripper flowed to the recirculation tank under the slightly positive pressure in the

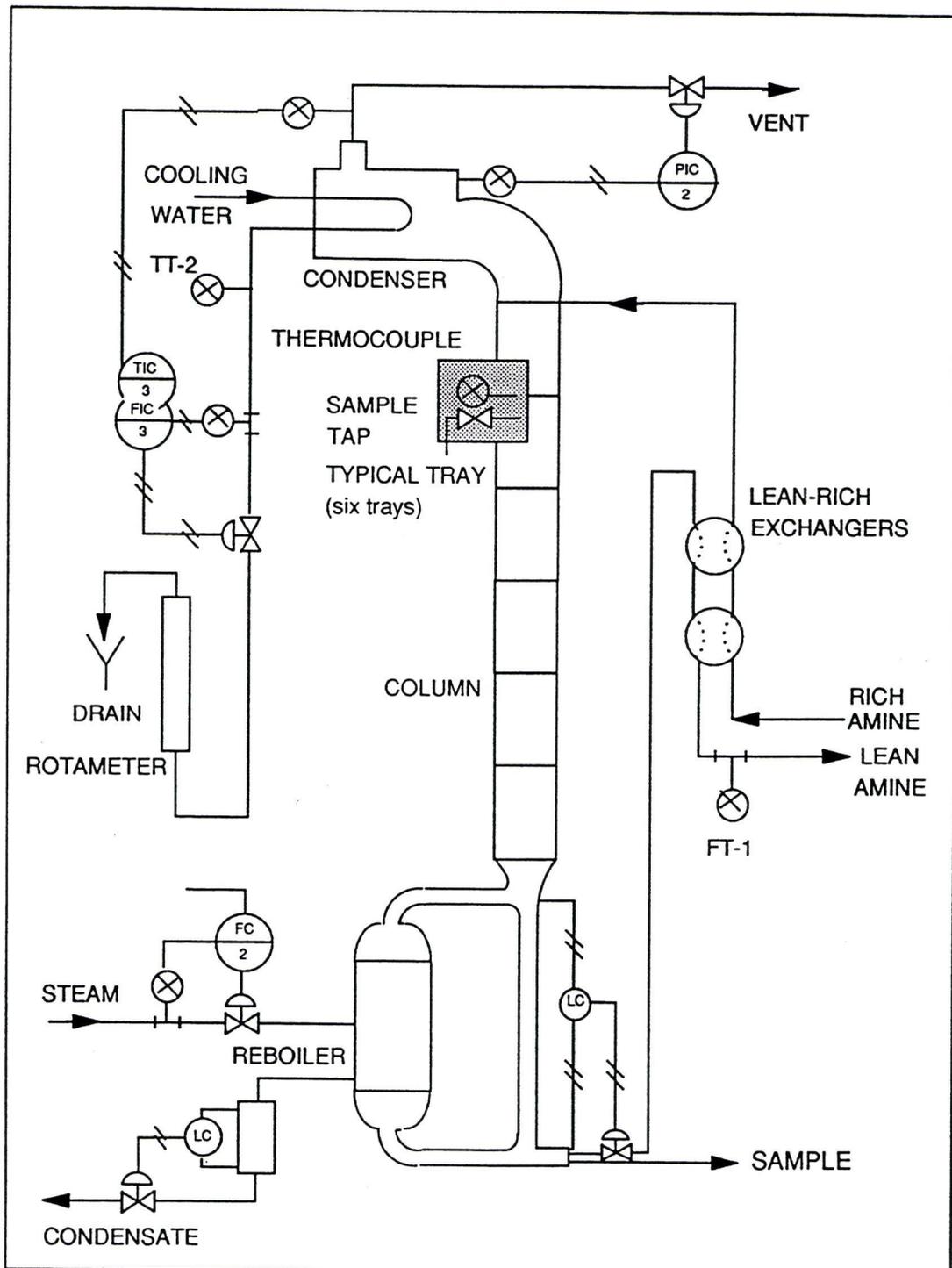


Figure 3.3 Regenerator configuration and instrumentation

column. Before entering the recirculation tank, the high temperature lean amine was made to exchange heat with the incoming rich amine in a set of two once through heat exchangers (HS-1 shown in Figure 3.1). The partially cooled lean amine was then further cooled by cooling water in another similar heat exchanger (HS-2 shown in Figure 3.1). The liberated gas in the stripper was vented through a pressure control valve, followed by a rotameter where flow could be locally read. This gas was passed through a knock out vessel to prevent liquid carry over before exiting the system. Rate of flow of cooling water was also read on a rotameter and on the screen. A part of the descending liquid in the stripper was routed through the reboiler. Steam was used as the heating medium in the reboiler. The reboiler was insulated with glass wool to avoid heat losses. Steam pressure and flow rate could be regulated by a pressure control valve and a flow control valve (FC-2), respectively, in the steam line. Consumption of steam was calculated from the amount of condensate collected within a specified time period.

The reboiler inventory was controlled by a level controller acting on the bottoms flow. Column pressure could be adjusted by manipulating the flow of non-condensable gas from the top of the condenser. Overhead composition control was effected by manipulating the condenser cooling water flow to maintain the vent vapour temperature. A constant vent vapour temperature ensured consistent water vapour pressure in the vent stream. Reboiler steam flow influenced the bottoms composition control. By design, liquid hold-up in the condenser was negligible, so that the reflux

ratio was a function of only the vapour leaving the feed plate. Thus, the interaction between the overhead and bottoms composition loops was reduced to a negligible amount (Bradley, 1972).

All the valves in the system were pneumatically controlled and were inspected from time to time for proper and accurate operation. Remote operation of these valves was managed by the I/P converters. Also, the digital output of various parameters were locally tested to ensure reliable readings.

3.1.3 Control System

The control system as mentioned earlier, was a Univox system supplied by Fisher Systems Inc.. The following variables could be controlled by this system :

- 1) Absorber level
- 2) Amine flow rate
- 3) Steam flow rate
- 4) Reboiler level
- 5) Cooling water flow
- 6) Stripper pressure
- 7) CO₂ flow rate
- 8) Air flow rate
- 9) Percentage of CO₂ in inlet gas

In addition to these parameters, temperatures at the locations given in Table 3.1 could be read continuously.

3.2 Procedure

Experimental runs were carried out on an absorber and stripper. The pilot scale unit consisting of the absorber and stripper was, as described earlier in this chapter, equipped with associated controls and instrumentation. It was designed for continuous service. Reference can be made to Fig. 3.1 for a better understanding of the procedure.

3.2.1 Solvent preparation

Commercial grade MEA and MDEA were used to prepare the aqueous solutions of the amines. These amine solvents were supplied by Travis Chemicals, Calgary. Feed solution was prepared and stored in 80 gallon glass lined holding tanks and was thoroughly mixed before each run to ensure consistency of composition. The aqueous solutions of the amines prepared by weight percent (wt%) was charged into the recirculation tank. There were two storage tanks in parallel to provide more flexibility and easily controlled operation. Anti-foaming agent was added to the recirculation tank from time to time when excessive foaming was observed in the absorber.

Table 3.1 : Thermocouple locations in the system

Absorber	Stripper
Lean feed of amine	Condenser cooling water in
Plate # 1	Condenser cooling water out
Plate # 2	Rich amine to heat exchanger
Plate # 3	Stripper feed after heat exchanger
Plate # 4	Stripper Reboiler
Plate # 5	Tray # 1
Rich amine leaving absorber	Tray # 2
CO ₂ @ rotameter	Tray # 3
Air @ rotameter	Tray # 4
Absorber vent	Tray # 5
	Tray # 6
	Stripper vent
	Reboiler steam chest

The aqueous solutions of these alkanolamines were analyzed for their pH values and also for the total amine or impurities present. pH analysis was done on a pH meter (Fischer Acumet pH meter, Model 620). The total amine content was analyzed in a Gas-Chromatograph (Hewlett Packard Series 5890 A). This initial analysis of the amine solution served as a comparative standard to any changes in the characteristics of the solvent at a later stage. Samples of the amine solution were tested after every two runs to detect any changes in concentration of amine and also to find if any degradation products were being formed. However, the temperature in the reboiler section of the stripper was not allowed to rise above 120°C to avoid any thermal degradation to take place.

Ten to fifteen drops (1 drop \approx 1 ml) of anti-foaming agent was added to the solvent if excessive foaming was observed. This small amount of anti-foaming agent did not affect the solvent composition in any noticeable way. Make-up water was added to the solution to maintain the concentration, as and when required. This loss of water came from whatever water vapour was escaping through the vent line in the stripper.

3.2.2 Experimental Run on the Pilot Scale Unit

This section deals with a complete description of a typical run on the unit. The process parameters which have been controlled and recorded are mentioned.

3.3.2.1 Start-up Procedure and Complete Run

The absorber recirculation pump was started and the solvent allowed to flow from the top of the absorber through a liquid distributor. The flow control valve in this line was set at the flow rate desired. Also, the level control valve was set at a point normally a little below the packing height. This was because when the gas was later allowed to flow in, it raised the level of the liquid to almost cover the whole packing height. As a result, the entire packing height was utilized for the mass transfer operation.

The stripper pump was then started to pump solvent from the bottom of the absorber to the top of the stripping column. The liquid distributor in the stripper allowed the solvent to fall in small droplets and also evenly distributed it radially. Level was set in the bottom of the stripping column, just enough to allow boil over of the liquid from the reboiler into the main column. Recycle ratio of the solvent into the reboiler, however, could not be controlled. But it could be assumed that if the level in the stripper column was similar and the pressure was also same then the reflux ratio in two different runs was almost similar.

The stripping column vapour was partially condensed in the overhead condenser by circulating cold water. This minimized the loss of amine as well as water from the system, thereby maintaining the solvent concentration. reflux from the condenser

returned to the stripper by gravity.

At this point, steam was passed through the reboiler. The flow rate and downstream pressure of steam was adjusted so that the temperature of amine in the reboiler never exceeded 120-125°C. At a temperature above this thermal degradation of amine begins to take place.

Lean solvent from the stripper then flowed through a set of heat-exchangers under the existing pressure in the column. In this process, rich amine flowing into the stripper got preheated and lean amine exiting the stripper got cooled down. Preheating the rich amine reduced the consumption of energy in the stripper, while cooling down the lean amine leaving the stripper ensured better absorption in the absorber.

The circulation of solvent was continued for 1-1.5 hours until all the solvent became uniformly heated. CO₂ was then introduced from the bottom of the absorber through a gas distributor plate. Flow rate of CO₂ and air could be controlled by the flow control valves in the line. The concentration of CO₂ could be altered likewise by changing the ratio of the openings in the flow control valves in the CO₂ and air lines. The control system made it possible to adjust just one control valve and the other control valve was operated by an automatic cascade control mechanism to attain the set ratio. Standard cylinders with a fixed percentage of CO₂ could also be used. Fine tunings in the control valves made it possible to maintain the set conditions as long

as the run progressed.

An hour after the system stabilized liquid samples were taken from all five points in the absorber and gas samples from the absorber vent line (Refer Fig. 3.1 for sample locations). These samples were analyzed for CO₂ concentration. Samples were then taken every 30-40 minutes and analyzed. The process was considered to attain steady-state when CO₂ loadings became constant in the liquid and the exit gas concentration did not change. Temperature profiles in the absorber were recorded during the entire duration of a run. A constancy of temperature also indicated the attainment of steady-state. Normally, steady-state was reached within 3.5-4 hours after which final samples were taken from all the locations in the absorber as well as the stripper. Condensate from the consumed steam was collected within a certain time interval which gave a measure of the rate of steam consumption. This concluded a single run.

Runs were carried out by varying the essential parameters one by one to study the effect of each one of them. The effect of following parameters were studied in particular :

- CO₂ flow rate
- CO₂ concentration
- Amine flow rate
- Amine concentration

- CO₂ loading
- Steam consumption

After having completed all the required runs on single amine solvents MEA and MDEA, mixed amines were used. The introduction of mixed amines introduced yet another variable : the percentage ratio of each amine in solution.

3.3 Analytical Technique for the Determination of CO₂ Concentration

Experimental studies on the absorption of CO₂ by alkanolamines would be futile if one did not have confidence in the analytical technique used to measure the CO₂ concentration in the liquid and gas phase. Thus, immense importance has been laid on the development of an analytical technique which is both convenient and accurate.

An extensive discussion is presented in this section on the current methods of analysis. The method used in the course of this work is then described. The advantages and disadvantages of the various techniques have been enlisted in a comparative fashion and most of the shortcomings of other methods has been taken care of. The final procedure used is a combination of the existing methods taking care of the shortcomings of each one of them. Calibration curves prepared for the procedure have been included in Appendix-A.

3.3.1 Analysis of CO₂ in the Gas Phase

CO₂ concentration in the gas phase was determined using a Non-Dispersive Infrared Analyzer (Model 880) supplied by Rosemount Analytical Inc., California. It was calibrated using standard CO₂ calibration gas of varying concentrations for three different ranges (0-1%, 1-20%, and 20-100% CO₂ concentrations). Concentrations of CO₂ as low as .05% could be read in the gas phase. The readings obtained by the Infrared analyzer was confirmed from time to time by analysing the gas in a Gas Chromatograph (Hewlett Packard Series 5890 A). Use of the Infrared analyzer provided online monitoring of CO₂ concentration.

3.3.2 Analysis of CO₂ Concentration in the Liquid Phase

Current methods for the quantitative determination of acid gas in the alkanolamine are often time consuming, tedious and suffer from problems of reproducibility. Among the more common ones are the volumetric method well suited to routine analysis, quantitative precipitation of the dissolved gas as metal salt with simultaneous formation of an acid, and titrimetric methods. More often than not, when the sample contains very low concentrations of dissolved gases, none of these methods is entirely satisfactory. The acid gas used in this study was carbon dioxide and the amines used were MEA, MDEA and their mixtures. A brief description of these methods is given below:

3.3.2.1 Volumetric Method :

This method involves reacting a known amount of sample with a given concentration of sulphuric acid solution in a closed vessel. The volume of CO_2 evolved is measured and is converted to its mole equivalent at the existing temperature and pressure conditions. Typically, sample volumes of 2 ml. were reacted with a fixed volume of 30% w/w H_2SO_4 in a reactor where the temperature and pressure was recorded for further calculations. The buffer solution used in the manometer was either one of the mixtures listed later in this section, each of which was tested for CO_2 absorption and was found not to absorb any amount whatsoever. The analysis of carbon dioxide and other acid gases dissolved in bases, by acidification of the solution and measurement of the volume of evolved gas, necessitates corrections for temperature, pressure, static head, solubility etc. (Weiland and Trass, 1969). Swick et al. (1952) in describing a method of analysis for carbon dioxide in methylenediamine by this technique, reported 99.8 % recovery of the gas, but if the acidified solution was not kept hot all the gas could not be recovered. Reference can be made to Fig. 3.4 for the arrangement of the low pressure solubility apparatus.

By slowly sweeping the reactor with a pure inert gas, followed by absorption into aqueous sodium hydroxide or onto Ascarite, these complications are minimized, but only at the expense of increased analysis time.

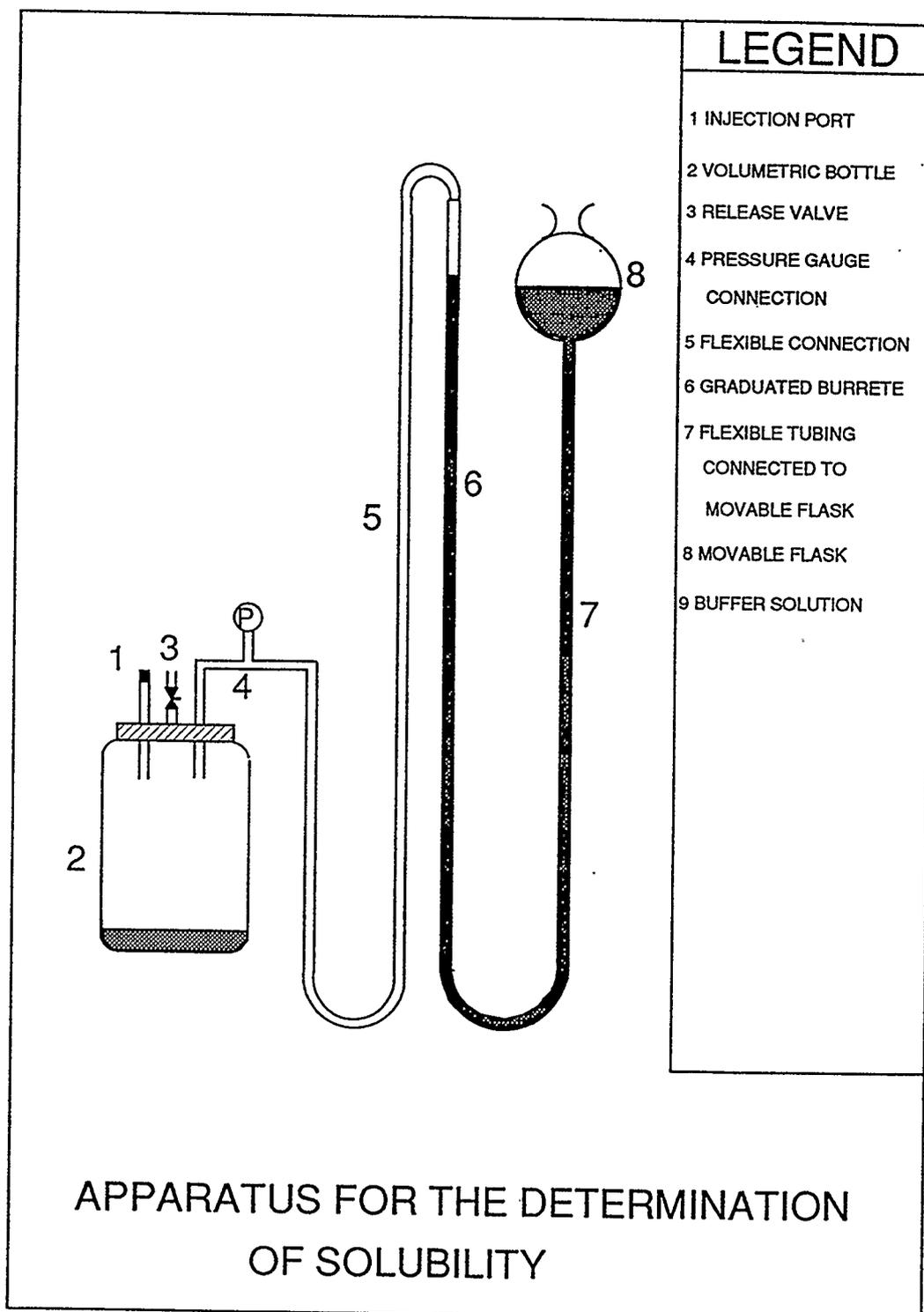


Fig. 3.4 : Low pressure solubility apparatus

Buffer Mixture I : Prepared by dissolving 100 grams of sodium sulphate in 500 ml. of water and adding 20 ml. of concentrated H_2SO_4 . 10 drops of methyl red is then added to the final solution.

Buffer Mixture II: This buffer is prepared by dissolving 100 grams of sodium chloride in 350 ml. of water and adding 1 gram of sodium bicarbonate. 2 ml. of Methyl orange indicator is finally added to the resulting solution.

The volumetric method, however, suffered from the following additional disadvantages :

i) Very small changes in the CO_2 concentration were indistinguishable, as it did not reflect in the volume of CO_2 evolved.

ii) Even the same solution tested repeatedly did not give the same volume of gas evolved.

iii) There is always a residual amount of CO_2 left in the sample, which can be confirmed by a gas chromatographic analysis, but only at the risk of letting H_2SO_4 enter the system. This residual CO_2 is not obtained even by mild heating of the solution. Though it is a very small amount it becomes appreciable when CO_2 loadings are low. The residual CO_2 is not a constant volume which can be determined once and added to the CO_2 volume finally obtained. It varies with the concentration of the amine as well as its loading.

3.3.2.2 BaCl₂ Precipitation Technique :

This method involves preparing a solution of 0.1 M BaCl₂ in water which has previously been heated and bubbled with nitrogen. At low pressure (close to atmospheric), the amine sample is directly added to excess of this solution to form barium carbonate precipitate. The precipitate so obtained is then filtered using Whatman 42 or Whatman 5 filter paper. All along the filtration process, the sample is kept covered to disallow any contact with air. After this, the filter paper along with the precipitate are washed with distilled water until the filtrate reaches a pH of 5-6. The precipitate is then dissolved in H₂O along with the filter paper until a pH of 4.0 is reached. It is then titrated against 0.1N HCl to determine the CO₂ content.

At high pressures, the sample is directly withdrawn into a 1 N caustic solution to fix the carbon-dioxide present in the carbonate form. But care has to be taken not to collect amine sample in excess of caustic. The NaOH amount should be just 2-3 times the amount of sample by volume.

A shortcut method in the precipitation technique is the gravimetric method whereby the precipitate is washed , dried and directly weighed to give the amount of CO₂ present. But this method does not give good results unless sufficient time is given for complete precipitation. Other problems include the loss of some of the precipitate while washing, filtering and drying. The method totally fails when the loading of

samples is very low.

A few other disadvantages of the precipitation technique combined with titration are as follows:

i) The whole procedure is very tedious and time consuming. A single sample analysis could take well above an hours time.

ii) This method, in general, seems to be applicable only at high loadings of CO₂.

iii) Also, it is generally observed that at low loadings, this technique shows higher than expected loadings.

3.3.2.3 GC Technique

All the above prevalent methods, inspite of their time consuming nature, give us an estimation of only the CO₂ content in the sample. With the increasing use of mixed amines which provide greater advantage over conventional amines from absorption capacity and energy savings point of view, an estimation of individual amine concentration too, in the solution has become important. Even in the case of single amine solutions, a track of the amine concentration has to be kept to ensure that the original amine concentration is preserved and no other conversions are taking place. In addition to this, one should also be able to estimate any degradation products in the sample. These requirements and most of the other shortcomings are almost

entirely taken care of by Chromatographic techniques. Much work, however, has not been reported in the open literature on the chromatographic analysis of carbonated alkanolamines, mainly because of sampling and calibration problems. In this work, we report the development of a GC based technique for such analysis.

Procedure for Preparing Calibration Curves :

Equipment used : A Hewlett Packard Series 5890 A Gas Chromatograph was used for analysis. It employs a 182 cm long Tenax GC Column. Temperature programming was done with an initial temperature of 35°C, initial time of 1 min., oven maximum temperature of 300°C, final temperature of 280°C, injector port temperature of 280°C, detector temperature of 300°C and the rate of rise in temperature was 30°C/min. Helium was used as the carrier gas with a fixed flow rate of 30 cc./min.

Procedure : Carbonated samples of different amines and their mixtures were prepared and injected into the GC column at 280°C. This vaporises the sample in the injection port. Dissolved and chemically combined CO₂ elute from the column first, followed by water and amine. Degradation products in the sample give distinct peaks and are easily identifiable. Calibration curves allow determination of concentration of each species.

Apart from the novel use of a suitable column and appropriate temperature

programming, the calibration curves hold the key to the success of this technique. The following calibration curves were prepared for individual and mixed amines as well as their CO₂ content. These curves are included in Appendix A.

Calibration Curve I : This is a calibration curve for the GC area vs. concentration (by wt%) of MEA in the sample. Thus, for any sample containing any quantity of MEA, the concentration can be determined from the area which appears under the MEA peak.

Calibration Curve II : This is a calibration curve for the GC area vs. concentration (by wt%) of MDEA in the sample. Thus, for any sample containing any quantity of MDEA, the concentration can be determined from the area which appears under the MDEA peak.

Calibration Curve III : This is a calibration curve for the GC area vs. moles of CO₂ in the gaseous phase. However, the GC areas that we obtain for CO₂ content in a sample of carbonated amine does not correspond to the GC area obtained for CO₂ in the gaseous phase. Therefore, this curve can only be used to interpret CO₂ concentrations in a purely gaseous phase.

Calibration Curve IV : This curve is for the GC area obtained for CO₂ in the solution state (physically + chemically combined CO₂) vs. the actual volume of CO₂

present in the sample. The calculation for the actual amount of CO_2 is performed with the help of existing data as well as actual measurements by volumetric and associated methods. The existing data comes from previously tested samples of carbonated amine solutions under equilibrium conditions reported in the literature.

The calibration curves for different amines showed that the concentration was not necessarily a linear function of the chromatographic area. Also, the chromatographic area of CO_2 present in amine solution does not correspond to that present in gaseous phase. This phenomenon is observed because all the CO_2 present in a physically or chemically combined state does elute as fast as that in the gaseous phase. This lag causes the chromatograph to over estimate the CO_2 content. However, once the calibration curves were plotted, the actual CO_2 content could be read accurately.

CHAPTER 4

Results and Discussion

This chapter consists of the results obtained from the experimental studies conducted on the pilot scale unit . The results have been presented in a systematic fashion so that the effect of each of the variables can be evidently observed. A discussion is presented for each of the runs involving single as well the mixed amine systems.

Experimental runs were performed using single solvents MEA and MDEA first, so that a distinction could be made between the advantages and disadvantages of each of the amines. This was followed by performing runs using the mixtures of MEA and MDEA.

The existing pilot scale unit had a few limitations as far as varying process variables were concerned. A few of the major limitations of the unit are qualitatively discussed below and the ways and means used to combat the problems are also explained.

In the absorber section there was no provision of taking gas samples from intermediate stages. Thus, only liquid samples were obtained and analyzed. There was not much flexibility in varying the gas flow rates because it caused flooding in the

column. Since the absorber had a small diameter as compared to the height (height/diameter ratio = 40) plug flow could not be exactly obtained. In absorbers of this type gas invariably causes flooding in the upper section of the column. Since the flow rate of the gas could not be exceeded above 40 L/min, the concentration of CO₂ in the gas mixture had to be increased to obtain a good concentration profile in the column. Thus a concentration value of 20% v/v of CO₂ was selected for all the runs except for those where the effect of concentration of CO₂ was being studied. It is, however, uncharacteristic of typical industrial applications to have very high CO₂ concentrations in gas streams.

Since the liquid from the absorber was pumped to the stripping column by the stripper pump, excessive liquid holdup in the absorber did not take place and the level could be maintained with ease. However, the solvent from the stripping column flowed to the recirculation tank under the pressure existing there. As a result very high flow rates of liquid in the system (above 64 kg/h) could not be handled by the stripping column and liquid build up started to take place there. Also, the pressure in the stripping column could not be manipulated within a broad range. At high pressure (above 80 kPa) in the column, the level could not be controlled in the bottom section and liquid level kept fluctuating in the reboiler. On the other hand, at low pressures (below 10 kPa), which was reached if very dilute CO₂ or very low flow rate of the gas was used, the solvent could not be pushed out of the column.

As a result of these shortcomings in the system, runs were carried out by varying the parameters to their limiting values and the range of operability was determined. The most optimum process variables were also, likewise decided and these parameters were kept constant, varying either one of them at a time. The following parameters were used as the most optimum ones for a particular solvent and they formed the base variables for each run. One variable at a time was changed, the others remaining constant, and the effect of each was observed. Thus, the graphs showing one particular variable changing have the remaining variables set at the values specified below.

Solvent MEA

MEA flow rate	= 32.0 kg/h
MEA conc.	= 20% w/w
CO ₂ flow rate	= 30 L/min
CO ₂ conc.	= 20% v/v

Solvent MDEA

MDEA flow rate	= 38.4 kg/h
MDEA conc.	= 50% w/w
CO ₂ flow rate	= 30 L/min
CO ₂ conc.	= 20% v/v

Mixed amine (MEA + MDEA)

Mixed Amine flow rate = 38.4 kg/h

Mixed Amine concentration :

MEA = 5% w/w

MDEA = 45% w/w

CO₂ flow rate = 30 L/min

CO₂ conc. = 20% v/v

Typical process parameters which were otherwise maintained constant in the system are presented in Table A.1 of the Appendix. The results of the experimental runs are mostly qualitatively discussed. The raw data obtained for the mixed solvent is undoubtedly very useful if they are to be used for designing and scaling up the process. Interpretation of the results can be confidently used for initial screening studies if a blended amine system consisting of MEA and MDEA is to be used.

4.1 Interpretation of Experimental Data**Loading of CO₂ Plots:**

The experimental data were expressed in the form of loading values of CO₂ along the dimensionless length of the absorber and stripper. Loading value for CO₂ can be defined as:

$$\text{Loading of CO}_2 = \text{moles of CO}_2 / \text{moles of amine}$$

In the case of mixed amine systems too, the results have been expressed in a similar fashion. Moles of amine, in the context of mixed amines stands for the sum of the moles of individual amines in the blend. Dimensionless length along the columns was chosen for the plots to make it possible to display the results for the absorber and stripper on the same plot.

Overall Gas Phase Mass-Transfer Coefficient ($K_g a$) Plots :

$K_g a$ or the overall gas phase mass-transfer coefficient for the absorber was calculated as shown below :

$$K_G a = \frac{G_M}{Ph} \int_{y_2}^{y_1} \frac{dy}{y - y_e} \quad (4.1)$$

where, G_M = molar mass velocity, g mol/m²h or kg mol/m²h

h = apparent packed height in the column, m

P = total pressure, kPa

y_1 and y_2 ≡ mole fraction of solute in the gas stream at the bottom and top of the column respectively

y_e ≡ mole fraction of solute in the gas stream at equilibrium with the bulk liquid phase composition

Absorption and Stripping Factor, 'P' : In order to compare various solvents in terms of their combined absorption and stripping characteristics a factor 'P' has been defined as follows :

$$P = (\sqrt{A} \times \sqrt{S})/E \quad (4.2)$$

$$A = (x1_a - x2_a) \quad (4.3)$$

$$S = (x1_s - x2_s) \quad (4.4)$$

where, $x1_a$, $x2_a$ are the loading values of CO₂ at the top and bottom of the absorption column (mol CO₂/mol amine), $x1_s$, $x2_s$ are the loading values of CO₂ at the top and bottom of the stripping column (mol CO₂/mol amine) and E is the rate of energy consumption in the reboiler (KJ/h).

It is desirable to have maximum absorption in the absorber and a maximum stripping in the stripper of the solute gas CO₂ along with the minimum energy consumption. Thus, by definition, the parameter 'P' has to be maximized to get the best absorption characteristics along with the best stripping qualities. The units of parameter 'P' are (mol CO₂/mol amine)(1/KJ/h). The units of this parameter symbolize it to be the molar CO₂ handling capacity per unit mole of the amine for a given heat duty. Another advantage of this parameter is that it reflects on the integrated unit rather than the absorber or stripper alone.

4.2 Effect of Process Variables (Solvent MEA)

The effect of various variables on the loading values of CO₂ along the dimensionless length of the absorber and stripper, and their effect on the overall gas phase mass-transfer coefficient are studied in this section. Fig. 4.1 shows the loading

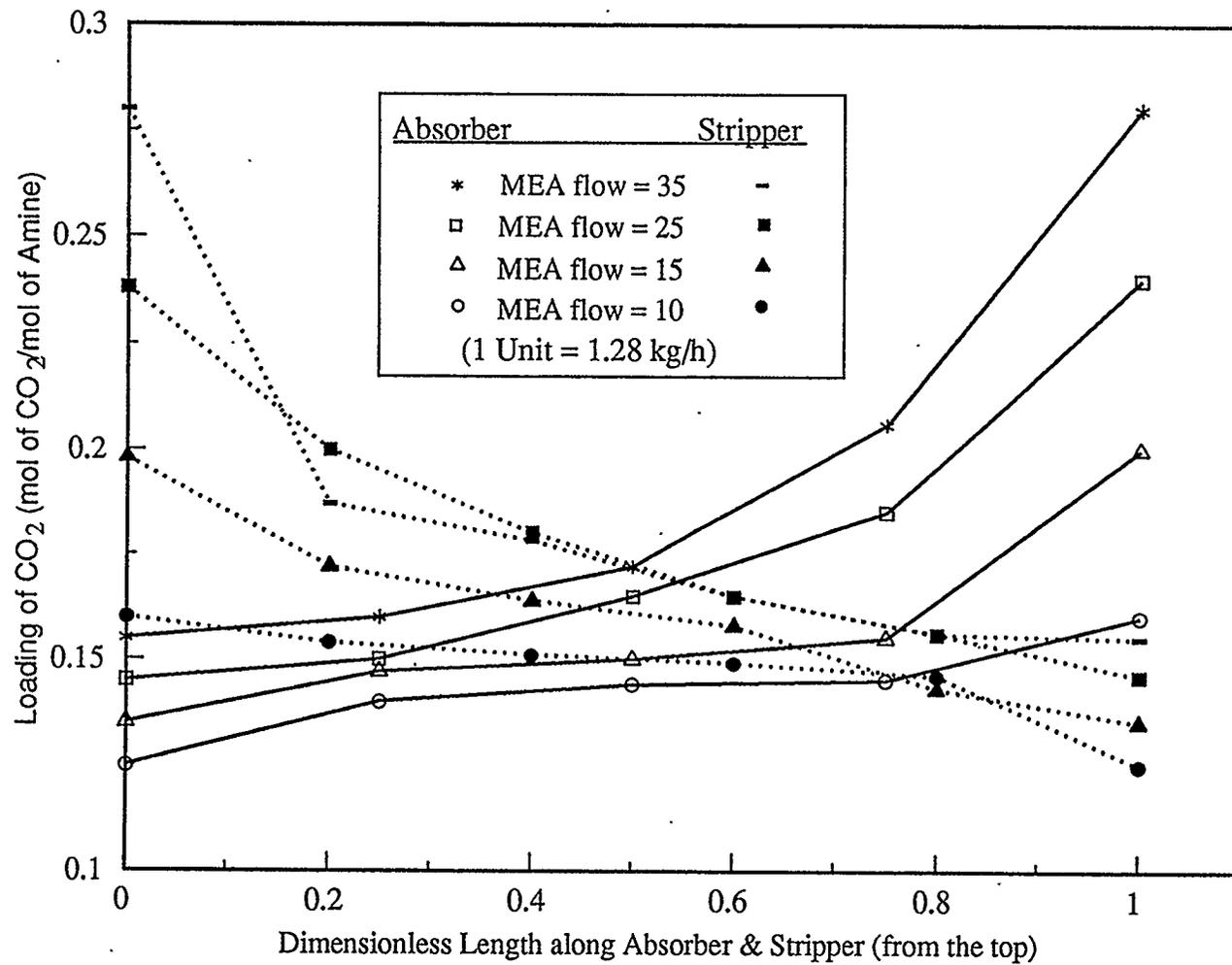


Fig. 4.1 Concentration profiles along the Absorber and Stripper for different MEA flow rates

profiles along the absorber and stripper for different flow rates of MEA. The first observation is that considerable absorption of CO_2 was obtained for MEA. This is in keeping with the fact that MEA has higher rate of reaction with CO_2 . As mentioned by Kohl and Riesenfeld (1979), CO_2 absorption in absorbers using MEA as the solvent can reach 70 - 80% of the equilibrium value. Though it is not true in the case of industrial absorbers, the pilot plant study conforms to the proclamation. The loading values along the absorber increased with increasing flow rates of MEA. This is because the rate of reaction of MEA with CO_2 is high enough not to be influenced by the small change in the residence time of the solvent in the column caused by an increased flow rate of amine. This increase in the loading values can also be explained based on the fact that the interfacial area for transfer of the solute increases with increasing flow rates of the solvent. There is also an increased turbulence in the system with increasing flow rates, which assists in the better contacting of the solvent and solute. The corresponding figure for the overall gas phase mass-transfer coefficient (Fig. 4.2) shows that the overall mass transfer coefficient also increases with increased MEA flow rate. However, as flow rate was increased the rate of increase in the mass-transfer coefficient decreases and tends to taper off. In general, increasing the liquid flow rate increases the interfacial area for mass transfer. However, this increase in the interfacial area is a non-linear function of the liquid flow rate, the former tending to rise but levelling off as the latter increases.

At increasing concentrations of MEA, the loading values increased all along the column (Fig. 4.3). Overall mass-transfer coefficients also increase with increasing

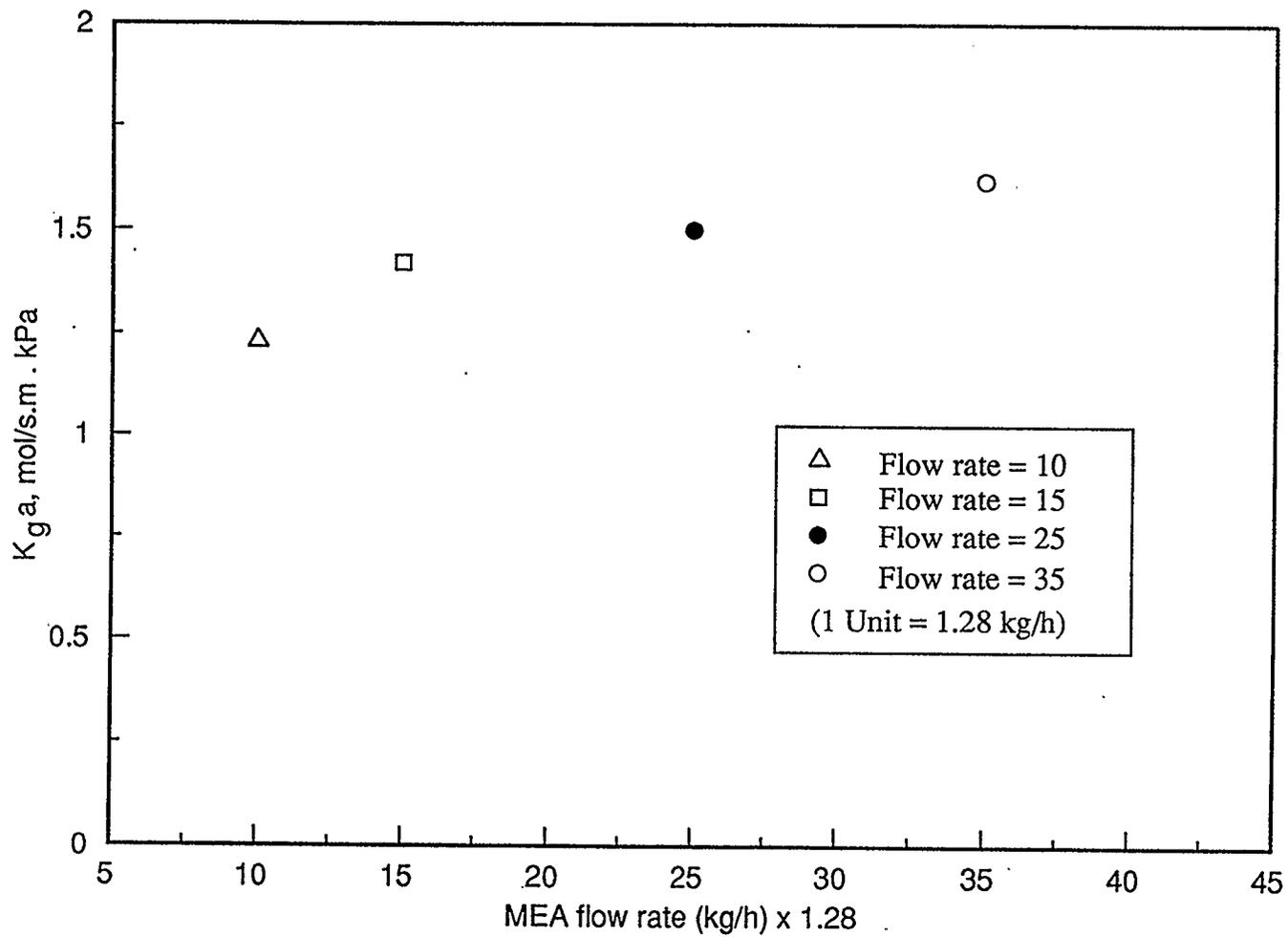


Fig. 4.2 Effect of MEA (20% w/w) flow rate on the overall gas phase mass transfer coefficient

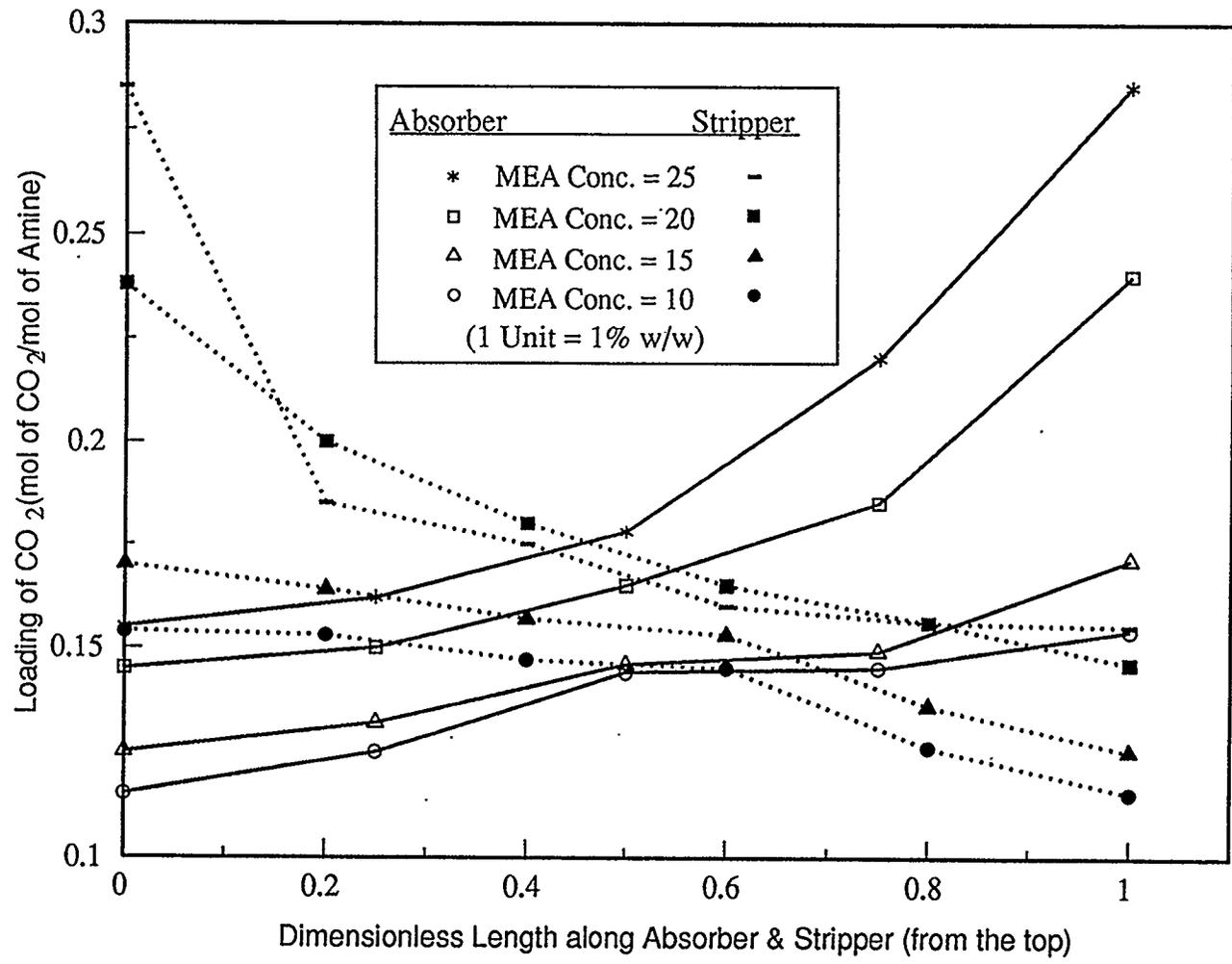


Fig. 4.3 Concentration profiles along the Absorber and Stripper for different MEA concentrations

solvent concentration (Fig. 4.4). The solution viscosity was not influenced to a large extent by the change in its concentration within the range of solvent concentrations employed. Increasing the solvent concentration increases the reactant availability for reaction with CO_2 . Kinetic effects over-ride the viscosity effects at the concentrations of MEA used. This should encourage one to further increase the concentration of solvent for best absorption results. But the corrosivity of the solution tends to increase very rapidly with increasing concentration for MEA. Moreover, at very high concentrations the heat of reaction causes the solution to heat up. Increased temperatures are, as mentioned earlier, not suitable for the forward reaction of MEA and CO_2 . Also, at very high concentrations, high viscosity values of the solvent are not suitable for the diffusion of CO_2 into the solvent (viscosity and diffusivity for liquids are related by an inverse relationship).

At increasing flow rates and concentration of CO_2 , loading values increased almost proportionally (Fig. 4.5 & Fig. 4.7). The corresponding mass-transfer coefficient values are plotted in Fig. 4.6 and Fig. 4.8 respectively. Excellent absorption reflected by a CO_2 loading of 0.31 was obtained for a concentration of 50% v/v CO_2 . However, MEA is not normally used to absorb CO_2 from its high concentrated gas mixtures. This is because at high loadings of CO_2 in MEA the corrosivity of the solution increases. Thus MEA is mostly used for low pressure conditions and where a stringent requirement is applied on the exit gas concentration. Under such operating conditions, MEA does not attain very high CO_2 loadings.

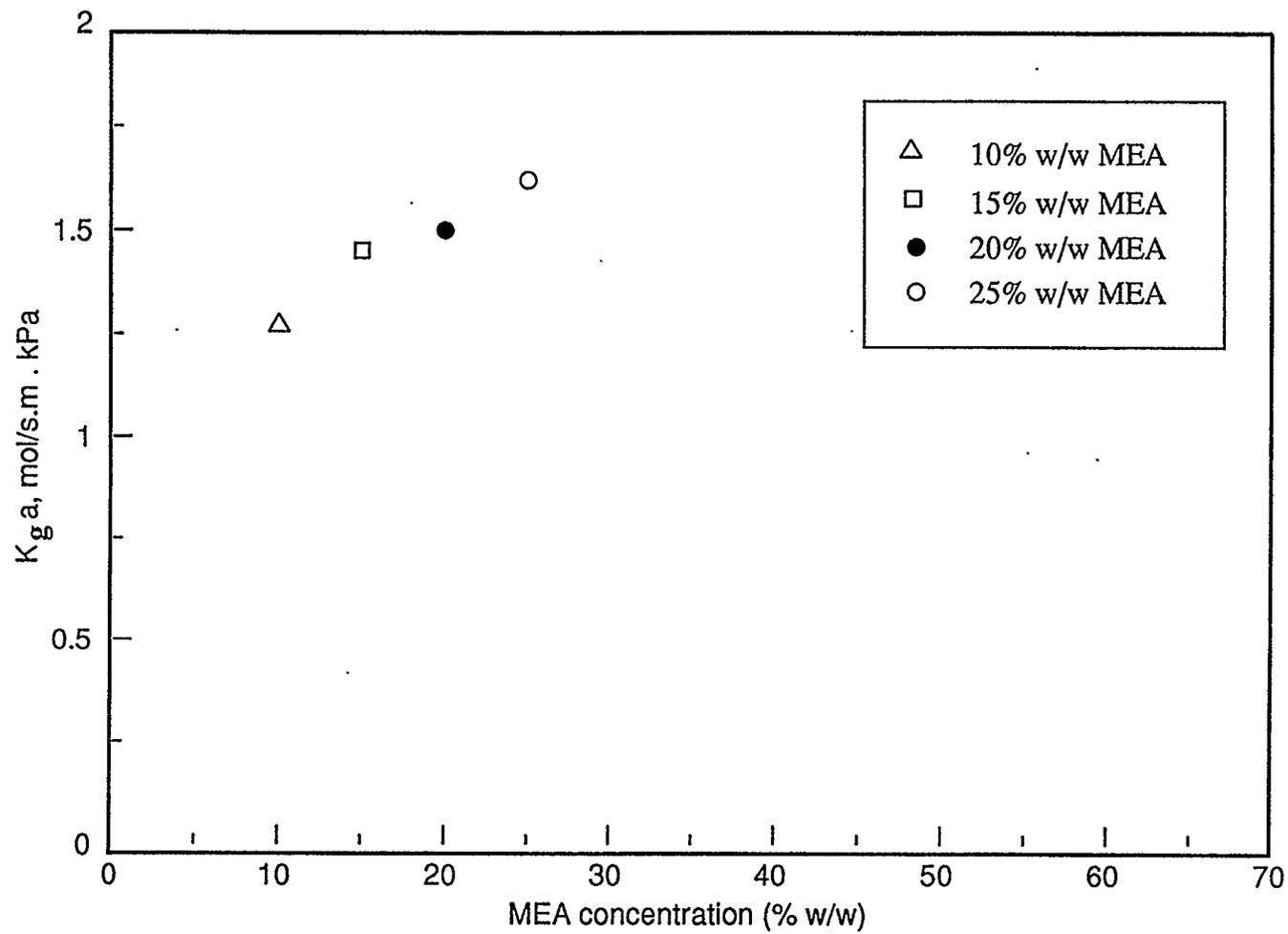


Fig. 4.4 Effect of MEA concentration on the overall gas phase mass transfer coefficient

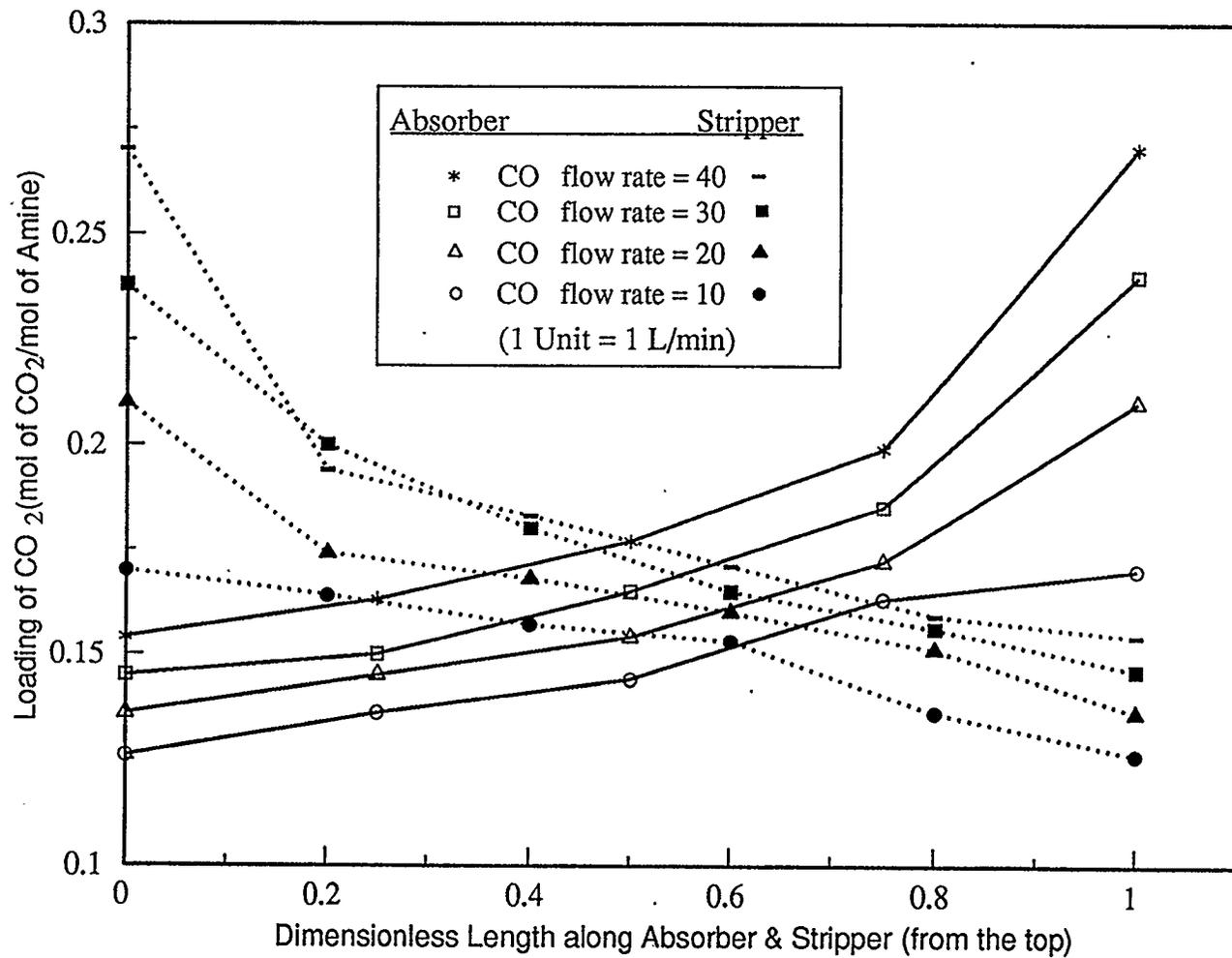


Fig. 4.5 Concentration profiles along the Absorber and Stripper for different flow rates of CO₂ (Solvent MEA)

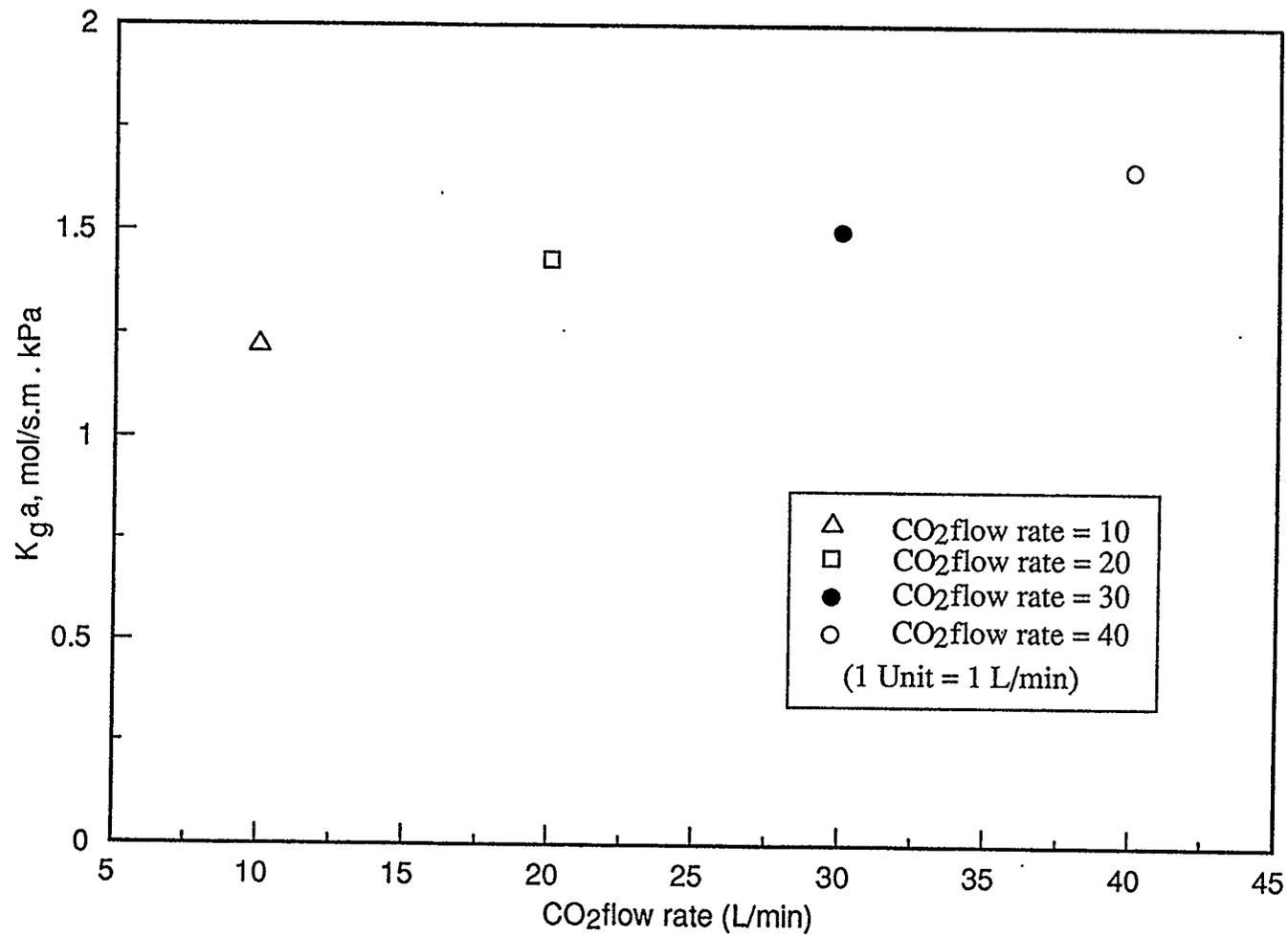


Fig. 4.6 Effect of CO₂ flow rate on the overall gas phase mass transfer coefficient for MEA (20% w/w)

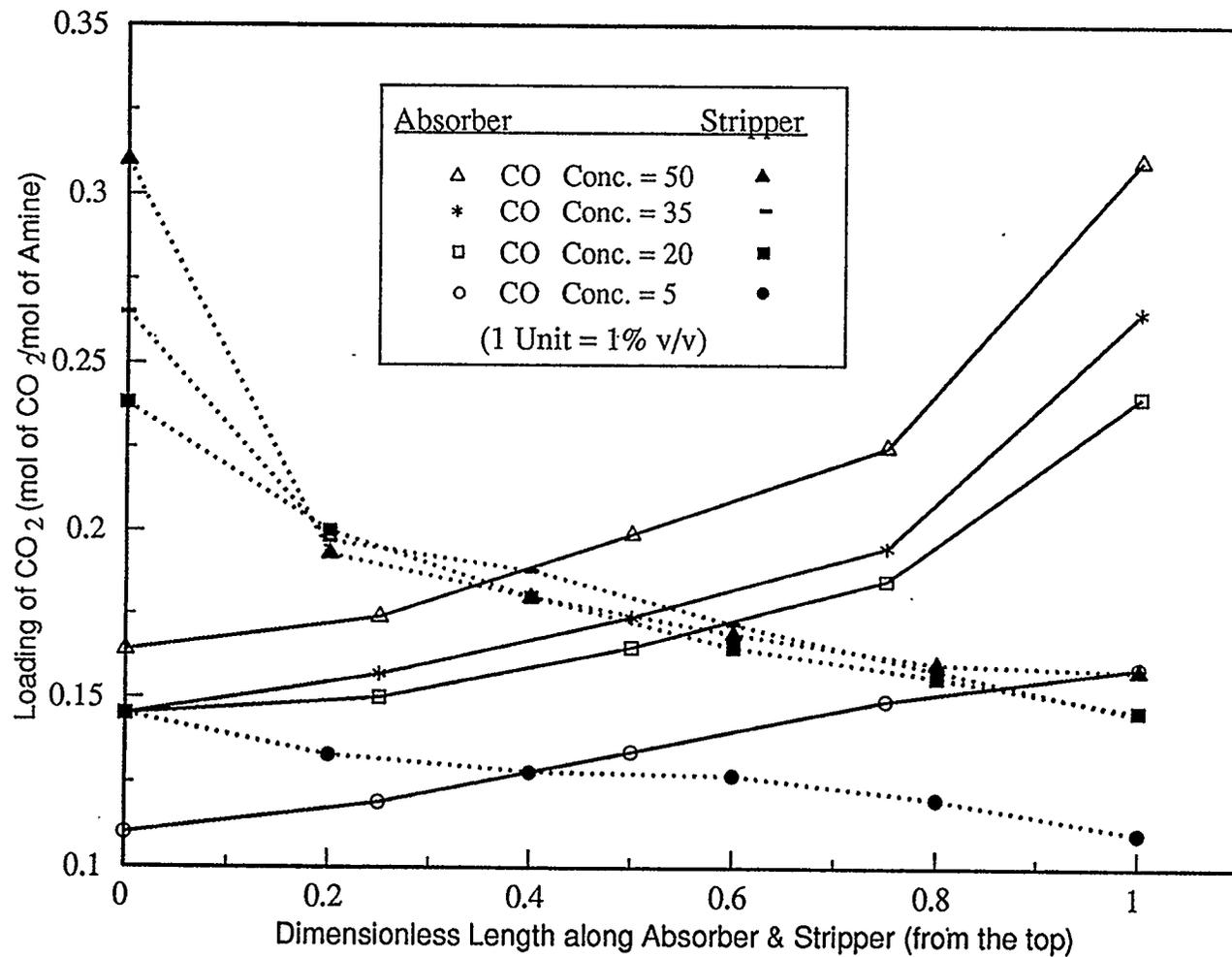


Fig. 4.7 Concentration profiles along the Absorber and Stripper for different concentrations of CO₂ (Solvent MEA)

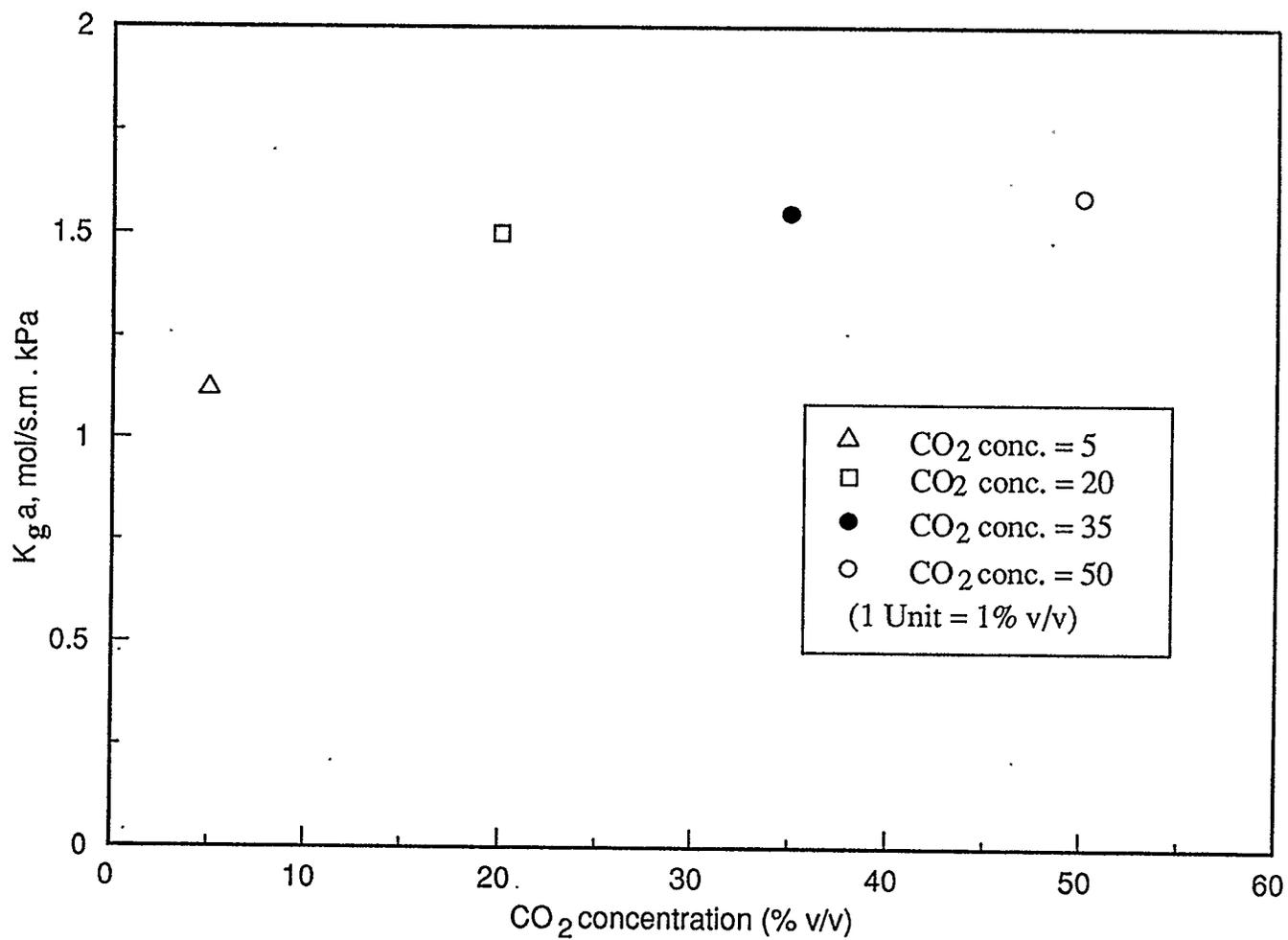


Fig. 4.8 Effect of CO₂ concentration on the overall gas phase mass transfer coefficient for MEA (20% w/w)

Increasing steam consumption rates improved the stripping process which is reflected by the decreasing CO₂ loadings in the exit solution from the stripper. The solution leaving the absorber, however, had almost similar CO₂ loadings (Fig. 4.9). When solution loadings are typically high near the top of the stripping column and low at the bottom, it is quite probable that the controlling resistance shifts from being liquid-side at the top to gas-side at the bottom (Weiland et al., 1982). Thus an increase in the boil up rate, for example, will improve column performance near the base but has little or no positive effect on stripping in the rest of the column so that the net effect of increased vapour rates can be disappointing in view of the additional costs involved. As can be seen from the temperature data (Table A.4, Appendix) the temperature of the solvent circulating in the system increased at higher steam consumption values. As a result, the lean amine entering the absorber was at a higher temperature at higher steam rates. Therefore, despite the fact that an increased driving force for transfer of CO₂ in this solution was present (due its lower CO₂ loading values), the high temperature reduced the extent of reaction.

4.3 Effect of Process Variables (Solvent MDEA)

This section describes the behaviour of the system while using MDEA as the solvent. The concentration profiles along the dimensionless length of the absorber and stripper (measured from the top of the columns), expressed as loading of CO₂ (moles of CO₂/moles of amine) as well as overall gas phase mass-transfer coefficients for are

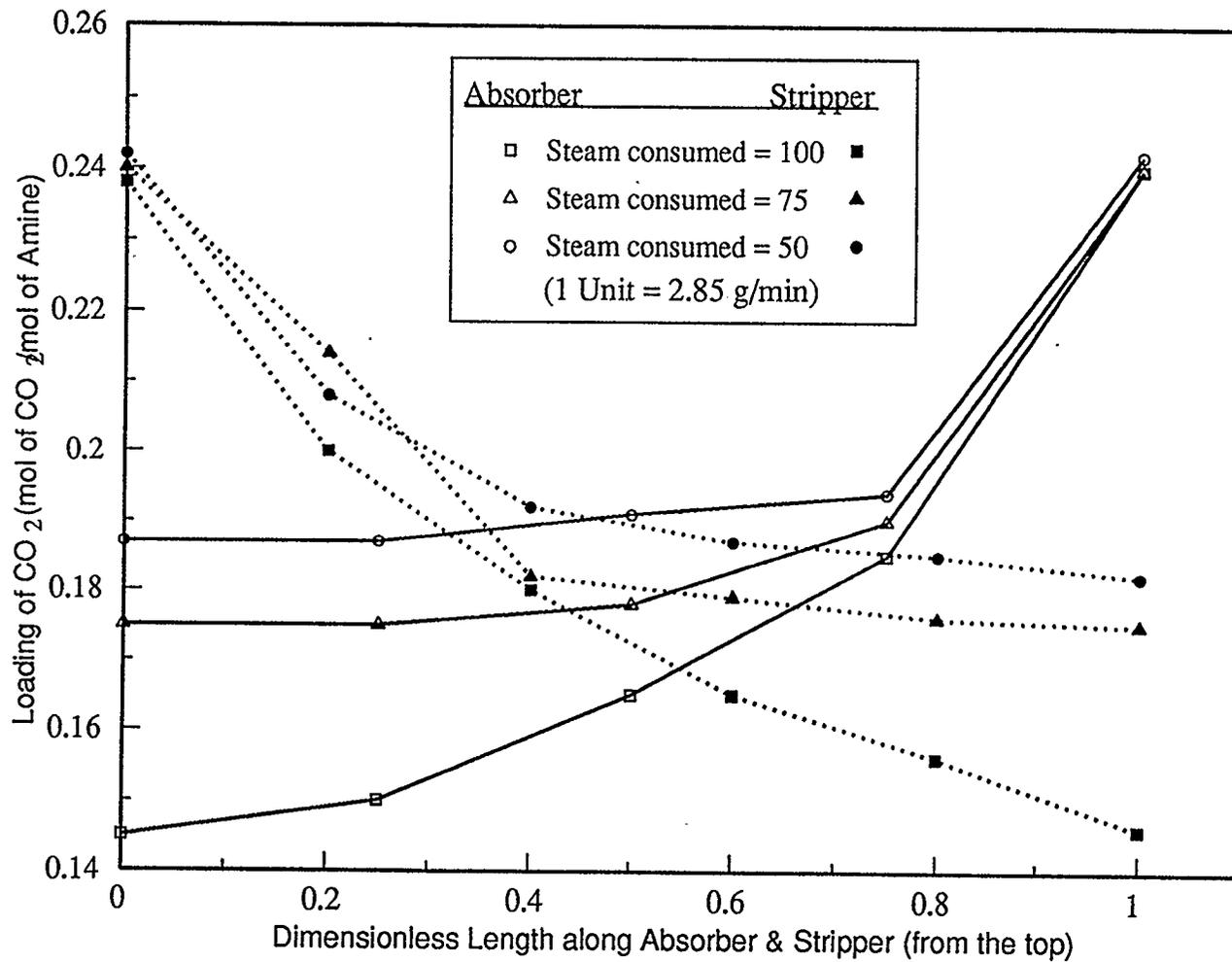


Fig. 4.9 Concentration profiles along the Absorber and Stripper for different steam consumption rates (Solvent MEA)

plotted for one process parameter changing at a time.

Fig. 4.10 shows the loading values along the absorber and the stripper for varying flow rates of MDEA (19.2 kg/h, 25.6 kg/h, 38.4 kg/h and 51.2 kg/h). The highest loadings at every point along the absorber were obtained at a flow rate of 38.4 kg/h. Decreasing flow rate of amines decreases the availability of unreacted MDEA molecules in the immediate vicinity of CO₂ molecules. Therefore, the rate of reaction, due to decreased availability of one of the reactants, is reduced. Initially, increasing the liquid flow rate resulting in increased interfacial area for mass transfer dominates the absorption mechanism, but later on the kinetic effects take over. At very high flow rates of the solvent, the residence time in the absorber for the solvent decreases. MDEA requires high contact time with CO₂ to react with it as a result of its slow reaction with CO₂. Thus, MDEA does not pick up as much CO₂. This explains the decreased loading values obtained at 51.2 kg/h as compared to that at 38.4 kg/h. Further, in the stripper the higher flow rate of amine (above 38.4 kg/h) causes lesser overall stripping since the solution cools down faster. This is because for the same heat supplied to the reboiler, more solvent volume per unit time has to be heated. Overall gas phase mass-transfer coefficient for varying concentrations of MDEA have been plotted in Fig. 4.11. These mass-transfer coefficients increase initially upto an amine flow rate of 38.4 kg/h but decrease with further increase in the flow rate. The effect of amine concentration is observed in Fig. 4.12 where the MDEA concentration is varied between 30, 40, 50 and 60% w/w and the corresponding overall gas phase mass-transfer coefficients have been

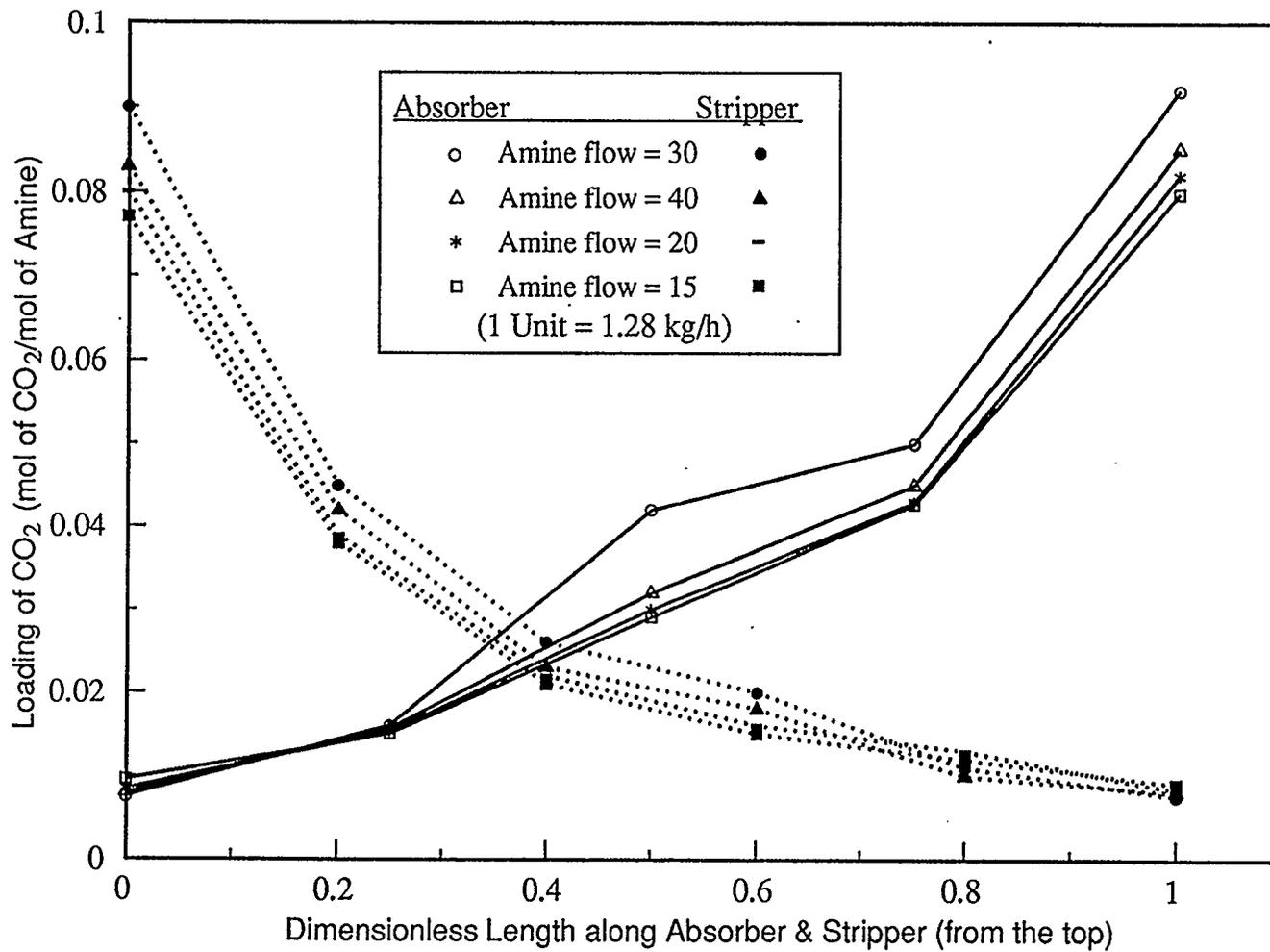


Fig. 4.10 Concentration profiles along the Absorber and Stripper for different flow rates of MDEA

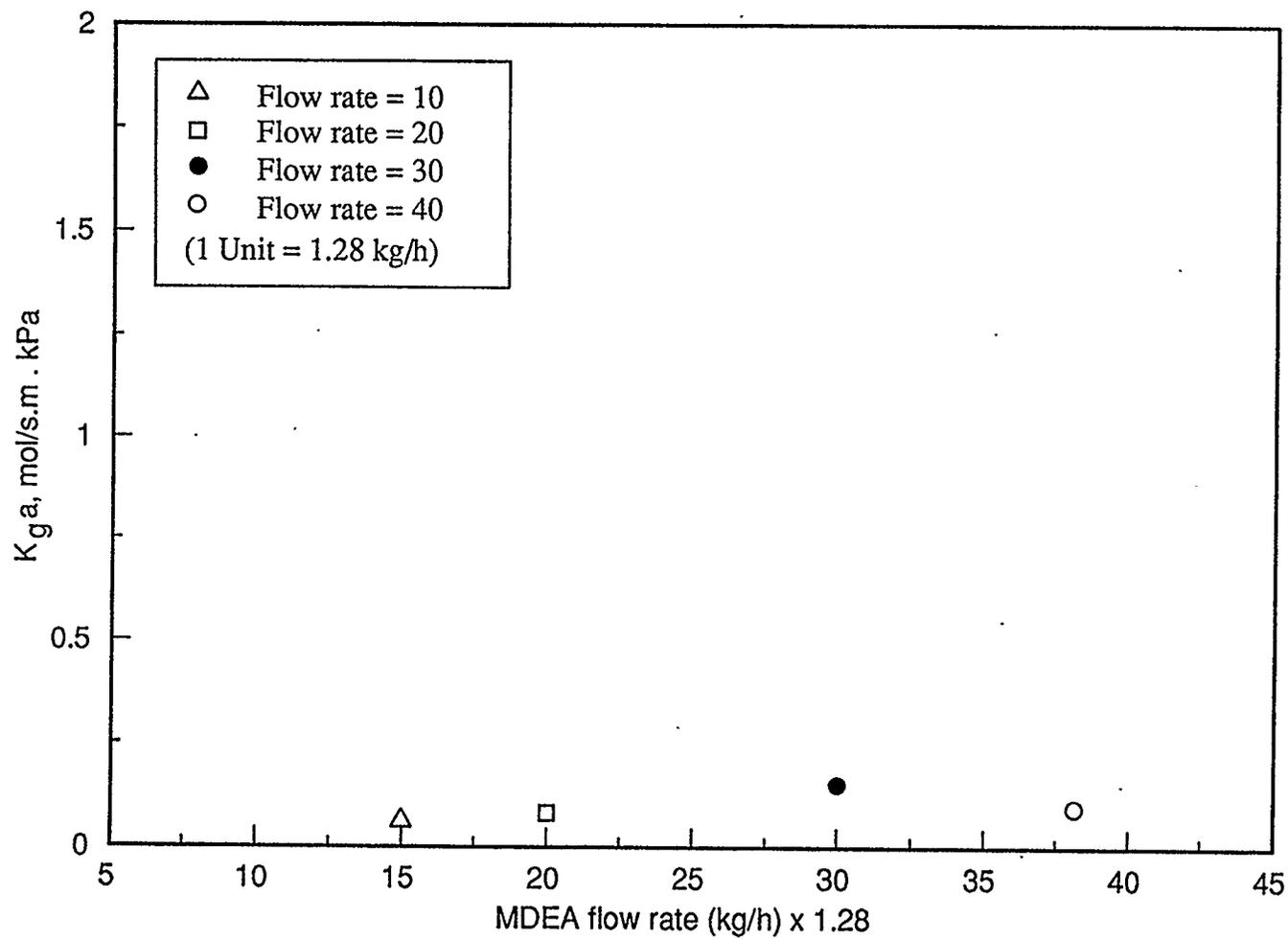


Fig. 4.11 Effect of MDEA (50% w/w) flow rate on the overall gas phase mass transfer coefficient

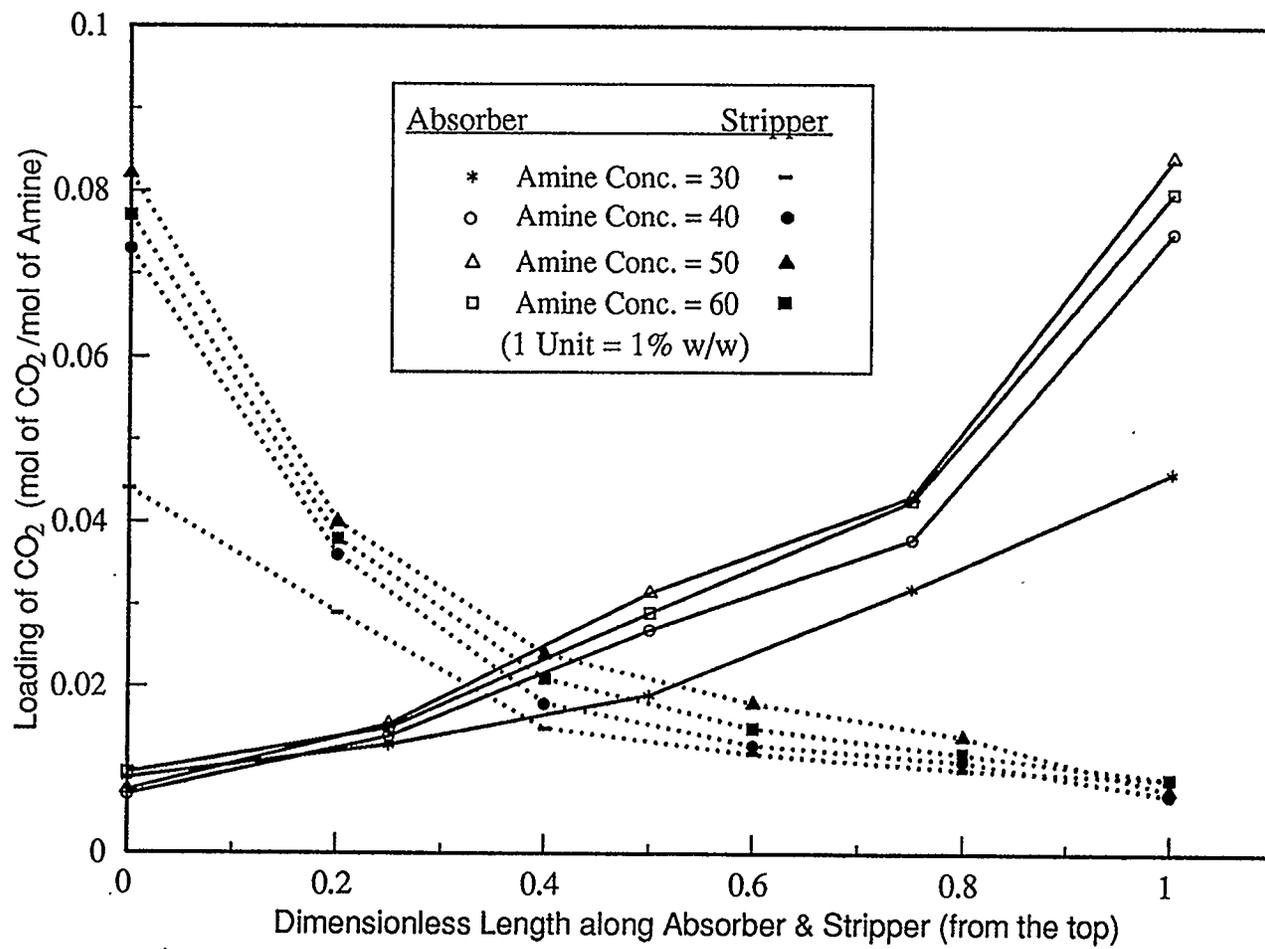


Fig. 4.12 Concentration profiles along the Absorber and Stripper for different concentrations of MDEA

plotted in Fig. 4.13. A normal expectation would be to get higher loadings at increasing strengths of the amine. This expectation is validated up to MDEA concentrations of 50% w/w. At higher MDEA concentration (60% w/w) the loading values are seen to drop. This is because the large increase in the viscosity of the solvent hinders the rate of mass transfer due to reduced rate of diffusion of CO₂ into the solvent. The increase in viscosity with increasing concentration of amine at a lower concentration range, however, is compensated by the increased availability of amine to react with CO₂.

When the flow rate of CO₂ is varied as shown in Fig. 4.14, loading values in general increase with CO₂ flow rate. Interestingly enough, at the highest flow = 40 L/min, the loading value of the solution exiting the absorber was lesser than at a flow rate of 30 L/min. However, it can be seen that the loading value was higher at a flow rate of 40 L/min in the upper section of the absorber. This is probably because most of the absorption in an absorption column takes place at the bottom. But due to the high flow rate at 40 L/min, sufficient contact time with the solvent was not possible. Thus the gas rising above to a higher stage had a higher partial pressure of CO₂ resulting in increased absorption there. Another reason is that the loading of the solution affects the absorption rates in the later section of the column. When a solution at higher loadings of CO₂ reaches the bottom, the gradient for mass transfer is lesser and thus the rate of mass transfer decreases. Overall mass-transfer coefficients initially increased but stopped increasing at very high flow rates (\cong 40 L/min) as can be seen in Fig. 4.15.

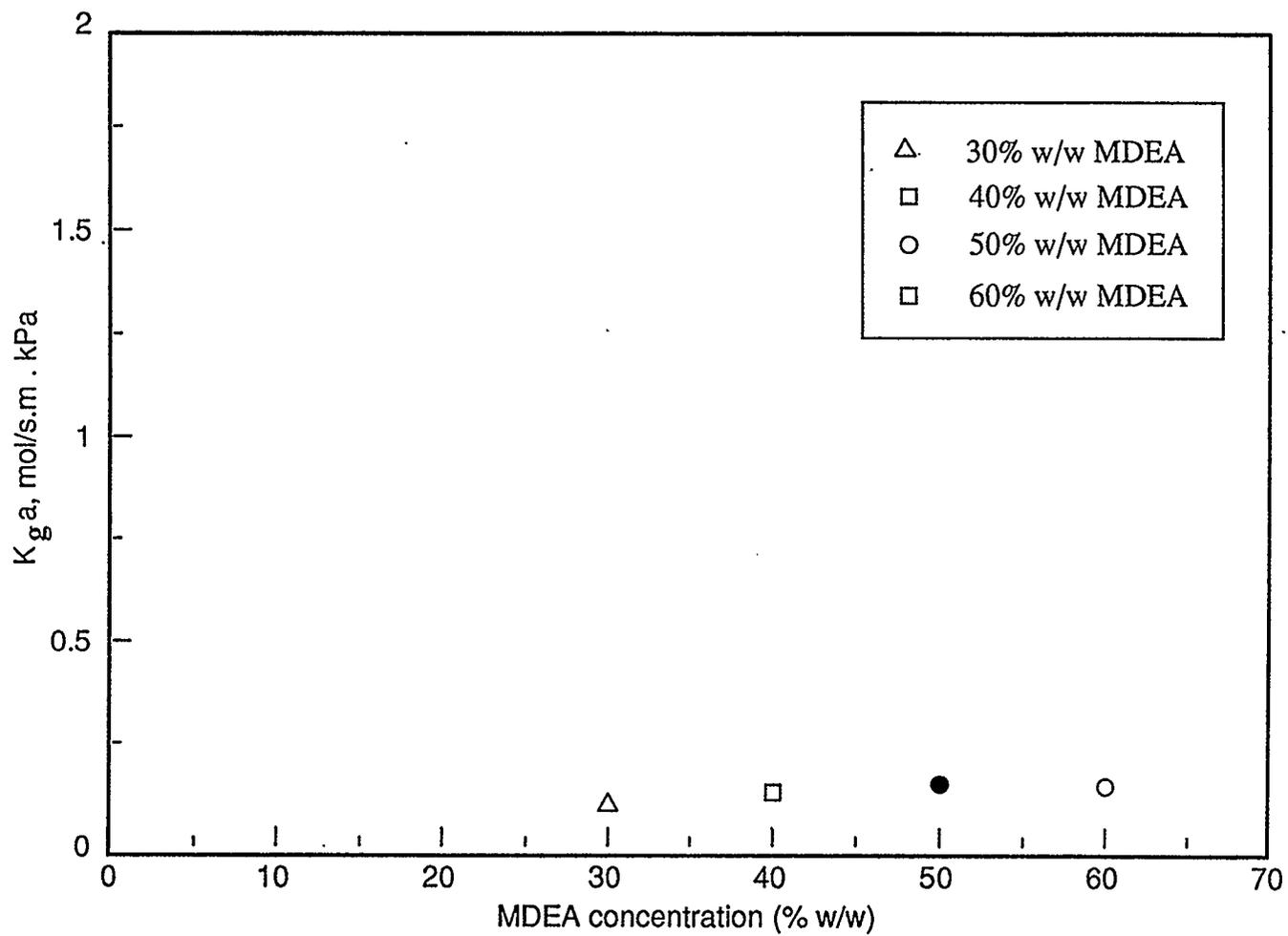


Fig. 4.13 Effect of MDEA concentration on the overall gas phase mass transfer coefficient

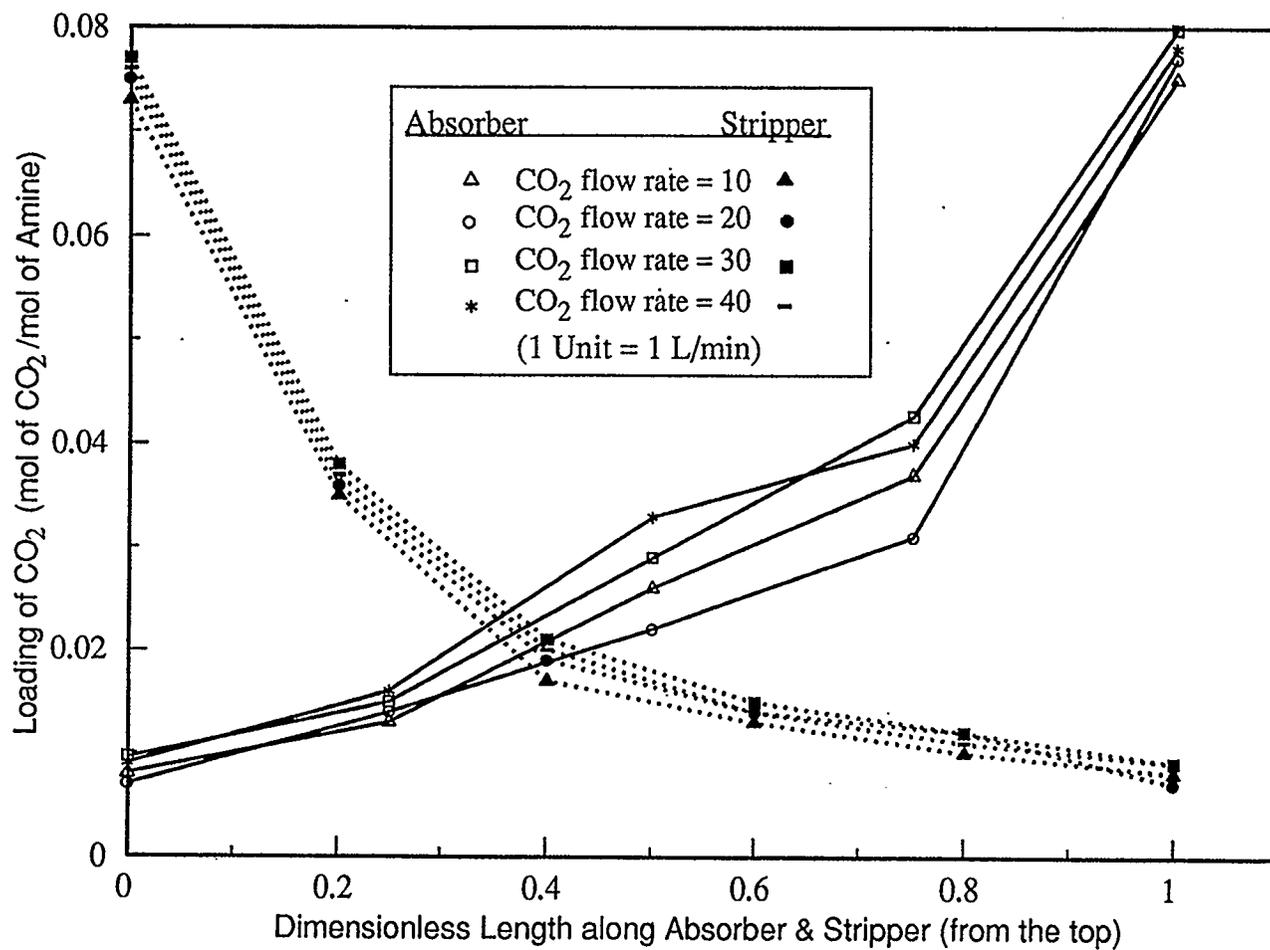


Fig. 4.14 Concentration profiles along the Absorber and Stripper for different flow rates of CO₂ (Solvent MDEA)

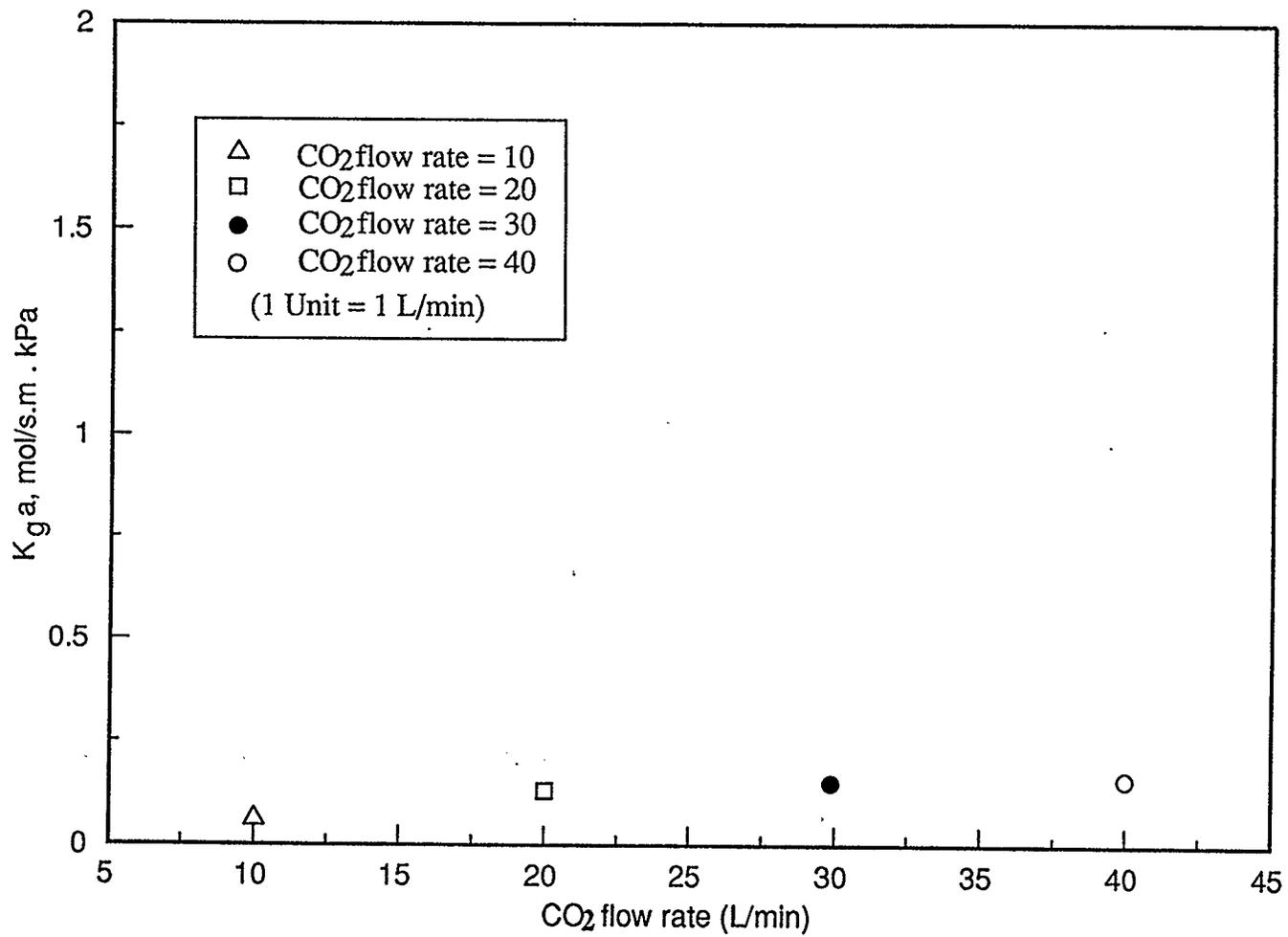


Fig. 4.15 Effect of CO₂ flow rate on the overall gas phase mass transfer coefficient for MDEA (50% w/w)

Fig. 4.16 shows the variation in loading values for different concentrations of CO_2 in the gas mixture. A higher concentration of CO_2 in general causes increased absorption of CO_2 due to an increase in the concentration gradient of CO_2 between the gas phase and the liquid phase. A particularly high loading value was obtained for a CO_2 concentration of 50% v/v. The mass transfer coefficient increased with increasing CO_2 concentrations too (Fig. 4.17).

The effect of steam consumption rates was studied at the base condition parameters for the MDEA system (Fig. 4.18). The stripping values obtained at steam consumption rates of 285 g/min and 142.5 g/min were in accordance with amount of steam consumed. The spread in loading values at the bottom of the stripper for solutions entering the stripper at similar loadings of CO_2 can be explained on the grounds that at higher steam consumption rates, the solvent circulating in the system attained a higher temperature. Measurement of temperatures confirmed this assertion (Table A.4, Appendix). The exit solution from the absorber reached almost the same loading value despite the fact that solutions entering it had different loadings. The solution entering the absorber at a higher temperature should be expected to absorb lesser CO_2 but since it entered the absorber at a lower loading of CO_2 , the driving force for mass transfer was larger.

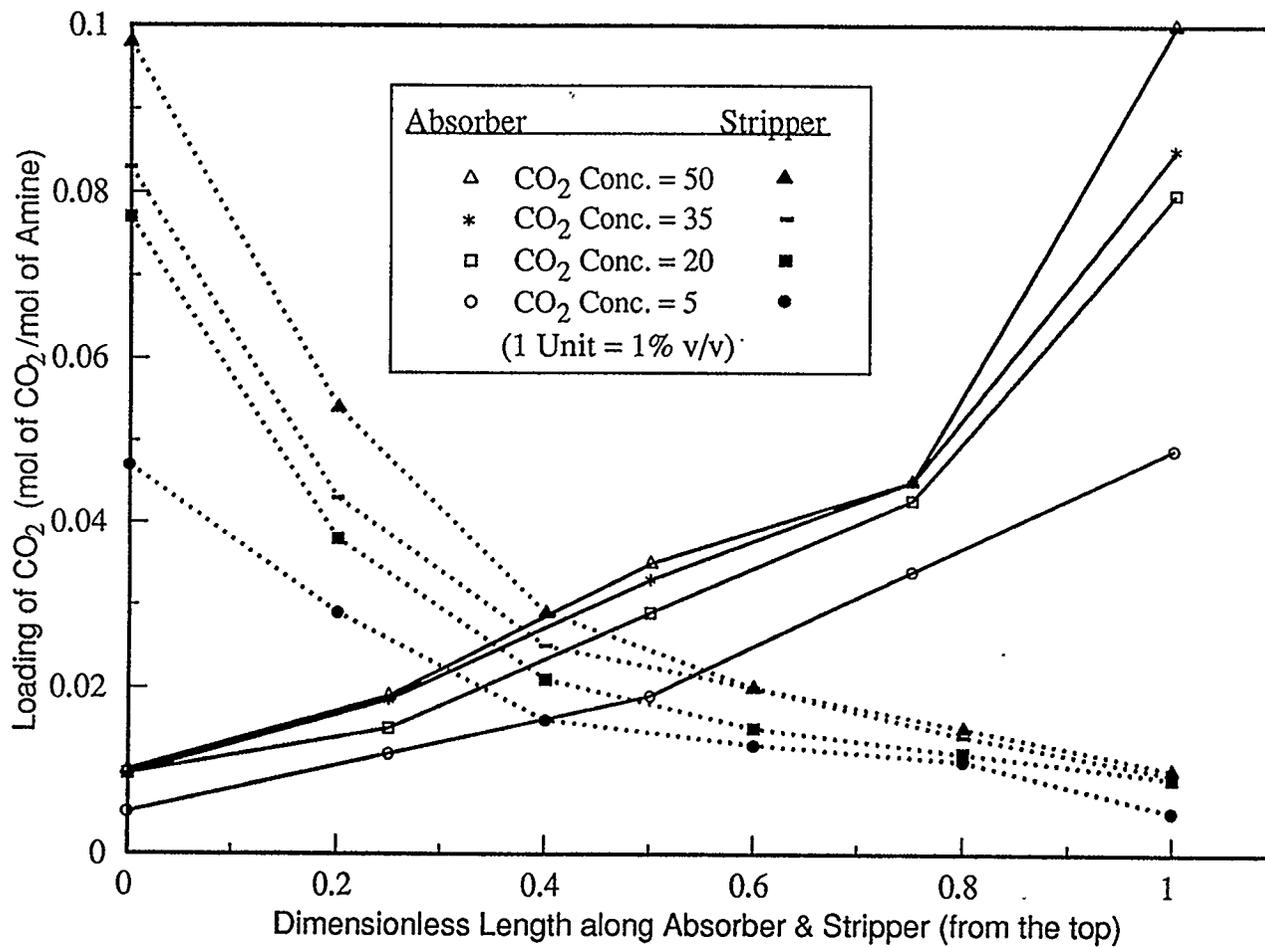


Fig. 4.16 Concentration profiles along the Absorber and Stripper for different concentrations of CO₂

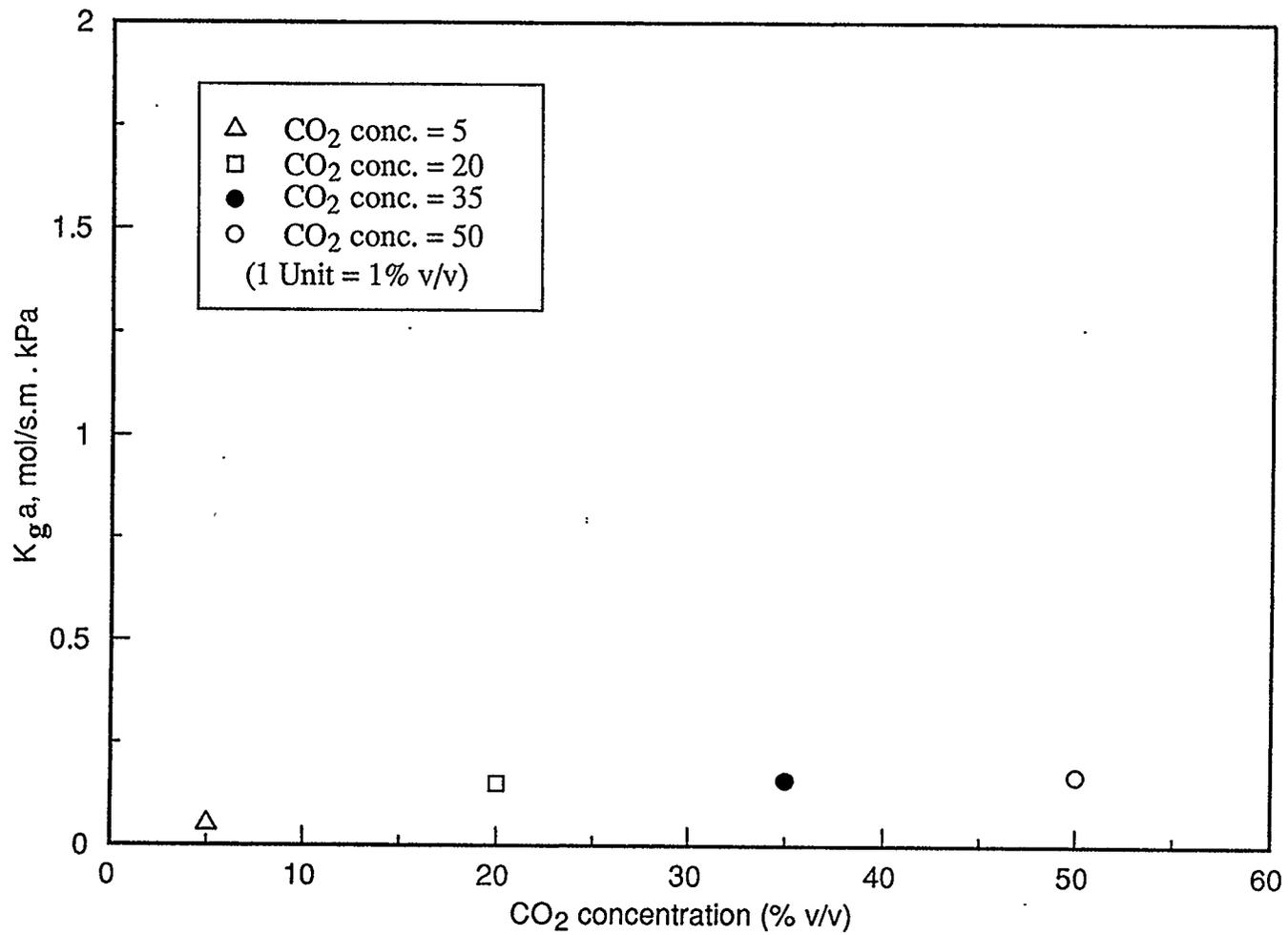


Fig. 4.17 Effect of CO₂ concentration on the overall gas phase mass transfer coefficient for MDEA (50% w/w)

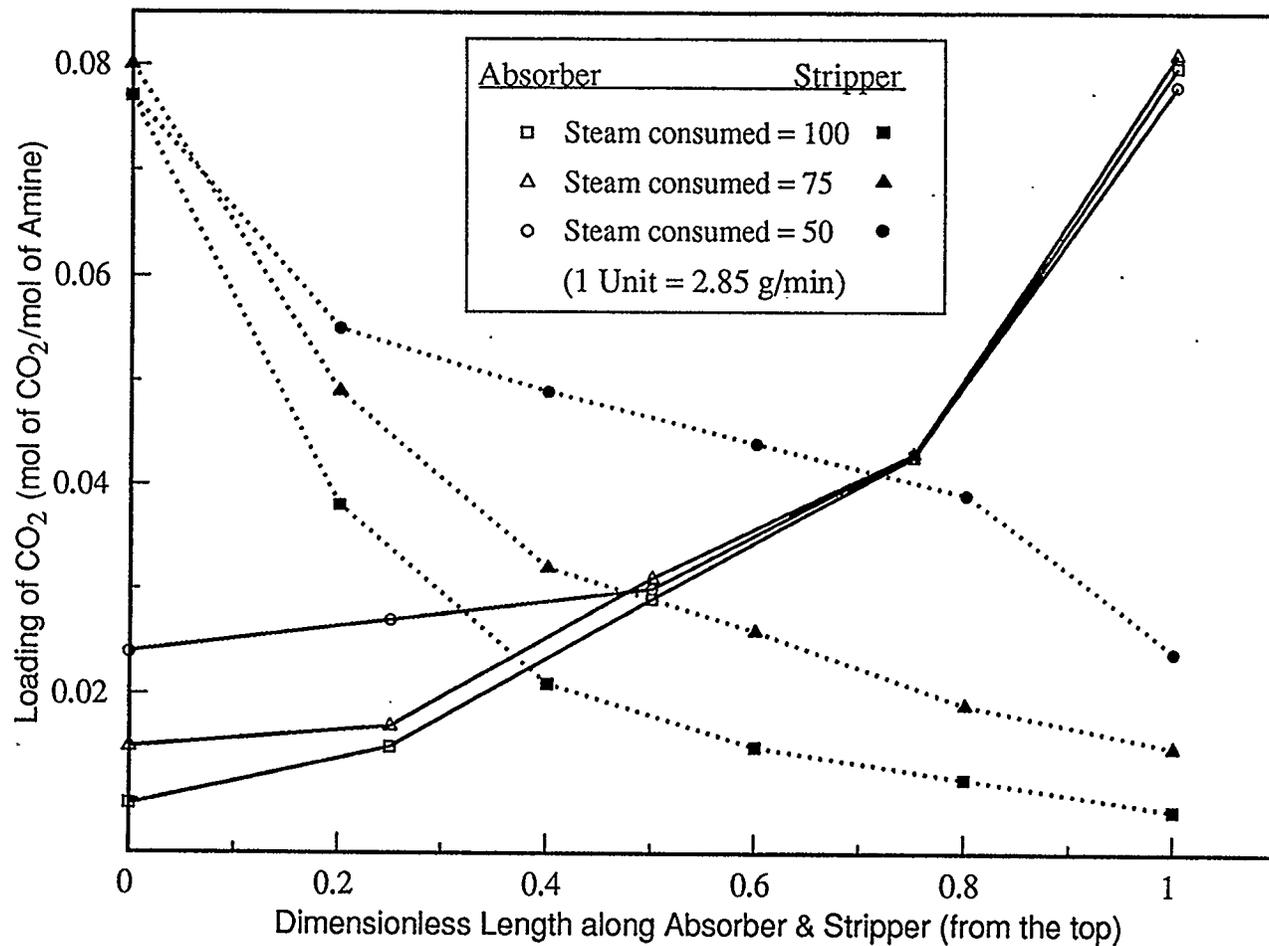


Fig. 4.18 Concentration profiles along the Absorber and Stripper for different steam consumption rates (Solvent MDEA)

4.4 Effect of Process Variables (Mixed Amine System)

All the runs using mixed amines (MEA + MDEA) gave very high solution loadings as compared to MDEA runs. The loading values all along the column increased with increasing concentration of MEA in the blend, when the total amine concentration was kept constant (Fig 4.19). Fig. 4.20 is plot of the parameter 'P' for various blends of amine. As discussed in section 4.1 a higher value of parameter 'P' means that the solvent has better absorption characteristics as well as superior stripping qualities. According to this criteria, the best stripping results combined with absorption characteristics was obtained in the case of a blend formulation of 45% w/w MDEA + 5% w/w MEA (Fig. 4.20). Fig. 4.21 shows the loading values for differing flow rates of a 5% w/w MEA + 45% w/w MDEA blend. The profiles were similar to that of MEA but the loading values at the exit of the stripper decreased almost ten-fold to a value even lower than that reached in the case of MDEA. The overall mass-transfer coefficients were also seen to increase with increasing flow rates (Fig. 4.22). The loading profiles in the absorber also changed. Much faster reaction rates than pure MDEA could be seen which can be inferred from the steeper slopes of the loading curves. It can also be speculated that by using a blend of these two amines, MDEA picks up considerable CO₂ at the bottom of the column while MEA mostly reacts with the CO₂ exiting the absorber at the top. MEA being more reactive immediately reacts with whatever CO₂ is leaving the absorber. MDEA on the other hand receives CO₂ from MEA as it flows along to the bottom of the absorber. This speculation is based on the

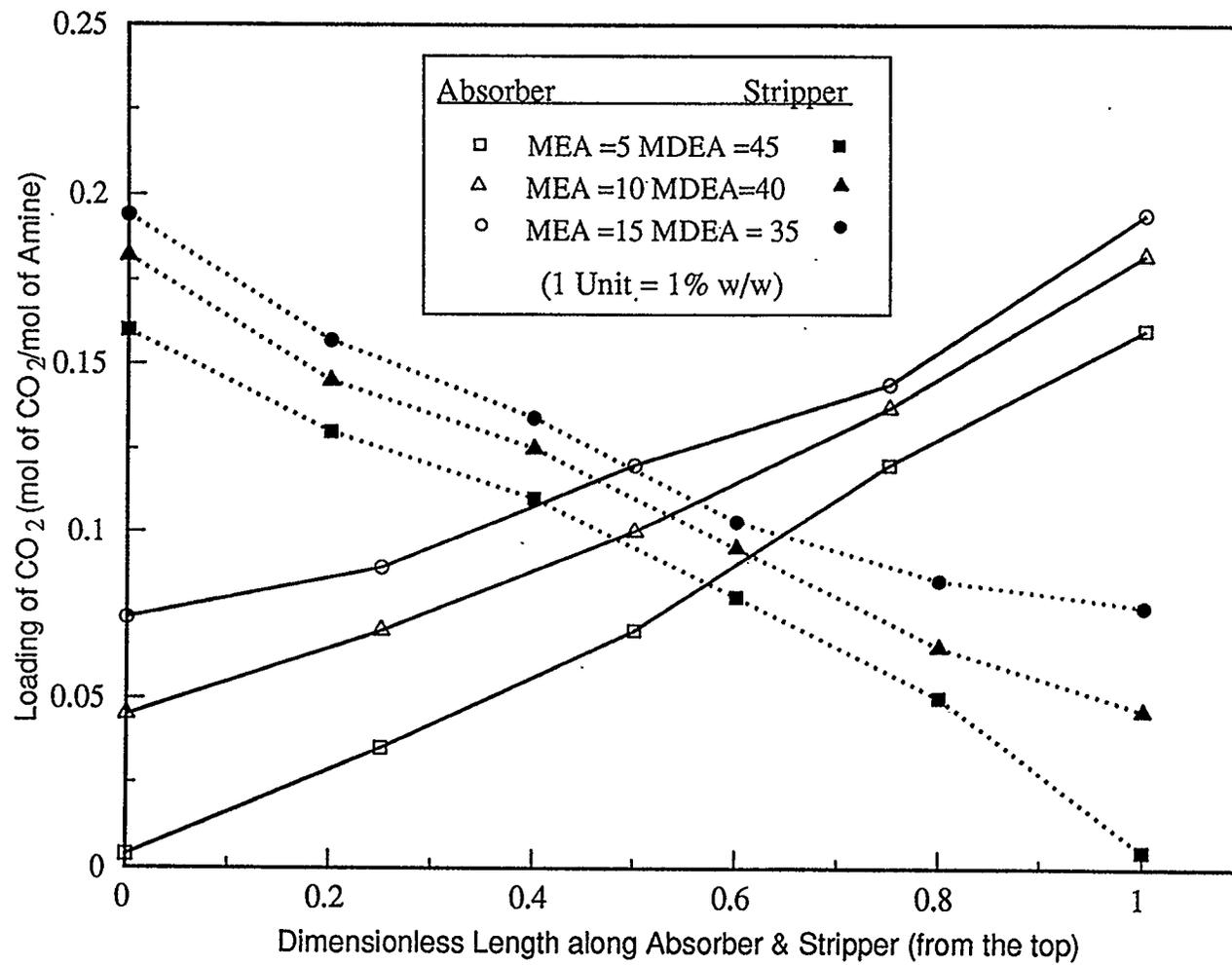


Fig. 4.19 Concentration profiles along the Absorber and Stripper for different wt % ratio of MEA and MDEA in the blend

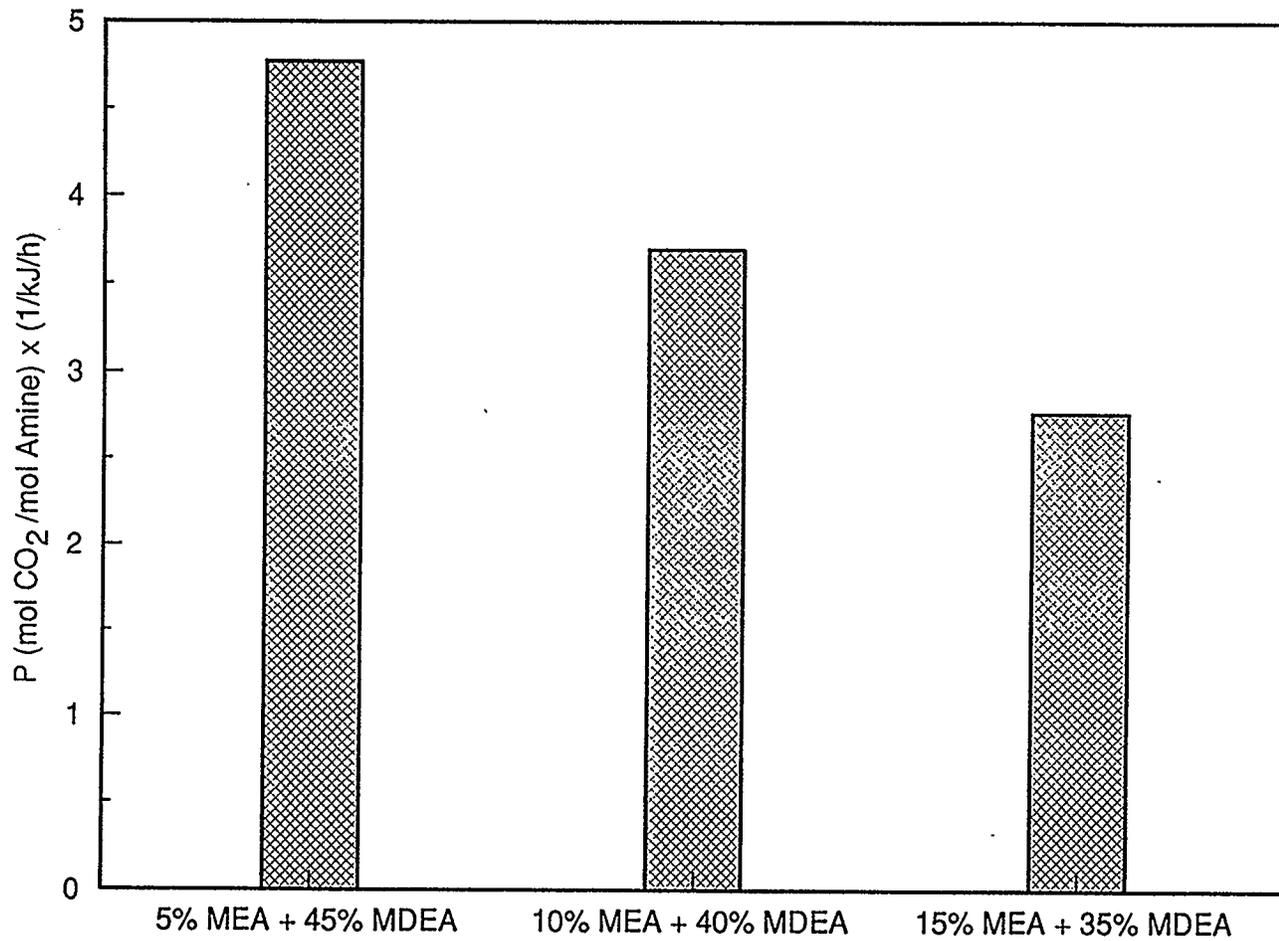


Fig. 4.20 : Effect of changing amine concentration ratio on parameter 'P' for same total concentration of amine solution

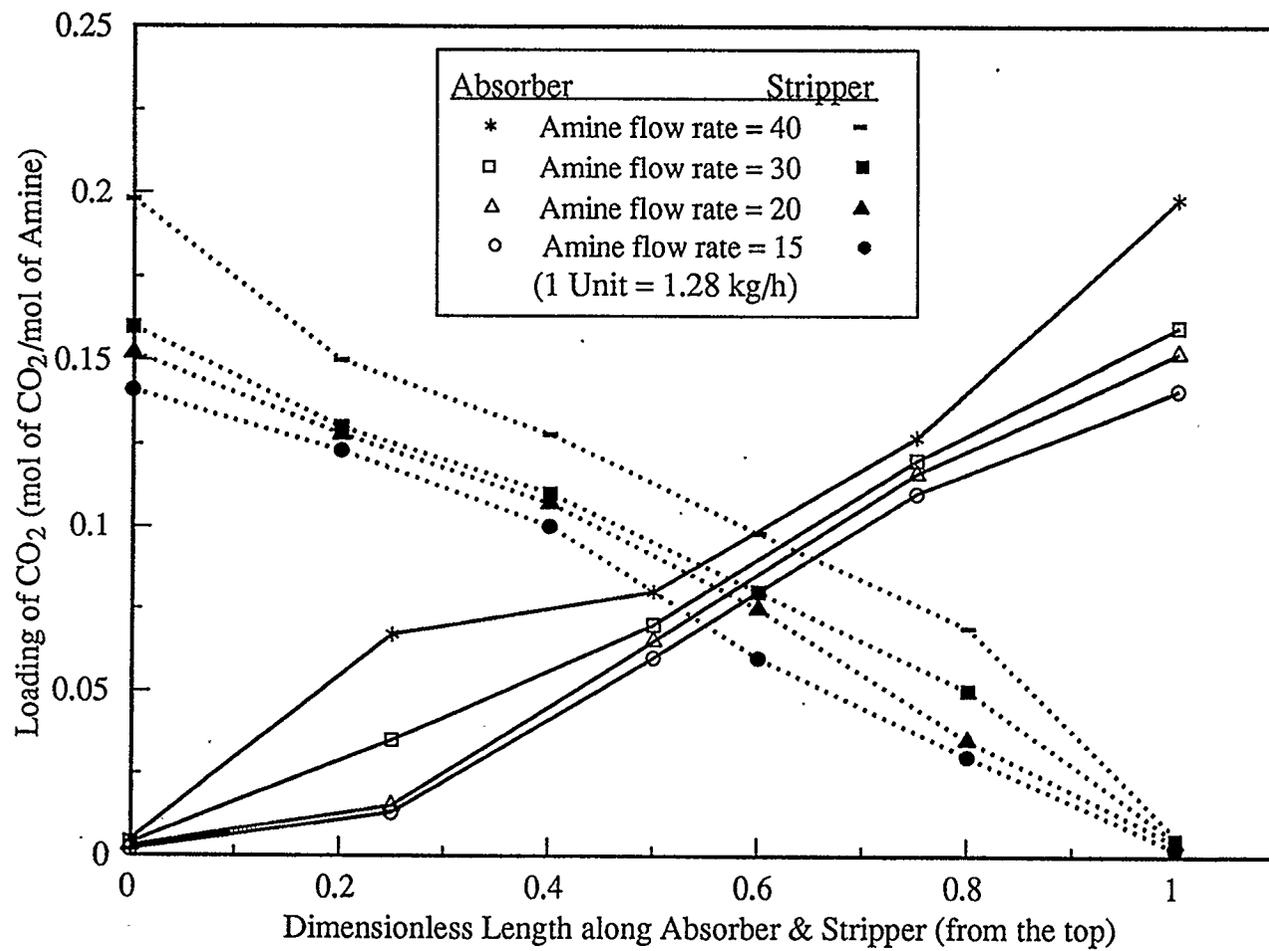


Fig. 4.21 Concentration profiles along the Absorber and Stripper for different flow rates of (5%MEA+45%MDEA) amine blend

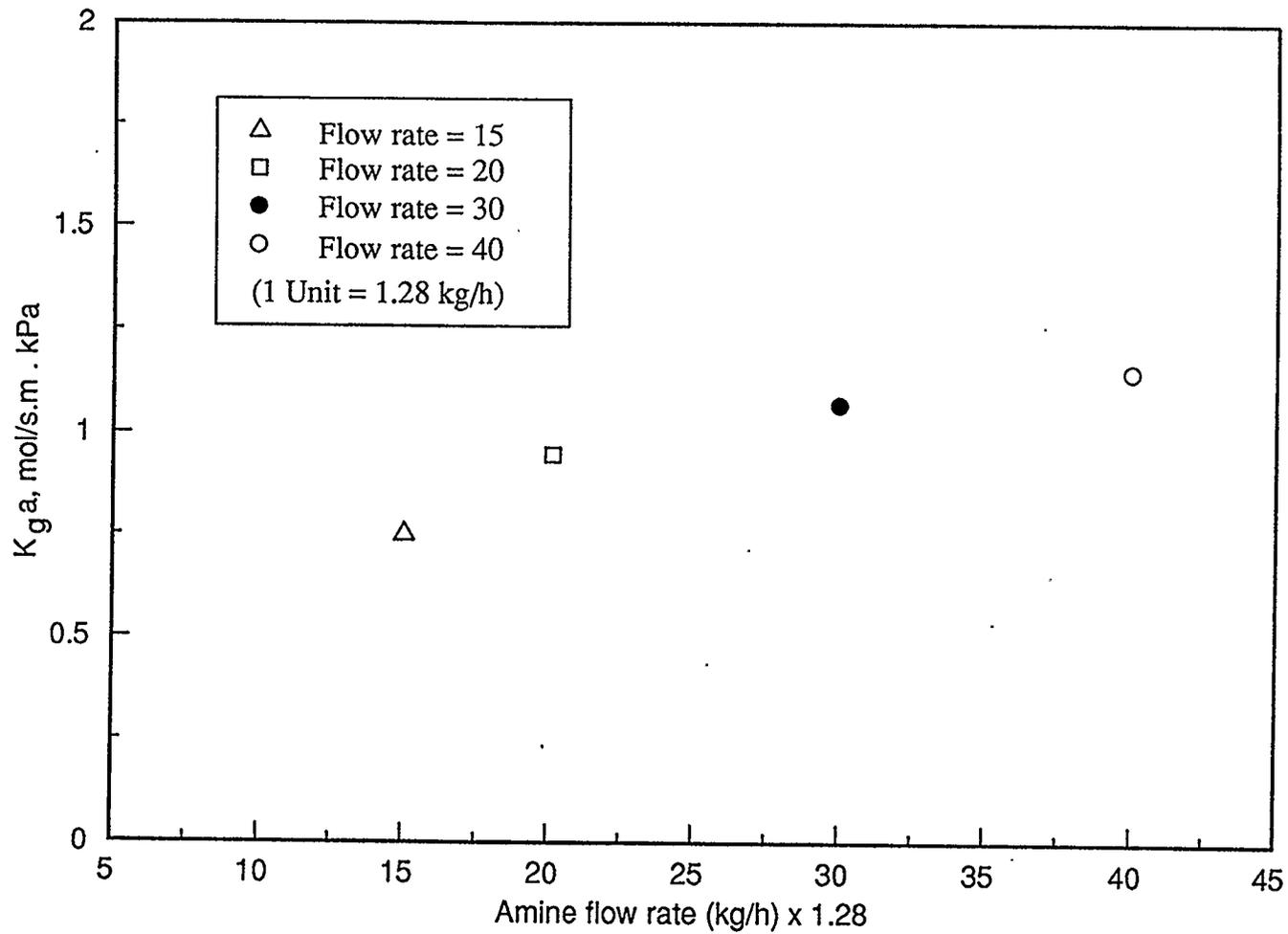


Fig. 4.22 Effect of amine flow rate on the overall gas phase mass transfer coefficient for (5% w/w MEA + 45% w/w MDEA) amine blend

'shuttle mechanism' (Astarita et al., 1981) where it is believed that MEA transports the CO_2 to MDEA in the bulk and regenerates itself for further reaction with CO_2 . Thus very low concentrations of CO_2 in the exit gas can be obtained.

When the total concentration of the amine is varied it shows better absorption characteristics in the case of the blend having higher MEA wt% (Fig. 4.23). But the use of such blends should be avoided because of the higher heat duty in the reboiler required for the stripping thereafter. When the total amine concentration was varied keeping the MEA wt% constant in the amine, the solution showed better absorption and stripping characteristics for a blend having higher wt% of MDEA. This can be inferred from the lower values of parameter 'P' for such blends (Fig. 4.24).

In the case of mixed amines, loading along the column increases upto a certain flow rate of CO_2 but later becomes either stable or decreases due to insufficient contact time for chemical reaction (Fig. 4.25). The overall mass transfer coefficient also decreases at high flow rates after increasing at lower flow rates of CO_2 (Fig. 4.26). CO_2 concentration affects loading values tremendously which can be observed for a 50% v/v CO_2 concentration where the loading value at the exit of the absorber reached a value of 0.26 (Fig. 4.27). The overall mass-transfer coefficients reach a stable value at high concentrations of CO_2 (Fig. 4.28).

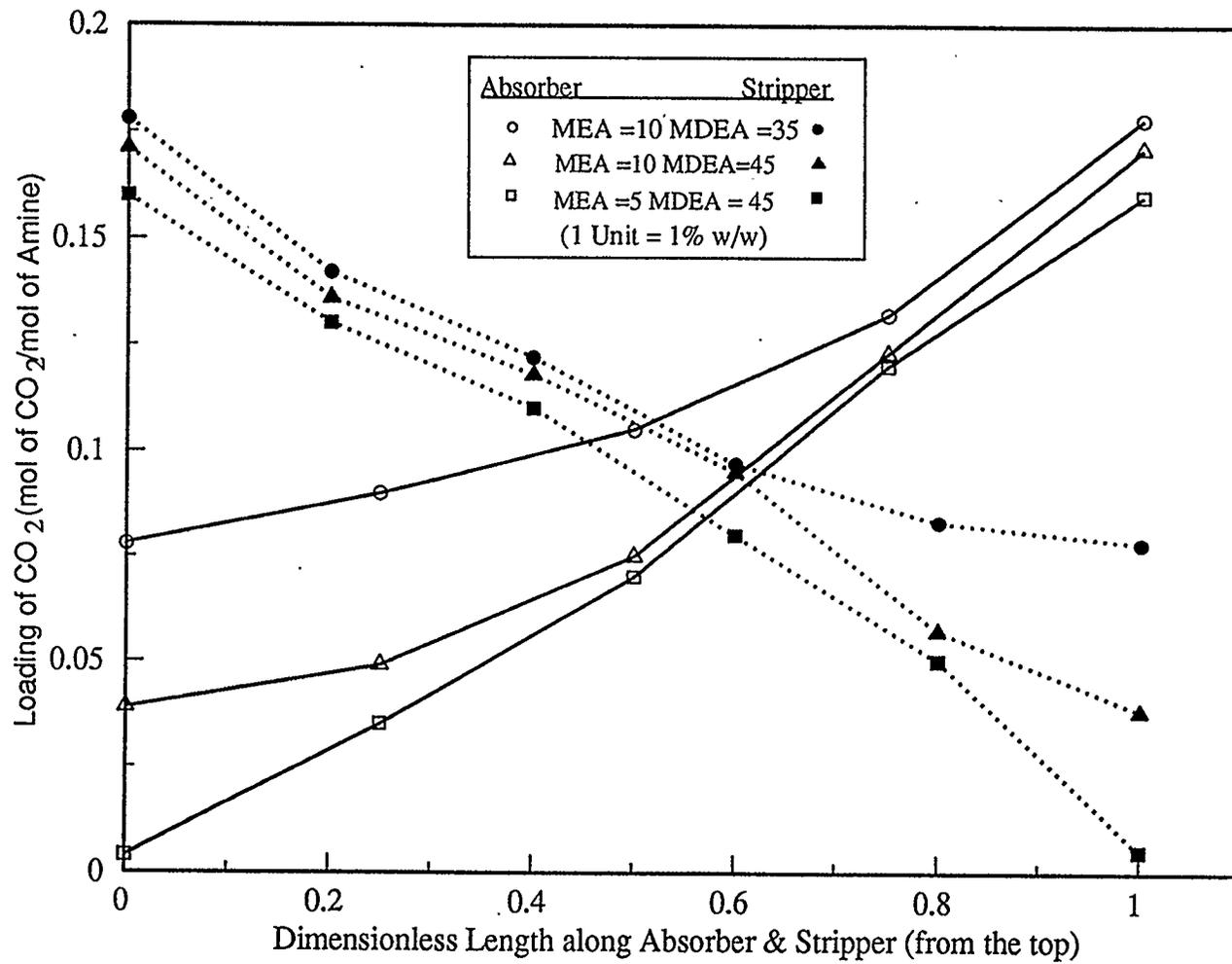


Fig. 4.23 Concentration profiles along the Absorber and Stripper for different wt% ratio of MEA and MDEA as well as varying total amine conc.

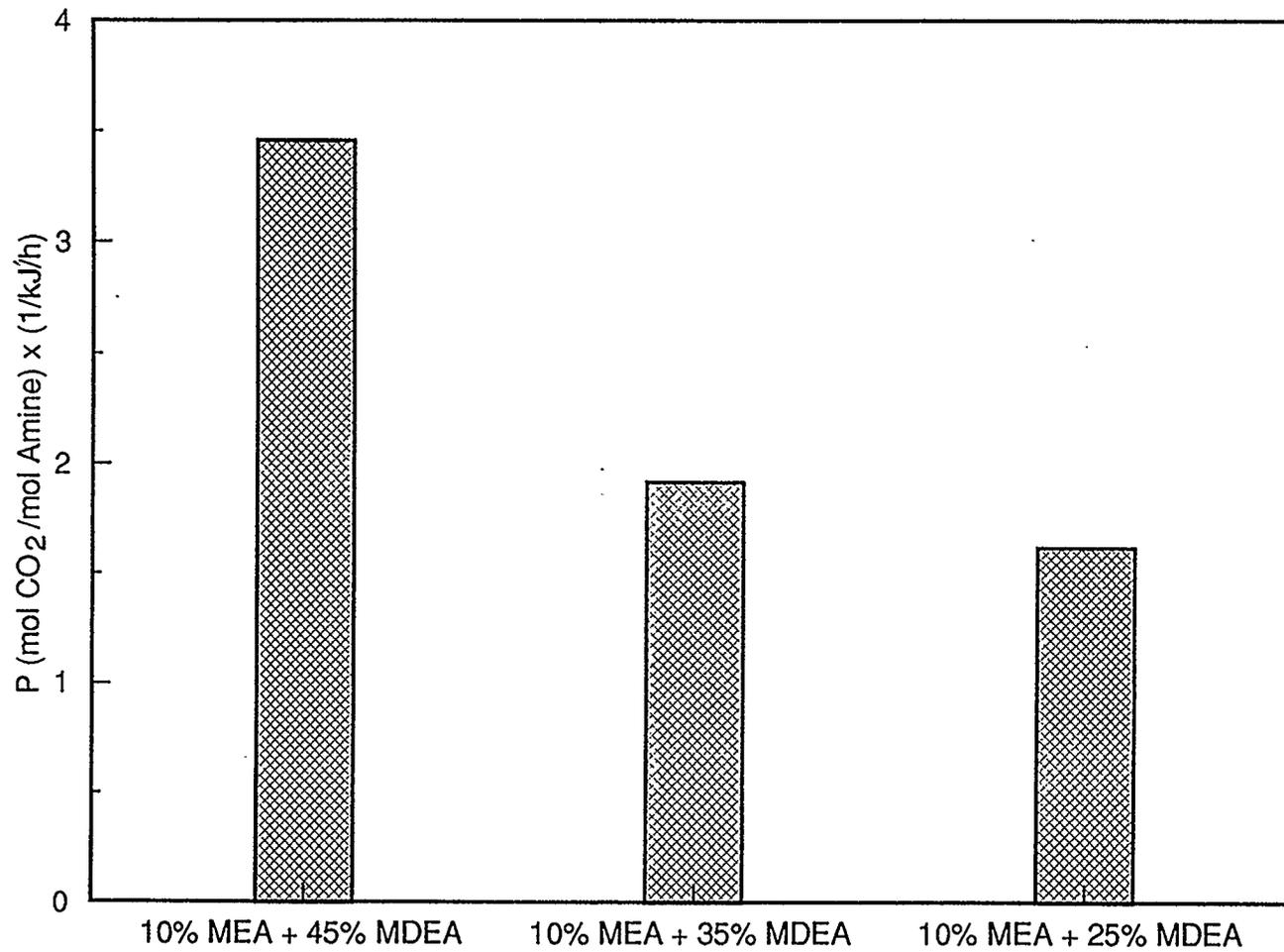


Fig. 4.24 : Effect of changing total amine concentration on parameter 'P' for changing MDEA concentration ratio in the amine solution

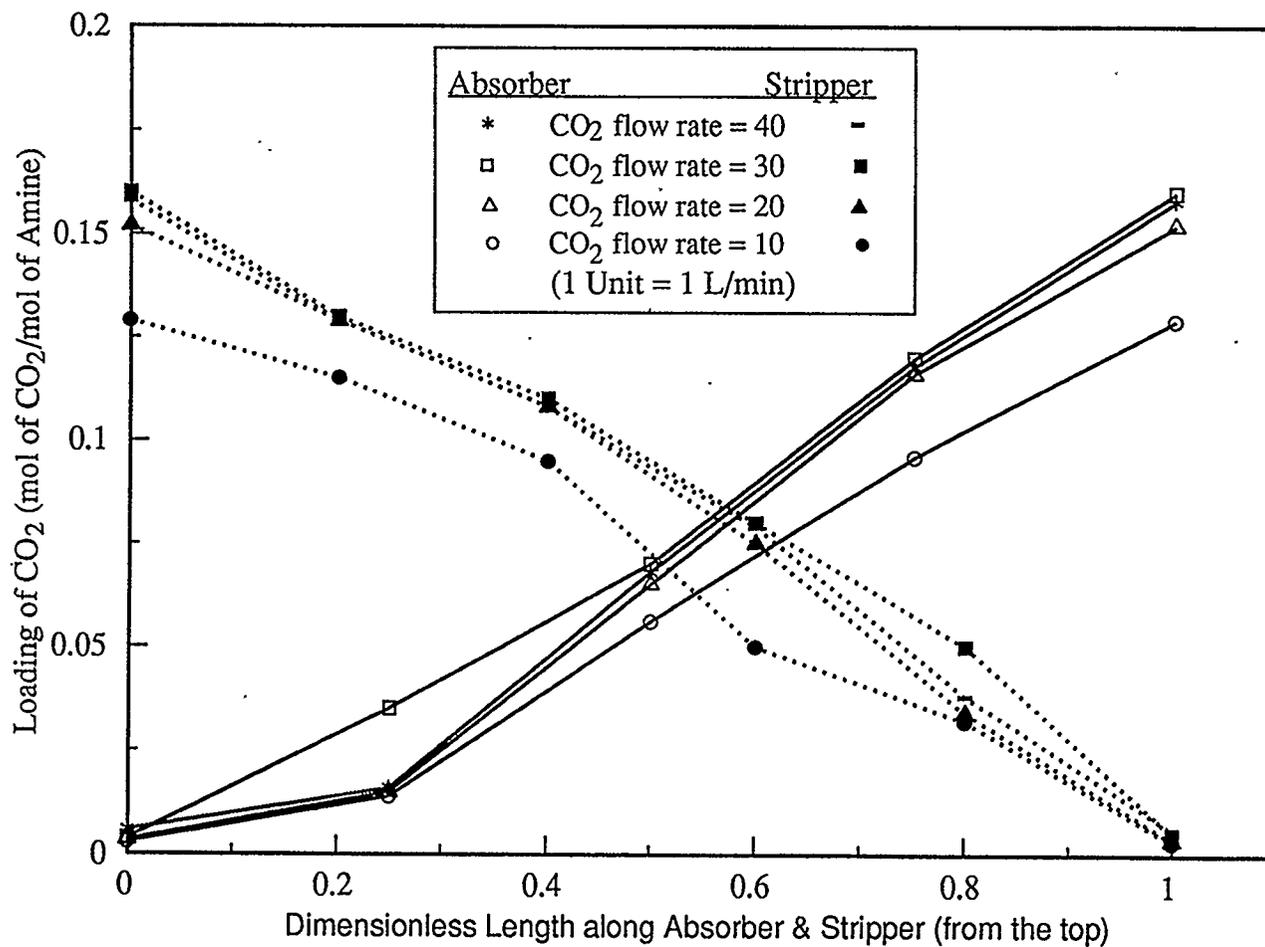


Fig. 4.25 Concentration profiles along the Absorber and Stripper for different flow rates of CO₂ (Solvent = 5% MEA + 45% MDEA)

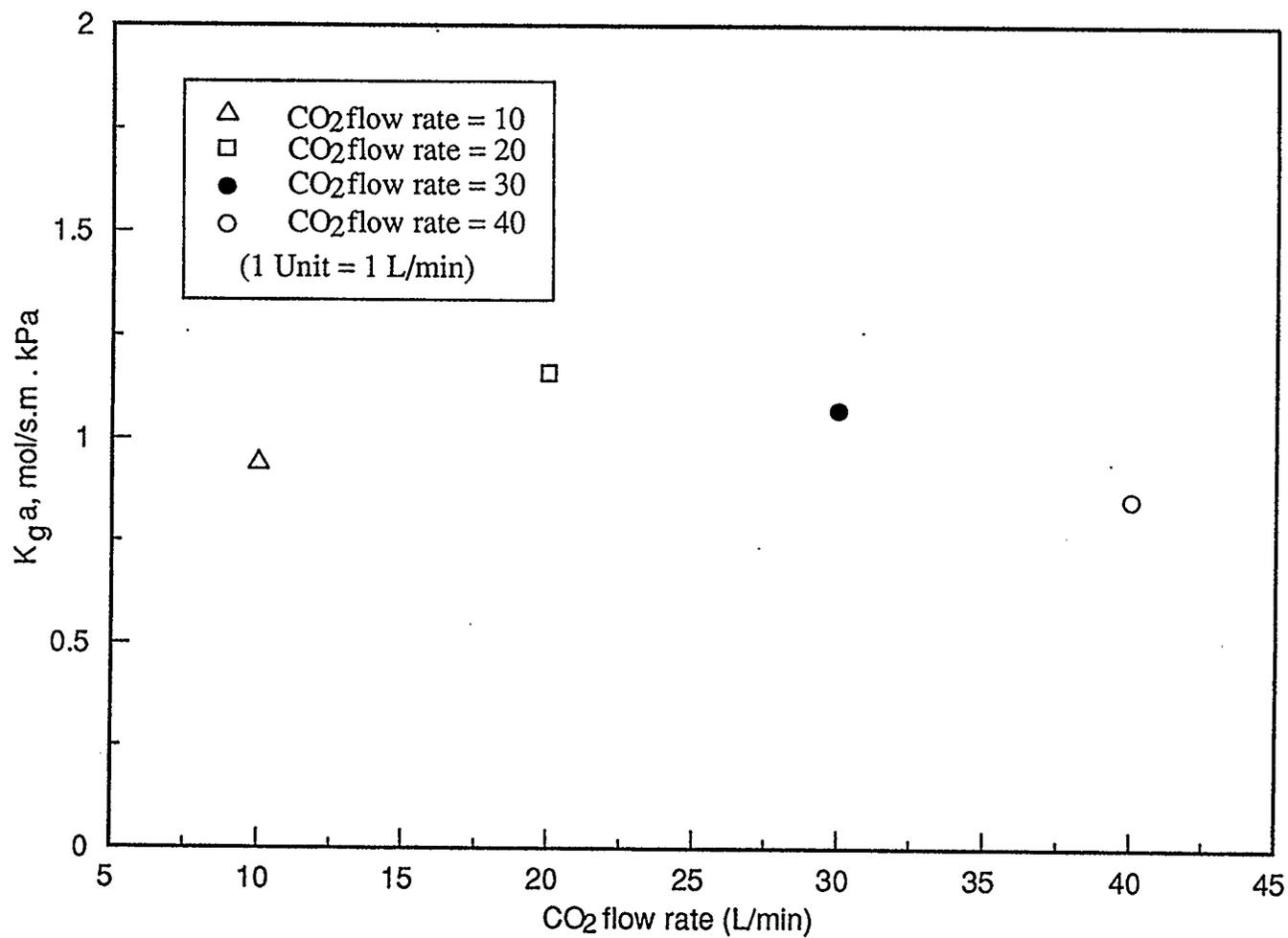


Fig. 4.26 Effect of CO₂ flow rate on the overall gas phase mass transfer coefficient for (5% w/w MEA + 45% w/w MDEA) amine blend

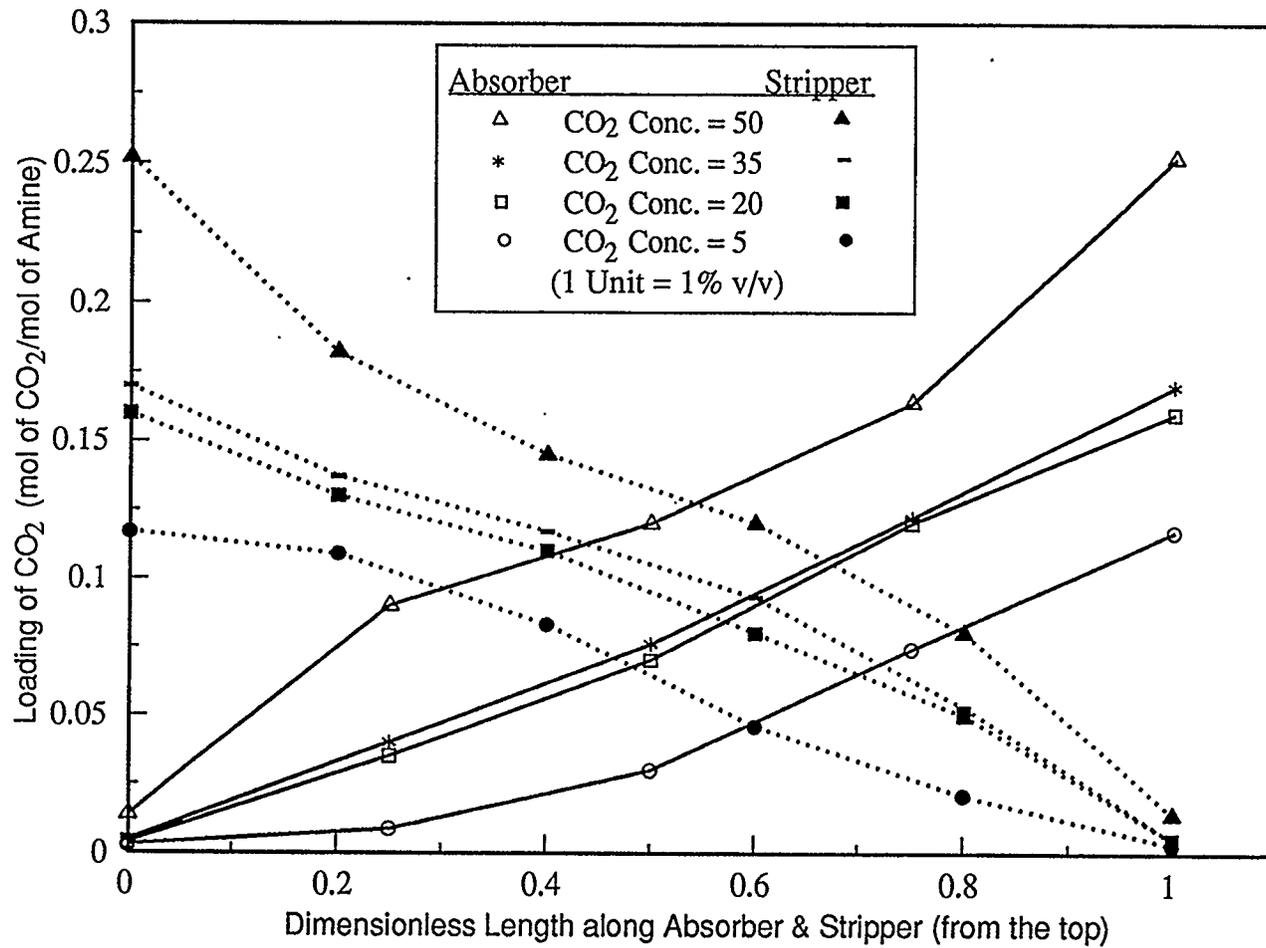


Fig. 4.27 Concentration profiles along the Absorber and Stripper for different concentrations of CO₂ (Solvent = 5% MEA + 45% MDEA)

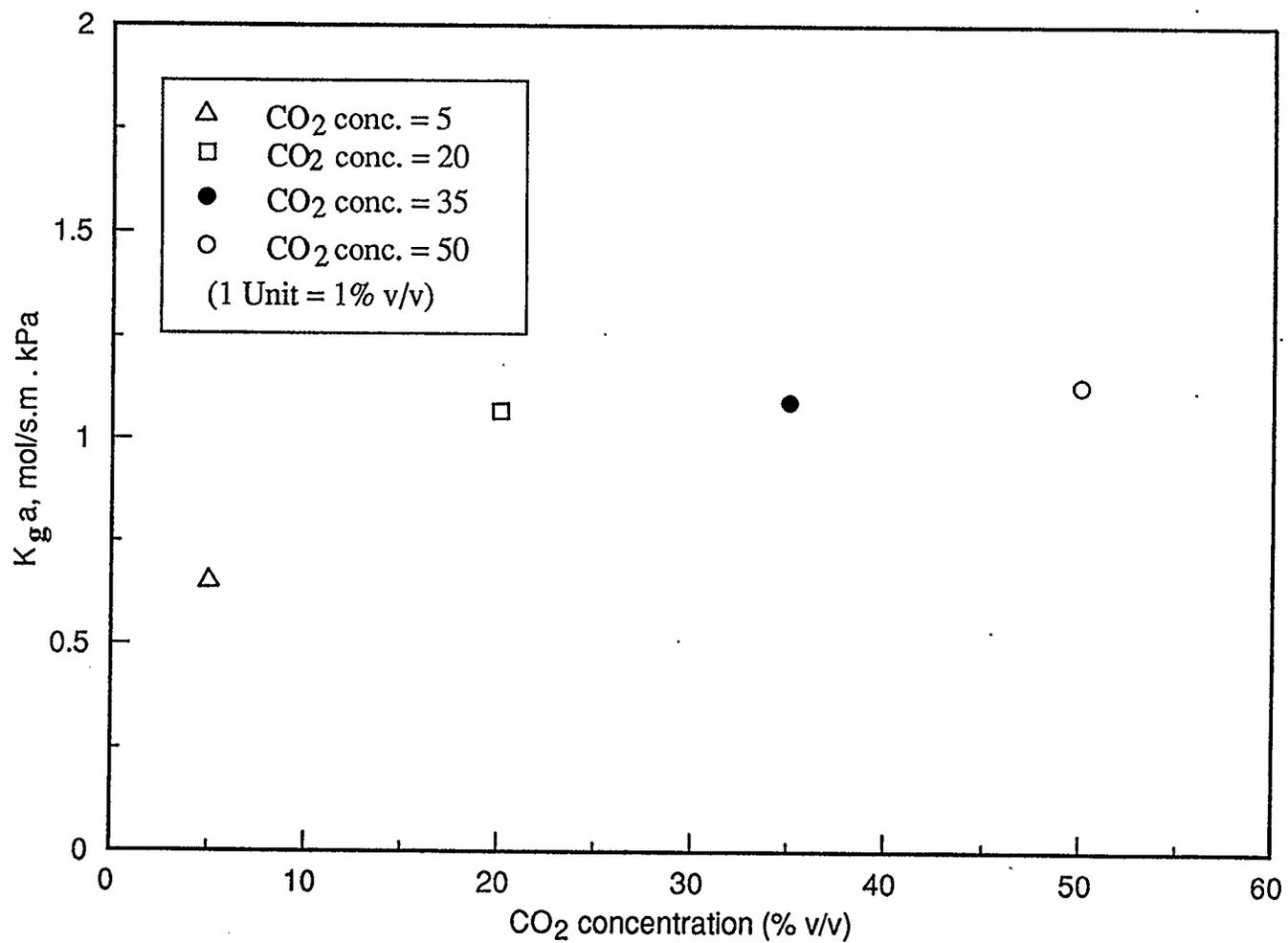


Fig. 4.28 Effect of CO₂ concentration on the overall gas phase mass transfer coefficient for (5% w/w MEA + 45% w/w MDEA) amine blend

Fig 4.29 shows the concentration profiles obtained at different steam consumption rates. It can be observed that the loading values in the absorber increased when the steam was reduced by 25% of the maximum value of 285 g/min. This was because the initial setting of the steam rate being used for the MEA and MDEA blend was too high. As a result, when the steam rate was decreased it brought about a general drop in the temperature in the system. When this cooler solution entered the absorber, it absorbed more CO₂. This is in keeping with the fact that the forward reaction of amines with CO₂ is favoured at high pressure and low temperature. However, the loading values at the exit of the stripper was almost the same for either steam rate as the steam supplied in all cases was sufficient to desorb that amount of CO₂.

4.5 Comparative Study of MEA, MDEA and their Blends

This section deals with a comparative study of MEA, MDEA and their blend (5% w/w MEA + 45% w/w MDEA). Comparative plots are shown for various process parameters.

4.5.1 Effect of various parameters on the K_ga values

The effect of amine flow rate, amine concentrations CO₂ flow rate and CO₂ concentration were studied on the K_ga values in the absorber. Fig. 4.30 shows the variation of K_ga for increasing concentrations of amines MEA and MDEA. It can be

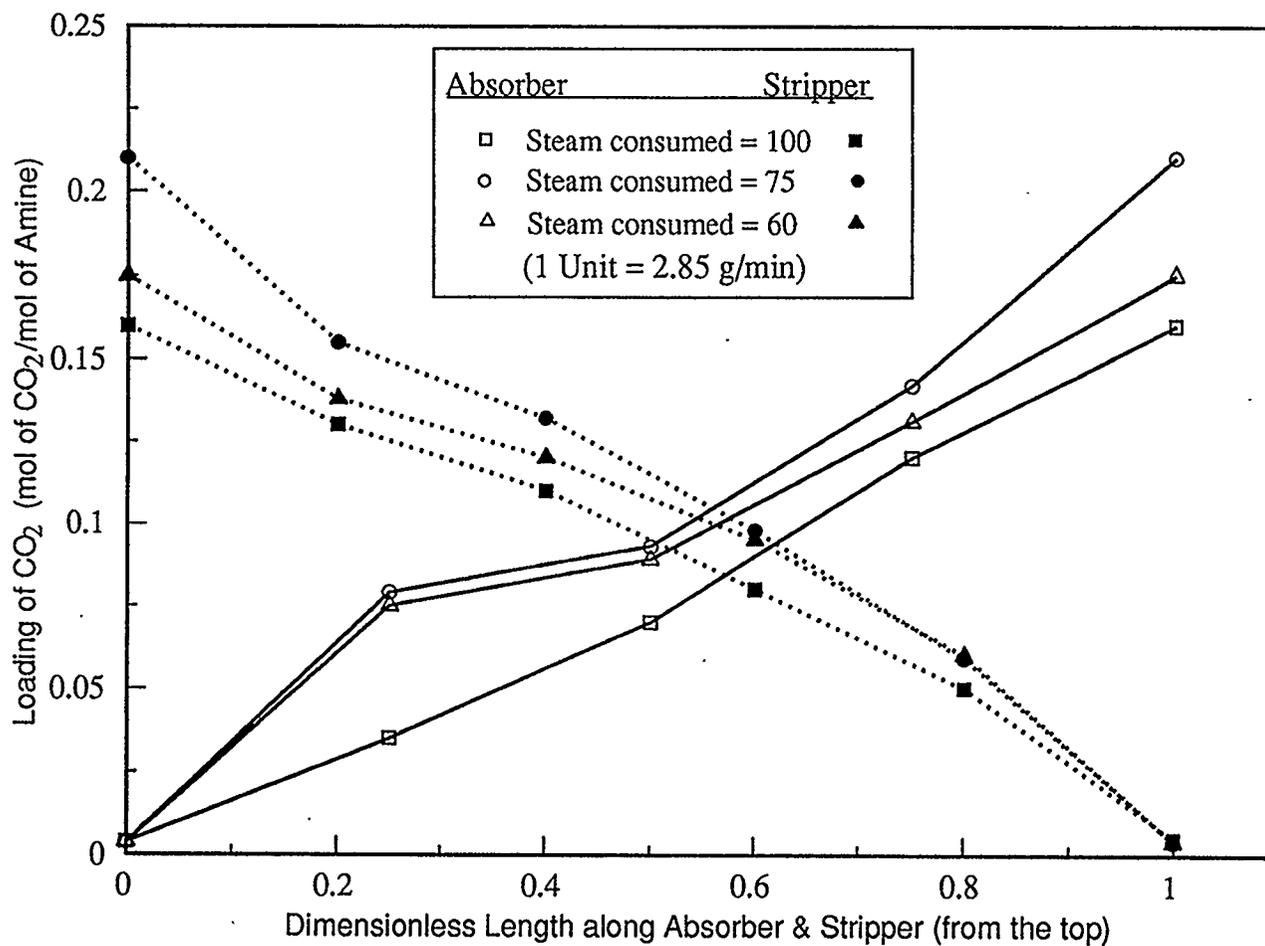


Fig. 4.29 Concentration profiles along the Absorber and Stripper for different steam consumption rates (Solvent = 5% MEA + 45% MDEA)

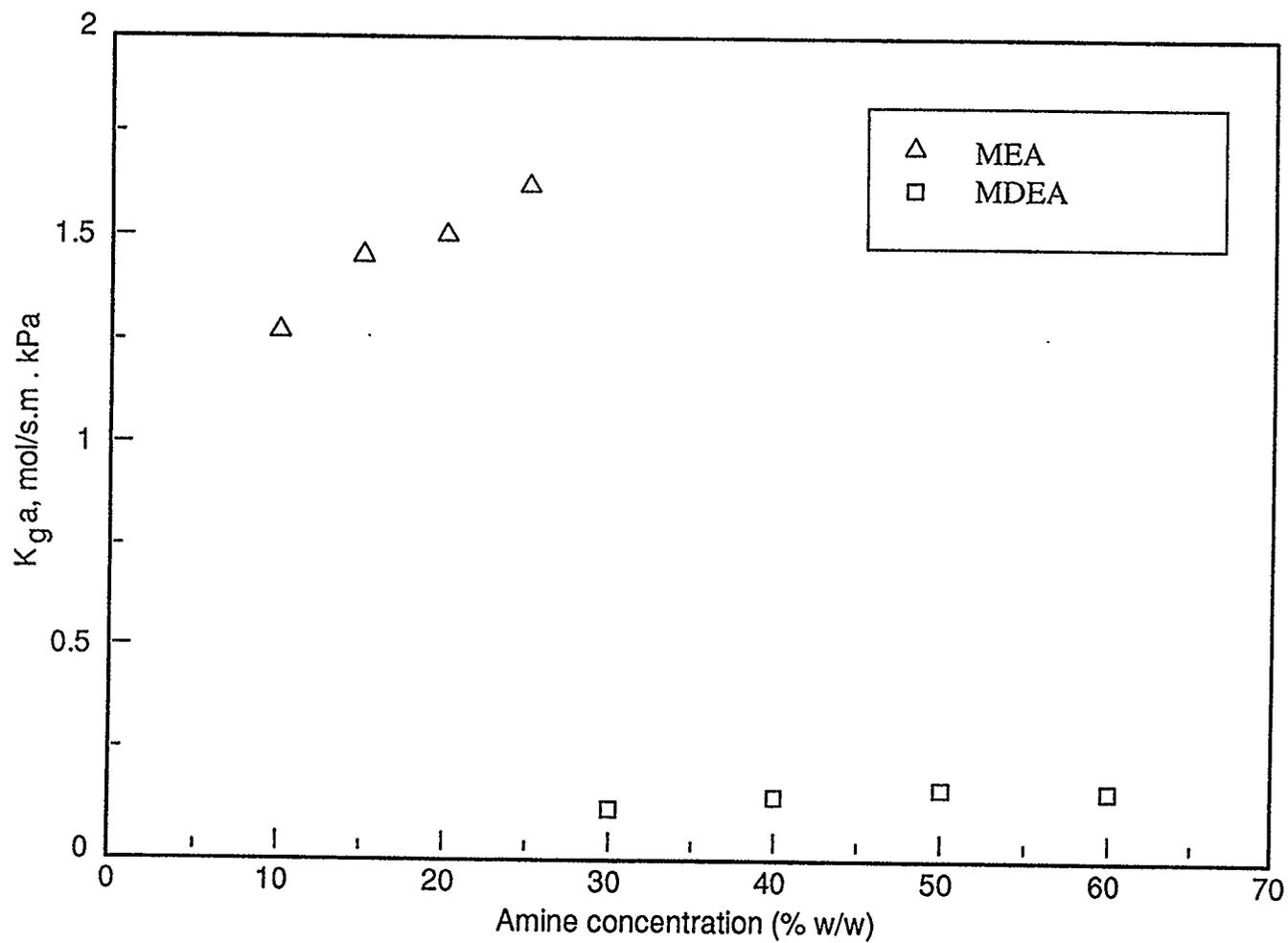


Fig. 4.30 Effect of amine concentration on the overall gas phase mass transfer coefficient for various amines

seen in the case of MEA that as the concentration of amine is increased, $K_g a$ values increase too. With the increased availability of MEA for the reaction an increase in the reaction with CO_2 takes place. In the case of MDEA, however there is an increase in the mass transfer coefficient with amine concentration initially. Later on, however, at higher concentrations of the amine, $K_g a$ reaches a maximum value and slowly decreases then after. This behaviour results from kinetic effects (reaction rate directly depends upon amine concentration) over-riding viscosity effects at initial increases in concentration of the amine. At increased viscosity, the diffusivity of CO_2 decreases rapidly resulting in reduced transfer of CO_2 . This effect is more pronounced in the case of MDEA because the viscosity of MDEA is almost four times that of MEA and any changes in its concentration in the solution has profound effect on viscosity (Refer Table A.2-Physical Properties of Alkanolamines, Appendix).

Fig. 4.31 shows the comparison of $K_g a$ values obtained for varying flow rates of the amines. The amine solutions compared are again 20% w/w MEA, 50% w/w MDEA and a blend consisting of 5% w/w MEA and 45% w/w MDEA. With increasing flow rates of MEA as well as the blended amine there is a general increase in the mass transfer coefficient. The increase in interfacial area which accompanies a higher liquid rate results in the improved mass transfer coefficient. In the case of MDEA, however, the mass transfer coefficient increases initially but becomes nearly constant later, or even starts to decrease. This is primarily because the reaction of CO_2 with MDEA is slow, and as a result, a minimum residence time of amine in the column has to be

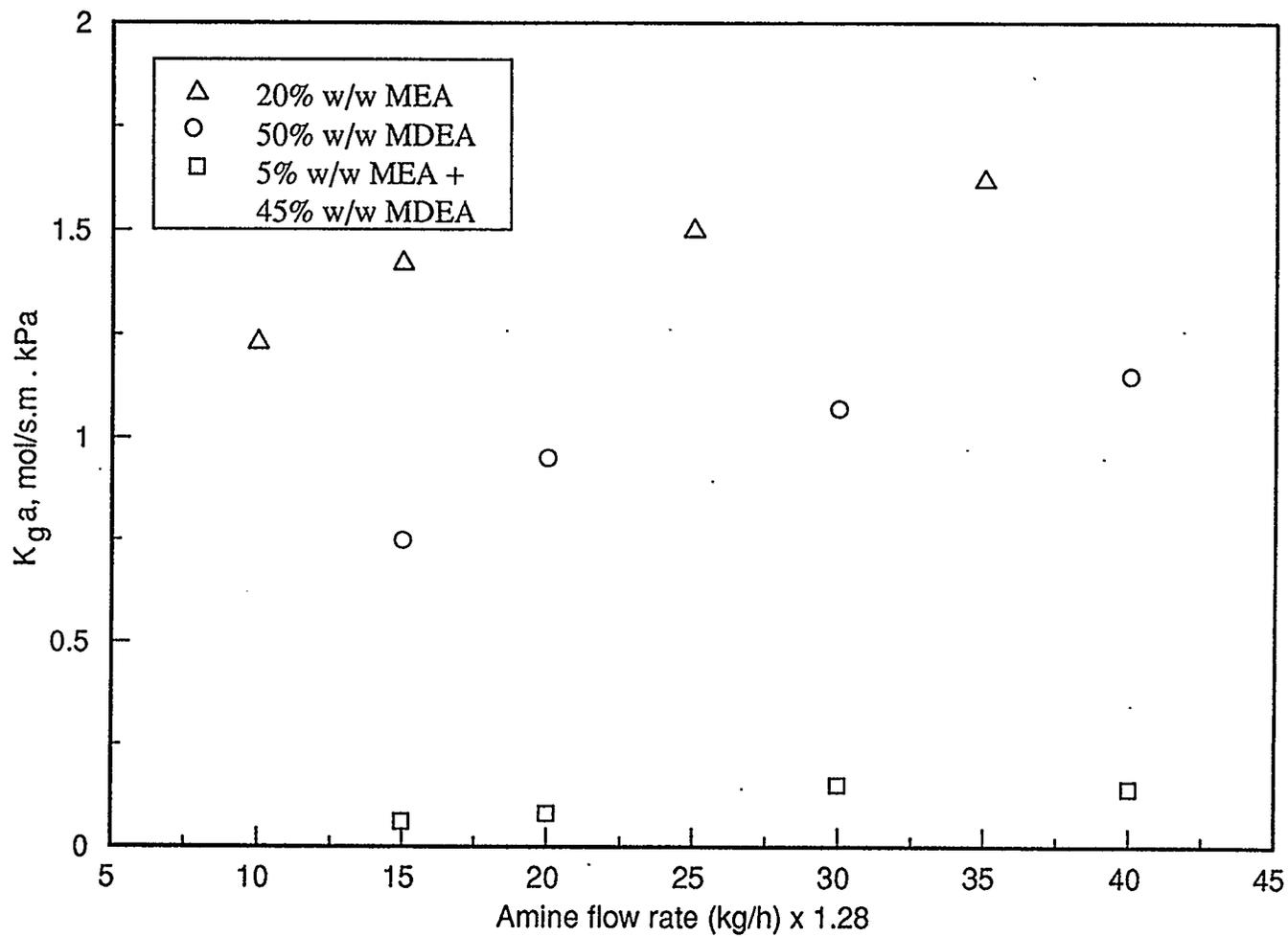


Fig. 4.31 Effect of amine flow rate on the overall gas phase mass transfer coefficient for various amines

provided for MDEA to react considerably. Increasing flow rates beyond 38.4 kg/h results in very short contact times for the amine in the absorber.

The effect of changing CO₂ concentrations on the overall mass-transfer coefficients can be seen in Fig. 4.32. For all the amines depicted in this graph, K_ga values increase initially but become almost constant at higher concentrations of CO₂. Increasing concentration of CO₂ increases its partial pressure thereby increasing the driving force for its transfer. When the concentration of CO₂ is raised above 20% v/v, the improvement in the mass-transfer coefficients are not as pronounced as expected. At higher concentrations of CO₂, the solution leaving the absorber is highly loaded. When this solution was being regenerated in the stripper very low loadings could not be attained at the exit of the stripper. As a result of this, the solution entering the absorber has a reduced driving force or transfer of CO₂. This results in a reduction in the overall transfer of CO₂ as compared to expected values.

Fig. 4.33 shows the effect of CO₂ flow rates on the K_ga values in the absorber. In the case of MEA there is an increase in K_ga values with flow rate but in the case of MDEA the increase is not as evident. In the case of both MDEA and the mixed solvent, a drop in K_ga values can be seen to occur at higher flow rates. The increase in K_ga with gas rate is caused principally by increased gas phase turbulence. An increase in liquid turbulence also assists in this effect. However, at high flow rates of CO₂, the contact time with the amine decreases and channelling effects are also caused. At very high flow

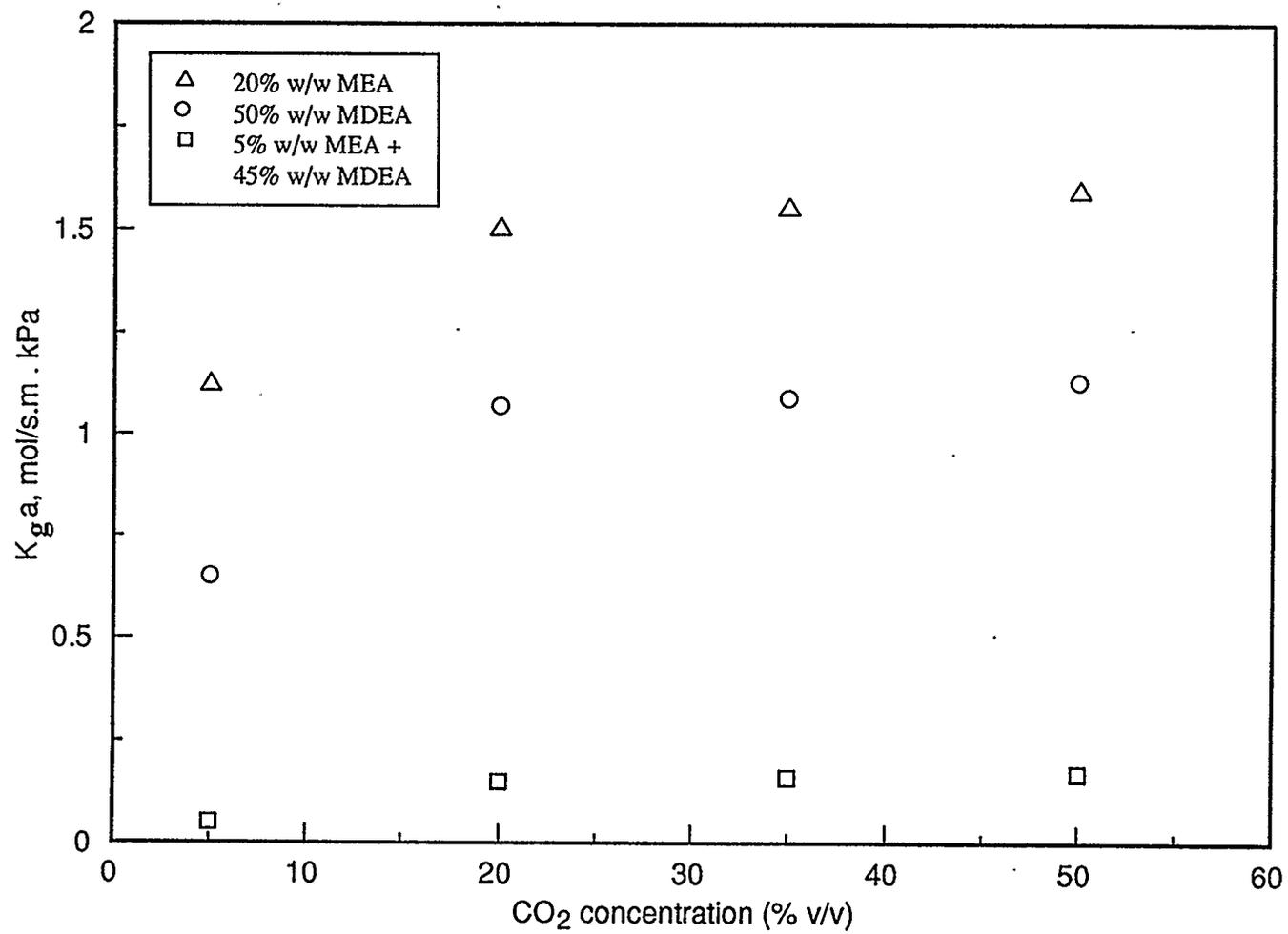


Fig. 4.32 Effect of CO₂ concentration on the overall gas phase mass transfer coefficient for various amines

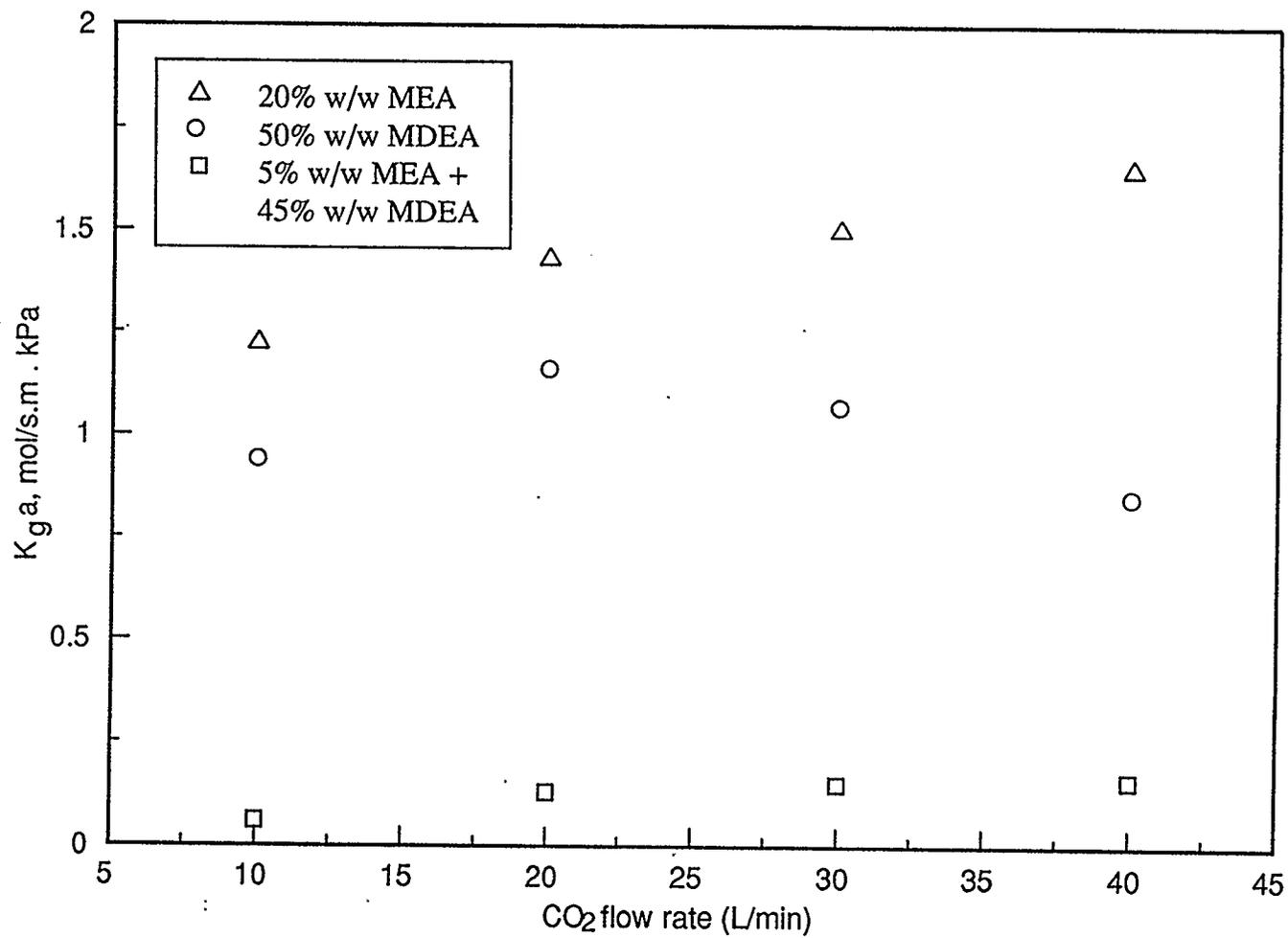


Fig. 4.33 Effect of CO₂ flow rate on the overall gas phase mass transfer coefficient for various amines

rates excessive foaming in the column may also result in reduced absorption of CO_2 .

4.5.2 Effect of Steam Consumption on K_{ga} :

The effect of steam consumption was studied on the CO_2 removal from the rich amine in the stripper. The data is presented in the form of energy input to the reboiler in terms of KJ/h against the CO_2 duty which is expressed in terms of moles of CO_2 removal per hour (Fig 4.34). This plot not only shows the energy consumption for a given CO_2 duty but also gives a comparison for the energy duty for various amine systems. An optimum value for the steam consumption is also obtained. A comparison for 20% w/w MEA, 50% w/w MDEA and 5% w/w MEA + 45% w/w MDEA solution shows that for the same heat duty considerably improved CO_2 removal can be obtained in the case of mixed amine solvent over that of single solvents MEA and MDEA.

The consumption of energy in the case of MEA is the highest followed by MDEA and the mixed amine. Increasing the heat input in the reboiler increases the CO_2 duty for MEA but the slope of the curve shows that the improvement is not much. This is because it is very difficult to reach very low loadings in the exiting solution for MEA. Also, when the heat input to the reboiler is increased, it results in a general rise in the temperature of the MEA solvent. As a result, reduced absorption takes place in the absorber and the incoming rich MEA entering the stripper has a lower loading of CO_2 . Consequently, overall removal of CO_2 i.e. the difference in the loading at the inlet and

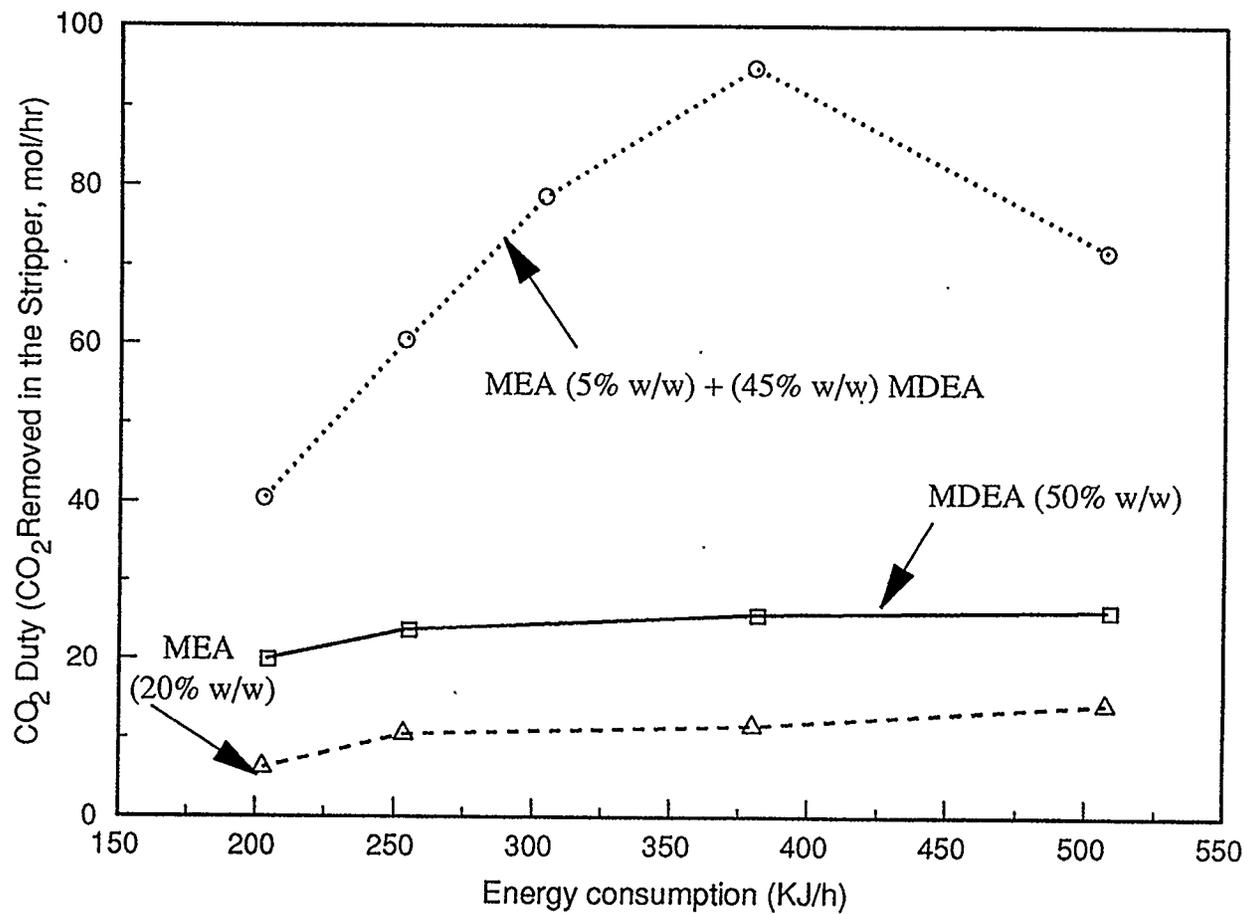


Fig. 4.34 Comparison of CO₂ duty for different amines at varying energy consumption rates

outlet streams of liquid actually decreases, though a slight improvement may be obtained in terms of a reduced CO₂ loading in the exit stream from the stripper.

A similar trend for CO₂ duty was obtained in the case of MDEA. Based on the fact that CO₂ strips relatively easily from carbonated MDEA solution and is more sensitive to energy input in the reboiler, a steeper slope was expected. However, in this case one must point out that we were dealing with very low CO₂ loadings in the solution which imposed a limitation on the measurement of loading values below 0.006 moles of CO₂ / moles of amine at the exit of the stripper. Moreover, it appears that almost all of the CO₂ was removed before the steam consumption rate was increased.

In the case of 5% w/w MEA + 45% w/w MDEA blend, a significant increase in the CO₂ duty was obtained with increase in heat duty in the reboiler. At the optimum heat input of 380 KJ/h for the blend, a ten-fold increase in CO₂ duty can be observed for the mixed amine as compared to MEA and a five-fold increase as compared to MDEA. Another noticeable feature in the case of the amine blend is that the CO₂ duty decreased with further increase in heat duty to 507 KJ/h. This is because, after having reached an optimum condition, the additional heat input increased the overall temperature of the circulating solution resulting in reduced absorption in the absorber and subsequently reduced loadings in the rich amine entering the stripping column.

CHAPTER 5

Solubility Modelling

5.1 Solubility Modelling

This section describes the development of a mathematical model for predicting CO₂ equilibrium solubility for a mixed amine system. The results of the model are useful in the design of absorbers using blended amines. The approach combines the method of Kent and Eisenberg (1976) and Chakma and Meisen (1990). The former carried out a curve fitting for the values of Equilibrium Constants and Henry's constant for CO₂/MEA/H₂O systems. Chakma (1989) provided an empirical relation for the equilibrium constant for CO₂/MDEA/H₂O systems. The expressions for equilibrium constants and Henry's constant were functions of temperature and/or free CO₂ concentration. The model ignores any non-ideality in the system which could be caused by the presence of ionic species in the system. The earlier work of Kent and Eisenberg (1976) was based on the postulate of McNeil and Danckwerts (1967) which states that the vapour pressure of the acid gas species is related to the free acid gas concentration in the liquid phase by a Henry's law relationship, and the free acid gas concentration is in turn determined by liquid phase ionic equilibria.

A comparison is then made with the predictions of Austgen et al. (1991) who used the electrolyte NRTL equation in the development of a physicochemical model for representing CO₂ solubility in aqueous mixtures of amines. The Electrolyte NRTL

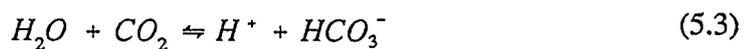
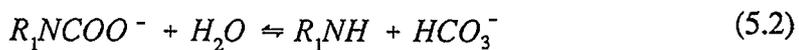
model is based upon both liquid-phase chemical equilibria and vapour-liquid equilibria and has widespread acceptance. It is however, quite cumbersome in its approach. Despite the fact that long range electrostatic interactions and short range binary molecular interactions are all considered in their model, uncertainties are introduced into the system by the introduction of adjustable binary energy interaction parameters fitted to experimental binary and ternary system VLE data.

5.1.1 Model Development

The determination of all the molecular and ionic species involves the simultaneous solution of a set of non-linear algebraic equations describing the chemical equilibria, electroneutrality and mass balance of all the species present in the aqueous solution.

5.1.2 Chemical Equilibrium

The equilibrium within the MEA/MDEA/H₂O/CO₂ system can be represented by the following set of well established chemical reactions. The chemical reactions for the system CO₂/H₂O/MEA have been given by Kent and Eisenberg (1976). The system of reactions has been written for the CO₂/H₂O/MEA/MDEA (mixed amine system).



The corresponding expressions for equilibrium constants are :

$$K_1 = \frac{[R_1NH][H^+]}{[R_1NH_2^+]} \quad (5.7)$$

$$K_2 = \frac{[R_1NH][HCO_3^-]}{[R_1NCOO^-]} \quad (5.8)$$

$$K_3 = \frac{[H^+][HCO_3^-]}{[CO_2]} \quad (5.9)$$

$$K_4 = [H^+][OH^-] \quad (5.10)$$

$$K_5 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (5.11)$$

$$K_6 = \frac{[R_3NH^+][HCO_3^-]}{[CO_2]} \quad (5.12)$$

The expressions for Henry's law relating acid gas partial pressure to physically dissolved gas concentration in the solvent is given by :

$$P_{CO_2} = H_{CO_2}[CO_2] \quad (5.13)$$

Equations for the total molar and charge balance for the system are :

$$[R_1NH_2^+] + [R_3NH^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [R_1NCOO^-] \quad (5.14)$$

$$[MEA] = [R_1NH] + [R_1NH_2^+] + [R_1NCOO^-] \quad (5.15)$$

$$[MDEA] = [R_3N] + [R_3NH^+] \quad (5.16)$$

$$[MEA + MDEA] \alpha_{CO_2} = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [R_1NCOO^-] \quad (5.17)$$

The empirical relations used for obtaining the equilibrium constants and Henry's constant are given below in SI units. These relations have been provided by Kent and Eisenberg (1976) and Chakma (1989) :

$$K_1 = \exp[-3.3636 - 5851.11T^{-1}] \quad (5.18)$$

$$K_2 = \exp[6.69425 - 3090.82T^{-1}] \quad (5.19)$$

$$K_3 = \exp[-241.818 + 298.253 \times 10^3 T^{-1} - 148.528 \times 10^6 T^{-2} + 332.648 \times 10^8 T^{-3} - 282.394 \times 10^{10} T^{-4}] \quad (5.20)$$

$$K_4 = \exp[39.554 - 987.9 \times 10^2 T^{-1} + 568.828 \times 10^5 T^{-2} - 146.451 \times 10^8 T^{-3} + 136.146 \times 10^{10} T^{-4}] \quad (5.21)$$

$$K_5 = \exp[-294.74 + 364.385 \times 10^3 T^{-1} - 184.158 \times 10^6 T^{-2} + 415.793 \times 10^8 T^{-3} - 354.291 \times 10^{10} T^{-4}] \quad (5.22)$$

$$K_6 = \exp[92.421453 - 1.49081486 \times 10^{-2} T + 40.847708 \times T^{-1} - 14.031652 \times \ln(T) - 9.8778738 \times 10^{-2} [CO_2] + 0.18275505 \times \ln([CO_2]) + 3.9862282 \times [MDEA] - 12.715421 \times \ln([MDEA])] \quad (5.23)$$

$$H_{CO_2} = \exp[22.2819 - 138.306 \times 10^2 T^{-1} + 691.346 \times 10^4 T^{-2} - 155.895 \times 10^7 T^{-3} + 120.037 \times 10^9 T^{-4}] / 7.50061 \quad (5.24)$$

The above mentioned set of equations (5.7 to 5.17) were solved, employing the values of K and H obtained from equations 5.18-5.24. There were, thus, eleven unknowns and eleven non-linear algebraic equations. The system of equations was solved by Newtons' method, which involves linearizing the system of equations and subsequently solving the resulting Jacobian matrix.

5.2 Results and Discussion of the Solubility Modelling

The solubility values were obtained from the model for which a FORTRAN program has been written. The solubility expressed as mole ratio of CO₂ and amine in the liquid was plotted against the corresponding CO₂ partial pressure (kPa). Solubility

values were first predicted by the model for single amine systems at conditions where experimental data was available. The predicted results were then compared to these experimental data to establish the validity of the model for single amine systems.

Fig. 5.1 shows the solubility values of CO₂ predicted by the model for 2.5N MEA solution at 40°C and 100°C and partial pressure range 0.01 - 5000 kPa. These predicted values are compared to the experimental data of Lee et al. (1976). Solubility is shown to decrease with increasing temperature as expected. The results of this prediction agree very well with the experimental data at both the temperatures.

Fig. 5.2 shows a comparison of predicted solubility values for CO₂ in an aqueous 2.5N MEA solution at 40°C and 100°C and low partial pressures (0.001-10 kPa) with the experimental data of Isaacs et al. (1980). The model predicts well above a CO₂ partial pressure of 0.01 kPa. However, good agreement is not seen at very low CO₂ partial pressures within the range 0.001 - 0.01 kPa. A comparison of model predictions for solubility of CO₂ in 2.5N MEA at 40°C and 80°C within the CO₂ partial pressure range 0.01 - 5000 kPa with the recent experimental data of Austgen et al. (1991) is depicted in Fig. 5.3. Excellent agreement within the entire range of parameters is observed.

A comparison of predicted solubility values of CO₂ in 2.0N MDEA solution within the temperature range 25°C - 100°C and partial pressure of CO₂ between 0.01 -

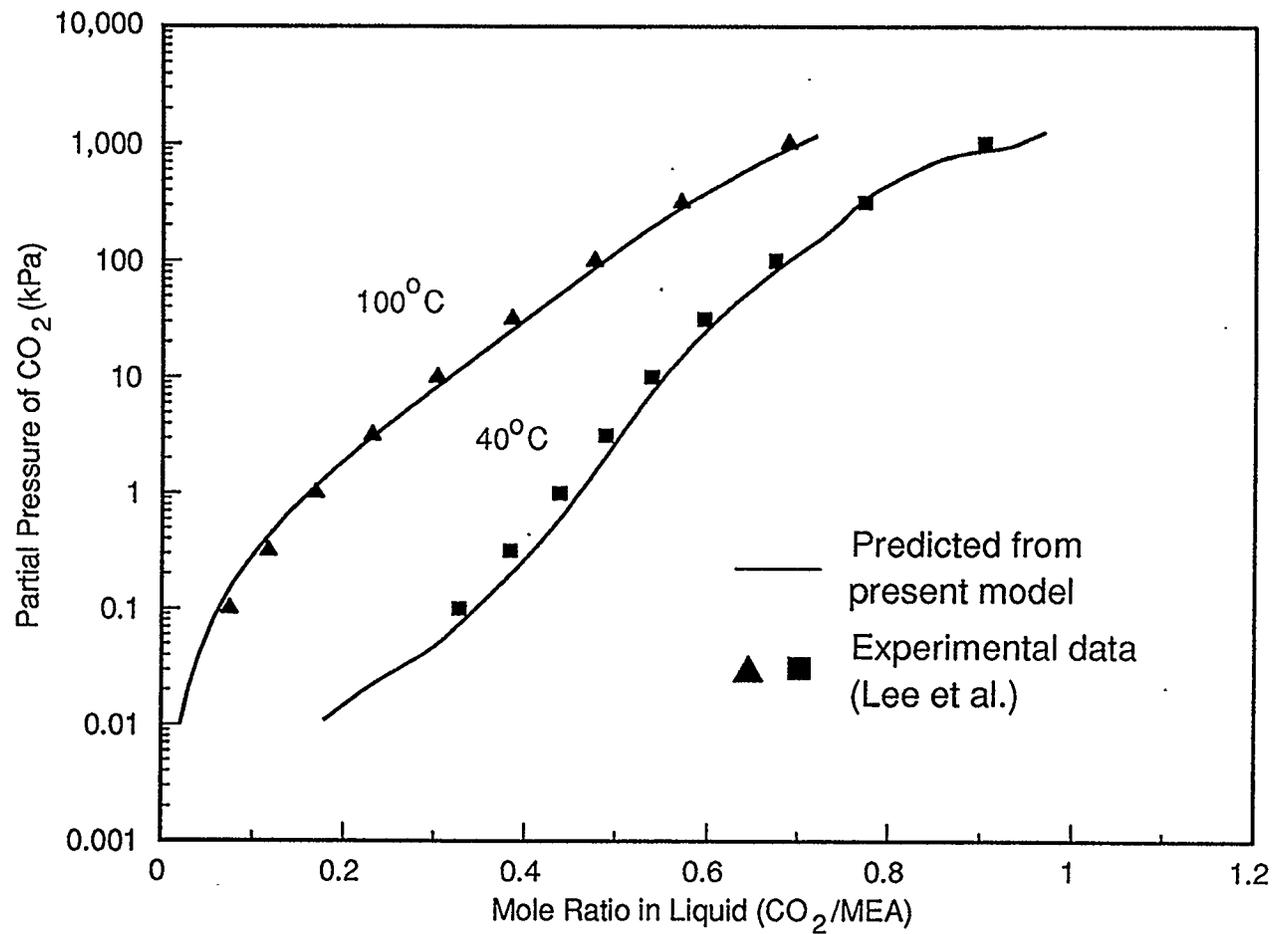


Fig. 5.1 Comparison of predicted solubility of CO₂ in 2.5N MEA solution at varying temperatures with experimental data of Lee et al., 1976

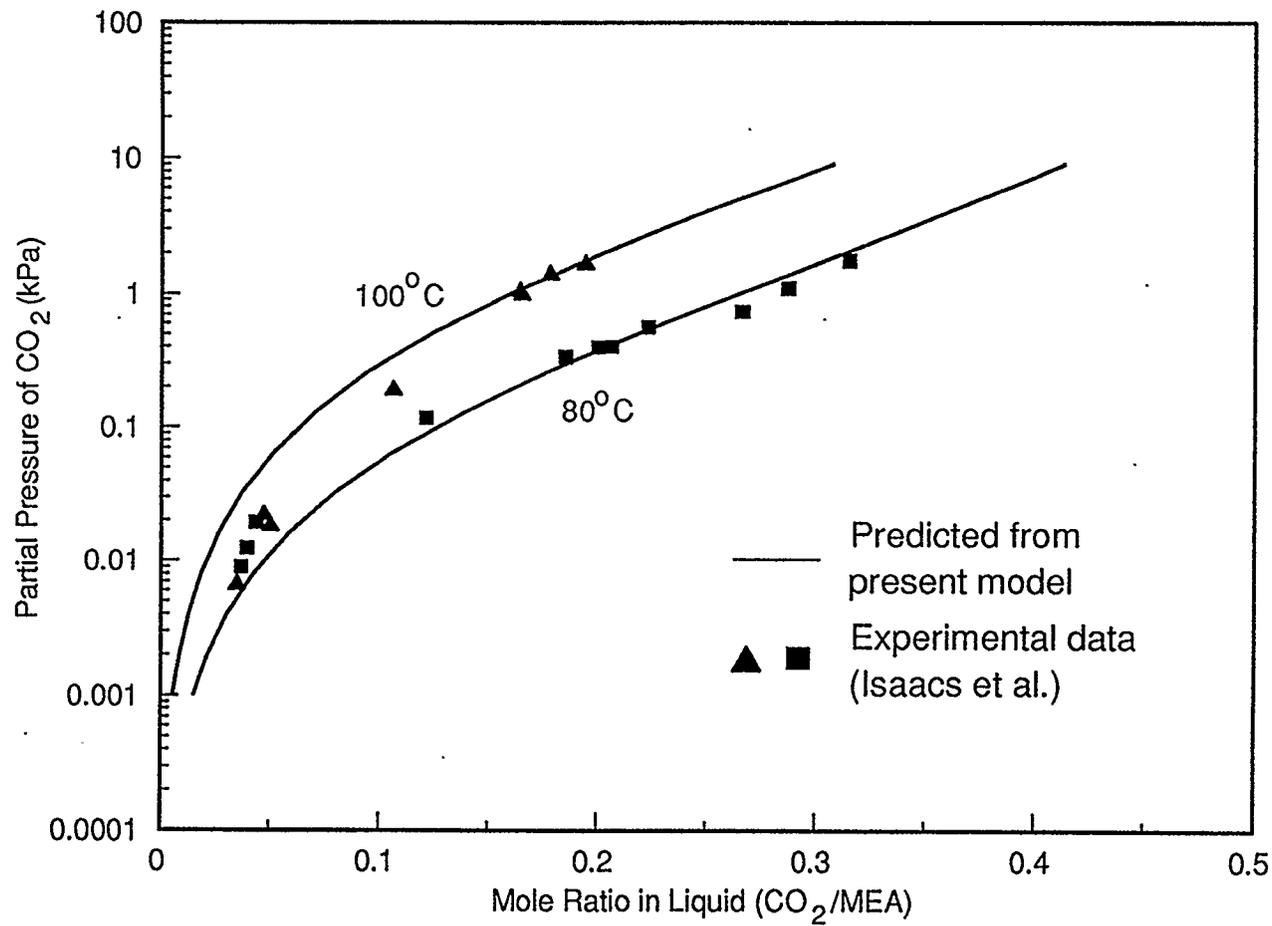


Fig. 5.2 Comparison of predicted solubility of CO₂ in 2.5N MEA solution at varying temperatures with experimental data of Isaacs et al., 1980

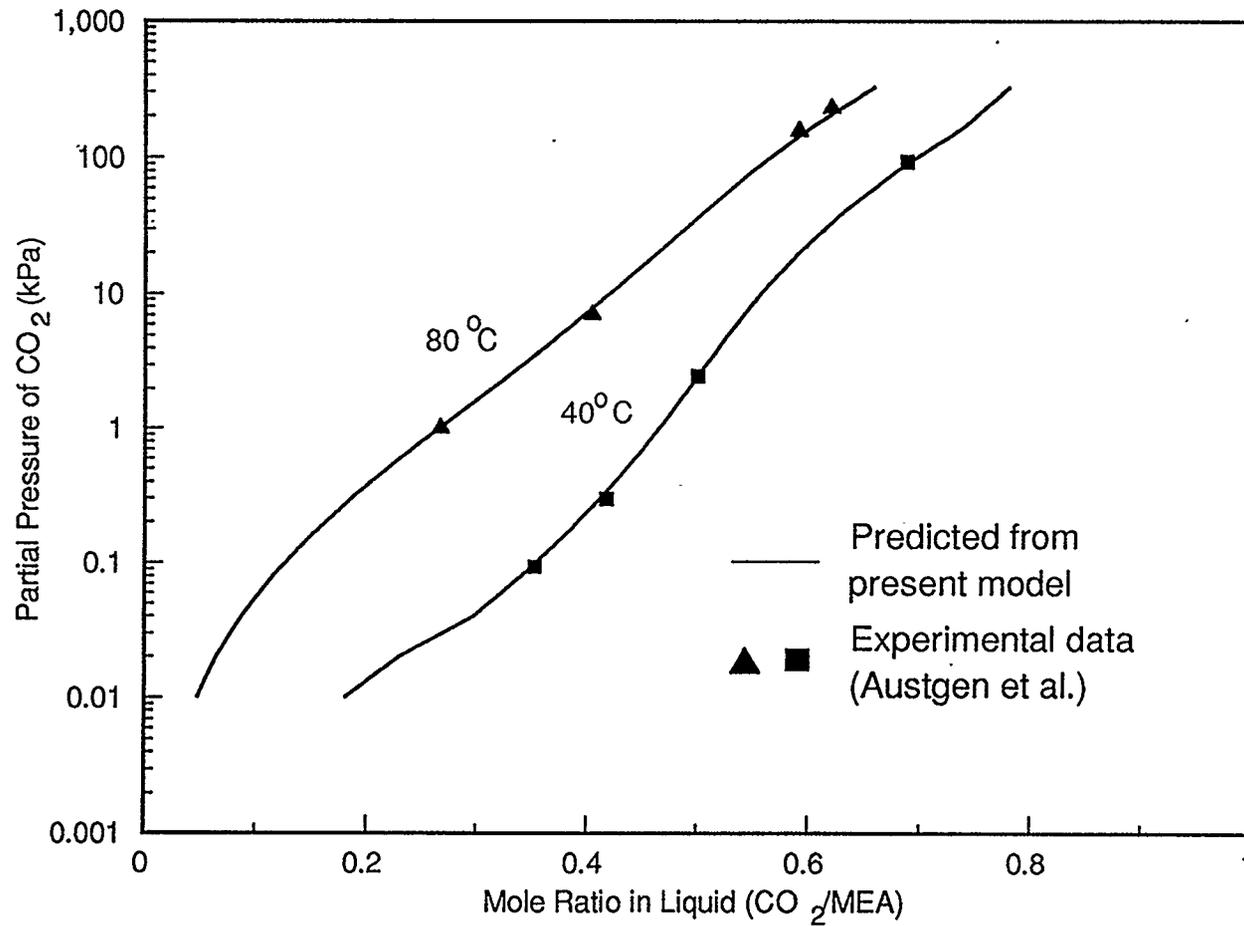


Fig. 5.3 Comparison of predicted solubility of CO₂ in 2.5N MEA solution at varying temperatures with experimental data of Austgen et al., 1991

5000 kPa with the experimental data of Jou et al. (1982) is shown in Fig. 5.4. A similar comparison of the solubility values of CO₂ in 4.28N MDEA with the experimental data of the same authors is made in Fig. 5.5. Here too, the predicted values are seen to over predict slightly. A comparison of the predicted solubility values at concentrations of 2.0N and 4.28N MDEA at 40°C with the experimental data of Austgen et al. (1991) shows excellent agreement (Fig. 5.6) The predicted values are seen to slightly over predict the experimental data at very high partial pressures.

Solubilities of CO₂ in mixed amine systems have been presented in Fig 5.7, Fig. 5.8 and Fig. 5.9 for different blends of MEA and MDEA at varying temperatures. The concentration ranges chosen for the predictions either signify the concentration values used in the actual experiments carried out for absorption and stripping studies or are for purely comparative purposes with existing experimental data. Comparison of the solubility has been made in different blends of MEA and MDEA in Fig 5.10. It can be inferred from this graph that solubility of CO₂ is higher in solutions having higher MEA concentration. However, at higher partial pressures of CO₂ the solubility of CO₂ in a 0.818 N MEA + 3.78 N MDEA amine blend surpasses that in other blends shown.

Fig 5.11 shows a comparison of the predicted solubility values for CO₂ in 4 N MEA and 4 N MDEA at 40°C with the model predictions of Austgen et al., 1991. It can be seen in Fig 5.11 that above a loading of 0.6 mol CO₂ /mol amine the solubility of

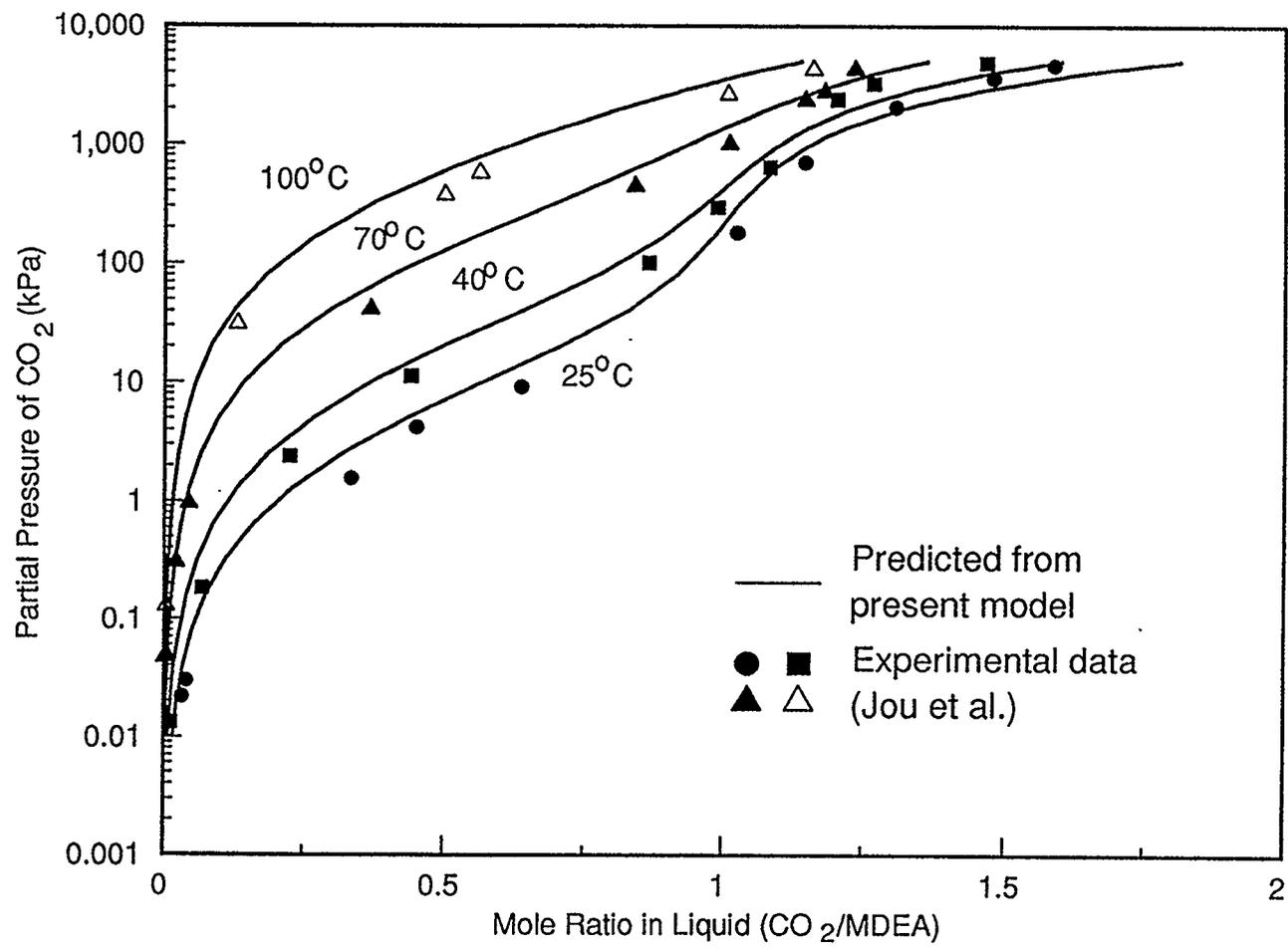


Fig. 5.4 Comparison of predicted solubility of CO₂ in 2.0N MDEA solution at varying temperatures with experimental data of Jou et al., 1982

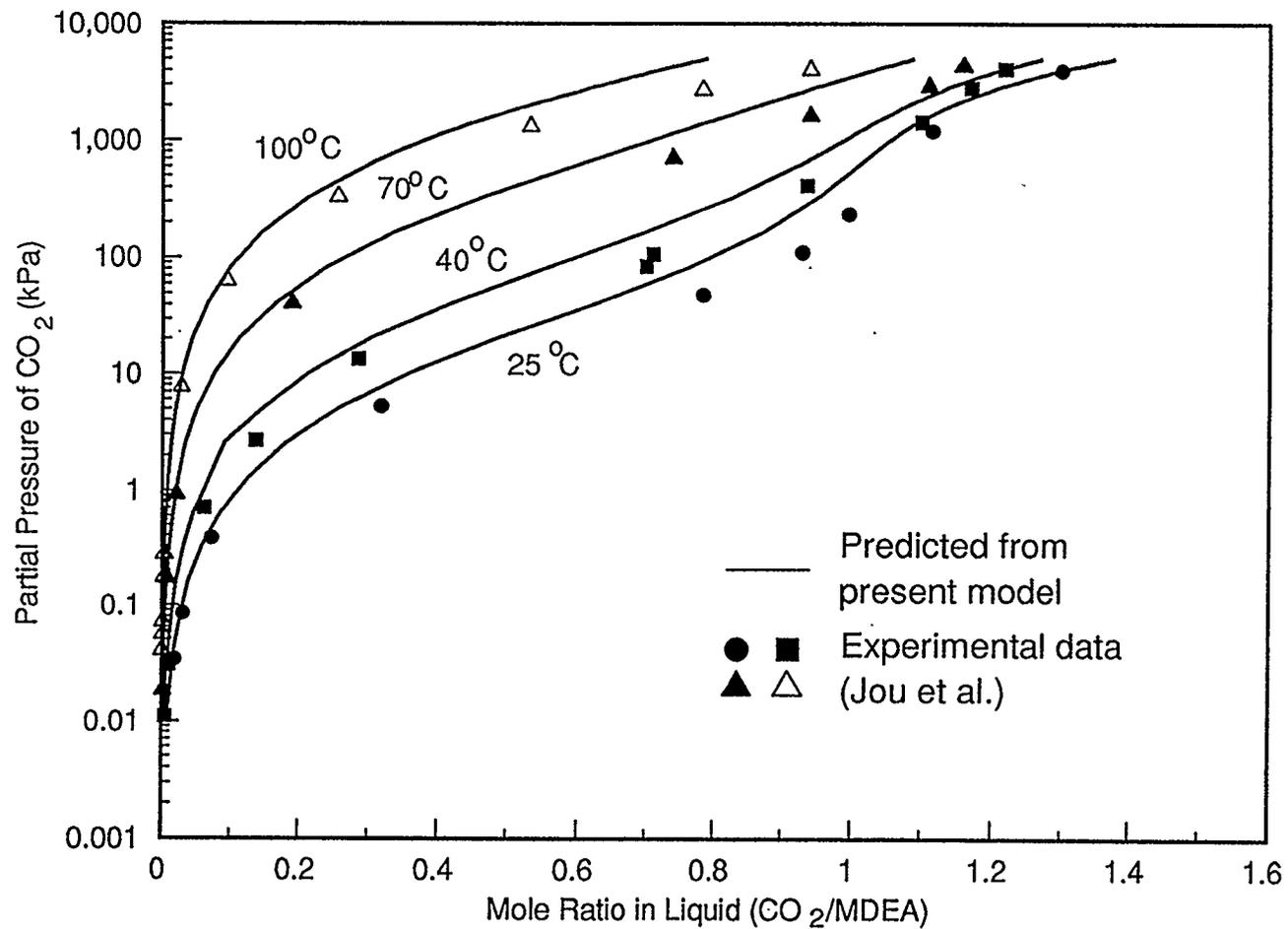


Fig. 5.5 Comparison of predicted solubility of CO₂ in 4.28N MDEA solution at varying temperatures with experimental data of Jou et al., 1982

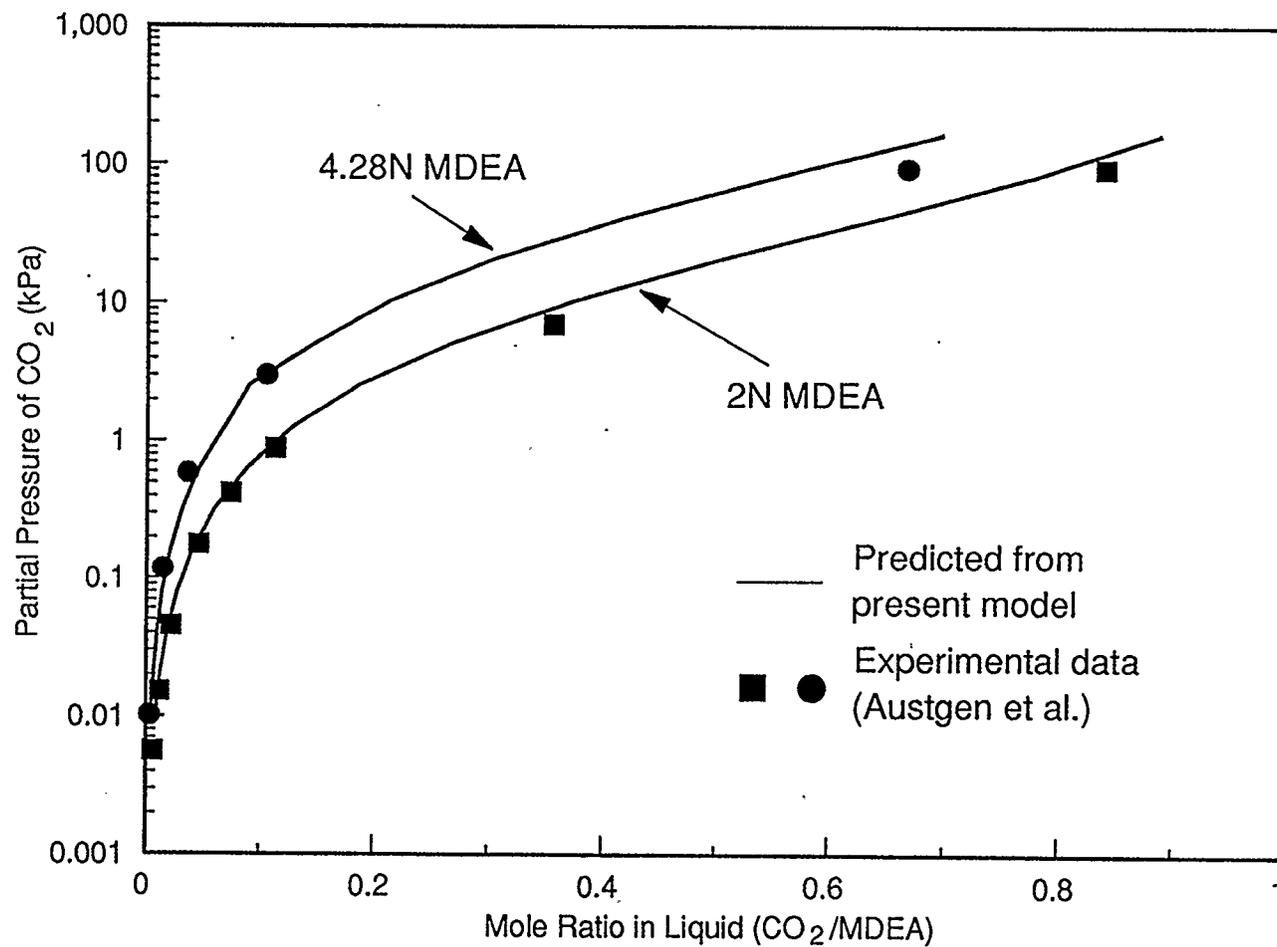


Fig. 5.6 Comparison of predicted solubility of CO₂ in 2.0N and 4.28N MDEA solution at 40°C with experimental data of Austgen et al., 1991

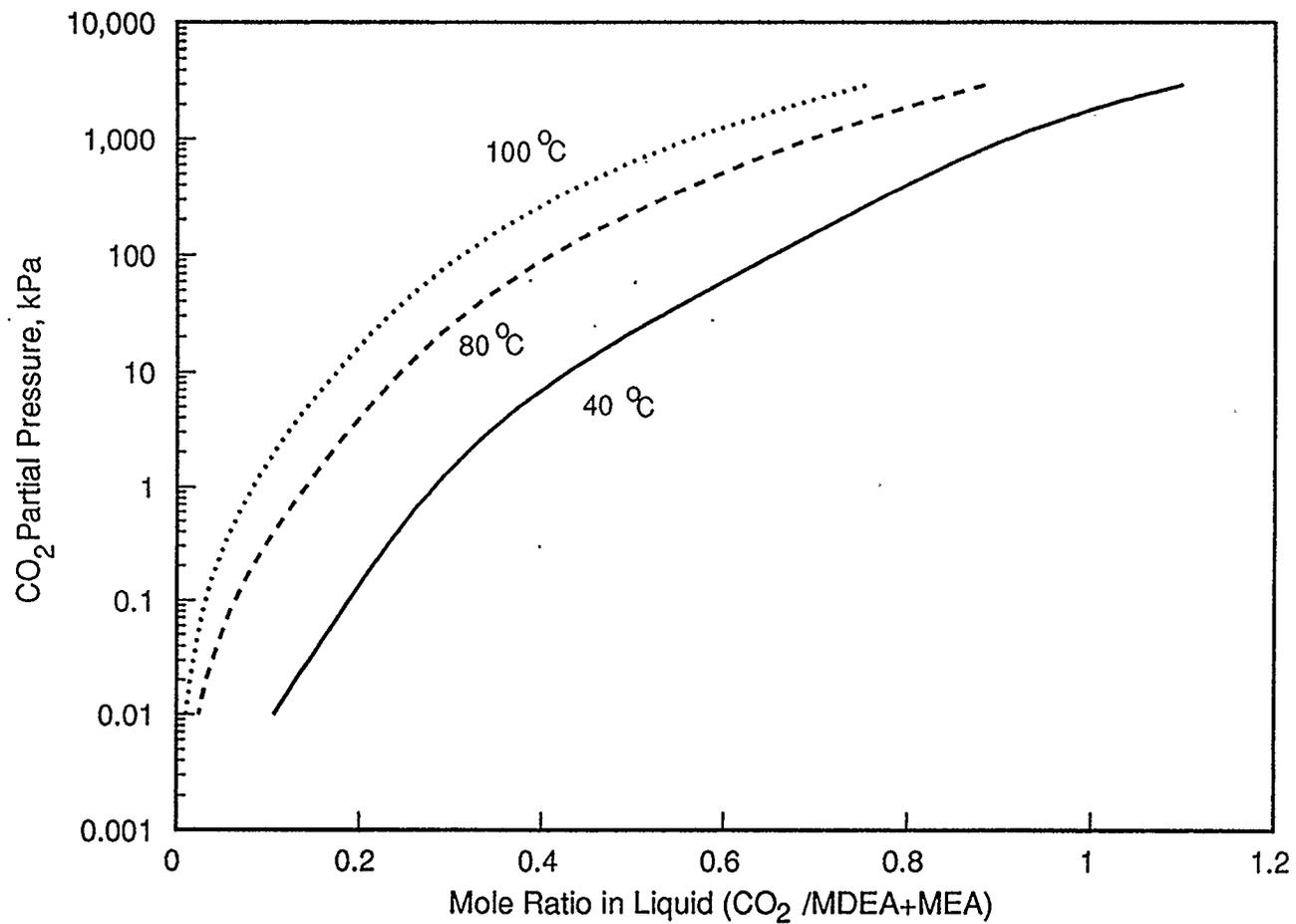


Fig. 5.7 Predicted solubility of CO₂ in a 2N MEA + 2N MDEA solution at varying temperatures

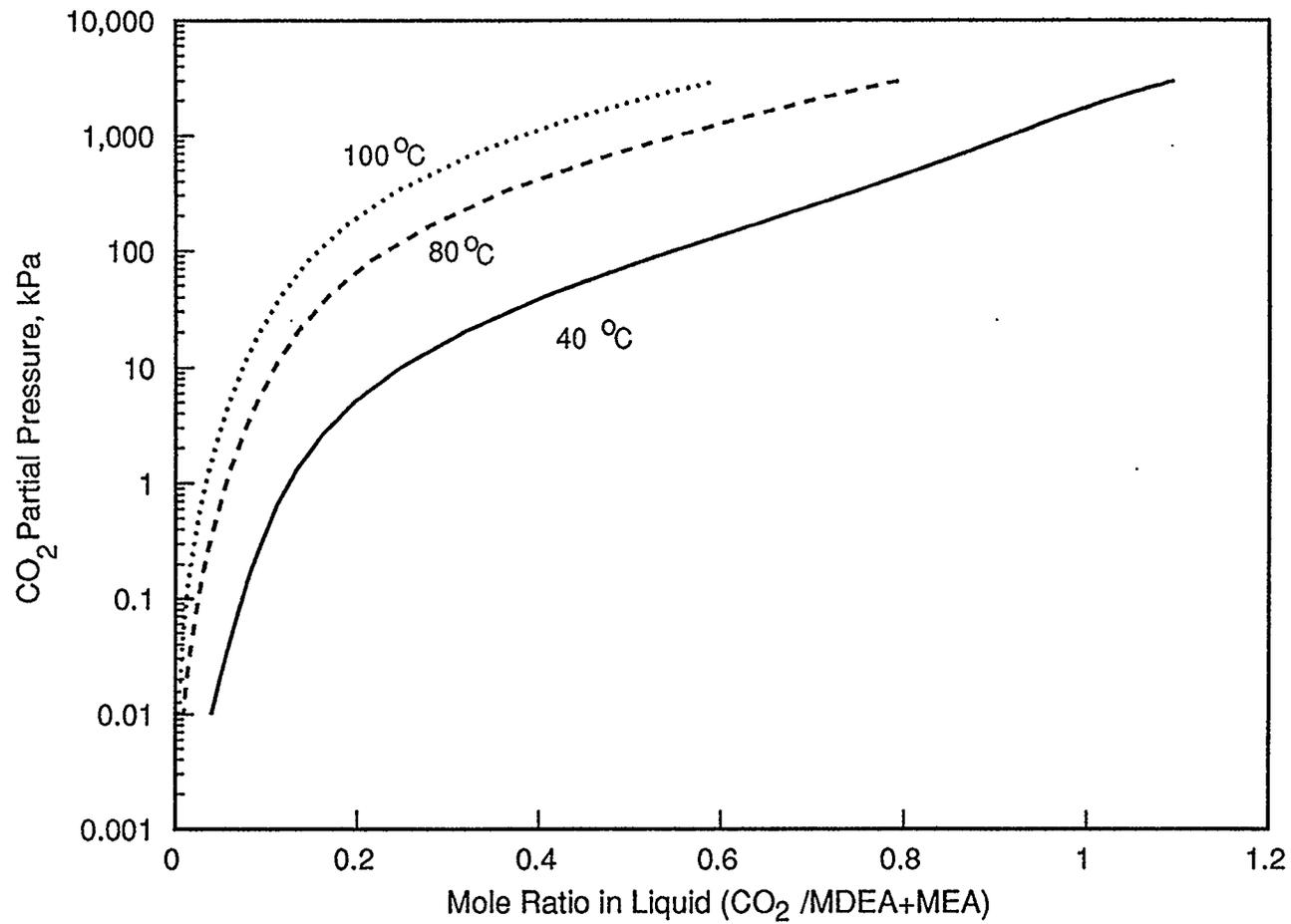


Fig. 5.8 Predicted solubility of CO₂ in a 0.818N MEA + 3.78N MDEA solution at varying temperatures

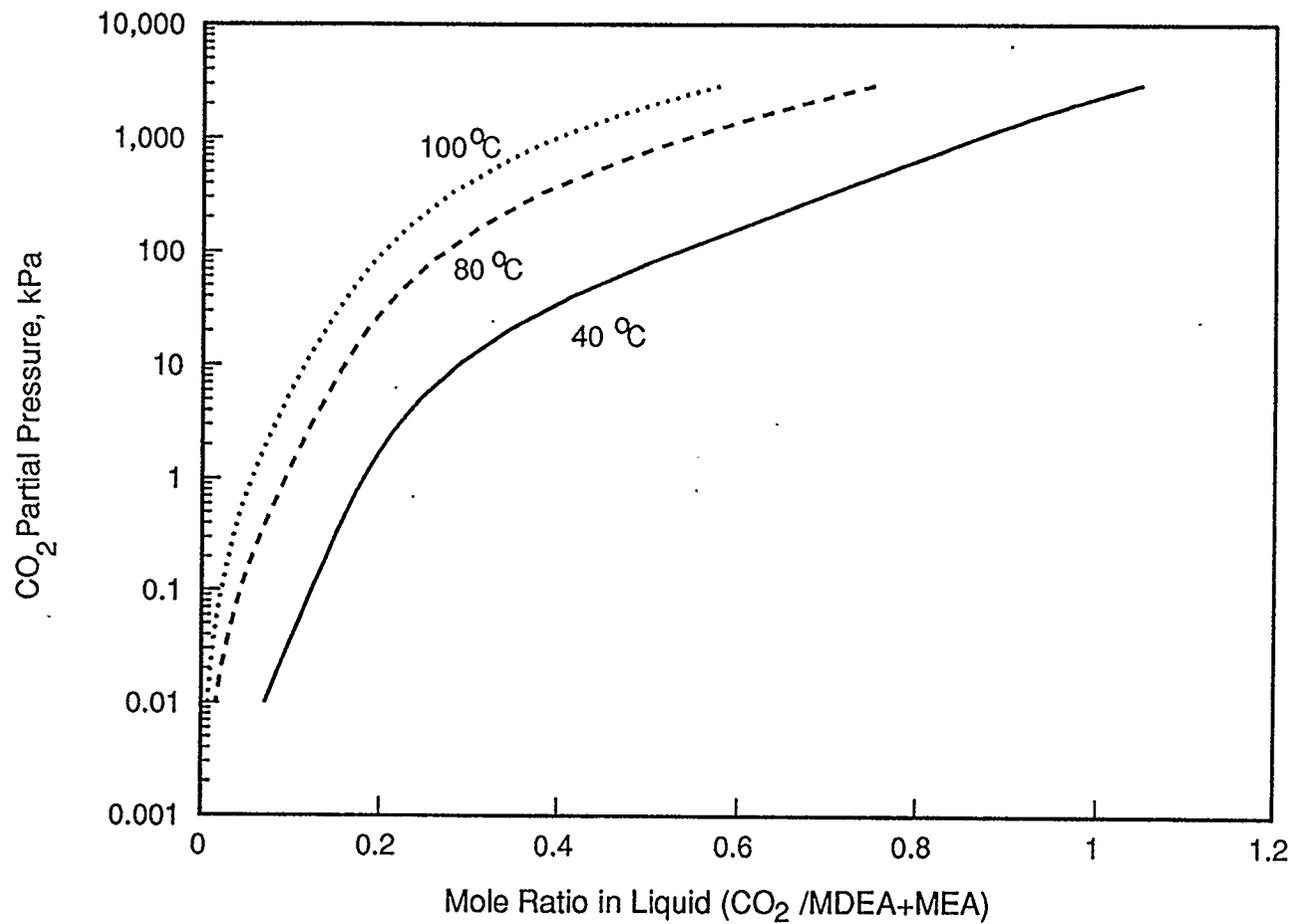


Fig. 5.9 Predicted solubility of CO₂ in a 1.64N MEA + 3.36N MDEA solution at varying temperatures

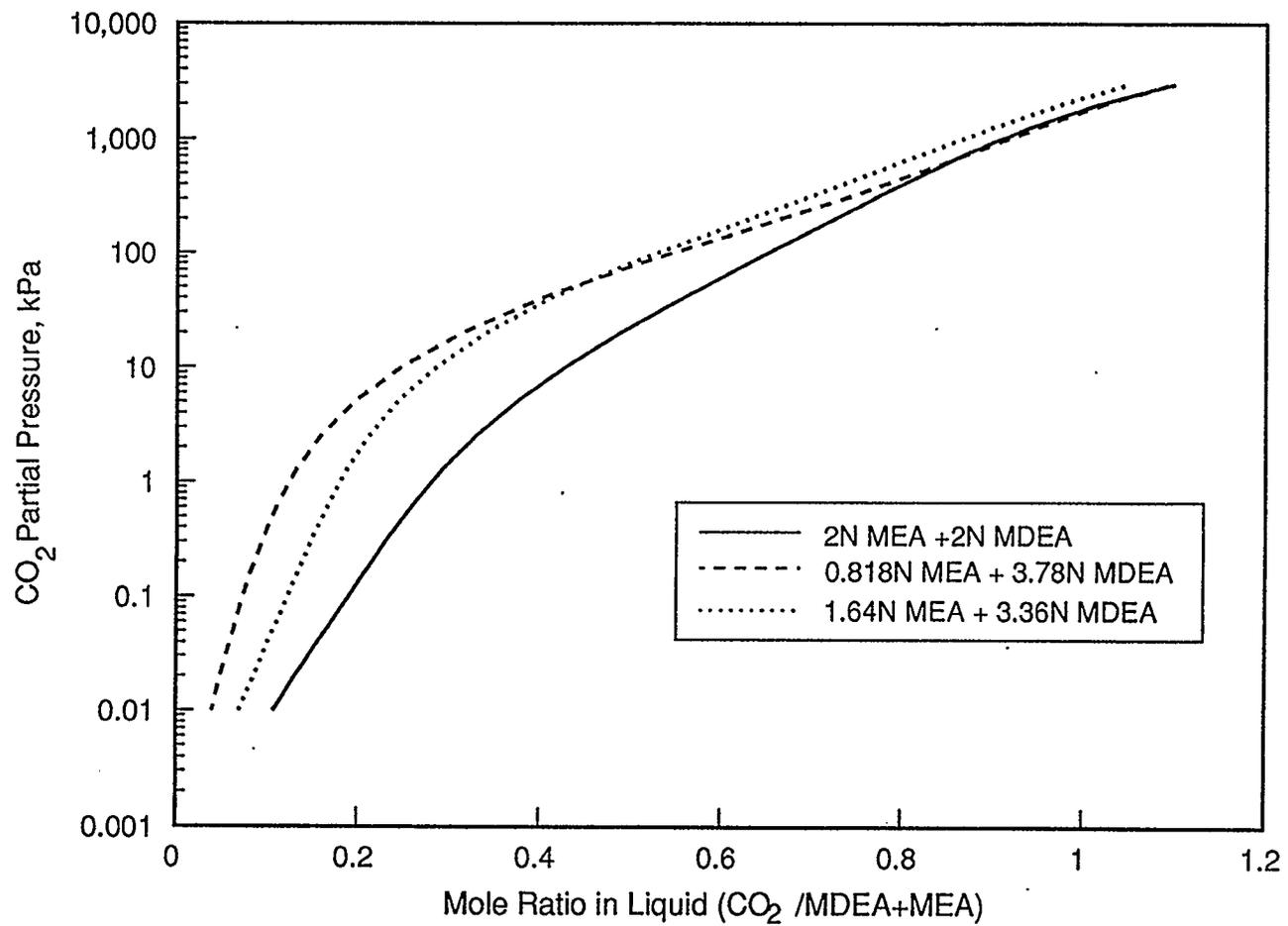


Fig. 5.10 Comparison of the predicted solubility of CO₂ in different blends of MEA and MDEA (Temperature = 40 °C)

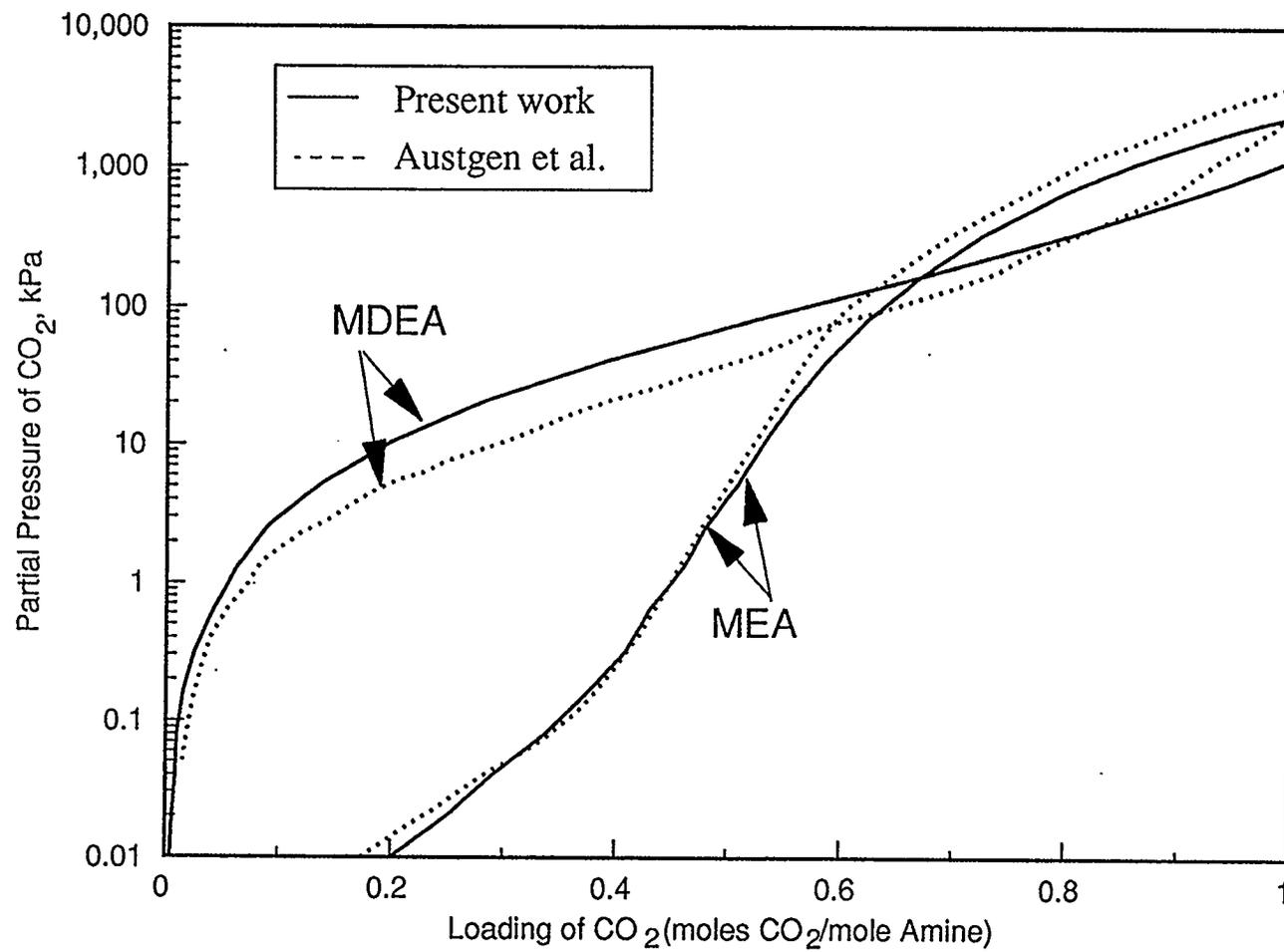


Fig. 5.11 Comparison of the predicted solubility of CO₂ in a 4N MEA and 4N MDEA solution at 40°C with model predictions of Austgen et al., 1991

CO₂ in MDEA exceeds that of MEA. This is due to the fact that MDEA does not form a stable carbamate upon reaction with CO₂. Stoichiometrically two molecules of MEA are required for every mole of CO₂ absorbed. Thus theoretically, it is reasonable to assume that the MEA will be completely converted to products at solution loadings above 0.5 mole of CO₂/mole of MEA. Since the carbamate is stable, it resists reverting to bicarbonate and an increase in the partial pressure of CO₂ results only in physical absorption. However, the physical solubility of CO₂ is very less in a non reacting system. On the other hand, the reaction of MDEA with CO₂ to form bicarbonate results in the conversion of only one amine molecule for each molecule of CO₂ absorbed. A certain amount of carbonate hydrolysis occurs with all amines so that even with MEA the loading may exceed 0.5, particularly at high pressures. Hydrolysis generates free amine which can react with additional CO₂, thus allowing the loading to exceed 0.5. Fig. 5.12 is a similar plot for 4 N MEA and 4 N MDEA at 80°C. The solubility of CO₂ in MDEA surpasses that in MEA at partial pressures above approximately 2000 kPa when the loading is almost 0.8 mol CO₂ /mol amine.

In the case of mixed amines the primary mechanism by which CO₂ is absorbed in the beginning is through reaction with promoter (MEA) to form carbamate of the promoter. As CO₂ loading increases, the ratio of molecular MDEA to promoter increases. Therefore, because of the law of mass action, both promoter and MDEA are seen to significantly affect the solubility of CO₂ at a given partial pressure. Above 0.6N MEA, reversion of carbamate to bicarbonate plays an important role.

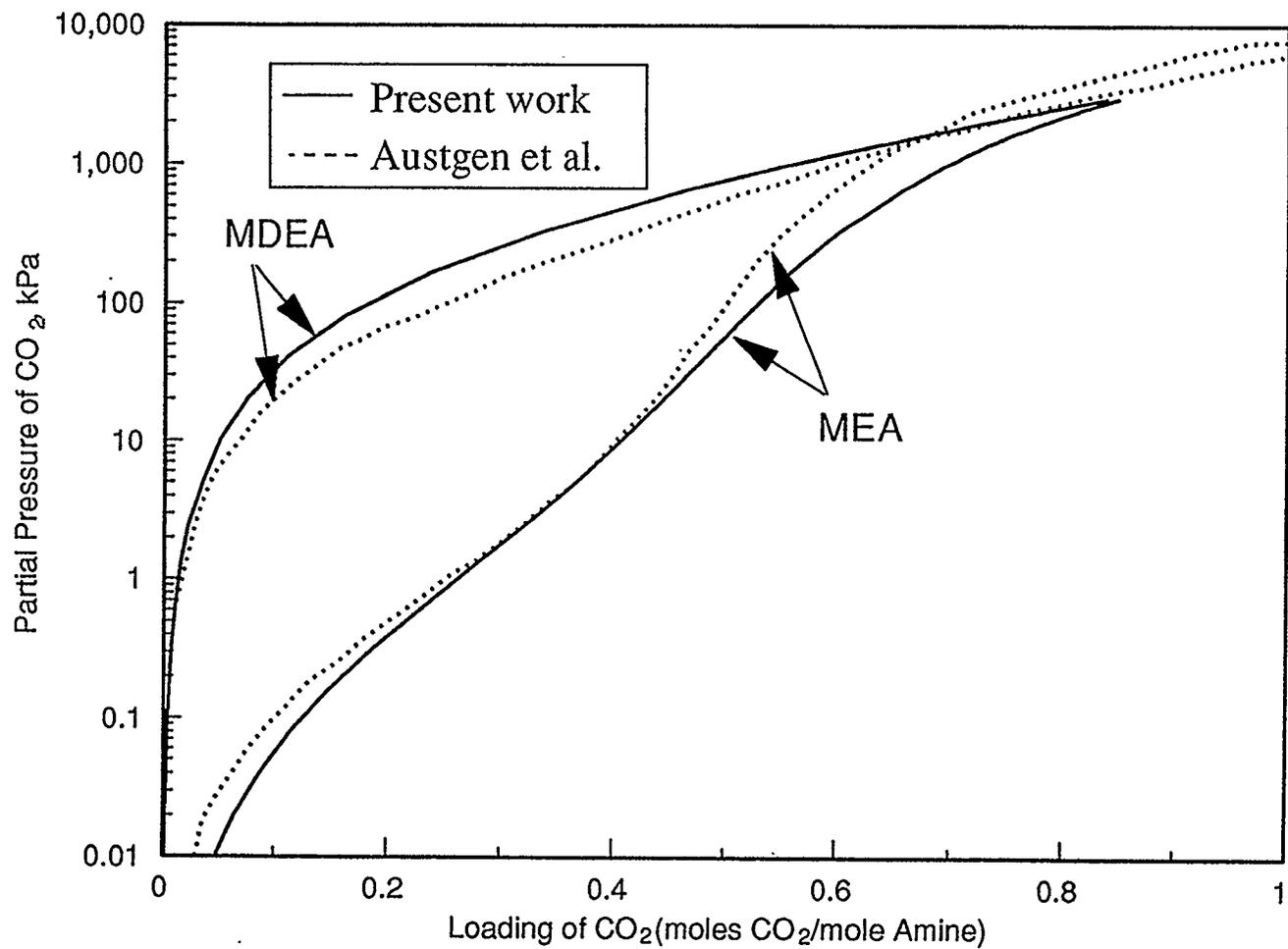


Fig. 5.12 Comparison of the predicted solubility of CO₂ in a 4N MEA and 4N MDEA solution at 80°C with model predictions of Austgen et al., 1991

Fig. 5.13 shows a comparison of the predicted solubility of CO_2 in a 2N MEA + 2N MDEA solution at 40°C with model predictions and experimental data of Austgen et al., 1991. Austgen's model predicts very well at low to moderate partial pressures of CO_2 (0.01 - 20 kPa). However the present model predictions are seen to agree quite well with experimental data at all ranges of partial pressure of the acid gas.

Plots for the species in the liquid phase are useful in analysis of the carbonated amine solution. These plots illustrate trends in the relative concentrations of the ionic and molecular species at equilibrium in the liquid phase. A speciation plot for the carbonated aqueous blend 3N MDEA and 1N MEA at 40°C has been plotted in Fig. 5.14. This plot also shows the pattern of the reaction of CO_2 with various other species in the solution as a function of its loading. At very low loadings, CO_2 mainly reacts with the primary amine MEA to form the carbamate of MEA. At higher loadings, the concentration of carbamate does not vary significantly while additionally absorbed CO_2 reacts primarily to form bicarbonate. At still higher loadings, the carbamate partially reverts due to the backward reaction favoured at increased concentration of the product (carbamate). At the same time, the concentration of bicarbonate further increases.

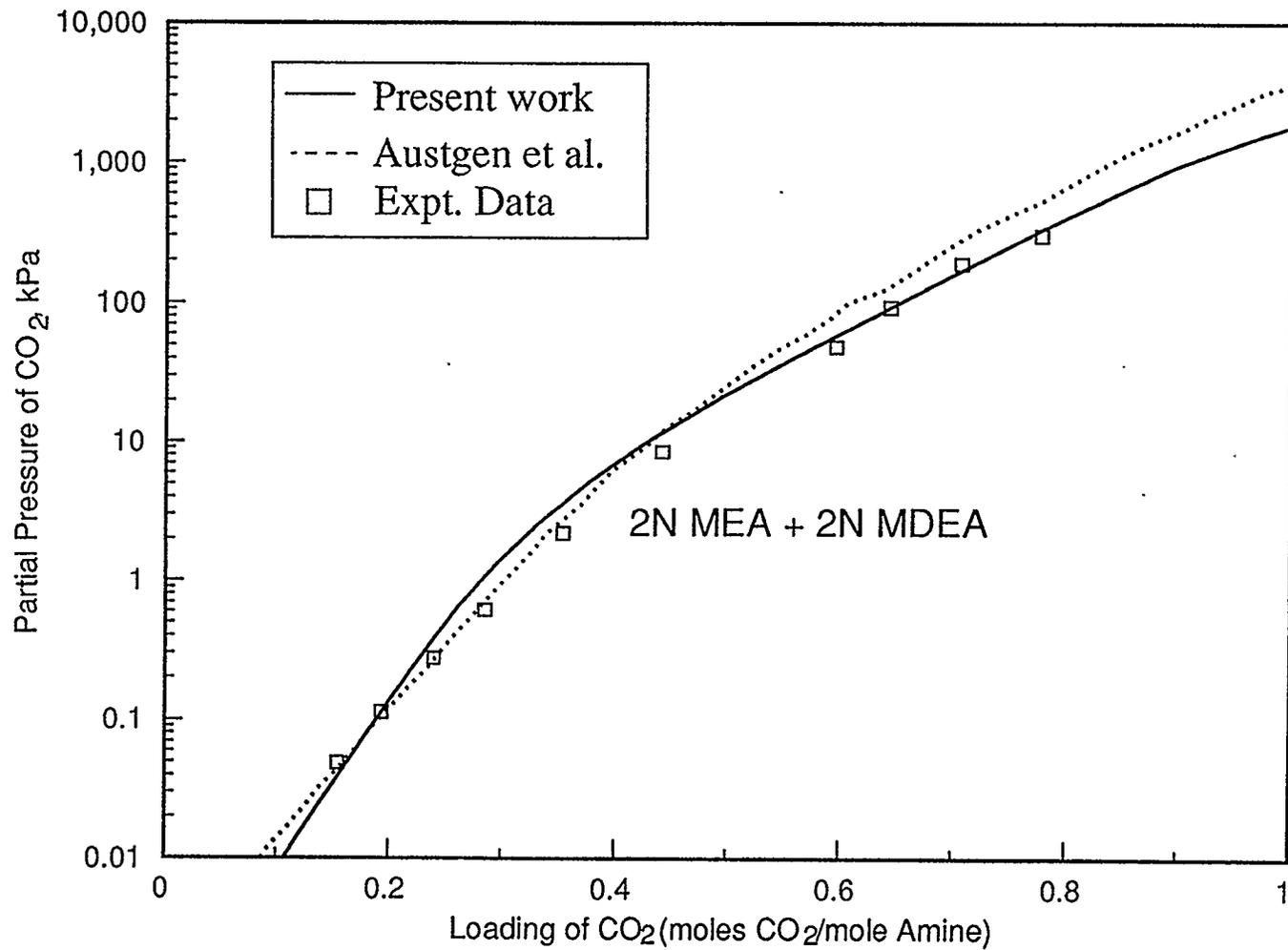


Fig. 5.13 Comparison of the predicted solubility of CO₂ in a 2N MEA + 2N MDEA solution at 40°C with model predictions and expt. data of Austgen et al., 1991

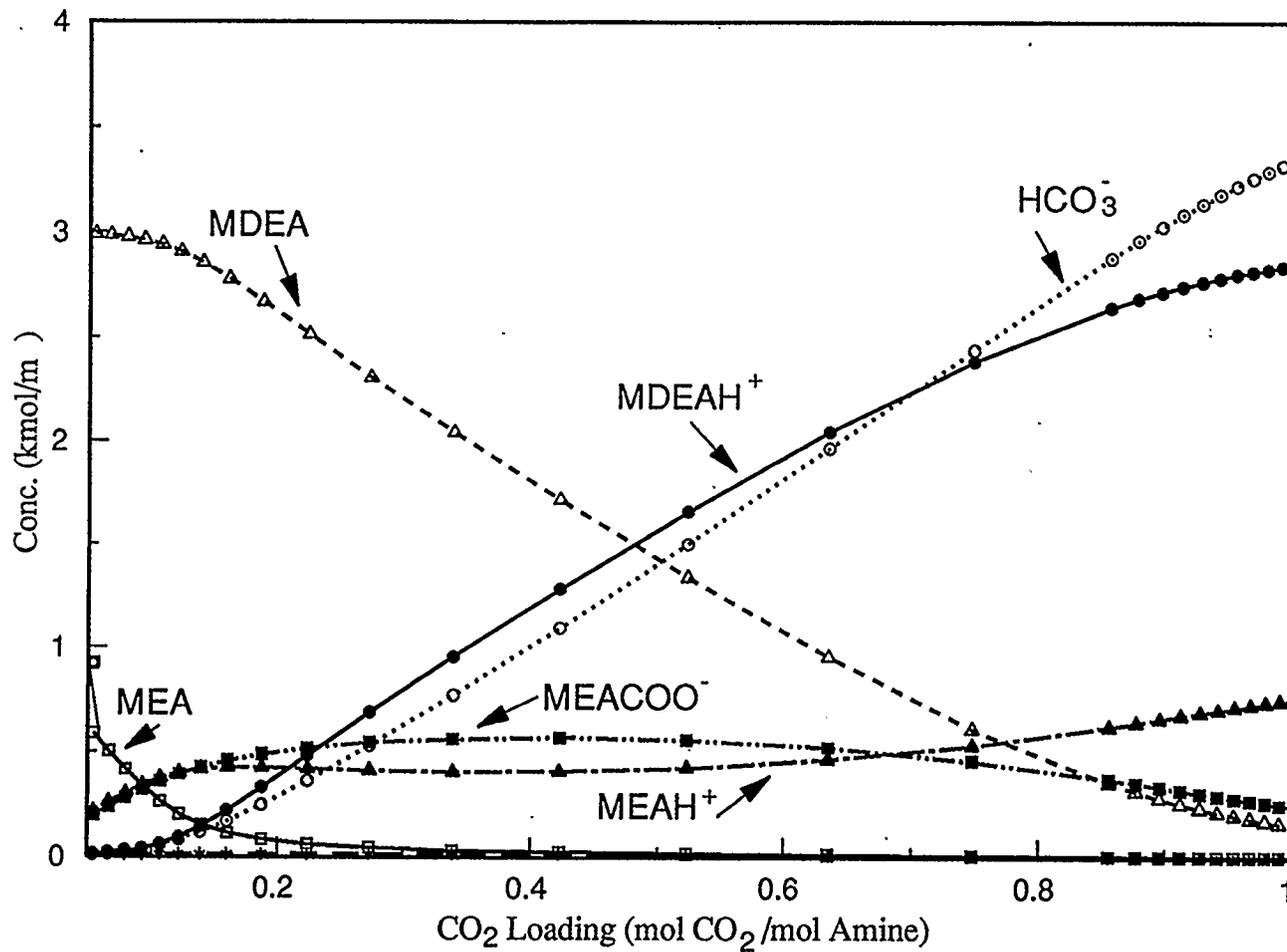


Fig. 5.14 Liquid-phase concentrations of a CO₂ loaded 3M MDEA
1M MEA aqueous mixture at 40°C.

CHAPTER 6

Conclusions and Recommendations

Conclusions

The following can be concluded from this study :

- ▶ A mixture of MEA and MDEA has vastly improved absorption characteristics and regeneration qualities. The enhancement of absorption rates can be attributed to the "shuttle-mechanism" (Astarita et al., 1981).

- ▶ A blend of 5% (by wt.) MEA and 45% (by wt.) MDEA showed the best absorption and stripping qualities.

- ▶ MEA has excellent absorption characteristics and is suitable for use in CO₂ absorption from gas mixtures, but the heat duty in the reboiler is too large to strip the carbonated amine solution and regenerate the solvent for further use.

- ▶ MDEA does not react fast with CO₂, but carbonated solutions of MDEA are very easy to strip with the expense of very less energy in the regenerator.

- ▶ Solubility of CO₂ in blends of MEA and MDEA can be accurately predicted by the model presented. Ionic concentrations of various species at different loadings of the

carbonated amine mixture can also be precisely obtained.

► By using a blend of MEA and MDEA, bulk removal of CO₂ is caused at the bottom of the column by MDEA, whereas absorption of CO₂ is caused by MEA at the top of the column. This is because MEA entering the system at the top can absorb CO₂ quite efficiently even at low partial pressures of the acid gas in the gas stream leaving the system.

Recommendations

A few recommendations can be made towards improving the existing experimental set-up, and the study of CO₂ removal by using blends of amines in general :

► More sampling points in the system could help in obtaining a better concentration profile in the column. Provision of gas sampling points along the absorber would give an improved picture of CO₂ absorption characteristics. This is because an exact calculation of the partial pressure drop of CO₂ in the column could be then be obtained.

► The experimental set-up should be made more flexible in terms of handling a wider range of process parameters like amine flow rate and gas flow rate.

► A rigorous modelling of the absorption and stripping columns for mixed amine use is required. Since the combinations of blends of amines is infinite, such a model would provide increased confidence in the data obtained as well as prove to be an important tool in extrapolation outside the range of actual experiments. But, for this purpose, it is essential to determine local mass transfer coefficients and fundamental physical properties of the system precisely.

REFERENCES

- Albrecht, J.J., "*Modelling Identification and Multivariable Control of an Absorption-Desorption System*", Ph.D. Thesis, Imperial College, London, (1977).
- Al-Ghawas, Hani A., Sandall, Orville C., "*Modelling the Simultaneous Transport of Two Acid Gases in Tertiary Amines with Reversible Reactions*", Sep. Sci. and Tech., 23(12&13), 1523-1540, (1988).
- Al-Ghawas, Hani A. and Sandall, Orville C., "*Simultaneous Absorption of Carbon-dioxide, Carbonyl Sulfide and Hydrogen Sulfide in Aqueous Methyl-diethanolamine*", Chem. Eng. Sci., Vol. 46, No. 2, 665-676, (1991).
- Astarita, G., "*The Influence of Carbonation Ratio and Total Amine Concentration on CO₂ Absorption in Aqueous Monoethanolamine Solutions*", Chem. Eng. Sci., 19, 95, (1964).
- Astarita, G., Savage, D.W., Bisio, A., "*Gas Treating with Chemical Solvents*", Wiley Interscience, New York, USA, 53, (1983).
- Astarita, G. and Savage, W.S., "*Gas Absorption and Desorption with Reversible Instantaneous Chemical Reaction*", Chem. Eng. Sci., Vol. 35, 1755-1764, (1980).
- Astarita, G. and Savage, W.S., "*Theory of Chemical Desorption*", Chem. Eng. Sci., Vol. 35, 649-656, (1990).
- Atwood, K., Arnold, M.R., Kindrick, R.C., "*Equilibria for the System, Ethanolamines-H₂S - Water*", Ind. Eng. Chem., 49 (7), pp 1439, (1957).
- Austgen, D.M., Rochelle, G.T., Peng, X. and Chen, C.C., "*Model of Vapour-Liquid Equilibrium for Aqueous Acid Gas-Alkolanolamine Systems Using the Electrolyte-NRTL Equation*", Ind. Eng. Chem. Res., Vol. 28, No. 7, pp 1060-1073, (1989).
- Austgen, D.M., Rochelle, G.T., and Chen, C.C., "*Model of Vapour-Liquid Equilibrium for Aqueous Acid Gas-Alkolanolamine Systems. 2. Representation of H₂S and CO₂ Solubility in Aqueous Mixtures of MDEA with MEA or DEA*", Ind. Eng. Chem. Res., Vol. 30, No. 3, pp 543-555, (1991).

- Ball, F.X., Furst, W., Renon, R.H., "An NRTL Model for Representation and Prediction of Deviation from Ideality in Electrolyte Solutions Compared to the Models of Chen (1982) and Pitzer (1973)", A.I.Ch.E. J., 31 (3), 392, (1985).
- Benitez-Garcia, Javier., Ruiz-Ibanez, Gabriel., Al-Ghawas, Hani A., Sandall, Orville C., "On the Effect of Basicity on the Kinetics of CO₂ Absorption in Tertiary Amines", Chem. Eng. Sci., Vol.46, No.11, 2927-2931, (1991).
- Beutier, D., Renon, H., "Representation of NH₃-H₂S-H₂O, NH₃-CO₂-H₂O and NH₃-SO₂-H₂O Vapor-Liquid Equilibria", Ind. Engng. Chem. Proc. Des. Dev., 17 (3), 220, (1978).
- Blauwhoff, P.M.M., Versteeg, G.F., Van Swaaij, W.P.M., "A Study on the Reaction Between CO₂ and Alkanolamines in Aqueous Solutions", Chem. Eng. Sci., Vol.39, No.2, 207-225, (1984).
- Bontozoglou, Vasilis and Karabelas, Anastasios J., "Numerical Calculation of Simultaneous Absorption of H₂S and CO₂ in Aqueous Hydroxide Solutions", Ind. Eng. Chem. Res., Vol. 30, No. 12, (1991).
- Bosch, H., Versteeg, G.F., Van Swaaij, W.P.M., "Gas-Liquid Mass Transfer with Parallel Reversible Reactions-II. Absorption of CO₂ into Amine-Promoted Carbonate Solutions", Chem. Eng. Sci., Vol.44, No.11, 2735-2743, (1989).
- Bosch, H., Versteeg, G.F., Van Swaaij, W.P.M., "Gas-Liquid Mass Transfer with Parallel Reversible Reactions-III. Absorption of CO₂ into Solutions of Blends of Amines", Chem. Eng. Sci., Vol.44, No.11, 2745-2750, (1989).
- Bosch, H., Versteeg, G.F., Van Swaaij, W.P.M., "Kinetics of the Reaction of CO₂ with the Sterically Hindered Amine 2-AMINO-2-METHYLPROPANOL at 298 K", Chem. Eng. Sci., Vol.45, No.5, 1167-1173, (1990).
- Bottoms, R.R., "Organic Bases for Gas Purification", Ind. Eng. Chem., 23, 501 (1983).
- Bradley, K.J., Andre, H., "A Dynamic Analysis of a Packed Gas Absorber", Can. J. Chem. Eng., 50, pp 528, (1972).
- Bright, R.L. and Leister, D.A., "Gas Treaters Need Clean Amines", Hydrocarbon Processing, Dec., pp 47-48, (1987).

- Bromley, L.A., "Approximate Individual Ion Values of B in Extended Debye-Huckel Theory for Uni-Univalent Aqueous Solutions at 293.15°K", J. Chem. Thermodyn., 4, 669, (1972).
- Bromley, L.A., "Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions", A.I.Ch.E. J., 19 (2), pp 313, (1973).
- Butwell, Kenneth F., "How to Maintain Effective MEA Solutions", Nat. Gas Proc., Vol. 47, No. 4, (1968).
- Chakma, A. and Meisen, A., "Improved Kent-Eisenberg Model for Predicting CO_2 Solubilities in Aqueous Diethanolamine [DEA] Solutions", Gas Separation and Purification, Vol.4, March, pp 37-40, (1990).
- Chakravarty, T., "Solubility Calculation for Acid Gases in Amine Blends", Ph.D. Dissertation, Clarkson College, (1985).
- Chakravarty, T., Phukan, U.K. and Weiland, R.H., "Reaction of Acid Gases with Mixtures of Amines", Chem. Eng. Prog., Vol. 81, pp 32, (1985).
- Chen, C.C., Britt, H.I., Boston, J.F., Evans, L.B., "Local Composition Model for Excess Gibbs Energy of Electrolyte Systems, Part 1 : Single Solvent, Single Completely Dissociated Electrolyte Systems", A.I.Ch.E. J., 28 (4), pp 588, (1982).
- Chen, C.C., Evans, L.B., "A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems", A.I.Ch.E. J., 32 (3), pp 444, (1986).
- Christensen, C., Sander, B., Fredenslund, A., Rasmussen, P., "Towards the Extension of Unifac to Mixtures with Electrolytes", Fluid Phase Equilib., 13, pp 297, (1983).
- Cornelisse, R., Beenackers, A.A.C.M., Van Beckum, F.P.H., Van Swaaij, W.P.M., "Numerical Calculation of Simultaneous Mass Transfer of Two Gases Accompanied by Complex Reversible Reactions", Chem. Eng. Sci., Vol. 35, pp 1245, (1980).
- Cornelissen, A.E., "Simulation of Absorption of H_2S and CO_2 into Aqueous Alkanolamines in Tray and Packed Columns", Trans. IChemE, Vol. 58, (1980).
- Cox, Lisa M., Weiland, Ralph H., Dingman, John C., " CO_2 Removal Using Blended Amines", Presented at Spring National Meeting of AIChE, New Orleans, LA, March 29-April 2, (1992).

- Critchfield, J.E., Rochelle, G.T., "*CO₂ Absorption into Aqueous MDEA and MDEA/MEA Solutions*", Presented at the AIChE National Meeting, Houston, TX, American Institute of Chemical Engineers: New York, NY, Paper No. 43e, (1987).
- Cruz, J., Renon, H., "*A New Thermodynamic Representation of Binary Electrolyte Solutions Nonideality in the Whole Range of Concentrations*", A.I.Ch.E. J., 24 (5), pp 817, (1978).
- Danckwerts, P.V., Sharma, M.M., "*The Absorption of Carbon-dioxide into Solutions of Alkalis and Amines (with some notes on Hydrogen Sulphide and Carbonyl Sulphide) - Review Series No. 2*", The Chem. Eng., October (1966).
- Danckwerts, P.V., McNeil, K.M., "*The Absorption of CO₂ into Aqueous Amine Solutions and the Effects of Catalysis*", Trans. Inst. Chem. Eng. (UK), 45, T32, (1983).
- Danckwerts, P.V., "*The Reaction of CO₂ with Ethanolamines*", Chem. Eng. Sci., Vol. 34, 443-446, (1979).
- De-Leye, L., Froment, G.F., "*Rigorous Simulation and Design of Columns for Gas Absorption and Chemical Reaction - I : Packed Columns*", Comput. & Chem. Engng., Vol. 10, No. 5, pp 493, (1986a).
- De-Leye, L., Froment, G.F., "*Rigorous Simulation and Design of Columns for Gas Absorption and Chemical Reaction - II : Plate Columns*", Comput. & Chem. Engng., Vol. 10, No. 5, pp 505, (1986b).
- Deshmukh, R.D. and Mather, A.E., "*A Mathematical Model for Equilibrium Solubility of Hydrogen Sulphide and Carbon dioxide in Aqueous Alkalonamine Solution*", Chem. Eng. Sci., Vol. 36, pp 355-362, (1981).
- Donaldson, T.L., Nguyen, Y.N., "*CO₂ Reaction Kinetics and Transport in Aqueous Amine Membranes*", Ind. Eng. Chem. Fundam., 19, pp 260, (1980).
- Edwards, T.J., Newman, J., Prausnitz, J.M., "*Thermodynamics of Aqueous Solutions Containing Volatile Weak Electrolytes*", A.I.Ch.E., 21 (2), 248, (1975).
- Edwards, T.J., Maurer, G., Newman, J., Prausnitz, J.M., "*Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes*", A.I.Ch.E., 24, 966, (1978).

- Escobilana, German P., Saez, Jorge A., Perez-Correa, Jose R. and Neuburg, Heinz J., "*Behaviour of Absorption/Stripping Columns for the CO₂-MEA System; Modelling and Experiments*", Can. J. Chem. Eng., Vol. 69, 969-977, August (1991).
- Goettler LLoyd A. and Pigford, Robert L., "*Computational Studies of the Simultaneous Chemical Absorption of Two Gases*", AIChE J., Vol. 17, No. 4, July (1971).
- Guggenheim, E.A., "*The Specific Thermodynamic Properties of Aqueous Solutions of Strong Electrolytes*", Phil. Mag., 19, 588, (1935).
- Haimour, N.K., Sandall, O.C., "*Absorption of Carbon Dioxide into Aqueous Methyl-diethanolamine*", Chem. Eng. Sci., Vol. 39, No. 12, 1791-1796, (1984).
- Haimour, N.K., Sandall, O.C., "*Absorption of H₂S into Aqueous Methyl-diethanolamine*", Chem. Engng. Commun., 59, pp 85, (1987).
- Haimour, N.K., Bidarian, A., Sandall, O.C., "*Kinetics of the Reaction Between CO₂ and Methyl-diethanolamine*", Chem. Engng. Sci., 42, pp 1393, (1987).
- Harned, H.S., Owen, B.B., "The Physical Chemistry of Electrolytic Solutions", 2nd ed., Reinhold, New York, (1958).
- Hermes, J.E., Rochelle, G.T., "A Mass Transfer Based Process Model of Acid gas Absorption/Stripping Using Methyl-diethanolamine", Presented at the ACS National Meeting, New Orleans, LA, (1987).
- Hikita, H., Asai, S., Ishikawa, H., Honda, M., "*The Kinetics of Reaction of CO₂ with Monoethanolamine, Diethanolamine and Triethanolamine by a Rapid Mixing Method*", Chem. Eng. J., 13, 7, (1977).
- Hikita, H., Asai, S., Katsu, Y. and Ikuno, S., "*Absorption of CO₂ into Aqueous Monoethanolamine Solutions*", AIChE J., Vol. 25, No. 5, 793-800, (1979).
- Isaacs, E.E., Otto, F.D. and Mather, A.E., "*Solubilities of Mixtures of H₂S and CO₂ in a Monoethanolamine Solution at Low Partial Pressures*", J. Chem. Eng. Data, Vol. 25, No. 2, pp 118-120, (1980).
- Jensen, M.B., Jorgensen, E., Faurholt, C., "*Reactions Between CO₂ and Amino Alcohols I. Monoethanolamine and Diethanolamine*", Acta. Chem. Scand., 8, 1141, (1954).

- Jones, J.H., Froning, H.R., Claytor, E.E., Jr., "*Solubility of Acidic Gases in Aqueous Monoethanolamine*", J. Chem. Engg. Data., 4 (1), pp 82, (1959).
- Jorgensen, E., Faurholt, C., "*Reaction between CO₂ and Amino Alcohols*", Acta. Chem. Scand., 8, pp 1141, (1954).
- Jou, Fang-Yuan., Mather, Alan E., Otto, F.D., "*Solubility of H₂S and CO₂ in Aqueous Methyl-diethanolamine Solutions*", Ind. Eng. Chem. Process Des. Dev., Vol. 21, 539-544, (1982).
- Kent, R.L. and Eisenberg, B., "*Better Data for Amine Treating*", Hydrocarbon Processing, pp 87-90, February (1976).
- Klyamer, S.D., Kolesnikova, T.L., Zhur. Fiz. Khim., 46, 1056, (1972).
- Klyamer, S.D., Kolesnikova, T.L., Rodin, Y.A., Gazov. Promst., 18 (2), 44, (1973).
- Kohl, Arthur L., "*Plate Efficiency with Chemical Reaction - Absorption of Carbon Dioxide in Monoethanolamine Solutions*", AIChE J., Vol. 2, No. 2, 264-270, June (1956).
- Kohl, A.L., Riesenfeld, F.C., "Gas Purification", 3rd ed., Gulf Publishing: Houston, TX, (1979) ; 4th ed. (1985)
- Laddha, S.S., Danckwerts, P.V., "*Reaction of CO₂ with Ethanolamines: Kinetics from Gas-Absorption*", Chem. Eng. Sci., Vol.36, 479-482, (1981).
- Lawson, J.D., Garst, A.W., "*Gas Sweetening Data : Equilibrium Solubility of H₂S and CO₂ in Aqueous Monoethanolamine and Aqueous Diethanolamine Solutions*", J. Chem. Eng. Data, 21 (1), pp 20, (1976).
- Lee, J.I., Otto, F.D. and Mather, A.E., "*Solubility of CO₂ in Aqueous Diethanolamine Solutions at High Pressures*", J. of Chem. Engg. Data, Vol. 17, No. 4, (1972).
- Lee, J.I., Otto F.D. and Mather, A.E., "*The Solubility of Mixtures of Carbondioxide and Hydrogen Sulphide in Aqueous Diethanolamine Solutions*", Can. J. Chem. Eng., Vol. 52, February (1974).
- Lee, J.I., Otto F.D. and Mather, A.E., "*The Solubility of H₂S and CO₂ in Aqueous Monoethanolamine Solutions*", Can. J. Chem. Eng., Vol. 52, December (1974).

- Lee, J.I., Otto F.D. and Mather, A.E., "*The Measurement and Purification of the Solubility of Mixture of Carbon-Dioxide and Hydrogen Sulphide in a 2.5 N Monoethanolamine Solution*", Can. J. Chem. Eng., Vol. 54, pp 214-219, June, (1976).
- Littel R.J., Filmer B., Versteeg G.F. and Swaaij, W.P.M., "*Modelling of Simultaneous Absorption of H^2S and CO_2 in Alkanolamine Solutions : The Influence of Parallel and Consecutive Reversible Reactions and the Coupled Diffusion of Ionic Species*", Chem. Eng. Sci., Vol. 46, No. 9, 2303-2313, (1991).
- Lyudkovskaya, M.A., Leibush, A.G., J. Appld. Chem. (U.S.S.R.), Vol. 22. No. 6, pp 558, (1949).
- Marini, L., Clement, K., Georgakis, C. and Suenson, Martin M., "*Experimental and Theoretical Investigation of an Absorber-Stripper Pilot Plant Under Nonequilibrium Conditions*", Ind. Eng. Chem. Fundam., Vol. 24, 296-301, (1985).
- Mason, J.W., Dodge, B.F., "*Equilibrium Absorption of CO_2 by Solutions of the Ethanolamines*", Trans. A.I.Ch.E., 32, 27, (1936).
- Meissner, H.P., Tester, J.W., "*Activity Coefficients of Strong Electrolytes in Aqueous Solutions*", Ind. Eng. Chem. Process Des. Dev., 11 (1), pp 128, (1972).
- Meissner, H.P., Kusik, C.L., Tester, J.W., "*Activity Coefficients of Strong Electrolytes in Aqueous Solution - Effect of Temperature*", A.I.Ch.E. J., 18 (3), pp 631, (1972).
- Mock, B., Evans, L.B. and Chen, C.C., "*Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems*", AIChE J., Vol. 32, No. 10, 1655-1664, October (1986).
- Muhlbauer, H.G., Monaghan, P.R., "*Sweetening Natural Gas With Ethanolamine Solutions*", Oil & Gas J., 55 (17), 139, (1957).
- Murzin, V.I., Leites, I.L., "*Partial Pressure of CO_2 over its Dilute Solutions in Aqueous 3-azapentane 1,5-diol*", Zhur. Fiz. Khim., 45, 2642, (1971).
- Nasir, P. and Mather, A.E., "*The Measurement and Prediction of the Solubility of Acid Gases in Monoethanolamine Solutions at Low Partial Pressures*", Can. J. Chem. Eng., Vol. 55, pp 715-717, December (1977).

- Pandya, J.D., "Adiabatic Gas Absorption and Stripping with Chemical Reaction in Packed Towers", Chem. Eng. Commun., Vol. 19, 343-361, (1983).
- Pinsent, B.R.W., Pearson, L., Roughton, F.J.W., Trans. Farad. Soc., 52, pp 1512, (1956).
- Pitzer, K.S., "Thermodynamic Electrolytes. I. Theoretical Basis and General Equations", J. Phys. Chem., 77, pp 268, (1973).
- Rangwala, H.A., Morrell, B.R., Mather, A.E., and Otto, F.D., "Absorption of CO₂ into Aqueous Tertiary Amine/MEA Solutions", Can. J. of Chem. Eng., Vol. 70, (1992).
- Reed, R.M., Wood, W.R., "Recent Design Development in Amine Gas Purification Plants", Trans. A.I.Ch.E., 37, 363, (1941).
- Renon, H., Prausnitz, J.M., "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", A.I.Ch.E. J., 14 (1), 135, (1968).
- Rochelle, G.T., "Research Needs for Acid Gas Kinetics and Equilibria in Alkanolamine Systems", Presented at the 70th Annual Gas Processors Association Convention, San Antonio, March 11-12, (1991).
- Sada, E., Kumazawa, H., Butt, M.A., "Chemical Absorption of CO₂ into Aqueous Solutions of Monoethanolamine", A.I.Ch.E. J., 22, 196, (1976).
- Sada, E., Kumazawa, H., Han, Z.Q., Matsuyama, H., "Chemical Kinetics of the Reaction of Carbon Dioxide with Etahanolamines in Nonaqueous Solvents", AIChE J., Vol.31, No.8, 1297-1303, August (1985).
- Sartori, G., Savage, D.W., "Sterically Hindered Amines for CO₂ Removal from Gases", Ind. Eng. Chem. Fundam., Vol. 22, No. 2, pp 239-249, (1983).
- Sharma, M.M., "Kinetics of Reactions of Carbonyl Sulphide and CO₂ with Amines and Catalysis by Bronsted Bases of the Hydrolysis of COS", Trans. Faraday Soc., 61, pp 681, (1965).
- Sivasubramanian, M.S., Sardar, H., Weiland, R.H., "Simulation of Fully-Integrated Amine Units for Acid Gas Removal", Presented at the AIChE National Meeting, Houston, TX, American Institute of Chemical Engineers, New York, NY, Paper No. 87e, (1985).

- Stewart, Paul B., Munjal, Prem K., Quiring, Frank., "Determination of Carbon Dioxide in Aqueous Solutions Under Pressure", Analytical Chemistry, Vol.41, No.12, October (1969).
- Suchak, N.J., Jethani, K.R., Joshi, J.B., "Modelling and Simulation of NO_x in Pilot-Scale Packed Columns", AIChE J., Vol. 37, No. 3, 323-339, March (1991).
- Suenson, Martin M., Georgakis, Christos and Evans, Lawrence B., "Steady-State and Dynamic Modelling of a Gas Absorber-Stripper System", Ind. Eng. Chem. Fundam., Vol. 24, 288-295, (1985).
- Tomcej, R.A., "Two Dimensional Model for Acid Gas Mass Transfer in Commercial Amine Contactors", Prepared for Presentation at the AIChE Spring National Meeting, March 29-April 2, (1992).
- Tomcej R.A., "Rate Based Model for Industrial Gas Sweetening Operations", Prepared for Presentation at the 41st Annual Canadian Chemical Engineering Conference, Vancouver, B.C., October 6-9, (1991).
- Tontiwachwuthikul, P., Pintola, T., Meisen, A. and Lim, C.J., "Modelling of CO_2 Absorbers Using a Sterically Hindered Amine", Prepared for Presentation at Canadian Chemical Engg. Conference, (1991).
- Tontiwachwuthikul, P., Meisen, A., Lim, C.J., " CO_2 Absorption by NaOH, Monoethanolamine and 2-Amino-2-Methyl-1-Propanol Solutions in a Packed Column", Chem. Eng. Sci., Vol. 47, No. 2, pp 381, (1992).
- Trass, Olev., Weiland, R.H., "Absorption of Carbon Dioxide in Ethylenediamine Solutions. II. Pilot Plant Study of Absorption and Regeneration", Can. J. of Chem. Eng., Vol.49, 773-781, (1971).
- Van Krevlen, D.W., Hofstijzer, P.J., Huntjens, F.J., "Composition and Vapor Pressures of Aqueous Solutions of Ammonia, Carbon Dioxide and Hydrogen Sulfide", Rec. Trav. Chim., 68, 191, (1949).
- Vanichseni, S. "Modelling and Parameter Estimation in the Absorption of CO_2 in Aqueous MEA Solution in a Pilot-Scale Packed Column", Ph.D. Thesis, Imperial College, London, (1977).
- Versteeg, G.F., Van Swaaij, W.P.M., "On Kinetics Between CO_2 and Alkanolamines both in Aqueous and Non-Aqueous Solutions-I. Primary and Secondary Amines", Chem. Eng. Sci., Vol.43, No.3, 573-585, (1988).

- Versteeg, G.F., Van Swaaij, W.P.M., "On the Kinetics Between CO_2 and Alkanolamines both in Aqueous and Non-Aqueous Solutions-II. Tertiary Amines", Chem. Eng. Sci., Vol.43, No.3, 587-591, (1988).
- Versteeg, Geert F., Van Swaaij, W.P.M., "Solubility and Diffusivity of Acid Gases (CO_2 , NO_2) in Aqueous Alkanolamines Solutions", J. Chem. Data, Vol. 33, 29-34, (1988).
- Weiland, R.H., Rawal, M., Rice, R.G., "Stripping of CO_2 from MEA Solutions in a Packed Column", AIChE J., Vol. 28, No. 6, (1982).
- Weiland, R.H., Trass, Olev., "Titrimetric Determination of Acid Gases in Alkali Hydroxides and Amines", Analytical Chemistry, Vol.41, No.12, October (1969).
- Xu, S., Wang, Yi-wei, Otto, Frederick D. and Mather, Alan E., "Rate of Absorption of CO_2 in a Mixed Solvent", Ind. Eng. Chem. Res., Vol. 30, 1213-1217, (1991).
- Xu, Shuo., Otto, D. Fredrick., Mather, Alan E., "Physical Properties of Aqueous AMP Solutions", J. Chem. Engg. Data., Vol. 36, 71-75, (1991).
- Zhang, D., Razzaghi, M., Ng, H.J., "Modelling of Acid Gas Treating with Blended Amines", Presented at Gas Processors Association 72nd Annual Convention, San Antonio, Texas, March 15-17 (1993).

APPENDIX A

Gas Chromatographic Technique

The gas chromatographic technique has been explained in the experimental section. This section describes the equipment and operating conditions as well as the calibration graphs.

Analytical equipment

- ◆ Gas Chromatograph (Model Hewlett Packard Series 5890 A)
- ◆ Integrator (Model HP 3396A, Hewlett Packard)
- ◆ Chromatographic column 6 ft. long
- ◆ Packing material, Tenax GC
- ◆ 20 μ L syringe (Model 7102KN, Hamilton Co.) with 2 μ L fixed needle and Chaney adapter

Operating conditions

The following operating conditions were used to get good resolution and better separation :

- ◆ Carrier gas - Helium
- ◆ Carrier gas flow rate - 30 ml/min.
- ◆ Detector - Thermal conductivity detector
- ◆ Detector port temperature - 300°C
- ◆ Injection port temperature - 280°C
- ◆ Column temperature:

Initial temperature - 35°C ; Initial time - 1 min.

Final temperature - 280°C ; Rate of rise of temp. - 30°C/min

Sample injection

A 20 µL precision syringe (Model 7102KN, Hamilton Co.) fitted with a Chaney adapter and 2 µL needle (Model 7102RN, Hamilton Co.) were used for sample injection. The injected sample size was 0.5 µL. Each analysis took about 35 min., including the cooling down period of the column. Each sample was injected at least three times and the peak areas of the components were averaged. The septum at the injection port was changed after every 20-25 injections to prevent any leakage.

Calibration

The calibration curves as discussed in the experimental section are presented.

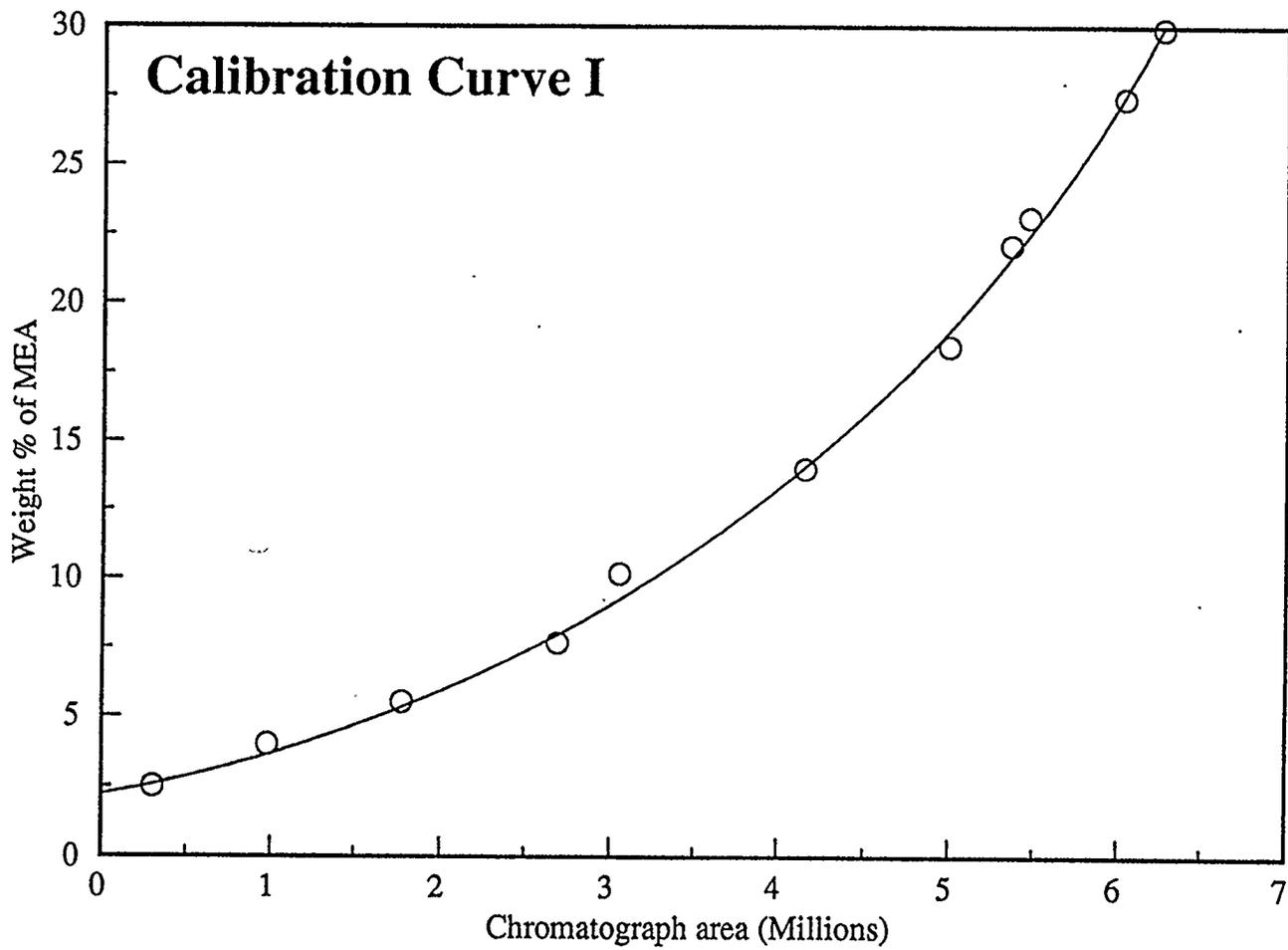


Fig. A.1 Calibration Curve for MEA present as wt. % against Chromatograph area

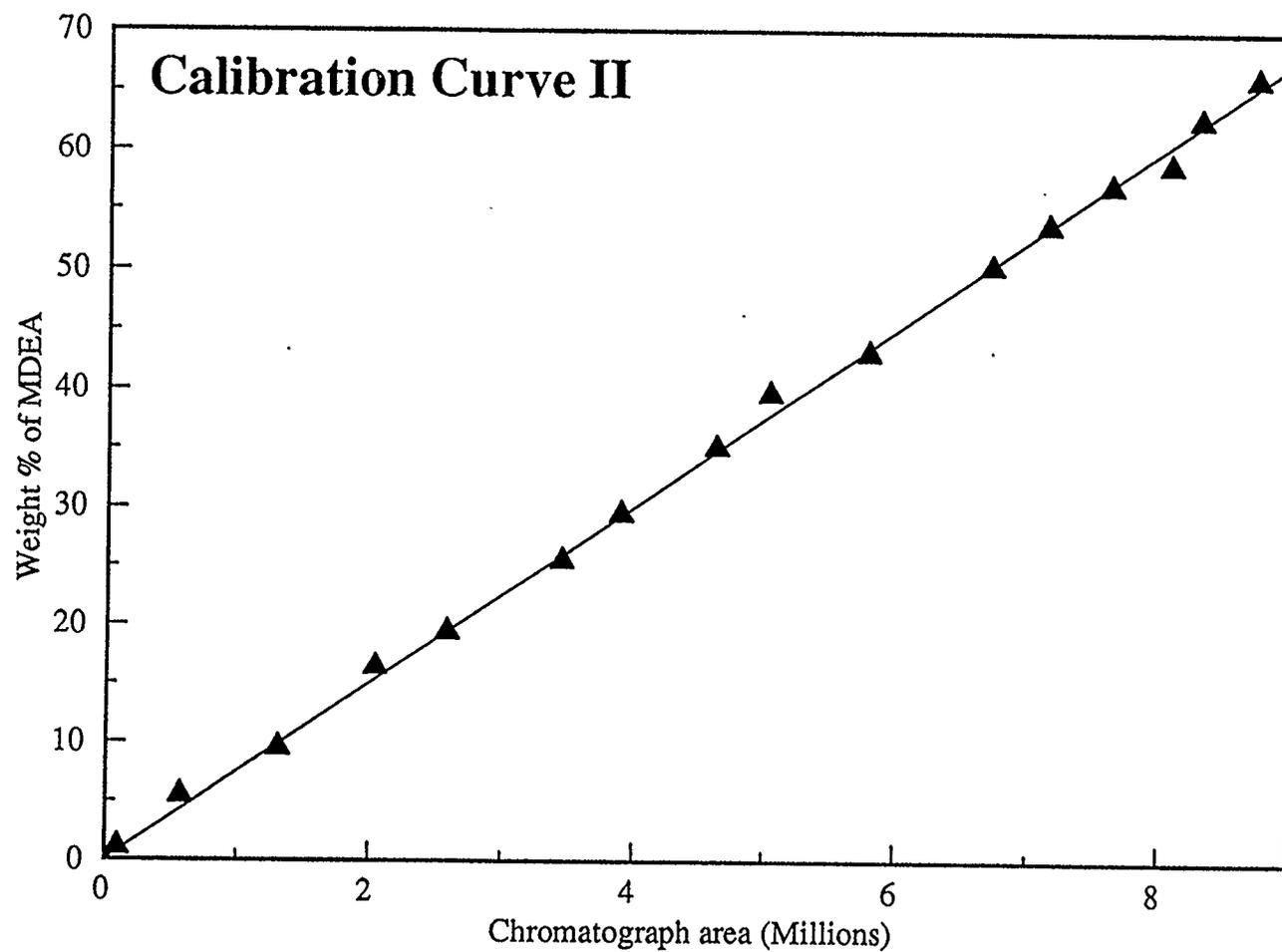


Fig. A.2 Calibration Curve for MDEA present as wt. % against Chromatograph area

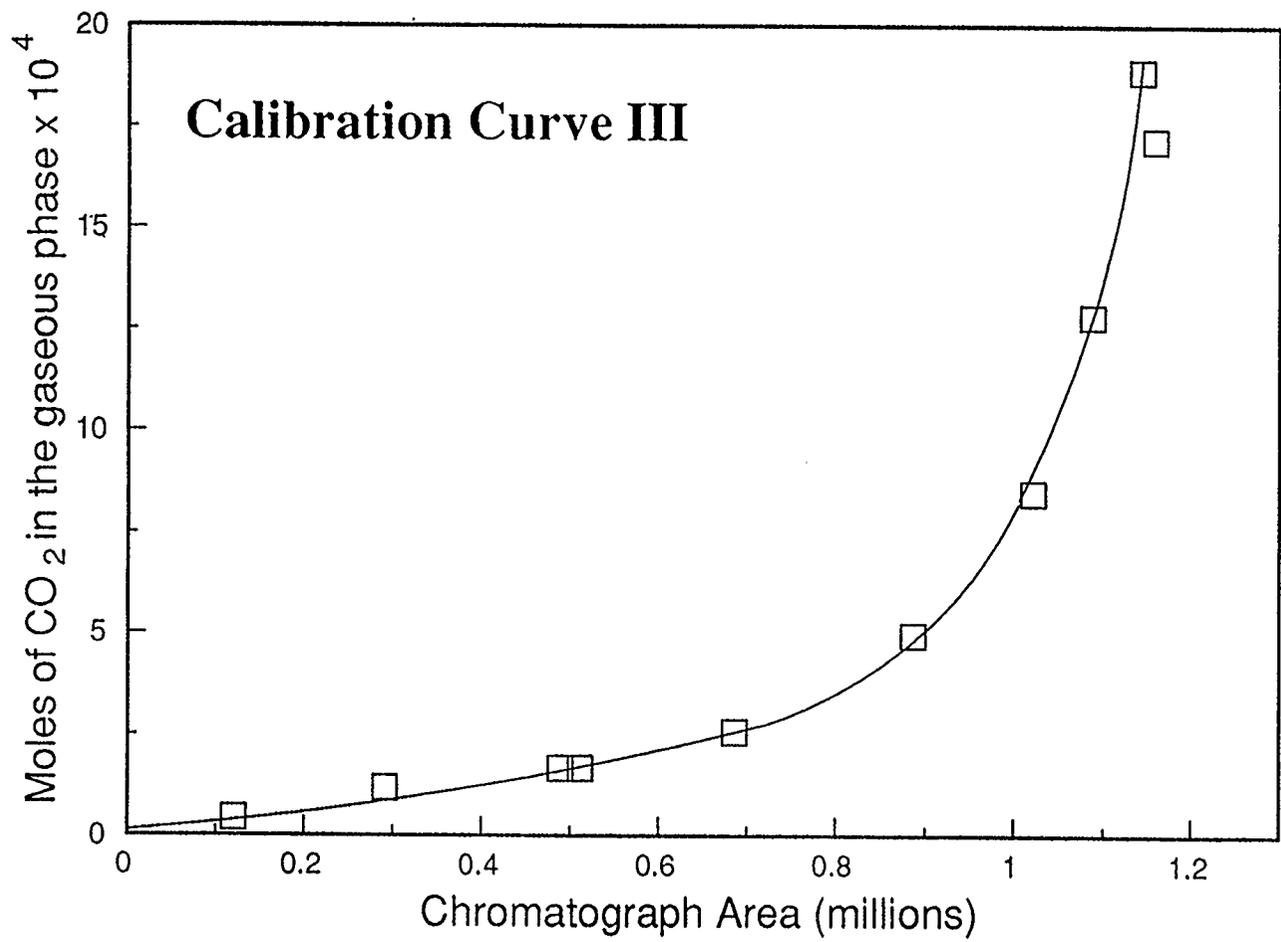


Fig. A.3 Calibration Curve for the Chromatograph Area obtained vs. Moles of CO₂ in the gaseous sample

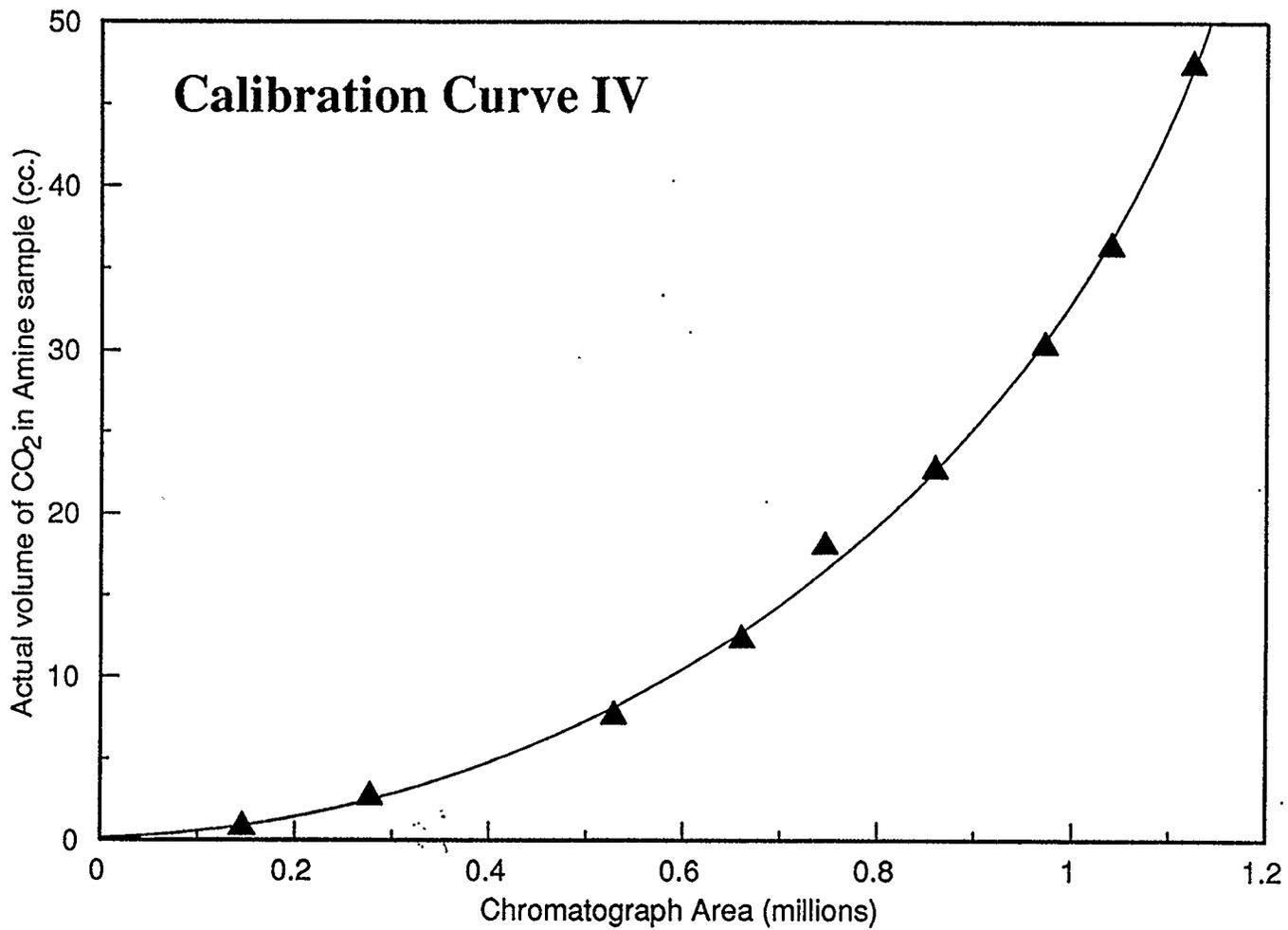


Fig. A.4 Calibration Curve for Chromatograph area obtained vs. the Actual Volume of CO₂ in the Amine Sample

APPENDIX B

Table A.1 Process parameters kept constant in the system for all runs

Stripper Pressure	45 kPa
Absorber Pressure	10 - 11 kPa
Reboiler Level	60%
Cooling Water Flow Rate	35L/min
Steam Pressure Upstream of PCV	340 kPa
Steam Pressure Downstream of PCV (in the reboiler jacket)	225 kPa
Apparent Height of Solvent in the Absorber	1.85 m
Absorber Level (Before introducing gas)	80%
Steam condensate	285 g/min

Table A.2 : Physical Properties of Alkanolamines**

Property	MEA*	MDEA*
Mol. weight	61.09	119.17
Specific gravity, 20/20 °C	1.0179	1.0418
Boiling point, °C		
760 mm Hg	171	247.2
50 mm Hg	100	164
10 mm Hg	69	128
Vapor pressure, mm Hg at 20°C	0.36	0.01
Freezing point, °C	10.5	-21.0
Solubility in water, % by weight at 20°C	Complete	Complete
Absolute Viscosity, g/cm s at 20°C	.241	1.01
Heat of Vaporization, KJ/kg at 1 atm.	825.7	518.7
Approximate cost, \$/kg	1.03	2.14
* Data of Carbide Chemicals Company		
** Table from Kohl and Riesenfeld (Gas Separation and Purification)		

Table A.3 : Heats of Reaction and Absorption of CO₂ in Alkanolamine Solutions

Acid Gas	Amine	Heat of Reaction KJ/kg gas
CO ₂	MEA	1918.9**
CO ₂	MDEA	1104.8

** Calculated for 0.4 mole of CO₂ per mole of MEA.

* Data reproduced from Kohl and Riesenfeld, 1979 (Gas Separation and Purification)

Reference	Temperature range (°C)	[MEA] (mole/l)	k_2 (l/mole.s)	Experimental technique
Hikita et al. (1977)	5.6-35.4	0.0152-0.177	$\log k_2 = 10.99 - 2152/T$	Rapid mixing
Jensen et al. (1954)	18	0.1,0.2	4065	Competition method
Danckwerts and Sharma (1966) Sharma (1964)	18	1.0	5100	Laminar jet
Alvarez-Fuster et al. (1980)	20	0.2-2.02	4300	Wetted wall column
Astarita (1961)	21.5	0.25-2.0	5400	Laminar jet
Clarke (1964)	25	1.6,3.2,4.8	7500	Laminar jet
Donaldson and Nguyen (1980)	25	0.0265-.0828	6000	Facilitated transport
Groothuis (1966)	25	2.0	6500	Stirred cell
Laddha and Danckwerts (1981)	25	0.49-1.71	5720	Stirred cell
Sada et al. (1976)	25	0.245-1.905	8400	Laminar jet
Sada et al. (1976)	25	0.2-1.9	7140	Laminar jet
Sharma (1964) Danckwerts and Sharma (1966)	25	1.0	7600	Laminar jet
Sharma (1964) Danckwerts and Sharma (1966)	35	1.0	9700 13000	Laminar jet
Leder (1971)	80		9.4×10^4	Stirred cell

Table A.4 : Literature data on the reaction between CO₂ and aqueous MEA (Compiled by Blauwhoff et al., 1984)