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EQUILIBRIUM SOLUBILITY OF HYDROGEN SULPHIDE AND CARBON DIOXIDE IN A MIXED SOLVENT

by

Ⓒ Rosalynn J. MacGregor

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Abstract

The solubility of hydrogen sulphide, carbon dioxide, and their mixtures has been measured at 40° and 100°C in a mixed solvent consisting of 20.9 wt% MDEA (methyldiethanolamine), 30.5 wt% sulfolane (tetrahydrothiophene-1,1-dioxide), and 48.6 wt% water. The results have been compared with those for aqueous 2.0 M MDEA and an analogous mixed solvent, containing AMP (2-amino-2-methyl-1-propanol), which are available in the literature.

At solution loadings less than 1 mol acid gas/mol MDEA, the solubility of the acid gas was lower in the mixed solvent than in the corresponding aqueous MDEA solvent; at solution loadings greater than 1 mol acid gas/mol MDEA, the reverse was true. At all loadings and at both temperatures studied, the mixed MDEA solvent absorbed equal or lesser quantities of acid gas than the comparable mixed AMP solvent. However, the shapes of the solubility curves show that the mixed MDEA solvent would be a better choice for certain industrial applications.

These data were used to modify the solubility model of Deshmukh and Mather to account for the mixed solvent effects on the system thermodynamics. Results show that the model is useful as a first approximation in predicting acid gas solubilities; agreement with experiment was generally found to be within ±15%.

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1. Introduction

The removal of acid gases from refinery and natural gases using mixed solvents continues to be of interest. H_2S is toxic and corrosive, and tends to act as a poison to many catalysts. CO_2, while much less reactive than H_2S, is undesirable as well since it dilutes other streams such as natural gas, hydrogen, or refinery fuel gases. In addition effective separation of H_2S and CO_2 from hydrocarbon and hydrogen streams, and from each other, can be profitable in terms of sulphur production for the fertilizer and other industries, and in terms of CO_2 production for enhanced oil recovery schemes.

A common process used for effecting the separation of acid gases from hydrogen or hydrocarbon streams is absorption of the acid gases into a liquid solvent. The absorber in such a process is generally a trayed or packed column in which the solvent contacts the gas countercurrently, absorbing the acid gas components as it travels down the absorber. Sweetened gas exits the top of the absorber, while rich solvent exits the bottom. To strip the acid gases from the rich solvent, the pressure is reduced and heat is applied. This process occurs in a regenerating column. The acid gases emerge from the top of the regenerator, while the lean solvent exits the bottom, to circulate back to the absorber. The solvent thus travels repeatedly around a circuit, absorbing acid gases at low temperatures and high pressures, and desorbing the acid gases at elevated temperatures and low pressures.

Desirable solvent properties include thermal stability, high affinity for acid gases at absorption conditions (and low affinity for hydrocarbons), low vapour pressure to minimize solvent losses in the regenerator, and low heat of absorption, heat capacity, corrosivity, toxicity, and cost.

Aqueous amine solvents such as MEA and DEA (see glossary) have been commonly used in acid gas treating units, possessing all of the above criteria to a certain extent. Because these amine solvents absorb acid gases by chemically reacting with them in aqueous solution, they may be called "chemical solvents." Another class of solvents exists as well: physical solvents. Methanol, sulfolane, and propylene carbonate are examples of physical solvents, which absorb acid gases, including mercaptans and other sulphur compounds, without chemically reacting with them. In strict terms, water may be classified as a physical solvent, but its capacity for acid gas absorption is too low to be of much commercial interest.

Acid gas solvents vary in composition according to the application, since feedstocks and product specifications are variable. For this reason, there exists no single "best" solvent. In recent years, studies of mixed solvents have been of interest. Mixed solvent formulations are aimed at marrying the separate advantages of chemical and physical solvents. Chemical solvents excel in reducing the H_2S and CO_2 content in gas streams to low levels, resulting in "sharp" separation of these acid gases from hydrocarbon streams. This capacity is limited by the stoichiometry of the chemical reactions occurring between the chemical solvent and the two gases, H_2S and CO_2. Some of the advantages of physical solvents are that absorption is not stoichiometrically limited; absorption capacity is roughly proportional to the partial pressure of the acid gas in contact with the solvent.

This work investigates the equilibrium solubilities of H_2S and CO_2 and their mixtures in a mixed solvent consisting of 20.9 % MDEA, 30.5 % sulfolane, and 48.6 % water, on a weight basis. Sulfolane was chosen as the physical solvent because of its stability and good affinity for acid gases; MDEA was chosen because it is a tertiary amine and is thermodynamically and kinetically selective for H_2S in the presence of CO_2. The molar composition of the mixed solvent studied in this work was chosen to correspond with the work of Roberts (1983), who studied the equilibrium solubility of H_2S and CO_2 in a mixed solvent consisting of AMP (2-amino-2-methyl-1-propanol), sulfolane, and water. In addition, the mixed solvents in both studies may be seen as 2.0 M amine solutions, with sulfolane substituted in the place of some of the water (see Table 1.1).

The experimental results are used to modify the solubility model of Deshmukh and Mather (1981) to account for the effects of mixed solvent on the thermodynamics of the system. Good agreement between experimental and modelled data is achieved.

Table 1.1 Compositions of Mixed MDEA and Mixed AMP Solvents

component	wt %	mol. wt.	mol/100g sol'n	mol %
MDEA	20.9	119.16	0.1754	5.61
sulfolane	30.5	120.17	0.2538	8.12
water	48.6	18.016	2.6976	86.27
AMP	16.5	89.141	0.1851	5.61
sulfolane	32.2	120.17	0.2680	8.12
water	51.3	18.016	2.8475	86.27

Mixed MDEA: molality = 2.217 mol MDEA/1000 g (water + sulfolane)

Mixed AMP: molality = 2.217 mol AMP/1000 g (water + sulfolane)

By titration, both solutions are 2.0 M amine solutions, within experimental tolerances.

2. Basic Thermodynamics of Mixed Solvent Systems

By definition, mixed solvents are composed of a mixture of solvent materials; in this work, they are MDEA, the chemical solvent, and sulfolane and water, two physical solvents.

Vapour-liquid equilibria for gases in physical solvents may be described as

$$A_{(g)} = A_{(l)} \qquad (2.1)$$

At equilibrium, the fugacities of molecular species A in both phases are equal:

$$f_A^{\,v} = f_A^{\,l} \qquad (2.2)$$

where $$f_A^{\,v} = \phi_A y_A P \qquad (2.3)$$

and $$f_A^{\,l} = \gamma_A m_A H_A e^{\int_{P^s}^{P} \frac{\bar{V}_A}{RT} dP} \qquad (2.4)$$

The exponential term in (2.4), the Poynting factor, describes the dependence of liquid phase fugacity on pressure, and becomes significant only at high pressures. H, the Henry's constant, is defined

$$H_A = \lim_{m_A \to 0} f_A/m_A \qquad (2.5)$$

Equation (2.2) can be rewritten as

$$\phi_A y_A P = \gamma_A m_A H_A e^{\int_{P^s}^{P} \frac{\bar{V}_A}{RT} dP} \qquad (2.6)$$

Assuming ideal gas and liquid phases,

$$y_A P = m_A H_A \qquad (2.7)$$

Thus, the partial pressure of A is approximately directly proportional to its molality for physical solvents.

Chemical solvents add chemical equilibrium to (2.1):

$$A_{(g)} = A_{(l)} + B = \text{ions} \qquad (2.8)$$

For CO_2 absorption into MDEA, the chemical equilibria are:

$$\mathrm{MDEA} + \mathrm{CO_2} + \text{[illegible]}\mathrm{O} = \mathrm{MDEAH^+} + \mathrm{HCO_3^-} \qquad (2.9)$$

$$MDEA + CO_2 + H_2O = MDEAH^+ + HCO_3^- \qquad (2.9)$$

$$HCO_3^- + H^+ = CO_3^{2-} + 2H^+ \qquad (2.10)$$

MDEA is a tertiary amine; unlike primary and secondary amines, it does not form carbamates with CO_2, which simplifies the thermodynamics of the system.

The H_2S reaction with MDEA may be written

$$H_2S + MDEA = HS^- + MDEAH^+ \qquad (2.11)$$

Reaction (2.10) is fast, while reaction (2.9) occurs slowly and is thus the rate-controlling step in the absorption of CO_2 into solvents containing MDEA. Because reaction (2.11) involves only a proton transfer, it occurs much faster than either reactions (2.9) or (2.10). Because of these kinetics, MDEA exhibits selectivity for H_2S over CO_2; in addition to this kinetic selectivity, MDEA has some thermodynamic selectivity for H_2S absorption relative to CO_2.

The chemical equilibria for reactions (2.9) to (2.11) are dominant at low acid gas loadings; most of the absorbed acid gas will be in ionic form, since the above reactions favour product formation. The acid gas partial pressure will be low, since very little of the absorbed acid gas will be in molecular form, and both sides of equation (2.7) will thus be small.

While chemical forces dominate at low acid gas partial pressures, physical forces become important at high partial pressures, when the chemical solvent has been loaded to its stoichiometric limit, and significant concentrations of molecular acid gas exist in the liquid phase. At intermediate acid gas loadings and partial pressures, both chemical and physical forces are important.

Research into mixed solvents is directed at finding combinations of chemical and physical solvents which can exploit their individual absorbent properties to produce better overall solvents. It is the subject of this work.

3. Survey of the Literature

3.1 Survey of Previous Experimental Work

As has been stated elsewhere (Roberts, 1983), few experimental studies have been reported for mixed solvent systems. Also, temperature and pressure ranges covered in these works have been limited.

There are several published data on non-aqueous mixed solvent systems. Leites et al. (1972) conducted CO_2 solubility studies with solvents containing MEA (2.5 M) and various organic physical solvents at 20° and 30°C. It was found that the CO_2 solubility was greater in aqueous 2.5 M MEA than in any of the mixed solvents at the partial pressures studied ($\leq$100 kPa).

Banasiak (1981) compared the solubility at 30°C of CO_2 in 15 wt% MEA in water with 15 wt% MEA in methanol. Partial pressures ranged from 225 kPa to 325 kPa; the mixed solvent was found to absorb $\leq$25% more acid gas than aqueous MEA.

Measurements of the solubilities of CO_2 and H_2S in binary mixtures of one of the physical solvents, propylene carbonate, N-methyl-2-pyrrolidone, and sulfolane, with one of MEA and DGA were reported by Rivas and Prausnitz (1979). Temperatures ranged from -10° to 100°C, and partial pressures were below 100 kPa. The amine content of the mixed solvents was 5-15 %. As was found by Leites et al. (1972), acid gas solubilities were lower in the nonaqueous mixed solvents at low partial pressures than in aqueous MEA;

however, the MEA-NMP mixture absorbed more acid gas than did pure NMP. PC-NMP mixtures had lower capacities for acid gases, which was attributed to reaction between propylene carbonate and N-methyl-2-pyrrolidone to produce a glycol carbonate, thus reducing the solvent properties of the mixture. The sulfolane-amine solvent mixtures and the physical solvent-DGA mixtures were not discussed. The mixed solvents were found in general to be attractive alternatives to conventional solvents, mainly due to the larger variations in loading as a function of temperature, resulting in lower energy costs for solvent regeneration.

Further work on MEA-NMP and MEA-PC solutions, as well as on DEA-NMP and DEA-PC mixtures, was done by Murrieta-Guevara and Rodriguez (1984). The solubility of CO_2 at 25° and 50°C in these mixtures was measured; H_2S solubility in MEA-NMP at 50°C was also determined. Partial pressures ranged from 20 kPa to 200 kPa, while two chemical solvent concentrations were studied: 5.1 and 14.2 wt%. The investigators found that MEA mixtures absorbed more acid gas than DEA mixtures, and that solubility in MEA-NMP mixtures increased with increasing MEA content, supporting the results of Rivas and Prausnitz (1979). H_2S was more soluble than CO_2 in these mixtures. In contrast to the results of Rivas and Prausnitz, the presence of MEA in propylene carbonate solutions did not significantly influence gas solubility.

Slightly more work has been done on aqueous mixed solvent systems. Woertz (1972) investigated the solubility of CO_2 in various solvent-amine-water solutions at 27°C and over a small range of pressures (432-667 kPa); one data point per solvent mixture was reported. Amines studied were MEA, DEA, and DIPA; several physical solvents were studied, including sulfolane. The concentration of the amines was held constant at 1.5 M, while water content varied between 3 and 10 vol %. Only MEA-water-solvent solutions containing dimethyl formamide, N-methyl-pyrrolidone, or diethylene glycol exhibited CO_2 loadings greater than that for aqueous MEA. Triethylene glycol produced a similar solubility to that for the aqueous solution. Among the physical solvents which inhibited the MEA solubility was sulfolane, in which case the mixed solvent achieved a loading 3 % below that found for the aqueous solvent. For the DEA case, the amine-water-sulfolane system achieved a 7% lower CO_2 loading than for the aqueous solvent; this figure was 13 % when the amine involved was DIPA. No explanation for the apparent inhibitive action of the physical solvents on CO_2 solubility was offered.

The solubility of CO_2 in MEA-water-sulfolane mixtures at 30°C and 0-100 kPa was investigated by Yushko et al. (1973). MEA concentration was held constant at 2.5 M, while the sulfolane content ranged from 0 to 84 wt%. It was found that CO_2 solubility decreased as sulfolane content increased at the low loadings covered in this study. The difference in solubilities decreased at higher pressures.

The trend observed at low pressures by Yushko et al. was also observed by Dymov et al. (1976) for mixtures of MEA, water and one of ethylene glycol and NMP; however, absorptivities remained about the same as for aqueous MEA because the mixed solvents had better regenerability.

The solubilities of H_2S and CO_2 were measured over a wide range of pressures (5 - 3900 kPa for H_2S and 2.4 - 5700 kPa for CO_2) by Isaacs et al. (1977) in a Sulfinol solution. The solution consisted of 40 wt% DIPA, 40 wt% sulfolane, and 20 wt% water, and the solubilities were measured at 40° and 100°C. Comparison of the results with 2.5 M aqueous DIPA showed that the Sulfinol solution (effectively 3.4 M) exhibited higher acid gas solubility than the aqueous solution at high partial pressures of acid gas. A more direct comparison with 3.4 M aqueous DIPA was not made.

Flynn et al. (1981) reported qualitative experimental results comparing the performance of conventional Sulfinol (DIPA-sulfolane-water) to a new Sulfinol formulation (tertiary amine-sulfolane-water). The new Sulfinol exhibited solvent loading characteristics similar to a physical solvent and selectivity for H_2S over CO_2, thermodynamically rather than kinetically controlled. The tertiary amine used in the formulation was not named.

H_2S and CO_2 solubilities at 40° and 100°C in a mixed solvent of 16.5 wt% AMP, 32.2 wt% sulfolane, and 51.3 wt% water were measured by Roberts (1983). The solvent was effectively 2.0 M AMP, so results were compared with those for aqueous 2.0 M AMP to determine the effect of replacing some of the water in the aqueous solvent with sulfolane. The mixed solvent absorbed more acid gas than the aqueous solvent at acid gas loadings above 1 mol/mol amine, and less acid gas than the aqueous solvent at lower acid gas loadings. The difference in solubility between the aqueous and mixed solvents was greater for H_2S than for CO_2. Qualitative behaviour was the same at both temperatures studied.

Byeseda et al. (1985) reported that a series of solvents with absorption properties superior to those of Sulfinol with the same concentration of water have been prepared. These solvents are called Optisol I, II, and III, and their success is purported to be due to the proprietary physical solvents used in the amine-physical solvent-water mixtures. Solubility data for H_2S and CO_2 at 23.9°C and 102 kPa were provided in terms of volume of acid gas absorbed per volume of solvent. The water content was 25 vol %; little other information regarding the solvent compositions was given.

Weichert et al. (1986) reported the development of a hindered amine-organic solvent mixture, called Flexsorb PS, for H_2S and CO_2 removal at moderate to high pressures. In addition to an increased equilibrium capacity for acid gases over that of aqueous MEA, the authors reported that the rate of absorption was greater for Flexsorb PS, due to the molecular structure of the hindered amine. Substantial savings in energy costs were reported, due to lower regeneration heat requirements. No information regarding possible kinetic or thermodynamic selectivity for H_2S in the presence of CO_2 was offered.

Gazzi et al. (1986) reported the development of a process for selective H_2S removal, involving a tertiary amine-organic solvent-water mixture and known as the "Selefining" process. The water content of the solvent is low, such that CO_2 hydration and therefore CO_2 absorption is limited, and high selectivity results. In addition, energy costs for the Selefining process were reported to be at least 46 % lower than those for either aqueous MDEA or Selexol processes performing the same task. Because of the proprietary nature of the solvent, neither its composition nor any equilibrium solubility data were given.

The above references show that mixed solvent systems can be superior to aqueous solvent systems for certain applications. While the presence of physical solvents in the solvents enhances acid gas absorption at high pressures, absorption is decreased at low pressures. Superior regenerability characteristics and decreased steam costs for regeneration are advantages which mixed solvents have over aqueous solvents in general. Data on the solubility of acid gases in mixed solvents systems over wide temperature and pressure ranges is scarce, and new solvent mixtures continue to be developed.

3.2 Survey of Models for Acid Gas Absorption

The earliest models for acid gas absorption were empirical in nature, due to lack of experimental data and computing power. Improvements have gradually been introduced; the models developed recently make fewer assumptions of ideality in both liquid and gas phases, and tend to rely on more fundamental data, such as Henry's constants, ionic dissociation constants, and gas phase fugacity coefficients. Because of this, more recent models are more flexible in terms of the solvent systems and temperature and loading ranges they can deal with.

Van Krevelen et al. (1949) studied ammonia-rich aqueous systems containing H_2S and/or CO_2. Systems lean in ammonia cannot be handled by this model, due to the very restrictive approximations applied. The predictions were made using pseudo-equilibrium constants, which were functions of ionic strength.

Atwood et al. (1957) modelled the absorption of H_2S in MEA, DEA, and TEA solutions. Activity coefficients for the amines were correlated in terms of ionic strength of solution; one curve described all three amines. Due to lack of experimental data, the amine dissociation constants given in the paper could not be considered to be precise. Several additional assumptions were made: salts were completely ionized in the liquid phase; activity coefficients of different ions were equal and independent of temperature; and the concentration of several of the species present in small amounts could be neglected.

The work of Atwood et al. was extended by Klyamer and Kolesnikova (1972) to model CO_2-MEA and CO_2-DEA systems. Results were found to agree with experimental data to within ±20% in terms of CO_2 partial pressures.

The equilibrium solubilities of H_2S and CO_2 in aqueous MDEA were modelled by Yu et al. (1985). The experimental data of Jou et al. (1982) formed the basis for the empirical model, which used a series of algebraic expressions involving equilibrium constants, molar concentrations, and Henry's constants. The resulting empirical model was then applied to mass transfer rate problems; prediction of equilibrium solubility data was reported to fit all available data within ±8%.

Kent and Eisenberg (1976) modelled the solubility of H_2S and CO_2 in aqueous MEA and DEA. None of the liquid phase species was neglected, and ionic equilibrium constants were used instead of empirical relations. The gas phase was assumed to be ideal, and non-idealities in the liquid phase were lumped together in the amine dissociation constant expressions; these were fitted to existing experimental data. Equilibrium constants were expressed in terms of molarities instead of activities. Henry's law was used to relate the concentrations of species found in both phases.

Zitz and Huemer (1982) used regression analysis to estimate Henry's constants and all ionic equilibrium constants as functions of temperature for the CO_2-H_2O-MDEA system.

While Kent and Eisenberg (1976) lumped non-idealities into two equilibrium constants, Zitz and Huemer's method fitted all ionic equilibrium constants and Henry's constants to the experimental data of interest. The temperature-dependence of these constants was expressed in the form ln K = A/T + B, and produced a very good fit of available data; however, the individual values of the various constants did not approach previously published experimental values. For instance, the authors found that the fitted dissociation constant of water was 1.7×10^{-14} over the temperature range 40-100°C; the generally accepted value varies between 2.4×10^{-14} and 4.9×10^{-14}. Thus, the approach taken by Zitz and Huemer is of value in interpolation of available data, but does not appear to represent the details of the system thermodynamics; extrapolation of the data to other solvents, or even extrapolation in temperature or concentration would be risky.

The thermodynamics of several acid gases in equilibrium with water was modelled by Edwards et al. (1975) for the temperature range 0° to 100°C and for ionic strengths to 0.5 molal. In contrast to the Kent and Eisenberg model, liquid phase ionic equilibrium constants were based on activities, and gas phase fugacities were determined using the virial equation of state.

The liquid phase activity coefficients were calculated by means of an extended form of the Debye-Hückel equation:

$$\ln\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+\sqrt{I}} + \sum_{k\neq w}\beta_{ik}m_k \qquad (3.1)$$

In this way, both liquid phase and vapour phase non-idealities were considered. Henry's constants were found as functions of temperature by fitting published data, and the Krichevsky-Kasarnovsky equation was used to describe their dependence on pressure. Interaction parameters (β's) were determined from experimental data and by making some assumptions suggested by Bromley (1972) and Pitzer (1973).

Edwards et al. (1978) extended their previous work to model aqueous acid gas solubilities between 0° and 170°C, and for much more concentrated solutions (ionic strengths to 6 molal). The theory of Pitzer (1973) and Pitzer and Kim (1974) was used for determining solute activity coefficients in the liquid phase. While providing the means to predict the behaviour of more concentrated aqueous solutions, the activity coefficient relations required more parameter evaluation, and slightly more calculation.

Beutier and Renon (1978) modelled systems similar to those modelled by Edwards et al., also using Pitzer's equations; however, Beutier and Renon extended the equation to allow ternary interactions between liquid phase species to be considered. The ternary interaction parameters were evaluated from experimental data, and their inclusion in the model improved the predictions. One drawback was that water must be the solvent used, and that its mole fraction in the liquid phase must be greater than 0.7.

Chen et al. (1979) extended the Pitzer equation, in its modified form, to model the activities of strong electrolyte solutions, particularly potassium carbonate and potassium bicarbonate solutions. The extended form reduces to the standard equation when no weak electrolytes are present in the system.

Ma[illegible]rer (1980) modelled multicomponent acid gas solubilities in water to about 10 or 20 molal and approximate[illegible] 70°C. The Poynting correction was used and fugacity coefficients were calculated from the equation of state by Nakamura et al. (1976). Liquid phase activities were calculated according to Pitzer (1973), and while two-body interactions between all solute species were considered, ternary interactions were neglected. Some of the binary interactions given by Edwards et al. (1978) were changed slightly, based on previously unused data.

Rivas and Prausnitz (1979) modelled solubility behaviour of acid gases in non-aqueous binary mixed solvents. Liquid phase activity coefficients for each solvent were determined from a fit of experimental data, using the two-suffix Margules equation. Vapour phase non-idealities were accounted for by using a virial equation. Henry's constants corresponding to the solvents studied had to be calculated, and a relation from O'Connell and Prausnitz (1964) was used:

$$\ln H_{2,M} = x_1 \ln H_{2,1} + x_3 \ln H_{2,3} - a_{13}x_1x_3 \qquad (3.2)$$

2 = solute; 1, 3 = solvent species

Regression was used to determine the equilibrium constants for the amine-acid gas ionic equilibria in the liquid phase.

Deshmukh and Mather (1981) proposed a rigourous thermodynamic model for the solubility of H_2S and CO_2 in alkanolamine solutions in the range 25-120°C. The extended Debye-Hückel equation used by Edwards et al. (1975) was applied; fugacities of vapour-phase components were calculated using the Peng-Robinson equation of state.

Equilibrium constants are based on activities of species, and two assumptions are made regarding water: its activity in the liquid phase is equal to its mole fraction; and its fugacity in the vapour phase is not a function of pressure. The interaction parameters for use in the extended Debye-Hückel equation determined by Edwards et al. (1975) were not used; no parameters had been determined for the amines and their salts in solution, and thermodynamic data were lacking. Instead, a least squares fit of available experimental data was performed for each amine studied, to determine salting-out parameters for the interactions of interest. Species present in very low concentrations were assumed to interact to a negligible extent with other species. The objective function used in the fitting was the difference between calculated and experimental acid gas partial pressures.

The resulting system of non-linear equations was solved by Brown's method [Brown, (1969), (1973)].

The model of Deshmukh and Mather was modified by Roberts (1983) to model the solubilities of H_2S and CO_2 in a mixed solvent consisting of AMP, sulfolane, and water. Because AMP is a hindered amine and therefore does not form a carbamate ion upon reaction with CO_2 [see Sartori and Savage, (1983)], this equilibrium expression was deleted from the system of non-linear equations to be solved. Again, interaction parameters in the extended Debye-Hückel equation were determined from a least squares fit of experimental data, this time using the objective function

$$\text{Error} = \Sigma|(\ln P_{calc} - \ln P_{expt})| \qquad (3.3)$$

As before, only species present in significant concentrations were assumed to influence activity coefficients. Because the physical solvent sulfolane was present as well as water, Henry's constants were also evaluated from a least squares fit of experimental data. As well, the influence of sulfolane on the dielectric constant of the solvent (used in the calculation of activity coefficients in solution) was accounted for by the use of an empirical expression based on experimental data on sulfolane-water mixtures [Covington and Dickinson, (1973)]. The influence of the mixed solvent on the dissociation constant of AMP, first dissociation of H_2S, and both dissociations of CO_2 were quantified by least squares analyses as well. Equilibrium constants dealing with all other species were set equal to those found in pure water, since these species are present in only very small concentrations.

A modified form of the Deshmukh-Mather model was used by Chakravarty (1985) to model the solubilities of acid gases in amine blends. The interaction parameters in the extended Debye-Hückel equation were refit using a larger data base and the objective function used by Roberts (1983), effectively normalizing the errors over the entire acid gas partial pressure range. Instead of Brown's method, a rearranged system of fewer non-linear equations was solved using a Newton-Raphson algorithm. Chakravarty's interaction parameters were chosen by their influence on pressure predictions; only those parameters which had a significant effect on the predictions were fitted; as well, parameter values were confined to the range -0.1 to +0.1.

Katti and Langfitt (1986) developed a simulator for commercial absorbers based on a mass transfer rate approach. The simulator requires VLE data predictions, and the model of Deshmukh and Mather was applied. The solvent studied was aqueous MDEA; H_2S and CO_2 solubilities were modelled. A separate model was used at low acid gas loadings; the reasons for this were not given. As well, the nonlinear system of equations was solved using a similar modification to that used by Chakravarty (1985). The authors reported a large decrease in CPU time required compared to that required by the Deshmukh-Mather model in its original form, due to these modifications. The interaction parameters and equilibrium constants used were taken from the work of Chakravarty.

Because of its rigour, the Deshmukh-Mather model was the choice of Chakravarty; other models did not have the theoretical basis allowing them the flexibility to be easily adapted to new solvent systems. For the same reason, this model was also chosen by Roberts (1983) and for this work.

4. Experimental Procedure

4.1 Apparatus

The apparatus used to collect the experimental data for this work has been described by Roberts (1983). The apparatus consisted of a closed system in which the gas of interest was circulated and bubbled through the solvent of interest by means of a magnetically driven pump (see Figure 4.1). The solvent was contained in a windowed equilibrium cell, consisting of a Jerguson liquid level gauge with a 250-cm^3 tubular gas reservoir mounted on the top. The temperature of the cell and pump were controlled to within ±0.5°C by means of an air bath. Analogue Heise Bourdon tube gauges (0-400 and 0-1000 psig) were used to measure the cell pressure.

4.2 Preparation for Sampling

After cleaning with distilled water and drying overnight, the cell was rinsed with about 20 ml of the solvent of interest, while nitrogen gas was circulated through the system with the pump running to purge traces of air for ½ - 1 hour. The solvent was then drained and fresh solvent added to the cell to the desired level. Nitrogen gas was again bubbled through the system for 10-15 minutes to remove traces of air from the solvent.

To minimize water loss from the solvent, the procedure to this point was done at room temperature. The pump was

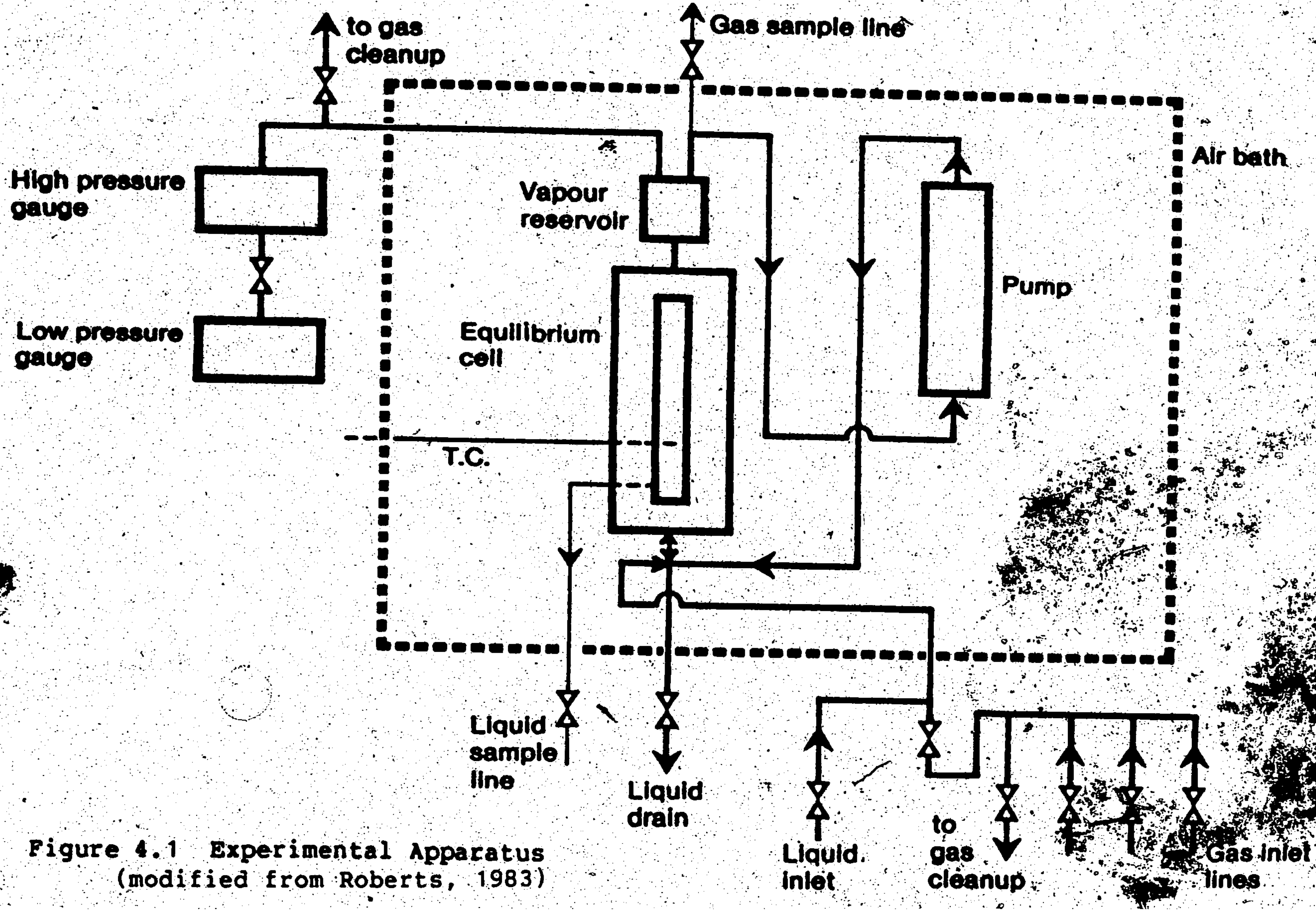

Figure 4.1 Experimental Apparatus
(modified from Roberts, 1983)

then started and the temperature control was turned on. When the cell had reached the temperature of interest, the desired partial pressure of CO_2 and/or H_2S was determined. If it was below approximately 200 kPa, nitrogen gas was fed to the cell to 150-200 kPa, and the acid gas was added afterward. This was done to keep the cell under enough pressure to take gas and liquid samples once equilibrium had been established, and for accurate cell pressure readings to be recorded.

Several data points could be collected using a single solvent cell charge by adding more acid gas to the system after each sample and obtaining a new, higher equilibrium partial pressure of acid gas. In general, equilibrium was approached from lower pressures in this way rather than from higher pressures. To approach equilibrium from higher pressures, acid gas had to be bled from the cell, which would be accompanied by a loss of water from the solvent in the form of water vapour, particularly at higher temperatures. Because of this loss, the solvent composition was checked for amine molarity at each data point, and a maximum of two data points was taken with this approach before the solution was changed.

After the addition of the acid gas to the cell, the pump was allowed to circulate the gas through the solvent overnight to reach equilibrium.

4.3 Sampling

The cell was left circulating overnight to attain equilibrium. Since little change in cell presures was noted after only 2 hours of circulation, equilibrium was certain to have been achieved during this time period.

Once equilibrium had been established, the pump was turned off. Atmospheric pressure, cell pressure, and cell temperature were recorded; the gas phase sample was then taken. This consisted of between 3 and 10 injections of cell gas into the sampling column of a model 5710A Hewlett Packard gas chromatograph (see Appendix I). Generally, between 7 and 30 kPa of cell pressure was lost during gas phase sampling.

The liquid phase sample was taken last. At partial pressures of acid gas greater than 300 kPa, a 40 cm^3 high pressure stainless steel sampling bomb containing 20-25 ml of 1 or 2 M sodium hydroxide (depending on acid gas loading) and fitted with a stainless steel needle valve was used; at lower acid gas partial pressures, a 50 cm^3 Erlenmeyer flask containing 20 ml of 1 M sodium hydroxide and fitted with a rubber septum was used.

The collection vessel was weighed empty to the nearest 0.1 mg on an analytical balance. The caustic solution was added, and the vessel was reweighed. Approximately 2 g of the cell liquid was withdrawn from the cell to purge the sampling line. At low loadings, the end of the sampling line was pushed through the septum and into the caustic solution.

The flask was agitated while the sampling valve was opened to bleed between 2 and 5 g of the cell liquid into the sampling flask, depending on solution loading. At higher loadings, the sampling bomb valve was attached to the sampling valve, and the two valves opened to allow the cell liquid into the sampling bomb. The valves were then closed and the bomb disconnected and agitated to mix the sample with the caustic. The sampling vessel was then reweighed to determine the mass of sample collected. Depending on loading, 2 to 20 g of the vessel contents were withdrawn for analysis.

4.3.1 Analysis for CO_2

A 250 cm^3 Erlenmeyer flask was prepared for CO_2 analysis with 50 ml distilled water and 25 ml 0.5 M $BaCl_2$ solution. An aliquot of sample was added, and the flask stoppered and allowed to stand for 48 to 72 hrs. The barium carbonate precipitate was filtered using #5 Whatman filter paper and a 75 mm glass funnel. During filtration, the funnel was covered with a watchglass to minimize exposure to atmospheric CO_2. The precipitate was washed with distilled water until Duotest pH paper indicated a filtrate pH of 5.9, generally requiring about 300 ml of water. The filter paper and precipitate were then transferred to a 250 cm^3 Erlenmeyer flask, and topped up with distilled water to the 100 ml mark. A magnetic stirring bar was used to shred the filter paper. Two to three drops of methyl orange-xylene cyanol indicator were added and the mixture was titrated to a grey-green endpoint against standard 0.100 N HCl.

A sample calculation for the above procedure is detailed in Appendix II. In the analysis, correction is made for the presence of carbonate in the caustic used; a small correction for the change in pH of pure water during titration is also made, generally amounting to the subtraction of 0.2 to 0.3 cm^3, or 5-10 vol%, from the volume of 0.100 N HCl used.

4.3.2 Analysis for H_2S

A 250 cm^3 Erlenmeyer flask was prepared for H_2S analysis with 100 ml distilled water, 2 to 3 ml glacial acetic acid, and a small stirrer bar. An excess of standard 0.100 N iodine solution, generally 10 to 25 cm^3, was pipetted into the flask. The aliquot sample of basic sulphide solution was then added to the flask while its contents were being stirred; the tip of the pipette was placed directly into the liquid to minimize H_2S losses. This solution was titrated against standard 0.100 N sodium thiosulphate. When the solution was pale yellow, a small amount (approximately 0.5 g) of thyodene indicator was added and the titration continued to a white or clear endpoint.

A sample calculation for the above procedure is detailed in Appendix II.

4.3.3 Amine Analysis

After the cell had reached the temperature of interest, and before any acid gas had been added, a 7 to 10 g sample of solvent was withdrawn for analysis. The sampling bottle was stoppered after sampling to allow the sample to reach room temperature. A 5 cm^3 sample was then taken up with a syringe and weighed to determine solvent density. The solution was then injected into a 250 cm^3 flask containing 50 ml distilled water, and titrated against standard 1.00 N HCl to a pink endpoint to determine amine normality using methyl red indicator.

This check confirmed that the soltion had remained at the target compositon; no dilution had occurred due to residual pockets of rinse water, and evaporation of water from the solution had been insignificant during the nitrogen purge step.

4.4 Laboratory Materials

The aqueous MDEA solution was prepared using practical grade MDEA (97% purity) supplied by Aldrich. The sulfolane was also supplied by Aldrich, and was of 99% purity. Both chemicals were used without purification.

The 1 and 2 M caustic solutions were prepared from distilled water and reagent grade NaOH pellets. The 0.5 M $BaCl_2$ solution was prepared from commercially purified $BaCl_2$ dissolved in distilled water, and filtered before use.

The sodium thiosulphate, iodine, and hydrochloric acid solutions used were certified standard solutions.

The N_2 and CO_2 gases were supplied by Linde and had purities of 99.997% and 99.9% respectively. The H_2S gas was supplied by Matheson and was 99.5% pure.

5. Experimental Results

5.1 Preliminary Results

The solubilities of H_2S and CO_2 in aqueous 2.0 M MDEA were measured at 40°C to verify the laboratory techniques used, and to ensure that analytical equipment was operating correctly. These results are tabulated in Tables 5.1 and 5.2, below, and are compared with those of Jou et al. (1982) in Figures 5.1 and 5.2. The curves on the plots in this chapter are computer-generated spline interpolations of the data points; in Figures 5.1 and 5.2 only the data of Jou et al. (1982) has been interpolated.

Table 5.1 Solubility of CO_2 in 2.0 M Aqueous MDEA at 40°C

α (mol CO_2/mol MDEA)	P_{CO_2} (kPa)
0.124	1.17
0.267	4.15
0.686	48.9
0.969	588.
1.203	3770.

As can be seen from Figures 5.1 and 5.2, good agreement was achieved between the results found in this work and those reported by Jou et al. (1982) for aqueous 2.0 M MDEA.

5.2 Mixed Solvent Results

The mixed solvent studied consisted of 20.9 wt% MDEA (2.0 M), 30.5 wt% sulfolane, and 48.6 wt% water. The particular composition chosen for study had the same mole fraction

Table 5.2 Solubility of H_2S in 2.0 M Aqueous MDEA at 40°C

α (mol H_2S/mol MDEA)	P_{H_2S} (kPa)
0.130	0.52
0.206	0.84
0.236	2.30
0.297	3.18
0.309	3.14
0.316	3.37
0.382	6.11
0.411	5.60
0.442	8.58
0.452	9.55
0.483	13.2
0.485	13.3
0.489	13.5
0.513	17.5
0.519	18.4
0.528	16.5
0.528	14.2
0.590	21.1
0.672	28.4
0.742	39.7
0.774	31.5
0.895	108.
0.975	145.
1.003	168.
1.051	157.
1.311	630.
1.725	1600.

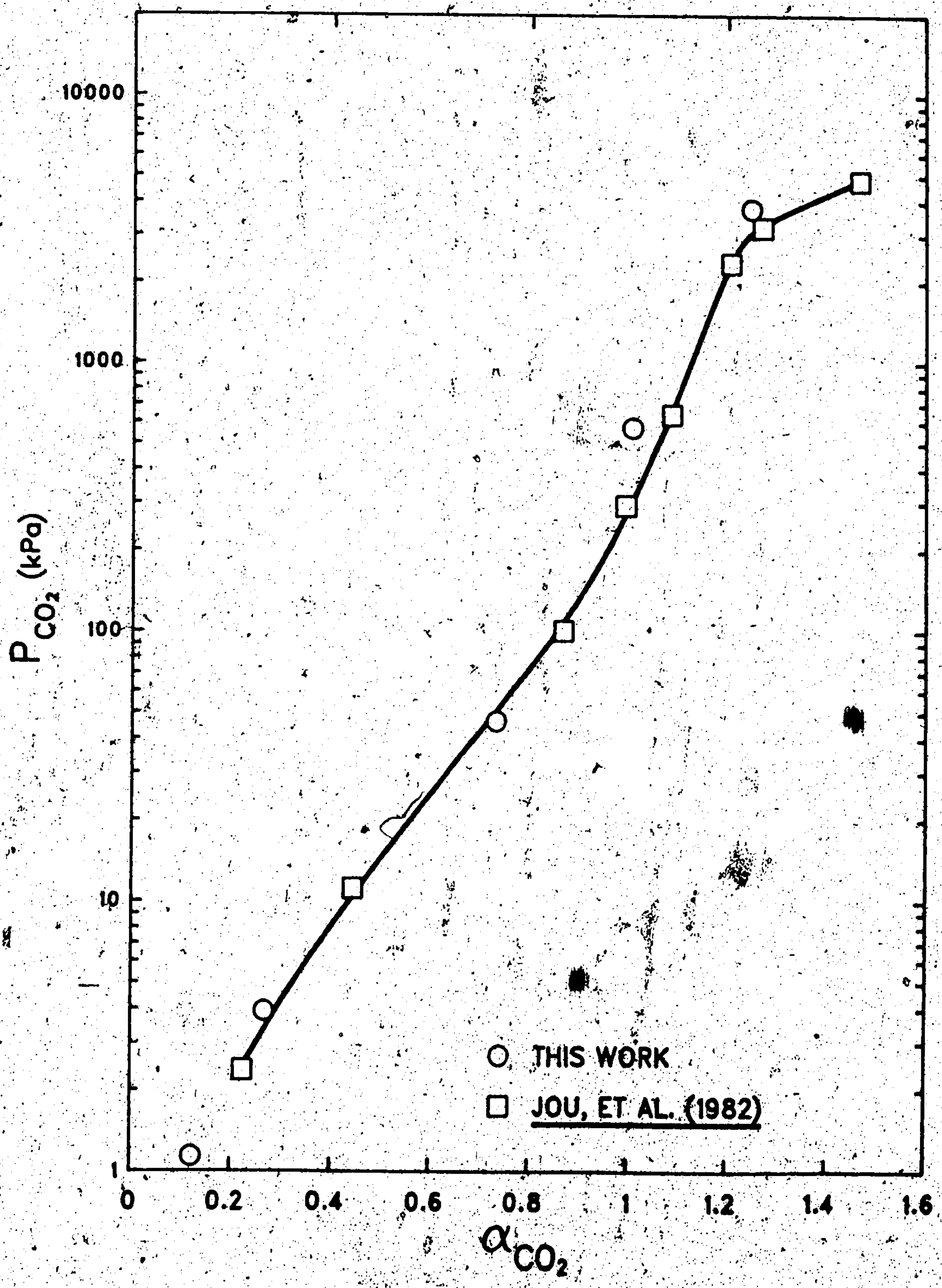

Figure 5.1 Comparison of Experimental Results for Carbon Dioxide Solubility in Aqueous 2.0 M MDEA at 40°C

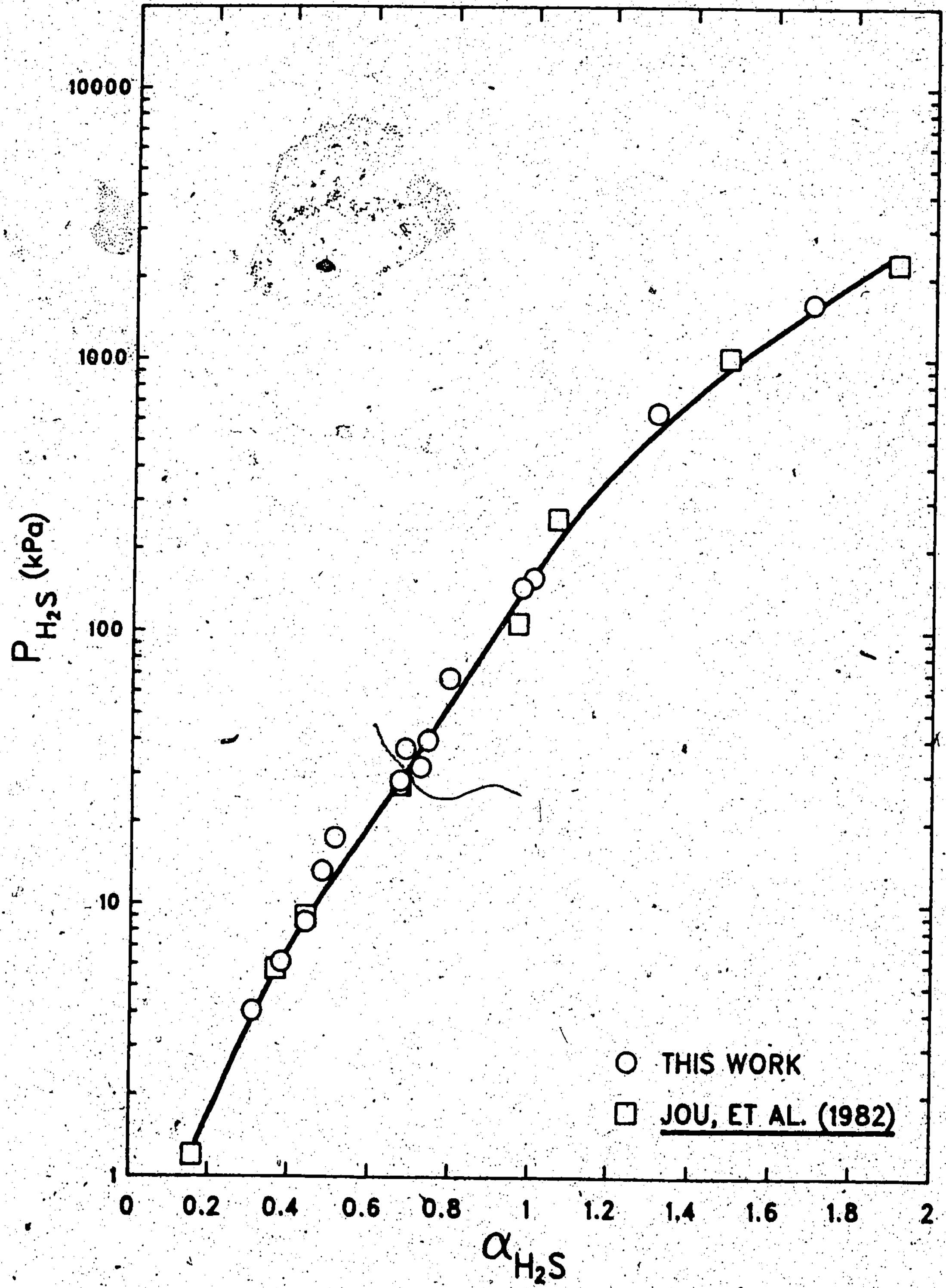

Figure 5.2 Comparison of Experimental Results for Hydrogen Sulphide Solubility in Aqueous 2.0 M MDEA at 40°C

composition as the mixed AMP solvent studied by Roberts (1983), thus allowing direct comparison of the two solvents.

The equilibrium solubilities of CO_2, H_2S, and mixtures of CO_2 and H_2S in the mixed solvent were measured at 40° and 100°C. The results are displayed in Figures 5.3 through 5.8 and Tables 5.3 through 5.7. Loadings are expressed in terms of moles acid gas absorbed per mole amine (α).

Two liquid phases were observed at high CO_2 loadings at 40°C, and at high H_2S loadings at 100°C. For the CO_2 case, the second liquid phase appeared between 1900 and 2900 kPa; for the H_2S case, the second liquid phase appeared between 2500 and 3200 kPa. In both cases the second liquid phase had a much smaller volume and a lower density than the first liquid phase, and was similar in colour and clarity to the first liquid phase. The two phases were also similar in viscosity and density, since the second phase was easily broken into droplets dispersed in the original phase, and coalescence was a slow process, taking about 5 minutes.

Smooth solubility behaviour (see Figures 5.3 and 5.6) made it unnecessary to exclude the LLV three-phase data from the modelling of the system. It is important to note that the solubilities reported here are from analysis of the larger, more dense phases only, and that the compositions of the second, lighter phases were not determined; because of their small volumes relative to the original liquid phases (≃1-2 vol%), they could be neglected in the data analysis.

Table 5.3 Solubility of CO_2 in 2.0 M Mixed Solvent at 40°C

α (mol CO_2/mol MDEA)	P_{CO_2} (kPa)
0.048	0.43
0.061	0.94
0.102	2.00
0.148	3.47
0.181	4.84
0.230	7.19
0.231	7.36
0.279	9.92
0.307	12.2
0.319	14.9
0.435	23.7
0.491	38.3
0.492	38.0
0.529	42.0
0.573	55.3
0.573	55.4
0.678	84.3
0.764	138.
0.785	122.
0.806	136.
0.898	367.
0.922	566.
0.924	356.
0.935	446.
0.944	474.
0.966	446.
1.004	694.
1.010	850.
1.093	1190.
1.167	1870.
1.255†	2900.
1.381†	4050.
1.567†	5770.

†two liquid phases observed

Table 5.4 Solubility of CO_2 in 2.0 M Mixed Solvent at 100°C

α (mol CO_2/mol MDEA)	P_{CO_2} (kPa)	α (mol CO_2/mol MDEA)	P_{CO_2} (kPa)
0.003	0.99	0.781	2680.
0.039	18.1	0.804	2680.
0.071	44.5	0.814	3010.
0.108	74.4	0.826	2400.
0.115	101.	0.829	3010.
0.161	149.	0.838	2400.
0.203	245.	0.870	2400.
0.256	350.	0.874	3280.
0.326	463.	0.895	3560.
0.343	509.	0.896	3560.
0.346	509.	0.902	3770.
0.369	674.	0.920	3510.
0.462	901.	0.933	3510
0.478	901.	0.935	4500.
0.508	901.	0.938	3010.
0.565	1560.	0.940	3010.
0.654	1810.	0.956	4520.
0.655	1810.	0.971	3560.
0.660	1860.	0.974	3560.
0.673	2050.	0.984	4110.
0.674	2000.	1.000	3510.
0.675	2000.	1.006	3510.
0.676	2000.	1.032	5120.
0.699	1860.	1.033	4520.
0.706	1860.	1.058	5470.
0.728	2090.	1.070	5580.
0.731	2090.	1.077	5580.
0.731	2090.	1.124	5580.
0.736	2220.	1.127	5580.

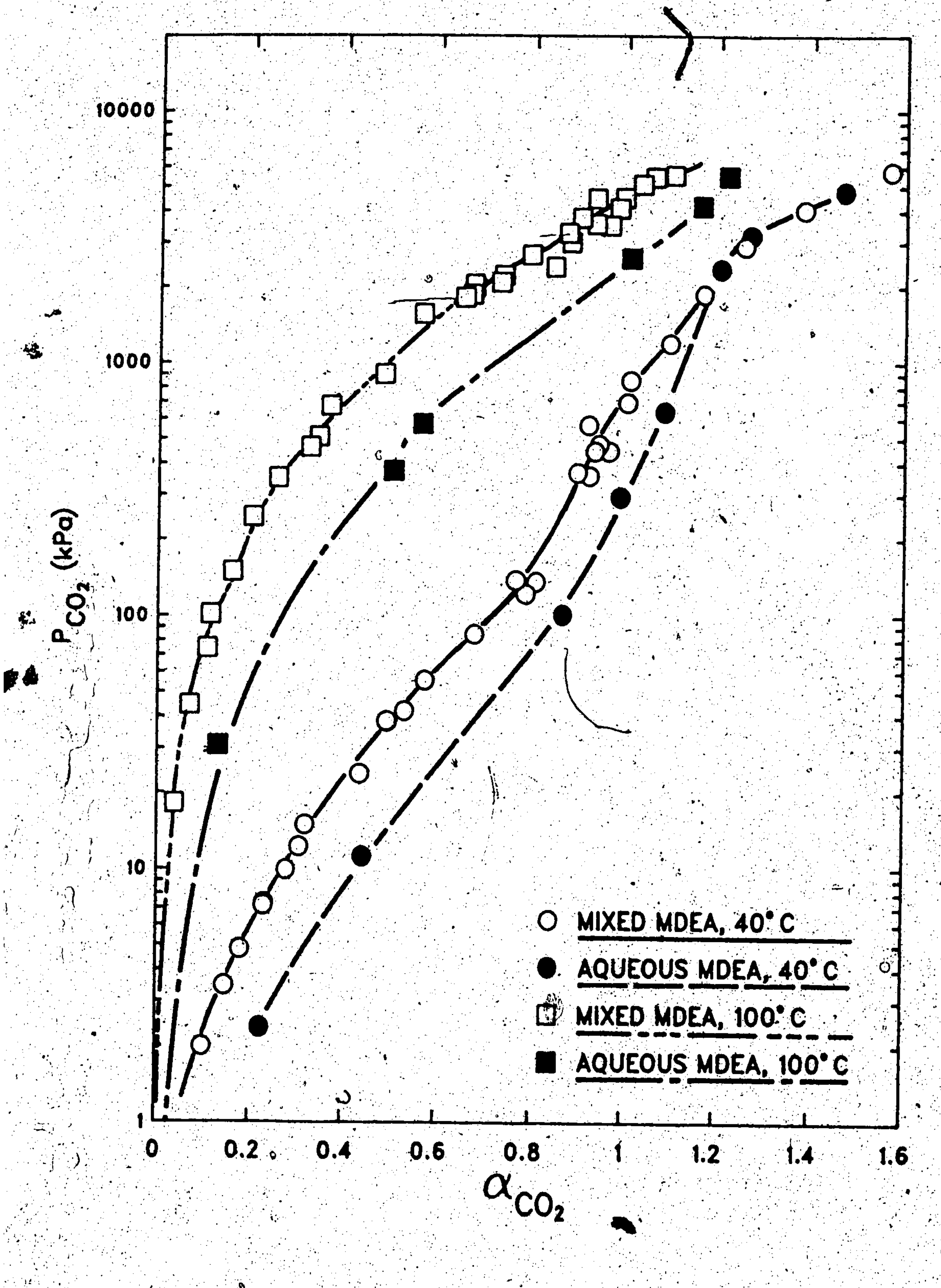

Figure 5.3 Comparison of Experimental Results for Carbon Dioxide Solubility in Aqueous and Mixed 2.0 M MDEA

Tables 5.3 and 5.4 contain solubility results for CO_2 in mixed MDEA at 40° and 100°C; these results are compared with those for aqueous MDEA in Figure 5.3. For clarity, the mean of the α's is plotted for cases in which more than one liquid phase analysis was done at a given partial pressure. At low partial pressures, solubility is greater in the aqueous solvent; the presence of sulfolane inhibits absorption in this range. Solubilities are nearly equal for partial pressures above 2000 kPa at 40°C; at 100°C, this "crossing-over" point occurs above 4500 kPa. It can be seen that at high inlet partial pressures of CO_2, the mixed solvent has a higher "cyclic capacity" than its aqueous counterpart. The cyclic capacity of a solvent is defined by Astarita et al. (1983) to be the "maximum total number of moles of acid gas...that can be extracted from the gas stream by a unit volume of the solvent." While the aqueous and mixed solvents exhibit the same behaviour at high pressures at 40°C, solubility is much lower at lower pressures at 100°C in the mixed solvent, indicating better regenerability and thus a higher cyclic capacity.

Table 5.5 contains solubility results for H_2S in mixed MDEA at 40° and 100°C, and again these results are compared with solubilities in aqueous MDEA in Figure 5.4.

The H_2S partial pressures at which the mixed and aqueous MDEA solutions have the same solubilities are 250 kPa at 40°C and 1500 kPa at 100°C. Below these pressures, aqueous MDEA absorbs more H_2S at both temperatures; above

Table 5.5 Solubility of H_2S at 40°C and 100°C in 2.0 M Mixed Solvent

40°C		100°C	
α (mol H_2S/mol MDEA)	P_{H_2S} (kPa)	α (mol H_2S/mol MDEA)	P_{H_2S} (kPa)
0.098	1.30	0.024	1.58
0.129	2.50	0.033	2.66
0.190	4.22	0.055	7.21
0.245	7.39	0.073	13.4
0.251	7.39	0.121	23.4
0.336	11.5	0.177	46.0
0.412	17.0	0.243	75.2
0.424	18.2	0.311	113.
0.480	30.6	0.443	225.
0.524	30.6	0.605	395.
0.581	38.1	0.804	671.
0.584	30.6	0.972	1020.
0.673	55.0	1.193	1440.
0.719	68.9	1.370	1940.
0.827	107.	1.590	2460.
0.917	154.	1.887†	3210.
1.042	258.		
1.131	373.		
1.135	373.		
1.232	512.		
1.360	678.		
1.697	1070.		
2.073	1470.		

†two liquid phases observed

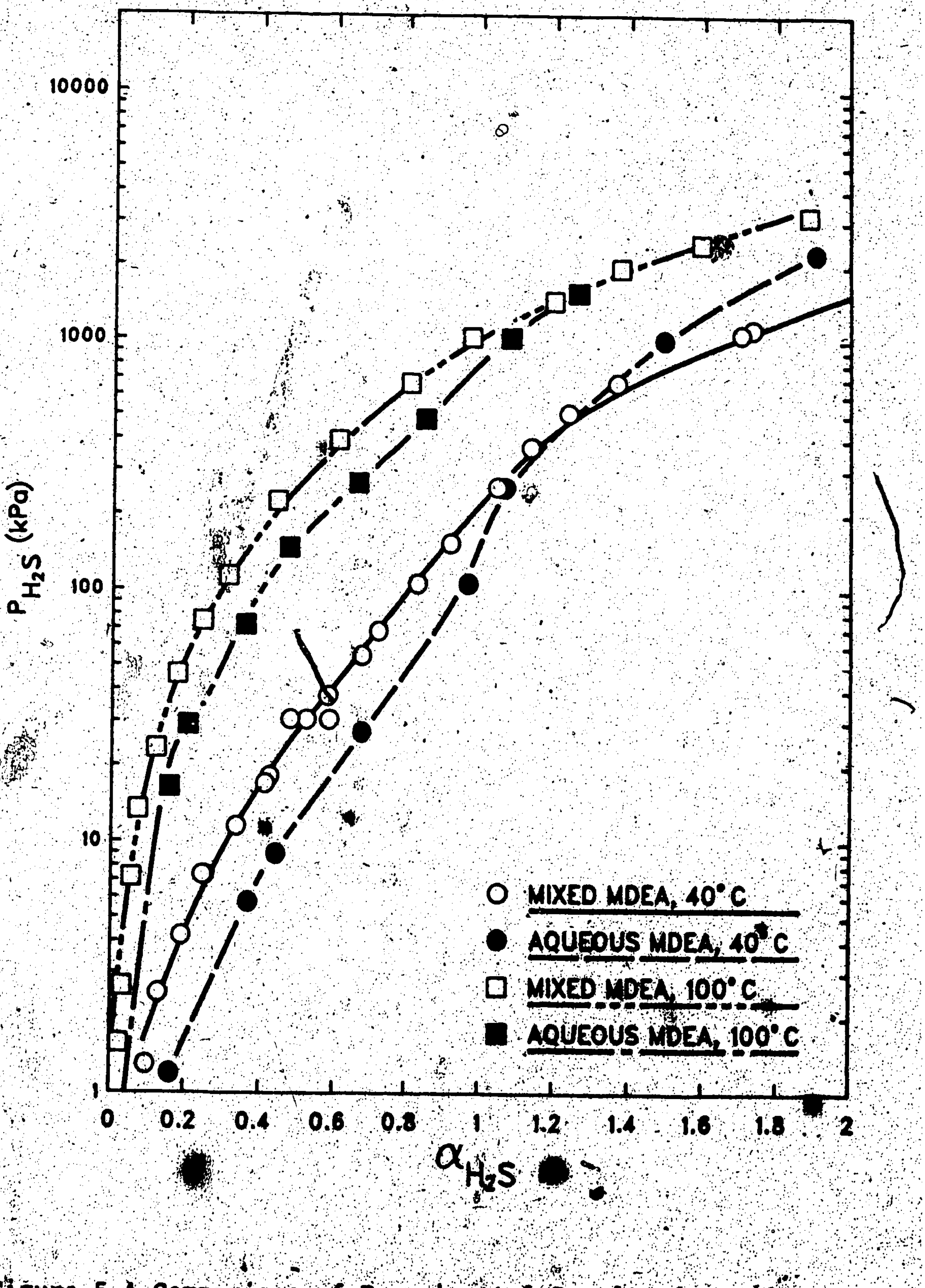

Figure 5.4 Comparison of Experimental Results for Hydrogen Sulphide Solubility in Aqueous and Mixed 2.0 M MDEA

them, it absorbs less. At H_2S pressures greater than 250 kPa in the absorber feed stream, the mixed MDEA solution would be the solvent of choice; higher solubility in the absorber and lower solubility in the regenerator would yield a higher cyclic capacity than for aqueous MDEA. Cyclic capacities are approximately equal for the two solvents below inlet H_2S partial pressures of 250 kPa; since equilibrium solubility of H_2S is lower in the mixed solvent than in the aqueous solvent at these conditions, the aqueous solvent would be preferred, energy costs being equal.

Equilibrium solubilities of H_2S are greater than those for CO_2 in both aqueous and mixed MDEA, and at both temperatures studied, demonstrating the thermodynamic selectivity of the tertiary amine for H_2S.

The effect of changing the chemical solvent in a mixed solvent can be seen in Figures 5.5 and 5.6. The AMP-sulfolane-water solvent studied by Roberts(1983) is compared with the MDEA-sulfolane-water solvent examined in this work; since the molal compositions of both solvents are the same, direct comparison of MDEA is possible. Figures 5.7 and 5.8 display the solubilities of CO_2 and H_2S in aqueous 2.0 M MDEA and AMP solutions, for comparison.

In general, equilibrium solubilities of acid gases are at least equal, and in many cases greater, in mixed AMP than in mixed MDEA. Differences in solubilities decrease as acid gas partial pressures increase; at 40°C and high pressures, solubilities are the same in both solvents.

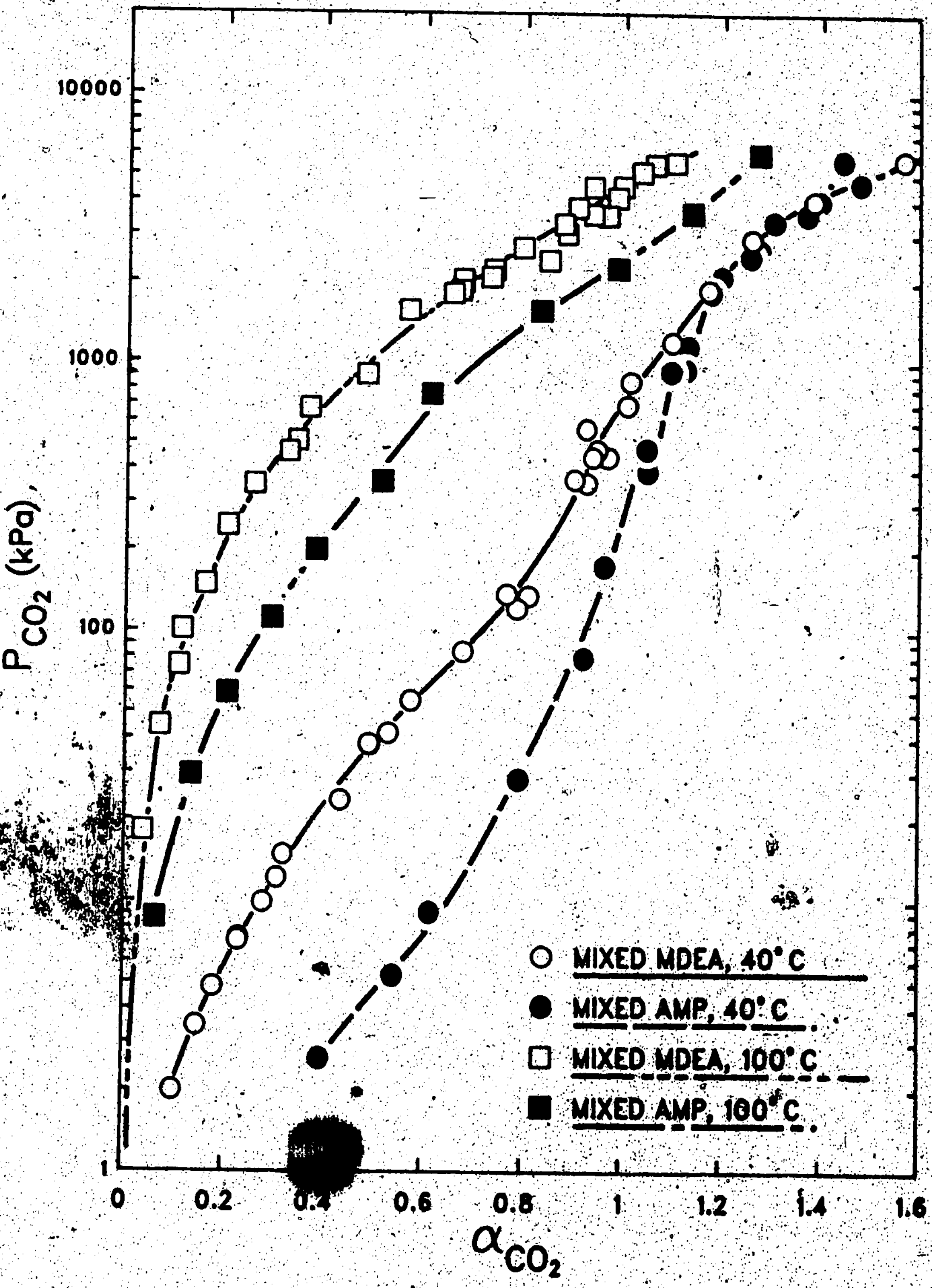

Figure 5.5 Comparison of Experimental Results for Carbon Dioxide Solubility in Mixed 2.0 M MDEA and Mixed 2.0 M AMP

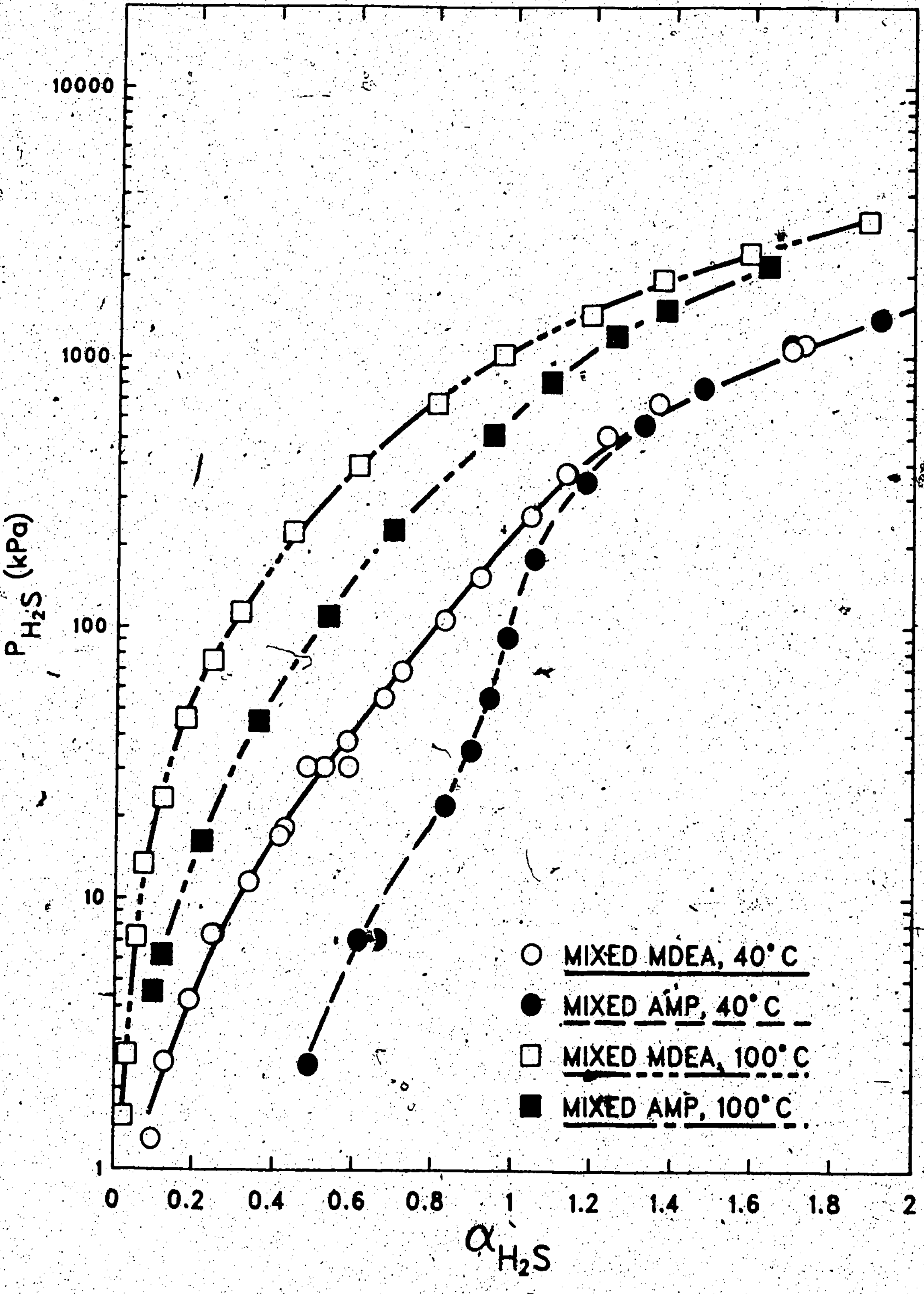

Figure 5.6 Comparison of Experimental Results for Hydrogen Sulphide Solubility in Mixed 2.0 M MDEA and Mixed 2.0 M AMP

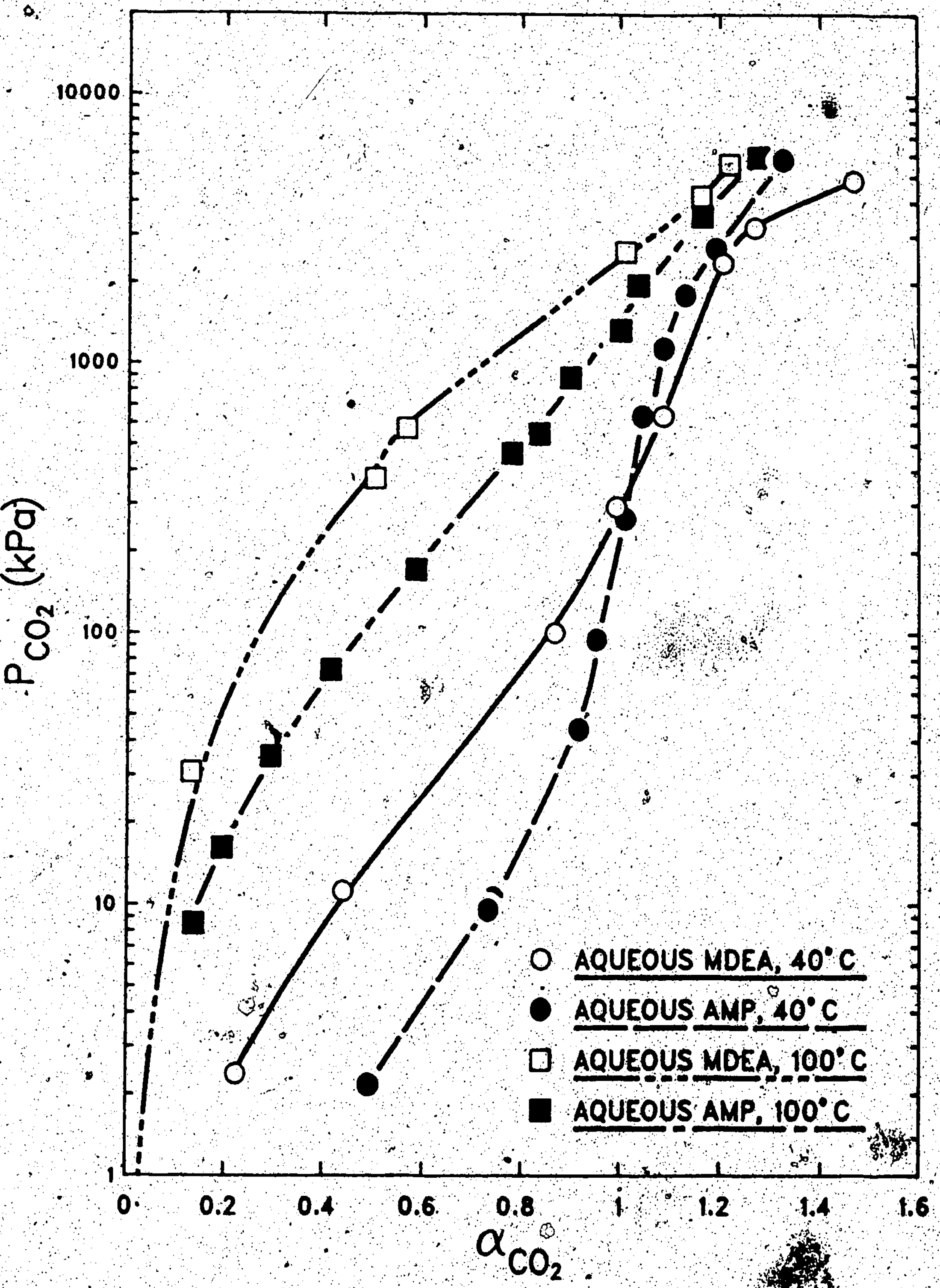

Figure 5.7 Comparison of Experimental Results for Carbon Dioxide Solubility in Aqueous 2.0 M MDEA and AMP

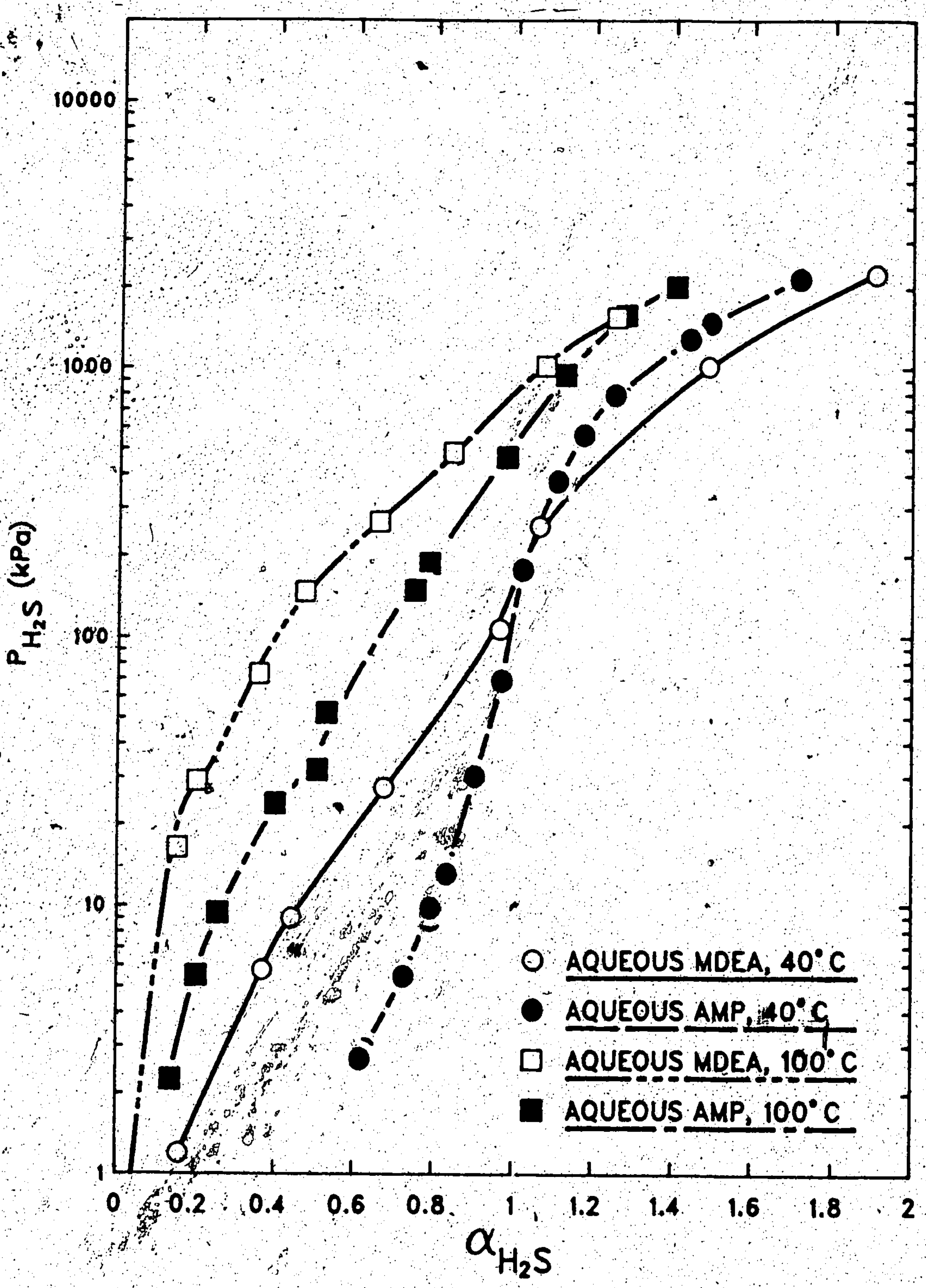

Figure 5.8 Comparison of Experimental Results for Hydrogen Sulphide Solubility in Aqueous 2.0 M MDEA and AMP

In all cases except that of H_2S solubilities at 100°C, the solubility behaviour in the two mixed solvents is qualitatively similar to that in the aqueous solvents. In the case of H_2S at 100°C, AMP absorbs more H_2S throughout the pressure range studied in the mixed solvent case, whereas the aqueous solvents have the same performance at pressures above 3500 kPa.

Because the mixed AMP solvent absorbs more acid gas than the mixed MDEA solvent at 100°C, the latter has the advantage of being more readily regenerated. A trade-off exists, however, between the superior regenerability of mixed MDEA, and its inability to reduce the partial pressure of acid gas in the absorber outlet stream to the levels which can be achieved by the mixed AMP solvent.

Replacement of MDEA with AMP in this amine-sulfolane-water solvent alters the absorption capabilities of the solvent in a predictable manner. Qualitative performance will be the same as that for changing from one aqueous chemical solvent to another. Thus, it appears that on a molecular level, sulfolane-MDEA interactions are qualitatively similar to sulfolane-AMP interactions.

Tables 5.6 and 5.7 show the solubility of CO_2 in the presence of H_2S and vice versa. In comparing the mixed acid gas results with those for the single acid gases, it can be seen that solvent loading capacities are reduced when there is more than one acid gas competing for absorption. These results are discussed further in Section 6.4, where they are

Table 5.6 Solubility of CO_2 and H_2S in 2.0 M Mixed Solvent at 40°C

α (mol CO_2/mol MDEA)	P_{CO_2} (kPa)	α (mol H_2S/mol MDEA)	P_{H_2S} (kPa)
0.360	25.8	0.108	5.29
0.089	3.56	0.109	2.50
0.407	43.8	0.217	23.8
0.069	3.97	0.240	9.12
0.675	193.	0.328	52.7
0.167	12.5	0.349	17.4
1.009	1910.	0.492	449.
0.356	58.1	0.499	56.4
0.781	940.	0.553	334.
0.616	628.	0.604	303.
0.537	438.	0.658	272.
0.456	312.	0.665	230.
0.418	277.	0.694	238.
0.341	178.	0.719	207.
0.381	355.	0.948	460.
0.225	301.	1.100	564.
0.148	148.	1.152	550.
0.236	359.	1.229	770.
0.258	367.	1.543	981.
0.154	298.	1.769	1310.

Table 5.7 Solubility of CO_2 and H_2S in 2.0 M Mixed Solvent at 100°C

α (mol CO_2/mol MDEA)	P_{CO_2} (kPa)	α (mol H_2S/mol MDEA)	P_{H_2S} (kPa)
0.033	387.	0.789	1830.
0.046	50.2	0.160	45.9
0.053	52.0	0.113	27.9
0.070	83.8	0.162	46.8
0.101	224.	0.504	322.
0.138	464.	1.102	1290.
0.140	795.	1.229	1740.
0.148	291.	0.123	96.5
0.162	548.	0.777	687.
0.186	559.	0.517	364.
0.209	343.	0.107	36.9
0.249	608.	0.224	117.
0.317	1560.	1.129	1610.
0.354	769.	0.094	46.1
0.364	1530.	0.499	446.
0.395	1210.	0.325	198.
0.546	1980.	0.270	223.
0.572	3620.	0.834	1250.
0.588	2600.	0.496	528.
0.662	2420.	0.579	1200.
0.863	4680.	0.372	509.
0.887	4840.	0.269	366.
1.017	5180.	0.179	247.
1.450	5460.	0.109	84.3

compared graphically with modelling results.

5.3 Reproducibility of Experimental Results and Error Analysis

The accuracy of the data is influenced by the accuracy of the following measured quantities: acid gas content of the liquid sample; amine solution concentration and density; vapour phase mole fraction; and total system pressure. Some of these measurements themselves depend on the accuracy of other measurements; for instance, the vapour phase mole fraction calculation requires response factors, which are determined in the laboratory and have errors associated with them.

Some reproducibility studies were done to determine where, in practise, experimental error accumulated in the laboratory analyses. It was found that errors in the determination of acid gas loadings (α's) are greatest at high pressures ($P_{acid\ gas}$>2000 kPa), due to limitations of the sampling equipment. At these pressures, half of the error associated with an acid gas loading calculation appears to originate with the actual sampling step.

Once the sample is in the bomb, reproducibility studies indicate that errors in α are relatively constant over the loading range studied. The average error in α was determined to be ≈±3%; maximum error was found to be ±5%.

In contrast, the errors in measuring the vapour phase mole fractions of acid gas are largest at low acid gas mole fractions, corresponding to low loadings. This is due to the method used for the determination of response factors; because the gas mixtures used in determining response factors are prepared by weighing the gases used, low concentrations of acid gas will have high relative errors associated with them. This does not occur at high acid gas loadings because nitrogen gas diluent, and therefore response factors, are not necessary. For these reasons, data much below 1 kPa partial pressure of acid gas were not taken, and partial pressures below 10 kPa will have as much as 10% error associated with them. These errors will be larger for H_2S than for CO_2, due to the shape of the H_2S response factor curve at low H_2S concentrations.

A more detailed and quantitative analysis of the errors associated with the experimental results reported here can be found in Appendix IV. Unfortunately, the errors incurred in liquid phase sampling itself under high pressures could not be quantified. As stated above, ±5% error in α measurements is estimated for this step.

6. Modelling of Experimental Results

Thermodynamic models are available for the prediction of acid gas solubilities in various solvents, and were discussed in Section 3.2. Models allow the investigator to interpolate and, more importantly, to extrapolate known experimental data. The development of mixed acid gas solvents makes thermodynamic modelling of solvent systems even more pertinent:

> "There exists an infinite variety of blend formulations. This makes detailed experimentation and pilot-plant trials an utterly infeasible approach to blend selection for each application. It is, therefore, essential to develop realistic theoretical models for the VLE behavior of solvent blends...." (Chakravarty, 1985)

The model of Deshmukh and Mather was chosen for the modelling of the solubilities of CO_2 and H_2S in the mixed solvent studied in this work. Because the model makes few thermodynamic assumptions and is easily adaptable to mixed solvents, it is useful in studying mixed solvent behaviour.

Two basic ways of modelling the system using the Deshmukh-Mather model were possible: sulfolane could be considered to be a solvent or a solute. Each procedure has requirements and limitations. Because sulfolane is present in large quantities, and is known widely as an acid gas solvent, it can easily be considered to be a solvent in the system. In this case the solvent is a water-sulfolane mixture, and Henry's constants, dielectric constants, and ionic equilibrium constants are influenced.

An alternative is to consider the sulfolane to be a solute in the system. The Henry's constants and dielectric constants of an aqueous system could then be used. However, more interaction parameters in the extended Debye-Hückel equation would need to be evaluated; sulfolane-MDEA and sulfolane-HCO_3^- interactions are examples.

Because of the ease of evaluating Henry's constants, the dielectric constant, and ionic equilibrium constants for a mixed water-sulfolane solvent, as opposed to the difficulty of evaluating more interaction parameters, the former method of modelling the system thermodynamics was chosen. The modification procedure developed by Roberts (1983) to adapt the model for a mixed AMP solvent was generally used in this work. Briefly, the modifications entailed:

1. fitting of aqueous MDEA data to extract selected interaction parameters ~~to be~~ used in the calculation of activity coefficients; and
2. fitting high-loading fugacity versus molality mixed solvent data to obtain Henry's constants for the mixed system;
3. regression analysis to determine the values of selected equilibrium constants for the mixed solvent system.

6.1 Henry's Constant Evaluation from Single Acid Gas Data

Because sulfolane and water are both physical solvents for CO_2 and H_2S, the Henry's constant for water alone insufficiently describes the VLE behaviour of the mixed solvent. Expressions for estimation of the Henry's constants of various gases in mixed solvents systems are available in the literature, based on different solution theories.

Several investigators have used Wohl's expansion as a basis for developing mixing rules for mixed solvent Henry's constants. O'Connell and Prausnitz (1964) suggested the following expression for simple, non-polar binary solvent mixtures:

$$\ln H_{2,M} = x_1 \ln H_{2,1} + x_3 \ln H_{2,3} - a_{13} x_1 x_3 \qquad (6.1)$$

2=solute; 1, 3=solvent species

The parameter a_{13} is empirically determined and equals zero for ideal solvent mixtures. The authors stated that other expressions could be developed for more complex and/or polar systems. Rivas and Prausnitz (1979) used a modification of equation (6.1) in which the parameter a_{13} becomes a function of temperature: $a_{13} = A_{13}/RT$. The expression was used to calculate the solubilities of acid gases in various non-aqueous physical organic solvent-amine mixtures.

Nitta et al. (1973) developed an expression for Henry's constants for mixed solvents, also based on Wohl's expansion, requiring molar volume data and a Flory interaction parameter. Some other methods which have been proposed include one based on statistical-mechanical solution theory [O'Connell (1971)] and a simplification of perturbation theory [Tiepel and Gubbins (1972)].

For several reasons, accurate estimations of the Henry's constants of acid gases in a sulfolane-water solvent in which substantial amounts of the solute species MDEA and protonated MDEA are present are not possible using the above methods. Most components involved are polar, and thus there are electrostatic forces in the solution which are difficult to predict, and since MDEA is considered to be a solute species in the analysis, it is difficult to include its contribution to the Henry's constant. The empirical technique used by Roberts (1983) was therefore used in this work as well.

The Henry's constant can be extracted from experimental VLE data with linear regression analysis on fugacity versus liquid phase mole fraction. Since mole fraction is proportional to molality at the low concentrations of dissolved molecular CO_2 and H_2S studied in this work, regression was performed using the more easily calculated molality data. These data were extracted from α vs P data by assuming that all acid gas below loadings of 1 mol/mol amine reacts, and $m_{\text{acid gas}} = 0$, and that all further acid gas absorbed does not react, but remains in molecular form. This assumption is supported by the work of Yu et al. (1985), which states that "at very high equilibrium partial pressures, the total content of CO_2 in the liquid phase is dominated by the physically dissolved form, and therefore values of H can be extracted from vapor-liquid equilibrium data." The Peng-Robinson equation of state was used to calculate the fugacities of the acid gases. The effect of pressure on H was assumed to be negligible.

The above procedure produced the Henry's constants displayed in Table 6.1. The Henry's constants for the mixed AMP-sulfolane-water system of Roberts (1983) are also given, for comparison. It can be seen that the MDEA mixed solvent follows the same trends as the AMP mixed solvent.

Table 6.1 Mixed MDEA and AMP Solvent Henry's Constants

	40°C			100°C		
gas	H (MPa-kg /mol)	corr. coeff.	no. data pairs used	H (MPa-kg /mol)	corr. coeff.	no. data pairs used
CO_2	2.851 (3.92)†	0.9959	7	4.460 (5.98)	0.7689	8
H_2S	0.4[illegible]0 (0.667)	0.9972	6	0.864 (1.35)	0.9947	4

†values in parentheses are for mixed AMP

The maximum expected error in H, estimated by regression analysis, was for H_{CO_2} at 100°C, at 33.9%; the other three Henry's constants had expected maximum errors near 5%. These Henry's constants were incorporated into the model as functions of temperature of the form

$$\ln H = A/T + B \tag{6.1}$$

Comparison of the values of the Henry's constants for the AMP-sulfolane-water solvent of Roberts (1983) with those for the MDEA-sulfolane-water solvent of this work indicates that the amines play a role in the physical properties of a solvent as well as in its chemical properties. Therefore, the use of the H's for water in the case of the modelling of aqueous MDEA data is itself an approximation.

6.2 Evaluation of Parameters in the Extended Debye-Hückel Equation

The form of the extended Debye-Hückel equation used in this work is:

$$\ln\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+\sqrt{I}} + \sum_{k\neq w}\beta_{ik}m_k \qquad (6.2)$$

The first term accounts for the electrostatic effects of the solvent on the solute species at infinite dilution. The coefficient A is a function of the dielectric constant of the solvent, as well as several other variables. The remaining terms represent the short range (van der Waals) two-body interactions between solute species; the β's are interaction, or "salting-out" parameters, determined empirically. Thus values for the β's and the solvent dielectric constant are required.

6.2.1 Dielectric Constant Evaluation

Activity coefficients of all ionic solute species are a function of the dielectric constant of the medium, which is in turn a function of temperature and of the composition of the medium. A temperature-dependent mixing rule for water-sulfolane mixtures was not available in the literature. The predictive equation suggested by Franks (1972) was tested, but found to be unsatisfactory for this system. An empirical relationship was developed, based on sulfolane-water mixture data at 25°C (Covington and Dickinson, 1973):

$$\epsilon_{mixture} = \epsilon_{ideal} + \epsilon_{excess} \qquad (6.3)$$

where

$$\epsilon_{ideal} = x_{sulf}\epsilon_{sulf} + x_{water}\epsilon_{water} \text{ and}$$

$$\epsilon_{excess} = -4.341x_{water} - 70.940(x_{water})^2 + 74.683(x_{water})^3$$

The expression fitted the available data with a maximum error of 3% in $\epsilon_{mixture}$. It was assumed that ϵ_{excess} is independent of temperature in the range 25° to 100°C.

6.2.2 Interaction Parameter Evaluation

Interaction parameters (β's) were reported for the MDEA-water-H_2S-CO_2 system by Chakravarty (1985). Because the β's were limited to between +0.1 and -0.1, an investigation of the region outside these limits was conducted prior to accepting the values of Chakravarty for use in this work.

The same experimental data, that of Jou et al. (1982), was used in both studies; due to the investigatory nature of this work, only a few representative data pairs for each acid gas were used in the analysis.

A regression analysis was done using these data sets and the objective function

$$\text{Error} = \Sigma|(\ln P_{calc} - \ln P_{expt})| \qquad (3.3)$$

to yield the interaction parameters listed in Table 6.2, which are assumed to be the parameters which have the greatest influence on the activity coefficients of the solute species. Species present in negligible concentrations and interactions between neutral molecules or ions of the same sign were assumed to have negligible effects on the activity coefficients; their interaction parameters were therefore set to zero.

Table 6.2 Interaction Parameters

species pair	Chakravarty (1985)	this work
H_2S-$MDEAH^+$	-0.0934	0
HS^--MDEA	0	-0.1701
HS^--$MDEAH^+$	-0.01156	-0.0523
CO_2-$MDEAH^+$	-0.08868	0
HCO_3^--MDEA	-0.01379	-0.2474
HCO_3^--$MDEAH^+$	-0.01406	-0.07454

The sets of values in Table 6.2 were tested by calculating acid gas partial pressures given the loadings reported by Jou et al. (1982), and evaluating the objective function given in equation (3.1). Results are given in Table 6.3.

Table 6.3 Goodness of Fit for Interaction Parameters

Acid Gas	Value of Objective Function All β's=0	 β's of Chakravarty (1985)	 β's of this work
CO_2	[a]29.9777	[b]27.0949	[b]37.0329
H_2S	80.0671	18.6431	[c]18.5664

[a] 9 of 58 runs did not converge
[b] 7 of 58 runs did not converge
[c] 1 of 56 runs did not converge

The value of the objective function for the β's of this work in the CO_2 case is greater than that for the case in which all β's were set equal to zero, indicating that choosing 8 representative data pairs out of a potential of 58 to fit these parameters is insufficient. The fact that the set of β's developed by Chakravarty (1985) yields an objective function only 10% lower than that for the case in which all β's are set equal to zero indicates that there is possibly a problem with some individual equilibrium constant values, or that the extended Debye-Hückel equation is an unsatisfactory activity coefficient expression for the ~~CO_2 case~~, if very accurate P_{CO_2} predictions are to be obtained. In addition, 7 of 58 runs did not converge for the non-zero β sets; non-convergence occurred at high loadings, and was more prevalent at the two lowest temperatures, 25° and 40°C. When the values of the objective functions for the two acid gases are compared, it can be seen that, although the CO_2 objective functions are larger, they are not too different from those for H_2S, and are therefore acceptable.

In contrast to the minimal improvement in partial pressure predictions evidenced in the CO_2 case, predictions of H_2S partial pressures were easily and markedly improved by adjusting the β's. The β's found by regression analysis on 5 selected experimental data points were sufficient to reduce the value of the objective function by a factor of 4.3, which was in fact slightly lower than that found by using the set of β's suggested by Chakravarty (1985). There are two reasons, however, to prefer the previously published set over that determined in this work: all of the runs converged, and the distribution of individual activity coefficients was clustered around unity to a larger extent for the β's of Chakravarty. The latter point is also true for the CO_2 case. Since little is known of the true activity coefficients for the system of interest, activity coefficients which are not far from unity are desirable.

Because the set yields the closest agreement with experiment, the β's suggested by Chakravarty (1985) for the CO_2 system were used in this work; because of the activity coefficient argument discussed above, the Chakravarty β's for the H_2S system were adopted as well.

The agreement between experiment and the Deshmukh-Mather model modified using the above findings is shown in Figures 6.1 and 6.2. It can be seen that a marginally satisfactory fit of the experimental data is achieved.

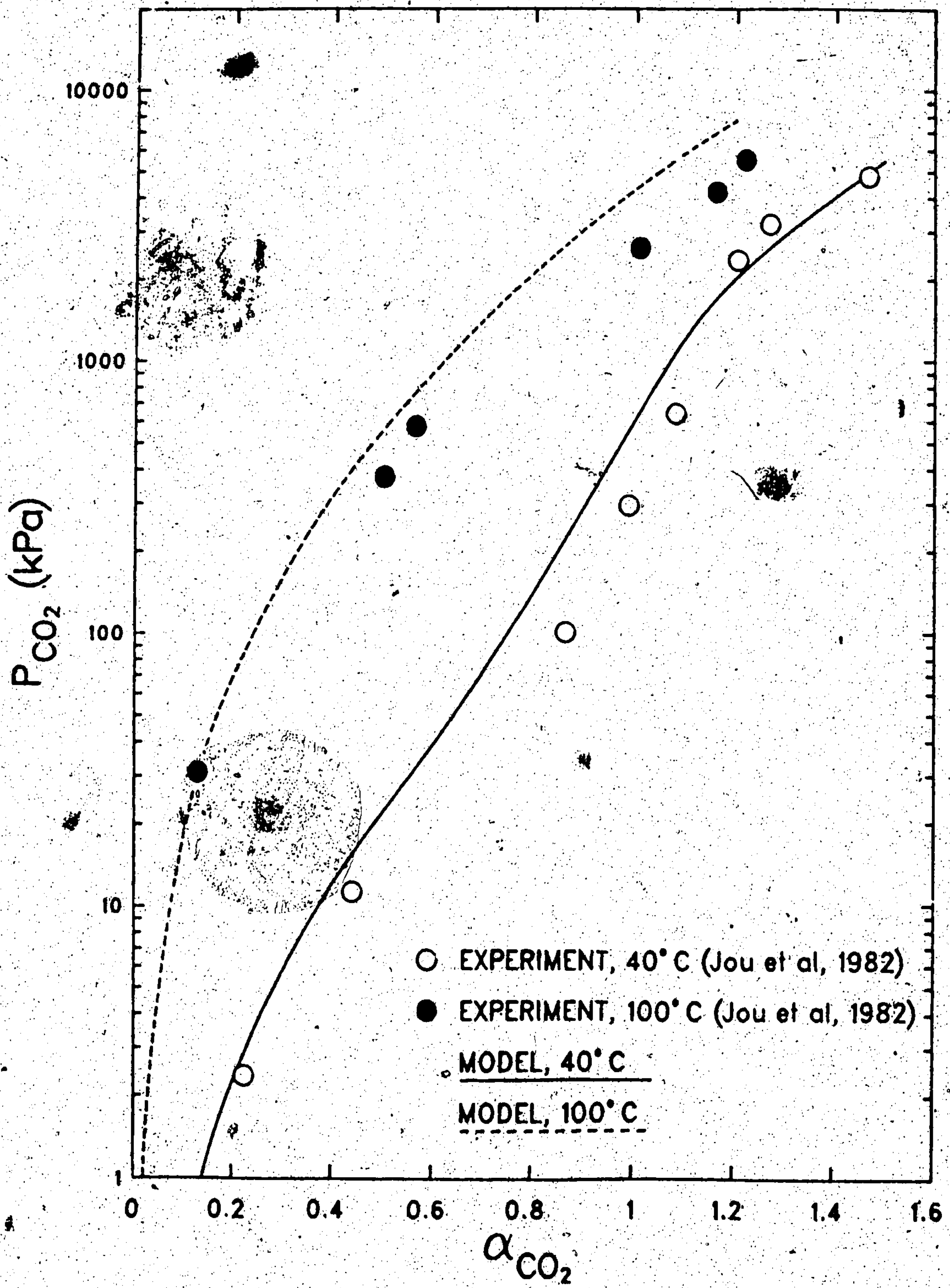

Figure 6.1 Comparison of Modelled and Experimental Results for Carbon Dioxide Solubility in Aqueous 2.0 M MDEA

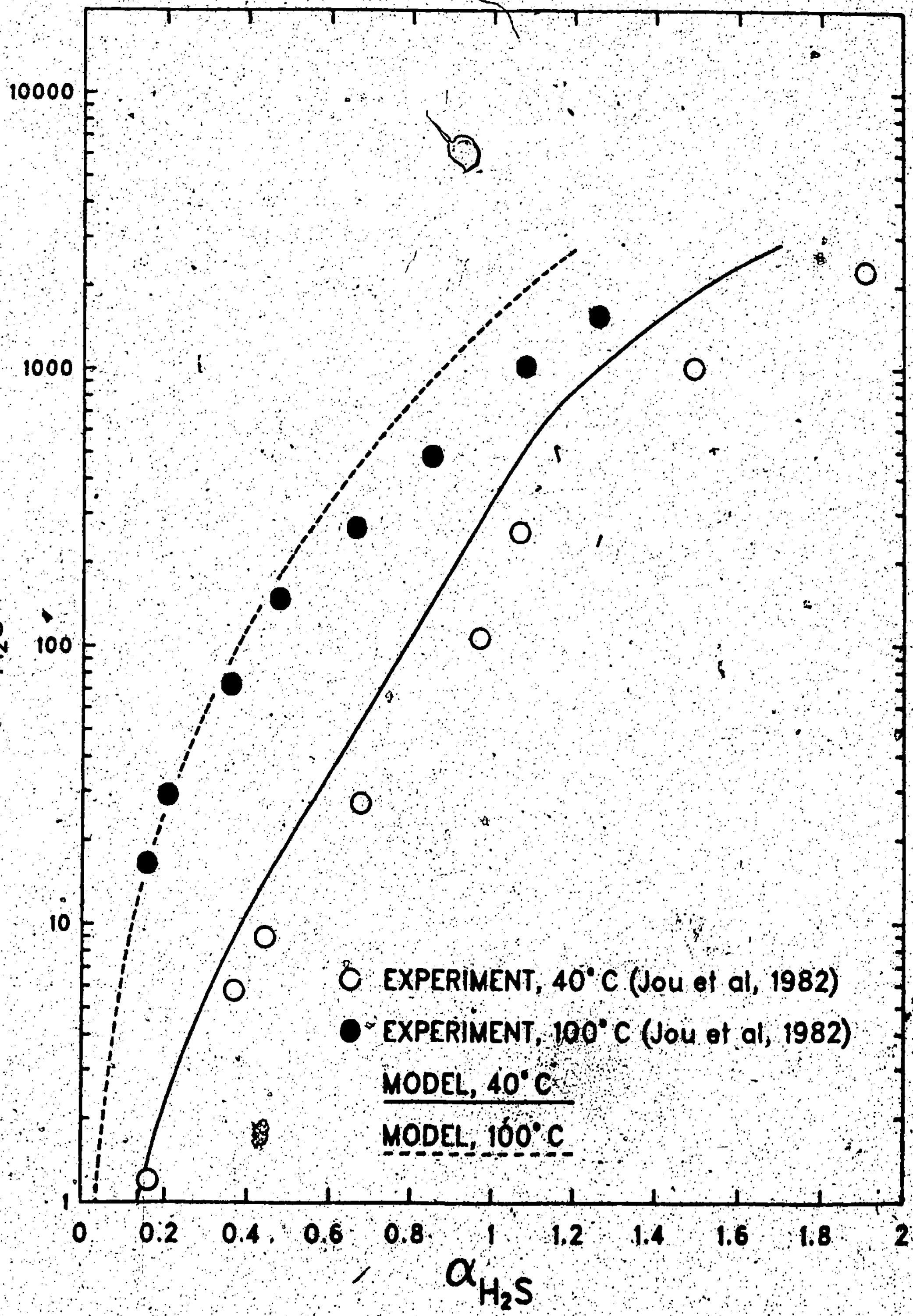

Figure 6.2 Comparison of Modelled and Experimental Results for Hydrogen Sulphide Solubility in Aqueous 2.0 M MDEA

6.3 Equilibrium Constant Evaluation from Single Acid Gas Data

As discussed previously, the extended Debye-Hückel equation yields the activity coefficients of solute species in the mixed solvent at infinite dilution; the extended form of the equation describes the van der Waals forces between solute species at all solute concentrations. However, the mixed solvent of this work is not infinitely dilute in sulfolane, the non-aqueous solvent in the system. The effect of substantial amounts of sulfolane on the activity coefficients of the solute species is known as the "secondary medium effect" [Sen et al. (1979)], and is not represented in the Debye-Hückel equation. Instead, it has in the past been represented by altering the apparent ionic equilibria:

$$K_{(\text{in mixture})} = Q_{\gamma} \times K_{(\text{in water})} \qquad (6.4)$$

where Q_{γ} is a multiplier on the product of the activity coefficients of the aqueous system. Thus, the equilibrium constant observed in the mixed solvent will differ from that for the aqueous solvent. This difference increases with increasing sulfolane concentration, and attendant decrease in dielectric constant of the solution.

The ionic equilibria for the mixed solvent system were adjusted only for the system's dominant reactions:

$$MDEAH^{+} = MDEA + H^{+} \qquad (6.5)$$

$$H_2S = H^{+} + HS^{-} \qquad (6.6)$$

$$CO_2 + H_2O = HCO_3^{-} + H^{+} \qquad (6.7)$$

$$HCO_3^- = CO_3^{2-} + H^+ \tag{6.8}$$

The remaining ionic equilibria were described using aqueous system equilibrium constants.

The mixed solvent data for H_2S solubility at 40° and 100°C were used to adjust the equilibrium constants for (6.5) and (6.6); using the result for (6.5), the solubility data for CO_2 in the mixed solvent at 40° and 100°C were used to adjust the equilibrium constants for (6.7) and (6.8).

Dependence on temperature for the above equilibrium constants was expressed as

$$\ln K = A/T + B \tag{6.9}$$

The objective function described by (3.3) was used to determine the constants. The procedure consisted of using the β's and the Henry's constants determined previously, using experimental data for H_2S solubility in the mixed solvent, and adjusting the equilibrium constants for (6.5) and (6.6) to yield the lowest value of the objective function, for each of 40° and 100°C. Emphasis was placed on the middle loading range, since experimental errors are lowest in this region. The resulting equilibrium constants were then incorporated into the model and the analogous procedure used to determine the equilibrium constants for (6.7) and (6.8) from the CO_2 mixed solvent solubility data. The results of these exercises are given below.

Table 6.4 Mixed-Solvent Equilibrium and Henry's Constants from Single Acid Gas Data

parameter	40°C	100°C
K(MDEA prot.)	1.387×10^{-6}	1.520×10^{-6}
K(H_2S diss.)	5.354×10^{-8}	9.275×10^{-8}
K(CO_2 diss.)	2.660×10^{-7}	1.003×10^{-7}
K(HCO_3 diss.)	2.384×10^{-11}	7.536×10^{-11}
H(CO_2), MPa-kg/mol	3.689	4.686
H(H_2S), MPa-kg/mol	0.5035	1.080

It was found that the predicted partial pressures of H_2S at high loadings were insensitive to the equilibrium constants, and that the H_{H_2S} found by linear regression (discussed in 6.1) had a pronounced effect on the predicted partial pressures at high loadings, while having a lesser influence at low loadings. The Henry's constant for H_2S was subsequently increased to yield better predictions at high loadings; in this way, a set of equilibrium and Henry's constants was converged upon which yielded a satisfactory fit to the experimental data throughout the loading range studied.

In contrast, the Henry's constant and equilibrium constants for the CO_2-mixed solvent system showed little dependence on acid gas loading. As well, similar to the results from the interaction parameter study, the CO_2-mixed solvent system was much more difficult to fit using the modified Deshmukh-Mather model, as will be shown below.

6.4 Mixed Acid Gases in the Mixed Solvent

As a test on the modelling constants determined above and displayed in Table 6.4, the modified Deshmukh-Mather model was run using loadings for the mixed acid gas experimental data, and comparing the predicted acid gas partial pressures with the experimentally-determined acid gas partial pressures. As can be seen in Figures 6.3 and 6.4, good agreement between predicted and experimental partial pressures was found for the 100°C case. However, consistently high partial pressures were obtained for the 40°C case, for both CO_2 and H_2S. Since the set of equilibrium constants and Henry's constants arrived upon above is not unique, a sensitivity analysis was done to determine a better set of these constants, using the objective function (equation (3.3)) as a guide. It was found that small adjustments to the dissociation constant and Henry's constant for CO_2 improved the model substantially; the modelled results for mixed acid gases were closer to the experimental results, as were those for CO_2 alone. Since no changes were made to the equilibrium or Henry's constants for H_2S, the modelled results for this acid gas remained the same. Results are displayed in Tables 6.5 and 6.6.

Table 6.5 Mixed Solvent Equilibrium and Henry's Constants from Mixed Acid Gas Data

parameter	40°C	100°C
K(MDEA prot.)	1.387×10^{-6}	1.520×10^{-6}
K(H_2S diss.)	5.354×10^{-8}	9.275×10^{-8}
K(CO_2 diss.)	3.059×10^{-7}	1.003×10^{-7}
K(HCO_3 diss.)	2.384×10^{-11}	7.536×10^{-11}
H(CO_2), MPa-kg/mol	3.136	4.686
H(H_2S), MPa-kg/mol	0.5035	1.080

Table 6.6 Goodness of Fit for Modelled Mixed Acid Gas Partial Pressures at 40°C

	Value of Objective Function	
Acid Gas	Using Table 6.4 Constants	Using Table 6.5 Constants
CO_2	2.08	1.55
H_2S	5.24	4.81

Figures 6.3 and 6.4 have been plotted using the constants in Table 6.5 incorporated into the modified Deshmukh-Mather model. As mentioned above, these constants yielded an equal or lower value of the objective function as calculated using all of the experimental data. The values in Table 6.4, in contrast, were determined from an objective function neglecting the highest and lowest loadings, which are the regions of highest experimental error. It appears that the use of more data is more important to the fitting exercise than the use of the data portion with the smallest experimental error. In particular, the highest loadings are

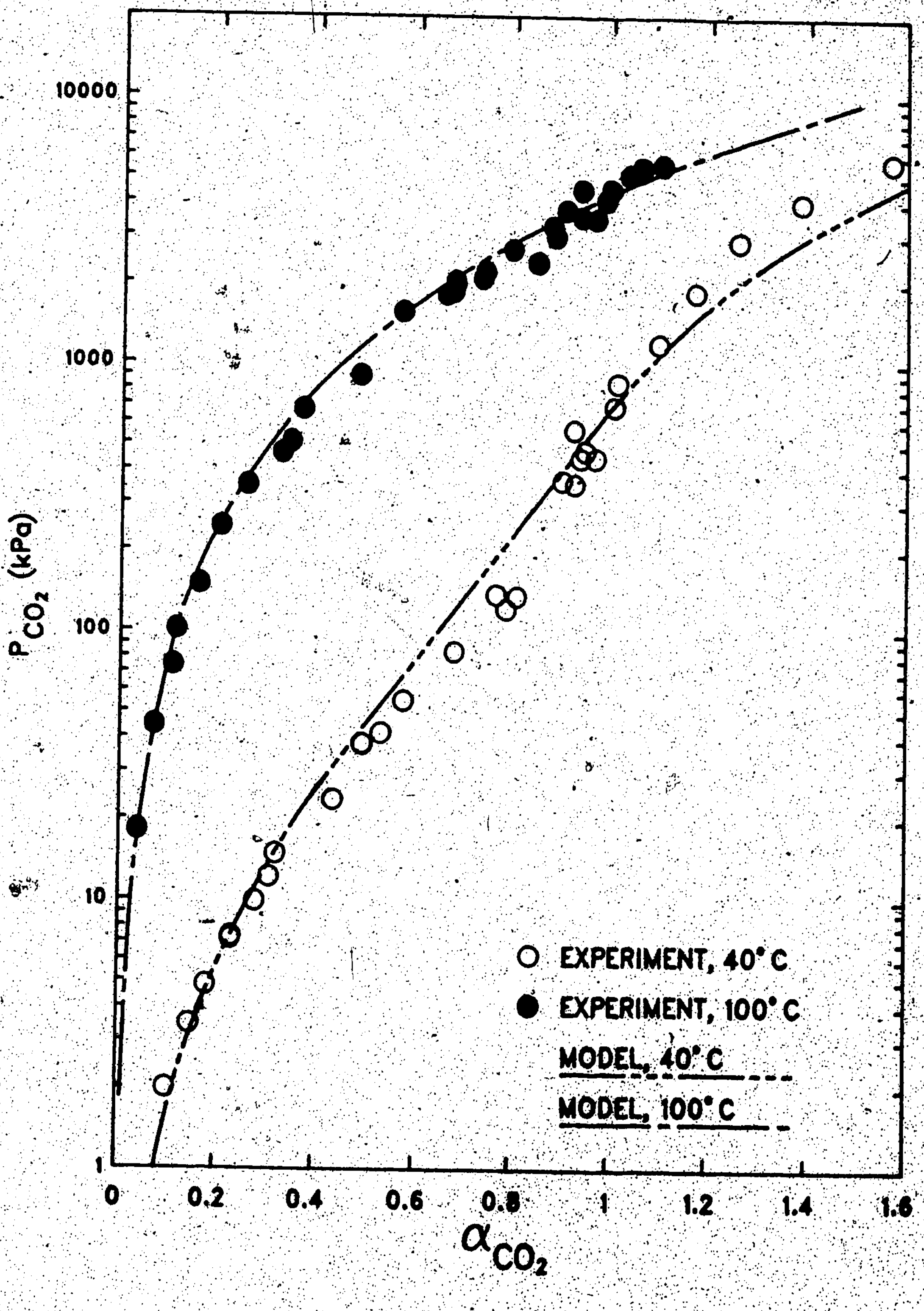

Figure 6.3 Comparison of Modelled and Experimental Results for CO_2 in Mixed 2.0 M MDEA

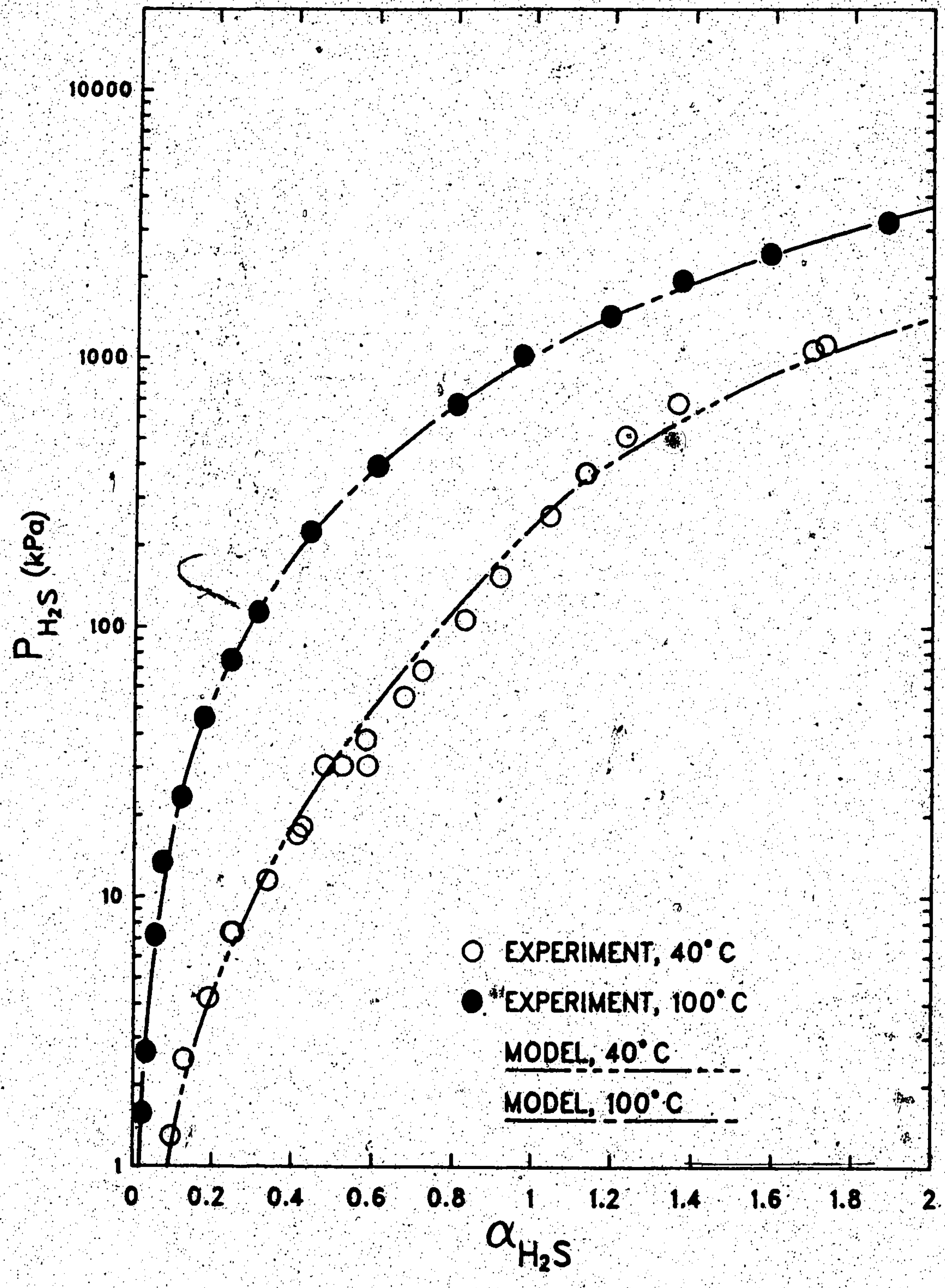

Figure 6.4 Comparison of Modelled and Experimental Results for H_2S in Mixed 2.0 M MDEA

important for use in determining the best Henry's constants, as discussed in Section 6.1.

Figures 6.3 and 6.4, then, were generated from the set of Henry's constants and selected equilibrium constants adjusted to yield the lowest objective function for each acid gas. The agreement between modelled and experimental results is acceptable for both gases at both 40° and 100°C. The computer code for the Deshmukh-Mather modelling program is available o[illegible] from the author, or from the University of Alb[illegible]artment of Chemical Engineering. The above-menti[illegible]al set of Henry's constants and equilibrium constants have been incorporated into the final code.

The Deshmukh-Mather model can be used to describe the experimental results in thermodynamic terms. The sulfolane in the mixed MDEA solvent acts to decrease the Henry's constant for the acid gas in contact with the solvent, tending to increase its solubility. However, the sulfolane also acts to decrease the dielectric constant of the solvent, which is a controlling factor in the degree of ionization which will occur. Since the acid gases ionize upon absorption into solution, the presence of sulfolane would tend to inhibit this ionization and thus tend to decrease the acid gas solubility in the mixed solvent. Since chemical forces dominate at low loadings, solubility is lower at low partial pressures in the mixed solvent than in aqueous MDEA. Since physical forces dominate at high loadings and the Henry's

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Appendix I: Gas Chromatograph

A. Gas Chromatograph Settings

A model 5710A Hewlett Packard gas chromatograph was used to analyse the gas phase samples in this work. It was equipped with a six port Valco gas sampling valve used for injecting sampling loop contents into the chromatograph column. A thermal conductivity detector measured the relative amounts of the separated gases. Each response peak was integrated by a 3380A Hewlett Packard integrator and reported in terms of area percent.

The operating conditions of the gas chromatograph were:

column temperature: 80°C (CO_2)
110°C (H_2S)
detector temperature: 150°C
sample loop volume: 2.0 cm^3
column dimensions: 8 ft (2.44m) × 1/8 in. (3.18mm) OD
column packing: 80-100 mesh Chromasorb 104
detector current: 110-120 mA
carrier gas flow: 35-40 cm^3/min He

B. Response Factor Determination

Response factors for H_2S and CO_2 relative to nitrogen were used for gas chromatograph calibration, and were determined as per Roberts (1983). H_2S/N_2 and CO_2/N_2 mixtures of known composition were prepared and analysed in terms of percent area by the gas chromatograph; since the mole percent composition of each mixture was known, the response factors could be determined:

$$RF = \frac{\text{area \% acid gas } (100 - \text{mole \% acid gas})}{(100 - \text{area \% acid gas}) \text{ mole \% acid gas}}$$

The response factors were a function of composition, and are tabulated in tables A1.1 and A1.2.

An independent check of the above method was [illegible]formed using a gas cylinder containing 0.99±0.02 % H_2S, 0.98±0.02 % CH_4, and the remainder N_2. The mixture was supplied by Matheson. The concentration of H_2S in the gas was verified using a wet chemistry method as follows: the regulator on the cylinder was attached to a 1/8-in. stainless steel line, which led to two well-stirred flasks containing 2 M NaOH and arranged in series. The second flask contained a sparger to increase gas-liquid mass transfer. The amount of caustic in the flasks totalled a 600-fold excess of that required to neutralize the expected throughput of H_2S. The outlet from the second flask entered a model DTM-115 Singer American Meter Division positive displacement gas meter. The outlet from the gas meter was vented to a fume hood.

The volume of gas used in the test was 3.66 l at approximately atmospheric pressure. Iodometric titration (see Section 4.3 and Appendix II) yielded a result of 0.7003 mmol H_2S absorbed by the caustic; the mole percent of H_2S leaving the gas cylinder was calculated to be 0.5754 mole %.

The same cylinder was attached to the gas chromatograph and the response factor was determined. A sample was also withdrawn into the sampling bomb used for determining response factors as described by Roberts (1983); both methods yielded a response factor of 0.5721, which agrees with the trend observed above (see also Table A1.2).

Table A1.1: CO_2 Response Factors as a Function of Composition

Mixture	area %	mole %	RF
1	47.368	44.947	1.109
2	87.017	85.686	1.120
3	46.779	45.195	1.066
4	45.740	43.496	1.095
5	33.390	3.0474	1.116
6	64.434	62.456	1.089

Table A1.2: H_2S Response Factors as a Function of Composition

Mixture	area %	mole %	RF
1†	0.330	0.5754	0.5751
2	54.878	53.831	1.043
3	31.210	30.102	1.054
4	8.0183	8.1900	0.977
5	19.411	18.936	1.031
6	3.4621	3.7857	0.9016
7	91.535	90.734	1.104
8	77.606	76.591	1.059
9	5.5863	6.1710	0.8996

†Evaluation using wet chemistry method on gas mixture in Matheson cylinder.

Appendix II: Sample Calculations for Laboratory Data

The following calculations apply to both aqueous and mixed solvent data.

A. Data for H_2S and CO_2 Liquid Phase Analysis:

mass of sample from cell: 1.8612 g
total mass, caustic + cell sample: 22.6893 g
mass of sample aliquot: 5.1729 g
density of amine solution (23°C): 1.0902 g/cm^3
concentration of amine solution (23°C):
2.00 moles amine/l

B. Sample Calculation for H_2S:

Data:
volume 0.100 N iodine solution used: 25 cm^3
volume 0.100 N thiosulphate solution required: 11.5 cm^3

- moles H_2S in sample aliquot =

$$\frac{(25.0 - 11.5)}{20.0} = 6.75\times10^{-4}$$

- moles H_2S in total sample =

$$(6.75\times10^{-4}) \times \frac{22.6893}{5.1729} = 2.9607\times10^{-3}$$

- mass of amine in total sample =

$$(1.8612 - (34 \times 2.9607\times10^{-3})) = 1.7605 \text{ g}$$

- moles of lean amine solution in total sample =

$$\frac{2.00}{1.0902} \times 1.7605 = 3.2298\times10^{-3}$$

$$\therefore \alpha = \frac{2.9607\times10^{-3}}{3.2298\times10^{-3}} = 0.9167 \text{ mol } H_2S\text{/mol amine}$$

C. Sample Calculation for CO_2:

Data:
volume 0.100 N HCl required(corrected, see p 24): 7.28 cm³
volume 1 N NaOH used: 20 ml
carbonate content of NaOH solution: 2.0×10^{-6} moles/ml

- moles CO_2 in sample aliquot =

$$\frac{7.28 \times 0.1}{1000 \times 2} = 3.64\times10^{-4}$$

- moles CO_2 in liquid sample + caustic solution =

$$3.64\times10^{-4} \times \frac{22.6893}{5.1729} = 1.5966\times10^{-3}$$

- moles CO_2 in liquid sample alone =

$$1.5966\times10^{-3} - 2.0\times10^{-6} \times 20 = 1.5566\times10^{-3}$$

- moles amine in total sample =

$$(1.8612 - (44 \times 1.5566\times10^{-3}))\times \frac{2.00}{1.0902} = 3.2888\times10^{-3}$$

$$\therefore \alpha = \frac{1.5566\times10^{-3}}{3.2888\times10^{-3}} = 0.4733 \text{ mol } CO_2/\text{mol amine}$$

D. Sample Calculation for Acid Gas Partial Pressures

Data:
cell pressure: 513.3 kPa
area % H_2S: 31.1448
response factor: 1.037
water mole fraction (liq): 0.8081
water saturation pressure: 7.376 kPa

- mole fraction H_2S =

$$\frac{31.1448/1.037}{31.1448/1.037 + (100 - 31.1448)} = 0.3037$$

- water partial pressure =

$$0.8081 \times 7.376 = 5.96 \text{ kPa}$$

- H_2S partial pressure =

$$0.3037 \times (513.3 - 5.96) = 154.1 \text{ kPa}$$

(The calculations for CO_2 partial pressure are analogous)

Appendix VII: Raw Experimental Data

Table A2.1 Raw Data - Solubility of Carbon Dioxide in 2.0 M Aqueous MDEA at 40 C

Mass liquid sample (g)	mmol CO2 in liq.	MDEA mol.	mmol MDEA in liq.	x water	Mole ratio	Total P (kpa)	Partial P H20 (kPa)	y CO2	Partial P CO2(kPa)
7.908E+00	1.96E+00	2.06	1.59E+01	9.486E-01	1.236E-01	4.487E+02	6.996E+00	2.604E-03	1.168E+00
5.370E+00	2.84E+00	2.06	1.06E+01	9.424E-01	2.668E-01	5.357E+02	6.951E+00	7.740E-03	4.146E+00
2.991E+00	3.92E+00	2.06	5.72E+00	9.248E-01	6.859E-01	5.557E+02	6.821E+00	8.815E-02	4.898E+01
2.730E+00	4.94E+00	2.06	5.10E+00	9.133E-01	9.686E-01	1.006E+03	6.736E+00	5.848E-01	5.884E+02
3.119E+00	6.88E+00	2.06	5.72E+00	9.039E-01	1.203E+00	3.998E+03	6.667E+00	9.436E-01	3.773E+03

Table A3.2 Raw Data - Solubility of Hydrogen Sulphide in 2.0 M Aqueous MDEA at 40 C

Mass liquid sample (g)	mmol H2S in liq.	MDEA mol.	mmol MDEA in liq.	x water	Mole ratio	Total P (kPa)	Partial P H20 (kPa)	y H2S	Partial P H2S(kPa)
7.979E+00	1.10E+01	2.00	1.49E+01	9.257E-01	7.415E-01	3.817E+02	6.828E+00	1.040E-01	3.972E+01
3.672E+00	8.68E+00	2.00	6.62E+00	9.038E-01	1.311E+00	8.714E+02	6.666E+00	7.226E-01	6.297E+02
3.239E+00	9.82E+00	2.00	5.69E+00	8.885E-01	1.725E+00	1.683E+03	6.553E+00	9.523E-01	1.602E+03
3.872E+00	7.13E+00	2.00	7.11E+00	9.155E-01	1.003E+00	4.541E+02	6.753E+00	3.692E-01	1.676E+02
1.618E+00	2.33E+00	2.00	3.02E+00	9.245E-01	7.735E-01	4.592E+02	6.819E+00	6.850E-02	3.146E+01
4.752E+00	4.00E+00	2.00	9.04E+00	9.377E-01	4.424E-01	4.558E+02	6.916E+00	1.883E-02	8.581E+00
3.866E+00	2.36E+00	1.99	7.46E+00	9.424E-01	3.162E-01	4.314E+02	6.951E+00	7.805E-03	3.367E+00
4.048E+00	2.42E+00	1.99	7.82E+00	9.427E-01	3.092E-01	4.025E+02	6.953E+00	7.805E-03	3.142E+00
4.441E+00	5.63E+00	1.99	8.38E+00	9.280E-01	6.723E-01	3.972E+02	6.844E+00	7.140E-02	2.836E+01
4.120E+00	7.97E+00	1.99	7.59E+00	9.131E-01	1.051E+00	4.871E+02	6.735E+00	3.222E-01	1.570E+02
4.203E+00	7.45E+00	2.01	7.64E+00	9.179E-01	9.747E-01	4.097E+02	6.770E+00	3.532E-01	1.447E+02
2.937E+00	1.68E+00	2.00	5.65E+00	9.435E-01	2.970E-01	4.302E+02	6.959E+00	7.385E-03	3.177E+00
3.960E+00	3.86E+00	2.00	7.51E+00	9.347E-01	5.134E-01	4.161E+02	6.894E+00	4.193E-02	1.745E+01
4.106E+00	4.04E+00	2.00	7.79E+00	9.345E-01	5.190E-01	3.943E+02	6.892E+00	4.655E-02	1.836E+01
3.722E+00	3.62E+00	1.96	6.85E+00	9.365E-01	5.279E-01	5.104E+02	6.907E+00	3.225E-02	1.646E+01
3.629E+00	3.29E+00	2.00	6.82E+00	9.369E-01	4.825E-01	4.705E+02	6.910E+00	2.794E-02	1.315E+01
3.414E+00	3.11E+00	2.00	6.41E+00	9.369E-01	4.846E-01	4.232E+02	6.910E+00	3.133E-02	1.326E+01
4.856E+00	4.45E+00	2.00	9.12E+00	9.367E-01	4.885E-01	4.127E+02	6.909E+00	3.273E-02	1.351E+01
4.297E+00	3.07E+00	1.96	8.03E+00	9.418E-01	3.821E-01	4.577E+02	6.946E+00	1.334E-02	6.108E+00
2.414E+00	1.85E+00	1.98	4.50E+00	9.407E-01	4.110E-01	4.177E+02	6.938E+00	1.342E-02	5.604E+00
3.710E+00	6.14E+00	2.00	6.87E+00	9.197E-01	8.949E-01	5.366E+02	6.783E+00	2.016E-01	1.082E+02
3.479E+00	3.87E+00	2.00	6.56E+00	9.317E-01	5.895E-01	4.415E+02	6.872E+00	4.785E-02	2.112E+01
3.789E+00	3.79E+00	2.02	7.17E+00	9.343E-01	5.280E-01	4.619E+02	6.891E+00	3.067E-02	1.417E+01
2.932E+00	2.52E+00	2.02	5.58E+00	9.373E-01	4.517E-01	4.748E+02	6.913E+00	2.011E-02	9.547E+00
4.773E+00	2.19E+00	2.02	9.28E+00	9.456E-01	2.357E-01	5.280E+02	6.974E+00	4.361E-03	2.303E+00
4.497E+00	1.81E+00	2.02	8.76E+00	9.469E-01	2.062E-01	4.972E+02	6.984E+00	1.691E-03	8.406E-01
4.170E+00	1.06E+00	2.00	8.11E+00	9.504E-01	1.301E-01	4.474E+02	7.010E+00	1.172E-03	5.244E-01

Table A3.3 Raw Data - Solubility of Carbon Dioxide in 2.0 M Mixed Solvent at 40 C

Mass liquid sample (g)	mmol CO2 in liq.	MDEA mol.	mmol MDEA in liq.	x water	Mole ratio	Total P (kpa)	Partial P H2O (kPa)	y CO2	Partial P CO2 (kPa)
5.832E+00	6.41E-01	1.98	1.05E+01	8.528E-01	6.091E-02	4.257E+02	6.290E+00	2.210E-03	9.410E-01
4.004E+00	1.30E+00	1.98	7.16E+00	8.468E-01	1.809E-01	4.087E+02	6.245E+00	1.184E-02	4.840E+00
4.194E+00	1.72E+00	1.98	7.47E+00	8.443E-01	2.308E-01	4.004E+02	6.227E+00	1.837E-02	[illegible]
[illegible]	[illegible]	1.98	7.68E+00	8.406E-01	3.067E-01	3.786E+02	6.200E+00	3.231E-02	1.223E+01
[illegible]	3.07E+00	1.98	7.07E+00	8.343E-01	4.345E-01	3.785E+02	6.154E+00	6.256E-02	2.368E+01
[illegible]	3.71E+00	1.98	7.02E+00	8.298E-01	5.288E-01	3.848E+02	6.120E+00	1.091E-01	4.197E+01
[illegible]	[illegible]	2.02	1.12E+01	8.468E-01	4.828E-02	[illegible]	6.245E+00	1.037E-03	[illegible]
[illegible]	8.99E-01	2.02	8.83E+00	8.440E-01	1.018E-01	4.040E+02	6.225E+00	4.940E-03	1.996E+00
[illegible]	1.07E+00	2.02	7.18E+00	8.416E-01	1.484E-01	3.909E+02	6.207E+00	8.864E-03	3.465E+00
[illegible]	1.68E+00	2.02	7.30E+00	8.374E-01	2.300E-01	3.791E+02	6.176E+00	1.895E-02	7.186E+00
[illegible]	[illegible]	2.02	5.69E+00	8.349E-01	2.786E-01	3.684E+02	6.158E+00	2.707E-02	9.917E+00
[illegible]	[illegible]	2.00	5.13E+00	8.279E-01	7.547E-01	2.782E+02	6.106E+00	4.383E-01	[illegible]
[illegible]	[illegible]	1.98	7.53E+00	8.111E-01	8.977E-01	3.672E+02	5.982E+00	1.000E+00	3.672E+02
[illegible]	[illegible]	1.98	3.57E+00	8.098E-01	[illegible]	3.562E+02	5.973E+00	1.000E+00	3.562E+02
[illegible]	[illegible]	1.98	3.96E+00	8.090E-01	[illegible]	4.742E+02	5.966E+00	1.000E+00	4.742E+02
[illegible]	[illegible]	1.98	3.93E+00	8.100E-01	9.218E-01	5.662E+02	5.974E+00	1.000E+00	5.662E+02
[illegible]	[illegible]	1.98	4.36E+00	8.062E-01	1.004E+00	6.943E+02	5.946E+00	1.000E+00	6.943E+02
[illegible]	[illegible]	1.98	3.23E+00	8.060E-01	1.010E+00	8.501E+02	5.944E+00	1.000E+00	8.501E+02
[illegible]	[illegible]	1.98	2.40E+00	8.022E-01	1.093E+00	1.193E+03	5.917E+00	1.000E+00	1.193E+03
[illegible]	[illegible]	1.98	2.45E+00	8.189E-01	1.187E+00	1.669E+03	6.025E+00	1.000E+00	1.669E+03
[illegible]	[illegible]	1.98	3.89E+00	8.132E-01	1.255E+00	2.902E+03	5.998E+00	1.000E+00	2.902E+03
[illegible]	[illegible]	1.98	3.54E+00	8.081E-01	1.381E+00	4.054E+03	5.990E+00	1.000E+00	4.054E+03
[illegible]	[illegible]	1.98	3.04E+00	8.004E-01	1.567E+00	5.772E+03	5.903E+00	1.000E+00	5.772E+03
[illegible]	[illegible]	2.00	[illegible]	8.373E-01	2.192E-01	4.591E+02	6.175E+00	3.241E-02	[illegible]
[illegible]	[illegible]	2.00	[illegible]	8.288E-01	4.922E-01	4.631E+02	6.113E+00	8.200E-02	[illegible]
[illegible]	[illegible]	2.00	6.27E+00	8.288E-01	4.908E-01	4.469E+02	6.113E+00	8.579E-02	[illegible]
[illegible]	[illegible]	2.00	4.34E+00	8.249E-01	5.731E-01	4.459E+02	6.084E+00	1.239E-01	[illegible]
[illegible]	[illegible]	2.00	8.39E+00	[illegible]	5.730E-01	4.329E+02	6.084E+00	1.280E-01	5.540E+01
[illegible]	[illegible]	2.00	7.71E+00	[illegible]	6.782E-01	4.468E+02	6.047E+00	[illegible]	8.426E+01
[illegible]	[illegible]	2.00	5.82E+00	8.158E-01	7.839E-01	4.842E+02	6.017E+00	[illegible]	[illegible]
[illegible]	[illegible]	2.00	3.73E+00	8.138E-01	8.064E-01	4.727E+02	6.002E+00	2.873E-01	[illegible]
[illegible]	2.80E+00	2.00	2.99E+00	8.078E-01	9.352E-01	[illegible]	[illegible]	5.126E-01	4.455E+02
[illegible]	2.88E+00	2.00	2.98E+00	8.064E-01	9.655E-01	7.272E+02	5.948E+00	5.126E-01	4.455E+02

Table A3.4 Raw Data - Solubility of Carbon Dioxide in 2.0 M Mixed Solvent at 100 C

Mass liquid sample (g)	mmol CO2 in liq.	MDEA mol.	mmol MDEA in liq.	x water	Mole ratio	Total P (kpa)	Partial P H2O (kPa)	y CO2	Partial P CO2 (kPa)
3.701E+00	1.74E-02	2.01	6.80E+00	8.522E-01	2.564E-03	3.171E+02	8.635E+01	3.126E-03	9.915E-01
3.425E+00	2.42E-01	2.01	6.28E+00	8.503E-01	3.850E-02	3.198E+02	8.616E+01	5.671E-02	1.814E+01
3.320E+00	4.31E-01	2.01	6.07E+00	8.487E-01	7.101E-02	3.199E+02	8.599E+01	1.391E-01	4.450E+01
2.688E+00	5.31E-01	2.01	4.90E+00	8.468E-01	1.083E-01	3.229E+02	8.580E+01	2.304E-01	7.441E+01
2.192E+00	4.58E-01	2.01	3.99E+00	8.464E-01	1.148E-01	3.392E+02	8.576E+01	2.987E-01	1.013E+02
2.710E+00	7.90E-01	2.01	4.92E+00	8.441E-01	1.605E-01	3.409E+02	8.553E+01	4.377E-01	1.492E+02
2.872E+00	1.06E+00	2.01	5.19E+00	8.419E-01	2.034E-01	6.797E+02	8.531E+01	3.608E-01	2.452E+02
2.004E+00	9.25E-01	2.01	3.61E+00	8.393E-01	2.562E-01	7.513E+02	8.504E+01	4.657E-01	3.499E+02
2.337E+00	1.37E+00	2.01	4.19E+00	8.358E-01	3.263E-01	8.349E+02	8.468E+01	5.544E-01	4.629E+02
1.062E+00	7.00E-01	2.01	1.90E+00	8.337E-01	3.688E-01	1.012E+03	8.447E+01	6.662E-01	6.744E+02
1.335E+00	1.61E+00	2.01	2.32E+00	8.178E-01	6.948E-01	3.[illegible]E+03	8.287E+01	9.358E-01	2.937E+03
1.932E+00	1.55E+00	1.99	3.31E+00	8.388E-01	4.694E-01	9.816E+02	8.499E+01	1.000E+00	9.816E+02
2.792E+00	2.68E+00	1.99	4.75E+00	8.343E-01	5.652E-01	1.562E+03	8.454E+01	1.000E+00	1.562E+03
1.955E+00	2.46E+00	1.99	3.35E+00	8.265E-01	7.355E-01	2.223E+03	8.375E+01	1.000E+00	2.223E+03
3.647E+00	4.26E+00	2.01	6.33E+00	8.202E-01	6.734E-01	2.313E+03	8.311E+01	8.855E-01	2.048E+03
2.370E+00	3.95E+00	2.01	4.02E+00	8.057E-01	9.838E-01	4.316E+03	8.164E+01	9.512E-01	4.105E+03
1.957E+00	3.41E+00	2.01	3.31E+00	8.035E-01	1.032E+00	5.304E+03	8.142E+01	9.646E-01	5.117E+03
2.276E+00	2.58E+00	1.99	3.92E+00	8.240E-01	6.595E-01	1.863E+03	8.349E+01	1.000E+00	1.863E+03
2.631E+00	3.16E+00	1.99	4.52E+00	8.222E-01	6.987E-01	1.864E+03	8.330E+01	1.000E+00	1.864E+03
2.631E+00	3.19E+00	1.99	4.51E+00	8.218E-01	7.059E-01	1.864E+03	8.327E+01	1.000E+00	1.864E+03
2.229E+00	2.79E+00	1.99	3.82E+00	8.207E-01	7.308E-01	2.089E+03	8.315E+01	1.000E+00	2.089E+03
5.303E+00	6.64E+00	1.99	9.08E+00	8.207E-01	7.309E-01	2.089E+03	8.315E+01	1.000E+00	2.089E+03
5.303E+00	6.61E+00	1.99	9.08E+00	8.208E-01	7.277E-01	2.089E+03	8.317E+01	1.000E+00	2.089E+03
4.229E+00	6.01E+00	1.99	7.24E+00	8.148E-01	8.290E-01	3.009E+03	8.256E+01	1.000E+00	3.009E+03
4.229E+00	5.91E+00	1.99	7.25E+00	8.155E-01	8.144E-01	3.009E+03	8.263E+01	1.000E+00	3.009E+03
2.925E+00	4.67E+00	1.99	4.97E+00	8.097E-01	9.404E-01	3.009E+03	8.204E+01	1.000E+00	3.009E+03
2.925E+00	4.66E+00	1.99	4.97E+00	8.098E-01	9.380E-01	3.009E+03	8.205E+01	1.000E+00	3.009E+03
3.713E+00	5.67E+00	1.99	6.33E+00	8.117E-01	8.963E-01	3.555E+03	8.225E+01	1.000E+00	3.555E+03
3.713E+00	5.67E+00	1.99	6.33E+00	8.118E-01	8.953E-01	3.555E+03	8.225E+01	1.000E+00	3.555E+03
2.551E+00	4.20E+00	1.99	4.32E+00	8.083E-01	9.709E-01	3.556E+03	8.190E+01	1.000E+00	3.556E+03
2.551E+00	4.21E+00	1.99	4.32E+00	8.082E-01	9.738E-01	3.556E+03	8.189E+01	1.000E+00	3.556E+03
3.073E+00	4.98E+00	1.99	5.21E+00	8.090E-01	9.555E-01	4.521E+03	8.197E+01	1.000E+00	4.521E+03

Table A3.4 cont'd

Mass liquid sample (g)	mmol CO2 in liq.	MDEA mol.	mmol MDEA in liq.	x water	Mole ratio	Total P (kpa)	Partial P H2O (kPa)	y CO2	Partial P CO2 (kPa)
3.073E+00	5.38E+00	1.99	5.18E+00	8.055E-01	1.038E+00	4.521E+03	8.161E+01	1.000E+00	4.521E+03
2.985E+00	5.39E+00	1.99	5.04E+00	8.038E-01	1.070E+00	5.584E+03	8.144E+01	1.000E+00	5.584E+03
2.995E+00	5.42E+00	1.99	5.04E+00	8.035E-01	1.077E+00	5.584E+03	8.141E+01	1.000E+00	5.584E+03
[illegible]	6.93E+00	1.99	6.14E+00	8.012E-01	1.127E+00	5.584E+03	8.119E+01	1.000E+00	5.584E+03
[illegible]	6.91E+00	1.99	6.15E+00	8.014E-01	1.124E+00	5.584E+03	8.120E+01	1.000E+00	5.584E+03
3.444E+00	5.39E+00	1.99	5.86E+00	8.106E-01	9.198E-01	3.507E+03	8.214E+01	1.000E+00	3.507E+03
3.444E+00	5.46E+00	1.99	5.85E+00	8.100E-01	9.333E-01	3.507E+03	8.208E+01	1.000E+00	3.507E+03
1.771E+00	3.01E+00	1.99	2.99E+00	8.067E-01	1.006E+00	3.508E+03	8.174E+01	1.000E+00	3.508E+03
1.771E+00	3.00E+00	1.99	2.99E+00	8.070E-01	1.000E+00	3.508E+03	[illegible]	1.000E+00	3.508E+03
[illegible]	3.15E+00	1.99	3.62E+00	8.130E-01	8.696E-01	2.403E+03	[illegible]	1.000E+00	2.403E+03
[illegible]	3.04E+00	1.99	3.63E+00	8.144E-01	8.381E-01	2.403E+03	8.252E+01	1.000E+00	2.403E+03
[illegible]	4.68E+00	1.99	5.67E+00	8.150E-01	8.255E-01	2.403E+03	8.258E+01	1.000E+00	2.403E+03
[illegible]	1.26E+00	1.97	3.67E+00	8.402E-01	3.426E-01	6.860E+02	8.514E+01	7.419E-01	5.089E+02
[illegible]	1.27E+00	1.97	3.67E+00	8.401E-01	3.457E-01	6.860E+02	8.512E+01	7.419E-01	5.089E+02
[illegible]	1.32E+00	1.97	3.66E+00	8.384E-01	3.608E-01	6.861E+02	8.505E+01	7.419E-01	5.090E+02
[illegible]	1.40E+00	1.97	2.76E+00	8.323E-01	5.078E-01	1.019E+03	8.423E+01	8.841E-01	9.009E+02
[illegible]	1.32E+00	1.97	2.76E+00	8.337E-01	4.778E-01	1.019E+03	8.448E+01	8.841E-01	9.008E+02
[illegible]	1.28E+00	1.97	2.77E+00	8.348E-01	4.620E-01	1.019E+03	8.455E+01	8.841E-01	9.007E+02
[illegible]	2.55E+00	1.97	4.06E+00	8.266E-01	6.279E-01	1.894E+03	8.376E+01	9.577E-01	1.814E+03
[illegible]	2.65E+00	1.97	4.05E+00	8.254E-01	6.542E-01	1.895E+03	8.363E+01	9.577E-01	1.814E+03
[illegible]	2.66E+00	1.97	4.06E+00	8.253E-01	6.549E-01	1.895E+03	8.363E+01	9.577E-01	1.814E+03
[illegible]	3.53E+00	1.97	5.23E+00	8.244E-01	6.758E-01	2.078E+03	8.353E+01	9.644E-01	2.004E+03
[illegible]	3.53E+00	1.97	5.23E+00	8.244E-01	6.751E-01	2.078E+03	8.353E+01	9.644E-01	2.004E+03
[illegible]	3.52E+00	1.97	5.23E+00	8.244E-01	6.741E-01	2.078E+03	8.354E+01	9.644E-01	2.004E+03
[illegible]	4.07E+00	1.97	5.07E+00	8.186E-01	8.036E-01	2.748E+03	8.283E+01	9.759E-01	2.682E+03
[illegible]	3.97E+00	1.97	5.08E+00	8.195E-01	7.817E-01	2.748E+03	8.308E+01	9.759E-01	2.682E+03
[illegible]	4.80E+00	1.97	5.49E+00	8.152E-01	8.742E-01	3.346E+03	8.260E+01	9.801E-01	3.279E+03
[illegible]	4.97E+00	1.97	5.61E+00	8.138E-01	[illegible]	3.825E+03	8.247E+01	9.854E-01	3.769E+03
[illegible]	5.41E+00	1.97	5.85E+00	8.124E-01	9.251E-01	4.549E+03	8.232E+01	9.888E-01	4.498E+03
[illegible]	5.68E+00	1.97	5.37E+00	8.059E-01	1.058E+00	5.527E+03	8.175E+01	9.895E-01	5.469E+03

Table A3.5 Raw Data - Solubility of Hydrogen Sulphide in 2.0 M Mixed Solvent at 40 C

Mass liquid sample (g)	mmol H2S in liq.	MDEA mol.	mmol MDEA in liq.	x water	Mole ratio	Total P (kpa)	Partial P H20 (kPa)	y H2S	Partial P H2S (kPa)
4.565E+00	2.03E+00	2.00	8.29E+00	8.404E-01	2.454E-01	3.381E+02	6.199E+00	2.185E-02	7.386E+00
5.889E+00	2.67E+00	2.00	1.06E+01	8.401E-01	2.514E-01	3.381E+02	6.196E+00	2.185E-02	7.386E+00
3.520E+00	2.12E+00	2.00	6.32E+00	8.359E-01	3.356E-01	4.213E+02	6.165E+00	2.730E-02	1.150E+01
3.670E+00	2.71E+00	2.00	6.56E+00	8.322E-01	4.121E-01	4.185E+02	6.138E+00	4.065E-02	1.701E+01
1.381E+00	1.18E+00	2.00	2.46E+00	8.288E-01	4.799E-01	4.214E+02	6.113E+00	7.266E-02	3.062E+01
1.381E+00	1.28E+00	2.00	2.45E+00	8.267E-01	5.236E-01	4.215E+02	6.097E+00	7.266E-02	3.062E+01
1.381E+00	1.43E+00	2.00	2.44E+00	8.238E-01	5.840E-01	4.215E+02	6.076E+00	7.266E-02	3.063E+01
2.478E+00	2.94E+00	2.00	4.36E+00	8.195E-01	6.734E-01	4.396E+02	6.044E+00	1.251E-01	5.499E+01
1.758E+00	2.22E+00	2.00	3.09E+00	8.174E-01	7.190E-01	4.434E+02	6.028E+00	1.554E-01	6.888E+01
2.015E+00	2.91E+00	2.00	3.52E+00	8.123E-01	8.268E-01	4.723E+02	5.991E+00	2.255E-01	1.065E+02
1.861E+00	2.96E+00	2.00	3.23E+00	8.081E-01	9.167E-[illegible]	5.073E+02	5.960E+00	3.031E-01	1.538E+02
3.696E+00	6.63E+00	2.00	6.37E+00	8.023E-01	1.042E+0[illegible]	5.942E+02	5.918E+00	4.349E-01	2.584E+02
3.164E+00	6.15E+00	2.00	5.42E+00	7.981E-01	1.135E+00	6.856E+02	5.886E+00	5.437E-01	3.727E+02
3.164E+00	6.13E+00	2.00	5.42E+00	7.983E-01	1.131E+00	6.856E+02	5.888E+00	5.437E-01	3.727E+02
2.106E+00	4.43E+00	2.00	3.59E+00	7.937E-01	1.232E+00	7:985E+02	5.854E+00	6.414E-01	5.122E+02
2.545E+00	5.85E+00	2.00	4.30E+00	7.880E-01	1.360E+00	9.442E+02	5.812E+00	7.182E-01	6.781E+02
1.554E+00	4.37E+00	2.00	2.58E+00	7.735E-01	1.697E+00	1.073E+03	5.705E+00	1.000E+00	1.073E+03
1.489E+00	5.01E+00	2.00	2.42E+00	7.579E-01	2.073E+00	1.469E+03	5.590E+00	1.000E+00	1.469E+03
3.903E+00	1.33E+00	1.98	6.98E+00	8.419E-01	1.904E-01	3.625E+02	6.210E+00	1.164E-02	4.219E+00
7.253E+00	1.27E+00	1.98	1.31E+01	8.466E-01	9.764E-02	3.627E+02	6.244E+00	3.583E-03	1.300E+00
4.312E+00	1.00E+00	1.98	7.74E+00	8.450E-01	1.293E-01	3.326E+02	6.232E+00	7.529E-03	2.504E+00
2.943E+00	2.20E+00	1.98	5.19E+00	8.304E-01	4.242E-01	3.250E+02	6.125E+00	5.587E-02	1.816E+01
3.025E+00	3.07E+00	1.98	5.29E+00	8.229E-01	5.807E-01	3.351E+02	6.069E+00	1.137E-01	3.811E+01
2.914E+00	8.32E+00	2.00	4.81E+00	7.675E-01	1.728E+00	1.180E+03	5.661E+00	9.523E-01	1.124E+03

Table A3.6 Raw Data - Solubility of Hydrogen Sulphide in 2.0 M Mixed Solvent at 100 C

Mass liquid sample (g)	mmol H2S in liq.	MDEA mol.	mmol MDEA in liq.	x water	Mole ratio	Total P (kpa)	Partial P H2O (kPa)	y H2S	Partial P H2S (kPa)
1.934E+00	4.48E+00	2.00	3.27E+00	7.820E-01	1.370E+00	1.943E+03	7.924E+01	1.000E+00	1.943E+03
4.442E+00	9.64E-01	1.98	7.98E+00	8.454E-01	1.208E-01	2.693E+02	8.566E+01	8.698E-02	2.342E+01
2.401E+00	7.61E-01	1.98	4.30E+00	8.426E-01	1.770E-01	2.332E+02	8.538E+01	1.973E-01	4.602E+01
3.056E+00	1.34E+00	1.98	5.50E+00	8.393E-01	2.433E-01	3.726E+02	8.504E+01	2.018E-01	7.520E+01
5.359E+00	7.14E-01	2.00	9.82E+00	8.448E-01	7.270E-02	3.156E+02	8.560E+01	4.250E-02	1.341E+01
3.695E+00	2.06E+00	2.00	6.63E+00	8.327E-01	3.107E-01	3.867E+02	8.438E+01	2.929E-01	1.133E+02
3.285E+00	2.59E+00	2.00	5.85E+00	8.262E-01	4.426E-01	4.650E+02	8.372E+01	4.831E-01	2.247E+02
3.625E+00	3.87E+00	2.00	6.39E+00	8.183E-01	6.050E-01	6.083E+02	8.291E+01	6.490E-01	3.948E+02
3.876E+00	5.43E+00	2.00	6.75E+00	8.088E-01	8.042E-01	8.486E+02	8.195E+01	7.901E-01	6.705E+02
2.266E+00	3.80E+00	2.00	3.91E+00	8.010E-01	9.715E-01	1.178E+03	8.116E+01	8.674E-01	1.022E+03
3.380E+00	6.87E+00	2.00	5.76E+00	7.909E-01	1.193E+00	1.567E+03	8.014E+01	9.158E-01	1.435E+03
2.026E+00	6.26E+00	2.00	3.32E+00	7.608E-01	1.887E+00	3.243E+03	7.709E+01	9.886E-01	3.206E+03
2.743E+00	7.26E+00	2.00	4.57E+00	7.734E-01	1.590E+00	2.521E+03	7.836E+01	9.738E-01	2.455E+03
4.611E+00	2.75E-01	1.96	8.29E+00	8.510E-01	3.321E-02	2.710E+02	8.623E+01	9.807E-03	2.657E+00
5.896E+00	2.55E-01	1.96	1.06E+01	8.515E-01	2.406E-02	2.673E+02	8.628E+01	5.904E-03	1.578E+00
5.797E+00	5.78E-01	1.96	1.04E+01	8.499E-01	5.549E-02	2.596E+02	8.611E+01	2.779E-02	7.213E+00

Table A3.7 Raw Data - Solubility of Carbon Dioxide and Hydrogen Sulphide in 2.0 Mixed Solvent at 40 C

Mass liquid sample (g)	MDEA mol.	mmol MDEA in liq.	x water	Total P (kpa)	Partial P H2O (kPa)	Mole Ratio H2S	Partial P H2S (kPa)	Mole Ratio CO2	Partial P CO2 (kPa)
4.945E+00	1.98	8.85E+00	8.41E-01	3.317E+02	6.202E+00	1.085E-01	2.503E+00	8.871E-02	3.561E+00
3.532E+00	1.98	6.19E+00	8.28E-01	3.495E+02	6.104E+00	1.076E-01	5.285E+00	3.602E-01	2.579E+01
8.817E-01	1.98	1.53E+00	8.20E-01	3.760E+02	6.049E+00	2.168E-01	2.376E+01	4.073E-01	4.378E+01
1.808E+00	1.98	3.06E+00	8.02E-01	5.356E+02	5.919E+00	3.279E-01	5.272E+01	6.747E-01	1.934E+02
1.467E+00	1.98	2.47E+00	7.97E-01	8.026E+02	5.879E+00	6.649E-01	2.301E+02	4.563E-01	3.121E+02
2.688E+00	1.98	4.48E+00	7.88E-01	1.064E+03	5.811E+00	9.484E-01	4.595E+02	3.806E-01	3.554E+02
3.150E+00	1.98	5.12E+00	7.68E-01	1.570E+03	5.662E+00	1.543E+00	9.814E+02	2.581E-01	3.666E+02
3.861E+00	1.92	6.66E+00	8.47E-01	3.496E+02	6.249E+00	2.400E-01	9.116E+00	6.856E-02	3.987E+00
4.190E+00	1.92	7.13E+00	8.38E-01	3.402E+02	6.178E+00	3.487E-01	1.739E+01	1.668E-01	1.249E+01
3.990E+00	1.92	6.64E+00	8.22E-01	4.033E+02	6.066E+00	4.986E-01	5.637E+01	3.583E-01	5.813E+01
2.811E+00	1.92	4.82E+00	8.13E-01	6.216E+02	6.000E+00	7.186E-01	2.068E+02	3.412E-01	1.779E+02
2.408E+00	1.92	3.94E+00	8.11E-01	7.413E+02	5.983E+00	6.941E-01	2.381E+02	4.180E-01	2.766E+02
2.024E+00	1.92	3.29E+00	8.08E-01	9.135E+02	5.957E+00	6.575E-01	2.723E+02	5.374E-01	4.379E+02
2.944E+00	1.92	4.78E+00	8.07E-01	1.129E+03	5.949E+00	6.036E-01	3.034E+02	6.157E-01	6.278E+02
2.068E+00	1.92	3.33E+00	8.02E-01	1.462E+03	5.913E+00	5.528E-01	3.339E+02	7.807E-01	9.403E+02
2.382E+00	1.92	3.78E+00	7.98E-01	2.529E+03	5.862E+00	4.916E-01	4.487E+02	1.00[illegible]E+00	1.914[illegible]
1.891E+00	2.04	3.25E+00	7.84E-01	7.617E+02	5.784E+00	1.152E+00	5.502E+02	1.484E-01	1.481E+02
1.649E+00	2.04	2.83E+00	7.83E-01	9.336E+02	5.776E+00	1.100E+00	5.641E+02	2.247E-01	3.012E+02
2.530E+00	2.04	4.31E+00	7.77E-01	1.202E+03	5.729E+00	1.229E+00	7.697E+02	2.362E-01	3.587E+02
1.868E+00	2.04	3.10E+00	7.57E-01	1.676E+03	5.583E+00	1.769E+00	1.311E+03	1.540E-01	2.980E+02

Table A3.8 Raw Data - Solubility of Carbon Dioxide and Hydrogen Sulphide in 2.0 Mixed Solvent at 100 C

Mass liquid sample (g)	MDEA mol.	mmol MDEA in liq.	x water	Total P (kpa)	Partial P H2O (kPa)	Mole Ratio H2S	Partial P H2S (kPa)	Mole Ratio CO2	Partial P CO2 (kPa)
4.881E+00	1.96	8.31E+00	8.44E-01	3.093E+02	8.555E+01	1.126E-01	2.789E+01	5.348E-02	5.197E+01
2.779E+00	1.96	4.89E+00	8.37E-01	5.541E+02	8.481E+01	1.065E-01	3.689E+01	2.094E-01	3.428E+02
2.290E+00	1.96	3.94E+00	8.31E-01	9.771E+02	8.415E+01	9.427E-02	4.610E+01	3.541E-01	7.688E+02
8.110E-01	1.96	9.82E-01	7.80E-01	5.627E+03	7.907E+01	1.088E-01	8.427E+01	1.450E+00	5.459E+03
[illegible]	1.98	4.10E+00	8.17E-01	1.583E+03	8.278E+01	3.249E-01	1.978E+02	3.945E-01	1.211E+03
[illegible]	1.98	6.29E+00	8.12E-01	2.317E+03	8.232E+01	2.701E-01	2.226E+02	5.461E-01	1.975E+03
[illegible]	1.98	2.19E+00	7.95E-01	5.502E+03	8.058E+01	1.786E-01	2.468E+02	1.017E+00	5.176E+03
[illegible]	1.98	4.58E+00	8.10E-01	2.040E+03	8.210E+01	4.994E-01	4.457E+02	3.838E-01	[illegible]
[illegible]	1.98	4.37E+00	7.97E-01	5.244E+03	8.076E+01	2.693E-01	3.657E+02	8.869E-01	[illegible]
[illegible]	1.98	3.11E+00	8.27E-01	9.848E+02	8.383E+01	2.244E-01	1.170E+02	2.492E-01	6.083E+02
[illegible]	1.98	3.05E+00	8.16E-01	1.200E+03	8.272E+01	5.169E-01	3.637E+02	1.858E-01	5.593E+02
1.900E+00	1.98	3.25E+00	8.05E-01	1.498E+03	8.160E+01	7.769E-01	6.873E+02	1.822E-01	5.477E+02
3.458E+00	1.92	5.71E+00	8.12E-01	3.316E+03	8.232E+01	4.957E-01	5.278E+02	5.879E-01	2.596E+03
3.038E+00	1.92	4.91E+00	8.06E-01	5.348E+03	8.166E+01	3.720E-01	5.087E+02	8.633E-01	4.679E+03
2.461E+00	2.04	4.25E+00	7.81E-01	2.635E+03	7.914E+01	1.229E+00	1.736E+03	1.397E-01	7.853E+02
2.080E+00	2.04	3.44E+00	7.78E-01	3.268E+03	7.879E+01	1.129E+00	1.606E+03	3.168E-01	1.556E+03
2.372E+00	2.04	4.03E+00	7.79E-01	5.030E+03	7.897E+01	8.340E-01	1.254E+03	5.718E-01	3.616E+03
3.021E+00	2.01	5.45E+00	8.43E-01	3.747E+02	8.542E+01	1.599E-01	4.592E+01	4.618E-02	5.022E+01
2.738E+00	2.01	4.93E+00	8.42E-01	3.789E+02	8.529E+01	1.619E-01	4.680E+01	7.012E-02	8.380E+01
2.870E+00	2.01	5.05E+00	8.24E-01	7.244E+02	8.344E+01	5.038E-01	3.219E+02	1.007E-01	2.241E+02

Appendix IV: Detailed Error Analysis

A. Error in Determination of Acid Gas Loadings

The following variables are defined:

m_{ag} = moles acid gas

m_{MDEA} = moles amine

α = mole ratio, acid gas/MDEA

V = volume of titrant, cm^3

T = temperature, K

B = background CO_2 correction, mol CO_2

C = amine concentration, mol MDEA/g solvent

W = mass of sample used for titration, g

M = CO_2 molecular weight

D = dilution factor

C_t = concentration of titrant, mol/l

Assumptions:

i) error in molecular weight of CO_2 negligible;

ii) error in concentration of standard solutions negligible.

The following equations are used to calculate the solubilities of the acid gases:

$$m_{ag} = \frac{VC_tD}{2\times1000} - B \qquad \text{(A4.1)}$$

$$m_{MDEA} = (W - m_{ag}\times M)C \qquad \text{(A4.2)}$$

$$\alpha = m_{ag}/m_{MDEA} \qquad (A4.3)$$

The error in α can be expressed thus:

$$\Delta\alpha \approx \left|\left(\frac{\partial\alpha}{\partial T}\right)\Delta T\right| + \left|\left(\frac{\partial\alpha}{\partial C}\right)\Delta C\right| + \left|\left(\frac{\partial\alpha}{\partial B}\right)\Delta B\right| + \left|\left(\frac{\partial\alpha}{\partial W}\right)\Delta W\right|$$

$$+ \left|\left(\frac{\partial\alpha}{\partial D}\right)\Delta D\right| + \left|\left(\frac{\partial\alpha}{\partial V}\right)\Delta V\right| \qquad (A4.4)$$

Sample Calculation:

Values for various variables and their estimated errors(see Appendix II):

$V = 7.28$	$\Delta V = 0.071\ cm^3$
$\left(\frac{\partial\alpha}{\partial T}\right) = 0.008\ K^{-1}$	$\Delta T = 0.5\ K$
$B = 4\times10^{-5}$ (= 0 for H_2S)	$\Delta B = 6\times10^{-6}$ mol CO_2
$C = 1.8345\times10^{-3}$	$\Delta C = 3.902\times10^{-5}$ mol MDEA/mol solvent
$W = 1.8612$	$\Delta W = 1.45\times10^{-4}$ g
$M = 44$	
$D = 0.4386$	$\Delta D = 1.4725\times10^{-5}$

$m_{ag} = 1.5566\times10^{-3}$ mol CO_2

$m_{MDEA} = 3.2888\times10^{-3}$ mol MDEA

$\alpha = 0.4733$

Equations (A4.1) through (A4.3) yield the following:

$$\frac{\partial\alpha}{\partial C} = \frac{-m_{ag}}{m_s C} = -258.00 \qquad \text{(A4.5)}$$

$$\frac{\partial\alpha}{\partial B} = \frac{-m_{ag}}{m_s^2} \times (1 - M\times C) = -155.53 \qquad \text{(A4.6)}$$

$$\frac{\partial\alpha}{\partial W} = \frac{-m_{ag}}{m_s^2} \times C = 0.2640 \qquad \text{(A4.7)}$$

$$\frac{\partial\alpha}{\partial D} = \frac{VC_t}{2000} \times \left[\frac{m_s + MCm_{ag}}{m_s^2}\right] = 0.1149 \qquad \text{(A4.8)}$$

$$\frac{\partial\alpha}{\partial V} = \frac{DC_t}{2000} \times \left[\frac{m_s + MCm_{ag}}{m_s^2}\right] = 6.923\times10^{-3} \qquad \text{(A4.9)}$$

Substitution of equations (A4.5) through (A4.9) into (A4.4) yields

$$\Delta\alpha = 1.554\times10^{-3} \qquad (3.3\%)$$

B. Error in Determination of Acid Gas Partial Pressures

The following variables are defined:

P_t = total cell pressure (kPa)

y_a = mole fraction acid gas

P_w = partial pressure of water (kPa)

P_a = partial pressure of acid gas (kPa)

The acid gas partial pressure is calculated:

$$P_a = (P_t - P_w)\times y_a \qquad \text{(A4.10)}$$

The uncertainty in the acid gas partial pressure is estimated in equation (A4.11):

$$\Delta P_a \simeq \left|\left(\frac{\partial P_a}{\partial P_t}\right)\Delta P_t\right| + \left|\left(\frac{\partial P_a}{\partial P_w}\right)\Delta P_w\right| + \left|\left(\frac{\partial P_a}{\partial y_a}\right)\Delta y_a\right| \qquad (A4.11)$$

Equation (A4.10) yields

$$\frac{\partial P_a}{\partial P_t} = y_a \qquad (A4.12)$$

$$\frac{\partial P_a}{\partial P_w} = -y_a \qquad (A4.13)$$

$$\frac{\partial P_a}{\partial y_a} = (P_t - P_w) \qquad (A4.14)$$

Estimated errors are:

ΔP_t = 10 kPa ($2500 < P_t < 6000$ kPa)
= 3.5 kPa ($P_t < 2500$ kPa)

ΔP_w = 3 kPa (T_{cell} = 100°C)
= 1 kPa (T_{cell} = 40°C)

Δy_a = 0.003

The error in acid gas partial pressure at 100°C is calculated for a range of total pressures using the above uncertainties and equations (A4.10) through (A4.14).

P_t(kPa)	P_w(kPa)	y_a	P_a(kPa)	ΔP_a(kPa)	% ΔP_a
6000.	83.	0.990	5860.	29.1	0.50
2000.	83.	0.960	1840.	12.0	0.65
800.	83.	0.700	502.	6.7	1.3
350.	83.	0.100	26.7	1.42	5.3
350.	83.	0.020	5.34	0.931	17.4