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THE UNIVERSITY OF ALBERTA

EQUILIBRIUM SOLUBILITY OF CARBON DIOXIDE IN PHYSICAL AND MIXED SOLVENTS

by

Amr Henni ©

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE
IN
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A.E. Mather, Supervisor

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T.W. Forest

Date : 5 August 1994

Abstract

The solubility of carbon dioxide has been measured in two physical solvents. Solubility data were collected at a temperature of 40°C for methanol and at 40°C, 70°C and 100°C for triethylene glycol monomethyl ether (TEGMME). The experimental data collected were correlated with the Peng-Robinson equation of state. The solubility of carbon dioxide at 40°C has also been measured in a mixture of 50 wt % of MDEA (methyldiethanolamine) and methanol and in another mixture of 50 wt % of MDEA and TEGMME .

Finally data were gathered at 40°C and 100°C for the solubility of carbon dioxide in a mixture of 40 wt % MDEA, 40 wt % methanol and 20 wt % water and in a second mixture of 40 wt % MDEA, 40 wt % TEGMME and 20 wt % water. The experimental data for the TEGMME system at 40°C and 100°C were correlated using the Deshmukh-Mather model.

Dedication

To

My wife Fatma-Zohra and my daughters Amina and Jihane, my mother Amina Assem and my father Mustafa, my sisters Maha Sidhoum and Hala Cheniouni, my brothers Tarek and late Oussama .

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Nomenclature

a	activity
b	constant in Debye-HÜckel expression
f	fugacity, Pa
m	molality, mol / kg
v	partial molar volume, m^3 / mol
v^∞	partial molar volume at infinite dilution , m^3 / mol
x	mole fraction in liquid
w	mass fraction
y	mole fraction in vapour phase
z	electric charge
A	constant in Debye-Hückel expression
H	Henry's constant, Pa-kg / mol
I	ionic strength, mol / kg
K	chemical equilibrium constant
P	pressure, Pa
R	gas constant, J / mol K
T	temperature, K

Greek letters

α	mole ratio in liquid
β	binary interaction parameter in the extended Debye-Hückel equation
γ	activity coefficient
δ	binary interaction parameter in the Peng-Robinson equation of state
ϵ	dielectric constant
ϕ	fugacity coefficient
ω	acentric factor

Subscripts

i	component i
j	component j
m	mixture
w	water
A	component A

Superscripts

l	liquid
s	saturated
v	vapour
o	reference state

1.Introduction

The removal of acidic impurities like CO_2, H_2S and COS from gas streams is a very important operation for the petrochemical, oil refineries, ammonia manufacture, coal gasification and natural gas purification plants .
In general the removal requirement for H_2S is very severe e.g. 4 ppm by volume for pipeline gas at 1490 MPa and 0.1 ppm for chemical applications such as ammonia synthesis. The CO_2 specification is less severe e.g. less than 1% for natural gas and 10 ppm for ammonia and 100 ppm for LNG manufacture to prevent freezing-up in the cryogenic heat exchanger (Astarita et al., 1983). Removal of mercaptans down to 100 ppm per volume has been an accepted norm for pipeline and to a lower specification if the gas is used as a chemical feedstock.

Acid gases are considered as poisons for a catalyst and have to be removed from oil refineries streams, flue gas and tail gas streams in order to meet pollution standards.

The processes available to remove acid gas impurities have been categorized into the following classes by Astarita et al.(1983):

-Physical Solvents		Trade Names
	-Propylene carbonate	Fluor
	-Polyethylene glycol dimethyl ether	Selexol
	-N-methyl 2 pyrrolidone	Purisol

	-methanol	Rectisol
-Chemical Solvents		
	-MEA (20-35 wt % in water)	
	-DEA (30 wt % in water)	
	-DGA (60 wt % in water)	Econamine
	-DIPA	ADIP
	-MDEA	
	-Promoted K_2CO_3 (25-30 % K_2CO_3, 5 % promoter)	Benfield, Catacarb
	-AMP(in water)	
-Hybrid Systems (Chemical and Physical solvents)	-DIPA-sulfolane-water (40-40-20 wt %)	Sulfinol D
	-MDEA-sulfolane-water (40-40-20 wt %)	Sulfinol M
	-MEA or DEA-methanol	Amisol
	-DIPAM (diisopropylamine) or DETA (diethylamine)-methanol	Improved Amisol
	-AMP-sulfolane-water	

-Dry bed Process

-Iron oxide

-Molecular sieves (zeolites)

-Cryogenic Distillation

-Membranes

Solvent selection:

In physical solvent processes the gas to be treated is washed with solvent under pressure. The solution is then regenerated by reduction in pressure with as little stripping as possible.

Physical solvents are economical in the treatment of gases in which the partial pressure of acid gases is high and where the removal to low levels is not required.

Aqueous alkanolamines (chemical solvents) are used in more than 1000 gas treating plants. This accounts for more than half of the installations (Astarita et al., 1983). As of 1987, DEA-based solvents were used to process 47 % of the treated gas volume while MEA and MDEA were used to process 23 % and 17 % respectively (Carey et al., 1991).

Historically DEA and MEA have dominated acid gas treating applications. A smaller number of plants uses DGA and DIPA.

The mutual solubilities of solvents and hydrocarbons are a function of the molecular structure of the amines and their concentrations. The larger the number of hydroxyl groups, the more is the water solubility and the lower is the hydrocarbon solubility. The presence of more aliphatic groups tends to raise hydrocarbon solubility and lower water solubility (Butwell et al., 1982).

	Number of groups		
	Amino(-NH)	**Hydroxyl(-OH)**	**Aliphatic(-CH_m)**
MEA	1	1	2
DGA	1	1	4
DEA	1	2	4
DIPA	1	2	6
MDEA	1	2	5
AMP	1	1	4

Figure 1 shows the conventional process configuration for a gas treating system using aqueous alkanolamine solution.

Acid gas loading of MEA is usually limited to 0.3 - 0.4 moles of acid per mole of amine for carbon steel. MEA is a primary amine and thus has a high pH which enables it to reduce H_2S to a very low specification. For a 15-20 % MEA solution the heat of reaction is very high about 1919 J/g CO_2 (below 0.5 mole acid gas/mole amine). A high heat of reaction implies a need for a large steam rate in the desorber.

The degradation products of DEA are much less corrosive than those of MEA. As a secondary amine, DEA has a reduced affinity for CO_2 and H_2S. The

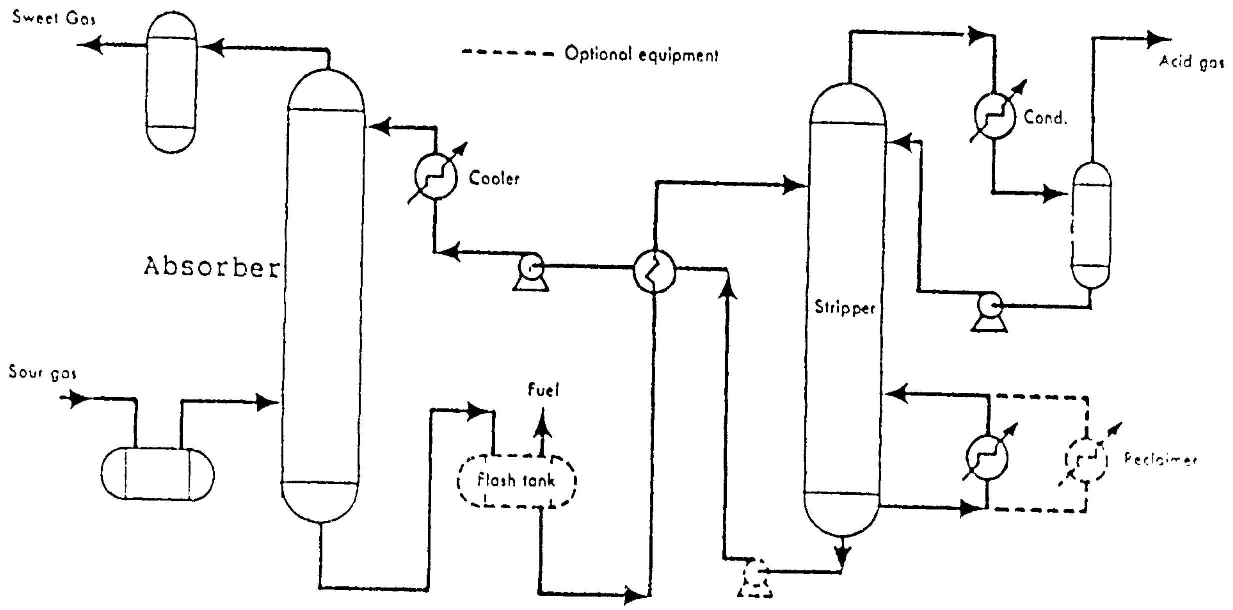

Figure 1. Basic flowsheet for acid gas removal

heat of reaction of DEA with CO_2 is about 1477 J/g CO_2 which is 25% less than that of MEA (Polasek et al., 1985).

DGA (40-60 wt %) tends to preferentially react with CO_2 over H_2S. It has a higher pH than MEA and thus also allows it to achieve a very low H_2S removal specification. Unlike MEA and DEA it is not likely to react irreversibly with COS and methyl and ethyl mercaptans. The heat of reaction is 1977 J/g with CO_2. The advantage of DGA is that it can be operated at a concentration as high as 60 wt % which results in lower circulation rates and reduced heat requirements for regeneration .

Despite major improvements including the addition of rate enhancers, the use of corrosion inhibitors for higher loadings and improved heat recovery, MDEA and hindered amines and blends of MDEA with primary or secondary amines are replacing DEA and MEA in existing new systems (Rochelle, 1991). The increasing concern over air pollution and the need to process both crude oil and natural gas that contain much higher levels of H_2S has made it necessary to boost the capacity of existing units. These demands led to the wide acceptance of MDEA-based solutions. Because of the high cost of MDEA relative to MEA and DEA, its use as a treating solution did not follow immediately after it was described as such by Frazier and Kohl (1950). MDEA is mainly kinetically selective for H_2S in the presence of CO_2. This selectivity arises because of the absence of any hydrogen atom on the nitrogen prevents it from reacting directly with CO_2 to form a carbamate ($RNHCOO^-$). CO_2 reacts first with water to form a bicarbonate which is then neutralized by the amine.

$CO_2+H_2O+R_2NCH_3 \rightleftharpoons HCO_3^- + R_2NHCH_3^+$

The acid gas and amine combine to form an acid-base complex called a salt, thus, removing the acid gas from the process stream.

The reaction with H_2S is that of an instantaneous proton transfer mechanism.

$H_2S + R_2NCH_3 \rightleftharpoons R_2NHCH_3^+ + HS^-$

Unlike the absorption in primary and secondary amines, the absorption in MDEA can reach 1 mole of CO_2 per mole of amine. While the high CO_2 loading is very attractive, the low rates of absorption of CO_2 in tertiary amines may limit their use. This disadvantage can be overcome by the addition of a small amount (5-10 %) of primary or secondary amine to an MDEA based solution. This blending enhances the overall reaction rate (Chakravarty 1985, Polasek et al., 1985).

Ballard (1980) argues that switching from MEA or DEA to MDEA in large amine units saves over a million dollars in energy saving per year without the damaging corrosion.

Sterically hindered amines are said to approach the stoichiometric loading of 1 mole CO_2/mole amine combined with the absorption rates characteristic of primary and secondary amines. The high loading is obtain by destabilizing the carbamate thanks to the presence of a bulky substituent next to the nitrogen atom. An example of a hindered primary amino alcohol is 2-amino-2-methyl-1-propanol (AMP). 2-Piperidine ethanol (PE) is an example of a hindered secondary amino alcohol. An example of a hindered diamine is 1,8-p-menthane diamine (MDA).

In order to combine the advantages of both physical and chemical solvents, mixed solvents have been proposed for effectively treating acid gases.This combination allows for a higher CO_2 loading, a lower solution circulation rate and regeneration energy. Since the regeneration section costs at least 50 % of the total capital cost (Sigmund et al., 1981) and that steam cost makes 70% of the variable costs (Astarita et al., 1983), any small improvement in this area will translate into considerable financial savings. The chemically reactive alkanolamine makes possible achieving very low residual levels of H_2S and CO_2 even at relatively low total pressure, while the physical solvent component makes possible not only the removal of mercaptans and other organic impurities to low levels, but also the removal of part of the H_2S and CO_2 with only small heat effects during absorption and regeneration. Examples of mixed solvents are Amisol (MEA or DEA with methanol), the improved Amisol (DIPAM or DETA and methanol) and Sulfinol (DIPA, sulfolane and water or MDEA, sulfolane and water). Rivas (1978) and Astarita et al.(1983) have discussed the advantages of using mixed solvents for gas absorption enhancement.

The objective of this study is to provide data on the solubility of CO_2 in two physical solvents : methanol and triethylene glycol monomethyl ether. This will help in understanding the part played by the physical solvents in the mixed systems. The solubility of CO_2 is measured in mixtures of MDEA (50 wt %) and methanol and MDEA (50 wt %) and triethylene glycol monomethyl ether in order to isolate the influence of MDEA on the physical solvents. Finally the solubility of CO_2 is measured in two aqueous mixed solvents at typical absorption and regeneration temperatures and over a wide range of partial pressures. The mixed solvents studied were composed of an amine, N-methydiethanolamine (40 wt %), water (20 wt %) and methanol (40 wt %) as a physical solvent in one case and triethylene glycol monomethyl ether (40 wt %) as the physical solvent in the second case.

Background information on the solubility of acid gases in MDEA-based mixed solvents is presented in chapter 1. A literature survey is presented in chapter 2. Chapter 3 describes the experimental procedures used to obtain the data. Experimental results and discussion are presented in chapter 4. The results of the model used to correlate the data are presented in chapter 5. Finally chapter 6 is a summary of the conclusions which can be drawn from the results of this study.

2. General background

2.1 Thermodynamic framework of mixed solvents

The mixed solvent used in this study is composed of a chemical solvent, MDEA, and two physical solvents : water and methanol in one case and water and TEGMME in another case.

At equilibrium the fugacities of a dissolved gas in a physical solvent are equal in both phases:

$$f_A^V = f_A^L \tag{2. 1}$$

$$\text{with } f_A^V = \phi_A\, y_A\, P \tag{2. 2}$$

$$f_A^L = \gamma_A\, m_A\, H_A \exp\int_{ps}^{P} (\, v_A \,/\, RT\,)\, dP \quad . \quad . \tag{2. 3}$$

$$\text{Where } H_A = \lim_{m_A \to 0} \; f_A \,/\, m_A \tag{2. 4}$$

When the 2 phases are considered as ideal:

$$\phi_A = \gamma_A \exp\int_{ps}^{P} (v_A \,/\, RT\,)\; dP = 1 \quad . \quad . \tag{2. 5}$$

$$\text{Thus :} \quad p_A = y_A P = m_A H_A \tag{2. 6}$$

At low concentrations, the solubility of the acid gas in a pure physical solvent can be described by Henry's law. In order to successfully correlate the solubility at high concentrations, an equation of state valid for the solvent and dilute solution can be used. In this study the Peng-Robinson (1976) equation of state is used. A description of the Peng-Robinson equation of state is given in appendix I. For mixtures of components with strong intermolecular interactions a modification of P-R equation, the Peng-Robinson-Stryjek-Vera (1986) equation will be used. There is a very large number of equations available in the literature for mixtures containing polar fluids such as water, ammonia and alcohols [Peng-Robinson-Stryjek-Vera (1986), Patel-Teja (1982)...].

When water is present , CO_2 reacts chemically with the amine. The chemical equilibrium can be represented by:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D \tag{2. 7}$$

The equilibrium constant is :

$$K=(m_c^{C}\, m_D^{d} / m_A^{a}\, m_B^{b}).\ (\gamma_C^{c}\ \ \gamma_D^{d} /\ \ \gamma_A^{a}\ \ \gamma_B^{b}) \tag{2. 8}$$

For MDEA, a tertiary amine, which does not form carbamate ($RNHCOO^-$) a theoretical loading of 1 mole of acid /mole of amine is possible.

The reactions taking place have the following form:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \tag{2. 9}$$

$$CO_2 + H_2O + R_2NCH_3 \rightleftharpoons HCO_3^- + R_2NHCH_3^+ \tag{2.10}$$

2.2 Literature survey

2.2.1 Solubility of acid gases in tertiary amines

A general survey of the literature dealing with the solubility of acid gases in alkanolamines in general and mixed solvents in particular was presented by MacGregor (1988), Roberts (1983) and Bosch (1989).

This survey will deal with the solubility of acid gases in aqueous MDEA and tertiary amines based mixed solvents in general.

The solubility of H_2S and CO_2 in aqueous MDEA has been studied by

Jou et al. (1982, 1993) and Bhairi (1984), Austgen (1989) and Chakma and Meisen (1987).

The solubility of mixed acid gases, H_2S and CO_2 in MDEA was measured by Jou et al.(1993) and Ho and Eguren (1988).

Flynn et al.(1981) studied a new Sulfinol solvent (tertiary amine-sulfolane-water) and compared the performance to that of the conventional Sulfinol (DIPA-sulfolane-water).

Gazzi et al.(1980) reported the development of the "Selefining" process. Energy costs reported were 46 % lower than those of aqueous MDEA or Selexol processes performing the same task.

MacGregor (1988) reported the solubility of CO_2 and H_2S and their mixtures in a mixed solvent (MDEA-sulfolane-water).

From the study done by Leites et al.(1972), it appears that among all the mixed solvents studied MEA-methanol mixtures yielded the highest capacity for CO_2. At higher pressures an enhancement of the solubility of CO_2 by the physical solvent component of the aqueous mixtures of monoethylamine and methanol was shown by Banasiak et al.(1981).

Subsequently the first mixed solvent chosen in this study was composed of MDEA and methanol and water.

Woertz's work (1972) showed that the solubility of CO_2 in MEA and water with diethylene glycol was greater than the corresponding aqueous solutions. Sweny and Valentine (1970) reported on the successful use of the dimethyl ether of polyethylene glycol (Selexol process) as a physical solvent. For all those reasons, the second mixed solvent in our study was chosen to be a mixture of MDEA, TEGMME (triethylene glycol monomethyl ether) and water.

2.2.2 VLE models for acid gases absorption

In 1936, Mason and Dodge used a curve fitting approach to correlate the solubility of CO_2 in aqueous ethanolamine. Van Krevelen et al.(1949) related pseudo-equilibrium constants to the ionic strength of the solution . He was then able to predict the partial pressure of H_2S in aqueous ammonia in the ammonia rich region. The "apparent" equilibrium constants were related to the component concentrations rather than to the activities. The activity coefficients were set equal to unity. This approach was used by Danckwerts and McNeil (1967) to predict the partial pressure of CO_2 over carbonated amine solutions. Atwood et al.(1957) proposed a method to predict the equilibrium composition of the CO_2-H_2S-Alkanolamine-H_2O system. Activity coefficients of all ionic species were assumed to be equal. This simple "mean" ionic activity coefficient was correlated with the ionic strength. Their method was generalized by Klyamer et al.(1973).

Edwards et al.(1975) used a Guggenheim-type equation to represent the activity coefficients. In this model, chemical equilibria was represented using activities rather than concentrations. Molecule-molecule binary interaction parameters were regressed from experimental data. Both long range and short range effects were considered. The model was valid for concentrations less than 2 M.

One of the most popular model, because of its computational simplicity, was developed by Kent and Eisenberg (1976). All activity and fugacity coefficients were set to unity. All the equilibrium and Henry's law constants were taken from the literature with the exception of the equilibrium constants for the reactions involving the amines which were fitted to the experimental data. The non-idealities were then lumped into these fitted constants.

An improved Kent-Eisenberg model was proposed by Chakma and Meisen (1990). As stated by Jou et al. (1982) and Chakma and Meisen (1987), the equilibrium constants governing the main amine reaction must not be only a function of the temperature (Kent-Eisenberg) but also depend on the gas partial pressure, solution loading and amine concentration (Hu and Chakma 1990a, 1990b).

Austgen et al.(1989) mentioned two drawbacks to the use of "apparent" equilibrium constants. First, the method cannot confidently be extended to composition outside the range over which the constants were adjusted. Second, the method cannot be used to accurately represent the true compositions of all liquid-phase species, ionic and molecular.

Edwards et al.(1978) extended his previous model in order to predict the solubility in much more concentrated solutions (above 10 molal). The work of Pitzer (1973) and Pitzer and Kim (1974) was used to determine the solute activity coefficients instead of the Debye-Hückel equation .

Beutier and Renon (1978) extended the use of Pitzer's equation and Edward's work to include ternary interactions between liquid phase species. Chen and Evans (1979) extended Pitzer's equation to model activity coefficients of strong electrolytes.

Austgen (1989) developed a model based on a generalized excess Gibbs energy. The vapour phase fugacity coefficients were calculated using the Redlich-Kwong Soave equation of state (1972). The electrolyte-NRTL equation [Chen and Evans(1986)] was used to represent the liquid phase activities. The model was later extended to describe CO_2 solubility in blends of amines.

Deshmukh and Mather (1981) proposed a rigorous thermodynamic model based on the extended Debye-Hückel equation. It is the model used in this study. In the liquid phase the chemical reactions are as follows :

$$MDEAH^+ \rightleftharpoons MDEA + H^+ \qquad (2.11)$$

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \qquad (2.12)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad (2.13)$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (2.14)$$

The equilibrium constants for reactions (1) to (4) are :

$$K_1 = (H^+)\ (MDEA)\ \gamma_H{}^+ \gamma_{MDEA} \,/\, (MDEAH^+)\ \gamma_{MDEAH}{}^+ \qquad (2.15)$$

$$K_2 = (H^+)\ (HCO_3^-)\ \gamma_H{}^+\ \gamma_{HCO3}{}^- \,/ (CO_2)\ \gamma_{CO2}\, a_w \qquad (2.16)$$

$$K_3 = (H^+)\ (CO_3^=)\ \gamma_H{}^+\ \gamma_{CO3}{}^= \,/\, (HCO_3^-)\ \gamma_{HCO3}{}^- \qquad (2.17)$$

$$K_4 = (H^+)\ (OH^-)\ \gamma_H{}^+\ \gamma_{OH}{}^- \,/\, a_w \qquad (2.18)$$

The vapour-liquid equilibria for CO_2 and water are:

$$\phi_{CO2}\, p_{CO2} = H_{CO2}\, m_{co2}\, \gamma_{CO2} \tag{2.19}$$

$$\phi_W\, y_W\, P = p_W\, x_W \tag{2.20}$$

The mass balance equations are :

$$m_A = (MDEA) + (MDEAH^+) \tag{2.21}$$

$$m_A\, \alpha_{CO2} = (CO_2) + (HCO_3^-) + (CO_3^=) \tag{2.22}$$

The equation of electroneutrality is :

$$(H^+) + (MDEAH^+) = (HCO_3^-) + 2(CO_2^=) + (OH^-) \tag{2.23}$$

There are eight species : H_2O, H^+, OH^- , CO_2 , HCO_3^- , $CO_3^=$, MDEA , $MDEAH^+$.

The number of unknowns is then fifteen : the activity coefficients and the concentrations of all species except water plus the water mole fraction. The independent equations are : three chemical equilibria equations (15-17), two vapour-liquid equations (19-20), two mass balance equations (21-22), one electroneutrality equation (23) and seven equations for the activity coefficients of the seven species for a total of fifteen equations.

The way to obtain the protonation constant of the amine, the dissociation constant of CO_2 and HCO_3^-, the interaction parameters of the extended Debye-Hückel equation and Henry's constant for the mixed solvent will be discussed in detail in the chapter 5. The physical solvent has an effect on the ionic strength of the solution and on the chemical equilibrium constants and is taken into account in the vapour-liquid equilibrium.

The method of Brown (1973) was used to solve the above system of non linear algebraic equations. It is based on a partial pivoting technique similar to Gaussian elimination in linear systems.

This model was used by Chakravarty (1985) to model the solubility of acid gases in amine blends. Roberts (1983) and Teng and Mather (1991) have also used the model to predict H_2S and CO_2 solubility in aqueous AMP and in mixed solvents of AMP, water and sulfolane.

MacGregor (1988) used it to correlate the solubility of CO_2 and H_2S and their mixtures in a solution of MDEA, sulfolane and water. Bosch (1989) utilised it to predict the solubility of H_2S and CO_2 in aqueous MDEA, DIPA, TEA, and MDEA solutions. More recently Weiland et al.(1993) used the model to fit all available phase equilibrium data for CO_2 and H_2S in aqueous solutions of MEA, DEA, DGA and MDEA.

3. Experimental section

The experimental apparatus is similar to that outlined by Jou et al.(1982). The experimental apparatus is shown in Figure 2. The liquid and vapour phases were brought to equilibrium in a windowed Jerguson cell. A 250 cm^3 cylindrical reservoir was attached to the top of the cell to increase the volume of the vapour phase. The vapour from the reservoir was circulated through the solvent by a magnetically driven pump similar to that devised by Ruska et al.(1970).

The cell and pump were enclosed in a 0.4 m^3 air bath maintained at ±0.1°C of the set point. The output of a calibrated iron-constantan thermocouple extended through the cell was measured by a Hewlett-Packard multimeter (3468A). The fluid pressure in the cell was measured with a calibrated Heise gauge which had an accuracy of ±0.1% of the scale span. A gas sample line extended from the reservoir to the sample loop of the gas chromatograph. The liquid sample line led from the bottom of the cell to a needle valve located outside the air bath.

Prior to the introduction of the fluid the apparatus was brought to the desired temperature and purged with nitrogen to remove traces of oxygen (when necessary the cell was first heated to 120°C to remove any water present). The solvent was fed by gravity to the equilibrium cell and carbon dioxide was then added. At low pressures of CO_2, nitrogen was added to keep the total pressure above atmospheric pressure. To ensure that equilibrium was reached, the vapour was bubbled through the liquid for at least 8 hours. The vapour and liquid were then sampled. The vapour was analyzed in a gas chromatograph (Hewlett-Packard 18714A) using a 3 m long, 6.35 mm O. D. column packed with Porapak QS and an oven operated at 120°C in the case of CO_2-methanol. In the case where MDEA or TEGMME were present a 3 m, 6.35 mm O. D. Chromosorb 104 packed column was used. The oven temperature was programmed to go from 120°C to 250°C, after the appearance of the water peak . When nitrogen was present in the gas phase, a Porapak S column was used and the oven temperature was set at 70°C and programmed to rise to

120°C if methanol and water were present.

The liquid phase was analyzed by withdrawing a sample of about 2 grams of solution into at least 10 grams of 50 wt % aqueous DEA (DGA when MDEA is present). Care was taken to make sure that the amount of DEA (or DGA) present was enough to absorb all the CO_2 present in the 40 cm^3 sampling container.

When the pressure was less than 100 kPa the liquid was sampled without dilution into aqueous DEA or DGA.

When a mixture of CO_2 and methanol in the vapour phase was present the response factor was found to be equal to 1.03. For the liquid phase, standardized solutions (20 μ l, 100 μ l, 200 μ l, 300 μ l, 500 μ l, 600 μ l, 1000 μ l of CO_2, 1 μ l of 8 , 20, 40, 55 wt % of aqueous MDEA or 1 μ l of 1, 5, 10, 15, 52 wt % of aqueous methanol or 1 μ l of 10, 15 wt % of aqueous TEGMME) were used depending on the system studied and the area count of the sample. In the case of MDEA and methanol the concentration was checked by titration using 0.1 N hydrochloric acid with methyl red as an indicator.

Each sample was analyzed five times for each equilibrium point. The average of each individual composition is reported as the equilibrium composition. For the binary systems, the repeatability of the vapor and liquid mole fraction was generally within ± 0.001 and ± 0.002, respectively. The vapor and liquid mole fractions for the ternary systems were reproducible to within± 0.002 and ±0.003, respecrively. The amine loadings in the quaternary systems were reproducible to within ±10 %.

Materials

The MDEA (99 % pure) was purchased from Aldrich Chemical Co. (Milwakee, WI). TEGMME (95 % pure), DEA (99 % pure), methanol (99.9 % pure) and anhydrous methanol (99+% pure , water $<$ 0.005 %) were bought from Aldrich Chemical Co. Carbon dioxide (99.9 % pure) was purchased from Linde (Edmonton, Alberta). DGA was purchased from Pfaltz & Bauer Inc. (Waterbury, CT). Water was distilled in our laboratory.

4. Experimental results and discussion

4.1 Preliminary results

4.1.1 Pure methanol results

The equilibrium solubility of CO_2 in methanol was measured at 40°C to provide a comparison with the values measured by Suzuki et al.(1990). The data are necessary to obtain the interaction parameter δ_{12} for CO_2 and methanol in the Peng-Robinson equation of state. The data are shown in Table 1 and plotted in Figure 3. The results are in very good agreement with those published by Suzuki et al.(1990). The solubility was correlated by PR equation. The objective function used to optimize the interaction parameter was of the type :

$$O\,F = \Sigma(\,|\, Pexp - Pcalc \,|\, / \,Pexp) \,/\, N \qquad (4.1)$$

N: Number of points

Table 1. Vapor-liquid equilibria at 40°C of CO_2(1)-methanol (2) system

P (kPa)	x_1	y_1
685	0.035	0.981
1125	0.052	0.983
2145	0.112	0.984
2896	0.164	0.986
4910	0.284	0.984
6954	0.467	0.977
7400	0.599	0.965
7713	0.674	0.948
8210†	0.965	0.965

† Critical point

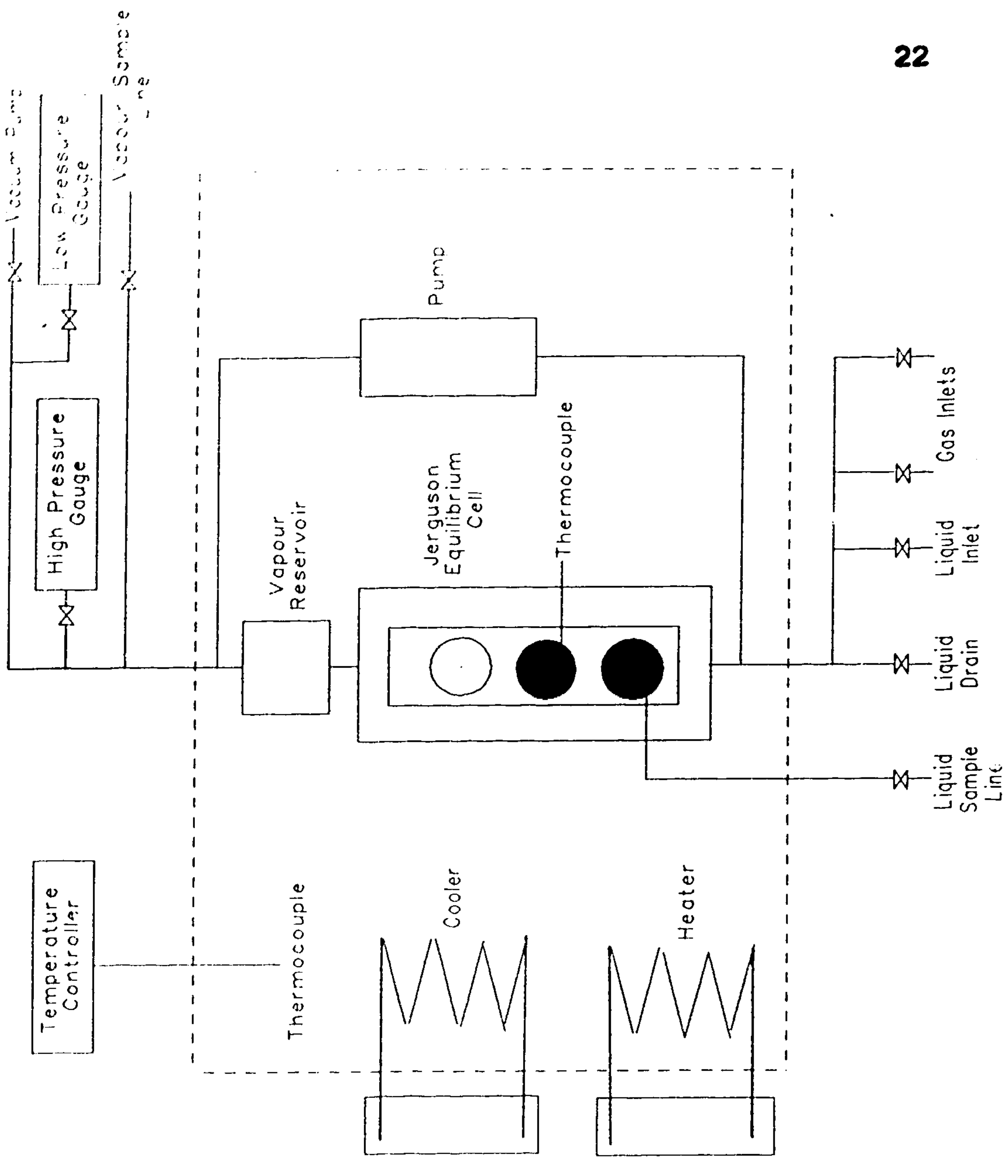

Figure 2. Experimental apparatus

Data published by Leu et al.(1991) (Figure 4) were used to obtain the values of the interaction parameters for other temperatures. The results of the optimization and the objective functions are presented Table 2.

The critical point experimentally found is plotted with those found in the literature in Figure 5.

Table 2. Peng-Robinson interaction parameters and objective functions for the CO_2(1)-methanol(2) system

T , K	δ_{12}	O F(%)
313.2	0.0685	3.82
323.2	0.073	2.70
352.6	0.085	4.22
394.6	0.110	5.49
477.6	0.184	1.92

4.1.2 Pure TEGMME results

The equilibrium solubility of CO_2 in TEGMME was also measured at 40 °C, 70°C and 100°C and the data are presented in Figure 6. The purpose of these measurements is to use the data to get the interaction parameter δ_{12} (CO_2-TEGMME) for the Peng-Robinson equation. The data are shown in Table 3. The critical pressures and temperatures of MDEA and TEGMME were

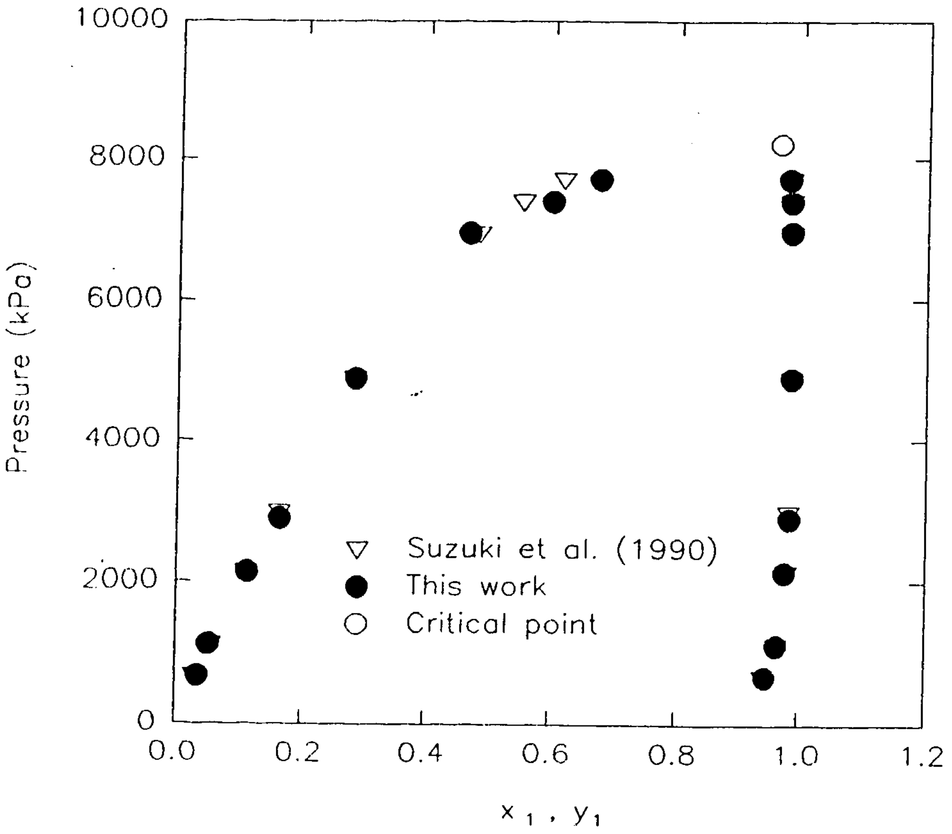

Figure 3. Phase diagram for CO_2 (1) and methanol (2) at 40°C .

estimated using Lydersen's correlation (Reid et al., 1987). The constants of the Antoine equation for TEGMME were reported by Troch et al.(1991). The acentric factors were obtained from Lee-Kesler correlation (Reid et al., 1987). The results are presented in Table 4. The interaction parameters and the objective functions are presented in Table 5.

Figure 7, 8 and 9 show the partial pressure of CO_2 versus the CO_2 mole fraction in the three physical solvents [sulfolane (Jou et al., 1990), TEGMME and methanol] at 40°C, 70°C and 100°C.

The objective functions for sulfolane and the interaction parameters are presented in Table 6. No TEGMME could be detected in the vapour phase. The vapour pressures of TEGMME at 40°C, 70°C and 100°C were estimated using the equation published by Troch et al.(1991) and found to equal to 2.9 Pa, 40.5 Pa and 315 Pa respectively.

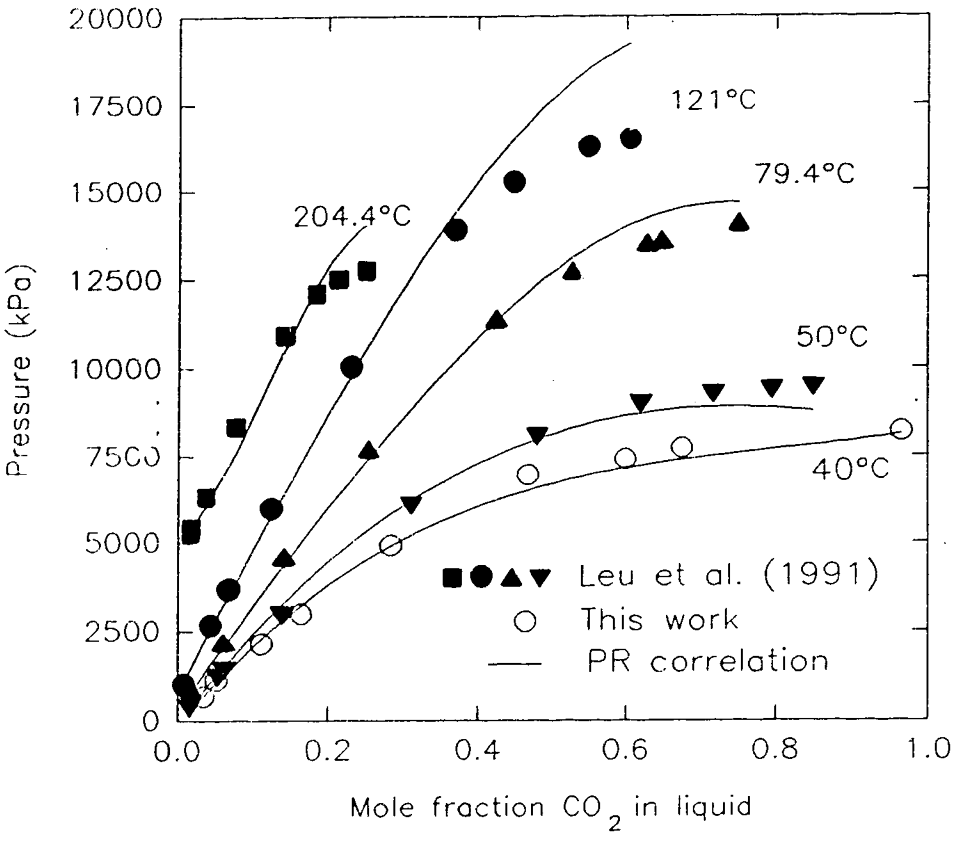

Figure 4. Solubility of CO_2 in methanol

Table 3. Solubility of $CO_2(1)$ in TEGMME(2).

40°C		70°C		100°C	
P(kPa)	x_1	P (kPa)	x_1	P (kPa)	x_1
783	0.100	443	0.051	300	0.025
1460	0.162	800	0.091	450	0.037
2108	0.228	1155	0.128	748	0.066
2782	0.278	2152	0.219	1392	0.100
3430	0.388	2682	0.274	2691	0.194
4097	0.482	3202	0.318	3083	0.225
5076	0.588	4143	0.385	3732	0.268
6209	0.662	4953	0.441	4518	0.298
7877	0.739	5734	0.507	5166	0.340
8794	0.817	7004	0.531	6063	0.375
				7282	0.422

Table 4. Pure component parameters for Peng-Robinson equation of state

Comp.	T_c (K)	P_c (kPa)	ω
MDEA	680.7	4053	1.125
TEGMME	682.4	3002	1.119

Table 5. Peng-Robinson interaction parameters and objective functions for the CO_2(1)-TEGMME(2) system

T , K	δ_{12}	O F(%)
313.2	-0.011	4.64
343.2	-0.053	2.21
373.2	-0.055	3.71

Table 6. Peng-Robinson interaction parameters and objective functions for the CO_2 (1)-sulfolane(2) system

T , K	δ_{12}	O F(%)
313.2	0.0272	2.90
343.2	0.0920	5.41
373.2	-0.0100	3.71

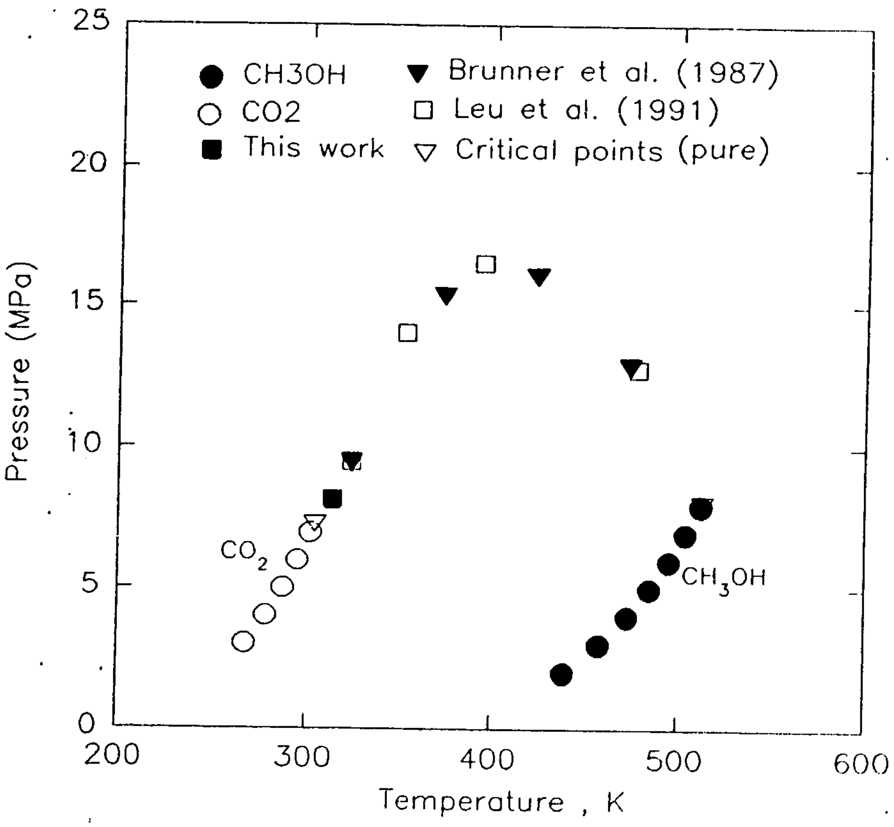

Figure 5. Critical locus of CO_2 and methanol mixtures

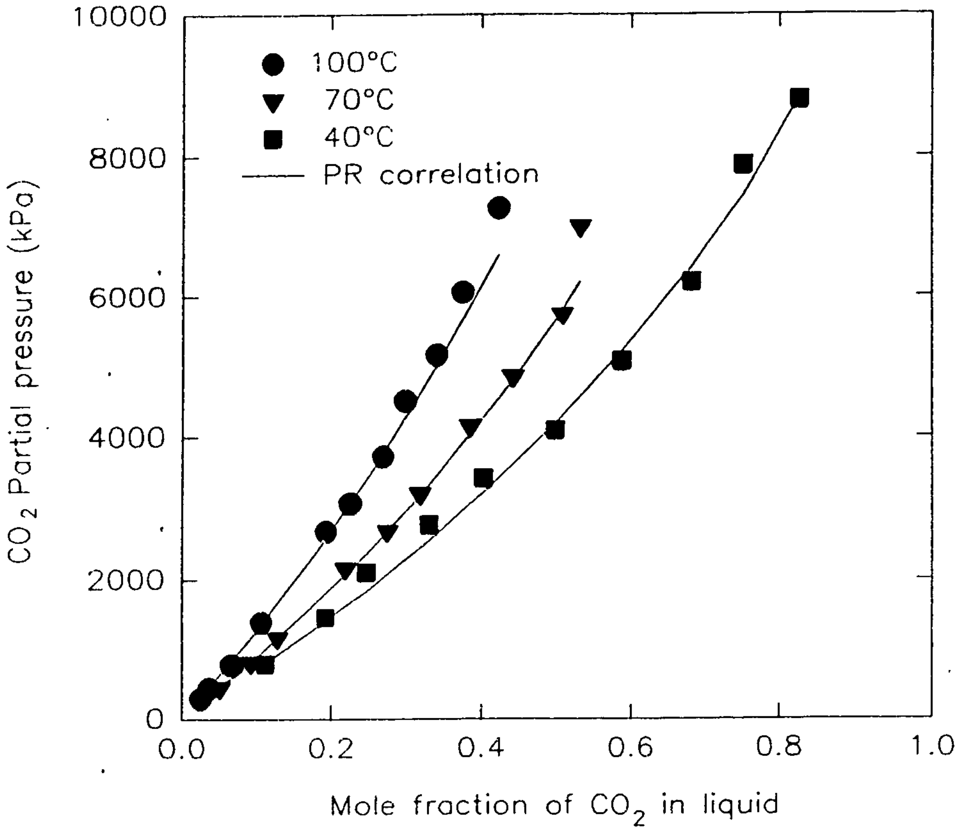

Figure 6. Solubility of CO_2 in TEGMME

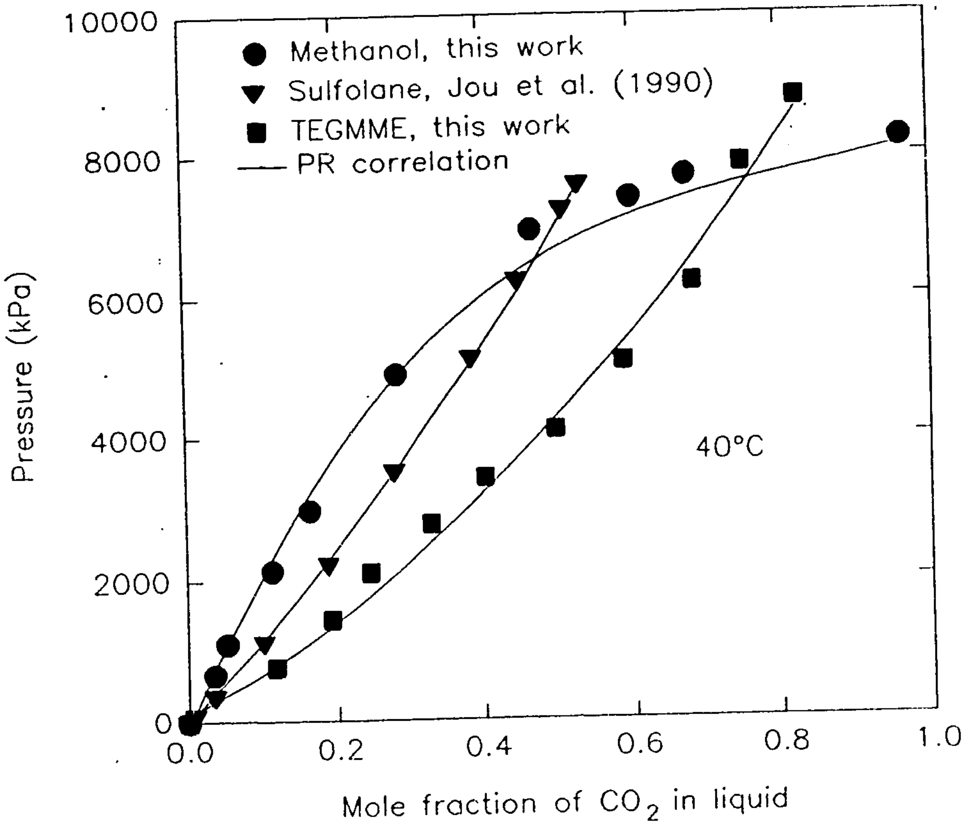

Figure 7. Solubility of CO_2 in physical solvents at 40°C.

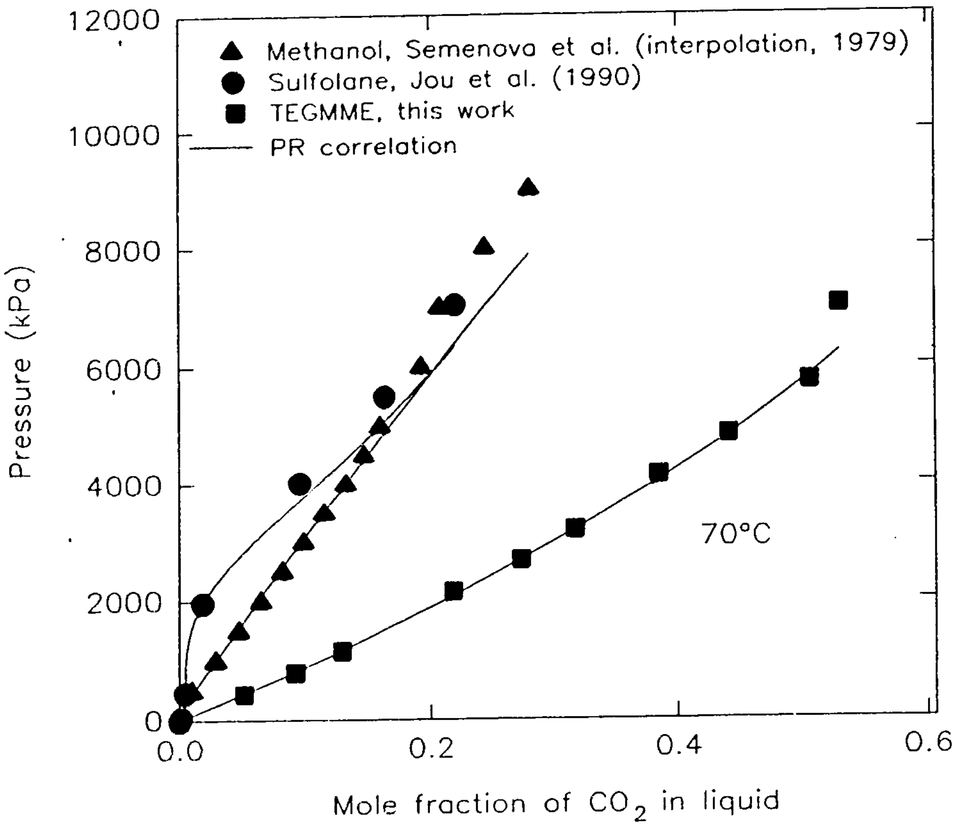

Figure 8. Solubility of CO_2 in physical solvents at 70°C.

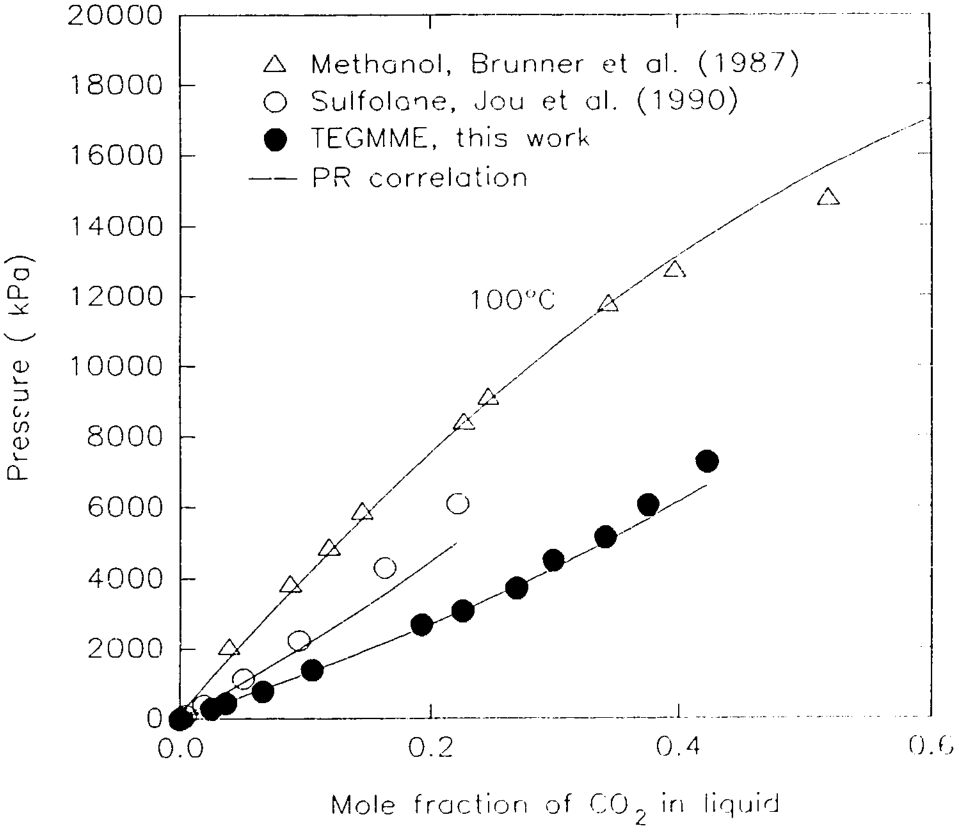

Figure 9. Solubility of CO_2 in physical solvents at 100°C.

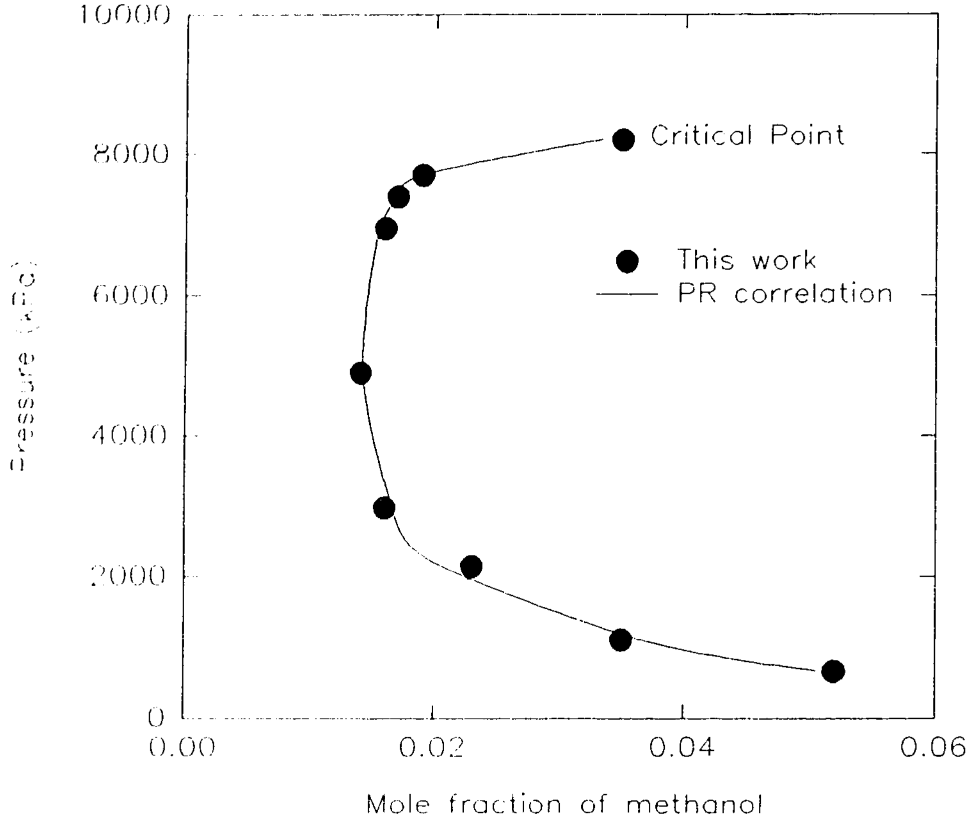

Figure 10. Mole fraction of methanol in the vapour phase at 40°C.

4.2 Experimental results

4.2.1 Methanol-MDEA mixture

The equilibrium solubility of CO_2 was measured in a mixture of 50 wt % of methanol and MDEA. Great care was taken in the cell to make the mixture water-free in order to avoid any chemical reaction between the CO_2 and the MDEA. The solvent was analyzed by chromatography and was found to be water-free.

The data are presented in Table 7 and in Figure 11. The data could not be well correlated by the Peng-Robinson equation.

Table 7. Solubility of carbon dioxide (1) in a mixture of MDEA (50 wt%) and methanol (2) (50 wt %) at 40°C

P_{CO_2}(kPa)	x_1	x_2
313	0.059	0.757
565	0.075	0.787
1161	0.118	0.744
1911	0.151	0.706
2596	0.1721	0.694
3496	0.195	0.657
4417	0.221	0.651
5813	0.246	0.613
7392	0.275	0.577

4.2.2 TEGMME-MDEA mixture

The equilibrium solubility of CO_2 was measured in a mixture of 50 wt % TEGMME and MDEA. Here also care was taken to insure that the mixture was water-free. The data are presented in Table 8 and in Figure 12.

The data could not be very well correlated by the PR equation and no improvement was found by using the PRSV equation of state. The objective functions for the two mixtures and the interaction parameters are presented in Table 9.

The failure to correlate the MDEA-methanol and MDEA-TEGMME mixtures could be explained by the formation of complexes. Sada et al. (1985, 1989) and Takeshita and Kitamoto (1988) claim that amines can react with CO_2 in a non-aqueous medium (polar or non-polar solvents). Sada et al.(1989) studied specifically the case of TEA with methanol and maintain that a chemical reaction occurs. This statement is in contrast with the finding of Versteeg and van Swaaij (1988).

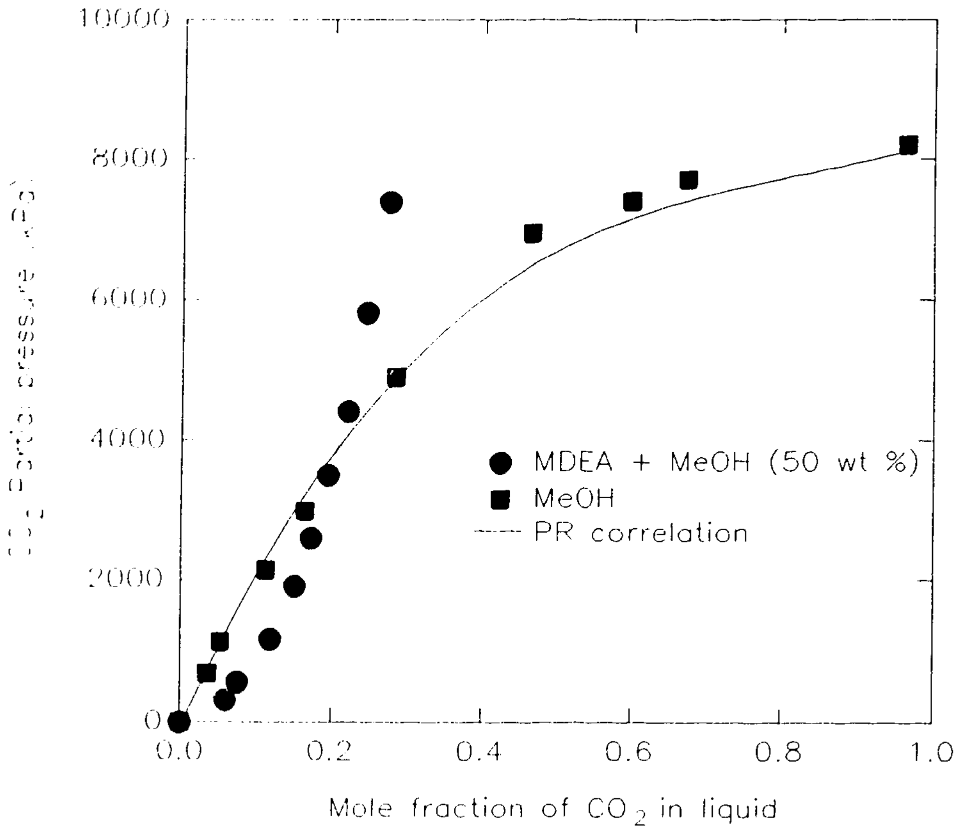

Figure 11. Effect of the addition of MDEA on the solubility of CO_2 in methanol at 40°C.

Table 8. Solubility of carbon dioxide (1) in a mixture of MDEA (50 wt %)(2) and TEGMME (50 wt %) at 40°C.

P (kPa)	x_1	x_2
294	0.053	0.613
583	0.129	0.571
1093	0.244	0.471
2875	0.324	0.451
4295	0.376	0.385
5245	0.399	0.374
6622	0.428	0.354
8403	0.506	0.304
10043	0.492	0.334

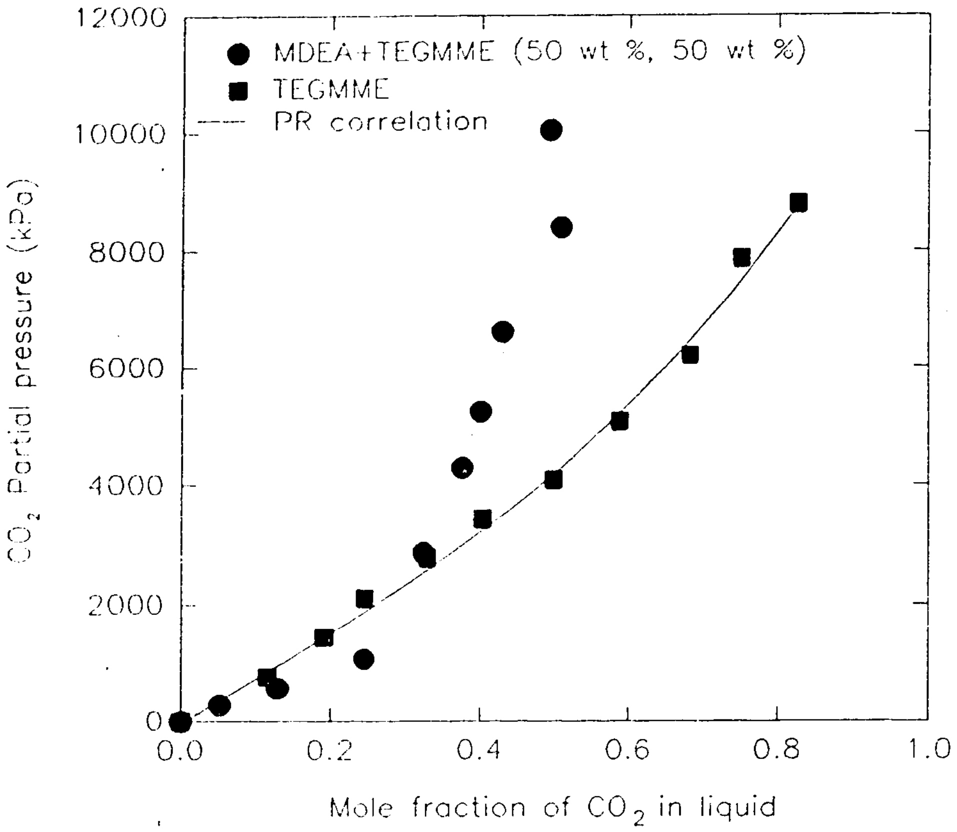

Figure 12. Effect of the addition of MDEA on the solubility of CO_2 in TEGMME at 40°(

Table 9. Interaction parameters for the Peng-Robinson equation of state and objective functions for CO_2-MDEA-MeOH and CO_2-MDEA-TEGMME mixtures at 40°C.

$CO_2(1)$/MEOH(2)/MDEA(3)		$CO_2(1)$/ MDEA(2)/TEGMME(3)
δ_{13}	-0.25	-0.011
δ_{32}	-0.05	-0.023
δ_{12}	0.0685	-0.14
OF	43.14%	39.78%

4.2.3 Methanol-MDEA-water mixed solvent results

The first mixed solvent studied consisted of 40 wt % MDEA, 40 wt % methanol and 20 wt % water. The data at 40°C and 100°C are displayed in Figure 14 and Table 10. The loading (α) is expressed in terms of moles of acid per mole of amine. Two experimental data were obtained at 120°C to check the fact that at high partial pressures of CO_2, the data obtained at 100°C almost cross those at 40°C.

Table 10. Solubility of CO_2 in mixture of MDEA (40 wt %) - methanol (40 wt %) - H_2O (20 wt %) at 40°C and 100°C.

P_{CO_2} (kPa)	α (mole CO_2/mole MDEA)	P_{CO_2} (kPa)	α (mole CO_2/mole MDEA)
40°C		100°C	
3	0.040	48	0.010
12	0.029	78.6	0.014
33	0.128	110.6	0.019
47.3	0.203	123.8	0.021
110.4	0.259	552.8	0.368
157	0.421	1641.2	0.567
305	0.732	1973	0.776
438	0.920	2313.7	1.057
537	0.991	3866	1.458
726	1.205	5367	1.734
1012	1.240	7044	1.752
2046	1.310		
3052	1.565		
4618	1.630		
5447	2.078		

4.2.4 TEGMME-MDEA-water mixed solvent results

The second mixed solvent studied was composed of 40 wt % TEGMME, 40 wt % MDEA and 20 wt % water. The solvent had the same weight composition as the previous mixed solvent, only the physical solvent, methanol, was replaced by TEGMME. Data have been obtained at 40°C and 100°C. The results are presented in Table 11 and in Figures 13 and 14. At 100°C, the experiment was carried to the highest pressure possible for the cell without reaching a value of unity for the amine loading.

5. Correlation of experimental data

5.1 Henry's constants evaluation

5.1.1 Pure solvents Henry's constants

The Henry 's constant can be extracted from experimental VLE data . The fugacity versus the pressure could be well correlated by the Krichevsky - Kasarnovsky equation (1935). The form of the equation is given in appendix I. The fugacity was calculated using the Peng-Robinson equation of state. Plots of ln (f_2/x_2) versus $(P - P_1^\circ)$ at 40°C, 70°C and 100°C are shown in Figure 15. The results of the regression are displayed in Table 12.

Table 11. Solubility of CO_2 in mixture of MDEA (40 wt %) - TEGMME (40 wt%) - H_2O (20 wt %) at 40°C and 100°C.

P_{CO_2} (kPa)	α (mole CO_2/mole MDEA)	P_{CO_2} (kPa)	α (mole CO_2/mole MDEA)
	40°C		100°C
3.4	0.013	25.6	0.005
7.7	0.021	27.3	0.067
27.3	0.068	79.4	0.007
48.8	0.109	178	0.012
124	0.193	219	0.017
133	0.218	273	0.019
159	0.238	482	0.044
165	0.259	882	0.079
196	0.355	1323	0.104
234	0.411	1929	0.147
619	0.493	3446	0.249
749	0.627	4128	0.273
1048	0.715	5432	0.285
1408	0.884	5956	0.305
2239	0.942	8091	0.619
†4370	0.980	10765	0.724
†5270	1.000	12626	0.738
†6330	1.126		
†7725	1.148		
†9980	1.211		

†two liquid phases observed

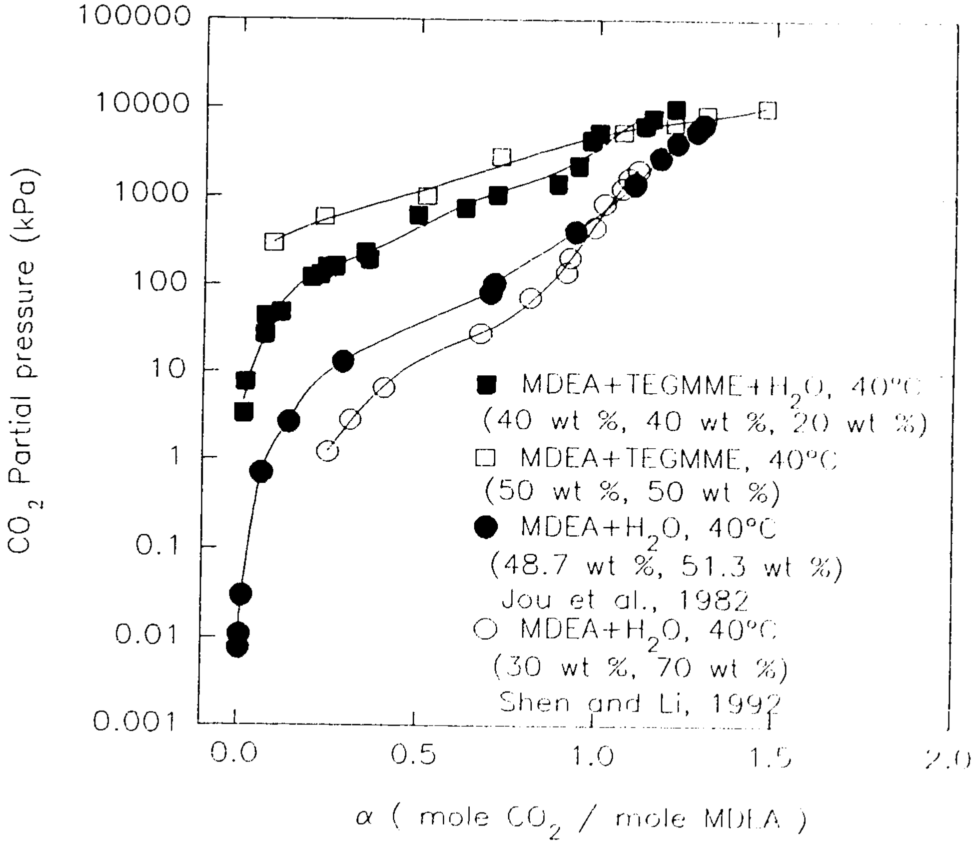

Figure 13. Effect on the solubility of CO_2 of the addition of water to TEGMME-MDEA mixture and the addition of TEGMME to water-MDEA mixture at 40°C.

Table 12. Henry's constants for $CO_2(2)$ in TEGMME(1).

Temperature (K)	H_{21}(MPa)
313.2	7.50
343.2	8.39
373.2	11.84

5.1.2 Mixed solvents Henry's constants

Mixed solvent Henry's constants for the TEGMME system were regressed from the experimental data at 40°C and 100°C. Only data for a loading greater than unity were used (physical solubility is dominant and no chemical reaction is taking place). Fugacity from PR equation is regressed versus the molality. The results of the regression are presented in Table 13 . Note that at 100°C, no experimental data could be obtained at α greater than unity. In order to obtain those data, an extrapolation was performed using the last three experimental points of highest loading.

Table 13. Henry's constants for CO_2 in MDEA-TEGMME-water system.

Temperature (K)	Henry's constant (MPa-kg/mol)
313.2	7.40
373.2	5.97

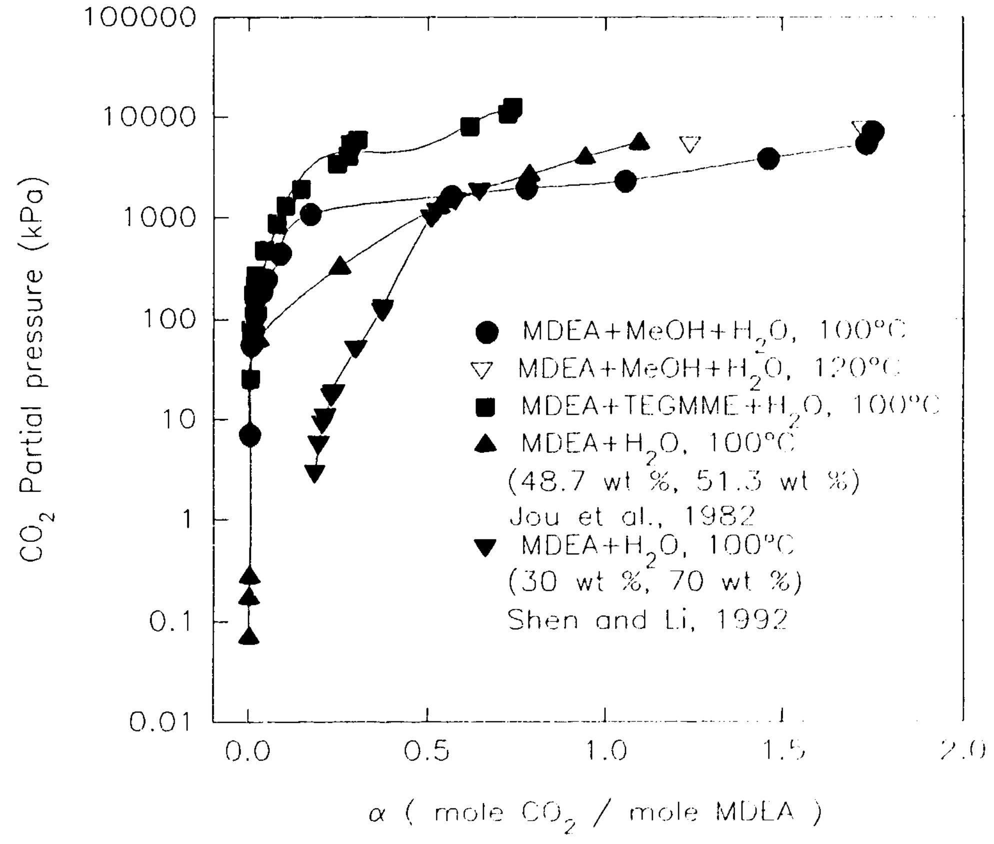

Figure 14. Solubility of CO_2 in mixed MDEA (40 wt %, 40 wt %, 20 wt %) and aqueous MDEA (48.7 wt % and 30 wt %).

5.2 Evaluation of dielectric constants

The dielectric constants of the solvent are used in the constants A and B of the Debye-Hückel equation :

$$\ln \gamma_i = (-A z_i^2 I^{0.5} / 1+b_i B I^{0.5}) + 2\sum_{k \neq w} \beta_{ij} m_k \qquad (5.1)$$

$A = -4.2 \times 10^6 (1 / \epsilon T)^{3/2}$

$B = 50.3 \times 10^8 (1 / \epsilon T)^{1/2}$

b_i :size of hydrated ions (Butler, 1964)

z_i: electric charge

β_{ij} : interaction parameters

m_k : molality, mol / kg

The dielectric constants for the mixture of methanol and water were correlated as a function of the weight composition . The raw data were published by Bates and Robinson (1966).

The dielectric constants of the mixture of ethylene glycol and water as reported by Franks (1973) were used in substitution to those of TEGMME and water.

The results of the regression are presented in Table 14.

Table 14 . Regression of the dielectric constants for the mixtures MeOH(1)-water(2) and ethylene glycol(1)-water(2).

$$\epsilon_m = ao + a1 * w_1^{\dagger} + a2 * (w_1)^2 + a3 * (w_1)^3$$

40°C	**ao**	**a1**	**a2**	**a3**
MeOH-water	73.168	-41.987	-1.2143	
TEGMME-water	73.168	-26.624	-1.3977	-10.19

100°C	**ao**	**a1**
MeOH-water	51.907	-33.930
TEGMME-water	55.674	-29.118

5.3 Interaction parameters evaluation

The interaction parameters for MDEA-water-CO_2 (Table 15) are the same as those reported by Chakravarty (1985) and MacGregor (1988). The parameters were fitted to the solubility of CO_2 in aqueous MDEA reported by Jou et al.(1982). The Debye-Hückel constants were obtained from Butler (1964).

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† mass fraction

Table 15. Interaction parameters for the extended Debye-Hückel equation

Species pairs	Chakravarty (1985)
CO_2-$MDEAH^+$	-0.08868
HCO_3^--MDEA	-0.01379
HCO_3^--$MDEAH^+$	-0.01406

5.4 Equilibrium constants evaluation for mixed solvent data

The equilibrium constant for the MDEA protonation was taken to be equal to the value optimized by MacGregor (1988) at 40°C and 100°C . The mixed solvent used in that work was a mixture of MDEA (30 wt %), sulfolane (20 wt %) and water (50 wt %). The MDEA protonation equilibrium constant could have been used as extra fitting parameter if another set of data was available with the present mixed solvent (MDEA, TEGMME and water). This would have certainly improved the correlation of the data by the model. The experimental data for the mixed solvents were used to obtain the optimized values for the dissociation constants of CO_2 and HCO_3^-. The objective function used in this case was:

$$OF = \sum \left| \left(\ln P_{Calc} - \ln P_{Expt.} \right) \right| \qquad (5.2)$$

The least squares problem was solved with the use of two complementary IMSL subroutines (one variable minimization DUVMIF and a multivariate function DUMINF) .The regressed parameters are listed in Table 16.

The prediction of the partial pressure was more sensitive to the constant for CO_2 dissociation than that for HCO_3^- dissociation. It was also noticed that the regression was very sensitive to the value of the dielectric constants.

Table 16. Equilibrium constants for the TEGMME mixed solvent system.

parameter	**40°C**	**100°C**
K (MDEA prot.)	1.387×10^{-6}	1.520×10^{-6}
K (CO_2 diss.)	4.22×10^{-8}	4.443×10^{-9}
K (HCO_3^- diss.)	1.14×10^{-12}	1.093×10^{-12}
OF	6.57	1.59

6. Conclusions

6.1 Physical solvent

The solubility of CO_2 in TEGMME at 40°C, 70°C and 100°C was higher than in methanol and sulfolane. TEGMME appears to be a promising physical solvent as it has a very low vapour pressure even at high temperature.

The CO_2-TEGMME system was very well correlated by the PR equation of state.

6.2 Non-aqueous mixed solvents

The non-aqueous systems of TEGMME-MDEA and methanol-MDEA could not be well correlated by the PR equation. The addition of MDEA to the physical solvents (TEGMME and methanol) in a 50 wt % proportion seems to enhance the solubility of CO_2 at low pressure only.

An addition of MDEA in a lower proportion (1-15 wt %) is proposed in order to enhance CO_2 solubility over all the pressure range. At very high partial pressures of CO_2, the solubility in the non aqueous mixed MDEA was equal if not greater than both the mixed and the aqueous MDEA solutions.

6.3 Aqueous mixed solvents

Pure TEGMME is a better solvent for CO_2 than pure methanol, used in a mixture with MDEA and water it has a tendency of absorbing less CO_2 (Figures 13 and 14) than the aqueous MDEA-methanol mixture. The advantage over the methanol system is that TEGMME losses to the vapor phase are negligible.

The addition of water to the TEGMME-MDEA and MeOH-MDEA systems enhances the solubility of CO_2. This enhancement disappears, as expected, at a loading of one for the TEGMME system (Figure 13) but continues above one for the methanol system (Figure 16). At high solution loadings(>1mole/mole MDEA) and for both 40°C and 100°C, CO_2 is more soluble in the MeOH-MDEA-water solution than in the aqueous amine solution (Figures 14 and 16). This can be explained by the greater power of absorption of methanol compared to water. At both 40°C and 100°C, the solubility of CO_2 in the aqueous MDEA is greater than in the TEGMME-MDEA-water system at any partial pressure (Figures 13 and 14). This behavior was unexpected.

The predictions of the Deshmukh-Mather model were in acceptable agreement with the experimental solubility of CO_2 in the MDEA-TEGMME-water system at 100°C (Figure 18). The model correlates less accurately the experimental data at 40°C (Figure 17). This was also the trend noticed by MacGregor (1988).

The measurement of the actual dielectric constants for the TEGMME-water mixture and the solubility of CO_2 at values of α above one at 100°C would certainly improve the prediction. The prediction of the model could also be improved if the protonation constants for MDEA were regressed from the experimental data.

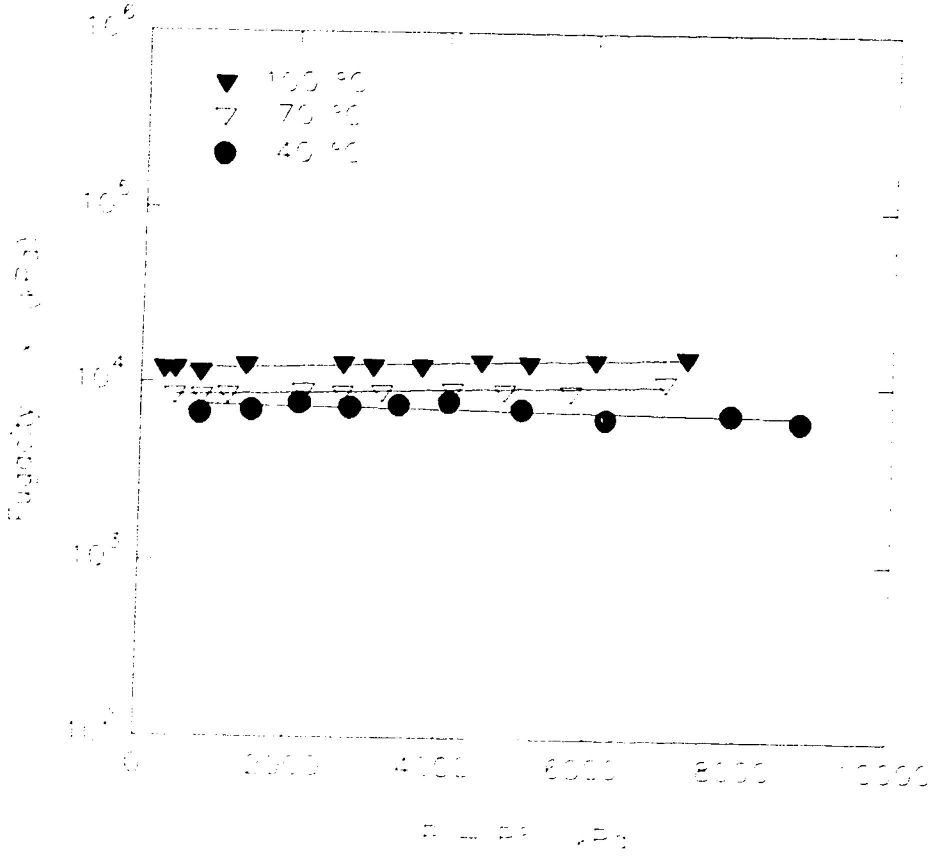

Figure 15. Fit of the fugacity of CO_2 in TEGMVE to K-K equation

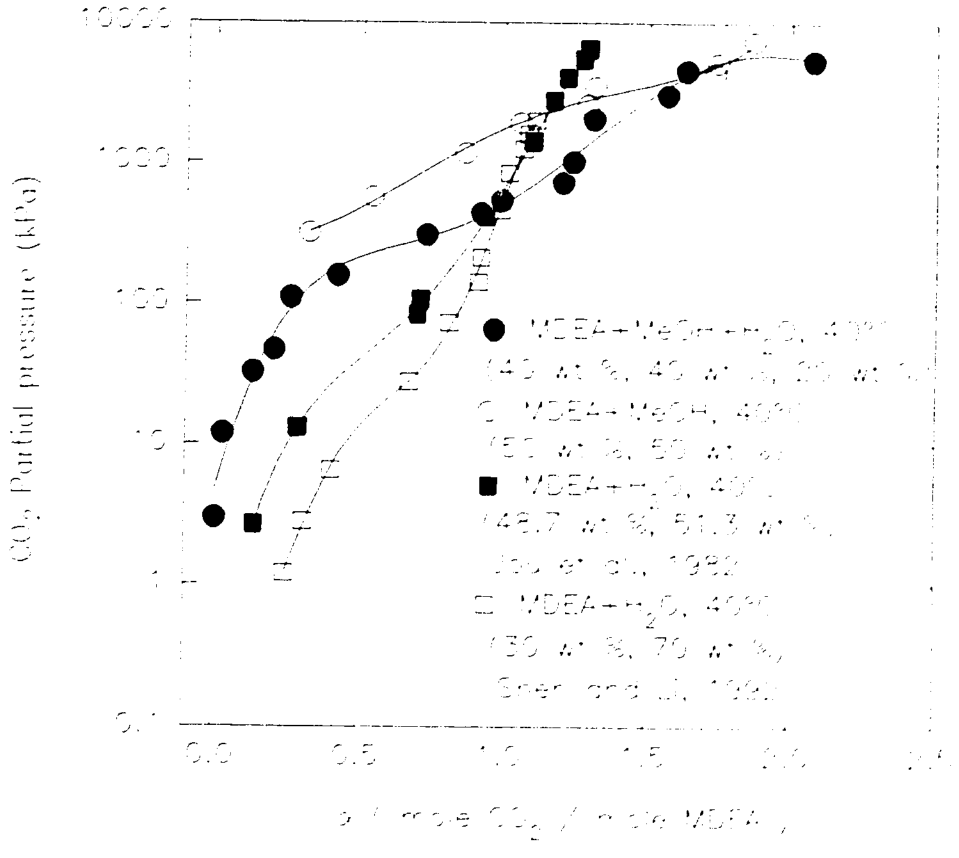

Figure 16. Effect on the solubility of CO_2 of the addition of water to MeOH-MDEA mixture and the addition of MeOH to water-MDEA mixture at 40°C.

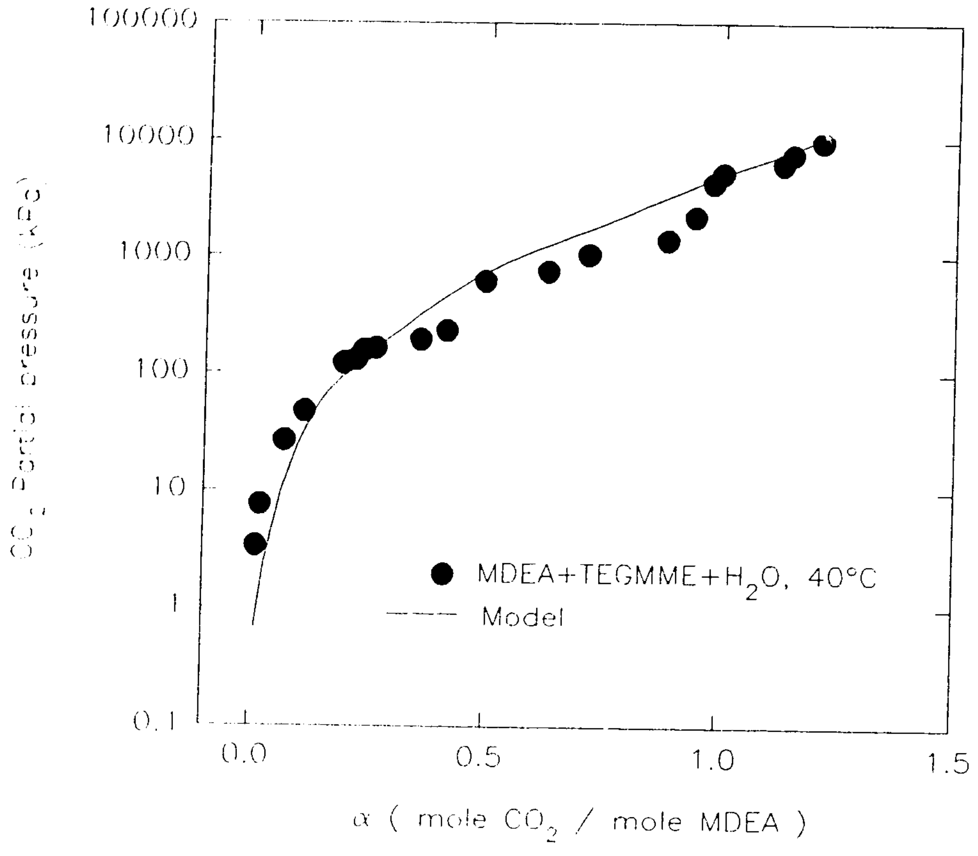

Figure 17. Solubility of CO_2 at 40°C in mixed solvent (40 wt %, 40 wt %, 20 wt %)

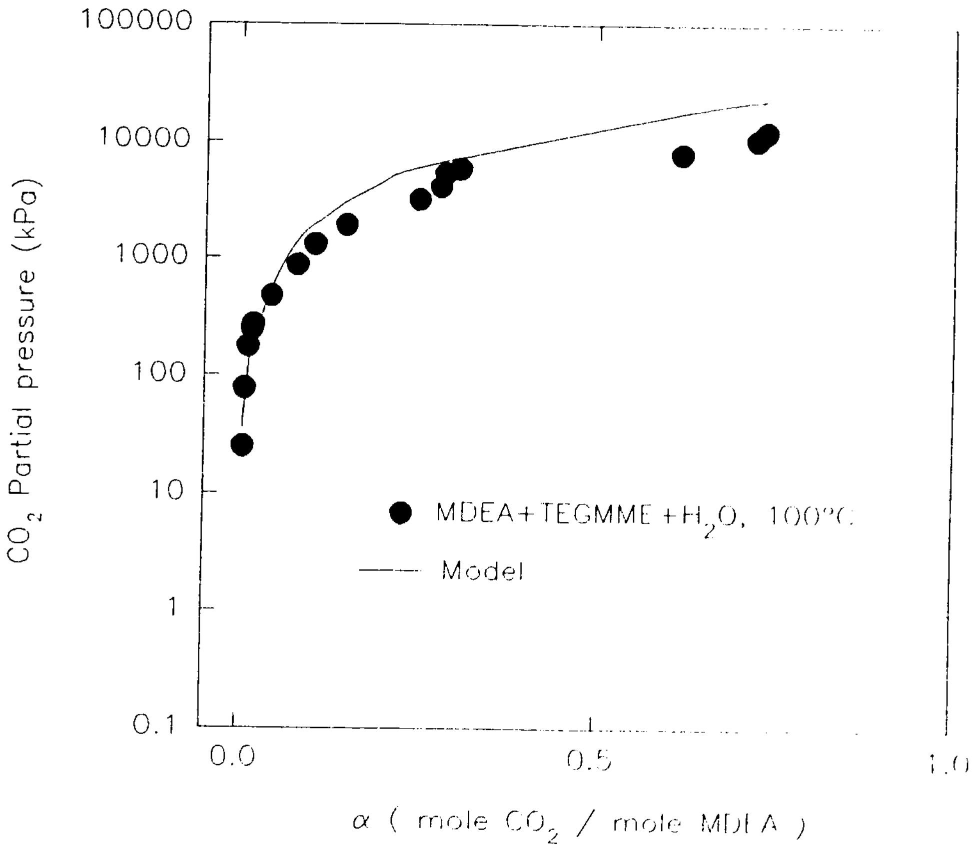

Figure 18. Solubility of CO_2 at 100°C in mixed solvent (40 wt %, 40 wt %, 20 wt %)

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Appendix I: Description of the Peng-Robinson equation of state and the Krichevsky-Kasarnovsky equation

The Peng-Robinson Equation of state is of the form:

$$P = \frac{RT}{(v - b)} - \frac{a(T)}{(v(v + b) + b(v - b))}$$

The fugacity coefficient of component i can be calculated from the following equation:

$$\ln\phi_i = \left(\frac{b_i}{b}\right)(Z - 1) - \ln(Z - B)\left(\frac{1}{\sqrt{8}}\right)\left(\frac{A}{B}\right)\left(\frac{2\sum y_i a_{ij}}{a} - \frac{b_i}{b}\right)\ln\frac{(Z + 2.414B)}{(Z - 0.414B)}$$

where

$A = a P / R^2T^2$, $B = b P / RT$, $Z = P v / RT$, $a = \Sigma y_i y_j a_{ij}$, $b = \Sigma y_j b_j$

and

$a_{ij} = (1 - \delta_{ij})(a_i a_j)^{0.5}$

$a(T) = a(Tc)\ \alpha(Tr, \omega)$

$b(T) = b(Tc)$

$a(Tc) = 0.45724\ R^2 (Tc)^2 / Pc$

$b(Tc) = 0.07780\ R\ Tc / Pc$

$\alpha^{0.5}(Tr, \omega) = 1 + \kappa\,[1 - (Tr)^{0.5}]$

$\kappa = 0.37464 + 1.54226\,\omega - 0.26922\,\omega^2$

The Krichevsky-Kasarnovsky equation is of the form:

$$\ln\frac{f_i}{x_i} = \ln H_{i,solvent} + \frac{V_i^{\infty}(P - P^s_{solvent})}{RT}$$

Appendix II : Sample calculations for laboratory data

1. Methanol - CO_2 system

a. CO_2 content in liquid sample:

data : P=685 kPa (total)
T=40°C
area count CO_2 : 1041
area count MeOH : 17338
area count CO_2 standard (0.1ml): 56889
area count MeOH (1.35 mg, 1.05 wt %): 3926

$$\text{mole } CO_2 = \frac{1041 \times 701 \times 0.1}{56889 \times 82.05 \times 296 \times 760} = 6.9495887\ \text{E-8}$$

$$\text{mole MeOH} = \frac{17730 \times 1.05 \times 1.30^{\dagger}}{3926 \times 100 \times 1000 \times 32.04} = 2.8534061\ \text{E-6}$$

$$\text{mole fraction of } CO_2 = \frac{6.9495887\ \text{E-8}}{6.9495887\ \text{E-6} + 2.8534061\ \text{E-6}} = 0.0348$$

b. CO_2 content in vapour sample:

data : P=685 kPa (total)
area count CO_2 : 98.04 %
area count MeOH : 1.96 %

$$\text{mole fraction of MeOH} = \frac{1.96}{1.96 + 98.04 \times 1.03^{\dagger}} = 0.019$$

mole fraction of CO_2 : $y_{CO2} = 1 - y_{MeOH} = 0.981$

partial pressure of CO_2 : $p_{CO2} = P\ (\text{total})\ y_{CO2} = 685 \times 0.981 = 672$ kPa

† response factor

2. TEGMME - CO_2 system :

a. CO_2 content in liquid sample :

data : P = 689 kPa (total)
P atm = 700 mm Hg
T= 40 °C
Mw (TEGMME) : 164.2
area count CO_2 : 2168
area count CO_2 std. (0.1ml) : 47283
area count TEGMME : 88007
area count TEGMME std. (1.7 mg,14.96 wt %) : 86902

$$\text{mole of } CO_2 = \frac{2168 \times 702 \times 0.1}{47283 \times 760 \times 82.05 \times 296} = 1.7438433 \text{ E-7}$$

$$\text{mole of TEGMME} = \frac{88007 \times 14.96 \times 1.7}{86902 \times 100 \times 1000 \times 164.2} = 1.56837 \text{ E-6}$$

$$\text{mole fraction of } CO_2 = \frac{1.7438422 \text{ E-7}}{1.7438422 \text{ E-7} + 1.56837 \text{ E-6}} = 0.10005$$

b. CO_2 content in vapour phase:

No traces of TEGMME were found in the vapour phase.

partial pressure of CO_2 : p_{CO_2} = P = 689 kPa

3. MDEA - MeOH - CO_2 system :

a. CO_2 content in liquid sample:

data : P = 363.5 kPa (kPa)
P atm. = 701 mm Hg
area count CO_2 : 73278
area count CO_2 std. (0.1 ml) : 5525
area count MeOH: 41425
area count MeOH(1.5 mg, 9.74 wt %) : 61898
liquid sample +(DGA+water) : 12.471 g
liquid sample in syringe : 1.6 E-3 g

$$\text{g } CO_2 = \frac{5525 \times 0.1 \times 701 \times 44}{73278 \times 760 \times 82.05 \times 296} = 1.2599272 \text{ E-5}$$

$$\text{g MeOH} = \frac{46960 \times 1.6 \times 9.74}{61898 \times 1000 \times 100} = 1.1823074 \text{ E-4}$$

Total =1.2599272 E-5 + 1.1823074 E-5 =1.3083001 E-4 g

$$\text{mass of MDEA} = 1.8512 - 1.3083001\text{E-4}\ \frac{12.471}{1.6 \text{ E-3}} = 0.831461818 \text{ g}$$

$$\text{mass of } CO_2 \text{ in liquid sample} = \frac{1.2599272 \text{ E-5} \times 12.471}{1.6 \text{ E-3}} = 0.09820345 \text{ g}$$

$$\text{mass of MeOH in liquid sample} = 1.1823074 \text{ E-4}\ \frac{12.471}{1.6 \text{ E-3}} = 0.921534724 \text{ g}$$

$$\text{mole fraction of } CO_2 = \frac{0.09820345/44}{0.09820345/44 + 0.921534724/32.04 + 0.831461818/119.16}$$

$$= 0.0588$$

$$\text{mole fraction of MeOH} = \frac{0.921534724/32.04}{0.921534724/32.04 + 0.09820345/44 + 0.831461818/119.16}$$

$$= 0.7575$$

mole fraction of MDEA= 1 - (0.0588 + 0.7575) = 0.1837

b. CO_2 content in vapour phase :

data : water partial pressure= water vapour pressure x water mole fraction
=7.38 kPa x 0.4120 = 3.04 kPa
area count CO_2 : 832456
area count CO_2 std. (0.1 ml) : 86798
area count MeOH : 67714
area count MeOH std.(1.6 , 9.74 wt %): 59618

$$\text{mole } CO_2 = \frac{832 \times 0.1 \times 701}{86798 \times 760 \times 82.06 \times 296} = 3.64193988 \text{ E-5}$$

$$\text{mole MeOH} = \frac{67714 \times 1.6 \times 9.74}{59618 \times 1000 \times 100} = 5.5244303 \text{ E-6}$$

$$\text{mole fraction of } CO_2 = \frac{3.64193988 \text{ E-5}}{3.64193988 \text{ E-5} + 5.5244303 \text{ E-6}} = 0.8683$$

partial pressure of CO_2 : p_{CO2} = (363.46 - 3.04) 0.8683 = 313 kpa

4. MDEA - TEGMME - CO_2 system :

a. CO_2 content in liquid sample :

data :P = 294 kPa (total)
P atm. = 706 mm Hg
area count CO_2 : 902
area count CO_2 std. (0.1 ml) : 46926
area count TEGMME : 30992
area count TEGMME std. (1.4 mg, 10.13 wt %) :
area count MDEA : 20257
area count MDEA std. (1.7 mg , 8 wt %) : 30610

$$\text{mole of } CO_2 = \frac{902 \times 0.1 \times 706}{46926 \times 760 \times 82.05 \times 296} = 7.3521407 \text{ E-8}$$

$$\text{mole of TEGMME} = \frac{30992 \times 1.4 \times 10.13}{57327 \times 1000 \times 100 \times 164.2} = 4.6693515 \text{ E-7}$$

$$\text{mole of MDEA} = \frac{22958 \times 1.7 \times 8}{30610 \times 1000 \times 100 \times 119.16} = 8.5601057 \text{ E-7}$$

$$\text{mole fraction of } CO_2 = \frac{7.352107\ E\ \text{-}8}{7.352107\ E\ \text{-}8 + 4.6693314\ E\text{-}7 + 7.5530345\ E\text{-}7}$$

$$=0.0526$$

$$\text{mole fraction of TEGMME} = \frac{4.6693315\ E\text{-}7}{4.6693315\ E\text{-}7 + 7.352107\ E\text{-}8 + 7.5530345\ E\text{-}7}$$

$$= 0.3343$$

mole fraction of MDEA = 1 - (0.0526 + 0.3343) = 0.6129

5. MDEA - MeOH - CO_2 - water system :

a. CO_2 content in liquid phase :

data : P = 205 kPa (total)
P atm. = 710 mm Hg
area count CO_2 : 3507
area count CO_2 std. (20 μl) : 19469
area count MDEA : 189745
area count MDEA std. (1.8 , 40.81 wt %) : 245094

$$\text{mole fraction of } CO_2 = \frac{3507 \times 20 \times 710}{19469 \times 1000 \times 296 \times 760 \times 82.05} = 1.3857872\ E\text{-}7$$

$$\text{mole fraction of MDEA} = \frac{189745 \times 40.81 \times 1.8}{245094 \times 100 \times 1000 \times 119.16} = 4.7725034\ E\text{-}6$$

$$\text{amine loading } \alpha = \frac{1.3857872\ E\text{-}7}{4.7725034\ E\text{-}6} = 0.029 \text{ mole } CO_2 \text{ / mole amine}$$

b. CO_2 content in vapour phase (low pressure)

data : area count CO_2 : 40578
area count CO_2 std. (60 μl) : 116010
area count N_2 :1580835
area count N_2 std. (700 μl) :1202267
area count MeOH : 181564
area count MeOH std. (1.7 mg, 9.74 wt %): 96295

$$\text{mole of } CO_2 = \frac{40578 \times 60 \times 710}{11601 \times 1000 \times 296 \times 760 \times 82.05} = 8.0727391 \text{ E-7}$$

$$\text{mole of } N_2 = \frac{1580835 \times 700 \times 710}{1202267 \times 1000 \times 296 \times 760 \times 82.05} = 3.5404359 \text{ E-6}$$

$$\text{mole of MeOH} = \frac{181564 \times 9.74 \times 1.7}{96295 \times 100 \times 1000 \times 32.04} = 9.7440919 \text{ E-6}$$

$$\text{mole fraction of } CO_2 = \frac{8.0727391 \text{ E-7}}{8.0727391\text{E-7} + 3.5404359 \text{ E-6} + 9.7440919 \text{ E-6}}$$

$$= 0.0573$$

partail pressure of CO_2 : p_{CO2} = (205 - 3.04) 0.0573 = 11.57 kPa

c. CO_2 content in vapour phase :

data : P = 193.7 kPa (total)
P atm. = 700 mm Hg
area count CO_2 = 474832
area count CO_2 std. (700μl) = 429465
area count MeOH = 53942
area count MeOH std. (1.7mg, 9.74 wt %) : 44852

$$\text{mole of } CO_2 = \frac{474832 \times 700 \times 698}{44852 \times 100 \times 32.04 \times 1000} = 2.926724\ E\text{-}5$$

$$\text{mole of MeOH} = \frac{53942 \times 9.74 \times 1.7}{44852 \times 100 \times 32.04 \times 1000} = 6.2152786\ E\text{-}6$$

$$\text{mole fraction of } CO_2 = \frac{2.926724\ E\text{-}5}{2.926724\ E\text{-}5 + 6.2152786\ E\text{-}6} = 0.8248$$

partial pressure of CO_2 : $p_{CO2} = (193.7 - 3.04)\ 0.8248 = 157.2$ kPa

Appendix III: Raw experimental data

Table A1 -Raw Data- Solubility of carbon dioxide in TEGMME at 40°C.

Liquid phase

P/P atm kPa/mm Hg	Area/Area/Vol CO_2/Std./(µl)	Mole CO_2	Area/Area/Mass/Comp. TEGMME /Std./(mg)/wt%	Mole TEGMME	Mole Fraction CO_2
783/702	2168/47283/100	1.7438437E-7	88007/86902/1.7/14.96	1.4762702E-6	0.1000
1450/710	4037/51010/100	3.0442390E-7	88208/86902/1.7/14.96	1.5721195E-6	0.1622
2103/709	5264/50894/100	3.9729366E-7	75340/86902/1.7/14.96	1.3427748E-6	0.2283
2782/701	11511/51717/100	8.4530580E-7	12289/86902/1.7/14.96	2.1902875E-6	0.2785
3430/701	8155/49182/100	6.2972640E-7	55701/86902/1.7/14.96	9.9275156E-7	0.3881
4097/703	6206/38072/100	6.2083689E-6	18243/86902/1.7/14.96	1.6595145E-7	0.4825
5076/704	14820/47248/100	1.1963370E-6	50030/86902/1.7/14.96	8.3922643E-7	0.5877
6209/702	23661/45444/100	1.9802032E-6	56624/86902/1.7/14.96	1.0092010E-6	0.6624
7877/698	43070/45527/100	3.5774812E-6	70685/86902/1.7/14.96	1.2598093E-6	0.7396
8794/699	19663/51113/100	3.2514256E-7	18243/86902/1.7/14.96	3.2514257E-7	0.8175

Table A2-Raw Data- Solubility of carbon dioxide in TEGMME at 70°C.

Liquid phase

P /P atm kPa/mm Hg	Area/Area/Vol CO_2/Std./(µl)	Mole CO_2	Area /Area/Mass/Comp. TEGMME/Std./(g)/wt%	Mole TEGMME	Mole Fraction CO_2
443/710	1453/12790/20	8.7397602E-8	111184/105958/1.7/14.96	1.6252215E-6	0.0510
800/710	3252/12790/20	2.2293832E-7	133149/105958/1.7/14.96	1.9462928E-6	0.0913
1155/710	3950/12790/20	2.1593763E-7	100552/105958/1.7/14.96	1.4698092E-6	0.1281
2152/710	5775/12790/20	3.3855843E-7	82707/105958/1.7/14.96	1.2072691E-6	0.2190
2682/710	8987/12790/20	5.2686139E-7	95462/105958/1.7/14.96	1.3934530E-6	0.2744
3202/708	9115/12790/20	5.3436537E-7	78551/105958/1.7/14.96	1.1466042E-6	0.3179
4143/697	11042/12790/20	6.5201272E-7	71304/105958/1.7/14.96	1.0408202E-6	0.3851
4943/697	14897/12790/20	8.7964432E-7	76301/105958/1.7/14.96	1.1137611E-6	0.4412
5734/707	15685/12790/20	9.3946240E-7	62585/105958/1.7/14.96	9.1354955E-7	0.5070
7004/703	21883/12790/20	1.3032797E-6	78836/105958/1.7/14.96	1.1507644E-6	0.5311

Table A3 -Raw Data- Solubility of Carbon dioxide in TEGMME at 100°C.

Liquid phase

P/P atm Kpa/mm Hg	Area /Area/Vol CO_2/Std./(µl)	Mole CO_2	Area /Area/Mass/Comp. TEGMME/Std./(mg)/wt%	Mole TEGMME	Mole Fraction
300/710	977/21772/20	3.4522337E-8	133157/151117/1.7/14.96	1.3647655E-6	0.0247
450/710	1927/21772/20	6.8055371E-8	173670/151117/1.7/14.96	1.7799526E-6	0.0368
748/710	2871/21772/20	1.0144702E-7	139488/151117/1.7/14.96	1.3427748E-6	0.0662
1392/692	5140/21772/20	1.7701983E-7	146423/151117/1.7/14.96	1.5007325E-6	0.1005
2691/692	5004/21772/20	1.7233603E-7	74812/151117/1.7/14.96	7.2342103E-7	0.1924
3083/692	5469/21772/20	1.8835047E-7	67043/151117/1.7/14.96	6.4829594E-7	0.2251
3732/697	6609/21772/20	2.2925627E-7	64798/60731/1.7/14.96	6.2658712E-7	0.2679
4518/697	8476/21772/20	2.9401969E-7	71823/60731/1.5/02.75	6.9246103E-7	0.2980
5166/700	14974/31656/20	5.2166122E-7	104581/151117/1.7/14.96	1.0112828E-6	0.3403
6063/707	22788/31656/20	5.5141473E-7	95137/151117/1.7/14.96	9.9199603E-7	0.3748
7282/700	18813/31656/20	4.5076629E-7	59210/60731/1.5/02.75	6.1738424E-7	0.4220

Table A4-Raw Data- Solubility of carbon dioxide in TEGMME/MDEA at 40°C.

Liquid phase

P/P atm Kpa/mm Hg	Area/Area/Vol CO_2/Std./(µl)	Mole CO_2	Area /Area/Mass/Comp. TEGMME/Std./(g)/wt%	Mole TEGMME	Area/Area/mass/Comp. MDEA/Std./(g)/wt%	Mole MDEA	Mole Fr. CO_2/MDEA
294/706	902/4626/100	7.352107E-8	30992/57327/1.4/10.13	4.6693300E-7	20257/30610/1.7/8	8.5601057E-7	05.26/61.29
583/700	2300/10340/100	1.687141E-7	32332/58566/1.4/10.13	3.9020259E-7	22452/34401/1.7/8	7.4489040E-7	12.94/57.13
1000/700	5077/16223/50	5.934172E-7	54131/67487/1.4/10.13	6.9277188E-7	41551/41462/1.7/8	1.1437724E-6	24.42/47.07
2780/713	9698/15837/30	7.532481E-7	37051/60952/1.4/10.13	5.2502540E-7	30754/33489/1.7/8	1.0411200E-6	32.37/45.06
4295/713	8926/15837/30	6.531469E-7	28288/58678/1.4/10.13	4.1638134E-7	22694/38750/1.7/8	6.6841741E-7	37.58/38.46
5245/713	14365/15837/30	1.051137E-6	40457/58678/1.4/10.13	5.9550128E-7	33447/38750/1.7/8	9.8513074E-7	39.94/37.43
6622/697	17613/16596/30	1.191951E-6	41286/58678/1.4/10.13	6.0770363E-7	33462/38750/1.7/8	9.8557255E-7	42.79/35.39
8403/697	17841/16596/30	1.127828E-6	30897/58678/1.4/10.13	4.5478416E-7	24861/38750/1.7/8	7.3224311E-7	50.64/30.45
10043/697	25078/16596/30	1.711826E-6	41160/58678/1.4/10.13	6.0584899E-7	39534/38750/1.7/8	1.1644141E-6	49.16/33.44

Table A5-Raw Data- Solubility of carbon dioxide in methanol/MDEA at 40°C.

Liquid phase

methanol standard solution, Area/Mass/wt% : 61898/1.6/9.74

P /P atm kPa/mm Hg	Area/Area/Vol CO_2/Std./(μl)	Mass CO_2(g)	Mass methanol(g)	Mass sample syringe(g)	Mass sample(g) bomb(Liq+DGA/Liq)	Mole fractions CO_2/methanol/MDEA
363/701	5525/73278/100	1.2599272E-5	1.1823074E-4	1.6E-3	12.4710/1.8512	0.0588/0.7575/0.1837
613/695	8307/75234/100	1.8292945E-5	1.4047956E-4	1.7E-3	12.0158/1.7700	0.0746/0.7873/0.1381
1212/695	15497/74558/100	3.4435546E-5	1.5763710E-4	1.7E-3	13.8836/2.4506	0.1184/0.7445/0.1371
1969/700	12992/70757/100	3.0638518E-5	1.0432048E-4	1.7E-3	11.9786/1.5058	0.1509/0.7058/0.1432
2598/704	12664/71399/100	2.9765982E-5	8.7436859E-5	1.7E-3	11.7238/1.2396	0.1721/0.6944/0.1335
3612/700	19518/14252/20	4.5875903E-5	1.1268790E-4	1.7E-3	12.8096/1.9064	0.1948/0.6569/0.1483
4563/700	16623/14799/20	3.7484100E-5	8.0561047E-5	1.8E-3	12.0379/1.1821	0.2208/0.6515/0.1276
5965/694	21530/15178/20	4.6934017E-5	8.5256390E-5	1.8E-3	13.2770/1.5145	0.2457/0.6129/0.1414
7395/714	22090/24822/20	5.7375873E-5	8.7655890E-5	1.8E-3	13.2090/1.6749	0.2752/0.5774/0.1474

Vapour phase

methanol standard solution, Area/Mass/wt%: 59618/1.6/9.74

P/P atm kPa/mm Hg	Area/Area/Vol CO_2 /Std./(μl)	Mole CO_2	Area methanol	Mole methanol	Mole Fraction CO_2	Partial Pressure CO_2 (kPa)
363/701	832456/86798/100	3.6419398E-5	67714	5.5244303E-6	0.8683	313
613/699	855806/88880/100	3.6460380E-5	35750	2.9166550E-6	0.9259	565
1212/695	850605/87633/100	3.6547793E-5	18716	1.5269403E-6	0.9599	1161
1969/704	849223/87995/100	3.6808873E-5	12863	1.0494247E-6	0.9723	1911
2598/702	1144141/786120/1000	5.5142356E-5	11073	9.0338801E-7	0.9839	2596
3612/691	799031/621331/800	3.8514543E-5	15229	1.2424542E-6	0.9687	3496
4563/700	799715/655459/800	3.7016371E-5	15350	1.2523260E-6	0.9673	4417
5965/713	858021/656027/800	4.0417721E-5	12704	1.0364527E-6	0.9750	5183
7395/711	852412/789128/1000	4.1609510E-5	12430	1.0140985E-6	0.9762	7392

Table A6-Raw Data- Solubility of carbon dioxide in methanol/MDEA/water at 40°C.

Liquid phase

P/P atm kPa/mm Hg	Area/Area/Vol. CO_2 /Std./(μl)	Mole CO_2	Area/Area MDEA/Mass/Comp. MDEA/Std./(g)/(wt %)	Mole MDEA	α Mole CO_2/ Mole MDEA	Partial Pressure CO_2 (kPa)
206/710	550/19469/20	2.1733189E-8	225249/245094/1.8/40.81	5.6655070E-6	0.004	2.77
205/710	3507/19469/20	1.3857872E-7	189745/245094/1.8/40.81	4.7725034E-6	0.029	11.6
245/710	17707/19469/20	6.9969016E-7	217074/245094/1.8/40.81	5.4598880E-6	0.128	32.9
268/710	29330/19469/20	1.1344854E-6	221712/245094/1.8/40.81	5.5765438E-6	0.203	47.3
323/697	37364/19469/20	1.4494011E-6	222341/245094/1.8/40.81	505923646E-6	0.259	110.4
194/703	5308/9843/20	4.1077581E-7	24157/28251/1.7/8.0	9.7592752E-7	0.421	155.3
344/702	4407/13129/30	3.8298862E-7	13990/30503/1.7/8.0	5.2346008E-7	0.732	302.9
763/702	5502/13129/30	4.7814918E-7	10601/30503/1.7/8.0	3.9665478E-7	1.205	723.6
1053/800	6787/13129/30	5.8982160E-7	12695/30503/1.7/8.0	4.7500541E-7	1.240	1009.3
2119/800	1164/13129/30	1.0778287E-6	20613/30503/1.7/8.0	8.6181959E-7	1.310	2041.8
3052/706	10300/13129/30	9.0021789E-7	15376/30503/1.7/8.0	5.7531967E-7	1.565	3048
4734/706	8410/13129/30	7.3503228E-7	12049/30503/1.7/8.0	4.5083420E-7	1.630	4611.9
5564/706	7715/13129/30	6.1468276E-7	7904/30503/1.7/8.0	2.9574185E-7	2.078	5440.3

Vapour phase

methanol standard solution, Area/Mass/wt% : 96295/1.7/9.74(with N_2, low pressure)
41280/1.7/9.74(high pressure, different helium flowrate)

P/Patm kPa/mm Hg	Area/Area/Vol CO_2 /Std./(μl)	Mole CO_2	Area/Area/Vol N_2 /Std./(μl)	Mole N_2	Area methanol	Mole methanol	Mole fraction CO_2
206/710	9672/116010/60	1.9241838E-7	1624652/1202267/700	3.6385683E-6	192769	1.0300659E-5	0.0136
205/710	40578/116010/60	8.0727391E-7	1580835/1202267/700	3.5404359E-6	181564	9.7440919E-6	0.0573
245/710	344987/116010/60	6.0717610E-6	1355706/1202267/700	3.0362348E-5	159277	8.5480036E-6	0.1356
268/710	435969/43477/200	7.7177965E-6	1249698/1202267/700	2.7988308E-5	139982	7.5124885E-6	0.1786
323/697	650565/575831/300	1.2798698E-5	948527/1202267/700	2.0854304E-5	63307	3.3975305E-6	0.3454
194/703	474832/429465/700	2.9267240E-5			53942	6.7530929E-6	0.8146
344/702	560110/487688/800	3.4944148E-5			34702	4.3444038E-6	0.8894
763/695	582241/487688/800	3.5962644E-5			14228	1.7822800E-6	0.9528
1053/697	583833/487688/800	3.6164748E-5			11601	1.4523493E-6	0.9614
2119/704	582014/487688/800	3.6414145E-5			10547	1.3203972E-6	0.9650
3124/704	583714/487688/800	3.6520506E-5			6963	8.7171009E-7	0.9767
4734/704	575966/487688/800	3.6035740E-5			7495	9.3830724E-7	0.9746
5564/704	579637/487688/800	3.6265426E-5			3754	8.0423172E-7	0.9783

Table A7-Raw Data- Solubility of carbon dioxide in methanol/MDEA/water at 100°C.

Liquid phase

P/P atm kPa/mm Hg	Area/Area/Vol. CO_2 /Std./(µl)	Mole CO_2	Area/Area MDEA/Mass/Comp. MDEA/Std./(g)/(wt %)	Mole MDEA	α Mole CO_2/ Mole MDEA	Partial Pressure CO_2 (kPa)
255/700	564/8503/10	2.5148120E-8	165161/103249/1.7/19.33	4.4113554E-6	0.006	7.0
272/700	1114/8503/10	4.9685213E-8	244584/103249/1.7/19.33	6.5326963E-6	0.008	55.8
469/695	1872/18133/20	7.7744040E-8	215813/102433/1.7/19.33	5.8101585E-6	0.014	78.6
493/704	2759/18133/20	1.1458109E-7	221405/102433/1.7/19.33	5.9607030E-6	0.019	110.6
501/706	2723/18133/20	1.1340727E-7	203222/102433/1.7/19.33	5.4711811E-6	0.021	123.8
436/700	5222/8503/10	2.3905001E-7	23961/103249/1.7/19.33	6.3290903E-6	0.037	185.9
59/700	6961/8503/10	3.1046566E-7	238047/103249/1.7/19.33	6.3580967E-6	0.049	248.6
1624/702	23647/8503/10	1.0572521E-6	227855/103249/1.7/19.33	6.0858956E-6	0.174	1087.2
2133/704	3693/15972/20	1.2252336E-7	11950/43834/1.6/8.0	4.5220870E-7	0.567	1641.2
2914/705	6854/15972/20	4.0818235E-7	18477/43834/1.6/8.0	5.2594786E-7	0.776	1973
3044/704	4301/15972/20	2.0541345E-7	7870/43834/1.6/8.0	1.9440333E-7	1.057	2313.7
4345/710	6329/15972/20	3.7958971E-7	9145/43834/1.6/8.0	2.6031245E-7	1.458	3866.0
6413/697	7612/13129/30	3.2557803E-7	7022/30503/1.7/8.0	1.8753254E-7	1.736	5367
7873/697	8800/13129/30	3.7639068E-7	8043/30503/1.7/8.0	2.1479980E-7	1.752	7044

Vapour phase

methanol standard solution, Area/Mass/wt% :710641/1.7/52.55;201346/1.7/20.59 (with N_2, low pressure)
206227/1.7/20.59 (high pressure)

P/Patm kPa/mm Hg	Area/Area/Vol CO_2 /Std./(µl)	Mole CO_2	Area/Area/Vol N_2 /Std./(µl)	Mole N_2	Area methanol	Mole methanol	Mole fraction CO_2
254/700	38139/38944/40	1.4856034E-6	286104/406797/400	1.06689160E-5	996472	4.1396874E-5	0.0277
272/700	182496/38944/40	1.0099490E-5	32507/406797/400	2.42175720E-6	739407	2.9010982E-5	0.2432
469/695	15182/11679/100	4.8946793E-6	43082/70331/500	1.15324060E-5	77643	1.0143227E-5	0.1842
493/704	23184/11679/100	7.5711631E-6	52982/70331/500	1.43661450E-5	68380	8.9331151E-6	0.2452
501/706	26099/11679/100	8.5473235E-6	46447/70331/500	1.26299490E-5	80789	1.0554218E-5	0.2694
436/700	319883/38944/40	1.7702607E-5	47983/406797/400	3.57471230E-6	415766	1.6312774E-5	0.4709
59/700	335667/38944/40	1.8576107E-5	44582/406797/400	3.32079170E-6	168133	1.2346342E-5	0.5425
1624/702	941837/38944/40	5.2271006E-5			323914	2.3785651E-5	0.6873
2133/701	903326/885750/800	3.1259119E-5			274878	8.5057047E-6	0.7840
2914/705	946535/885750/800	3.1391446E-5			159066	1.4306028E-5	0.6869
3044/704	1025065/1036509/900	3.5471838E-5			137114	4.2479560E-6	0.7707
4345/710	1063696/1036509/900	3,5527235E-5			79790	7.7161280E-6	0.8985
6413/697	1076408/1036509/900	3.5293541E-5			73425	6.603647E-6	0.8424
7873/697	1098199/1036509/900	3.6008029E-5			44726	4.022553E-6	0.8995

Table A8-Raw Data- Solubility of carbon dioxide in TEGMME/MDEA/water at 40°C.

Liquid phase

P/P atm kPa/mm Hg	Area/Area/Vol. CO_2 /Std./(μl)	Mole CO_2	Area/Area MDEA/Mass/Comp. MDEA/Std./(g)/(wt %)	Mole MDEA	α Mole CO_2/ Mole MDEA	Partial Pressure CO_2 (kPa)
208/692	1957/20883/20	7.0266793E-8	285535/325712/40.81/1.8	5.4042346E-6	0.013	3.4
204/706	2192/20883/20	8.0297804E-8	253422/143967/19.33/1.7	4.8543561E-6	0.016	7.7
203/689	10663/20883/20	3.8119908E-7	301704/325712/40.81/1.8	5.7102604E-6	0.067	27.3
234/697	10814/20883/20	3.9108608E-7	309012/325712/40.81/1.8	5.7582899E-6	0.068	44.8
237/706	16026/20883/20	5.8706779E-7	283238/143967/19.33/1.7	5.3607599E-6	0.109	48.8
248/689	32498/20883/20	1.1617938E-6	318005/143967/19.33/1.7	6.0187845E-5	0.193	124.0
304/706	33515/20883/20	1.2277285E-6	297804/143967/19.33/1.7	5.6344620E-6	0.218	133.7
327/695	36972/20883/30	1.3332480E-6	300182/325712/40.81/1.8	5.6814539E-6	0.238	159.1
338/695	41809/20883/20	1.5076752E-6	307145/325712/40.81/1.8	5.8132405E-6	0.259	164.7
201/685	3758/8043/20	3.4679041E-7	29356/32904/8.0/1.7	9.0763269E-7	0.355	196.4
292/693	7626/13302/20	4.3048616E-7	38300/32763/8.0/1.7	1.2557415E-6	0.411	324.5
624/706	18744/35076/20	4.0879259E-7	43803/60247/8.0/1.7	8.2980652E-7	0.493	619.0
754/706	15703/35076/20	3.4247066E-7	28844/60247/8.0/1.7	5.4642237E-7	0.627	749.3
1053/698	34591/35361/20	7.3984391E-7	73251/80828/8.0/1.7	1.0343324E-6	0.715	1048.2
1413/698	24450/35361/20	5.1866714E-7	41565/80828/8.0/1.7	5.8691386E-7	0.884	1408.2
2244/706	3775/9601/30	4.5117243E-7	7338/17496/8.0/1.7	4.7868228E-7	0.942	2239.0
4375/711	7594/9601/30	9.1403134E-7	14293/17496/8.0/1.7	9.3238018E-7	0.980	4370.0
5275/712	12571/9601/30	1.5152026E-6	23198/17496/8.0/1.7	1.5132831E-6	1.001	5270.0
6335/712	10238/9601/30	1.2340024E-6	16796/17496/8.0/1.7	1.0956592E-6	1.126	6330.0
7725/712	11134/9601/30	1.3419987E-6	17920/17496/8.0/1.7	1.1689815E-6	1.148	7720.0
9985/712	10156/9601/30	1.2241188E-6	15495/17496/8.0/1.7	1.0107906E-6	1.211	9980.0

vapour phase

P/Patm kPa/mm Hg	Area/Area/Vol CO_2 /Std./(μl)	Mole CO_2	Area/Area/Vol N_2 /Std./(μl)	Mole N_2	Mole fraction CO_2
203/699	17353/44014/40	5.9722366E-7	948153/608775/600	3.5388825E-5	0.0166
204/706	39207/44014/40	1.3628613E-6	874460/793438/800	3.3723896E-5	0.0388
203/689	154960/110381/100	5.2403380E-6	889770/608775/600	3.2734637E-5	0.1378
234/697	124769/110381/100	7.5522939E-6	766513/608775/600	3.1105964E-5	0.1953
237/706	237212/110381/100	7.8548837E-6	766749/608775/600	2.9559978E-5	0.2098
248/697	341335/394089/400	1.3082639E-5	602276/608775/600	2.2415007E-5	0.3685
304/706	447167/394089/400	1.7360261E-5	575189/608775/600	2.1415705E-5	0.4480
327/704	485606/394089/400	1.8799162E-5	518366/513652/500	1.9282110E-5	0.4941
338/695	477264/394089/400	1.8240018E-5	509102/513652/500	1.8659789E-5	0.4943

Table A9-Raw Data- Solubility of carbon dioxide in TEGMME/MDEA/water at 100°C.

Liquid phase

P/P atm kPa/mm Hg	Area/Area/Vol. CO_2 /Std./(µl)	Mole CO_2	Area/Area MDEA/Mass/Cor MDEA/Std./(g)/(wt %)	Mole MDEA	α Mole CO_2/Mole MDEA	Partial Pressure CO_2 (kPa)
207/700	1076/20883/20	3.9080807E-8	384781/325712/40.81/1.8	7.2826330E-6	0.005	25.6
250/700	993/20883/20	3.9958443E-8	435411/325712/40.81/1.8	8.2408916E-6	0.007	79.1
203/689	10663/20883/20	3.8119908E-7	301704/325712/40.81/1.8	5.7102604E-6	0.067	27.3
330/689	2067//20883/20	7.4967127E-8	413822/325712/40.81/1.8	6.1646525E-6	0.012	178.2
369/699	2500/20883/20	9.0671416E-8	361140/325712/40.81/1.8	5.3798556E-6	0.017	218.7
418/699	3268/20883/20	1.1852670E-7	407340/325712/40.81/1.8	6.0680909E-6	0.019	273.5
549/703	2655/20883/20	9.6844078E-8	67205/32763/8.0/1.6	2.2034205E-6	0.044	482.0
948/703	4279/20883/20	1.5608128E-7	59848/325712/8.0/1.6	1.9622098E-6	0.079	881.8
1389/703	4137/20883/20	1.5090167E-7	44389/325712/8.0/1.6	1.4553624E-6	0.104	1323.0
1996/701	4410/20883/20	1.6040201E-7	33270/325712/8.0/1.6	1.0908086E-6	0.147	1929.0
3513/705	9623/20883/20	3.7078195E-7	45439/325712/8.0/1.6	1.4897881E-6	0.249	3446.0
4195/705	10922/20883/20	4.1905027E-7	45932/325712/8.0/1.6	1.5059518E-6	0.278	4128.0
5498/710	12433/20883/20	4.8040676E-7	51470/325712/8.0/1.6	1.6875237E-6	0.285	5432.0
6022/710	9258/20883/20	3.5772587E-7	35802/325712/8.0/1.6	1.1738240E-6	0.305	5956.0
8158/705	6827/20883/20	3.2178255E-7	19158/325712/8.0/1.6	5.1984274E-7	0.619	8091.0
10832/698	12251/16207/20	4.6537363E-7	41917/40633/8.0/1.6	7.8969819E-7	0.724	10765
12692/697	4463/16207/20	2.0797117E-7	6485/5892/1.9/1.6	208197791E-7	0.738	12626

vapour phase

P/Patm kPa/mm Hg	Area/Area/Vol CO_2 /Std./(µl)	Mole CO_2	Area/Area/Vol N_2 /Std./(µl)	Mole N_2	Mole fraction CO_2
207/700	122533/110381/700	4.2099107E-6	510748/513652/500	1.8854796E-5	0.1825
250/700	221431/110381/700	7.2700076E-6	260601/231019/200	9.6203581E-6	0.0430
330/699	300409/394089/400	1.1547072E-5	150282/231019/200	5.5398916E-6	0.6758
369/699	392628/394089/400	1.5091770E-5	156586/231019/200	5.7722778E-6	0.7233
418/699	417081/394089/400	1.6316910E-5	12940/231019/200	4.6794282E-6	0.7771

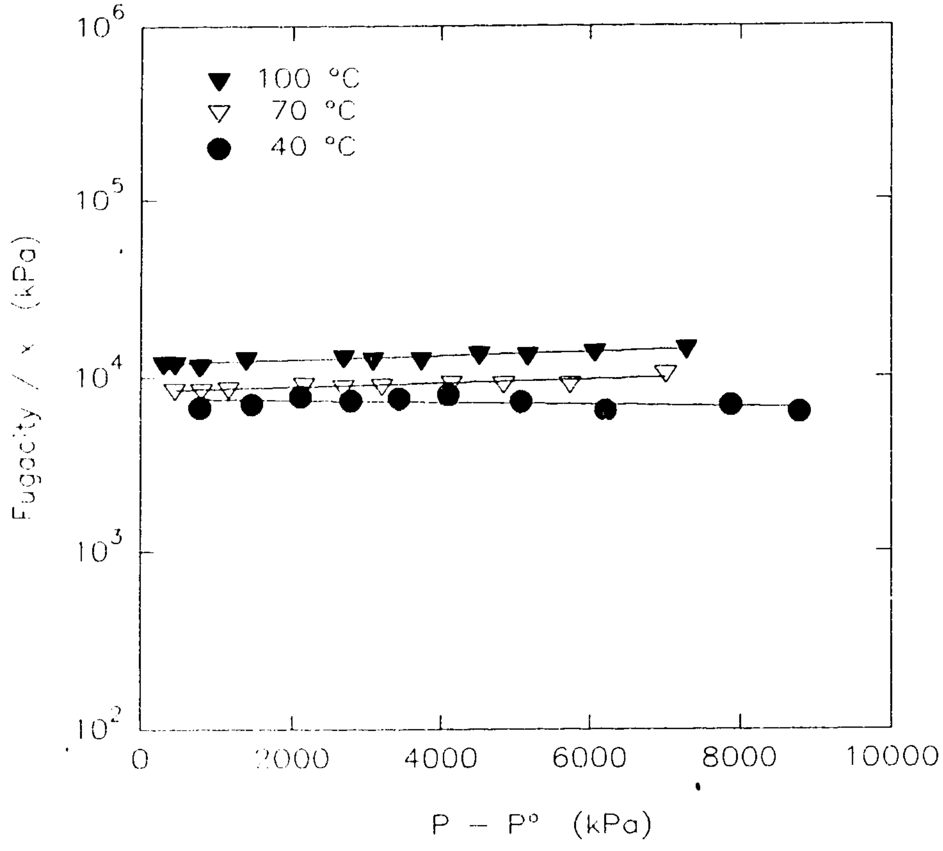

Figure 15. Fit of the fugacity of CO_2 in TEGMME to K–K equation