

2

**VOLUMETRIC PROPERTIES AND ABSORPTION OF
CARBON DIOXIDE IN AQUEOUS SOLUTIONS OF
PIPERAZINE AND ACTIVATED DIETHANOLAMINE.**

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I hereby declare that this thesis is based on the results found by me. Materials of work found by other researchers are mentioned by reference. This thesis is neither in whole or in part has been previously submitted for any degree.

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ABSTRACT

Removing acidic gases such as CO₂ is a very important process in many chemical industries today. One of the most widely methods used to remove the acidic gases is absorption using aqueous alkanolamine solutions. There are many types of alkanolamine-based solvents used in the industrial gas treating process. Among the amine solvents that have recently received great deal of attention are activated amines where piperazine has been used as the activator.

This work studied the volumetric properties of the aqueous solution of piperazine (PZ) and activated DEA in order to understand the interactions between its constituent molecules, which reflect the amine solvent behavior. Densities of aqueous piperazine, DEA + H₂O, DEA + PZ mixtures and activated DEA solutions were measured at temperature varying from 30 to 80 °C and the concentration of piperazine varies from 0.01 M to 1 M. The density behavior of piperazine-water mixture is different from DEA-Piperazine-water system, where the densities of the aqueous binary mixture of piperazine increase with an increase of piperazine composition but decrease in the aqueous ternary mixture of DEA-Piperazine-water system. Two distinct zones with separation line at mole fraction of piperazine equal to 0.0025 in the total amine concentration of 4M was observed in the ternary system. A Redlich-Kister correlation was used to represent the excess molar volumes of the binary and ternary systems.

In the CO₂ absorption study, solubility of CO₂ into aqueous solutions of piperazine and activated DEA has been measured systematically using a stirred cell reactor at

temperatures ranging from 20 to 50 °C with CO₂ partial pressures varying from 0.4 kPa to 96 kPa. The concentration of piperazine used ranged from 0.1 to 1 M. Generally the aqueous solutions of piperazine and activated DEA exhibited the same solubility curve trend as other amine solutions. Increasing the CO₂ partial pressure increased the gas loading; however, increasing either the temperature or piperazine concentration decreased the CO₂ loading. Compared with other amine mixtures, activated DEA was found to be a potential solvent for CO₂ removal. A mathematical model based on Kent-Eisenberg approach was applied to represent the vapor-liquid equilibrium of CO₂-piperazine-H₂O system. A good agreement between the model representation and the experimental values were achieved except in the region of high CO₂ partial pressure and low piperazine concentration which may be due to the dominant role of physical absorption. When applied to activated DEA system, the model gives reasonable predictions with the experimental data.

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TABLE OF CONTENT

Abstract	i
Acknowledgements	iii
List of Figures	viii
List of Tables	xii
List of Appendices	xiii
Nomenclature	xiv
CHAPTER 1	
INTRODUCTION	
1.1 Generalities	1
1.2 Aim and scope of work	4
1.3 Structure of thesis	6
CHAPTER 2	
LITERATURE REVIEW	
2.1 Historical background on amine gas treating	8
2.1.1 Structures and properties of alkanolamines	10
2.2 Theoretical background	
2.2.1 Development on density correlation	16
2.2.2 Chemical equilibrium	18
2.2.3 Equilibrium constant	19
2.2.4 The relationship of temperature with equilibrium constant	21
2.2.5 Characteristics of electrolyte solutions	27
2.2.6 Phase equilibrium	35

2.2.7	Equilibrium associate with CO ₂ -activated alkanolamine –water system	37
2.3	Reaction mechanism	
2.3.1	Reaction of CO ₂ with water	38
2.3.2	Reaction of CO ₂ with aqueous primary and secondary alkanolamine	40
2.3.3	Reaction of CO ₂ with aqueous piperazine	42
2.3.4	Modeling of VLE data in H ₂ O-CO ₂ -alkanolamine system	43
2.4	Method used to determine the solubility of CO ₂ in aqueous alkanolamine	49
2.5	A literature review on previous work	
2.5.1	Density	54
2.5.2	Solubility of CO ₂ in alkanolamine	56
2.6	Conclusion	64
CHAPTER 3		
EXPERIMENTAL METHODS AND TECHNIQUES		
3.1	Material	65
3.2	Solutions preparation	66
3.3	Methods and procedures	
3.3.1	Density measurement of aqueous piperazine, DEA-H ₂ O, DEA-PZ and activated DEA	66
3.3.2	Solubility of carbon dioxide into aqueous piperazine and activated DEA	
3.3.2.1	Experimental apparatus	67
3.3.2.2	Experimental procedure	69
3.3.2.3	Determination of amine concentration	70

3.3.2.4	CO ₂ loading analysis	73
3.3.2.5	Carbamate concentration	74
CHAPTER 4		
RESULTS AND DISCUSSION		
4.1 Volumetric Properties		
4.1.1	Density	78
4.1.1.1	Density of binary system	79
4.1.1.2	Density of tertiary system	84
4.1.2	Excess molar volume	87
4.1.2.1	PZ-H ₂ O system	87
4.1.2.2	DEA-H ₂ O system	90
4.1.2.3	DEA-PZ system	90
4.1.2.4	DEA-PZ- H ₂ O system	93
4.1.3	Comparison of volumetric properties in various amines studied	97
4.1.4	Density correlation	101
4.2 Solubility studies		
4.2.1	Solubility of CO ₂ in aqueous piperazine solution	108
4.2.1.1	Effect of partial pressure and concentration	108
4.2.1.2	Effect of temperature	114
4.2.1.3	Comparison with published data	114
4.2.2	Solubility of CO ₂ in aqueous activated DEA solutions	120
4.2.2.1	Effect of piperazine composition in activated DEA	120
4.2.2.2	Effect of partial pressure and temperature	121

4.2.2.3	Comparison between activated DEA and it single amine	126
4.2.2.4	Comparison between activated DEA and other amine mixtures	129
CHAPTER 5		
SOLUBILITY AND SPECIATION MODELING		
5.1	Modeling for the CO ₂ -PZ-H ₂ O system	132
5.2	Solubility model development	133
5.3	Results and discussion	139
5.4	Speciation in CO ₂ -PZ-H ₂ O system	
5.4.1	Speciation model assumptions	146
5.4.2	Species profile	147
5.4.3	Validation of speciation model	148
5.5	Applying the Kent and Eisenberg model to CO ₂ -PZ- DEA-H ₂ O system	155
CHAPTER 6		
CONCLUSIONS AND RECOMMENDATIONS		
6.1	Conclusions	158
6.2	Recommendations	160
REFERENCES		162
APPENDICES		176

LIST OF FIGURES.

Figure 2.1	Basic flow diagram of alkanolamine acid-gas removal process.	9
Figure 2.2	Molecular structures for different types of alkanolamine.	11
Figure 2.3	Absorption conditions of CO ₂ in vapor and liquid phase of activated DEA system.	38
Figure 2.4	Molecular structures of piperazine species.	43
Figure 2.5	Solubility apparatus used by Al-Ghawas et al.	51
Figure 3.1	The schematic diagram of the equipment.	68
Figure 3.2	The variation of pH as the function of time during the CO ₂ absorption process.	71
Figure 3.3	Typical titration curve of carbonated amine with 1 M HCl solution added to determine final amine concentration.	72
Figure 3.4	Typical titration curve of the sample with 1 M HCl solution added to determine the CO ₂ loading.	76
Figure 3.5	Typical titration curve of carbonated amine with 1 M NaOH added to determine the total carbamate.	77
Figure 4.1	Densities of aqueous piperazine solutions at different temperatures.	81
Figure 4.2	Densities of aqueous DEA solutions at different temperatures.	82
Figure 4.3	Densities of aqueous DEA + PZ mixtures at different temperatures.	83
Figure 4.4	Densities of 2 M mixture of PZ + DEA + H ₂ O solutions at different temperatures.	85
Figure 4.5	Densities of 4 M mixture of PZ + DEA + H ₂ O solutions at different temperatures.	86
Figure 4.6	Excess molar volumes of aqueous piperazine solutions at different temperatures.	89
Figure 4.7	Excess molar volumes of aqueous DEA solutions at different temperatures.	91

Figure 4.8	Excess molar volumes of DEA + PZ mixtures solutions at different temperatures.	92
Figure 4.9	Excess molar volumes of 2 M of PZ + DEA + H ₂ O mixtures solutions at different temperatures.	95
Figure 4.10	Excess molar volumes of 4 M of PZ + DEA + H ₂ O mixtures solutions at different temperatures.	96
Figure 4.11	Comparison of densities in various systems studied at 40 °C.	99
Figure 4.12	Comparison of excess molar volumes in various systems studied at 40 °C.	100
Figure 4.13	Comparison between experimental and calculated density values in aqueous piperazine solutions.	104
Figure 4.14	Comparison between experimental and calculated density values in aqueous DEA solutions.	105
Figure 4.15	Comparison between experimental and calculated density values in DEA + PZ mixtures.	106
Figure 4.16	Comparison between experimental and calculated density values in aqueous activated DEA solutions.	107
Figure 4.17	Solubility of CO ₂ into aqueous piperazine solutions at 20 °C.	110
Figure 4.18	Solubility of CO ₂ into aqueous piperazine solutions at 30 °C.	111
Figure 4.19	Solubility of CO ₂ into aqueous piperazine solutions at 40 °C.	112
Figure 4.20	Solubility of CO ₂ into aqueous piperazine solutions at 50 °C.	113
Figure 4.21	Solubility of CO ₂ into 1 M of aqueous piperazine solutions at various temperatures.	116
Figure 4.22	Solubility of CO ₂ into 0.6 M of aqueous piperazine solutions at various temperatures.	117
Figure 4.23	Comparison of the CO ₂ solubility in 0.6 M aqueous piperazine at 40 °C of the present work with that of Bishnoi and Rochelle (2000).	118
Figure 4.24	Solubility of CO ₂ in different types of amine solutions at 30 °C with total amine concentration of 2 M.	119

Figure 4.25 Solubility of CO ₂ in different types of amine solutions at 30 °C with different composition of piperazine in total amine concentration of 2 M.	122
Figure 4.26 Solubility of CO ₂ in different types of amine solutions at 30 °C with different composition of piperazine in total amine concentration of 4 M.	123
Figure 4.27 Solubility of CO ₂ into 0.2 M DEA + 0.9 M PZ aqueous solution at different temperatures.	124
Figure 4.28 Solubility of CO ₂ into 3.98 M DEA + 0.01 M PZ aqueous solution at different temperatures.	125
Figure 4.29 Solubility of CO ₂ in aqueous single amine and its mixtures at 40 °C with total amine concentration of 2 M.	128
Figure 4.30 Solubility of CO ₂ in various types of amine mixtures at 30 °C with total amine concentration of 2 M.	130
Figure 4.31 Solubility of CO ₂ in various types of amine mixtures at 30 °C with total amine concentration of 4 M.	131
Figure 5.1 Block diagram for the process of fitting the adjusted K's values of the piperazine carbamates.	138
Figure 5.2 The total CO ₂ loading calculated from the model and the experimental loading at 20 °C.	142
Figure 5.3 The total CO ₂ loading calculated from the model and the experimental loading at 30 °C.	143
Figure 5.4 The total CO ₂ loading calculated from the model and the experimental loading at 40 °C.	144
Figure 5.5 The total CO ₂ loading calculated from the model and the experimental loading at 50 °C.	145
Figure 5.6 Species concentration profile in 1 M of aqueous piperazine solution at 50 °C.	150
Figure 5.7 Species concentration profile in 0.6 M of aqueous piperazine solution at 50 °C.	151
Figure 5.8 Species concentration profile in 0.4 M of aqueous piperazine solution at 50 °C.	152

Figure 5.9 Species concentration profile in 0.2 M of aqueous piperazine solution at 50 °C.	153
Figure 5.10 Species concentration profile in 0.1 M of aqueous piperazine solution at 50 °C.	154
Figure 5.11 Comparison between the experimental and model CO ₂ loading values at amine concentration of 0.2 M DEA + 0.9 M PZ.	157

LIST OF TABLES.

Table 2.1	Experimental work on solubility of CO ₂ in aqueous DEA solutions.	57
Table 2.2	Experimental work on solubility of CO ₂ in aqueous MDEA solutions.	58
Table 2.3	Experimental work on solubility of CO ₂ in blended amines solutions.	60
Table 2.4	Experimental work on solubility of CO ₂ in aqueous activated amine solutions.	62
Table 4.1	Comparison of densities of aqueous DEA solutions measured with literature values.	79
Table 4.2	The binary interaction parameters using the Redlich-Kister equation of excess volume.	101
Table 4.3	Pure fluid parameters for the density equation.	102
Table 4.4	The density of pure fluid at various temperatures.	103
Table 5.1	Expression used for modeling.	137
Table 5.2	The coefficient of equilibrium constant for the piperazine carbamates.	139
Table 5.3	Comparison of piperazine carbamates equilibrium constant with literature values.	140
Table 5.4	Deviation between experimental and calculated total piperazine values.	149

LIST OF APPENDICES

A.	Density measurement and excess molar volumes of aqueous piperazine, DEA, DEA + PZ and activated DEA solutions.	176
B.	Correlation for the pure piperazine.	185
C.	Comparison between measured experimental density and calculated values.	187
D.	Solubility of carbon dioxide into aqueous piperazine solutions.	198
E.	Solubility of carbon dioxide into activated DEA solutions.	207
F.	Modeling program using MATLAB software for CO ₂ -PZ-H ₂ O system.	214
G.	Comparison between experimental and predicted carbon dioxide loading in aqueous piperazine solutions.	220
H.	Example of species calculations which is neglected in the model.	224
I.	Species concentrations profile in aqueous piperazine solutions.	226
J.	Comparison between the experimental and model total piperazine values.	233
K.	Modeling program using POLYMATH software for CO ₂ -PZ-DEA-H ₂ O system.	240
L.	Comparison between experimental and predicted carbon dioxide loading in CO ₂ -activated DEA system.	246

NOMENCLATURE.

PZ = Piperazine

PZH⁺ = Protonated piperazine

PZCOO⁻ = piperazine carbamate

H⁺PZCOO⁻ = Protonated piperazine carbamate

⁻OOC PZCOO⁻ = Piperazine dicarbamate

HCO₃⁻ = bicarbonate

DEA = Diethanolamine

MEA = Monoethanolamine

AMP = 2 amino-2methyl-1propanol amine

MDEA = Methyldiethanolamine

VLE = Vapor-liquid equilibrium

NRTL = Non-random two-liquid

NMR = Magnetic resonance

V^E = Excess molar volume

A_i = pair parameter

x_i = mole fraction of pure component

V_m = molar volume of liquid mixture

V_i^o = molar volume of pure fluid at the temperature of the system.

M_i = molar mass of pure component i

ρ = density

μ_i = chemical potential of species I

l, v = liquid and vapor phase respectively

B_i = chemical species

ν_i = stoichiometric coefficient

M = total reactions

N = total species

ΔG = change in free Gibbs energy

γ_i = activity coefficient of the species i .

m_i = molarity of the species i .

R = ideal gas constant

T = temperature

H_i° = standard enthalpy of species I

K = equilibrium constant

S = entropy

C_p = heat capacity

f = fugacity

$[i]$ = ion concentration

Z_i = charge of ion i

β = interaction parameter for the aqueous solutions

a = constant related to average hydrated radius ions

H_i = Henry's Law Constant