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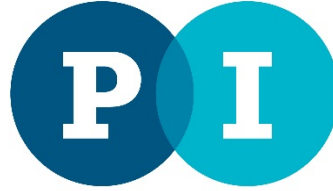
**Solubility of Hexane/Heptane in  
Methyldiethanolamine (MDEA) aqueous  
solution**

**Thesis Code No.: PICETS-15-07**

**By**

**Rana Jamal Danon**

**Submitted in partial fulfillment  
of the requirements for the Degree of  
MASTER OF SCIENCE IN CHEMICAL ENGINEERING  
Nov, 2015**



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## **DECLARATION**

The substance of this thesis is original work of the author and due reference and acknowledgement has been made, whenever necessary, to the work of others cited in this thesis. No part of the thesis has been submitted or accepted for any degree at the Petroleum Institute or at any other institution worldwide and is not concurrently submitted or will be submitted in candidature for any other degree.

*Rana Jamal Danon*

18<sup>th</sup> .Nov, 2015

**SOLUBILITY OF HEXANE/HEPTANE IN METHYLDIETHANOLAMINE  
(MDEA) AQUEOUS SOLUTION**

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## إهداء

الحمدُ لله الذي بنعمته تتمّ الصالحات و الصلاة و السلام على رسول الله محمد صلى الله

عليه و سلم

إلى أممي الغالية و أبيي الحنون

إلى زوجي و رفيقي فادي

إلى أولادي الأحباء

إلى أخي الحبيب مُحمّد

إلى أخواتي الرائعات ميس و ندير

إليكم أهدي ثمرة جهدي و أتمنّ غالباً و قوفاً إلي جانبي و دعمكم المتواصل لي

سعياً نحو العلم و طلباً له

شكراً من القلب

لا حزنكم أحترتي

## **DEDICATION**

At first, all Praise should be to ALLAH and prayers, peace be upon prophet Mohammad, and then after, I would like to dedicate this work to my parents, my husband who have supported me throughout the post graduate course and loved me unconditionally.

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## Table of Contents

List of figures.....	3
List of tables.....	5
List of abbreviations .....	7
Nomenclature.....	8
Abstract.....	9
1. Introduction.....	10
1.1. Background .....	10
1.2. Motivation.....	11
1.3. Objectives.....	12
1.3.1. Specific Objectives .....	12
1.4. Thesis Outline .....	14
2. Literature Review .....	14
2.1. Solubility of several hydrocarbons in water at VLLE. ....	15
2.2. Solubility of water in alkanes.....	22
2.3. Solubility of hydrocarbons in amine aqueous solutions. ....	22
2.4. Solubility of hexane in amine aqueous solutions. ....	28
3. Methodology.....	29
3.1. Apparatus & Experimental work. ....	29
3.2. Comparison between analytical and commercial (industrial) grade of MDEA using Mass spectroscopic technique- Direct Sample Analysis.....	35
4. Results & discussion – Hexane/ Heptane solubility in aqueous MDEA at VLLE. ..	38
4.1. Experimental results- hexane .....	38
4.1.1. Repeatability and reproducibility study.....	40
4.2. Reliability test .....	44
4.3. Experimental results- heptane .....	46
4.3.1. Repeatability and reproducibility study.....	48
4.4. Comparison between hexane and heptane solubility in MDEA aqueous solutions	53
5. Modeling approach .....	55

5.1. Modeling approach using Henry's constant.....	56
5.1.1. Henry's correlations for water-hydrocarbon systems.....	65
5.1.2. Henry's correlations for aqueous amine – hydrocarbon systems .....	67
5.2. GCA-EoS solubility prediction of n-hexane & n-heptane in aqueous MDEA solutions.....	71
6. Conclusions and Conclusion Remarks .....	75
7. Future work.....	75
8. References.....	77
Appendix A.....	80
Appendix B.....	81
Appendix C.....	82

## List of figures

<b>Figure 2.1:</b> The solubility of methane in water [4] .....	15
<b>Figure 2.2:</b> The solubility of ethane in water [4] .....	16
<b>Figure 2.3:</b> The solubility of propane in water vs. Temperature [4].....	17
<b>Figure 2.4:</b> P-T diagram of n-decane/water, ref [15].....	18
<b>Figure 2.5:</b> Solubility of C <sub>5</sub> -C <sub>9</sub> normal alkanes in water from 273 to 413 K .....	19
<b>Figure 2.6:</b> Solubility in mole fraction of hexane in water vs. temperature , — [18] , ---- [17] ..	21
<b>Figure 2.7:</b> Solubility in mole fraction of heptane in water vs. temperature, — [18] , ---- [17] ..	21
<b>Figure 2.8:</b> Solubility of methane in 50 wt% MDEA solution [4] .....	23
<b>Figure 2.9:</b> Solubility of ethane in a 50 wt% solution of MDEA [4] .....	23
<b>Figure 2.10:</b> Solubility of Propane in a 50 wt% solution of MDEA [4].....	24
<b>Figure 2.11:</b> Flow diagram of the equilibrium cell with pneumatic samplers for online gas chromatograph analysis [23].....	26
<b>Figure 2.12:</b> Example of thermodynamic diagram in conditions close to described, [24] .....	27
<b>Figure 3.1:</b> Equilibrium cells used for the experiments.....	30
<b>Figure 3.2:</b> Schematic diagram for the simple equilibrium cell .....	30
<b>Figure 3.3:</b> Analytic circuit.....	32
<b>Figure 3.4:</b> Thermal programming of the oven .....	33
<b>Figure 3.5:</b> Hexane area detector response vs. conc. ....	34
<b>Figure 3.6:</b> Heptane area detector response vs. conc.....	35
<b>Figure 3.7:</b> Mass spectrums of analytical and industrial MDEA.....	37
<b>Figure 4.1:</b> Solubility of hexane in 40, 45 & 50 wt % MDEA vs. temperature .....	39

<b>Figure 4.2:</b> Effect of amine weight percentage on solubility of hexane at constant temperatures	39
<b>Figure 4.3:</b> Repeatability of hexane solubility in 50 wt% MDEA .....	41
<b>Figure 4.4:</b> Effect of temperature in hexane activity coefficient at different MDEA wt % .....	42
<b>Figure 4.5:</b> Hexane activity coefficient natural log vs. temperature inverse .....	44
<b>Figure 4.6:</b> This work new data with data from ref [1] for the solubility of hexane in 50 wt % ...	45
<b>Figure 4.7:</b> Results of solubility of heptane in 40, 45 & 50 wt % MDEA vs. temperature.....	47
<b>Figure 4.8:</b> Salting -in effect at constant Temperatures.....	47
<b>Figure 4.9:</b> Repeatability of heptane solubility data points in 40 & 50 wt %.....	49
<b>Figure 4.10:</b> Heptane activity coefficient isopleths as a function of temperature .....	51
<b>Figure 4.11:</b> Heptane activity coefficient natural log vs. temperature inverse .....	52
<b>Figure 4.12:</b> Heptane/ Hexane solubility in 50 wt% aqueous MDEA.....	53
<b>Figure 4.13:</b> Solubility data of hexane/heptane in 40, 45 & 50 wt% aqueous MDEA solutions ..	54
<b>Figure 5.1:</b> Hexane-50 wt % VLLE total pressure .....	58
<b>Figure 5.2:</b> Calculated and fitted hexane Henry's constant as a function of temperature .....	66
<b>Figure 5.3:</b> Calculated and fitted heptane Henry's constant as a function of temperature .....	66
<b>Figure 5.4:</b> Natural logarithm of hexane salting-in ratio as a function of MDEA wt% .....	69
<b>Figure 5.5:</b> Natural logarithm of heptane salting-in ratio as a function of MDEA wt% .....	69
<b>Figure 5.6:</b> Hexane $k_i$ coefficient as a function of temperature.....	70
<b>Figure 5.7 :</b> Hexane $k_i$ coefficient as a function of temperature.....	70
<b>Figure 5.8:</b> GCA-EoS model prediction of hexane mole fraction in aqueous MDEA solutions...	74
<b>Figure 5.9:</b> GCA-EoS prediction of heptane mole fraction in aqueous MDEA solutions .....	74

## List of tables

<b>Table 1.1:</b> Specific data needed for the system.....	13
<b>Table 2.1:</b> n-Hexane-water VLLE system solubility data, ref [13] .....	18
<b>Table 2.2:</b> Values parameters of Tsonopoulos equation for n-alkanes C5 to C7, [17].....	20
<b>Table 2.3:</b> Solubility of n-hexane in the 25 wt % MDEA aqueous solution [1].....	28
<b>Table 2.4:</b> Solubility of n-hexane in 50 wt% MDEA aqueous solution [1].....	28
<b>Table 3.1:</b> Material origin and purity.....	31
<b>Table 3.2:</b> Actual prepared concentrations of aqueous amine solutions used for hexane measurements.....	31
<b>Table 3.3:</b> Actual prepared concentrations of aqueous amine solutions used for hexane measurements.....	32
<b>Table 3.4:</b> Thermal programming of the oven.....	33
<b>Table 4.1:</b> Solubility of hexane at different temperatures and amine concentrations .....	38
<b>Table 4.2:</b> Repeatability of the samples in hexane/ MDEA aqueous solutions .....	40
<b>Table 4.3:</b> Hexane- 50 wt% MDEA reproducibility check.....	41
<b>Table 4.4:</b> Activity coefficient of hexane in aqueous phase using the measured solubilities.....	42
<b>Table 4.5:</b> Parameters of the fitting equation.....	43
<b>Table 4.6:</b> Solubility of heptane at different temperatures and amine concentrations.....	46
<b>Table 4.7:</b> Repeatability of the samples in heptane/ MDEA aqueous solutions .....	48
<b>Table 4.8:</b> Heptane- 50 wt% MDEA reproducibility check .....	49
<b>Table 4.9:</b> Activity coefficient of heptane in aqueous phase using the measured solubilities.....	50
<b>Table 4.10:</b> Parameters of the fitting equation.....	51

<b>Table 5.1:</b> Hexane- water VLLE Henry's constant calculation.....	61
<b>Table 5.2:</b> Wagner eq. parameters [32].....	62
<b>Table 5.3:</b> Calculated vapor pressures corresponding to pure n-hexane according to Wagner eq.	62
<b>Table 5.4:</b> Calculated vapor pressures corresponding to pure n-heptane according to Wagner eq. .....	63
<b>Table 5.5:</b> Calculated vapor pressures corresponding to pure water according to Wagner eq.....	64
<b>Table 5.6:</b> Characteristic properties of pure species under interest .....	64
<b>Table 5.7:</b> Heptane- water VLLE Henry's constant calculation .....	65
<b>Table 5.8:</b> Coefficients of Henry's constant correlation .....	65
<b>Table 5.9:</b> Mole fractions of hexane in pure water and in different aqueous amine solutions at VLLE. ....	67
<b>Table 5.10:</b> Salting-in ratio for hexane in aqueous MDEA over that of hexane in pure water .....	67
<b>Table 5.11:</b> Mole fractions of heptane in pure water and in different aqueous amine solutions VLLE. ....	68
<b>Table 5.12:</b> Salting-in ratio for heptane in aqueous MDEA over that of heptane in pure water ...	68
<b>Table 5.13:</b> GCA-EoS prediction of hexane mole fraction in various aqueous MDEA solutions	72
<b>Table 5.14:</b> GCA-EoS prediction of heptane mole fraction in various aqueous MDEA solutions	73

## List of abbreviations

BTEX	Benzene, Toluene, Ethylbenzene & Xylene
MDEA	Methyldiethanolamine
VLLLE	Vapor/ Liquid/ Liquid equilibrium
FID	Flame Ionization Detector
TCD	Thermal Conductivity Detector
DEA	Diethanolamine
APCI	Atmospheric Pressure Chemical Ionization
DSA	Direct Sample Analysis
TOF	Time Of Flight
GT	Gravimetric determination



## Nomenclature

$T_o$	Arbitrary reference temperature
$\delta x$	Repeatability of sequential analyses
$x_i$	Component i mole fraction
$x_a$	Molarity of MDEA in the aqueous solution
$\varphi_i$	Fugacity coefficient
P	Total pressure of the system
$P_i^{sat}$	Saturation vapor pressure of component i
$P_w^0$	Vapor pressure of pure water at T (K)
$f_i$	fugacity
$f_i^0$	Fugacity of component I at some arbitrary condition
$\bar{\rho}$	Density of solution
$H_{iw}$	Henry's constant for the hydrocarbon species in water
$H_{ia}$	Henry's constant for the hydrocarbon species in amine
$\sigma_x$	Standard deviation of the x values
$H_i^E$	The partial molar excess enthalpy of component I
$v_w^0(T)$	Molar volume of pure water at T (K)
$v_w^0(298 K)$	Molar volume of pure water at 298 (K)
u(x)	Uncertainty of measured x
$\varphi_i^{sat}$	The fugacity coefficient of pure i at its vapor/liquid saturation pressure
RD	Relative deviation

## Abstract

Aqueous solutions of alkanolamines are commonly used in natural gas industry to absorb acid gases ( $\text{CO}_2$  and  $\text{H}_2\text{S}$ ) from natural gas and hydrocarbon liquids. The dissolved hydrocarbons in the alkanolamines are considered as lost product and must be minimized. Even though light hydrocarbons have higher solubility in the alkanolamines than heavy hydrocarbons; the heavy hydrocarbons contribute to the foaming problem which could significantly increase the hydrocarbons losses and decrease the absorption process efficiency. Thus, the solubility information for heavy hydrocarbon is of high importance not just to determine the magnitude of hydrocarbons losses but also for their influence on alkanolamines foaming. This thesis presents new experimental solubility data of hexane and heptane in aqueous amine solutions. Simple equilibrium cells were used to measure the solubility of hydrocarbons in aqueous amine systems in the range: 298–328 K. Analyses of aqueous liquid samples were performed using a gas chromatograph. It has been observed that hexane and heptane solubility in MDEA solutions increased with increasing temperature. Also, increasing amine concentration in the test solution increased the solubility of hexane and heptane. Simple models were developed in order to represent the activity coefficient of hexane and heptane in the aqueous MDEA solution in the range of 40 – 50 wt % MDEA. The Henry's law- based model allowed for a more direct comparison between the solubilities in pure water and in the aqueous solution of MDEA.

## 1. Introduction

### 1.1. Background

Methyldiethanolamine and alkanolamine solutions in general are used in gas sweetening process to strip acid gases, specifically carbon dioxide and hydrogen sulfide. As they are characterized by their high selectivity to absorb these acid gases [1], [2]. The acid gases are considered as corrosive agents; the existence of acid gases with liquid water in the process vessels and pipes threatens their structures from corrosion. The acid gases should be removed and kept below the design specification of 4-20 ppm H<sub>2</sub>S and <3% CO<sub>2</sub> [3].

One of the advantages of using alkanolamines solutions is that they dissolve selectively more acid gases than hydrocarbons. However, hydrocarbons have low solubility in alkanolamines solutions. This low solubility represents lost product in natural gas treating solvents. This work was undertaken to measure the solubility of n-alkanes C<sub>6</sub> and C<sub>7</sub> individually in 40, 45 and 50 wt% aqueous MDEA solutions at VLL equilibrium at temperature range of 298 K to 328 K.

Several hydrocarbons, i.e, lighter alkanes and BTEX were investigated in literature to compare between their solubility in aqueous MDEA or any alkanolamine on a hand and in pure water on the other hand. They had shown higher solubility but similar behavior to that in pure water [4].

## 1.2. Motivation

The accurate knowledge of the solubility of hydrocarbons in aqueous amine solutions is very important to determine the magnitude of hydrocarbons losses during the treating process. Indeed, hydrocarbons losses are more significant for light hydrocarbon i.e. C1 (methane), C2 (ethane), C3 (propane) and C4 (butane) than heavy liquid hydrocarbon i.e. C5 (pentane) C6 (hexane) and C7 (heptane). Most of the available data in literature is focused on light hydrocarbon solubility [2-5]. However, the solubility information for heavy hydrocarbon is of high importance not just to determine the magnitude of hydrocarbons losses but also for their influence on alkanolamines foaming.

Several works had been done in literature for various types of hydrocarbons to measure their solubility in pure water and in amine solutions to estimate the equilibrium losses and to be able to analyze process-operating problems that would result in excess losses. In addition, the presence of the hydrocarbon in the acid gas may cause problems elsewhere in the process [4, 5]. For example, hydrocarbons may cause fouling of the catalyst in the Claus reactors.

Foaming during gas sweetening is one of the most serious operational problems. Foaming can be induced by various contaminants including liquid hydrocarbon [6], [7]. Indeed, foaming generally leads to serious consequences such as loss of absorption capacity, reduced mass transfer area and efficiency and carryover of amine solution to the downstream plant [8]. Foamed alkanolamines may carry large amounts of hydrocarbons which contribute to hydrocarbons losses, which is far in excess of what would be expected from solubility alone [5]. A foam problem is enhanced when the solution has sufficient liquid organic/ chemical contaminants capable to increase the solution viscosity and density and reduce the solution surface tension [6], [9] and [10]

and the impact of liquid hydrocarbon comes from its solubility in the aqueous amine solution, which therefore reduces its surface tension [9]. When the surface tension is low, the solution can create a very thin film that is elastic in nature and capable of encapsulating a gas bubble [11]. The outcome of this thesis will be helpful for the reliable, more controlled operating of the sweetening processes.

This study arises as a part of the ongoing project studying the deterioration of solvent quality and foaming problem in Habshan Gas Sweetening Unit (HGSU), GASCO, Abu Dhabi. In GASCO 40-50 wt% MDEA is used for acid gas removal. So far light n-paraffins and BTEX were investigated in literature. This work extended the paraffins to hexane and heptane in aqueous MDEA solutions and was undertaken to measure the solubility of hexane /heptane in MDEA amine solutions and to quantify the effect of MDEA composition and system temperature on the hydrocarbon solubility.

### **1.3. Objectives**

The main objective of this thesis is to collect data regarding solubility of n-alkanes,  $C_6$  and  $C_7$  in 40, 45 and 50 wt % MDEA aqueous solutions. The collected solubility data are used to develop simple model for hexane and heptane solubility in aqueous MDEA solutions.

#### **1.3.1. Specific Objectives**

The specific targets of this project were:

- Producing  $x(P,T)$  data for hexane and heptane in different aqueous MDEA solutions as detailed in table 1.1:

**Table 1.1:** Specific data needed for the system

In 40wt % MDEA solution	n	Temperature	Pressure	x(P,T)	In 45wt % MDEA solution	n	Temperature	Pressure	x(P,T)
		298 K					298 K		
		308 K					308 K		
		318 K					318 K		
		328 K					328 K		
In 50wt % MDEA solution	n	Temperature	Pressure	x(P,T)					
		298 K							
		308 K							
		318 K							
		328 K							

- Studying the effect of temperature and amine concentration on the solubility of hexane/heptane in the aqueous solution.
- Comparing between the solubility of hexane in MDEA solution to that of heptane at the same conditions of temperature and MDEA concentration.
- Finding a correlation or fitting for the experimental data based on Henry's constant.

## 1.4. Thesis Outline

Chapter 1 provides a brief background and the objectives of the thesis.

Chapter 2 deals with the detailed literature review on the solubility of n-hexane and n-heptane in pure water under VLL equilibrium and any available data about their solubility in MDEA aqueous solutions. The chapter also deals with lighter alkanes and aromatic hydrocarbons solubility in MDEA solutions and in pure water as well. Chapter 3 introduces the experimental work, included to that a comparison between commercial and analytical grade of MDEA.

Chapter 4 presents all the results and discussions for the solubility calculations for n-hexane and n-heptane solubility in the aqueous MDEA respectively.

Chapter 5 presents the modeling approach used for the covered range of temperature and system pressure. Chapter 6 provides a summary of all the conclusions and concluding remarks.

Chapter 7 presents the recommendations for the future studies.

## 2. Literature Review

Hydrocarbons are in contact with water in reservoirs and during production, transportation and processing operations. A precise estimation of water- hydrocarbon phase behavior was required to design and operate natural gas facilities, crude oil refineries and petrochemical plants.

Data concerning water-n-alkane mutual solubility are required for the design of a variety of chemical engineering separation more specifically absorption operations. They are most of the time performed at high temperatures and pressures.

Most of the literature studies done so far have focused on alkanes ranging from  $C_1$  to  $C_4$  which have shown a similar trend in solubility. Generally hydrocarbons are sparingly soluble in aqueous solvents and to a first approximation their solubility can be described by the traditional

Henry's Law. For pure water as the solvent, Henry's law linearly relates the mole fraction in water to gas-phase partial pressure. The presence of amines in the aqueous phase increases hydrocarbon solubility over that in water, an effect referred to as (salting-in effect)[12]. Commercial amine treating solutions can contain as much as 25 mol % amine, i.e; 40-50 wt% MDEA , so it is important to take account of salting-in effect.

### 2.1. Solubility of several hydrocarbons in water at VLLE.

Carrol et al., 1998 [4] had built charts for the solubility of methane, ethane and propane in water and in aqueous solutions of various industrially important alkanolamines from a combination of a thermodynamic model and experimental data. They showed that the solubility of methane, ethane and propane in water share many common characteristics.

For methane the solubility is quite insensitive to the temperature, although at low temperatures it decreases with increasing temperature, but it is significantly affected by pressure as can be seen from figure 2.1.

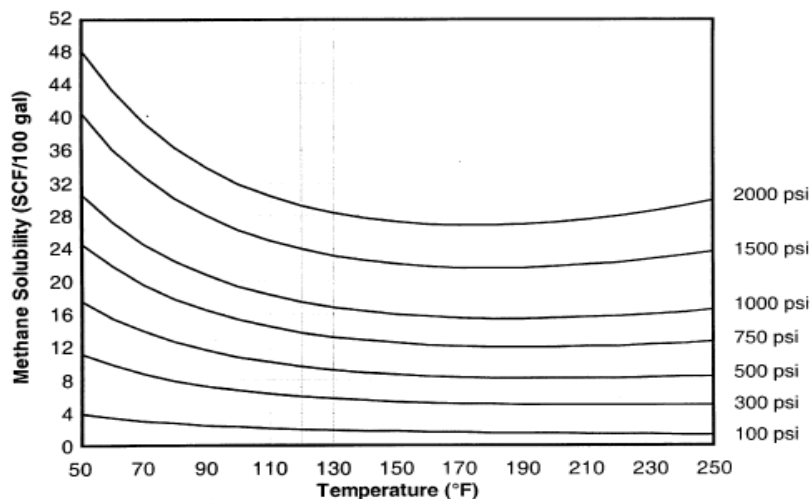
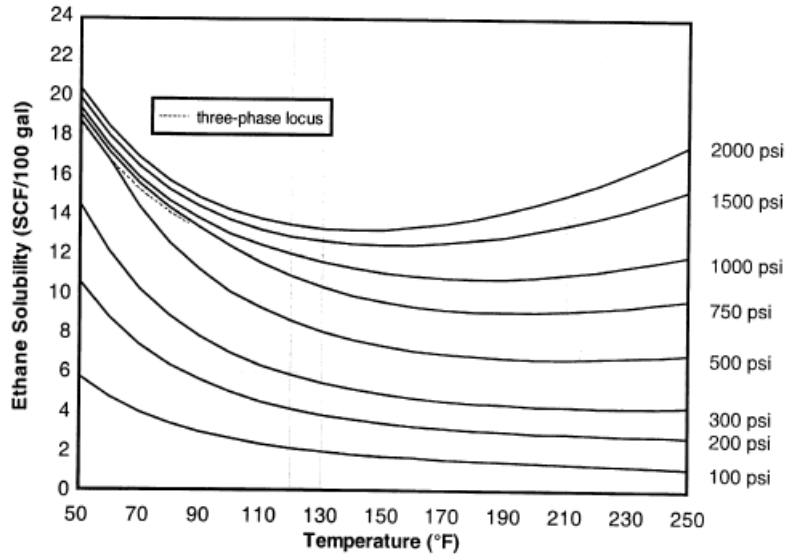


Figure 2.1: The solubility of methane in water [4]

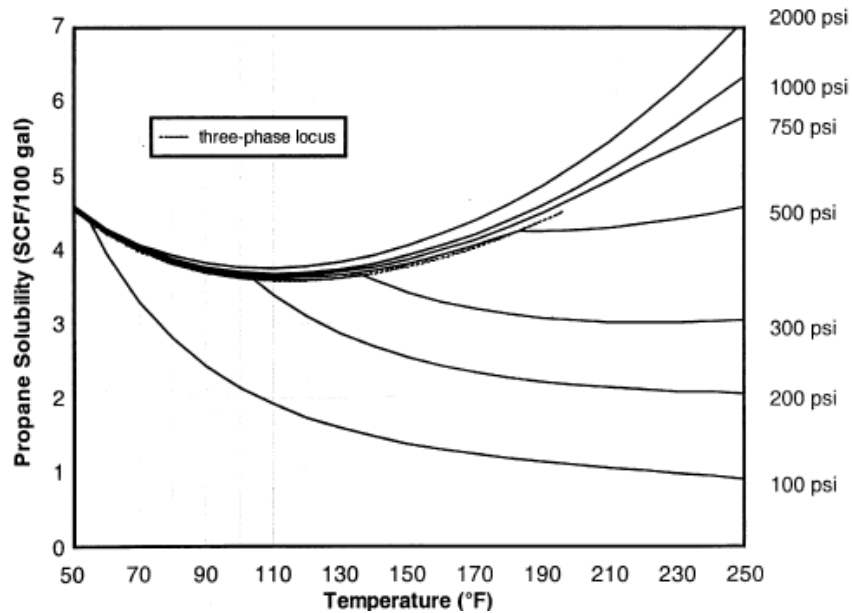


While, the solubility of ethane in water has a similar appearance to that for methane except for a small three phase (liquid- liquid-vapor) locus at low temperature, as can be seen from figure 2.2.



**Figure 2.2:** The solubility of ethane in water [4]

Even though the solubility of propane in water appears to be significantly different from the curves for either methane or ethane in water, it does share a few common characteristics. Figure 2.3 shows the solubility of propane in water at different temperatures.



**Figure 2.3:** The solubility of propane in water vs. Temperature [4]

Although the solubility of hydrocarbons in water has been extensively studied by several authors, very few studies are available concerning the solubility in the three phase region.

Salim Mokraoui et al., 2008. [1], [13] had reported solubility data in water for several hydrocarbons (ethane to hexane) as a function of temperature at VLLE conditions using a static-analytic method based apparatus, the minimum temperature of their experiments was 288 K, while the maximum temperature, for each system was lower than the critical temperature of the corresponding hydrocarbon. For ethane, propane and isobutene –water systems, the solubility was quite insensitive as the temperature and system vapor pressure increased, while it increased for n-butane, n-pentane and n-hexane- water systems. They had reported the solubility of n-hexane-water VLLE system as in table 2.1, also same results were obtained by [14] :

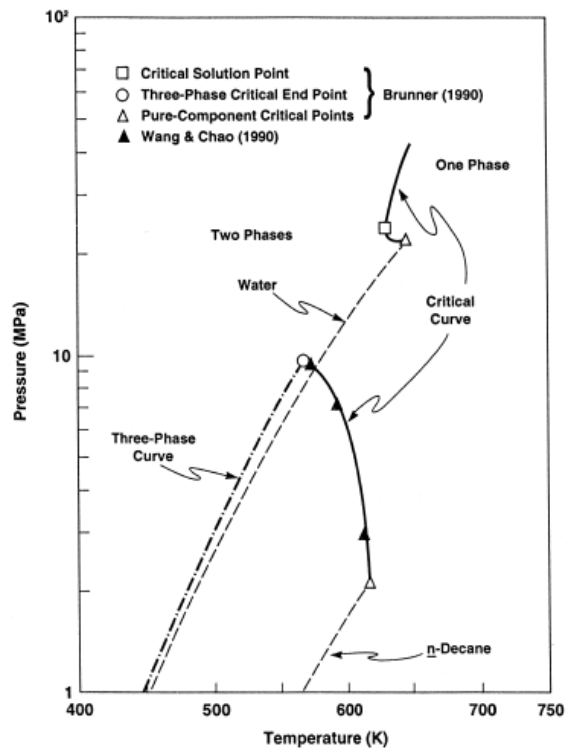
**Table 2.1:** n-Hexane-water VLLE system solubility data, ref [13]

T/K	$P_{exp}^a$ /MPa	$x_{exp} \times 10^6$	$x_{cal} \times 10^6$	rel. dev/ %	$\delta x^b \times 10^8$
298.09	0.4997	2.08	2.08	0.0	9
313.15	0.5028	2.33	2.33	0.0	6
333.15	0.5012	3.08	3.08	0.0	5
353.15	0.5028	4.58	4.58 <td 0.0	13	

<sup>a</sup> Total pressure adjusted with helium in order to allow convenient sampling.

<sup>b</sup> Repeatability of sequential analyses of the aqueous phase.

An example of the phase behavior of alkane/water binaries is given in figure 2.4 for n-decane/water [15].

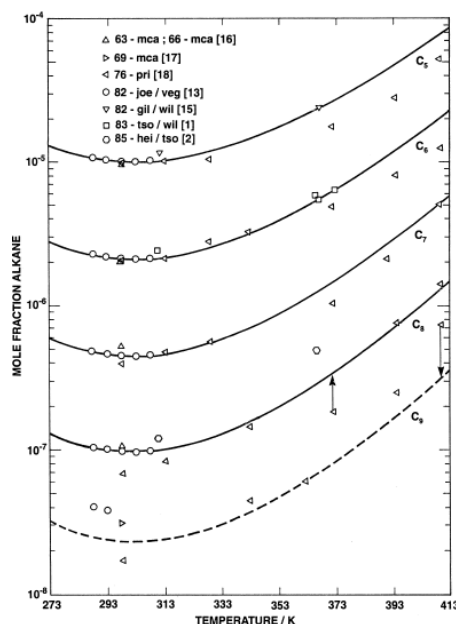


**Figure 2.4:** P-T diagram of n-decane/water, ref [15]

A point below the three phase equilibrium curve represents equilibrium between one liquid phase and the vapor, while a point above the line represents equilibrium between the hydrocarbon-rich and water- rich liquid phases.

All three phases are at equilibrium at  $P_3$ , which is the three phase equilibrium pressure. It was estimated for such systems that the mutual solubilities are only weakly pressure-dependent [15], [16].

Tsonopoulos [17], had investigated mutual solubility data for C5-C16 alkanes and water for temperature ranges close to 298 K, along with calorimetric heats of solution, as a function of the carbon number. He found that the solubility of alkanes in water at 298 K drops steeply with increasing CN (carbon number), but the rate of decrease becomes significantly smaller for CN >11. Both calorimetric and solubility data indicate a minimum in solubility (heat of solution =0) at around 303 K. see figure 2.5.



**Figure 2.5:** Solubility of C<sub>5</sub>-C<sub>9</sub> normal alkanes in water from 273 to 413 K

Correlations proposed by Tsonopoulos [17] were plotted which are expressed by:

$$\ln x = A + \frac{B}{T} + C \ln (T), T \text{ in K} \quad (2-1)$$

where  $x$  is the solubility of the hydrocarbon in water in mole fraction and  $A$ ,  $B$  &  $C$  parameters of these equations are reported for the temperature range 273 to 413 K, see table 2.2.

**Table 2.2:** Values parameters of Tsonopoulos equation for n-alkanes C5 to C7, [17]

Alkanes	A	B	C
Pentane	-333.59719	14537.472	47.97436
Hexane	-374.90804	16327.128	53.89582
Heptane	-396.93979	17232.298	56.95927

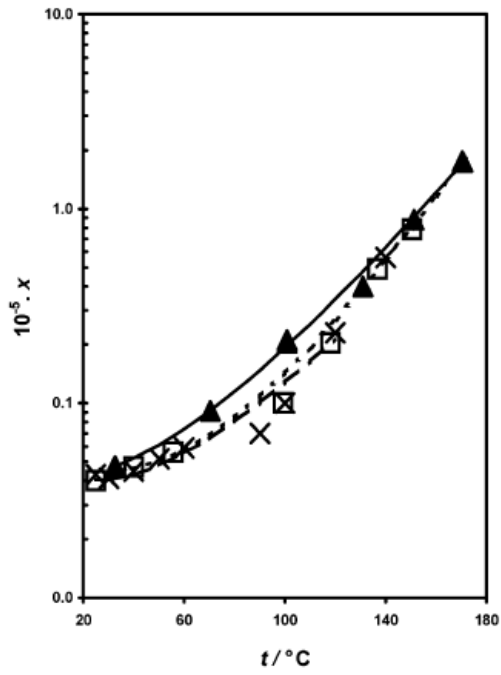
This correlation results from the relationship between solubility and heat of solution which is given by:

$$\left(\frac{\partial \ln x_i}{\partial T}\right) = \frac{H_i^E}{RT^2} \quad (2-2)$$

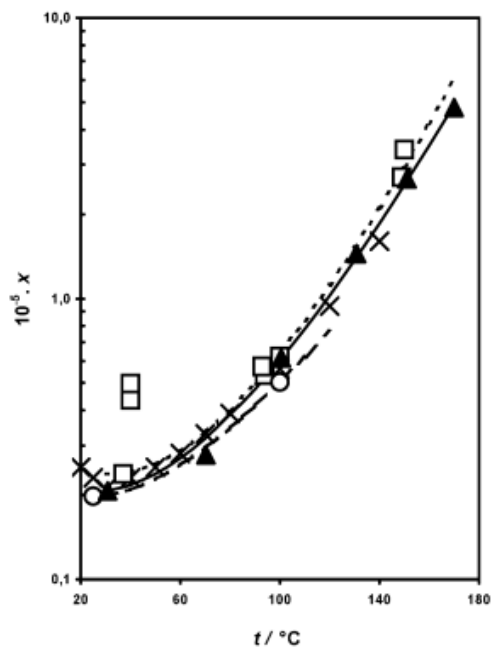
Where,  $H_i^E$  is the partial molar excess enthalpy of component  $i$ , expressed as a linear function of temperature, which after simple integration leads to Tsonopoulos equation.

The values of  $A$ ,  $B$  &  $C$  were obtained by fitting the experimental data using the least square method.

Celine Marche et al., 2003. [18] had determined the solubility of hexane and heptane in water at temperatures ranging from (30° to 180°C) and at the vapor pressure of the systems as can be seen from figures 2.6 & 2.7.



**Figure 2.6:** Solubility in mole fraction of hexane in water vs. temperature , — [18] , ---- [17]



**Figure 2.7:** Solubility in mole fraction of heptane in water vs. temperature, — [18] , ---- [17]

According to their work, detection of alkane trace low levels in water was possible by changing the sensitivity of the FID (flame ionization detector), since the hydrocarbon solubility in water is low.

However, increasing the sensitivity of the FID led to very poor reproducibility for the hexane chromatographic area because the detector signal was perturbed by water, so a modification of the sampling procedure was done by using the solid phase extraction method.

It was shown that solubilities of alkanes in water at 30 °C decrease with increasing carbon number. On the other hand, increasing temperature from 30 to 180 °C increases the solubility of hexane and heptane. i.e; increasing the temperature from (30 to 180) °C increases the solubilities by a factor of 23 for hexane.

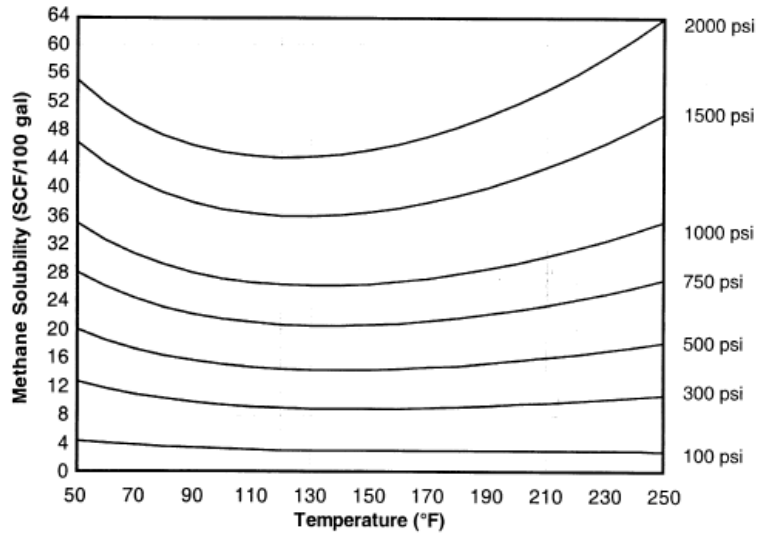
## **2.2. Solubility of water in alkanes.**

Tsonopoulos [17] has studied the solubility of water in alkanes and he concluded that among hydrocarbons, alkanes have the least affinity for water.

The solubility of water in alkanes at 298 K is fairly insensitive to carbon number, rising slightly with increasing carbon number while calorimetric measurements give a heat of solution that is nearly independent of temperature and carbon number.

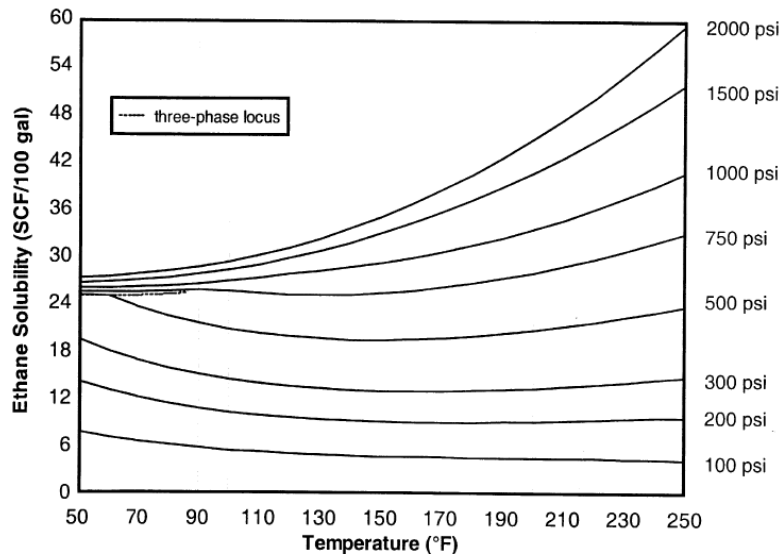
## **2.3. Solubility of hydrocarbons in amine aqueous solutions.**

Carroll et al., 1998. [4], [19] had compared between the solubility of methane, ethane and propane in 50 wt % MDEA to that in water. For example, the plot for the solubility of methane in MDEA solution looks very similar to that for pure water, see figures 2.1 and 2.8, it shows that the solubility increases with pressure and exhibits the characteristic minima. However, the presence of the amine changes the location of the minima.



**Figure 2.8:** Solubility of methane in 50 wt% MDEA solution [4]

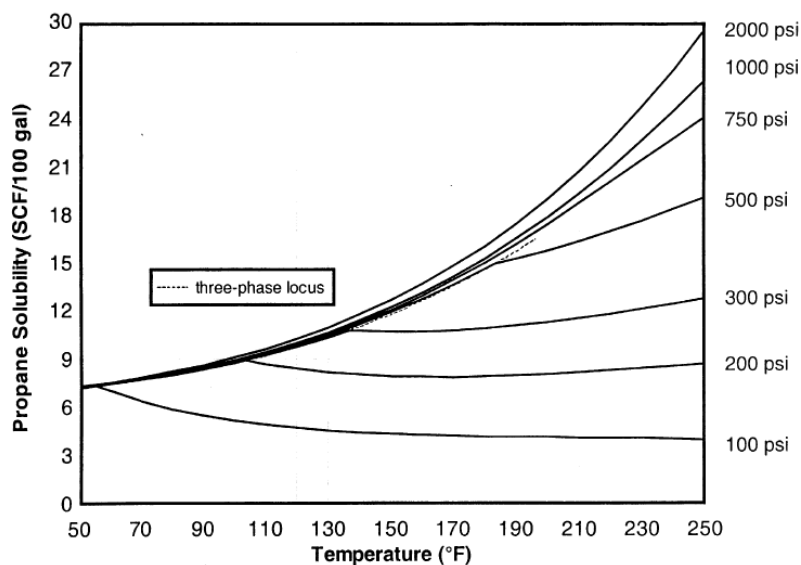
Interestingly, It was found that ethane solubility in MDEA solution is similar to that in pure water, it also includes a small three- phase locus at low temperature. See figures 2.2 & 2.9.



**Figure 2.9:** Solubility of ethane in a 50 wt% solution of MDEA [4]



Propane solubility in 50 wt% MDEA solution shows similar to that in water but is significantly larger, in addition, the solubility of liquid propane in the MDEA is quite insensitive to the pressure and it doesn't show the minima as it does in pure water see figures 2.3 & 2.10.



**Figure 2.10:** Solubility of Propane in a 50 wt% solution of MDEA [4].

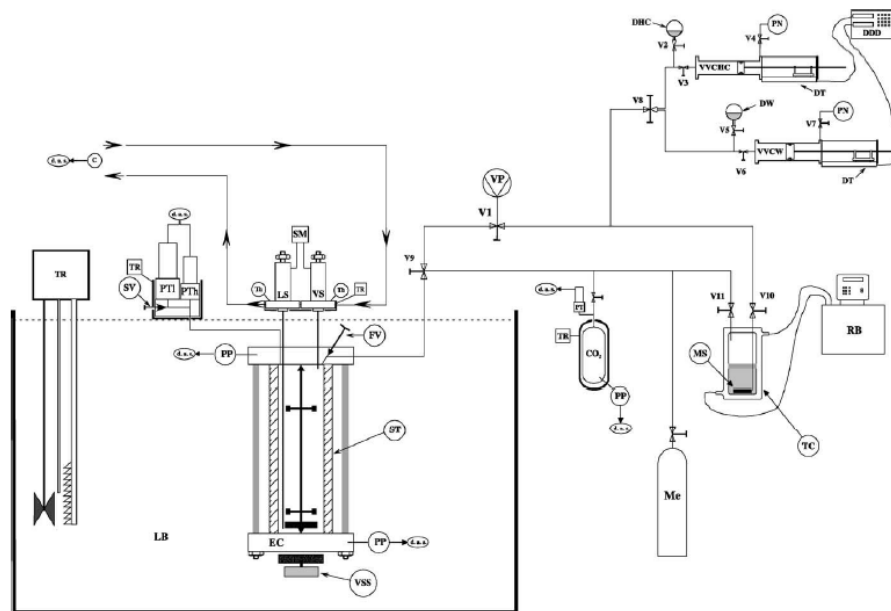
The solubility of each of ethane, propane, i- butane, n-butane, n-pentane and mixtures of them in 25 wt %, 50 wt% MDEA, 35 wt % DEA & 35 wt % MEA under VLLE , were investigated in [1], The used apparatus was the static-analytic equilibrium cell with pneumatic capillary auto samplers.

According to their work, increasing the temperature as well as the vapor pressure in each of 25 wt % MDEA and 35 wt % DEA decreased the solubility of Ethane under VLLE while the case was reversed in 50 wt % MDEA, the solubility increased and behaved similar to that in pure water, but was larger in the amine solution than water.

While the solubility of each of propane, butane, i-butane and pentane in the 25 and 50 wt % MDEA and in 35 wt % DEA was increasing with increasing the temperature as well as the total pressure which at some points differed from the system vapor pressure by adding helium, without which the sampling wouldn't be possible, specially that the solubility is a weak function of pressure up to 0.5 MPa.

Solubility of each of propane, propylene and n-butane in about 3-4 M MDEA and various alkanol amine solutions were also studied under VLE by Jou et al., 2002 [20], 2004 [21] & 1996 [22] .

For the solubility study of each of the BTEX compounds namely (benzene, toluene, ethylbenzene and xylene) in aqueous MDEA solution and in other amines Valtz et al., 2003-2008 [23], [24], [25] and [26] applied their experiments based on a static- analytic method with Rolsi pneumatic samplers for on line gas chromatograph analysis, see figure 2.11. The reliability of the measurements had been tested by measuring the solubility of each of the BTEX compounds in pure water and by comparing the results to literature data.



**Figure 2.11:** Flow diagram of the equilibrium cell with pneumatic samplers for online gas chromatograph analysis [23]

The analytic method was carried out by loading the evacuated cell with about 5 cm<sup>3</sup> of solvent (either distilled water or aqueous amine solution), followed by adding 2 cm<sup>3</sup> of hydrocarbon. In these conditions two liquid phases were present and at equilibrium, the total pressure was measured.

After that the total pressure was increased up to about 5 bar using methane and the solution was stirred vigorously for more than 1 hr to achieve phase equilibrium. Stirring was reduced for 1 hr and samples of aqueous phase were withdrawn and analyzed by gas chromatography. In the vapor phase samples, only the aromatics and methane were able to be detected (the concentrations of amine and water were considered to be negligible).

The solubility of aromatics was found to increase logarithmically with temperature in a manner similar to its behavior in water. However, the addition of an organic amine to water

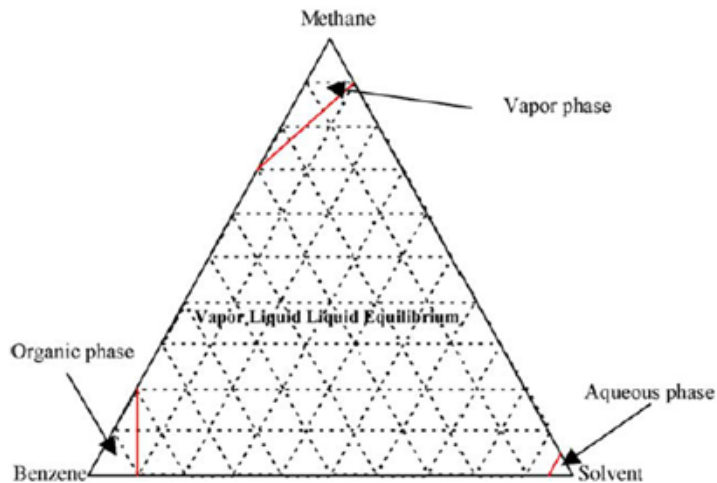
results in substantially higher solubility of the aromatic over that of water. In addition, they found that for a given amine concentration, the aromatic solubility decreases logarithmically with its number of carbon atoms.

With the same apparatus Valtz et al., 2006-2008. continued their experiment regarding toluene benzene, ethylbenzene and xylene solubility [24], [25], [26], they used a simple model based on activity coefficients.

It was stated that it is due to very low mutual solubilities in aqueous systems (solvent and hydrocarbon), it is very easy to reach (vapor, liquid, liquid) equilibrium conditions. They assumed the following:

- There is no significant amount of water or alkanolamine in the organic phase nor in the vapor phase.

For Ethylbenzene and xylene individually C. Coquelet et al., 2008 [26] had carried out the same experiments, in addition they used literature data to determine the temperature which corresponds to the minimum of solubility in pure water. See figure 2.12 for a typical three phase diagram for benzene-aqueous amine system, in which methane was used allow for sampling.



**Figure 2.12:** Example of thermodynamic diagram in conditions close to described, [24]

## 2.4. Solubility of hexane in amine aqueous solutions.

The solubility of n- hexane in 25wt%, 50 wt% MDEA and 35 wt% DEA was investigated in [1], the solubility increased with increasing temperature as well as total pressure which sometimes was adjusted with helium up to  $\approx 0.5$  MPa. As can be seen from table 2.3 and table 2.4.

**Table 2.3:** Solubility of n-hexane in the 25 wt % MDEA aqueous solution [1]

T/K	$P_{exp}^*/\text{MPa}$	$x_{exp} \times 10^5$	$\delta x^{**} \times 10^7$
298.09	0.5010	0.95	2
313.13	0.5135	1.16	2
333.14	0.5029	1.80	3
353.18	0.5132	2.91	3

\* Total pressures adjusted with helium

\*\* Repeatability calculated based on 10 samples analyzed on average

**Table 2.4:** Solubility of n-hexane in 50 wt% MDEA aqueous solution [1]

T/K	$P_{exp}^*/\text{MPa}$	$x_{exp} \times 10^4$	$\delta x^{**} \times 10^6$
298.34	0.5081	0.46	2
303.34	0.5154	0.52	0.9
313.24	0.5018	0.64	1
323.21	0.4991	0.90	4
333.23	0.5015	1.17	3
343.17	0.5392	1.50	3

\* Total pressures adjusted with helium

\*\* Repeatability calculated based on 10 samples analyzed on average

Despite the difference in pressure values, Table 2.4 is to be taken to test for reliability of this work, as long as this difference has a negligible effect on the solubility. To our knowledge, no data is available in literature for the solubility of heptane in amine solutions in general and in MDEA aqueous solutions specifically.

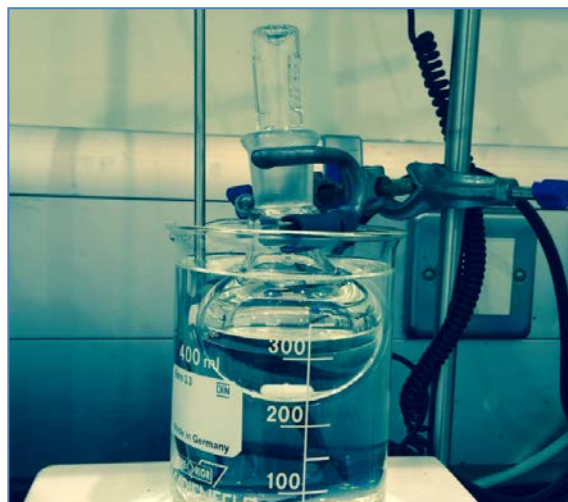
### **3. Methodology**

#### **3.1. Apparatus & Experimental work.**

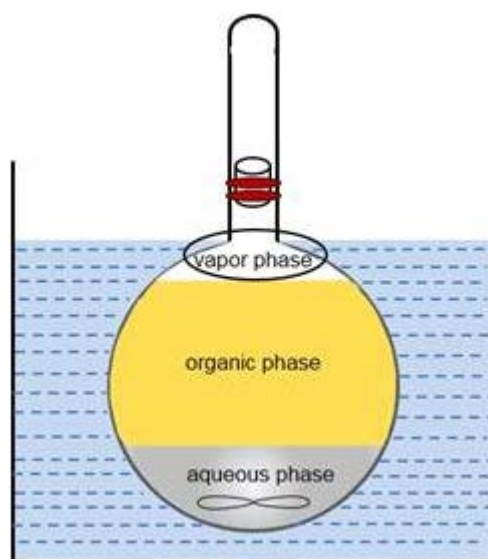
In the beginning of this work, about four months had been spent working on a static equilibrium cell with pneumatic auto sampler and online gas chromatography, however the use of this assembly was stopped for reasons out of control as there were no reliable data obtained consequently a simple equilibrium cell was used. The experimental setup simply consists of an equilibrium cell immersed in a high boiling temperature oil bath fixed at a set point temperature using a digital heater with uncertainty of 0.3 °C.

Three solutions of MDEA of 40, 45 and 50 wt % concentrations were prepared from commercial, fresh, unloaded MDEA, provided by GASCO, and filtered de-salted water, since the presence of ionic species would affect the solubility of hydrocarbons and reduce the solubility “salting-out” [5].

Under atmospheric pressure, 25 ml of 50 wt% MDEA solutions was taken and added to the equilibrium cell followed by 15 ml of Hexane/Heptane. (The same procedure was repeated for the 40 wt% and 45 wt% MDEA), figures 3.1 & 3.2 show the used cells and a schematic diagram of a single cell respectively.



**Figure 3.1:** Equilibrium cells used for the experiments



**Figure 3.2:** Schematic diagram for the simple equilibrium cell

To ensure the equilibrium at the specified temperature and pressure, the denser phase was stirred by magnetic stirrer with suitable rpm and left not less than 12 hours. Samples from the aqueous phase were withdrawn and analyzed by gas chromatography.

Several samples were analyzed to evaluate the repeatability of the results. Also selected cells were duplicated to test the reproducibility of the results. The origin and purity of compounds are reported in table 3.1:

**Table 3.1:** Material origin and purity

Compound	Formula	Furnisher	Purity
n-Hexane	C <sub>6</sub> H <sub>14</sub>	Merck	≥ 96.0%
n-Heptane	C <sub>7</sub> H <sub>16</sub>	Merck	≥ 96.0%
Commercial MDEA	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	GASCO-Dow	99.0 %

The compositions measurements of the amine aqueous solutions used for hexane solubility study were determined gravimetrically and are listed in table 3.2:

**Table 3.2:** Actual prepared concentrations of aqueous amine solutions used for hexane measurements

Aqueous mixture	Amine composition Gravimetric determination (wt%) ± 0.001
40 wt% MDEA	40.202
45 wt% MDEA	44.996
50 wt% MDEA	49.997

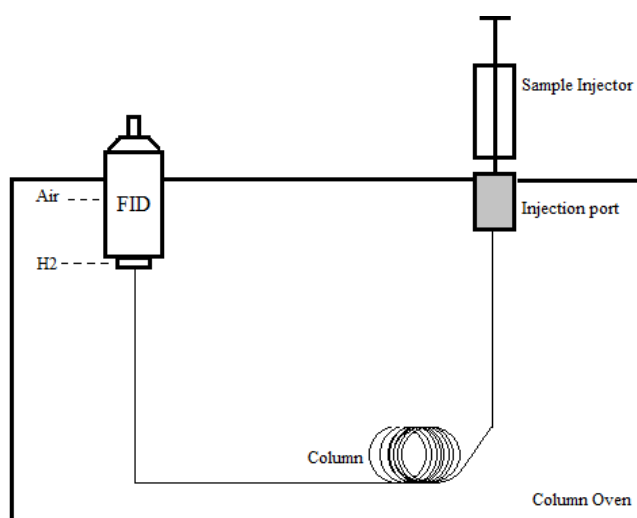
Also, the compositions of the aqueous amine solutions for heptane solubility study were determined gravimetrically as listed in the table 3.3:



**Table 3.3:** Actual prepared concentrations of aqueous amine solutions used for hexane measurements

Aqueous mixture	Amine composition Gravimetric determination (wt%) $\pm$ 0.001
40 wt% MDEA	40.035
45 wt% MDEA	44.943
50 wt% MDEA	49.890

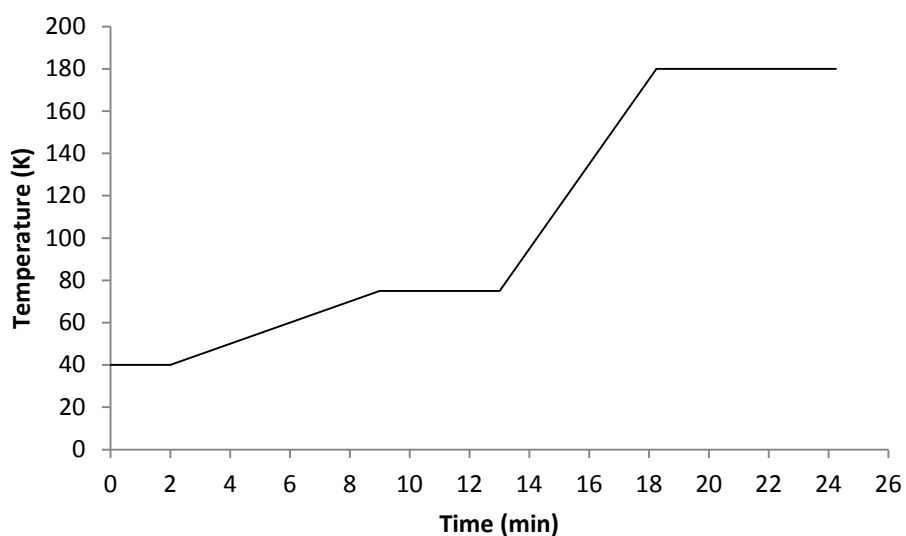
All analyses were performed using Agilent 6890 N gas chromatograph equipped with a flame ionization detector. Chromatographic separation was accomplished with an HP-5, 30 m, 0.32 mm i.d., 0.25  $\mu$ m film thickness. Split injection mode was used, the split mode provides a way to inject a normal-sample size, vaporize it, and then transfer only part of it to the column for analysis. The rest is vented to waste. The best split ratio to achieve good reproducibility was found to be 2 %, figure 3.3 shows the used analytical circuit and table 3.4 give the thermal programming followed in the GC analysis which is also shown in figure 3.4.



**Figure 3.3:** Analytic circuit

**Table 3.4:** Thermal programming of the oven

Steps	Ramp rate °C/min	Final temperature °C	Holding time-min
Starting	0	40	2
Ramp 1	5	75	4
Ramp 2	20	180	6

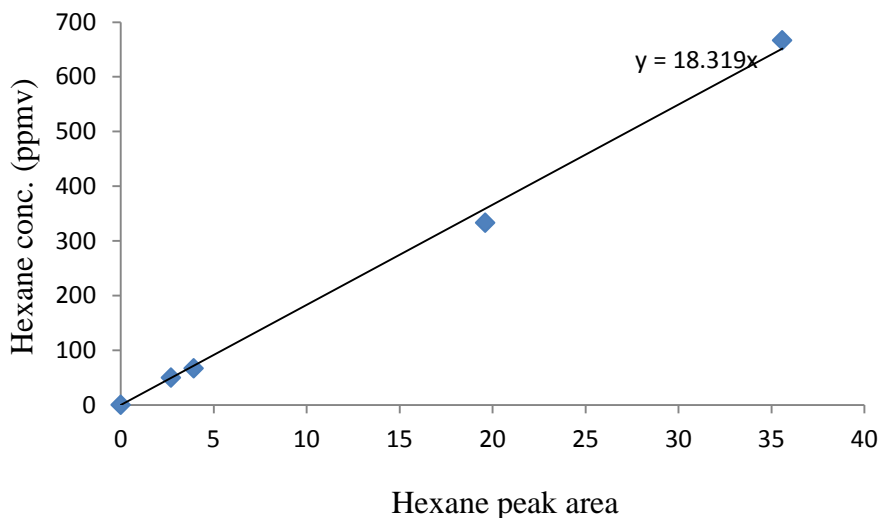


**Figure 3.4:** Thermal programming of the oven

In order to avoid or reduce the possibility of losing hydrocarbon by adsorption throughout the lining and the column itself, a blank injection was used frequently between samples measurements.

In addition, a 10 ml beaker filled with oil placed on the heater next to the equilibrium cell was used as a bus beaker to carry the vial samples to the GC and maintain the same conditions of temperature and pressure.

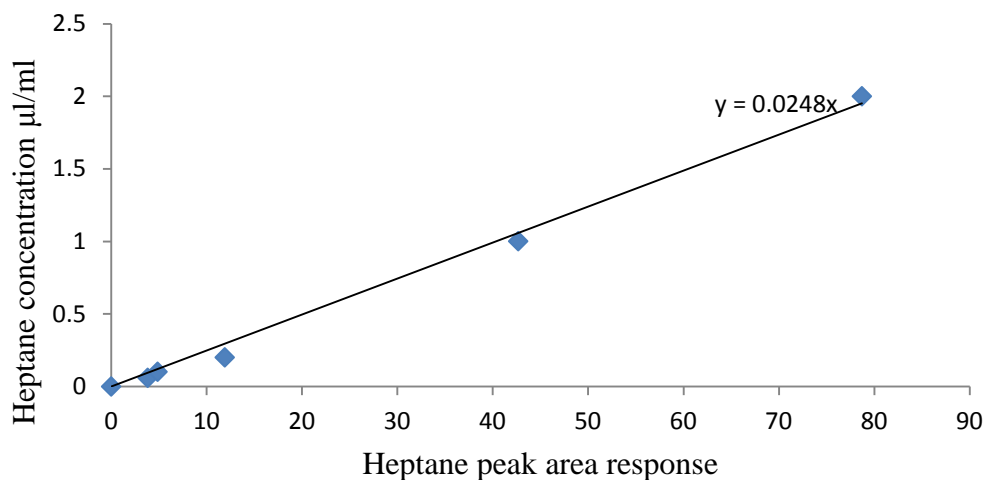
The FID was used in the analytical circuit and was calibrated by injecting known solutions of the hydrocarbon under interest. For hexane, five points calibration line was generated to calibrate the FID, as can be seen from figure 3.5.



**Figure 3.5:** Hexane area detector response vs. conc.

Also, For heptane, five points calibration line was generated to determine its detector response see figure 3.6.

The standard solutions of heptane were prepared gravimetrically over the range in which the actual analysis would be conducted and that required further dilution for the standard solutions prepared due to the lower solubility of heptane. All standards were immediately analyzed to establish a reliable calibration curve.



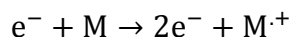
**Figure 3.6:** Heptane area detector response vs. conc.

### **3.2. Comparison between analytical and commercial (industrial) grade of MDEA using Mass spectroscopic technique- Direct Sample Analysis.**

The main interest of this study is to determine the solubility of hexane and heptane in commercial MDEA that is used in GASCO operation. However, a direct sample analysis linked to mass spectrometer was used to compare the composition of the analytical grade MDEA and the obtained MDEA from GASCO. The aim of this comparison was to make sure that any comparison between literature values that used analytical grade MDEA and our obtained values from GASCO commercial grade MDEA would be valid. Here is below a description of the used Mass spectroscopic technique linked to Direct Sample Analysis.

The mass spectrometer performs three essential functions:

1. The sample is introduced using a sample inlet system and molecules are exposed to a stream of high-energy electrons, converting some of the molecules to positive ions, by removing electrons from them, in an ionization chamber. The molecules are thus converted into radical-cations.

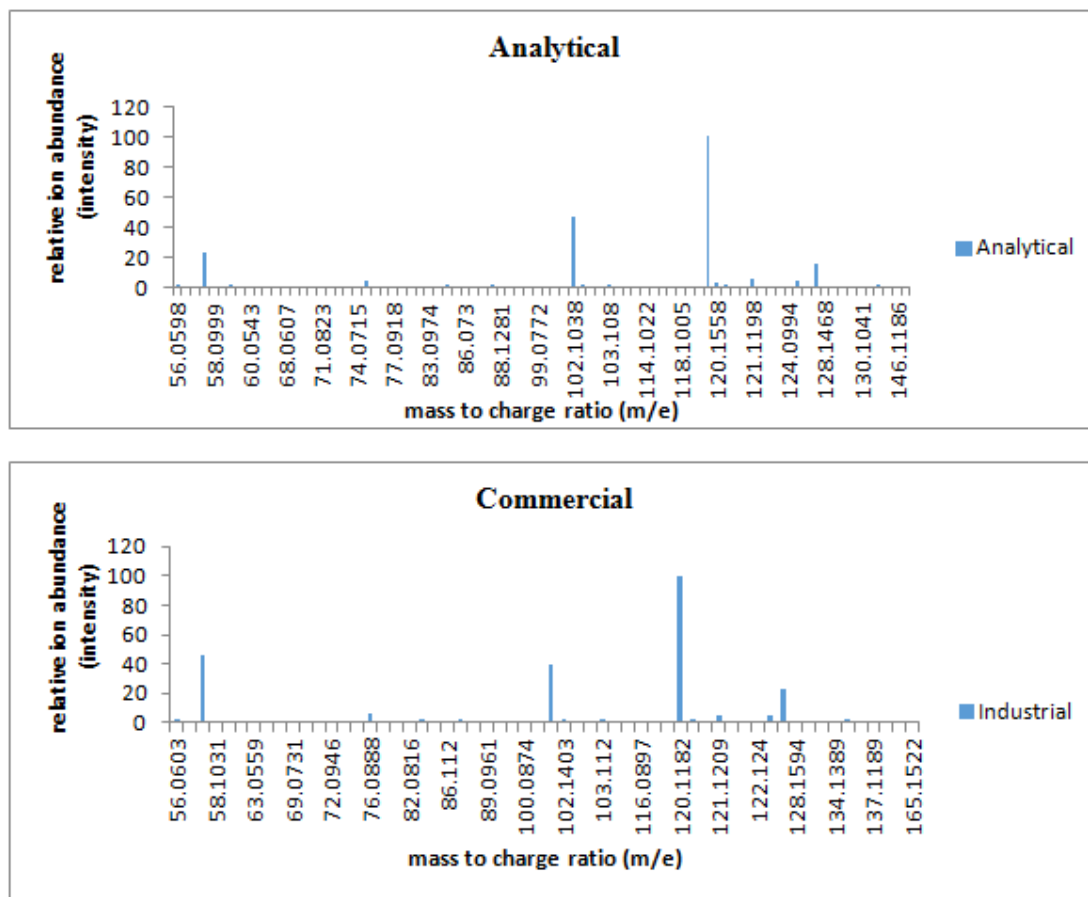


Because of their high energy, some of these ions fragment or break apart into smaller ions. Finally, all of these ions are accelerated in an electric field.

2. The accelerated ions are separated according to their mass-to-charge ratio in a magnetic or electric field.
3. The ions with a particular mass-to-charge ratio are detected by a device that is able to count the number of ions that strike it, by producing a proportional current [27].

The mass spectrum is a plot of ion abundance versus mass to charge (m/e) ratio. The most abundant ion formed in the ionization chamber gives rise to the tallest peak in the mass spectrum, called the base peak. Here we have used the direct sample analysis technique, in which the samples molecules were ionized through atmospheric pressure chemical ionization APCI, and then the ions were detected using TOF-MS detector technique, see figure 3.7.

For commercial MDEA, the base peak appeared at mass to charge ratio  $m/e = 120.1182$  while for the analytical, it appeared at 120.1172 which are referred to MDEA. From the below mass spectrums of both commercial and analytical MDEA, it can be concluded that their spectrums are very close to each other and the commercial MDEA is expected to behave similar to the analytical one.



**Figure 3.7:** Mass spectrums of analytical and industrial MDEA.

## 4. Results & discussion – Hexane/ Heptane solubility in aqueous MDEA at VLLE.

### 4.1. Experimental results- hexane

The influence of temperature and amine concentrations on the solubility of hexane in aqueous MDEA solutions has been studied. The results of this study are reported in table 4.1 and plotted in figure 4.1. The obtained solubility data for hexane in 50 wt% MDEA are in excellent agreement and fit well with the available data in [28] confirming the high level of reliability of the new data.

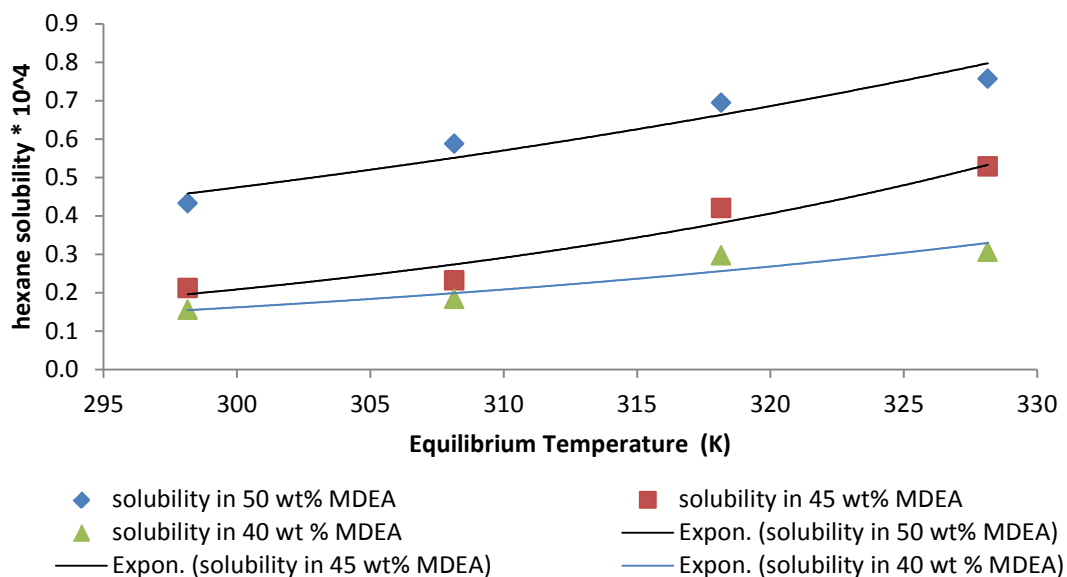
**Table 4.1:** Solubility of hexane at different temperatures and amine concentrations

40 wt% MDEA			45 wt% MDEA			50 wt% MDEA		
T(K)*	X <sub>Hexane</sub> × 10 <sup>4</sup>	Standard deviation**	T(K)*	X <sub>Hexane</sub> × 10 <sup>4</sup>	Standard deviation**	T(K)*	X <sub>Hexane</sub> × 10 <sup>4</sup>	Standard deviation**
298	0.16	0.0568	298	0.21	0.0462	298	0.44	0.0432
308	0.17	0.0143	308	0.23	0.0154	308	0.59	-
318	0.30	-	318	0.42	-	318	0.70	0.0247
328	0.31	-	328	0.53	-	328	0.81	0.0798

\* At around the atmospheric pressure.

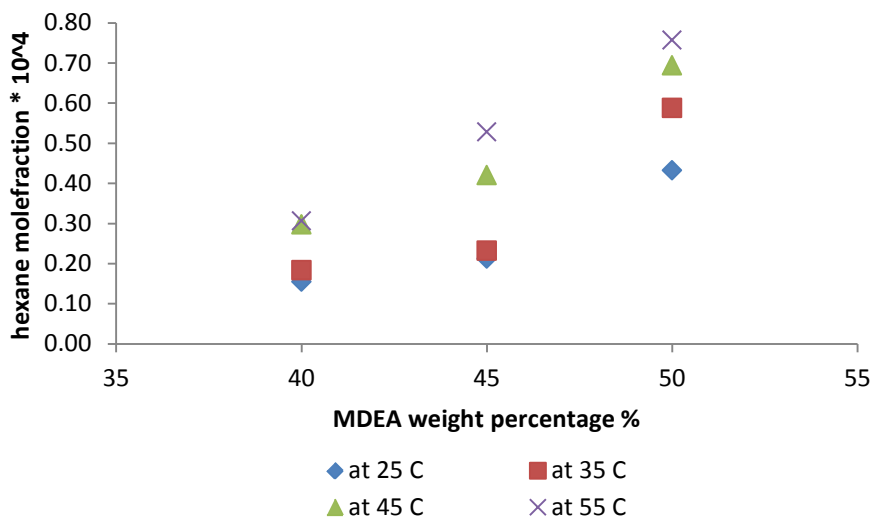
\*\*standard deviation  $\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$ , values × 10<sup>4</sup> are given, no. of samples three on average.

\*\*\* Standard uncertainty:  $u(x) \approx 0.05 \times 10^{-4}$ ;  $u(T) = 0.3K$ .



**Figure 4.1:** Solubility of hexane in 40, 45 & 50 wt % MDEA vs. temperature

Figure 4.1 indicates that the solubility of hexane increases exponentially with increasing equilibrium temperature. Also, it is important to investigate the effect of increasing amine concentration (Salting In) at the same temperature as in figure 4.2.



**Figure 4.2:** Effect of amine weight percentage on solubility of hexane at constant temperatures



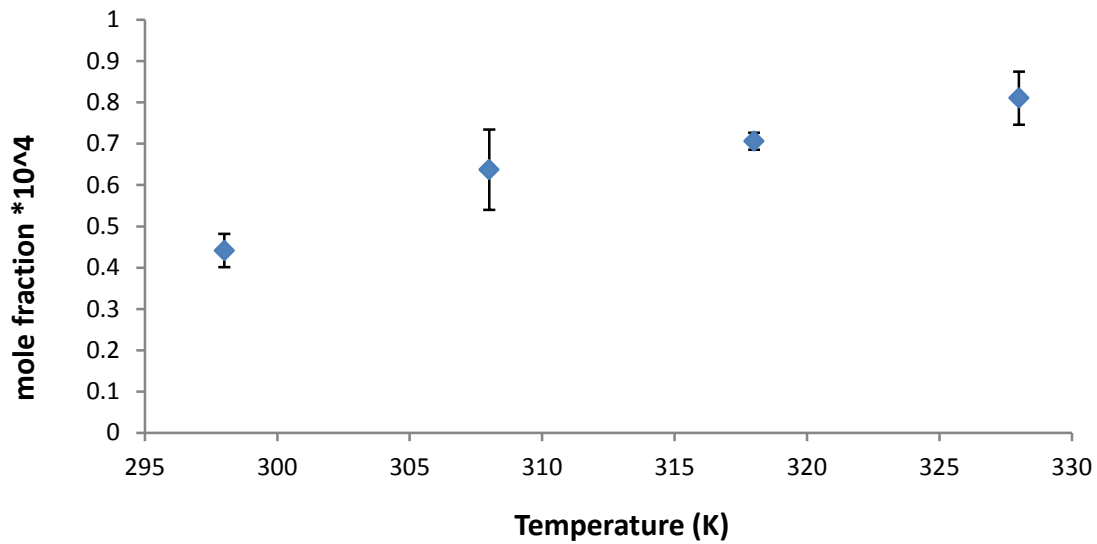
#### 4.1.1. Repeatability and reproducibility study.

The equilibria of (hexane / MDEA aqueous solution) was repeated at 25, 35, 45 and 55 °C and they were in a good agreement and they confirmed good repeatability of the saturation as in table 4.2. Also, figure 4.3 shows the standard error bars for the repeatability of hexane solubility in 50 wt% MDEA.

**Table 4.2:** Repeatability of the samples in hexane/ MDEA aqueous solutions

MDEA wt %	Temperature	Number of samples	Hexane mole fraction × 10 <sup>4</sup>			Standard deviation σ *
40 wt % MDEA	298	3	0.155	0.212	0.098	0.0568
	308	2	0.184	0.164	---	0.0143
45 wt% MDEA	298	2	0.179	0.245	---	0.0462
	308	2	0.243	0.221	---	0.0154
50 wt% MDEA	298	3	0.402	0.423	0.485	0.0432
	318	3	0.675	0.715	0.720	0.0247
	328	2	0.757	0.870	---	0.0798

$$* \sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \times 10^4$$



**Figure 4.3:** Repeatability of hexane solubility in 50 wt% MDEA

In addition hexane- 50% MDEA equilibria was duplicated to test for reproducibility at 25, 35, 45 and 55 °C and it confirmed good reproducibility of the saturation as in table 4.3.

**Table 4.3:** Hexane- 50 wt% MDEA reproducibility check

MDEA wt %	Temperature	Number of samples reproduced	Hexane mole fraction * 10 <sup>4</sup>		
50 wt % MDEA	298	3	0.393	0.424	0.521
	308	1	0.687	---	---
	318	1	0.714	---	---
	328	1	0.805	---	---

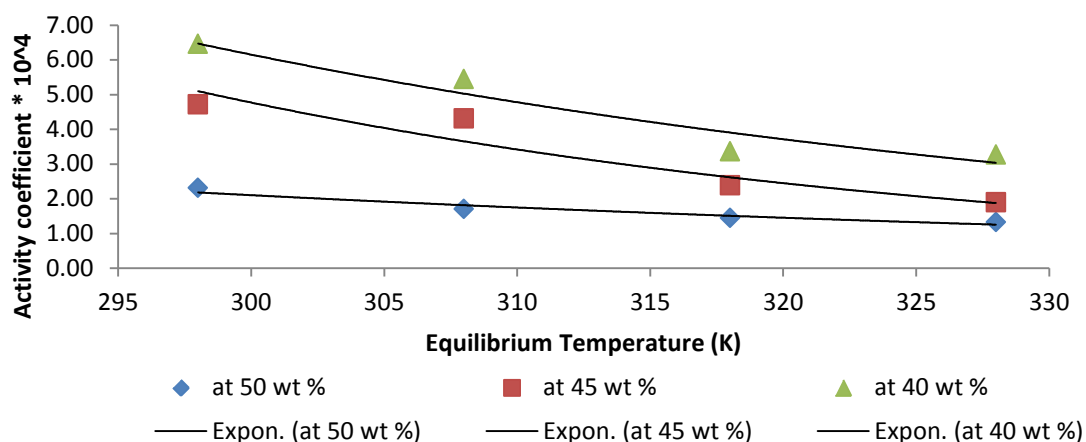
Activity coefficient of hexane in the aqueous phase can be now calculated through the following relation as in table 4.4:

$$\gamma_{Hexane}^{aq} = \frac{1}{x_{Hexane}^{aq}} \quad (4-1)$$

**Table 4.4:** Activity coefficient of hexane in aqueous phase using the measured solubilities

Temperature	Activity coefficient $\gamma_{Hexane}^{aq}$		
	40wt%	45wt%	50wt%
298	64523.83	47157.63	23125.82
308	54386.72	43114.69	17016.20
318	33638.79	23784.57	14402.80
328	32669.71	18932.47	13213.55

Plots of the activity coefficients are given against temperature in (K) for different amine concentration as in figure 4.4:



**Figure 4.4:** Effect of temperature in hexane activity coefficient at different MDEA wt %

The activity coefficients of hexane show a positive deviation from Raoult's law ( $\gamma \gg 1, g^E > 0$ ) [29] and decrease with increasing temperature  $\frac{\partial \gamma_i}{\partial T} < 0$ .

The above curves have been fitted into the following exponential formula:

$$\gamma_{Hexane}^{aq} = \hat{A} \exp(BT) \quad (4-2)$$

Taking the natural logarithm, in order to simplify the parameters, leads to:

$$\ln \gamma_{Hexane}^{aq} = \ln \hat{A} + BT = A + BT \quad (4-3)$$

A and B are amine concentration dependent parameters, The values of these parameters are listed in table 4.5:

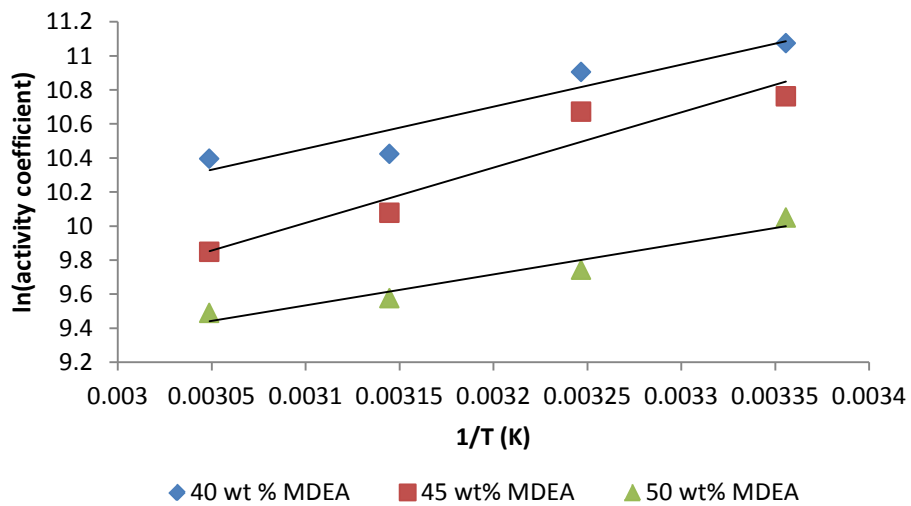
**Table 4.5:** Parameters of the fitting equation.

Solvent	A	B
40 wt % MDEA	18.421	-0.025
45 wt % MDEA	20.723	-0.033
50 wt % MDEA	15.425	-0.018

A plot of the natural logarithm of the activity coefficient versus the temperature inverse should give linear behavior for this narrow temperature range with a slope of the partial molar excess enthalpy divided by the universal gas constant:

$$\frac{\partial(\ln \gamma_i)}{\partial(\frac{1}{T})} = \frac{\bar{h}_i^E}{R} \quad (4-4)$$

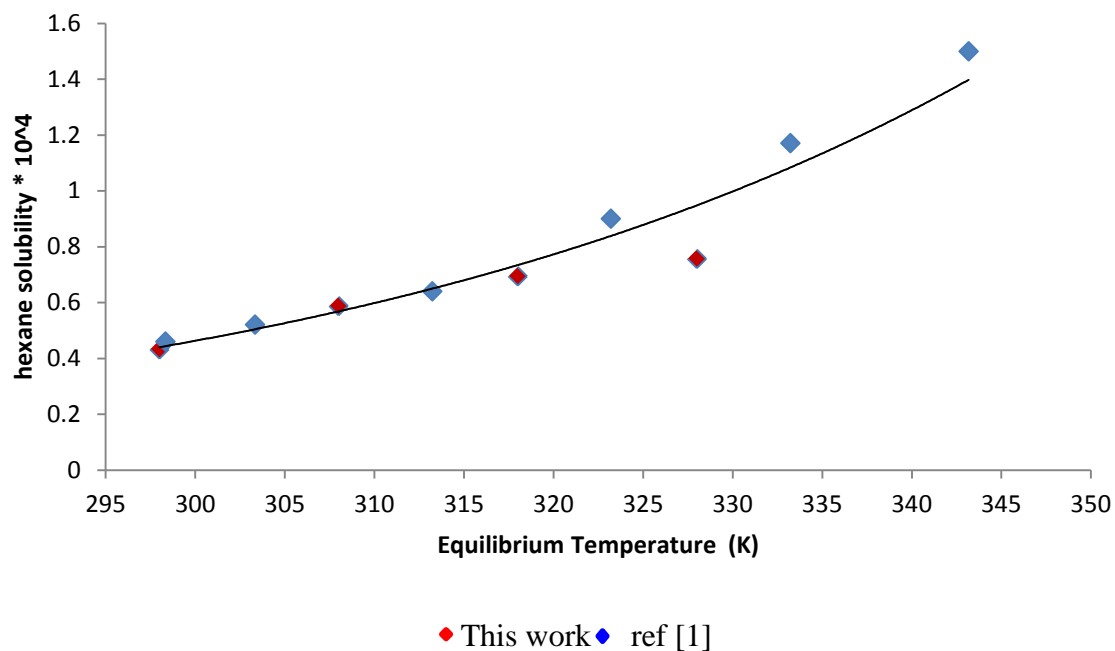
Figure 4.5 shows this relation and the data shows smooth transition between the different MDEA concentrations.



**Figure 4.5:** Hexane activity coefficient natural log vs. temperature inverse

#### 4.2. Reliability test

As mentioned in the literature review, hexane solubility in 50 wt % MDEA was investigated earlier by Makraoui et al., 2008 [1], Their results were in conformity with the results obtained from this work as shown in figure 4.6.



**Figure 4.6:** This work new data with data from ref [1] for the solubility of hexane in 50 wt %

MDEA show compatibility of the results.

### 4.3. Experimental results- heptane

Effect of temperature and amine concentration on the solubility of heptane in MDEA aqueous solutions was studied in this work. Table 4.6 shows the solubility of heptane at different temperatures and amine concentrations.

**Table 4.6:** Solubility of heptane at different temperatures and amine concentrations

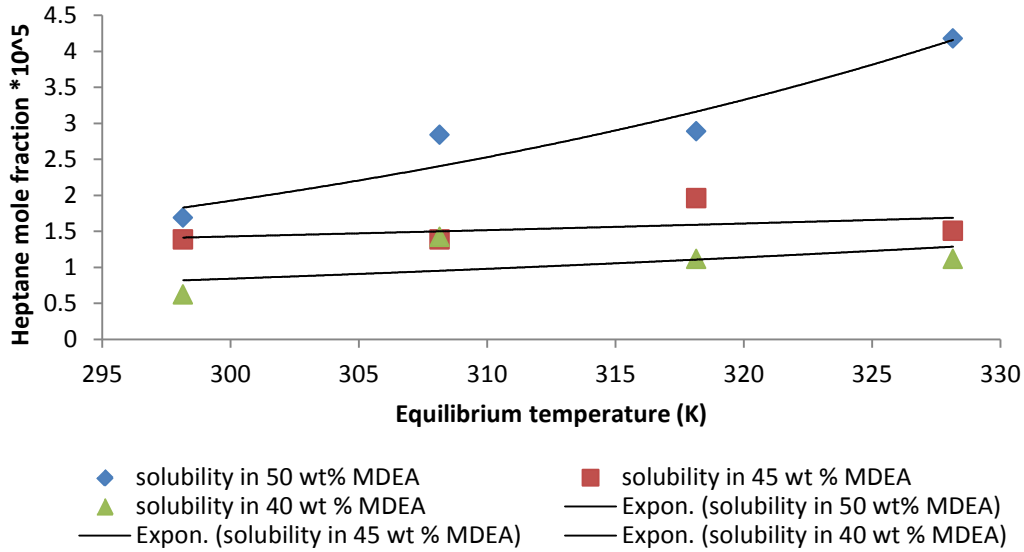
40 wt% MDEA			45 wt% MDEA			50 wt% MDEA		
T(K)*	$x_{\text{heptane}} \times 10^5$	$\sigma$ **	T(K)*	$x_{\text{heptane}} \times 10^5$	$\sigma$ **	T(K)*	$x_{\text{heptane}} \times 10^5$	$\sigma$ **
298	0.625	0.125	298	1.39	0.011	298	1.69	0.119
308	1.42	0.076	308	1.39	0.008	308	2.84	0.489
318	1.12	0.160	318	1.96	0.480	318	2.90	0.295
328	1.13	---	328	1.51	0.067	328	4.18	0.577

\* At about the atmospheric pressure.

\*\*standard deviation  $\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$ , values  $\times 10^5$  are given, no. of samples are three on average.

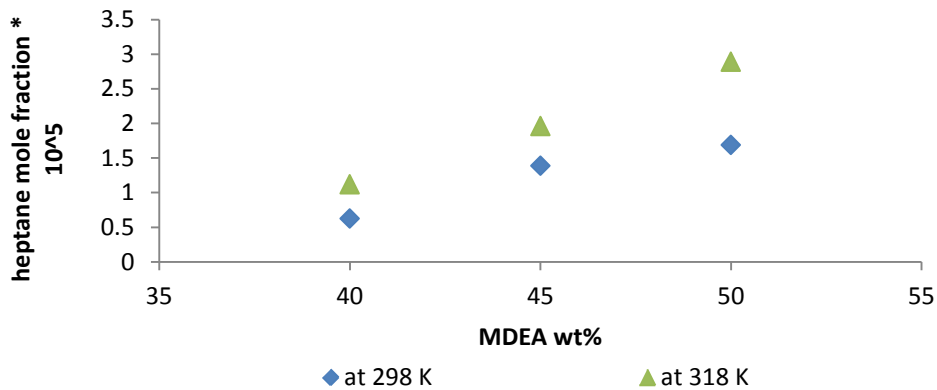
\*\*\* Standard uncertainty:  $u(x) \approx 0.03 \times 10^{-4}$ ;  $u(T) = 0.3$ .

Figure 4.7 shows the solubility of heptane in mole fraction versus the equilibrium temperature in K.



**Figure 4.7:** Results of solubility of heptane in 40, 45 & 50 wt % MDEA vs. temperature

As the isopleths curves show, the solubility of heptane is a weak function of temperature and vapor pressure in the 40 and 45 weight percent while it increases exponentially with increasing equilibrium temperature and pressure in the 50 weight percent aqueous phase. Also, figure 4.8 shows the effect of the increasing MDEA wt% on heptane solubility at 298 K and 318 K.



**Figure 4.8:** Salting -in effect at constant Temperatures



In general, the solubility of heptane increases with increasing amine weight percentage as this is well known as (Salting-In) effect; the more the amine percentage the more the solubility power of heptane.

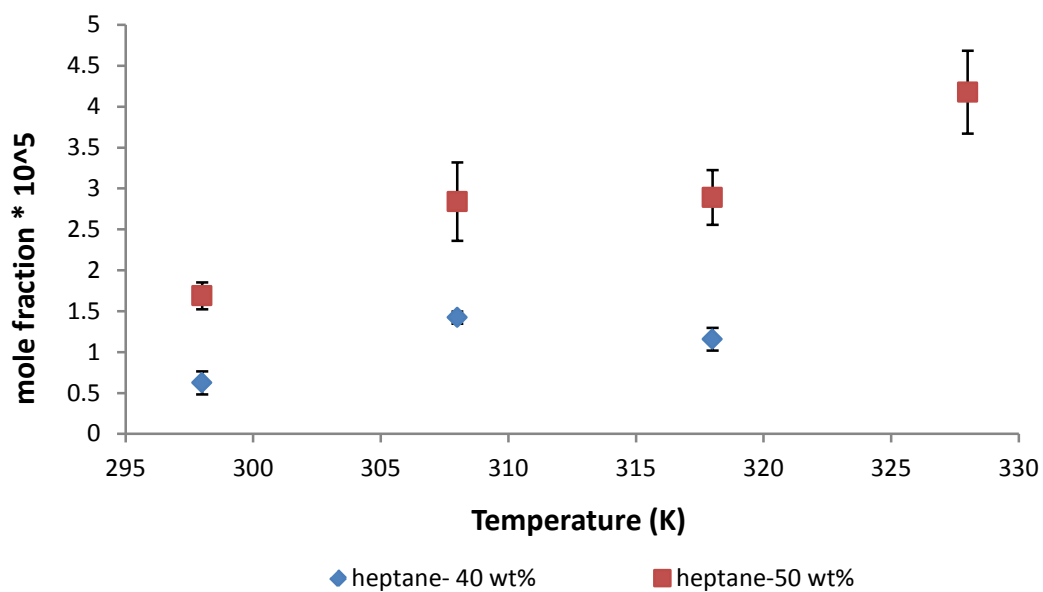
#### 4.3.1. Repeatability and reproducibility study

Several samples were analyzed to evaluate the repeatability and reproducibility of the results. Table 4.7 & 4.8 show the results of the repeatability and reproducibility studies, respectively. Also, figure 4.9 shows the standard error bars for heptane repeatability in 40 and 50 wt % MDEA.

**Table 4.7:** Repeatability of the samples in heptane/ MDEA aqueous solutions

MDEA wt%	Temperature	number of samples	Average heptane mole fraction * 10 <sup>5</sup>	Standard deviation $\sigma^*$
40 wt% MDEA	298	3	0.625	0.125
	308	4	1.42	0.076
	318	5	1.12	0.16
45 wt% MDEA	308	5	1.39	0.237
	318	4	1.96	0.48
	328	4	1.51	0.067
50 wt% MDEA	308	4	2.84	0.489
	318	3	2.89	0.295
	328	5	4.18	0.577

\*standard deviation  $\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$ , values \* 10<sup>5</sup> are given.



**Figure 4.9:** Repeatability of heptane solubility data points in 40 & 50 wt %

**Table 4.8:** Heptane- 50 wt% MDEA reproducibility check

Temperature	Number of reproduced samples	Heptane mole fraction * 10 <sup>5</sup>
298	1	1.77
328	1	3.77

Activity coefficient of heptane in the aqueous phase can be then calculated through the below equation. Table 4.9 shows the calculated activity coefficient of heptane based on the obtained solubility data.

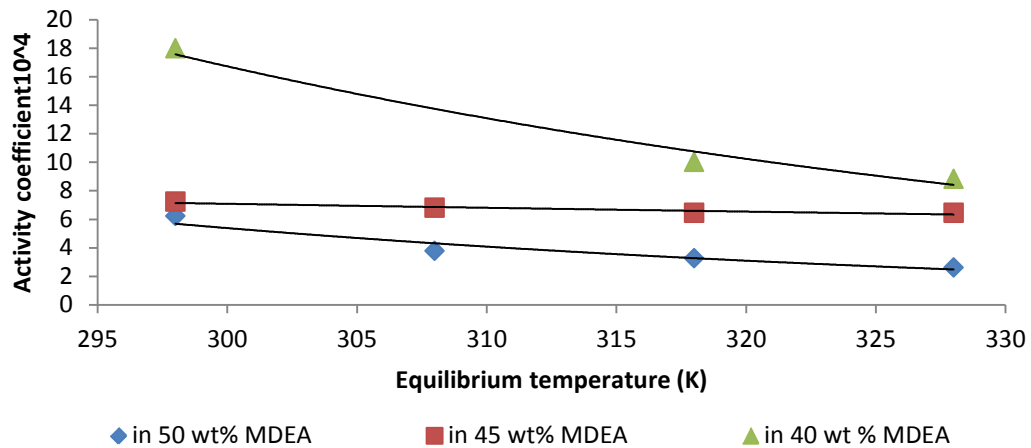
$$\gamma_{Heptane}^{aq} = \frac{1}{x_{Heptane}^{aq}} \quad (4-5)$$

**Table 4.9:** Activity coefficient of heptane in aqueous phase using the measured solubilities

Temperature (K)	Activity coefficient $\gamma_{Heptane}^{aq}$		
	40wt%	45wt%	50wt%
298	160005.30	72021.72	59247.83
308	70307.34	72052.96	35224.11
318	89395.69	50975.35	35224.11
328	88242.48	66333.11	23940.57

The activity coefficients of heptane show a positive deviation from Raoult's law ( $\gamma \gg 1, g^E > 0$ ) [29] and decrease with increasing temperature  $\frac{\partial \gamma_i}{\partial T} < 0$ .

Figure 4.10 shows effect of temperature on heptane activity coefficients at different amine concentrations.



**Figure 4.10:** Heptane activity coefficient isopleths as a function of temperature

The above curves have been fitted into the following exponential formula:

$$\gamma_{\text{Hexane}}^{\text{aq}} = \hat{A} \exp(BT) \quad (4-6)$$

Taking the natural logarithm, leads to:

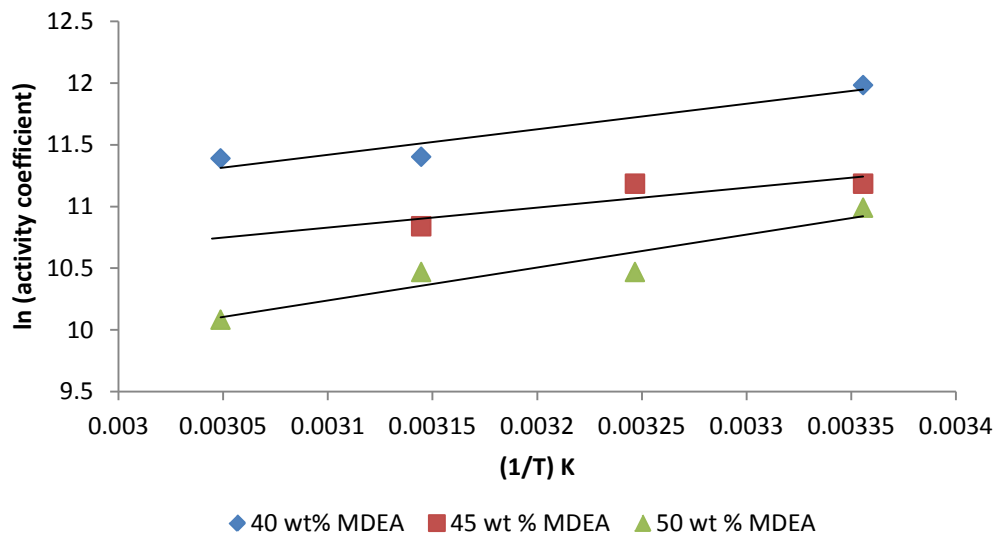
$$\ln \gamma_{\text{Hexane}}^{\text{aq}} = \ln \hat{A} + BT = A + BT \quad (4-7)$$

Where parameters A and B are amine weight concentration dependent, the values of these parameters are fitted as in table 4.10:

**Table 4.10:** Parameters of the fitting equation.

Solvent	A	B
40 wt % MDEA	19.519	-0.025
45 wt % MDEA	12.368	-0.004
50 wt % MDEA	19.114	-0.028

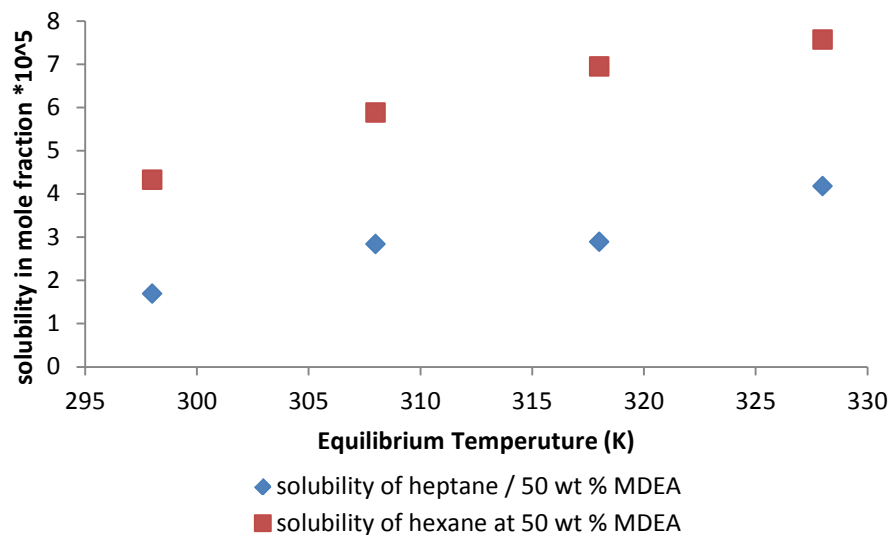
Figure 4.11 shows the linear relation between the natural logarithm of the activity coefficient and the temperature inverse and the data shows smooth transition between the different MDEA concentrations.



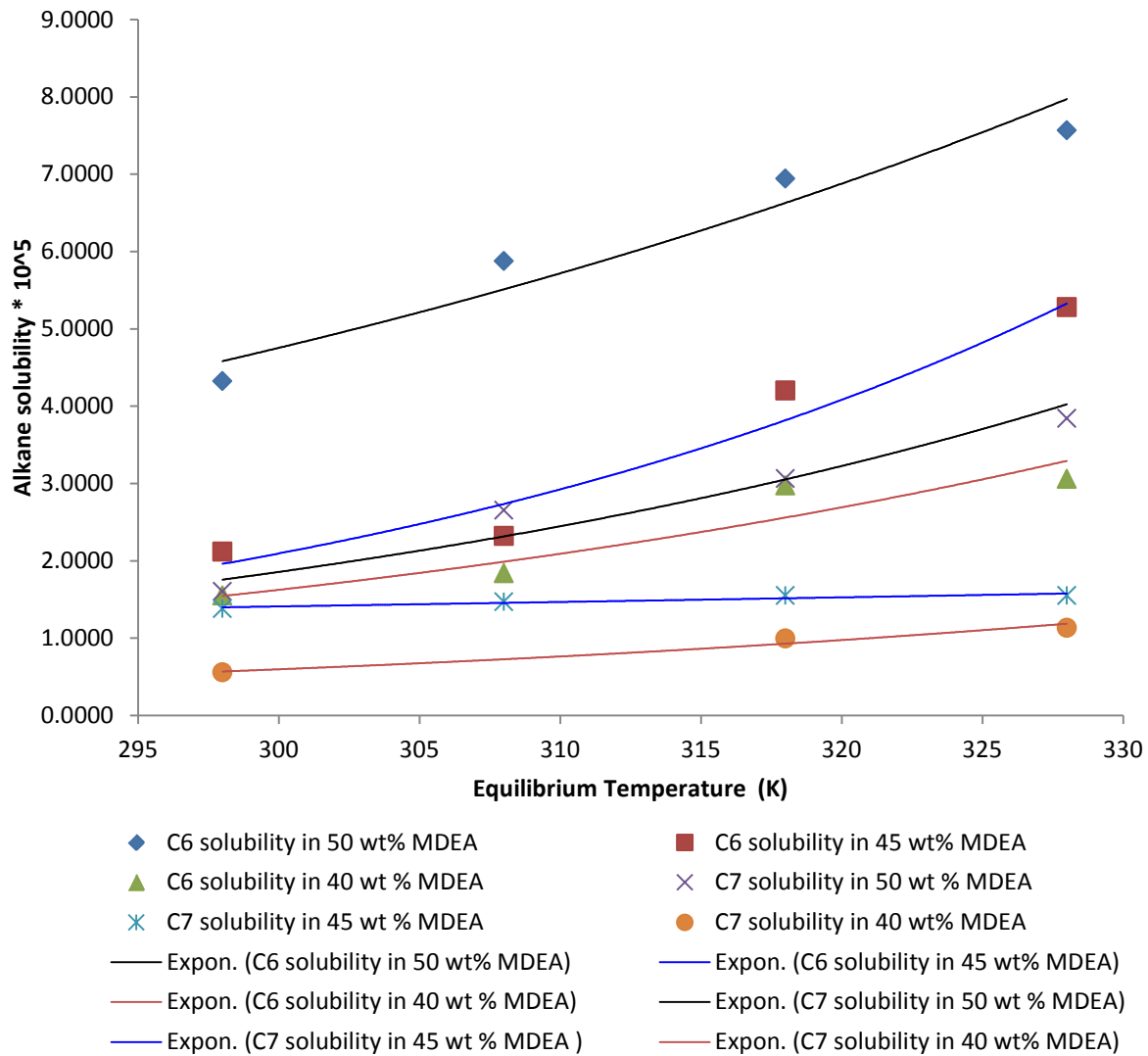
**Figure 4.11:** Heptane activity coefficient natural log vs. temperature inverse

#### 4.4. Comparison between hexane and heptane solubility in MDEA aqueous solutions

Heptane and hexane solubility in aqueous MDEA was compared for the same MDEA percentage under the same conditions of temperature and total pressure, heptane solubility was less than that of hexane as this was expected following the trend of the lighter alkanes i.e, as the carbon number increases, the solubility decreases. Moreover, they showed the same trend and nice parallelism of the curves; see figures 4.12 & 4.13.



**Figure 4.12:** Heptane/ Hexane solubility in 50 wt% aqueous MDEA



**Figure 4.13:** Solubility data of hexane/heptane in 40, 45 & 50 wt% aqueous MDEA solutions

## 5. Modeling approach

Equality of pressure, temperature and chemical potentials of components in different phases are the well known criteria of phase equilibria.

Thus thermodynamic equilibrium between different phases exists if the following conditions are fulfilled:

$$T^\alpha = T^\beta = \dots = T^\pi$$

$$P^\alpha = P^\beta = \dots = P^\pi$$

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi$$

Besides temperature and pressure, the chemical potential of each species must be equal in all phases. The chemical potential of a component is identical with the partial molar Gibbs energy.

$$\mu_i = \bar{g}_i$$

On the other hand, the partial molar Gibbs energy may be expressed by the fugacity:

$$\bar{g}_i(T, P, z_i) = g_i^{\text{pure}}(T, P^0) + RT \ln \frac{f_i(T, P, z_i)}{f_i^0(T, P^0)}$$

The properties of the pure component  $g_i^{\text{pure}}(T, P^0)$  and  $f_i^0$  are only functions of pressure and temperature; therefore, they show the same values in all phases.

Consequently, the conditions for phase equilibrium can be expressed by means of the fugacity as well:

$$\bar{g}_i^\alpha = \bar{g}_i^\beta = \dots = \bar{g}_i^\pi$$

$$f_i^\alpha = f_i^\beta = \dots = f_i^\pi$$

The last equation is the starting point for practically all phase equilibrium calculations.



### 5.1. Modeling approach using Henry's constant.

Due to very low mutual solubilities in aqueous solvent–hydrocarbon systems, it is very easy to reach vapor–liquid–liquid equilibrium (VLLE) conditions. The phase rule tells us that specification of a certain number of intensive properties of a system also fixes the values of all other intensive properties [30].

Intensive properties namely temperature, pressure and compositions (solubilities) are phase rule variables but they are not all independent.

For water, amine and hydrocarbon = three component mixture,  $c=3$ .

with three phases = L,L,V,  $\pi =3$ , applying phase rule  $F=2+c-\pi$ , gives  $2+3-3 =2$  freedom of choice for the possible combinations, namely,  $T(P,x)$ ,  $P(T,x)$ , more specifically  $x(P,T)$  as a ruled surfaces in  $x(P,T)$  space (bivariant equilibria), so it is necessary to have a correct knowledge of the (alkane-aqueous MDEA) mutual solubilities.

Although the solubility is a function of temperature and pressure, it is still a weakly pressure dependent function that is explained from the fact that neither MDEA nor water is available in a considerable amount in the vapor and in the hydrocarbon phase. And thus the vapor phase was estimated as containing only vapors of the hydrocarbon under study. This assumption was validated by the work of Salim Mokraoui et. al. [1], [13] for VLLE of hydrocarbon- water system as they calculated Henry's law constant once through the fugacity coefficient of the hydrocarbon species in the vapor phase  $\hat{\varphi}_i^V$  with respect to the hydrocarbon partial pressure, in the presence of water, second through the fugacity coefficient of the pure hydrocarbon species  $\varphi_i^V$  with the saturation vapor pressure of pure hydrocarbon, and they gave values that deviated from each other by less than 2 %. This small deviation makes the approximation convenient and satisfactory.

They also approximated the total pressure to be nearly the sum of the pure vapor pressures of each of the hydrocarbon plus water.

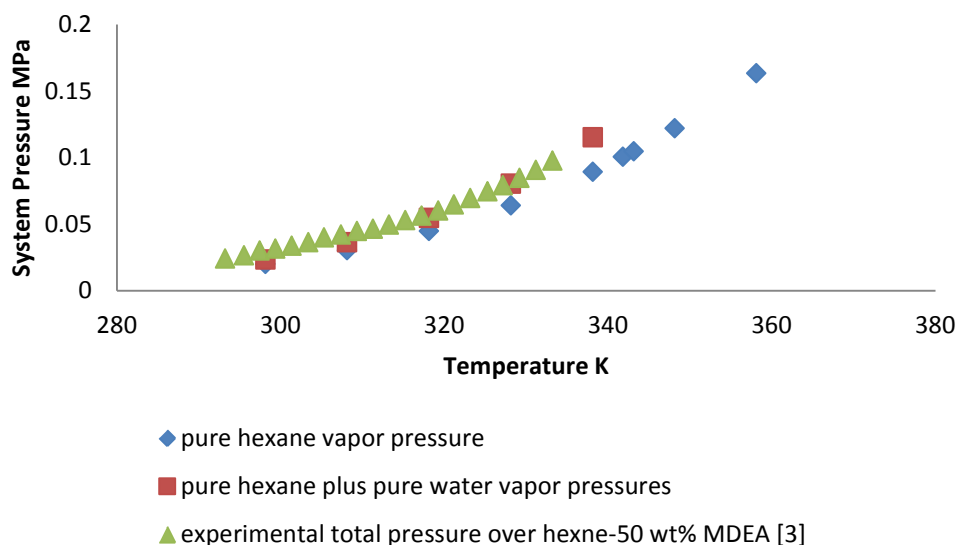
Also Tsonopoulos [16] has shown that the three phase equilibrium pressure can be approximated by the sum of the pure component vapor pressures up to high temperature for hydrocarbon-water VLLE systems.

Although our system is ternary VLLE by adding MDEA, its behavior looks like binary VLLE, in other meaning the actual degree of freedom is one instead of two due to the following prescribed assumptions:

- There is no significant amount of water or alkanolamine in the organic phase  
(this was proved by analysing samples from the organic phase) [1],[23-26].
- There is no significant amount of water or alkanolamine in the vapor phase.  
(since the organic phase is in direct contact with the vapor phase)[1, 23-26].

Based on the preceded discussion, the vapor phase of our cells can be assumed as pure hexane/heptane under atmospheric pressure.

S. Mokraoui et al., 2008 [1] had measured the total pressure of the VLLE hexane-50 wt% in a static-analytic equilibrium with pneumatic capillary auto samplers, and in order to check the validity of our assumption, we compared between the vapor pressure of pure hexane and the sum approximation of pure hexane and pure water with the actual measured system pressure, they were near to each other, deviated by not more than 1% for the pressure range covered for modeling, figure 5.1 shows this obviously.



**Figure 5.1:** Hexane-50 wt % VLLE total pressure

As discussed earlier, since the solubility in MDEA aqueous solution looks similar, but higher, to that in water, the traditional Henry’s law seems convenient to model such solubility. [5, 13, 31]

The presence of amines in the aqueous phase increases hydrocarbon solubility over that in water, an effect referred to as “salting-in”. [5]

The fugacity of a component i, which must be equal in each phase, is denoted as follows:

$\hat{f}_i^{V \text{ or } O \text{ or } aq}$  is the fugacity of component i in a phase either vapor phase V, or the hydrocarbon-rich liquid, H, or the aqueous liquid, aq.

$$\hat{f}_i^V = y_i P \hat{\phi}_i^V \quad (5-1)$$

$$\hat{f}_i^O = x_i^O P \hat{\phi}_i^O \quad (5-2)$$

$\hat{\phi}_i^V$  &  $\hat{\phi}_i^O$ , are to be calculated using an equation of state.

For the hydrocarbon species in the aqueous phase:

$$\hat{f}_i^{aq} = x_i H_{ia} \exp \left[ \frac{\bar{v}_i^\infty (P - P_w^0)}{RT} \right], \text{ for the hydrocarbon species} \quad (5-3)$$

$H_{ia}$  : Henry's constant for the hydrocarbon species in amine, adjusted with that in water as follows:

$$\frac{H_{iw}}{H_{ia}} = S_{ia} \quad (5-4)$$

$\bar{v}_i^\infty(T)$  :The partial molar volume of the hydrocarbon species at infinite dilution at T (K), calculated from the following approximation:

$$\bar{v}_i^\infty(T) = \bar{v}_i^\infty(298 K) \times (v_w^0(T)/v_w^0(298 K)) \quad (5-5)$$

Where the poynting factor (  $\exp \left[ \frac{\bar{v}_i^\infty (P - P_w^0)}{RT} \right]$  ) reflects the effect of pressure on the fugacity of pure liquid i,

$$\frac{f_i^l(P)}{f_i^l(P_i^{sat})} \quad (5-6)$$

With our system the pressures are not too high, hence the poynting factor  $\exp \left( \int_{P_i^{sat}}^P \left( \frac{\bar{v}_i^\infty}{RT} \right) dP \right)$  is close to unity.

Thus for hydrocarbon (hexane/ heptane), the thermodynamic equilibrium equations are:

$$f_{\text{Hydrocarbon}}^v = f_{\text{Hydrocarbon}}^o = f_{\text{Hydrocarbon}}^{\text{aq}} \quad (5-7)$$

$$\begin{aligned} Y_{\text{Hydrocarbon}} \phi_{\text{Hydrocarbon}} P &= x_{\text{Hydrocarbon}}^o \gamma_{\text{Hydrocarbon}}^o P_{\text{Hydrocarbon}}^{\text{sat}} = \\ &= x_{\text{Hydrocarbon}}^{\text{aq}} \gamma_{\text{Hydrocarbon}}^{\text{aq}} P_{\text{Hydrocarbon}}^{\text{sat}} \end{aligned} \quad (5-8)$$

The equilibrium between the aqueous phase and the organic phase can be expressed by:

$$x_{\text{Hydrocarbon}}^o \gamma_{\text{Hydrocarbon}}^o = x_{\text{Hydrocarbon}}^{\text{aq}} \gamma_{\text{Hydrocarbon}}^{\text{aq}} \quad (5-9)$$

Since the hydrocarbon phase is assumed pure hydrocarbon, then  $x_{\text{Hydrocarbon}}^o = 1$  and consequently the activity coefficient is also 1.

$$x_{\text{Hydrocarbon}}^o \gamma_{\text{Hydrocarbon}}^o = x_{\text{Hydrocarbon}}^{\text{aq}} \gamma_{\text{Hydrocarbon}}^{\text{aq}} = 1 \quad (5-10)$$

$$x_{\text{Hydrocarbon}}^{\text{aq}} * \gamma_{\text{Hydrocarbon}}^{\text{aq}} = 1 \quad (5-11)$$

$$\gamma_{\text{Hydrocarbon}}^{\text{aq}} = \frac{1}{x_{\text{Hydrocarbon}}^{\text{aq}}} \quad (5-12)$$

Where  $\gamma_{\text{Hydrocarbon}}^{\text{aq}}$  and  $\gamma_{\text{Hydrocarbon}}^o$  are activity coefficients of hydrocarbon species, in the aqueous and hydrocarbon rich liquid phase, respectively.

As the aqueous phase can be modeled either by Henry's law or the activity coefficient model, we can write:

$$x_i H_i(T) = x_i^{\text{aq}} \gamma_i^{\text{aq}} f_i^{\text{sat}} = 1 \times f_i^{\text{sat}} \quad (5-13)$$

The liquid fugacity of the pure hydrocarbon can be approximated as follows:

$$f_i^{\text{sat}} = \phi_i^{\text{sat}} \times P_i^{\text{sat}} \quad (5-14)$$

Then,

$$x_{iw}^* H_{iw}(T) = \phi_i^{\text{sat}} \times P_i^{\text{sat}} \quad (5-15)$$

The last equation can then be used to derive an equation for the Henry's constant for water-hydrocarbons system in the form

$$\ln H_w = A + \frac{B}{T} + C \ln T \quad (5-16)$$

The effect of alkanolamine on the solubility is modeled using the salting-in ratio ( $S_{ia}$ ). And for each system, Henry's constant for hydrocarbon in aqueous amine solution ( $H_{ia}$ ) is calculated using the salting-in ratio:

$$S_{ia} = \frac{H_{iw}}{H_{ia}} = \frac{x_{ia}}{x_{iw}} \quad (5-17)$$

For Hexane/water VLLE, see table 5.1.

**Table 5.1:** Hexane- water VLLE Henry's constant calculation

T (K)	$p_{i,calc}^{sat}$ * (MPa)	Tr	Pr	$\varphi_i^{sat}$ **	$(x_{iw} * 10^6)^{***}$	$H_{iw} = \frac{\varphi_i^{sat} \times P_i^{sat}}{x_i}$
308	0.030407708	0.607	0.01009	0.977377	2.10958	14088
318	0.044734238	0.626	0.01484	0.935051	2.23074	18751
328	0.064015595	0.646	0.02124	0.956908	2.47541	24746
338	0.089364831	0.666	0.02965	0.951331	2.86596	29664

\*Using Wagner eq.

\*\*Using Lee/ Kesler correlation [30].

\*\*\*Using Tsonopolous eq.

The Wagner eq. is one of the best available equations for an accurate representation of vapor pressure data over a wide temperature range, it expresses the reduced vapor pressure as a function of reduced temperature, see tables 5.2, 5.3, 5.4 & 5.5:

$$\ln P_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^{2.5} + D\tau^5}{1-\tau}, \tau \equiv 1 - T_r \quad (5-18)$$

**Table 5.2:** Wagner eq. parameters [32]

parameter species	A	B	C	D
Water	-7.77224	1.4568	-2.71942*	-1.41336*
Hexane	-7.53998	1.83759	-2.5438	-3.1630
Heptane	-7.77404	1.85614	-2.8298	-3.5070

\*For water the exponents on the last two terms are 3 and 6

**Table 5.3:** Calculated vapor pressures corresponding to pure n-hexane according to Wagner eq.

T (K)	P (MPa)
298.15	0.020039674
308.15	0.030407708
318.15	0.044734238
328.15	0.064015595
338.15	0.089364831
341.85*	0.100523411
343.15	0.104692819
348.15	0.122004204
358.15	0.163256838

\* Normal boiling point.

**Table 5.4:** Calculated vapor pressures corresponding to pure n-heptane according to Wagner eq.

T (K)	P (MPa)
298.15	0.006103467
308.15	0.009847778
318.15	0.015325438
328.15	0.023091492
338.15	0.033798641
343.15	0.040485815
348.15	0.048197122
358.15	0.067132421
363.15	0.078590692
368.15	0.091541336
371.55*	0.101266622
373.15	0.106114896

\* Normal boiling point.



**Table 5.5:** Calculated vapor pressures corresponding to pure water according to Wagner eq.

T (K)	P (MPa)
298.15	0.003176964
308.15	0.005640545
318.15	0.009611675
328.15	0.015783614
338.15	0.025066231
343.15	0.03122596
348.15	0.038619761

Lee/Kesler correlation as a function of  $T_r$  and  $P_r$ , provides reliable values of  $\varphi$  for any non polar or slightly polar gas.

Table 5.6 gives the needed characteristic properties of pure species under interest.

**Table 5.6:** Characteristic properties of pure species under interest

	$T_C$ (K)	$P_C$	$\omega$
water	647.1	220.55 bar	0.345
n-hexane	507.40	3.014 MPa $\equiv$ 30.35 bar	0.301
n-heptane	540.2	2.74 MPa $\equiv$ 27.35 bar	0.350

The same scenario was repeated for heptane/water VLLE as in table 5.7.

**Table 5.7:** Heptane- water VLLE Henry's constant calculation

T (K)	$P_{i,calc}^{sat}$ * (MPa)	Tr	Pr	$\varphi_i^{sat}$	$(x_{iw} * 10^7)^{***}$	$H_{iw} = \frac{\varphi_i^{sat} \times P_i^{sat}}{x_i}$
308	0.009847778	0.57049	0.00359408	1**	4.52729	21752.04
318	0.015325438	0.589003	0.005593225	1**	4.81374	31836.86
328	0.023091492	0.607516	0.008427552	1**	5.38519	42879.62
338	0.033798641	0.62603	0.012335271	0.945312	6.29991	50715.44

\*Using Wagner eq.

\*\*For reduced pressure less than 0.01, fugacity coefficients are assumed 1 confidently.

\*\*\*Using Tsonopolous eq.

### 5.1.1. Henry's correlations for water-hydrocarbon systems

The Henry's constant is derived in the following form:

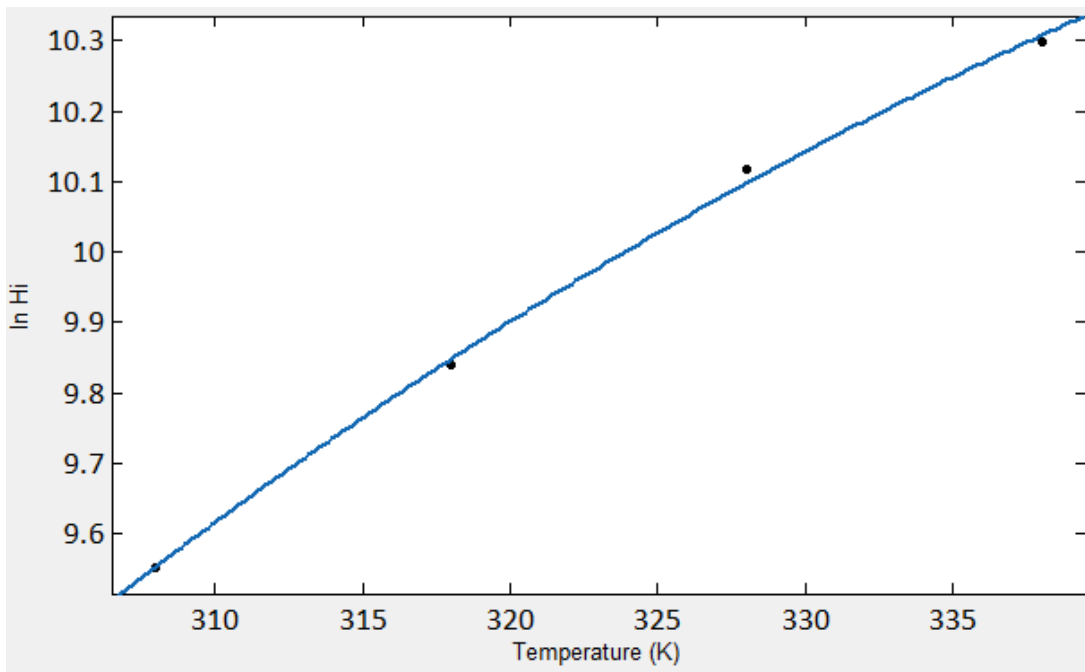
$$\ln H_{iw} = A + \frac{B}{T} + C \ln T \quad (5-19)$$

the parameters A,B and C are given in table 5.8,  $H_{iw}$  is expressed in MPa and T in Kelvin.

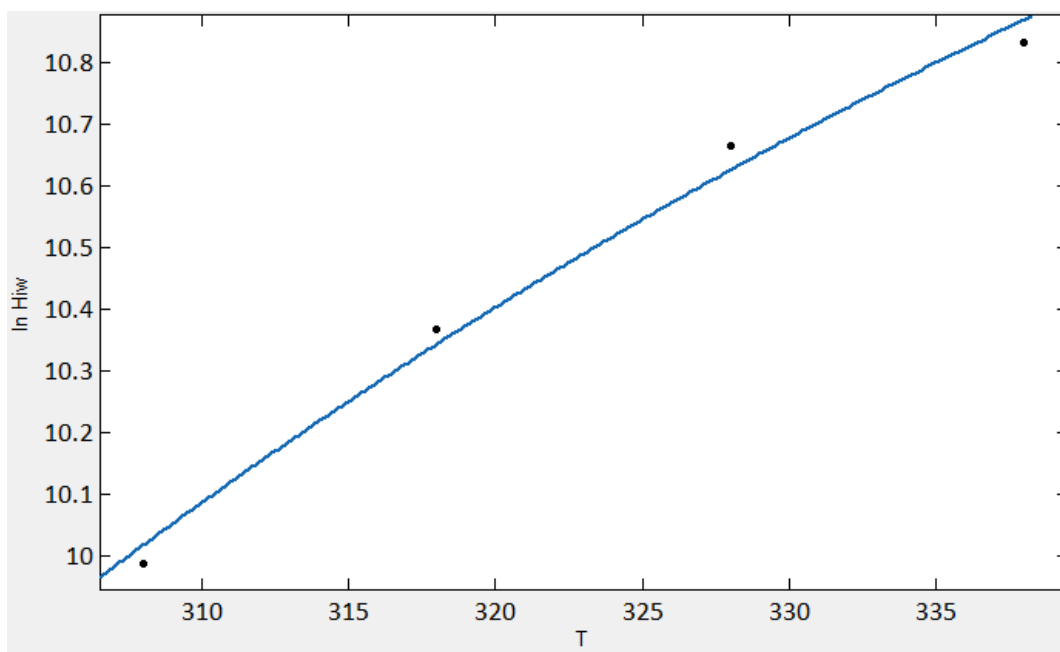
**Table 5.8:** Coefficients of Henry's constant correlation

Parameters Hydrocarbons	A	B(K)	C	Temperature range
Hexane	271.4	-14670	-37.38	(308-338) K
Heptane	186.3	-10890	-24.6	(308-338) K

This can be seen from figures 5.2 & 5.3 for calculated and fitted Henry's constants of hexane/ heptane respectively.



**Figure 5.2:** Calculated and fitted hexane Henry's constant as a function of temperature



**Figure 5.3:** Calculated and fitted heptane Henry's constant as a function of temperature

### 5.1.2. Henry's correlations for aqueous amine – hydrocarbon systems

The effect of alkanolamine on the solubility is modeled using the Salting-in ratios ( $S_{ia}$ ). For each system, Henry's constant for hydrocarbon in aqueous amine solution ( $H_{ia}$ ) is calculated using salting-in ratio,  $S_{ia}$ , see table 5.9.

**Table 5.9:** Mole fractions of hexane in pure water and in different aqueous amine solutions at VLLE.

T(K)	$x_{\text{hexane}} \times 10^6$ * in pure water at VLLE	$x_{\text{hexane}} \times 10^4$ ** in 40 wt% MDEA at VLLE	$x_{\text{hexane}} \times 10^4$ ** in 45 wt% MDEA at VLLE	$x_{\text{hexane}} \times 10^4$ ** in 50 wt% MDEA at VLLE
298	2.10765	0.155	0.212	0.437
308	2.10958	0.184	0.232	0.588
318	2.23074	0.297	0.420	0.694
328	2.47541	0.306	0.528	0.757

\* Calculated using Tsonpolous eq.

\*\* Our data.

From which, the salting-in ratios for the different aqueous systems can be calculated according to table 5.10.

**Table 5.10:** Salting-in ratio for hexane in aqueous MDEA over that of hexane in pure water

T(K)	$S_{ia}$ in 40 wt% MDEA solution	$S_{ia}$ in 45 wt% MDEA solution	$S_{ia}$ in 50 wt% MDEA solution
298	7.35	10.1	20.7
308	8.72	11.0	27.9
318	13.3	18.8	31.1
328	12.4	21.3	30.6

Also, the same scenario was repeated for heptane/water VLLE, see table 5.11.

**Table 5.11:** Mole fractions of heptane in pure water and in different aqueous amine solutions VLLE.

T(K)	$x_{\text{Heptane}} \times 10^7$ * in pure water at VLLE	$x_{\text{Heptane}} \times 10^5$ ** in 40 wt% MDEA at VLLE	$x_{\text{Heptane}} \times 10^5$ ** in 45 wt% MDEA at VLLE	$x_{\text{Heptane}} \times 10^5$ ** in 50 wt% MDEA at VLLE
298	4.512	0.625	1.39	1.69
308	4.527	1.42	1.39	2.84
318	4.814	1.12	1.96	2.89
328	5.385	1.13	1.51	4.18

\* Calculated using Tsonpolous eq.

\*\* Our data.

From which, the salting-in ratios for the different aqueous systems can be calculated according to table 5.12.

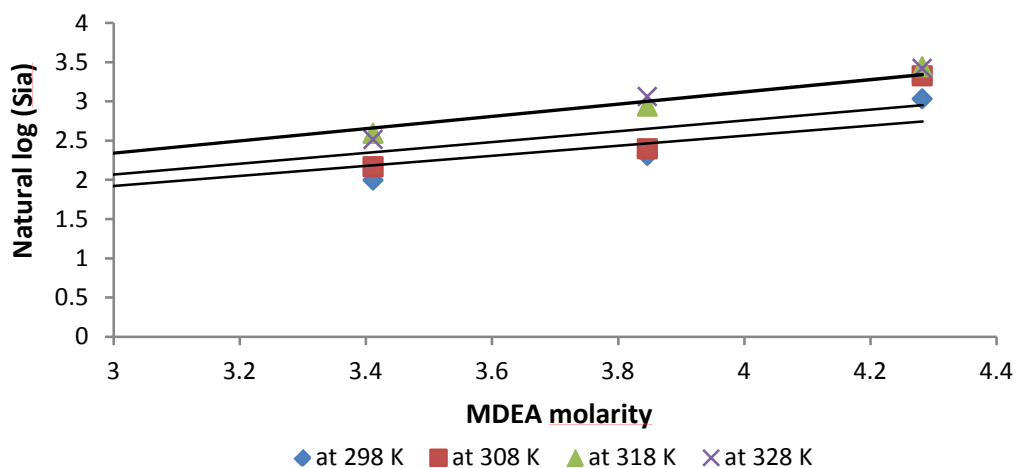
**Table 5.12:** Salting-in ratio for heptane in aqueous MDEA over that of heptane in pure water

T(K)	$S_{ia}$ in 40 wt% MDEA solution	$S_{ia}$ in 45 wt% MDEA solution	$S_{ia}$ in 50 wt% MDEA solution
298	13.9	30.8	37.5
308	31.4	30.7	62.7
318	23.2	40.8	60.1
328	21.0	28.0	77.6

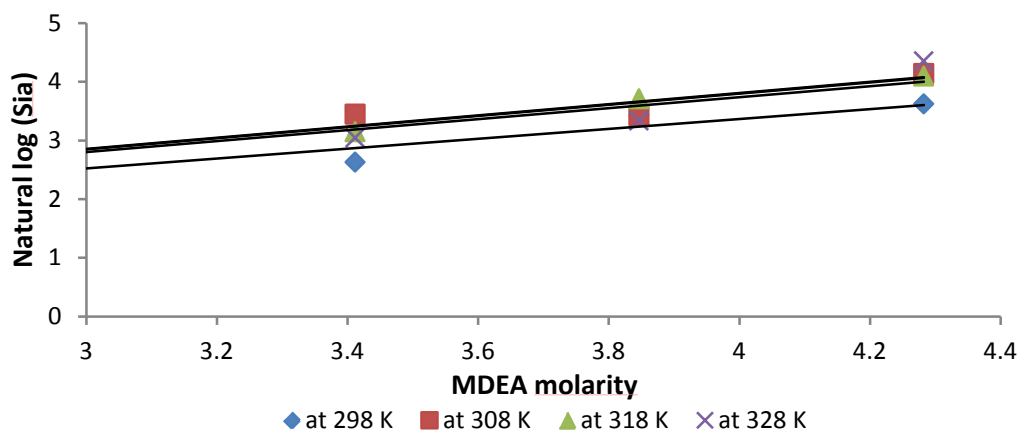
Correlations for the natural logarithm of the salting –in ratio ( $S_{ia}$ ) are derived in the following form [33], [34]:

$$\ln(S_{ia}) = k_i * x_a \tag{5-20}$$

where  $x_a$  is the molarity of MDEA in the aqueous solution, and  $k_i$  is a coefficient, see figures 5.4 & 5.5 for hexane and heptane respectively.

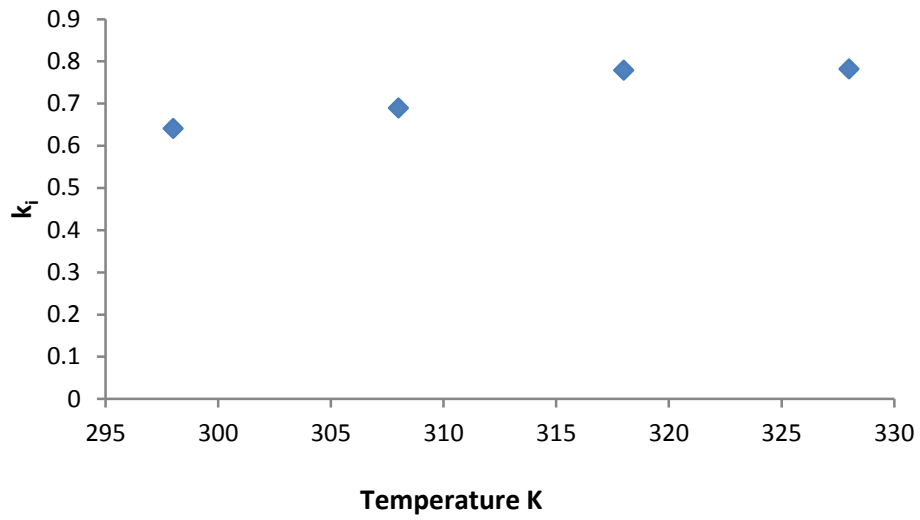


**Figure 5.4:** Natural logarithm of hexane salting-in ratio as a function of MDEA wt%

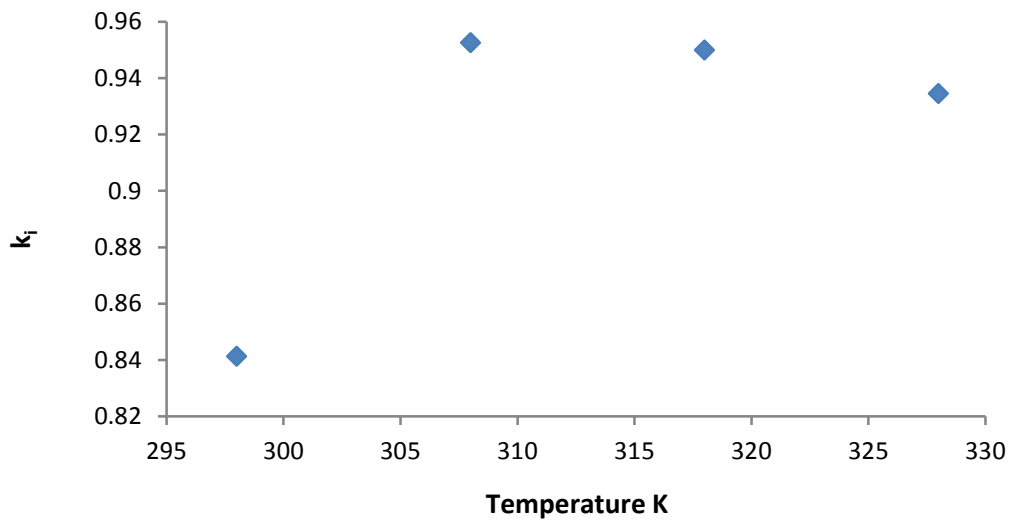


**Figure 5.5:** Natural logarithm of heptane salting-in ratio as a function of MDEA wt%

Plots for the  $k_i$  coefficients as a function of temperature are plotted in figures 5.6 & 5.7.



**Figure 5.6:** Hexane  $k_i$  coefficient as a function of temperature



**Figure 5.7 :** Hexane  $k_i$  coefficient as a function of temperature

## **5.2. GCA-EoS solubility prediction of n-hexane & n-heptane in aqueous MDEA solutions.**

GCA-EoS model [14, 35, 36] was applied to predict for the solubility of n-hexane and n-heptane in the MDEA aqueous solution.

It is an extension of the group contribution equation of state which is derived by combination of four well known equations and principles in phase equilibrium thermodynamics:

1. Van der waals EoS.
2. NRTL equation [37].
3. Carnahan starling expression for hard spheres [38].
4. Group contribution principle [39].

In group contribution method, it is assumed that the mixture doesn't consist of molecules but of functional groups, the number of the functional groups is much smaller than the number of possible molecules. The association is an attractive interaction between molecules of the same kind.

Predictions were made at 0.1-0.15 MPa. They were generally close to our results, and the comparison has been accepted, since the systems are believed weakly pressure dependent for the range up to 0.5 MPa. Tables 5.13 & 5.14 show the GCA-EoS prediction and the experimentally obtained solubility for hexane and heptane respectively, also see figures 5.8 & 5.9.



**Table 5.13:** GCA-EoS prediction of hexane mole fraction in various aqueous MDEA solutions

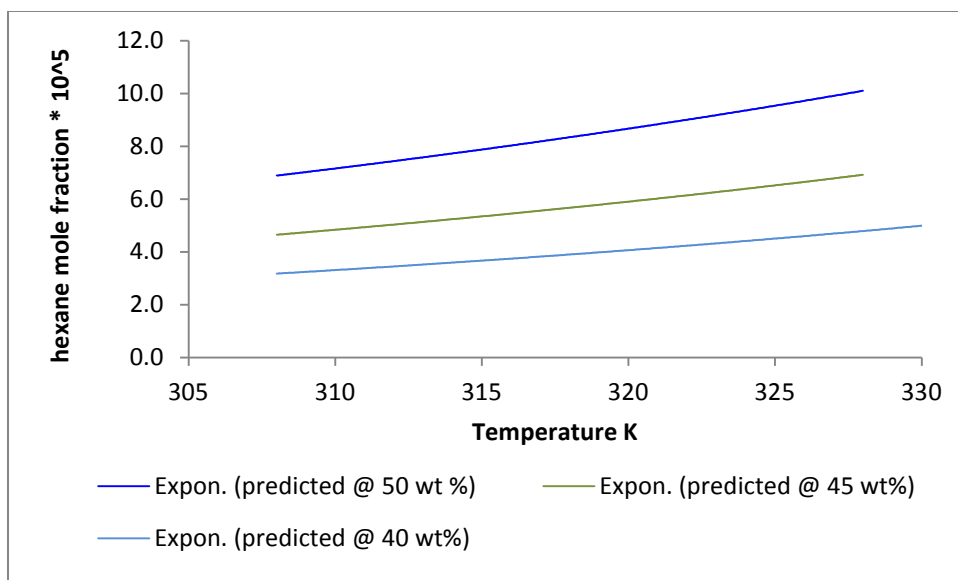
Temperature (K)	mole fraction (exp.)	Predicted mole fraction	RD*
40 wt% MDEA			
318	$2.97 * 10^{-5}$	$3.90 * 10^{-5}$	0.31
328	$3.06 * 10^{-5}$	$4.78 * 10^{-5}$	0.56
45 wt% MDEA			
308	$2.32 * 10^{-5}$	$4.65 * 10^{-5}$	1.00
318	$4.20 * 10^{-5}$	$5.67 * 10^{-5}$	0.35
328	$5.28 * 10^{-5}$	$6.92 * 10^{-5}$	0.31
50 wt % MDEA			
308	$5.88 * 10^{-5}$	$6.89 * 10^{-5}$	0.17
318	$6.94 * 10^{-5}$	$8.34 * 10^{-5}$	0.20
328	$0.757 * 10^{-4}$	$1.01 * 10^{-4}$	0.33

$$* RD = \sqrt{\frac{(\text{Experimental mole fraction} - \text{Predicted mole fraction})^2}{(\text{Experimental mole fraction})^2}}$$

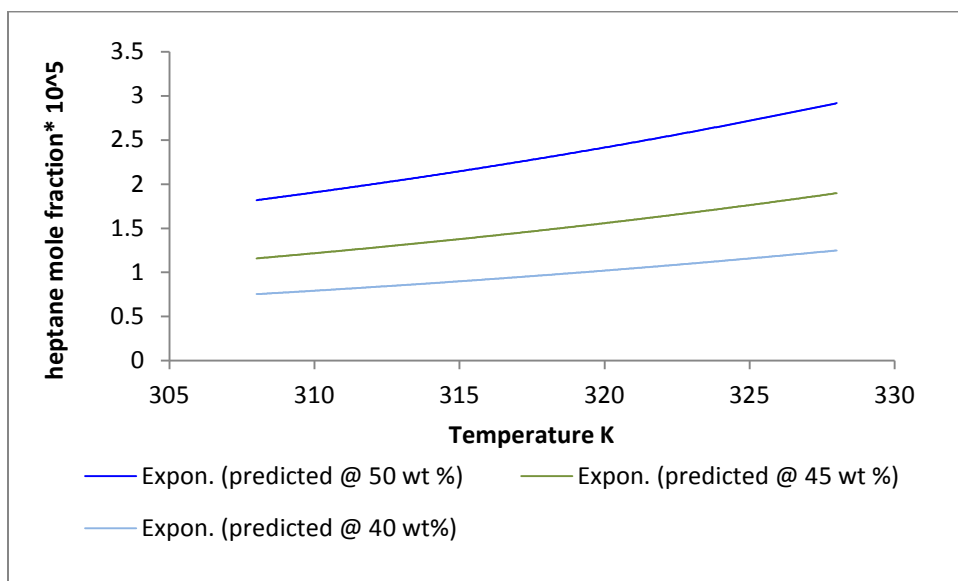
**Table 5.14:** GCA-EoS prediction of heptane mole fraction in various aqueous MDEA solutions

Temperature (K)	mole fraction (exp.)	Predicted mole fraction	RD*
40 wt% MDEA			
308	$1.42 * 10^{-5}$	$7.54 * 10^{-6}$	0.47
318	$1.12 * 10^{-5}$	$0.969 * 10^{-5}$	0.13
328	$1.13 * 10^{-5}$	$1.25 * 10^{-5}$	0.10
45 wt% MDEA			
308	$1.38 * 10^{-5}$	$1.16 * 10^{-5}$	0.16
318	$1.96 * 10^{-5}$	$1.48 * 10^{-5}$	0.25
328	$1.51 * 10^{-5}$	$1.90 * 10^{-5}$	0.26
50 wt % MDEA			
308	$2.84 * 10^{-5}$	$1.82 * 10^{-5}$	0.36
318	$2.89 * 10^{-5}$	$2.30 * 10^{-5}$	0.20
328	$4.18 * 10^{-5}$	$2.92 * 10^{-5}$	0.30

$$* RD = \sqrt{\frac{(\text{Experimental mole fraction} - \text{Predicted mole fraction})^2}{(\text{Experimental mole fraction})^2}}$$



**Figure 5.8:** GCA-EoS model prediction of hexane mole fraction in aqueous MDEA solutions



**Figure 5.9:** GCA-EoS prediction of heptane mole fraction in aqueous MDEA solutions

In general, the relative deviations between predicted and experimental values was a little high, however, they are still considered close to each other.

## 6. Conclusions and Conclusion Remarks

- The solubility of each of hexane and heptane follows the same trend as if they would be in water alone, but significantly larger values by one or two orders of magnitude due to the salting-In effect of the amine.
- Hexane and heptane solubility increased with increasing temperature and MDEA concentration.
- At the same temperature and amine concentration, the solubility of heptane is lower than the solubility of hexane; the solubility is inversely proportional to the chain length.
- Simple thermodynamic models were developed for the activity coefficient based on the obtained experiment data.
- GCA-EoS model has proved the capability to predict the solubility data of such systems.

## 7. Future work

- The present work has focused on temperature range between 298 to 328 K. However the typical absorbers operating temperature range is between 350- 473 K, [36], so it is highly recommended to study the equilibrium at these higher temperatures.
- Using a static analytic equilibrium cell with pneumatic capillary auto samplers with online gas chromatography is a necessity to cover these high temperatures and also to study solubility at elevated pressures and to give the possibility to study the effect of each of the temperature at isobaric conditions and the effect of pressure at isothermal conditions of the system under consideration.

- Extending the same work to include 25 wt% MDEA as well as other common used amines, might be the forwarded next step after this work.
- The higher paraffins as well as mixtures of different paraffins would be also investigated as a future research subject.
- Studies of the solubility of hydrocarbons in loaded amines with acid gases is necessary to better assess hydrocarbon solubilities in amine treating solutions, since loaded amine solvent with high ionic strength causes dissolved hydrocarbon concentrations to be much lower than would be expected simply on the basis of solubilities in unloaded amines, it may be low by a factor of more than ten at high loadings [5].

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## Appendix A

### Activity and Activity coefficient

The fugacity of component  $i$  in a liquid solution is most conveniently related to the mole fraction  $x_i$  by

$$f_i^l = \gamma_i x_i f_i^0$$

Where  $\gamma_i$  is the activity coefficient and  $f_i^0$  is the fugacity of  $i$  at some arbitrary condition known as the standard state.

At any composition, the activity coefficient depends on the choice of standard state and the numerical value of  $\gamma_i$  has no significance unless the numerical value of  $f_i^0$  is also specified.

Because the choice of standard state is arbitrary, it is convenient to choose  $f_i^0$  such that  $\gamma_i$  assumes values close to unity and when for a range of conditions,  $\gamma_i$  is exactly equal to unity, we say that the solution is ideal, thus the definition of solution ideality ( $\gamma_i = 1$ ) is not complete unless the choice of standard state is clearly indicated.

Either of two choices is frequently used. One of these leads to an ideal solution in the sense of Raoult's law and the other leads to an ideal solution in the sense of Henry's law.

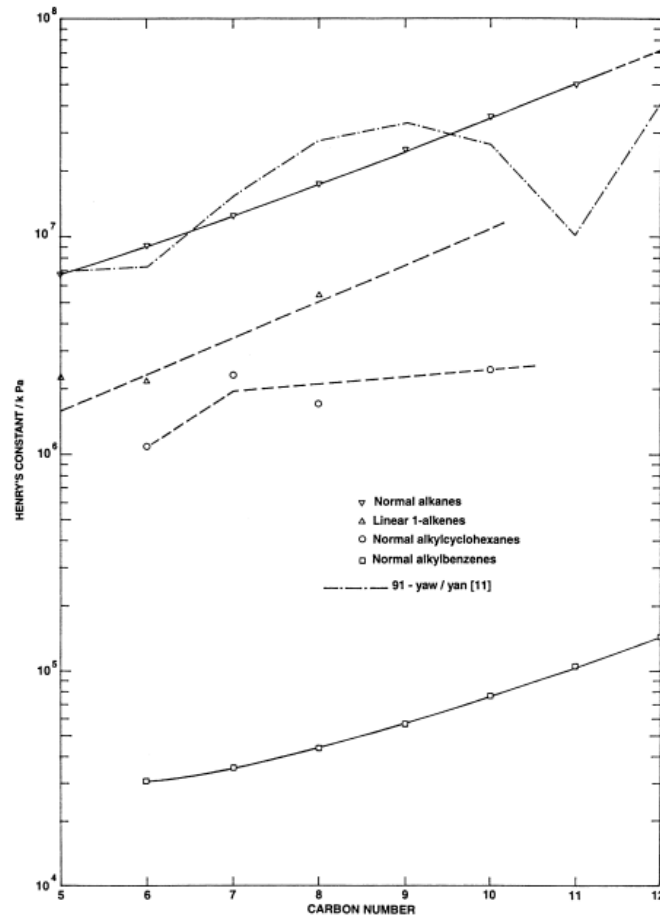
## Appendix B

### Henry's law

Application of Raoult's law to species  $i$  requires a value for  $P_i^{\text{sat}}$  at the temperature of application, and thus is not appropriate for a species whose critical temperature is less than the temperature of application. Henry's law states that the partial pressure of the species in the vapor phase is directly proportional to its liquid-phase mole fraction. Thus

$$y_i P = x_i H_i$$

Where  $H_i$  is Henry's constant, values of which come from experiment, see below figure.



Henry's constants for C5-C12alkanes & other hydrocarbons at 298.15 K [15]

## Appendix C

We consider, for convenience, that the ratio  $\frac{n_{H_2O}}{ml\ solution}$  is constant; also the MDEA ratio  $\frac{n_{MDEA}}{ml\ solution}$ , in the aqueous phase solution.

compound	Mwt (g/mol)	Density* (g/ml)
MDEA	119.19	1.0418
water	18.015	1
Hexane	86.16	0.678

\* assumed constant at the studied temperature range

The density of 50 wt % MDEA aqueous solution is calculated through

$$\bar{\rho} = \sum x_i \rho_i = x_{\text{water}} \times \rho_{\text{water}} + x_{\text{MDEA}} \times \rho_{\text{MDEA}}$$

, considering the actual weight percentage gives,

$$\bar{\rho} = 0.4997 \times 1 + (1 - 0.4997) \times 1.0418 = 1.0209 \text{ g/ml}$$

Amount of MDEA + water in 1 ml = 1.0209 g

Amount of MDEA in 1 ml = 1.0209 \* 0.4997 = 0.51014 g

Number of moles of MDEA contained in 1 ml =  $\frac{0.51014}{119.19} = 4.2801 \times 10^{-3}$ , assumed constant for convenience

Amount of water in 1 ml = 1.0209 \* (1 - 0.4997) = 0.51075 g

Number of moles of water contained in 1 ml =  $\frac{0.51075}{18.015} = 0.02835$  moles, assumed constant for convenience

Amount of hexane detected at 55 °C in 1 ml of 50 wt % MDEA aqueous solution = 0.0002127 g

Number of moles of hexane detected at 55 °C in 1 ml 50 wt % MDEA aqueous solution =  
 $2.469 * 10^{-6}$  moles

Total number of moles = 0.03262 moles

Mole fraction of hexane at 55 °C in 50 wt % MDEA aqueous solutions=  $0.7569 * 10^{-4}$ .