

**MEASUREMENT AND
THERMODYNAMIC MODELLING
OF VOLUMETRIC PROPERTIES
OF ALKANOLAMINE-WATER
MIXTURES**

A Thesis submitted for the award of the Degree

of

BACHELOR OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

by

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CERTIFICATE

This is to certify that the thesis entitled *Measurement and Thermodynamic Modelling of Volumetric properties of Alkanolamine-Water mixtures*, being submitted by **Mr. Arun Venkat** for the award of the B.Tech. Degree in Chemical Engineering is a record of bona fide research carried out by him at the Department of Chemical Engineering, National Institute of Technology, Rourkela, under my guidance and supervision. The work documented in this thesis has not been submitted to any other University or Institute for the award of any other degree or diploma.

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Abstract

The densities of aqueous binary mixtures of 2-(Methylamino) ethanol were measured at temperatures in the range of (298 to 323) K. The total concentration of the amine was restricted of 40 weight %. The experimentally measured densities were correlated as a function of temperature and mole fraction and excess molar volumes and partial molar volumes of the amine at infinite dilution in water were calculated. The derived densities of aqueous binary mixtures of 2-Piperidineethanol and Piperazine and aqueous ternary mixtures of 2-Piperidineethanol and Piperazine were also correlated as functions of temperature and concentration.

Chapter 1

Background

1.1 Introduction to the treatment of acid gases

An acid gas stream, as defined by chemical nomenclature is a stream of gas that contains significant amounts of acidic gases such as CO_2 and H_2S . With numerous process industries handling gas streams during operation and the heavy diminution of the calorific value, substantial increase in the cost of compression and transportation and various downstream processing difficulties of gas streams due to the presence of acid gases, the removal of acid gases from gas streams is of considerable importance. A variety of processes including physical and reactive absorption, carbon adsorption and cryogenic distillation have been developed for the removal of acid gases from gas streams.

1.2 Gas Treatment Techniques

Among the different separation techniques that have been developed for the removal of CO_2 , solvent absorption is the most widely employed method. On the basis of the modality of action, solvent absorption techniques are classified into physical absorption and reactive absorption.

Physical absorption makes use of the solubility of CO_2 in specific solvents such as methanol (Rectisol Process) for separation. Thermodynamic studies indicate that the solubility of CO_2 decreases with increasing temperatures. The efficiency of such operations thus, require the maintenance of very low

temperatures which necessitates the development of powerful refrigeration systems that render the operation highly energy intensive.

In reactive absorption, the solubility of CO₂ is enhanced through chemical reaction with the solvent. It is a process of interphase mass transfer enhanced by chemical reaction leading to a higher mass transfer coefficient. Besides the provision of better mass transfer, reactive absorption can be carried out at higher and more economically viable temperatures and thus is less energy intensive in comparison with physical absorption. For the removal of CO₂, the most commonly used solvents are alkanolamines.

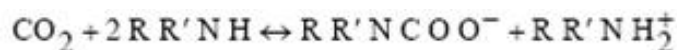
1.3 Chemistry of Alkanolamines

Amines that have two hydrogen atoms directly attached to a nitrogen atom, such as Monoethanolamine (MEA) and 2-(2-aminoethoxy) ethanol (DGA), are called *primary amines* and are generally the most alkaline. Diethanolamine (DEA) and Diisopropanolamine (DIPA) have one hydrogen atom directly attached to the nitrogen atom and are called *secondary amines*. Triethanolamine (TEA) and N-Methyldiethanolamine (MDEA) represent completely substituted ammonia molecules with no hydrogen atom directly attached to the nitrogen atoms, and are called *tertiary amines*. The amine group present in the alkanolamine provides the basicity and the hydroxyl group increases the solubility, thus reducing the vapour pressure of aqueous alkanolamine solutions. A hindered amine, such as 2-amino 2-methylpropanol (AMP), is defined as a primary amine in which the amino group is attached to a tertiary carbon atom, or a secondary amine in which the amino-group is attached to at least one secondary or tertiary carbon atom (*Sartori and Savage, 1983*).

In aqueous solutions of primary and secondary alkanolamines, the following reactions with CO₂ occur (*Danckwerts and Sharma, 1966; Danckwerts, 1979*).

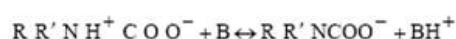
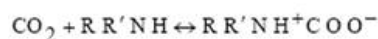
Carbamate formation:

The zwitterion mechanism originally proposed by *Caplow (1968)* and reintroduced by *Danckwerts (1979)* is generally accepted as the reaction mechanism



$\text{R}' = \text{H}$ for primary amines

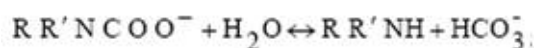
for the above reaction.



This mechanism comprises two steps: formation of the CO₂-amine zwitterion, followed by base catalyzed deprotonation of this zwitterion. Here B is a base, which could be amine, OH⁻, or H₂O (*Blauwhoff et al., 1984*). However, *Versteeg and van Swaij (1988)* argued that, for aqueous amine solutions, the contribution of the hydroxyl ion is minor due to its low concentration, and may be neglected without a substantial loss of accuracy. *Laddha and Danckwerts (1981)* considered only the amine as the base for aqueous alkanolamine solutions. Thus, the equilibrium loading capacities of primary and secondary alkanolamines are limited by the stoichiometry of the carbamate formation reaction to 0.5 mole of CO₂/mol of amine. For normal primary and secondary amines e.g. MEA, DEA etc. the carbamates formed are quite stable.

Carbamate Reversion Reaction:

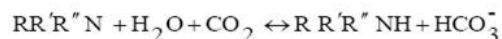
If the amine is hindered, the carbamate is unstable and it may undergo carbamate reversion reaction as follows (*Sartori and Savage, 1983*):



The above reaction means that for the hindered amines one mol of CO₂ is absorbed per mol of amine. However, a certain amount of carbamate hydrolysis occurs with all amines so that even with MEA and DEA the CO₂ loading may exceed 0.5, particularly at high pressures and higher contact times (*Sartori and Savage, 1983*).

Tertiary amines cannot form carbamates and therefore they act as chemical sink for CO₂ in aqueous solutions simply by providing basicity, the final

product being bicarbonate. Hence, the stoichiometry of the CO₂-tertiary amine reactions is 1 mol of CO₂ per mol of amine.



1.4 Choice of Solvent

The attainment of economy while achieving high degrees of separation is in general, the target set by most process industries. The regeneration of the solvent is necessary to economize the process. Despite faster reaction rates, primary amines such as MEA require more regeneration energy due to the formation of stable carbamates. Though, tertiary alkanolamines exhibit higher CO₂ equilibrium loading capacities, their slow reaction rates is indeed a matter of concern. In an attempt to minimize the drawbacks of both kinds of amine systems, a third category of solvents known as blended alkanolamine solvents has been developed. The increased CO₂ reaction rate has been demonstrated industrially by *promoting* a tertiary / sterically hindered alkanolamine solvent with a small amount of faster-reacting primary or secondary amine (*Kohl and Nielsen, 1997*).

1.5 Volumetric properties of (alkanolamine + water) system

For pure or mixed solvents, thermodynamic properties of interest in phase equilibria can be calculated from thermal and volumetric measurements. Volumetric measurements give information on how thermodynamic properties like U, H, S, G, A, and vary with pressure or density at constant temperature. Since volumetric properties of fluids are usually expressed by equations of state which are pressure explicit, it is more convenient to calculate thermodynamic properties in terms of the independent variables V and T. At constant temperature and composition, one of the Maxwell's relations can be used to render the effect of volume on energy and entropy. The other properties are then calculated from their definitions. Phase equilibria can also be completely described from volumetric data. But the equation of state

approach is often not promising due to the lack of sufficiently accurate volumetric properties of mixtures at high densities. In calculating the fugacity of a component in a mixture, volumetric data must be available, preferably in the form of an equation of state, at the temperature under consideration and as a function of composition and density (over the entire density range, starting from zero density to the density of the condensed phase including the two phase region) with an appropriate mixing rule. Our knowledge of molecular physics, is unfortunately, not sufficient to render a generic method for predicting the properties of a mixture using the knowledge of the properties of the pure components. It remains a tedious task to obtain such a huge volumetric data for liquid mixtures and very few data is available in the open literature.

An alternative technique to calculate the fugacity, hence the activity coefficient of pure or a liquid mixture is to use the excess function, a departure from the ideal behaviour. The excess functions arise due to the inequalities in intermolecular force of interactions. The present work is aimed to enhance our understanding of molecular interactions in alkanolamine + water systems using the volumetric data (generated in the present study as well as taken from open literature) in combination with the molecular theories and models. The excess molar volume is one of the fundamental thermodynamic quantities of liquid mixtures. Attempts have been made to describe along with all other excess properties of liquid mixtures with current solution theories like Flory theory, the cell model of Prigogine and co-workers, regular solution theory etc. These solution theories are almost successful for non-polar binary mixtures but mere quantitative agreement has been obtained for polar binary mixtures (*Kato and Suzuki, 1978*).

In an attempt to understand the molecular interactions and the non-ideality exhibited by polar liquid mixtures, the applications of which extend to the solution of one of the most pertinent issues of our time, the abatement of CO₂ pollution, the volumetric properties of four mixture systems, (2-Methylaminoethanol + Water), (2-Piperidineethanol + Water), (Piperazine + water) and (Piperazine + 2-Piperidineethanol + Water) have been analyzed.

1.6 Physicochemical properties of Alkanolamine-Water system

The determination of physicochemical properties of (alkanolamine + water) system at various system temperatures is highly essential for the design of gas absorption/desorption systems. Among the various physicochemical properties of aqueous alkanolamine solvents, the most pertinent ones with regard to gas treating equipment design are density, physical solubility of CO_2 in these solvents and surface tension. Since the density of the mixed amines is a strong function of relative compositions of amines, it is desirable to measure accurately the densities of blended aqueous alkanolamine solvents for a wide range of relative amine composition and temperature. The extent of utilization of membrane contactors is on the rise due to the attainment of high interfacial mass transfer areas. The surface tension of aqueous alkanolamine solutions is an important factor in the choice of the type of membrane material to be employed.

1.7 Objectives of the present work

The primary objective of this work is to measure the volumetric properties of 2-Methyl amino ethanol (MAE) - Water binary mixtures and correlate the same. The thermodynamic modelling of two other binary systems namely 2-Piperidineethanol (2-PE) - Water and Piperazine - Water will be carried out for a wide range of concentrations and temperatures. The use of MAE and 2-PE is elucidated by the sterically hindered structures of these amines. The inherent nature of piperazine to readily absorb CO_2 makes it a suitable solvent for the removal of CO_2 . Another major aim of this work is to correlate the density of aqueous ternary alkanolamine mixtures of (Piperazine + 2-Piperidineethanol + water). The thermodynamic modelling of this system is of considerable significance as it falls under the category of blended amine solvents.

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Chapter 2

Literature Survey and Thermodynamics

2.1 Literature Survey

Ever since the inception of the idea of utilizing the solvent properties of alkanolamine mixtures for the selective and reactive absorption of CO₂, significant work has been done by researchers from diverse backgrounds to study two major aspects of these mixtures, the first being the kinetics of the reaction between alkanolamine-water systems and CO₂ and the second aspect being the thermodynamics of these mixtures prior to reaction.

On the kinetics front, *Danckwerts and Sharma (1966)* and *Caplow (1968)* proposed a two step mechanism for the reaction between the alkanolamine mixture (consisting of normal primary or secondary alkanolamines) and CO₂ wherein, the amine first forms a carbamate which exists as zwitterion followed by its base catalyzed deprotonation. In 1981, *Laddha and Danckwerts* considered only the amine as the base, which lead to the conclusion that the average equilibrium loading capacity of the alkanolamine system was restricted to about 0.5 mol of CO₂/mol of alkanolamine mixture. In 1983, *Sartori and Savage* investigated the kinetics of sterically hindered primary and secondary amines and tertiary amines. Their study of sterically hindered primary and secondary amines suggested the possibility of the reversion of the formed carbamate due to its sterically hindered structure. With regard to tertiary amines, the formation of carbamates was ruled out which implied

that these amines merely provided the basicity required for the absorption of CO_2 . A consequence of this investigation was that it provided a new insight about the choice of solvents for absorption.

The thermodynamic aspect deals with the measurement of transport and physicochemical properties so as to understand the nature of the non-ideality exhibited by the alkanolamine mixtures. Thermodynamic correlations have widely been employed to accurately determine the values of transport and physicochemical properties of solutions over a range of concentrations and temperatures. The most commonly used thermodynamic correlation in the study of the volumetric properties of aqueous alkanolamine solutions is the Redlich-Kister correlation. Over the last two decades, extensive studies have been carried out on the properties of aqueous solutions of sterically hindered amines. *Xu et al (1992)* investigated the physicochemical properties of aqueous solutions of 2-piperidineethanol, a sterically hindered secondary amino alcohol. *Maham et al (1995)* extended their investigation of the volumetric properties of aqueous DEA solutions by computing the partial volume at infinite dilution and studying the molar expansivity of liquid mixtures. *Henni et al (2003)* measured the volumetric properties and viscosities of aqueous AMP mixtures which have been utilized for the experimental standardization of this work. In 2006, *Mandal and Paul* measured the properties of aqueous blends of (Piperazine + 2-piperidineethanol). In the same year, *Samanta and Bandopadhyay* measured the properties of (Piperazine + 2-Amino-2-methyl-1-propanol) and (Piperazine + N-Methyldiethanolamine). The density data of the aqueous solutions of (Piperazine + AMP) were correlated using a different approach so as to avert the measurement of the molar volumes of the pure fluids. *Li et al (2007)* presented the volumetric properties of aqueous solutions of 2-Methylaminoethanol.

2.2 Thermodynamics

A major aspect of the present work is the thermodynamic modelling of alkanolamine-water systems. Two models have been considered for this purpose. The conventional model proposed by Redlich and Kister correlates the excess of volume, a measure of non-ideality of mixtures as a function of temperature and concentration of the individual constituents. An important aspect of this model is that it considers the pure molar volumes of the con-

stituent fluids at the system temperature. This mandates the existence of the pure components of the mixture in the fluid state at the working temperature of the system.

With regard to the amine treatment of gaseous stream for the removal CO₂, amines like piperazine have been shown to possess good absorption capabilities. The present work defines the working temperature range of the mixture systems between 288 K and 356.65 K. As piperazine exists in the solid state in this range of temperatures, an alternative model was utilized to correlate the density of binary systems of (piperazine + water) and ternary mixtures of (2-Piperidineethanol + Piperazine + Water). The set of equations in section 2.2.1 are those used in the Redlich-Kister model and those in 2.2.2 are employed in the alternative model.

2.2.1 The Redlich-Kister Model

$$V_m = V^E + \sum x_i V_i^0 \quad (2.1)$$

$$V^E = \sum_{j,k=1, j \neq k}^n V_{jk}^E \quad (2.2)$$

$$V_{jk}^E = x_j x_k \sum_{i=1}^n A_i (x_j - x_k)^i \quad (2.3)$$

$$A_i = a + b(T/K) + c(T/K)^2 \quad (2.4)$$

$$V_m = \frac{\sum_{i=1}^n x_i M_i}{\rho_m} \quad (2.5)$$

Where V_m is the molar volume of the mixture; V_E is the excess volume of the mixture; x_i is the mole fraction of the individual component; V_i^0 is the pure fluid molar volume at system temperature; A_i is a temperature dependent correlation parameter; a,b,c are temperature and concentration independent parameters.

The last equation mentioned above, represents the most general way of computing the molar volume of a mixture from the experimental density data. This equation has been employed to compute the independent correlation

parameters through a computer programmed optimization, enunciated in later sections.

2.2.2 The Alternative(virial-type) Model

$$\rho = \sum_{i=1}^n A_i + B_i W^i (T/K) + C_i W^i (T/K)^2 \quad (2.6)$$

$$W = \sum_{i=1}^n S_i w_i \quad (2.7)$$

Where, ρ is the density of the mixture; T is the mixture temperature; A, B and C are correlation parameters; W is the total mass fraction of the amine in the mixture; S_i is the weighting factor of each amine; w_i is the mass fraction of each amine.

2.3 List of Symbols

Symbol	Meaning
A	Correlation coefficient
a	Correlation coefficient
B	Correlation coefficient
b	Correlation coefficient
C	Correlation coefficient
c	Correlation coefficient
W	Mass fraction of total amine
w_i	Mass fraction of individual amine
x	Mole fraction
VE	Excess molar volume
S	Weighting factor of amine
ρ	Density
V_i^∞	Partial Molar volume at infinite dilution

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Chapter 3

Experimental Work

3.1 Experimental Setup and Procedure

In an attempt to measure the volumetric properties of binary mixtures of 2-Methyl-amino ethanol (MAE) -Water at various concentrations and temperatures, a standard solution of MAE with 95% (w/w) purity manufactured by Merck Chemicals was used. The aqueous mixtures were made using Degasified Reverse Osmosis water. Prior to the generation of density data, the experimental setup had to be standardized and for this purpose, a standard solution of 2-Amino-2-methyl - 1-propanol (AMP) with 98% (w/w) was utilized. All mixtures were made in 50 ml volumetric flasks manufactured by Merck Specialities Limited. The densities of the various mixtures were measured using pycnometers of capacity 25.3 ml manufactured by Borosil Glass Works Limited. The temperature of the mixtures was maintained using a PID controlled programmable circulator with a capacity of 13 litres and operating temperature range of (-40 to 200) $^{\circ}\text{C}$ manufactured by PolyScience Inc., USA. An offset of 0.01°C was achieved during temperature control. Upon the attainment of satisfactory standardization results (see table 3.2.3), the densities of aqueous MAE mixtures with concentrations (10%, 17.8%, 25% and 40%) (w/w) within the temperature range of (298 to 333) K were measured. The weights of the pycnometers were measured using an analytical balance with an accuracy of 0.0001 g. The experimental observations are tabulated in section 3.2.

3.2 Observations

Table 3.1: Standard Solution Properties

Solution	Mol. Weight	Purity	Density	Molar Volume
2-Amino-2-Methyl Propanol	89.14	95%	0.932	95.644
2-Methyl Amino Ethanol	75.11	98%	0.94	79.904
Water	18.01	100%	0.997	18.064

Table 3.2: Pycnometer¹ Specs.

Property	Value
Volume	25.3 cc
Weight	20.232 g

Table 3.3: Standardization Data

Solution	Temperature	Measured Density	Actual Density ²	%Error
Pure AMP	313 K	920.2	919.65	0.06%
Pure MAE	303 K	931.56	932.26	-0.08%

Table 3.4: Measured Density Data

Solution Strength(w/w% MAE)	Temperature	Density(kg/m ³)
17.8	308 K	993.12
17.8	318 K	988.6
10	298 K	996.04
10	303 K	995.06
10	308 K	992.82
10	313 K	991.26
10	318 K	989.17
10	323 K	986.77
25	298 K	997.63
25	303 K	996.39
25	308 K	992.97
25	313 K	990.29
25	318 K	987.61
25	323 K	981.01
40	298 K	990
40	303 K	989.7
40	308 K	986.1
40	313 K	984.06
40	318 K	979.5
40	323 K	976.7

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Chapter 4

Modelling of Binary Systems

4.1 MAE - Water system

Two sets of density data, one measured and the other derived from *Li et al (2007)* were used for the mathematical modelling of the MAE-Water binary system. The total concentration (mole fraction) range for the model was from 0 to 0.8009 and the total temperature range was from 298.15 K through 323.15 K. The Redlich-Kister model (see 2.2.1) was used for the correlation of the molar volume of the binary mixtures as a function of concentration and system temperature. The temperature dependent parameters in the Redlich-Kister correlation were computed using the non-linear least squares optimization routine (lsqnonlin) in MATLAB 7.0. The results of the simulation of this system are presented in the following section.

4.2 2-Piperidineethanol - Water system

The density data required for the modelling of this system were derived from *Xu et al (1992)*. The concentration (mole fraction) range of 2-PE considered for correlation was from 0.065 to 1.0 and the total temperature range was from 298.15 0K through 356.65 0K. The Redlich-Kister methodology adopted previously was employed

in this system as well. The results yielded from the simulation of this system are tabulated in section 4.4.

4.3 Piperazine - Water System

The density data for this combination were derived from *Samanta and S.S. Bandyopadhyay (2006)*. As piperazine exists in the solid state till about 106 °C which is well past the working range of this work and the Redlich-Kister correlation requires the knowledge of the molar volumes of the pure fluids at different mixture temperatures, a different approach (see 2.2.2) was adopted for the correlation of the density of the aqueous mixtures. Presented in section 4.4, are the results of the simulation of the system of this combination.

4.4 Results

Figure 4.1: Variation of Excess Volume (V_E) with X_{MAE}

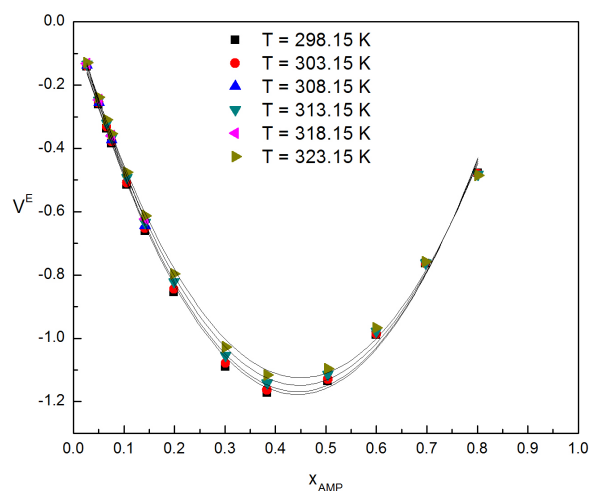


Table 4.1: R-K Parameters for MAE-Water System

Variables	Parameters	Value
A0	a	-0.286878522
	b	-0.033549644
	c	6.44708E-05
A1	a	0.323895604
	b	0.023078845
	c	-5.89036E-05
A2	a	-0.10953746
	b	0.007370155
	c	-1.18132E-05
Average	Correlation Error	0.1167%

4.5 Discussion

For the MAE - Water binary mixture system, the density data were correlated with an average error of correlation of 0.1167%. The excess volume versus MAE concentration plot (figure 1.1) reveals that the mixture tends towards minimal deviation from ideality at either very low concentrations of MAE or at very high concentrations. With respect to temperature, deviation from ideality increases with increment in system temperature. Figure 1.2 indicates a gradual fall in mixture density with incremental MAE concentration and temperature. The trend with respect to incremental MAE concentration is explained by the fact that the density of MAE is lesser than that of water. Volumetric expansion accounts for the fall in mixture density with increasing system temperatures.

For the binary mixture system of (2-PE + Water), a correlation error of 0.034 % was obtained. The trend observed in figure 1.4(fall in

Table 4.2: Partial Molar Volume of MAE at inf. dilution in Water

Temperature	Partial Molar Volume at Infinite dilution (V_i^∞)
298.15	74.74068
303.15	75.16715
308.15	75.60205
313.15	76.04541
318.15	76.50171
323.15	76.96662

mixture density with increasing temperature) is consistent with first principles. The average absolute error of correlation of the PZ-Water binary system was found to be 0.145%. The trend observed in figure 1.6 can be explained using the fact that the density of piperazine, by virtue of its solid state at the specified temperature range is greater than that of water. Hence with increasing concentrations of PZ, an increase in mixture density is observed.

Table 4.3: R-K Parameters for 2-PE - Water System

Variables	Parameters	Values
A0	a	7.514257956
	b	-0.031122704
	c	-2.29092E-06
A1	a	-48.25268454
	b	0.312928117
	c	-0.000482829
A2	a	92.37449935
	b	-0.618046214
	c	0.001009724
Average	Correlation error	0.034%

Table 4.4: Partial Molar Volume of 2-PE at inf. dilution in water

Temperature	Partial Molar Volume at Infinite Dilution in Water (V_i^∞)
298.15	121.6875315
303.75	123.6572002
308.85	123.9193138
313.85	124.2549849
323.15	125.049251
331.05	125.9397264
341.45	127.5164918
341.85	127.5807628
356.65	130.4124662
357.35	130.5695817

Table 4.5: Correlation Parameters for PZ -Water System

Parameter	Value
S	0.000423941
A0	0.724561228
B0	0.002080411
C0	-3.90836E-06
A1	2.709724604
B1	0.847037197
C1	-0.002296271
A2	-2.112849951
B2	30.53949237
C2	20.05598363
Average Correlation error	0.0145%

Figure 4.2: Variation of MAE Mixture Density with Temperature

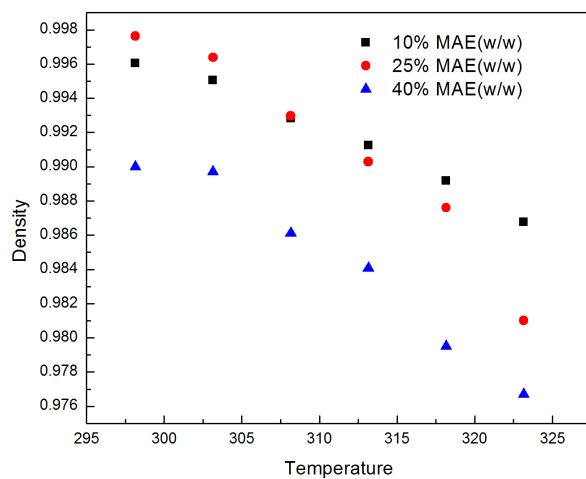


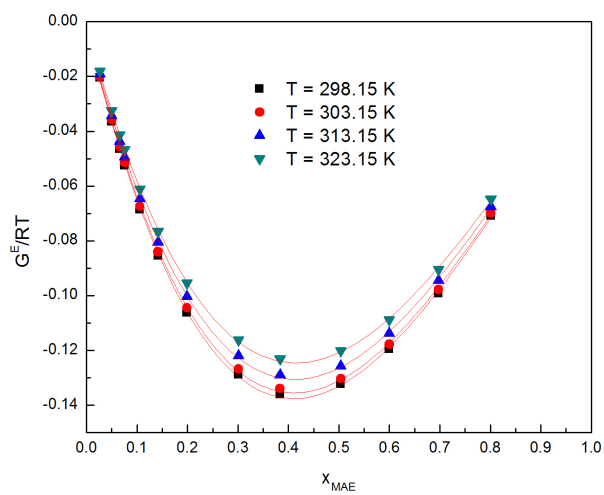
Figure 4.3: Variation of G^E/RT with MAE concentration

Figure 4.4: Variation of 2-PE - Water mixture density with Temperature

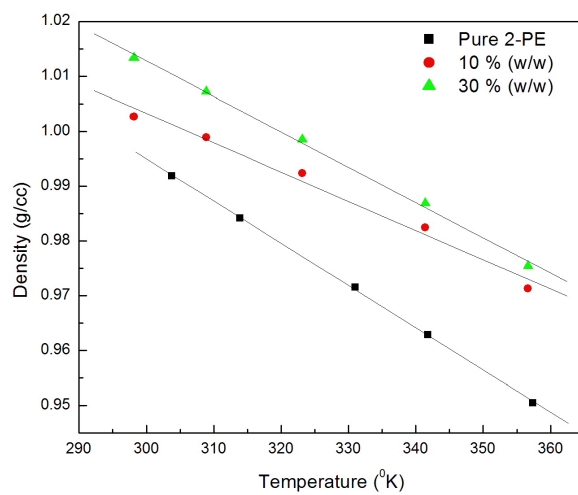


Figure 4.5: Variation of PZ - Water mixture density with Temperature

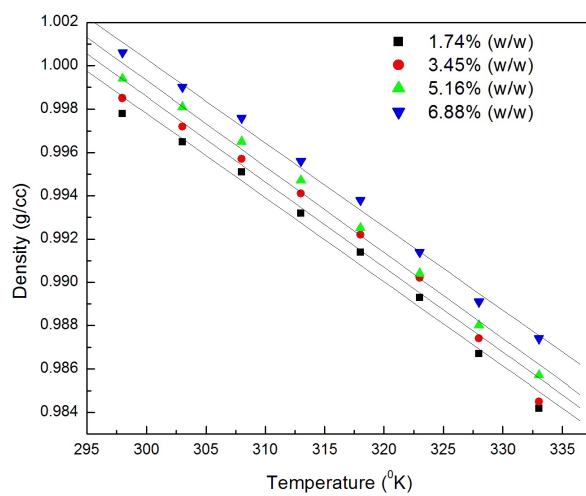
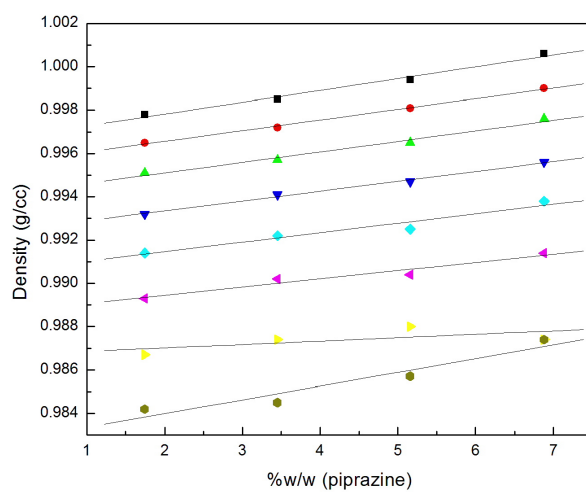


Figure 4.6: Variation of PZ - Water mixture density with PZ concentration



Bibliography

- [1] Juelin L, Mundhwa M, Paitoon T, Henni A; Volumetric Properties, Viscosities, and Refractive Indices for Aqueous 2-(Methlyamino)ethanol Solutions from (298.15 to 343.15) K, *J. Chem. Eng. Data* **2007**, 52, 560-565.
- [2] Samanta A, Bandyopadhyay S; Density and Viscosity of Aqueous Solutions of Piperazine and (2-Amino-2-methyl-1-propanol + Piperazine) from 298 to 333 K, *J. Chem. Eng. Data* **2006**, 51, 467-470.
- [3] Xu S, Wang Y, Otto F, Mather A; Physicochemical properties of 2-piperidineethanol and its aqueous solutions, *J. Chem. Eng. Data* **1992**, 37(4), 407-411.

Chapter 5

Modelling of Ternary systems

5.1 Piperazine - 2-Piperidineethanol - Water mixtures

The experimental data for the modelling of this system was derived from *Paul and Mandal (2006)*. As piperazine is a solid up to a temperature that is beyond the working temperature range of the current system, the alternative model described in Chapter 2 was considered. The simulation results have been presented in the following section.

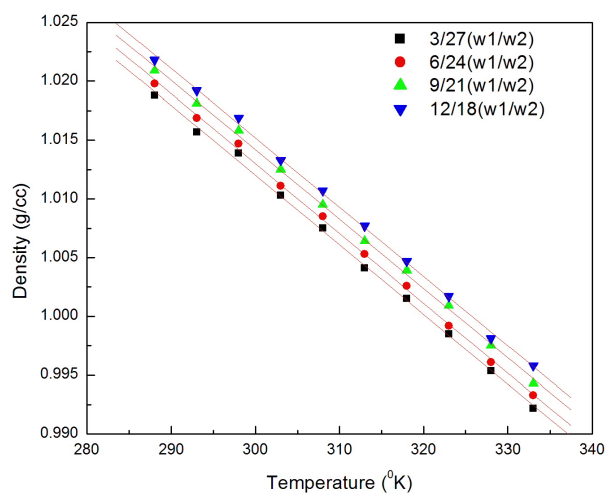
5.2 Results and Discussion

The density data were correlated using the `lsqnonlin` optimization routine in MATLAB 7.0. The average absolute error in correlation was calculated to be 0.0178%. The trend observed in *figure 5.1* is consistent with the fact that density decreases with increasing temperature due to volumetric expansion.

Table 5.1: Estimation of Correlation Parameters

Parameter	Value
S1	0.018382485
S2	0.012990383
A0	1.083566876
B0	-4.87058E-05
C0	-8.46311E-07
A1	1.139779551
B1	0.027501687
C1	-6.99298E-05
A2	0.630428074
B2	0.053598565
C2	0.004360658
Average Correlation Error	0.0178%

Figure 5.1: Variation of mixture density with temperature at various amine concentrations



Bibliography

- [1] Paul S, Mandal B; Density and Viscosity of Aqueous Solutions of (2-Piperidineethanol + Piperazine) from (288 to 333) K and Surface Tension of Aqueous Solutions of (N-Methyldiethanolamine + Piperazine), (2-Amino-2-methyl-1-propanol + Piperazine), and (2-Piperidinethanol + Piperazine) from (298 to 323) K, *J. Chem. Eng. Data* **2006**, 51, 2242-2245

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