PHENOMENA OF MIXING ETHYLENE GLYCOL /WATER SYSTEM FOR FREEZING POINT MEASUREMENTS

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by
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Certification

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Abstract

Experimental work is carried out to find the minimum value of freezing point that can be obtained for Ethylene Glycol – water solution. 5% wt. of methanol is added to the Ethylene glycol – water solution to investigate its effect on freezing temperature.

The experiments also included determination of boiling temperature of Ethylene Glycol – water solution with and without methanol at different ethylene glycol concentrations from 0 to 100 weight per cent at temperature 20°C and 1 atmosphere pressure.

The results revealed that increasing Ethylene Glycol percent from 0 to 55% leads to decrease in the freezing point. Above 80% the Ethylene Glycol cause a rise in freezing temperature.

Also the presences of 5% methanol decreases the freezing temperature for all values of ethylene glycol percents, while it cause little increase in the boiling temperature.

The freezing point and the boiling point that were measured experimentally are substituted in Lielmezs model to obtain the reduced temperature (T*):

$$T^* = \frac{\frac{T_F}{T} - 1}{\frac{T_F}{T_{NB}} - 1}$$

The range of solution temperature that investigated is from -130°C to 290°C.

Empirical correlations for estimating the freezing and boiling temperature for the solutions are obtained with error percents ranging from 2.25% to 9.9%. The results are compared with works of other authors that investigated other components. The correlations obtained are:

For Ethylene Glycol – water the freezing temperature is given by:

$$TF = -3.06189\times 10\wedge(-08\times C^{5}) + 3.806444\times 10\wedge(-05\times C^{4}) + 0.000274\times C^{3}$$
$$-0.0302\times C^{2} + 0.185096\times C - 0.744554$$

For Ethylene Glycol – water – Methanol the freezing temperature is given by:

$$TF = -5.1\times 10\wedge^{-10}\times C^{6} + 1.31\times 10\wedge^{-08}\times C^{5} + 1.69\times 10\wedge^{-05}\times C^{4} - 0.00173\times C^{3}$$
$$+0.048945\times C^{2} - 0.92848\times C + 0.294131$$

For Ethylene Glycol – water the boiling temperature is given by:

$$T_{B} = -12.2722\times 10\wedge(-09\times C^{6}) + 10.82779\times 10\wedge(-07\times C^{5}) + 10.82779\times 10\wedge(-05\times C^{4})$$
$$+0.000359\times C^{3} - 0.044008\times C^{2} + 1.729584\times C + 90.61662$$

For Ethylene Glycol – water – Methanol the boiling temperature is given by:

$$T_{B} = 2.17\times 10\wedge^{-07}\times C^{5} - 4.5\times 10\wedge^{-05}\times C^{4} + 0.003288\times C^{3} - 0.09532\times C^{2} + 1.160554\times C$$
$$+98.53581$$

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Notations

Symbols

a	parameter of the attractive forces between the molecules
b	parameter of the size of the molecules (hard body term)
Ωa, Ωb	Constants in eq. (2.3)
K_B	Boiling Point Elevation Constant. (°C /m)
K_F	Freezing-Point Depression Constant (°C /m)
M	molality of solution. (m)
P	Pressure (kg/cm^2)
P_C	Critical Pressure (kg/cm^2)
R	molar gas constant **(**joule/K. mole**)**
T*	Reduced Temperature (dimensionless)
T	Temperature (°C)
T_C	Critical Temperature (°C)
ΔT_B	Boiling Point Elevation (°C)
ΔT_F	Freezing-Point Depression (°C)
T_{NB}	Normal Boiling Temperature (°C)
V	Volume (m^3)

Subscripts

F	Freezing
B	Boiling
C	Critical

Abbreviations

EG	Ethylene Glycol
AF & CS	Antifreeze and Coolants
PET	Polyethylene Terphthalate
NB	Normal boiling point

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Chapter one

Introduction

Antifreeze is a liquid, which prevents freezing when mixed with water in cooling system. It also should provide year-round protection of the cooling system from rust and corrosion and does not harm rubber hoses and plastics [1].

Antifreeze is used to protect liquid-cooled internal-combustion engines to prevent freezing during the winter and boil-over during the summer and consequently damage to the engine water jacket and radiator.

Antifreeze and coolants contain mixture of additives designed to meet many requirements such as introducing of more efficient engines operating at higher temperatures, the use of light metals and plastics in the cooling system, and a growing concern relative to the toxicological and ecological aspects of the antifreezes and coolants themselves.

Water–ethylene glycol formulations are preferred AF and Cs (antifreeze and coolants) because they provide year-round, cost effective, freezing, boiling, and corrosion protection. In addition, they are chemically stable, and compatible with plastics used in the cooling system.

The essential requirements for acceptable antifreeze-coolant materials are :- (1) ability to lower the freezing point of water to the lowest winter operating temperatures likely to be encountered. (2) Incapability of imparting any undesirable properties to water that would interfere with its primary function of efficient engine cooling. (3) Satisfactory chemical stability and ability to protect cooling-system metals from the corrosive action of water. Additional desirable characteristics of antifreeze materials are: availability at low cost, minimum effect on rubber hose connections, low partial pressure, and freedom from unpleasant odor, minimum effect on automobile finishes, low coefficient of expansion [4].

Factors which will influence the future of antifreeze – coolant developments increase in heat loads, increased service life, and the increased use of aluminum in equipments manufacturing [4].

Antifreeze keeps the water in a car's radiator from freezing because the ethylene glycol molecules get in the way when water tries to crystallize into ice. Because it is more difficult for the ice crystals to form, the water freezes at lower temperature than if the glycol molecules were not present [2].

One function of coolant is to lower the freezing point of the mixture in the system. Another function of coolant is to raise the viscosity (thickness) of the coolant mixture. Higher viscosity mixtures will reduce cavitations at water pump.

The aim of this research is to study the effect of Ethylene Glycol on the freezing point. A 5% of methanol is added to different Ethylene Glycol-Water concentrations to investigate the lowering of freezing point and find generalized concentration -temperature correlation.

Also it is aimed to use the model of Lielmezs equation to determine reduced temperature T* from experimental boiling temperature and freezing temperature.

Chapter Two

Review of Literature and Theoretical Background

2.1 Antifreeze and Coolant

An antifreeze also known as engine coolant is a liquid substance that is added to a liquid – usually water to lower its freezing point and raises its boiling point which circulating through an internal combustion engine to cool it. It provides protection from rust, leaks, corrosion, and does not harm rubber hoses and plastics. In addition, it must be relatively low in cost, chemically stable, does not have unpleasant odor, and does not affect the cooling finishes **[1, 7, 9]**.

2.1.1 Antifreeze-Coolants Requirements and Compound

An acceptable antifreeze - coolant must specify many requirements. The most essential of these are: *(1)* an effective heat exchange fluid *(2)* capable of providing freezing and boiling protection, *(3)* capable of protecting metals against corrosion; *(4)* compatible with plastics and elastomers; *(5)* chemically stable at low and high temperatures; *(6)* compatible with hard water; *(7)* low foaming; and *(8)* ecological and toxicologically acceptable **[8, 2]**.

Because of its universal availability, cheapness, and high specific and latent heats, water was selected early as the coolant for most systems. Despite its valuable characteristics, water has two serious disadvantages: *(1)* its considerable corroding action on metals; and *(2)* the fact that on freezing, which can easily occur in the winter, it undergoes a volume expansion equal to about 9% of original volume, which is enough to cause rapture of the cooling system or even the engine block (in automobiles). So that, many materials found its way to appear through this problem to substitute water completely or partially [5].

Antifreeze - Coolant compounds used in the past have fallen into disuse for failure to meet one or more of these requirements. The low specific heats and thermal conductivities of mineral oils and kerosene plus their high viscosities at low temperatures called for a specially designed cooling system, and this discouraged their using in automobiles. Since the heat capacity of these materials is very low, cars using them as coolants tended to over heat in warm weather. Additional disadvantages of kerosene and lubricating oils are unpleasant odor, flammability, and undesirable effect on rubber hoses [5, 9].

In organic salts, such as sodium, calcium, and magnesium chlorides, although they are effective freeze-point depressants for water and very expensive, are too corrosive for satisfactory use in automotive cooling systems. Salt brines, however, can be used satisfactoly where operating conditions are less severe such as in ice making factories. There are no generally recognized inhibitor systems for salt–based antifreezes that will protect the variety of metals found in cooling systems. Solder and aluminum are practically difficult to protect. If the inhibitor concentration becomes depleted, these solutions become much more aggressive than the organic-based antifreeze. Another disadvantage of the brine antifreeze is that it has little effect on the boiling point [9].

Sugar and honey solutions, in addition to being thermally unstable, require such high concentrations to obtain even moderate freeze-point depression that the viscosity of the coolant is too high at low temperatures. The same disadvantages have disqualified glycerol for automotive use [9]. The first widely used automobile antifreeze was ethanol. But, at the other end of temperature scale, it did not raise the boiling point of water [28]. Ethanol and isopropyl alcohol, along with diethylene glycol are less effective and more expensive than methanol as freeze-point depressants. Diethylene glycol also dissolves paints [10]. In 1930, Methanol was widely used an antifreeze. While effective in preventing the coolant from freezing, its low boiling point and low specific heat capacity led to considerably less cooling than water alone. Also the concentration of methanol would tend to be reduced over time due to its greater tendency to evaporate than the water with which it was mixed. [21]

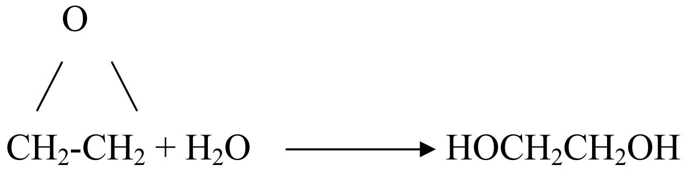
Methanol has no taste or color but it does have a slight odor and it is highly toxic. It is used as a fuel and antifreeze, and to make formaldehyde. It is the simplest alcohol compound, comprised of one carbon atom, one oxygen atom and four hydrogen (CH_3OH). It also referred to as wood alcohol, carbinol and methyl alcohol. [20, 22] In Alaska, 1989, methanol is used as antifreeze and deicer, and it is usually mixed with water. [24]

Propylene glycol has been used in pharmaceuticals, ice-cream, make-up, and soft drinks. Propylene glycol is not car antifreeze. Car antifreeze is ethylene glycol, which is highly poisonous and must never be used in a well with potable water. Using the water – propylene glycol mixture does two things for the motor: first it keeps the motor from freezing during storage second; it increases the lubricating properties of the water. The increased lubricity helps maintain longer bearing life. [24]

2.1.2 Ethylene Glycol as "Permanent" Antifreeze – Coolant

Ethylene glycol ($HOCH_2CH_2OH$) is odorless, practically odorless, low-volatility, low-viscosity, hygroscopic liquid. It is completely miscible with water and many organic liquids. [51]

It is the simplest and most important of glycols. It was first prepared in 1859 by Wurtz but did not become commercially important, however until 1925 when it was manufactured in large-scale quantities via the hydration of ethylene oxide:



$$CH_2\text{-}CH_2 + H_2O \longrightarrow HOCH_2CH_2OH$$

The major source of ethylene glycol today is the hydration of ethylene oxide. Smaller quantities are obtained by the reaction of product, glycolic acid, in the presence of a CuO-MgO catalyst at high temperatures and pressures. [11, 12]

$HCHO + CO + H_2O \longrightarrow CH_2OHCOOH$

$CH_2OHCOOH + ROH \longrightarrow CH_2OHCOOR + H_2O$

$CH_2OHCOOR + 2H_2 \longrightarrow HOCH_2CH2OH + ROH$ [11, 12]

Although from 1925 to 1927 the quantities available were small. In 1929, practically every manufacturer of dynamite in the United States was using ethylene glycol. The second commercial use for ethylene glycol was as an antifreeze material for automobile cooling system in 1930 by National Carbon Company, Inc. [5]

During 1950, methanol increased its market penetration annually to high point, after which it gradually decreased in use. At the same time, the term "permanent" become associated with ethylene glycol antifreeze-coolant because it's high boiling point and flash point reduced the risk of coolant loss when the cooling system under goes over heating. Moreover, the vapors from a hot glycol solution contain mostly water; so that, the Antifreeze base is not lost by evaporation and freezing protection is maintained [16]. In the years 1946-1960 the antifreeze market settled on two major products, methyl alcohol and ethylene glycol; by 1960 the glycol had increased its share of the market to over 90% [9, 5]. In 1953, however, some automobile companies began installing ethylene glycol antifreeze on the assembly lines, and this practice increased until, in late 1962, methanol was no longer used. All antifreeze put in new cars at the factory was ethylene glycol-based and most of car companies began putting ethylene glycol coolants in all their new cars all year round. [16]

Table 2.1 shows the best available information on consumption of ethylene glycol antifreeze in United States. This includes data Compiled by the chemical specialties manufactures association and industrial estimates.

One of the top 50 chemicals produced in 1995, was ethylene glycol. Ethylene glycol can be found in hydraulic brake fluids, adhesives, printer's inks, and wood stains. The chemical is also used to de-ice airplanes, synthesize safety explosives, and is used in softening agents for cellophane. It is used in the manufacture of polyester films and fibers, plasticizers, and elastomers. It is also an intermediate in the synthesis of PET (polyethylene terphthalate), the polymer used in soft drink bottles. However, the great need of ethylene glycol lies mainly in the great number of automobiles on the road, not only in the United States, but also across the globe. This chemical is mainly used as the active ingredient in antifreeze. In antifreeze, ethylene glycol decreases the freezing point and increases the boiling point of the fluids in a vehicle's radiator, thus preventing over boil and freezing. [50]

Table2.1 united states consumption of E.G antifreeze [9]

year	Consumption millions of liters
1965	534.4
1966	528.8
1967	538.2
1968	576.8
1969	618.8
1970	672.2
1971	731.3
1972	759.6
1973	789.2
1974	707.4
1975	824
1977	829.3
1978	874.3
1979	891.7
1980	909.5

Water –Ethylene glycol formulations are today's preferred antifreeze - coolant and the most popular one. Several of other substances are acceptable for special applications. Some of the physical properties of these compounds along with water are given in table 2.2 [4]

Table 2.2: Physical properties of acceptable antifreeze compounds [2]

Property	Water	Methanol	Ethanol	2-propanol	Glycerol	Ethylene glycol	Diethylene glycol	Propylene glycol
Molecular weight	18.016	32.04	46.07	60.09	92.09	62.07	106.12	76.09
Specific gravity,20/20°C	1.00	0.7924	0.7905	0.7861	1.2636	1.1155	1.1184	1.0381
Specific heat, J/gk	4.1742	2.51	2.43	2.7	2.41	2.40	2.31	2.51
Freezing point, °C								
Pure	0	-97.7	-117.3	-88.4	17.0	-13.3	-8.3	Sc
50% solution		-44.5	-30.6	-22.5	-22.0	-36.6	-26.1	-33.0
Boiling point, °C	100	64.5	78.4	82.3	290.0	197.3	244.8	187.2
Vapor pressure at 20°C, kPa	2.3322	12.8	5.87	4.39	0.000046	0.016	<0.001	0.024
Flash point, open-cap, °C		15.6	18.9	15.6	176.7	115.6	143.3	107.2
Viscosity at 20°C, mPa s(=Cp)	1.01	9.59	1.19	2.37	1499	20.9	35.7	60.5

2.1.3 Freezing Point of Antifreezes

For dilute ideal solutions of nonelectrolytes, the depression of the freezing point of solvent brought about by addition of a solute is proportional to the molar concentration of the solute and independent of the nature of the solute. $\Delta T_F = K_F \times m$; Where ΔT_F is freezing-point depression; K_F is molal freezing-point lowering of the solvent (1.86°C m^{-1}. for water); m is molality of solution. Although this equation is strictly applicable to dilute ideal solutions, fair results can be obtained by its use for nonelectrolyic antifreezes. However, the exact determination of the freezing points of antifreeze solutions must be done experimentally. The results of determinations on antifreeze solutions of commercial importance are given in figure (2.1). All of these materials, with the exception of isopropyl alcohol, are capable of giving protection to -50°F., the lowest atmospheric temperature likely to be encountered. For unit volume, the order of decreasing effectiveness for commercial antifreeze materials is methanol, ethylene glycol, ethyl alcohol, propylene glycol, glycerol, and isopropyl alcohol [9, 5].

An accurate method for freeze-point determination has been developed by the American Society for Testing and materials (ASTM) [9, 47].

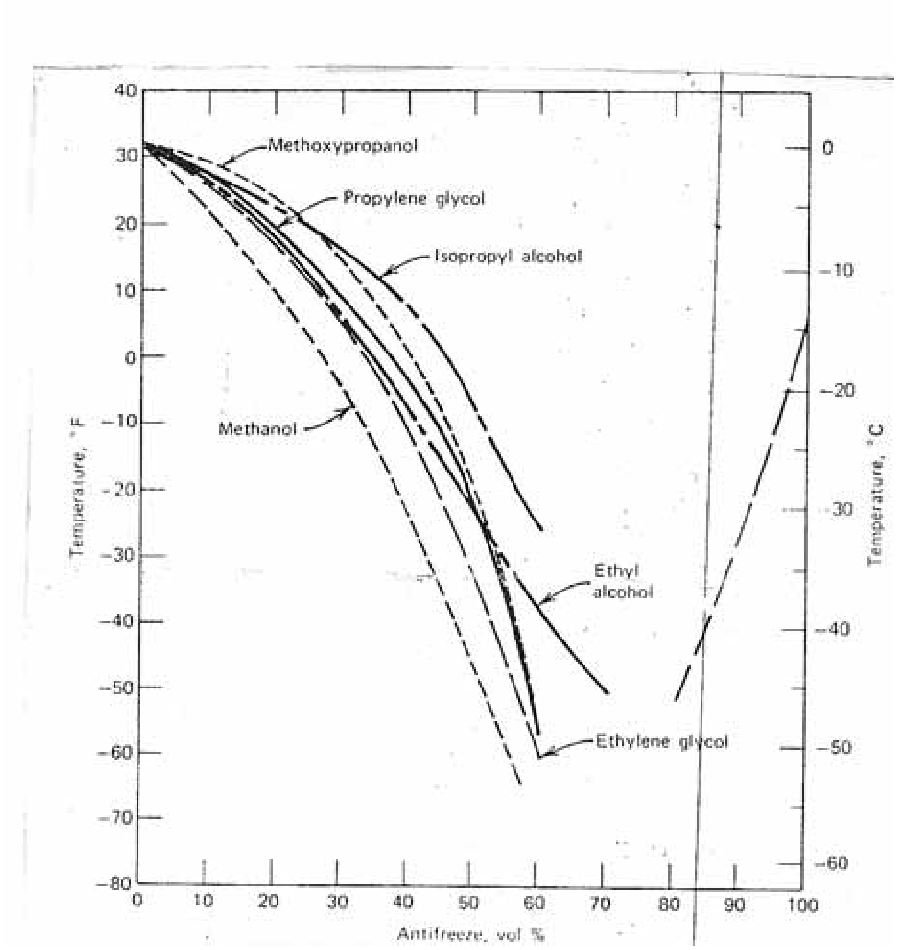


Fig 2.1 Freezing point of antifreeze/coolant solutions [9, 16]

2.1.4 Freezing Protection

Unlike pure water, antifreeze/coolant solutions do not solidify when exposed to temperatures several degrees below their freezing point [13]. If an antifreeze – coolant solution is exposed to a temperature, say 10° C below its freezing point, ice crystals form in the solution and the mixture becomes slush instead of solid material. As the temperature is lowered, more ice crystals form and the antifreeze material will become a stiff mush but never crystalline solid. This is due to the fact that the solid phase coming out is pure water. This removes water from the solution and, in effect, concentrates the remaining antifreeze/coolant solution and thereby lowers its freezing point.

The freezing point reported is the temperature at which the first ice crystals appear, but the mixture will only become completely solid at the eutectic temperature, although it may become very stiff before this is reached. For practical purposes, therefore, it may be said that antifreeze/coolant solutions have a *freezing range* rather than freezing point. While it is true that this phenomenon practically eliminates the possibility of block breakage and cooling system is protected, for stiff slush's can not be circulated and therefore will not transfer heat as they should; this leads to boil over, local overheating, and block breakage due to excessive heat[1,5].

Freezing protection of given antifreeze – coolant solution is taken to mean the lowest temperature at which the solution operates satisfactory as coolant. The difference between the freezing point (point at which the first ice crystals appear) and the protection point varies with the nature of the antifreeze – coolant and its concentration. Generally speaking, the greater concentration, the greater the spread between freezing point and protection point [5, 14].

In practice, depending upon the climate, freezing protection ranging from -20 to -40°C (-4 to -40°F) will be required.

2.1.5 Boiling Point of Antifreezes

The boiling point of an antifreeze, and more important, of the coolant solution used in the engine, can greatly influence the performance of the engine. The low boiling point of methanol solutions (80°C for a concentration of 35%) has practically eliminated it as antifreeze in high-pressure cooling systems. Vehicles operating with methanol as an antifreeze must be equipped with a low-temperature (70°C) thermostat whether the system is pressurized or not. Since most automobiles today are equipped with hot water circulating heaters, the higher the coolant temperature the more effectively the passenger compartment is heated in cold weather.

The boiling point is also important as it affects evaporation losses of the coolant, water pump cavitations caused by flash boiling on the suction side of pump, and after-boil. After-boil is boiling of coolant after a hand run when the coolant temperature is relatively high and the engine is quite hot. It is caused by residual heat form the shut off engine soaking into the coolant, which is not being circulated. Although after-boil can occur with any coolant, it is much more frequent with low boiling materials.[9]

For dilute ideal solutions of nonelectrolytes, the boiling point elevation of a solvent brought about by addition of a solute is proportional to molar concentration of the solute and independent of the nature of the solute.

$$\Delta T_B = K_B \times m;$$

Where:

ΔT_B is the boiling point elevation; K_B is boiling point elevation constant ($0.51°C*m^{-1}$ for water), m is molality of the solution.[49]

2.1.6 Boiling Protection

As the power increased, more heat must be rejected through the cooling system. Additional cooling can be provided in two ways – by enlarging the cooling capacity of the system, or by increasing the cooling system pressure (and thus the boiling point of the coolant) and following the coolant to circulate at higher maximum temperature. Within reasonable limits, a higher coolant temperature also helps increase the operating efficiency of the system since less heat rejected to the coolant and more is available to power the system. This temperature increase also has been shown to improve lubrication and reduce engine wear. Practical limits obviously exist, e.g. as the coolant temperature increases there is a commensurate increase in the operating temperature of the lubricating oil. If this temperature is increased too much, rapid oxidation of oil occurs with a decrease in lubricating efficiency.

The elevated boiling point of ethylene glycol antifreeze – coolant relative to water is important because it reduces evaporation losses, water pump cavitations caused by flash boiling on the suction side of the pump and after-boil caused by residual heat from a shut-off of the system [9, 1, 16].

2.2 Antifreeze – Coolant Applications

Antifreeze – coolants have many areas in addition to cooling systems where freeze-retarding substances are needed such as, stationary engines used in pipelines service, refrigeration systems, snow-melting system, hot-water heating systems, air conditioning systems, solar energy units, freezing and freeze drying units. Hydraulic systems often have antifreeze installed when the operation of the equipment is intermittent and the possibility of freezing exist.

In many of these cases, the antifreeze – coolant used as a heat transfer fluid and is designed to operate at temperatures below the freezing point of water. In choosing antifreeze – coolant for one of these operations, consideration should be given to the types of metals in the system, possible fire hazards, and the operating conditions which may influence the selection of the antifreeze base or the inhibitors used in it [9, 17, 18].

Ethylene glycol however remains the most important of the antifreezes – coolants. While the biggest outlet for ethylene glycol is anti-freeze for automobile-engine cooling systems, it has many applications. Its use as an airplane-engine coolant developed rapidly during the World War II. It is consumed as ethylene glycol dint rate in the manufacture of explosives.

Polyethylene glycols, alkyl resins, and other miscellaneous materials are manufactured form it. Consumption is significant in cellophane, hydraulic fluids, adhesives, and radio condenser pastes. Newer applications in crude its use as an intermediate for the synthetic fiber "Dacron" and for glyoxal **[19]**.

2.2.1 Aircraft Deicing

Many liquids have been tested for their ability to melt ice from aircraft surfaces, the more satisfactory ones being ethylene glycol, propylene glycol, 1,3-butylene glycol and glycerol. Of these, ethylene glycol and propylene glycol are the most widely used. Diethylene glycol, triethylene glycol, dipropylene glycol, and glycerol are used in some commercial deicing fluids, but the first three, when used as the major component, have a tendency to mar acrylic plastics, doped fabric finishes, and certain painted surfaces.

An ideal deicing fluid should: *(1)* display superior ice removing ability, *(2)* be noncorrosive to metals, and *(3)* not craze or discolor plastics, painted surfaces, or elastomers or otherwise cause deterioration of any of the materials of construction.

Most products are based on ethylene glycol with propylene glycol, corrosion inhibitors, a wetting agent, in some cases a thickener, and a small amount of water. Some customers request an added dye. Many formulations contain a triazole compound to reduce the hazard of glycol decomposition on noble metal electrodes.

The ethylene glycol provides most of the freezing point depression. It may contain small amounts (5-10 %) of higher glycols incidental to its manufacture; these seem to have little effect on the overall performance of the formulation. The propylene glycol reduces the low temperature pour point of the solution. Propylene glycol is being increasingly used because it is much less toxic than ethylene glycol. The corrosion inhibitors may include phosphates, nitrites, nitrates, borax, and silicates. Because of their superior performance on metal surfaces, nonionic and anionic surfactants are preferred to cationics as wetting agents. The water serves to solubilize the additives, depresses the pour point of the fluid, raises the flash point, and reduces the cost. Dye is often used to identify various solutions and to reduce the hazard of accidental misapplication of fluid. It also serves to demarcate the areas that have been treated. [9, 17]

2.3 Ethylene Glycol and Corrosion Problem

Ethylene glycol, which is the major antifreeze material, oxidized to a mixture of corrosive acids of which the formic acid and oxalic acid are the major constituents. This oxidation is promoted by mechanical defects, such as air suction at pump shaft seal, bad hose connection, and exhaust gas leakage. The resulting solution will be much more corrosive than tap water to which no antifreeze has been added. The factors responsible for the rapid oxidation of the antifreeze – coolant also are excessive aeration, the presence of local hot spots in the cooling system, and operating of the antifreeze – coolant at consistently high temperatures. It is proved that the addition of ethylene glycol gives higher corrosion rate for many metals than when water alone is used. This increase was especially the case for aluminum. [25, 26]

Thus, uninhibited solutions of ethylene glycol and water are corrosive to metals contained in cooling system, requiring the addition of an effective corrosion inhibitor package. The metals that need to be protected are of four classes:

1. Iron, steel, and gray cast iron
2. Aluminum alloys in cast and wrought forms

3. Copper and brass
4. Lead based solders

So that, many corrosion problems may arise such as pitting, crevice, deposition of corrosion products, cavitations in coolant pumps, and high temperature corrosion. This means that several inhibitors are required in a balanced formulation to protect the aluminum, steel, cast iron, solder and brass cooling system components it may encounter in service. [1, 27]

2.4 Characteristics of Some Freezing Point Depressant Additives

Ethylene glycol is slightly flammable and harmful. The minimum lethal dose is 1-1.5 ml/kg or approximately 100 ml for an adult. Short-term exposure can result in irritation to eyes, skin and respiratory tract. Repeated or long-term exposure can bring about effects on the central nervous system and eyes.

Propylene glycol is slightly water-polluting but practically non-toxic to humans. The minimum lethal dose of pure propylene glycol for human adults is more than 15 times greater than with ethylene glycol. Propylene glycol has lower fire hazard when exposed to heat or flame. Propylene glycol can have quite a low pH that might affect the corrosion potential.

Ethyl alcohol is highly flammable and therefore dangerous when exposed to heat and flame. Vapours may form explosive mixtures with air. Most vapours are heavier than air. Ethyl alcohol has very low surface tension, which may cause leakage in sealing devices and foaming.

Methyl alcohol is like ethyl alcohol highly flammable. Methyl alcohol is toxic. The chemical is a skin and eye irritant. The substance may be fatal if inhaled, ingested or absorbed through the skin. Ingestion can also cause blindness. The minimum lethal dose for human adults, in absence of medical treatment, is between 0.3 and 1 g/kg. Methyl alcohol is not compatible with elastomers made of 100% FKM (Viton A), soft rubber or polyether-urethane (EU).

Ammonia causes strong irritation to eyes, skin and the respiratory tract. Swallowing the liquid is corrosive to the mouth, throat and stomach. Exposure to high concentrations can cause temporary blindness and eye damage. Ammonia is highly toxic to aquatic organisms. Ammonia is not compatible with elastomers made of 100% soft rubber, isoprene (IR), natural rubber (GRS), polyurethane (AU) or silicon rubbers. Ammonia is not compatible with copper [57].

2.5 Cooling System Basics

The cooling system includes the water jackets, water pump, radiator, fan, fan shroud, heater, thermostat, coolant, radiator cap, overflow reservoir, and various hoses that circulate the coolant. Modern cooling systems are closed systems, which mean they use a coolant recovery reservoir. When the engine is shut off and cools downs, a vacuum is created as the coolant contracts. This opens a valve in the radiator cap and sucks the overflow into the reservoir. When the engine warms up again, the process reverses.

A water and antifreeze – coolant mixture cools the engine. It circulates through the water passages while the water pump pushes the hot coolant into the radiator. The radiator cools the mixture as much as possible before it returns to the engine. All the little fins dissipate heat, which is carried away by the air flowing through the radiator. Air enters through the grille as you drive, and the fan helps pull it in. The fan also draws air when the vehicle is stopped. When the fluid reaches the lower radiator hose, it is cooled and ready to re-enter the water pump where it's pushed back into the engine's water jackets.

A cold engine has cold coolant. It needs to reach normal operating temperatures as quickly as possible. The thermostat is a temperature-controlled valve. When the coolant is too cold, the thermostat closes and the water pump only circulates coolant in the block. When the coolant reaches operating temperature, usually between 180 and 195°F (82.2 and 90.6 °C), the thermostat opens and the coolant makes the full trip through the radiator.

When the truck's heater is on, a second valve opens allowing coolant through a small radiator mounted either on the firewall or under the dash, known as the heater core. The heater pulls warm coolant away from the engine and uses it to heat the cab. The battling serious overheating situation, turning the heater on high will pull heat out of the engine. It may sound sadistic to crank up the heater on a day hot enough to make the engine boil over, but sometimes the cooling system needs all the help it can get. When the choice is between getting home sweaty or being stranded, we'll gladly turn on the heater. Combustion produces a heat in the engine. Average combustion-chamber temperatures are around 1,500°F (815.6°C) with extremes as high as 6000°F (3315.6°C). Since water boils at 212°F (100°C), there's a big gap that requires a lot of cooling.

Pressure raises the boiling point of coolant, so most radiator caps are designed to raise the pressure to about 15 psi (1.02 atm.). This adds 40 degrees to the boiling point, which is why it's important to replace defective radiator caps. A cap with a bad pressure valve makes the engine run substantially hotter. Elevation lowers the boiling point of coolant. For every 1,000 feet (3600 m) above sea level, the boiling point drops 3 degrees.

Antifreeze alone can reach 330°F (165.5°C) before it boils. Pure antifreeze doesn’t absorb heat as well as water, so most manufactures recommend mixing the two. While the coolant protects against heat, antifreeze protects against the extremely cold temperatures encountered when the vehicle is parked. Water freezes at 32°F (0°C), and antifreeze is good down to 0 degrees. Interestingly, a 1:1 mix offers protection down to about -34°F (-36.7°C). People in extreme climates can use 60% antifreeze to lower the freezing point to about -60°F (-51.1°C), but heat absorption suffers. That's a satisfactory trade-off in frigid climates, but the most vehicles should stick with the stand 1:1 mix. [9, 30, 31]

2.6 Future Trends

The antifreeze market will continue to be divided into two main categories: low priced volatile antifreezes, and relatively high-priced permanent antifreezes. In the volatile field, methanol-based antifreezes are expected to increase in popularity due to their superior antifreeze efficiency, low cost, and lack of odor. This increase will be dependent primarily upon the rate at which synthetic methanol is made available for antifreeze work. In the nonvolatile field, Ethylene glycol-based antifreezes will continue to predominate, because of the antifreeze efficiency of ethylene glycol and it's relatively low cost as compared to its only close competitor, glycerol, which has many other important commercial uses. It is expected that permanent-type antifreezes will make further inroads on the business now held by the volatile type, although the difference in manufacturing costs insures the continued use of volatile antifreezes. Automotive manufactures are considering the use of factory-sealed cooling system, in which case both the types and quantities of antifreeze materials would be affected. [5]

2.7 Other Antifreezes

The American Society for Testing Materials (ASTM) [17] is currently working on developing standards for propylene glycol antifreeze and coolants because propylene glycol has as high a boiling point and low freezing point. Cecilia Hagg[57] proved that when water freezes out after the temperature of the fluid has passed below the freezing point, the concentration of the additive increases in the liquid-phase. The increased additive concentration implies that the freezing point of the remaining liquid-phase is further lowered and in order to freeze out more ice the temperature of the fluid has to be further lowered below the current freezing point of the liquid. The result is that the fluid has no definitive freezing point but rather a freezing range. She used in her work different antifreezes mixed with water like potassium formate, potassium acetate calcium chloride, potassium carbonate, ammonia, glycerol, methyl alcohol, ethyl alcohol, and propylene glycol.

Duus[14] used methanol in automobile cooling system because the boiling point of methanol 65°C is lower than that of other antifreeze material such as alcohol 77.8°C, isopropanol 82.2°C, or glycerol 291°C. Nevertheless, because of its low molecular weight, approximately 20 to 25% less volume of methanol is required to affect a given lowering of the freezing point than of glycol or denatured alcohol; this is an economic advantage.

2.8 Modified Redlich-Kwong equation of state for saturated vapour-liquid equilibrium

Defining the dimensionless temperature T* as

$$T^* = \frac{\frac{T_C}{T} - 1}{\frac{T_C}{T_{NB}} - 1} \qquad \ldots (2.9)$$

Where T* is reduced temperature, T_C is critical temperature, and T_{NB} is normal boiling point.

The modified Redlich-Kwong equation predicts the saturated liquid vapour equilibrium states accurately over the entire liquid range from triple point up to critical point.

The Redlich-Kwong equation of state **[1]** has been widely used in the last years in chemical engineering for predicting the vapour-liquid equilibria and volumetric properties **[32, 33]**. As a matter of fact, many attempts have been made to improve the original Redlich-Kwong equation **[32, 34]**. One of the most interesting developments along these lines has been the work of Soave **[34, 35]** who introduced a modified temperature dependence of the attractive force term. This procedure has been developed by Peng and Robinson **[36, 37]**, Usdin and McAuliff **[38]** and Raimondi **[39]**. In the work of Lielmezs **[41]** the temperature dependence of the attractive force term of the Redlich-Kwong equation is introduced by means of new reduced temperature T* term expressed as a function of temperature T, the normal boiling point temperature T_{NB}, the critical point temperature T_C and two form saturated vapour-liquid equilibrium derived substance dependent constants.

This modification predicts the saturated liquid vapour equilibrium states for all types off liquids accurately over the entire liquid range from the triple point up to the critical point. [41]

The original two parameter relation of Redlich-Kwong [40] is

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5} \times V \times (V+b)} \quad \ldots (2.1)$$

If eq. (2.1) is applied, the critical state thermodynamic criteria for stability

$$(\frac{\partial P}{\partial V})_T = 0$$

$$(\frac{\partial^2 P}{\partial^2 V})_T = 0 \quad \ldots$$

(2.2)

For one component system

$$a = \Omega a \times \frac{R^2 \times Tc^{2.5}}{P}$$

... (2.3)

$$b = \Omega b \times \frac{R \times Tc}{Pc}$$

For pure compounds, equations (2.1)-(2.3) yield the following Ω_a and Ω_b values [42]:

$$\Omega a = \frac{1}{9 \times 2^{1/3} - 1} = 0.42748 \qquad \ldots (2.4)$$

And

$$\Omega b = \frac{2^{1/3} - 1}{3} = 0.08664 \qquad \ldots (2.5)$$

Assuming that parameter b remains constant, combining eqns. (2.3) and (2.5) and have

$$b = 0.08664 \times \frac{R \times T_C}{P} \qquad \ldots (2.6)$$

If, on the other hand, let parameter a to be temperature dependent, it is defined as a product of two terms

$$a(T) = a(\frac{T_C}{P_C}) \propto (T^*) \qquad \ldots (2.7)$$

Applying eqns (2.3) and (2.4) to express term a (T_C, P_C) as

$$a(T_C, P_C) = 0.4248 \times \frac{R^2 \times T_C{}^2}{P_C} \qquad \ldots (2.8)$$

To express the a(T*) in term of eq (2.7) as a continuous temperature dependent function, the previously proposed reduced temperature T* is introduced, which is defined as:

$$T^* = \frac{\frac{T_C}{T} - 1}{\frac{T_C}{T_{NB}} - 1} \qquad \ldots (2.9)$$

Where T, T_C and T_{NB} are the temperatures, in K, of the given state, the critical point, and normal boiling point, respectively [43, 44, 45, 46].

Chapter Three

Experimental Work

3.1 Material used

3.1.1 Liquids

The liquid used in the experiment is annular Ethylene Glycol Produced by Fluka Company. The physical and thermo chemical properties of Ethylene Glycol are shown in Table 3.1.

Table 3.1 Physical and Thermo chemical Properties of E.G.

Formula	$HOCH_2CH_2OH$
Purity	98 % (H_2O<0.2 %)
Molecular weight	62.07
Freezing point	-12°C
Boiling point	197°C
Refractive index, nD^{20}	1.43
Specific gravity(60°F/60°F)	1.113

3.1.2 Additives

The Methanol is added to the solution to reduce the freezing point in this work. It is annular produced by BDH Company in England. The physical and thermo chemical properties of methanol are shown in Table 3.2.

Table 3.2 Physical and Thermo chemical Properties of Methanol

Formula	CH_3OH
Molecular weight	32.04
Boiling point, 760mm, °C	64.5C TO 65.5
Freezing point, °C	-97.7C
Refractive index, nD^{20}	1.328 TO 1.33
Specific gravity(60°F/60°F)	0.796 TO 0.797
Maximum limits of impurities	
Acidity	0.02 ml N/1%
Alkalinity	0.02 ml N/1%
Non volatile matter	0.0005%
Aldehydes and ketones[(CH3)2CO]	0.005%
Organic impurities passes test	0.0005%
water	0.1%

3.2 Procedure of mixing

The ethylene glycol is mixed with water at different percentages

The following mixtures were prepared in this study:-

A. Binary mixture of water with (0-100) wt% of ethylene glycol.

B. Mixture of water with (0-100) wt% of ethylene glycol with 5% methanol.

The solution is mixed well before measuring the freezing temperature and boiling temperature.

3.3 System Description to Measure the Freezing Point

Cooling system (chiller) was used to control and reduce the temperature of the liquids that decrease through circulation. The chiller used is shown in figure 3.1. The chiller is composed of bath and vacuum. In the experimental work the bath is used to measure the freezing point of the samples. The temperature range of the chiller is from 70°C to -100°C and the pressure range is 0.5 to 1000 mbar, made in Danmarc Company of He tosicc.

3.4 Experimental Procedure

The sample solutions are mixed well before test then it is placed in the bath of the chiller and the chiller is then switched on to cool the solution. The temperature is measured by thermometer during it's decrease until the freezing temperature is reached. Also an alcohol thermometer of range 20 to -80°C is used to check the chiller's thermometer reading. The chiller's temperature reaches to -58°C. The procedure is repeated for each sample. Each experiment is doublicated for more accuracy.

Fig. 3.1: The chiller

3.5 System Description to Measure the Boiling Point

The flow system apparatus used for measuring the boiling temperature is composed of thermometer, capillary tube, stirrer, beaker, elastic band, test tube, oil bath, pipette, burner, and clamp.

3.6 Experimental Procedure

The boiling point of smaller quantities of liquid may be determined by using the following technique. Seal the end of 5 cm length and 4mm inside diameter thin-walled glass tubing to make a small test-tube (outer jacket) and attach to a thermometer with tape or an elastic band such that the sealed end of the tube is in level with the bulb of the thermometer. The capillary tube is cut about 2 cm from the sealed end. Mercury thermometer and attached tube is immersed in oil bath. Finally, by a pipette, an Ethylene Glycol – Water solution is introduced to measure the boiling point to a depth of a bout 1 cm. Figure 3.2a.and 3.2b.

Oil bath is heated with stirring and the tip of the inner tube is observed carefully. Initially, a slow erratic stream of air bubbles will be seen to leave the tube as the air inside warms up and expands, but this will eventually be replaced by a steady rapid stream of bubbles as the solution reaches its boiling point. At this point the heating is stopped and the sample stays in the oil bath the temperature of which will continue to rise for a short time, while depending on the rate of heating and the actual temperature of the bath. As the temperature begins to fall, the temperature is recorded at which the stream of bubbles stops and the sample just begins to rise up within the inner capillary tube, this is the boiling point of the sample. The procedure is then repeated by using new capillary tube and another sample to measure its boiling point. This experiment is done at atmospheric pressure. Each test is carried out twice.

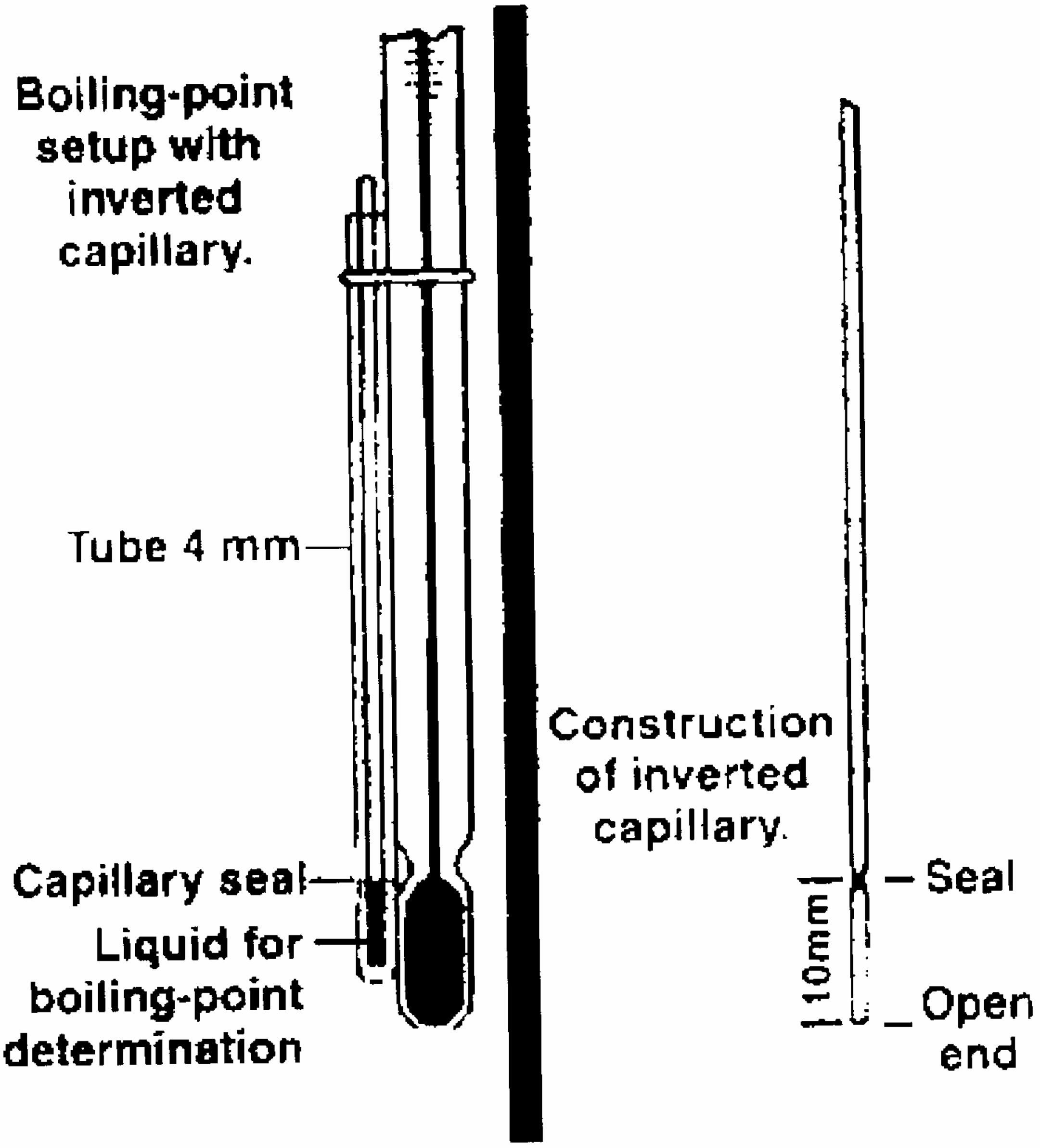


Fig 3.2a: Boiling Point measurements

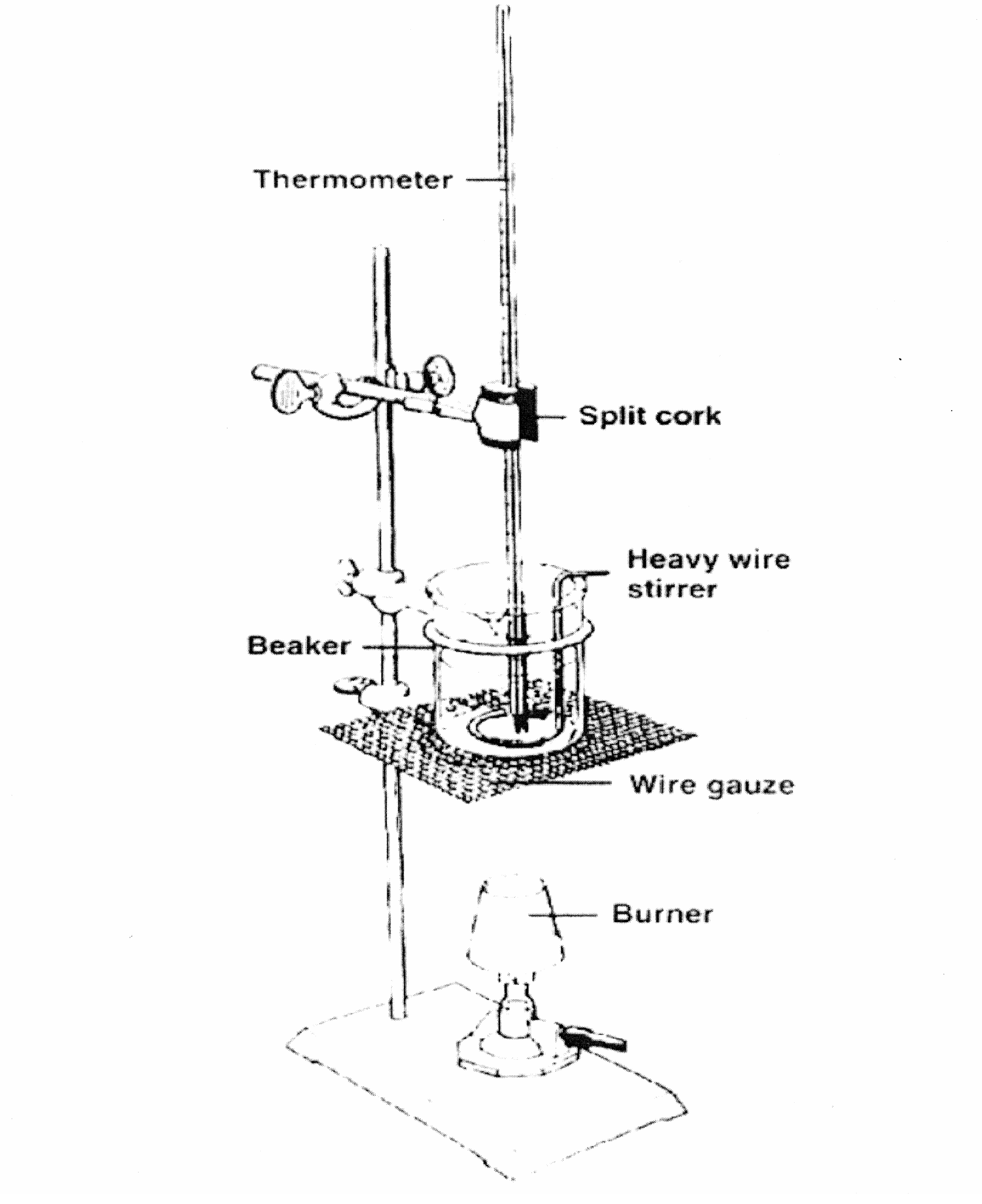


Fig 3.2b: Boiling Point systems

Chapter four

Results and discussion

The experimental results are presented in tables A.1 and A.2
In appendix A

4.1 Freezing point

4.1.1 Effect of Ethylene Glycol Concentration on the Freezing Point

Figure 4.1 shows the relation of freezing point (T_F) with the weight percent of Ethylene Glycol.

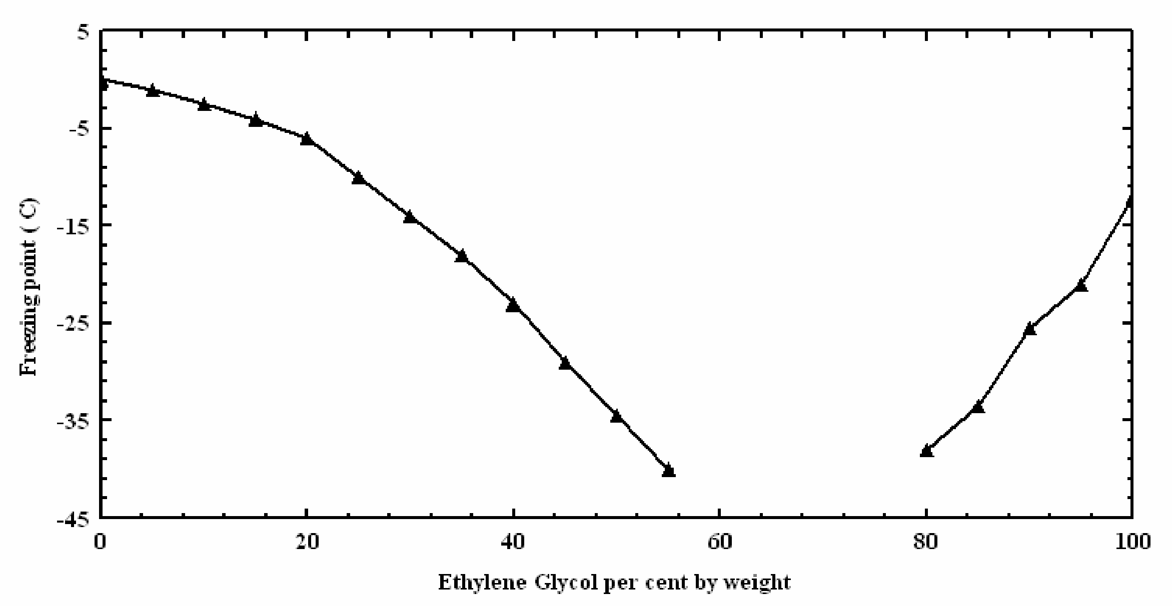


Fig 4.1 Freezing point (°C) vs. Weight % of Ethylene Glycol

The freezing point (T_F) of water decreases gradually with increasing ethylene glycol percent until 55% E.G add. In 60%, 65%, 70%, 75% and 80% of Ethylene Glycol the solutions stay in liquid state so the freezing point is noticeable.

Above 80% of Ethylene Glycol the increase in Ethylene Glycol results in an increase in the freezing point (T_F).

Johnston Services, Inc. [56] proved that the freezing point of propylene glycol decreases with increasing it's weight percent, But over than of ethylene glycol.

Cecilia Hägg[57] proved that the freezing point of different components like Potassium formate, potassium acetate, calcium chloride, potassium carbonate, ammonia, glycerol, methyl alcohol, ethyl alcohol, and propylene glycol increased with increasing their weight percent with water.

4.1.2 Addition of Methanol

Figure 4.2 shows the effect of addition of 5% methanol to the solution of various percentages of Ethylene Glycol.

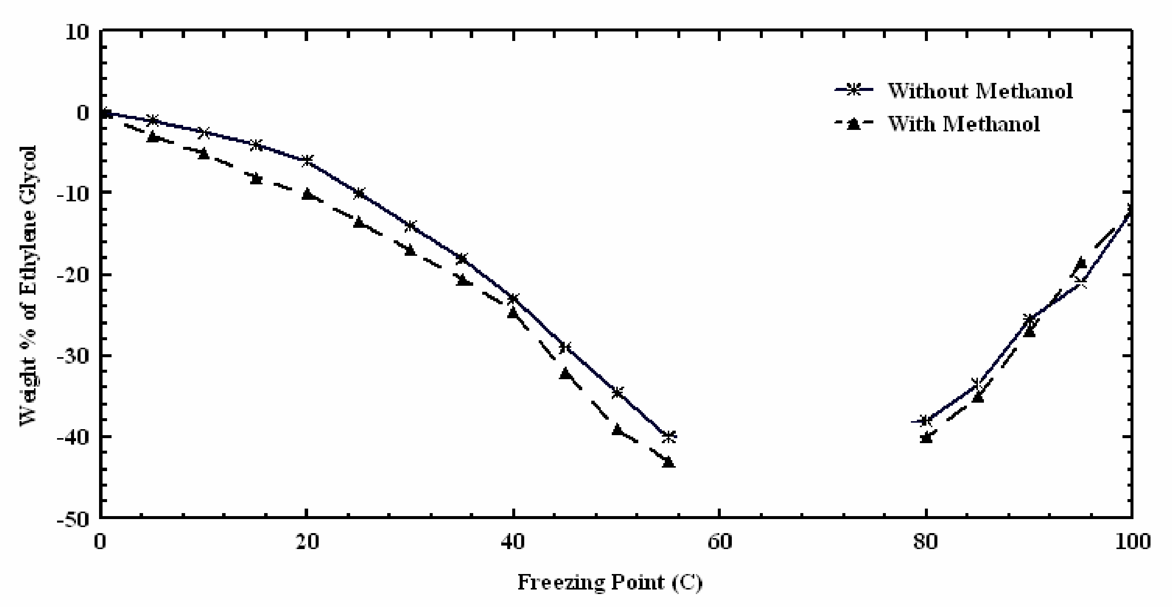


Fig 4.2 Freezing point (°C) vs. Weight % of Ethylene Glycol

It is evident that the freezing points (T_F) decreases with the increase in the weight % of Ethylene Glycol to about 55%.

In Figure 4.2, the Ethylene Glycol and water form eutectic mixture in the range 55% to 80% Ethylene Glycol by weight, although the exact eutectic composition and the temperature have not been accurately defined because the solution remain liquid at temperature below their freezing points.

The range from 80% to 100% of Ethylene Glycol the freezing point increases when the percent of Ethylene Glycol increased.

Also the figure reveals that the presence of methanol leads to decrease in the freezing point below that when no methanol is added for the whole range of Ethylene Glycol composition.

4.2 Boiling Point

The experimental work includes the investigation of the effect of addition of ethylene glycol and the methanol on the boiling point.

4.3 Effect of Ethylene Glycol Concentration on Boiling Point (T_B)

Figure 4.3 shows the effect of the ethylene glycol percent on the boiling point of the solution.

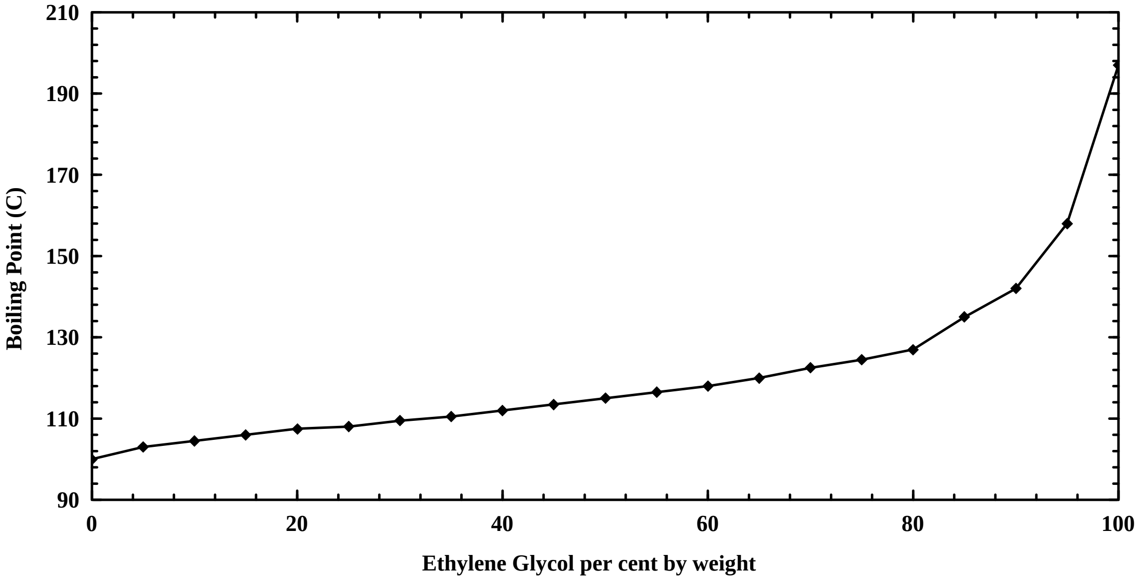


Fig 4.3 Boiling point vs. weight % of Ethylene Glycol

Figure 4.3 reveals that the boiling point increases with increasing the composition of Ethylene Glycol.

Kallgren, R. W. [16] showed that the boiling point of methanol decreases with increasing the weight percent.

Zink, D. G. [5] showed that the boiling point of the solution of methanol with water and the solution of ethyl alcohol with water decreases with increasing the weight percent.

4.2.2 Addition of Methanol

Figure 4.4 shows the effect of addition of 5% of methanol to the system of different percentages of Ethylene Glycol.

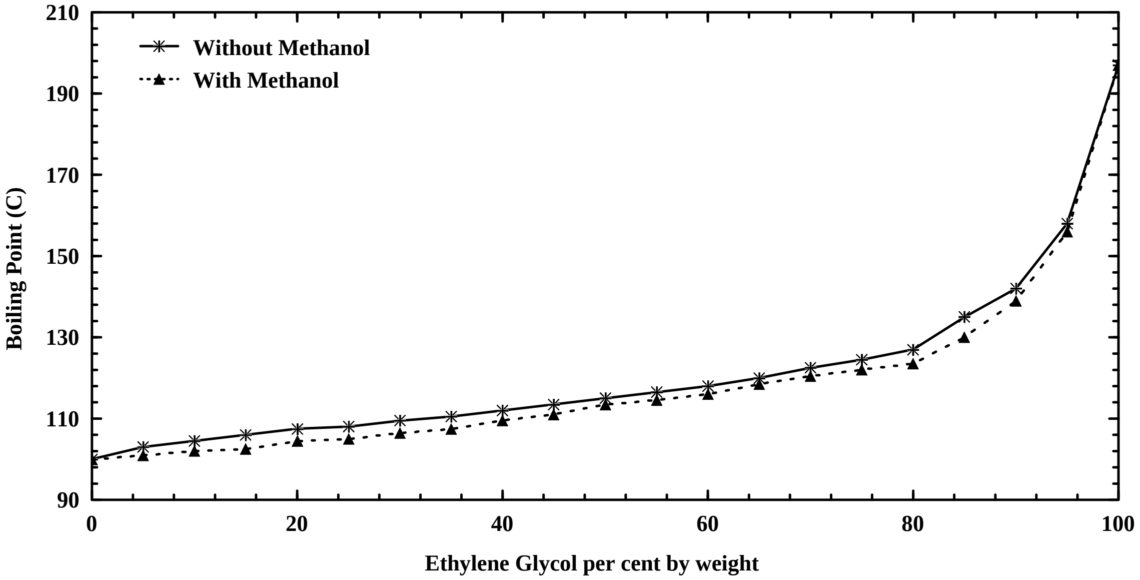


Fig 4.4 Boiling Point vs. Weight % of Ethylene Glycol

Figure 4.4 indicates that when the weight percentage of Ethylene Glycol increase the boiling point increases. It is evident that the presence of methanol leads to decrease the boiling point below that when no methanol is added for the whole range of Ethylene Glycol percent.

4.3 Comparison between Experimental Results of Ethylene Glycol/water and Propylene Glycol of Union Carbide Corp Results Graphically

4.3.1 Determination of the Freezing Point at Different E.G /Distilled water Concentration and Propylene Glycol/water concentration.

The freezing point was measured for different concentrations of E.G. The results were shown in Figure 4.5 which compares the present results with Propylene Glycol of Union Carbide Corp results [29].

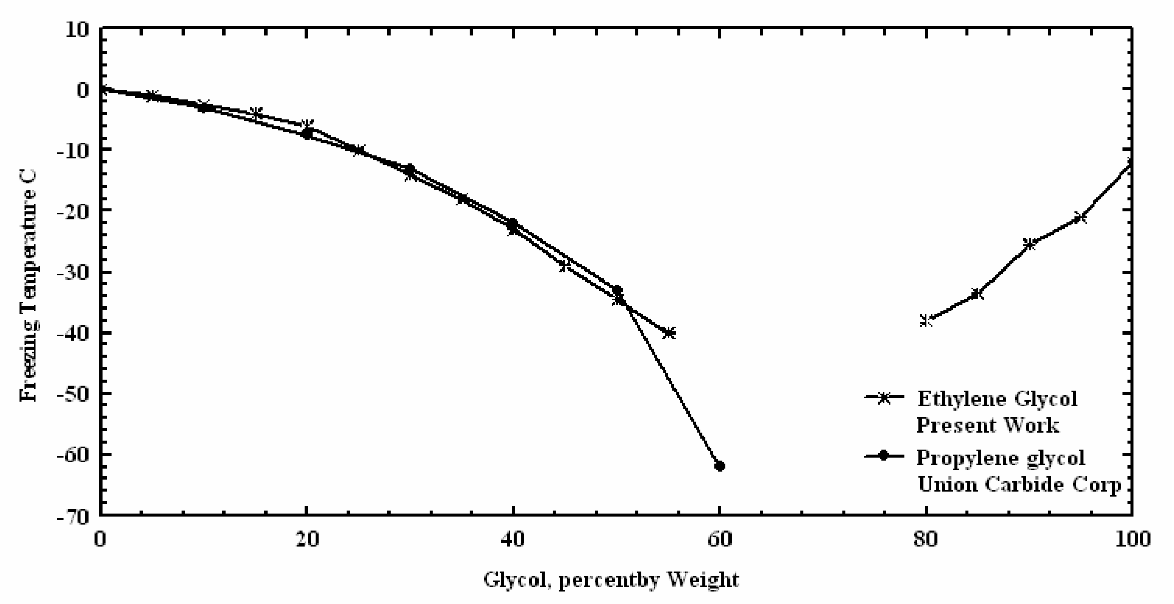


Fig 4.5 Freezing Point vs. weight % for aqueous solution of E.G/water as compared with Propylene Glycol /water of Union Carbide Corp results

The figure reveals that the curve of Propylene Glycol of Union Carbide Corp is higher than the curve of the present results.

4.3.2 Determination of the Boiling Point at Different E.G/ Distilled water Concentration and Propylene Glycol/water concentration.

The boiling point was measured for different concentrations of E.G. and the results are compared with those of Propylene Glycol of Union Carbide Corp [29].

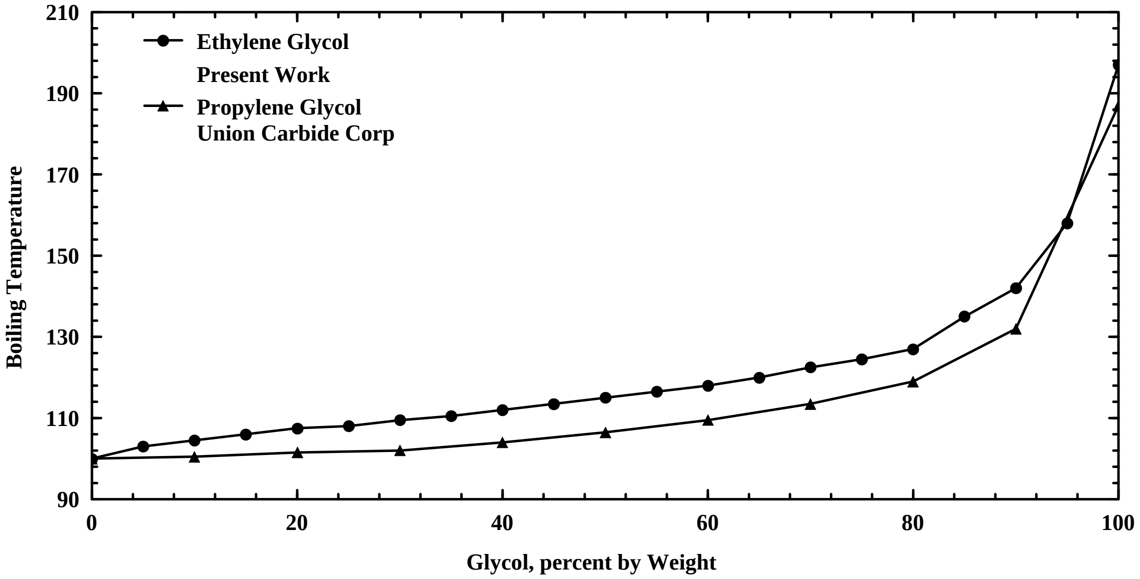


Fig 4.6 Boiling Point vs. weight % for aqueous solutions of E.G/water as compared with Propylene Glycol /water of Union Carbide Corp results

It can be noted that an increase in the concentration of E.G in distilled water results in significant increase in the boiling point.

Also the figure reveals that the results of Propylene Glycol of Union Carbide Corp are less than those of the present results.

4.4 The use of Leilmezs model to predict the reduced temperature (T*)

Lielmiezs's proposed the following equation to predict T* [41]

$$T^* = \frac{\frac{T_C}{T} - 1}{\frac{T_C}{T_B} - 1} \qquad \ldots (4.1)$$

Where

T* = reduced temperature, T_c = critical point of liquid,T_B = boiling point of liquid, and T = the temperature of liquid

The Leilmezs equation is modified in the present work to estimate the T* from freezing point and boiling point as follows

$$T^* = \frac{\frac{T_F}{T} - 1}{\frac{T_F}{T_B} - 1} \qquad \ldots (4.2)$$

Where: T_F = freezing point of liquid

$$T^* = \frac{T_F - T}{T} \times \frac{T_B}{T_F - T_B} \qquad \ldots (4.3)$$

$$T^* = \frac{T_F \times T_B - T \times T_B}{T \times (T_F - T_B)} \qquad \ldots (4.4)$$

$$T^* = \frac{T_F \times T_B}{T_F - T_B} \times \frac{1}{T} - \frac{T_B}{T_F - T_B} \qquad \ldots (4.5)$$

The line equation is:

$$Y = m \times x + b \qquad \ldots (4.6)$$

If equation (4.5) equals equation (4.6) then

$$T^* = Y$$

$$X = \frac{1}{T}$$

$$m = \frac{T_F \times T_B}{T_F - T_B}$$

$$b = -\frac{T_B}{T_F - T_B}$$

Now the equation (4.5) become

$$T^* = m \times \frac{1}{T} + b \qquad \dots (4.7)$$

Substitutition of the freezing point and the boiling point that were measured experimentally, gives the slop m, the intercept b and to obtain the reduced temperature T* from equation (4.7) the results are shown in appendix (B)

For Ethylene glycol /water system

Table 4.1 Ethylene glycol /water system

The substances	T_F (K)	T_B (K)
Water	273.15	373.15
E.G	261.15	470.15
50% mixture	238.65	388.15

For water the equation (4.7) becomes

$$T^* = -1019.2592 \times \frac{1}{T} + 3.7315 \qquad \dots (4.8)$$

For E.G the equation (4.7) becomes

$$T^* = -587.4625 \times \frac{1}{T} + 2.2495 \qquad \dots (4.9)$$

For 50% of E.G mixture the equation (4.7) becomes

$$T^* = -619.6120 \times \frac{1}{T} + 1.5963 \qquad \dots (4.10)$$

The initial value of temperature T is 143.15 K (-130°C) to 563.15 K (290°C). Substitutition these temperatures in equations (4.8), (4.9) and (4.10) gives the reduced temperature T*

The results are presented in appendix B in table B_1.

Plotting T* from equations 4.8, 4.9, and 4.10 gives figure 4.7

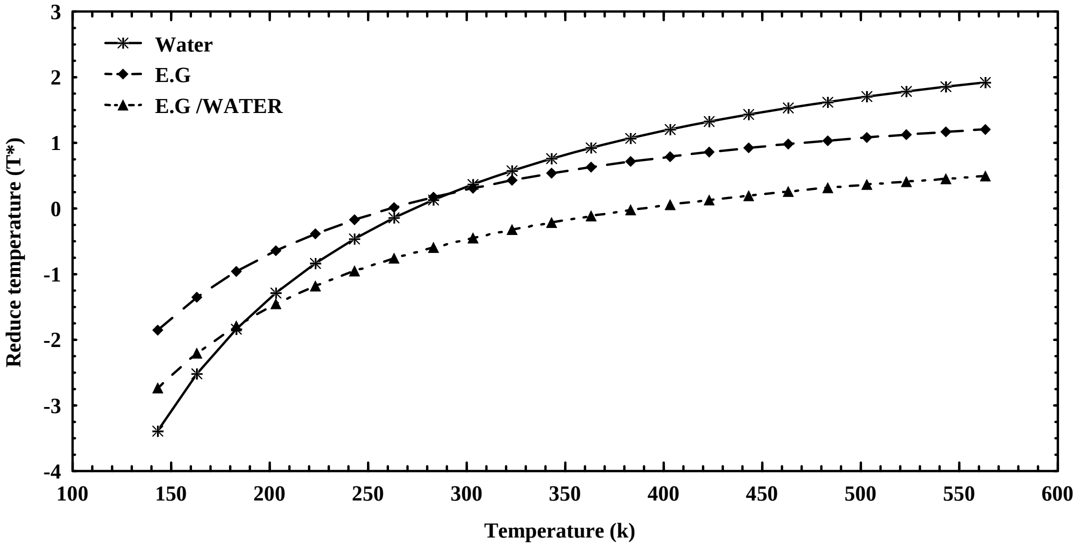


Fig 4.7: Reduced temperature (T*) vs. temperature (K)

Figure 4.7 indicates that an increase in temperature results in significant increase in the reduced temperature for the three solutions.

Also the figure reveals that from 143.15 to 283.15 K the reduced temperature T* of ethylene glycol increased with increasing the temperature more than of increasing the water alone and the mixture of ethylene glycol with water.

Then from 283.15 to 563.15 K the reduced temperature T* of ethylene glycol increased with increasing the temperature less than of increasing the water alone and the mixture of ethylene glycol with water.

For E.G /water/methanol system

Table 4.2 ethylene glycol /water/ methanol system

The substances	T_F (K)	T_B (K)
Water	273.15	373.15
E.G	261.15	470.15
5%methanol/50%E.G/45%water	234.15	386.15

For water the equation (4.7) becomes

$$T^* = -1019.2592 \times \frac{1}{T} + 3.7315 \qquad \text{… (4.8)}$$

For E.G the equation (4.7) becomes

$$T^* = -587.4625 \times \frac{1}{T} + 2.2495 \qquad \text{… (4.9)}$$

For 5%methanol/50% of E.G/ 45%water mixture the equation (4.7) becomes

$$T^* = -594.8488 \times \frac{1}{T} + 2.5405 \qquad \text{… (4.11)}$$

The initial value of temperature (T) is 143.15 K (-130°C) to 563.15 K (290°C). Substitutition of these temperatures in these equations (4.8), (4.9) and (4.11) gives the reduced temperature (T*)

The results are listed in table B_2 in appendix B.

Figure (4.8) shows the variation of T* with solution temperature for the three solution

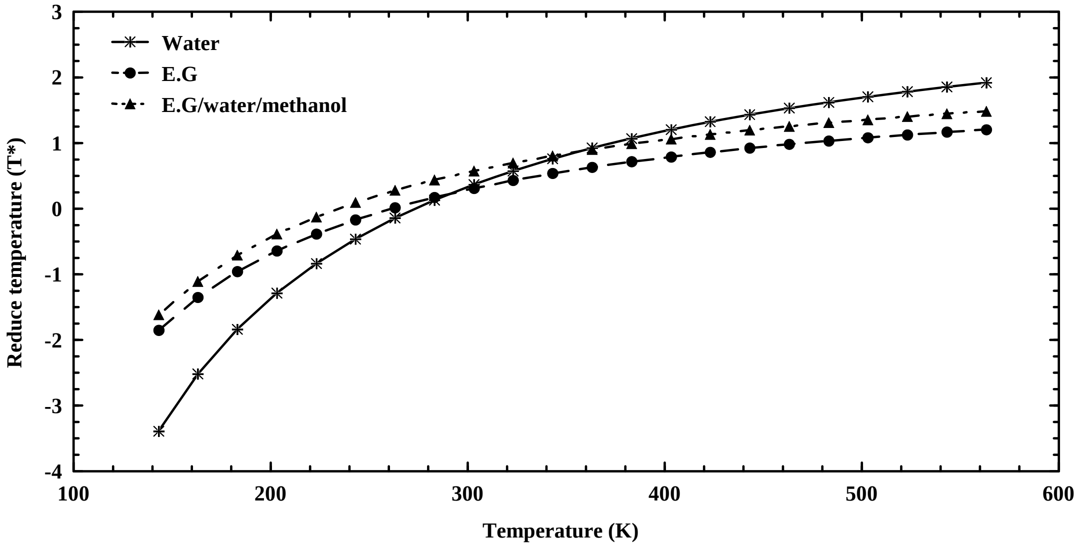


Fig 4.8 Reduced temperature (T*) vs. Temperature (K) in presence of Methanol

Figure 4.8 indicates that when the temperature increases the reduced temperature increases.

It is evident that between 143.15 to 363.15 K the mixture of E.G/water with methanol gives higher values of reduced temperature than that when the water alone and the E.G alone. From 363.15 to 563.15 the reduced temperature T*of the mixture becomes between water and ethylene glycol. Tables (4.3) to (4.7) shows the values of freezing temperature and boiling temperature obtained from the work of the other authors [54, 55, 52, 58, 53].

For 2-propanol (1sopropanol)/water system

Table 4.3: 2-propanol (1sopropanol)/water system [54]

The substances	T_F (K)	T_B (K)
Water	273.15	373.15
2-propanol	184.75	355.45
50% mixture	248.86	375.11

For water the equation (4.7) becomes

$$T^* = -1019.2592 \times \frac{1}{T} + 3.7315 \qquad \dots (4.8)$$

For 2-propanol the equation (4.7) becomes

$$T^* = -384.7064 \times \frac{1}{T} + 2.0823 \qquad \dots (4.12)$$

For 50% of 2-propanol mixture the equation (4.7) becomes

$$T^* = -739.4049 \times \frac{1}{T} + 2.9712 \qquad \dots (4.13)$$

The initial value of temperature (T) is 143.15 K (-130°C) to 563.15 K (290°C). Substitutition of these temperatures in these equations (4.8), (4.12) and (4.13) gives the reduced temperature (T*)

The results are presented in appendix B in table B_3.

Plotting T* from equations 4.8, 4.12, and 4.13 gives figure 4.9 for the three solution

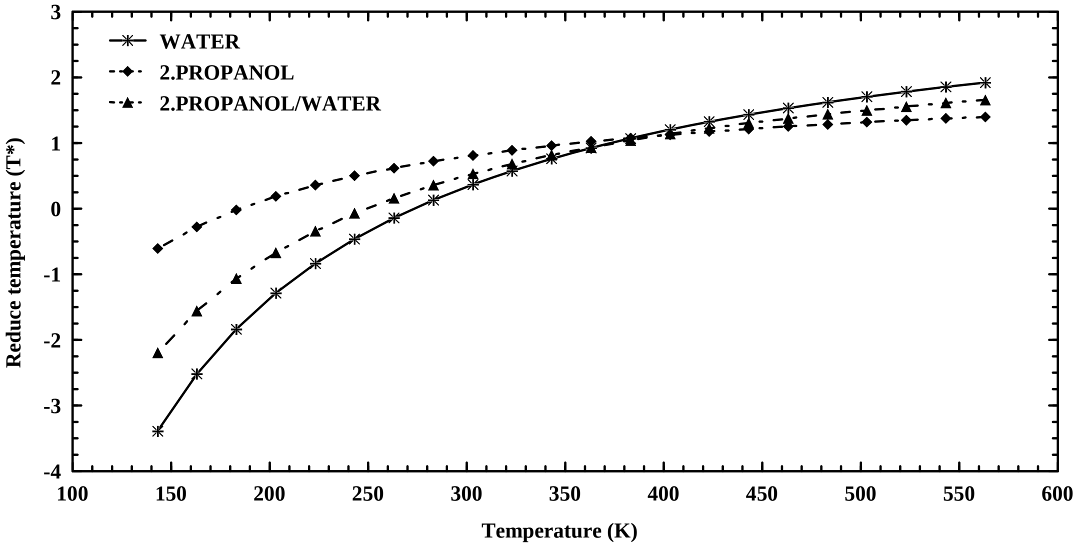


Fig 4.9: Reduced Temperature (T*) vs. Temperature (K)

Figure 4.9: reveals that the reduced temperature increases with increasing the temperature.

Also the figure reveals that in low temperatures the reduced temperature T* of 2-propanol is higher than of water and the mixture. In high temperatures the reduced temperature T* of 2-propanol is lower than of water and the mixture.

For Diethylene glycol/water system

Table 4.4 Diethylene glycol /water system [55]

The substances	T_F (K)	T_B (K)
Water	273.15	373.15
Diethylene glycol	264.85	517.98
50% mixture	253.55	374.73

For water the equation (4.7) becomes

$$T^* = -1019.2592 \times \frac{1}{T} + 3.7315 \qquad \ldots (4.8)$$

For Diethylene glycol the equation (4.7) becomes

$$T^* = -541.9955 \times \frac{1}{T} + 2.0464 \qquad \ldots (4.14)$$

For 50% of Diethylene glycol mixture the equation (4.7) becomes

$$T^* = -784.0633 \times \frac{1}{T} + 3.0923 \qquad \ldots (4.15)$$

The initial value of temperature (T) that is 143.15 K (-130°C) to 563.15 K (290°C). Substitutition of these temperatures in these equations (4.8), (4.14) and (4.15) gives the reduced temperature (T*)

The results are listed in table B_4 in appendix B.

Figure 4.10 shows the variation of T* with solution temperature for the three solution

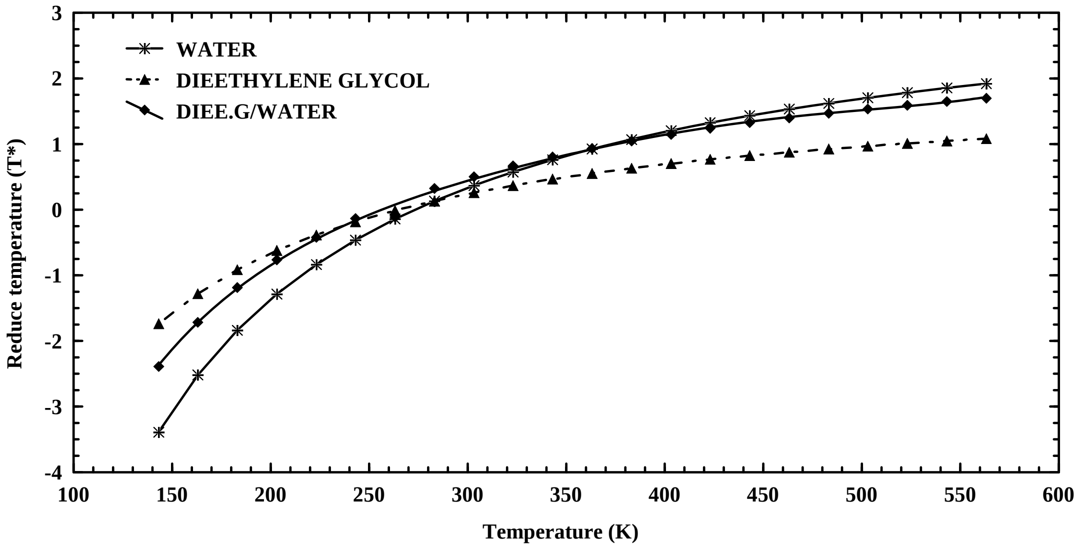


Fig 4.10: Reduced Temperature (T*) vs. Temperature (K)

Figure 4.10: indicates that when the temperature increases the reduced temperature increased.

It is evident that the mixture of Diethylene with water from 143.15 to 203.15 K leads to an increase in the reduced temperature T* over than that of water and less than of diethylene glycol. From 363.15 to 563.15 K the reduced temperature T* of the mixture is below than that when every one alone.

For Ethanol/water system

Table 4.5 Ethanol /water system [52]

The substances	T_F (K)	T_B (K)
Water	273.15	373.15
Ethanol	155.85	351.55
50/50% mixture	242.55	355.45

For water the equation (4.7) becomes

$$T^* = -1019.2592 \times \frac{1}{T} + 3.7315 \quad \ldots (4.8)$$

For Ethanol the equation (4.7) becomes

$$T^* = -279.9646 \times \frac{1}{T} + 1.7964 \quad \ldots (4.16)$$

For 50% of Ethanol mixture the equation (4.7) becomes

$$T^* = -782.2794 \times \frac{1}{T} + 3.2252 \quad \ldots (4.17)$$

The initial value of temperature (T) is 143.15 K (-130°C) to 563.15 K (290°C). Substitutition of these temperatures in these equations (4.8), (4.16) and (4.17) gives the reduced temperature (T*)

The results are presented in appendix B in table B_5.

Plotting T* from equations 4.8, 4.16, and 4.17 gives figure 4.11 for the three solution

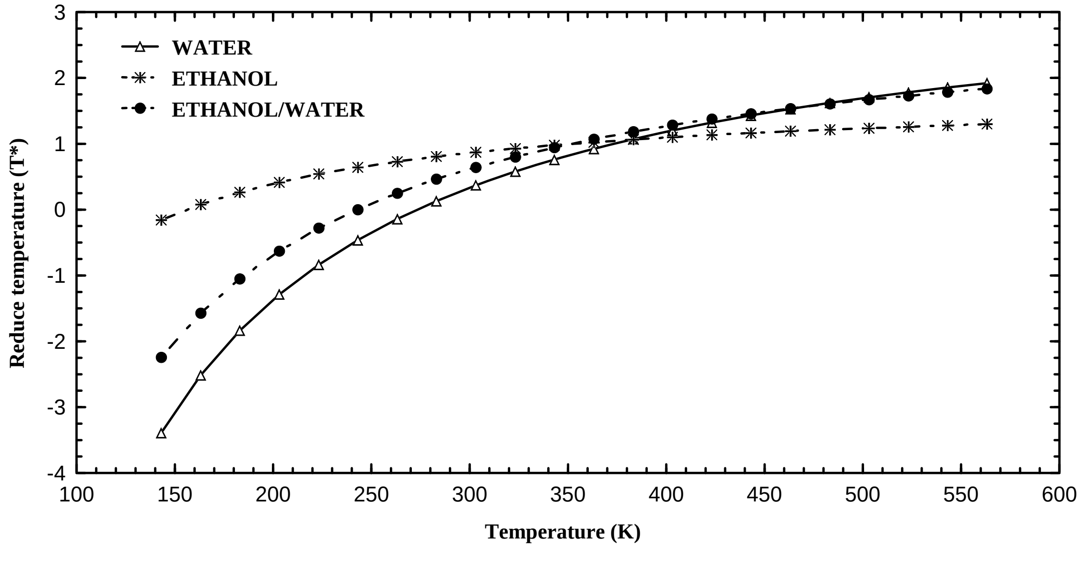


Fig 4.11: Reduced Temperature (T*) vs. Temperature (K)

Fig. 4.11: indicates that an increase in temperature results in significant increase in the reduced temperature.

Also the figure reveals that from 143.15 to 343.15 K the reduced temperature T* of the mixture increases with increasing the temperature more than of water alone and less than of ethanol alone and from 343.15 to 563.15 K the reduced temperature of the mixture increased higher than that of the ethanol.

For Glycerol/water system

Table 4.6 Glycerol /water system [58]

The substances	T_F (K)	T_B (K)
Water	273.15	373.15
Glycerol	290.15	563.15
50% mixture	247.69	375.72

For water the equation (4.7) becomes

$$T^* = -1019.2592 \times \frac{1}{T} + 3.7315 \qquad \ldots (4.8)$$

For Glycerol the equation (4.7) becomes

$$T^* = -598.5274 \times \frac{1}{T} + 2.0628 \qquad \ldots (4.18)$$

For 50% of Glycerol mixture the equation (4.7) becomes

$$T^* = -726.8772 \times \frac{1}{T} + 2.9346 \qquad \ldots (4.19)$$

The initial value of temperature (T) is 143.15 K (-130°C) to 563.15 K (290°C). Substitutition of these temperatures in these equations (4.4.8), (4.18) and (4.19) gives the reduced temperature (T*)

The results are listed in table B_6 in appendix B.

Figure 4.12 shows the variation of T* with solution temperature for the three solutions.

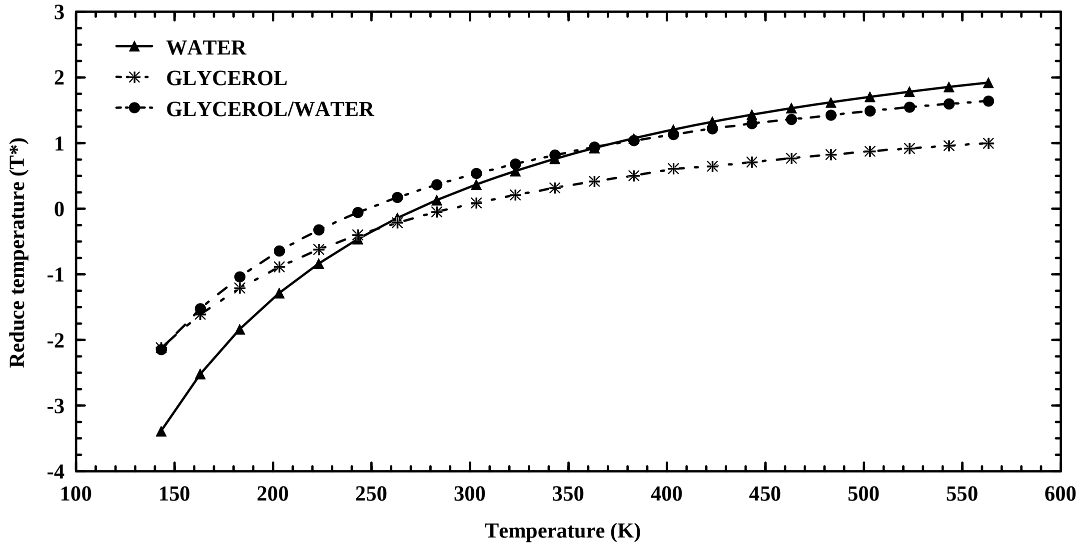


Fig 4.12: Reduced Temperature (T*) vs. Temperature (K)

Figure 4.12: reveals that the reduced temperature increases with increasing the temperature.

It is evident that the temperature of the mixture glycerol with water from 143.15 to 363.15 K leads to an increase is the reduced temperature T*over than that when every one is alone and from 363.15 to 563.15 K the reduced temperature T*of the mixture is below than of water and higher than of glycerol.

For Methanol/water system

Table 4.7 Methanol /water system [53]

The substances	T_F (K)	T_B (K)
Water	273.15	373.15
Methanol	175.45	337.65
50% mixture	227.15	376.86

For water the equation (4.7) becomes

$$T^* = -1019.2592 \times \frac{1}{T} + 3.7315 \qquad \ldots (4.8)$$

For Methanol the equation (4.7) becomes

$$T^* = -365.2324 \times \frac{1}{T} + 2.0817 \qquad \ldots (4.20)$$

For 50% of Methanol mixture the equation (4.7) becomes

$$T^* = -571.9239 \times \frac{1}{T} + 2.5176 \qquad \ldots (4.21)$$

The initial value of temperature (T) is 143.15 K (-130°C) to 563.15 K (290°C). Substitutition of these temperatures in these equations (4.8), (4.20) and (4.21) gives the reduced temperature (T*)

The results are presented in appendix B in table B_7.

Plotting T* from equations 4.8, 4.20, and 4.21 gives figure 4.13 for the three solution

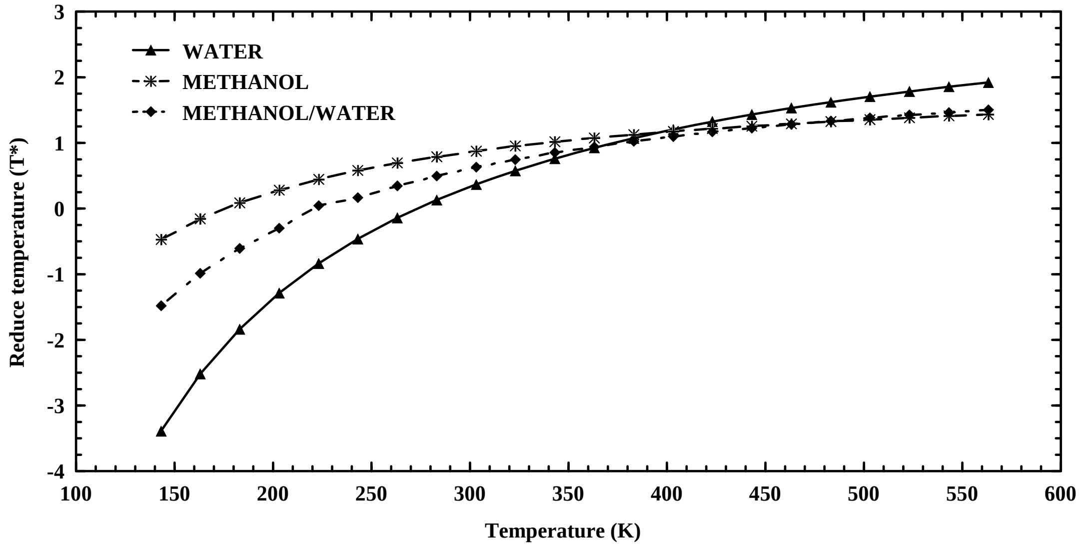


Fig 4.13: Reduce Temperature (T*) vs. Temperature (K)

Figure 4.13: indicates that when the temperature increases the reduced temperature increases.

The figure reveals that from 143.15 to 383.15 K the reduced temperature T* of the mixture is increased with increasing the temperature more than that of water and less than of methanol. Between 383.15 to 563.15 K the reduced temperature of mixture is higher than of methanol and less than of water.

Determination of the reduced temperature among different pure components is compared in figure 4.14. The results are listed in table C_1 in appendix C.

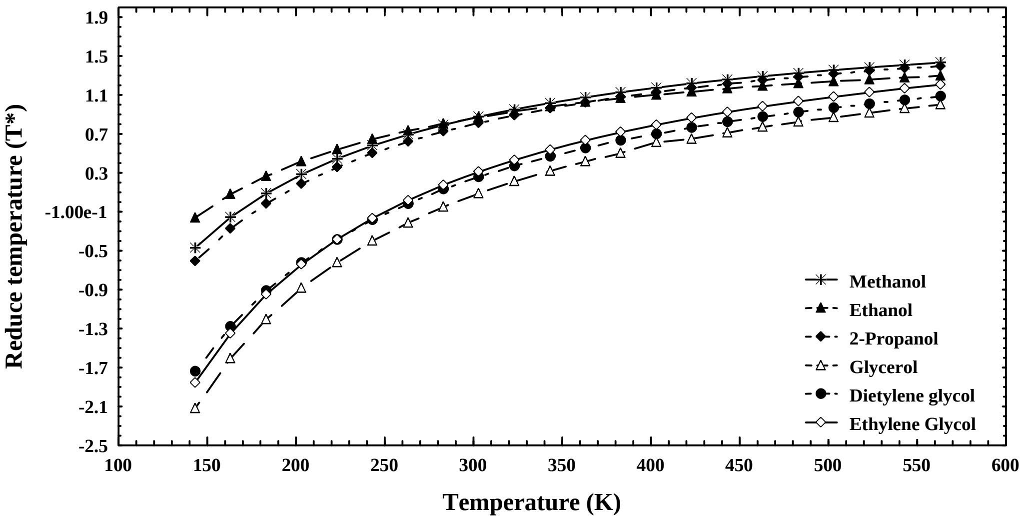


Fig 4.14: Reduce Temperature (T*) vs. Temperature (K) for pure component

Figure 4.14: reveals that the reduced temperature increases with increasing the temperature for pure component.

It is evident that the glycerol gives reduced temperature values less than other components. The E.G gives values of the reduced temperature more than of diethylene glycol or glycerol and less than of 2-propanol, ethanol, and methanol. In higher temperature the reduced temperature T* of methanol recorded degrees higher than other pure component.

Determination of the reduced temperature among different mixture components with water is compared in figure 4.14. The results are presented in appendix C in tableC_2.

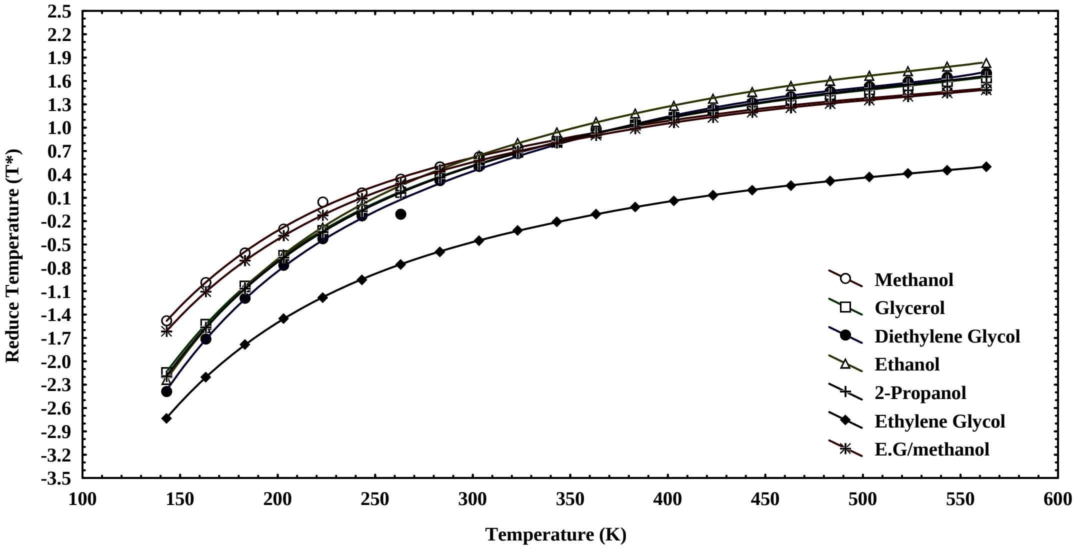


Fig 4.15: Reduce Temperature (T*) vs. Temperature (K) for mixture with water

Fig. 4.15: indicates that an increase in solution temperature results in significant increase in the reduced temperature for the solutions.

It is evident that the ethylene glycol with water recorded is less than other mixtures. In low temperatures the mixture methanol with water recorded more than of other mixtures. In higher temperature the reduced temperature T* of ethanol recorded degrees higher than other mixtures.

4.5 Correlation

In this work the statistica computer program was used to obtain the correlations describing the system.

In addition these correlations can be used without performing the experiments. It was noticed that the freezing temperature T_F is affected by weight percent of Ethylene Glycol C. This relation can be expressed as follows:

$$T_F = f(C^b) \qquad \ldots (4.22)$$

Statistical analysis of experimented results using Rosenbrok and Quasi-Newton method gives the following relation to predict the freezing temperature for water – ethylene glycol solution at 25°C.

$$T_F = A_1 \times 10\wedge(-08 \times C^5) + A_2 \times 10\wedge(-05 \times C^4) + A_3 \times C^3 + A_4 \times C^2 + A_5 \times C + A_6 \qquad \ldots (4.23)$$

Where: T_F is the freezing temperature (°C), and C is the weight percent of ethylene glycol. Table 4.8 shows the values of the constants. Figure 4.16 shows the relation between the values of T_F taken from experimental results and the theoretical results from mathematical correlation. It can be noticed that most points lie at or close to the 45° straight line with ±9.9 percent error.

Table 4.8 Values of the constants in Eq.(4.23)and the corrleation coefficient

Constants	Values	Variance (V%)	Correlation coefficient (R)
A1	-3.06189	99.59	0.9928
A2	3.806444		
A3	0.000247		
A4	-0.0302		
A5	0.185096		
A6	-0.744554		

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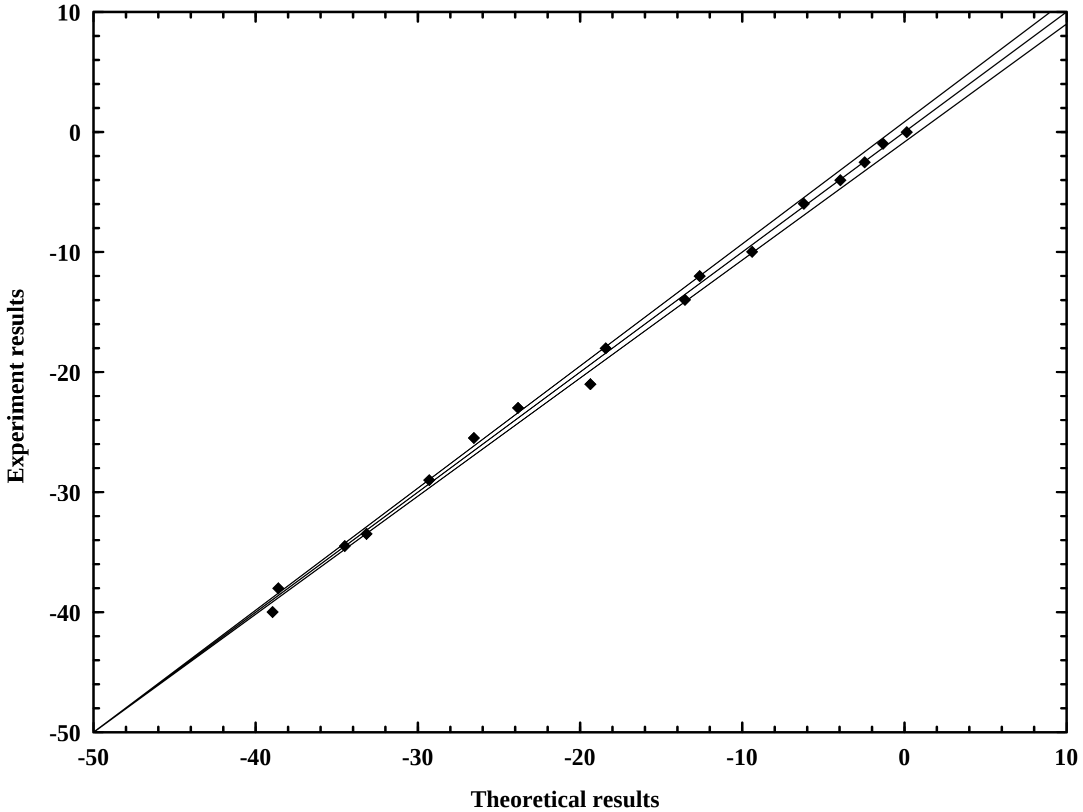

Fig 4.16 Temperature experimental results vs. theoretical results

The freezing temperature T_F is affected by the weight percent of Ethylene Glycol with methanol C.

Statistical analysis (Rosenbrok and Quasi-Newton method) gives the following relation of water, ethylene glycol, and 5% methanol solution:

$$T_F = A_1 \times C^6 + A_2 \times C^5 + A_3 \times C^4 + A_4 \times C^3 + A_5 \times C^2 + A_6 \times C + A_7 \qquad \ldots (4.24)$$

Where:

C is the weight percent of ethylene glycol.

Table 4.9 shows the values of the constants of Eq. 4.24. Figure 4.17 shows the relation between the values of T_F taken from experimental data and the predicted values from mathematical correlation. The percent error is ±2.3%.

Table 4.9 Values of the correlations coefficients in Eq.(4.24)

Constants	Values	Variance (V %)	Correlation coefficient (R)
A1	-5.1×10^{-10}	99.669	0.998
A2	1.31×10^{-08}		
A3	1.69×10^{-05}		
A4	-0.00173		
A5	0.048945		
A6	-0.92848		
A7	0.294131		

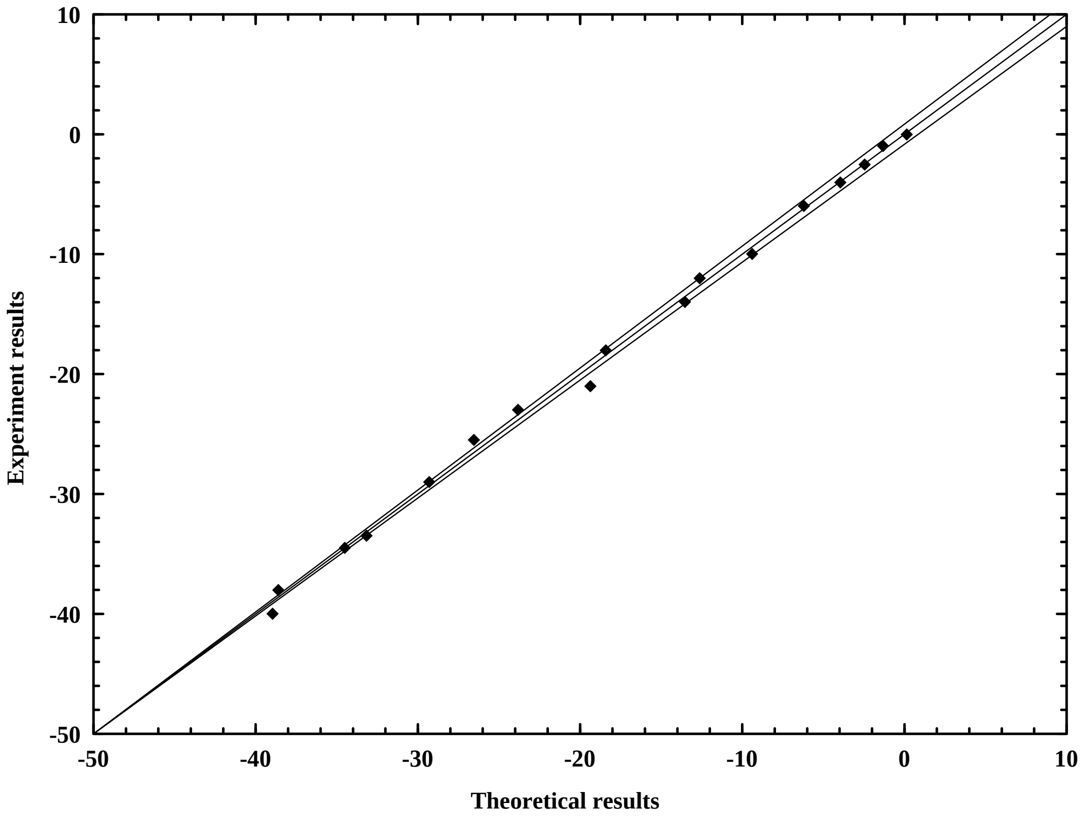

Fig 4.17: Temperature of experimental data vs. temperature of theoretical data

The boiling temperature T_B is affected by the weight percent of Ethylene Glycol C. This relation can be expressed as follows:

Statistical analysis (Rosenbrok and Quasi-Newton method) gives the following relation to obtain the boiling temperature for water – ethylene glycol solution at 25°C.

$$T_B = A_1 \times 10\wedge(-09 \times C^6) + A_2 \times 10\wedge(-07 \times C^5) + A_3 \times 10\wedge(-05 \times C^4) + A_4 \times C^3 + A_5 \times C^2 + A_6 \times C + A_7$$

… (4.25)

Table 4.10 shows the values of the constants. Figure 4.18 shows the relation between the values of T_B taken from experimental data and the predicted values from mathematical correlation. It can be noticed that most point lie at or close to the 45° straight line ±7.92% error.

Table (4.10) Values of the corrleations coefficients in Eq.(4.25)

Constants	Values	Variance (V%)	Correlation coefficient (R)
A1	-12.2722	99.48	0.992
A2	10.82779		
A3	10.82779		
A4	0.000359		
A5	-0.044008		
A6	1.729584		
A7	90.61662		

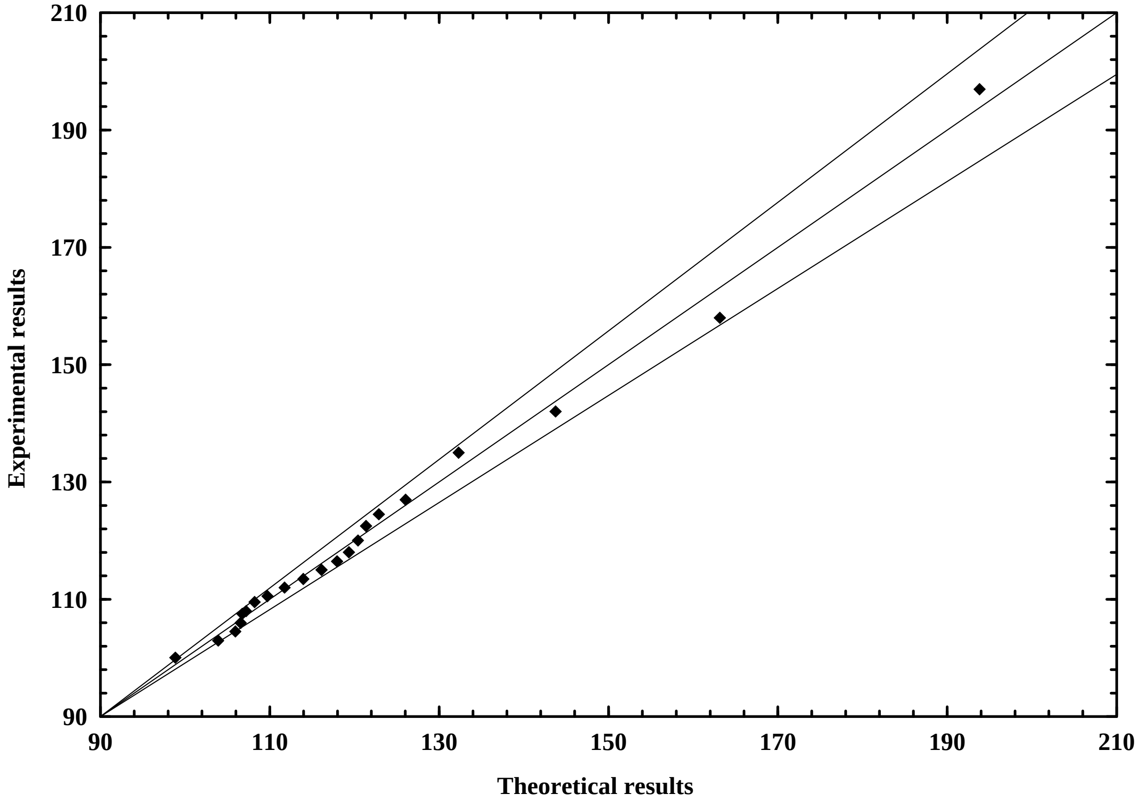

Fig 4.18: Temperature of experimental data vs. temperature of theoretical data

The following relation is obtained for boiling temperature in the presence of 5% methanol.

$$T_B = A_1 \times C^5 + A_2 \times C^4 + A_3 \times C^3 + A_4 \times C^2 + A_5 \times C + A_6 \qquad \ldots (4.26)$$

Table 4.11 shows the values of the constants. Figure 4.19 show the relation between the values of T_B taken from experimental data and the predicted values from mathematical correlation. The error presence is ±2.25%.

Table 4.11 Values of the correlations coefficients in Eq. (4.26)

Constants	Values	Variance (V%)	Correlation coefficient (R)
A1	2.17×10^{-07}	99.366	0.9968
A2	-4.5×10^{-05}		
A3	0.003288		
A4	-0.09532		
A5	1.160554		
A6	98.53581		

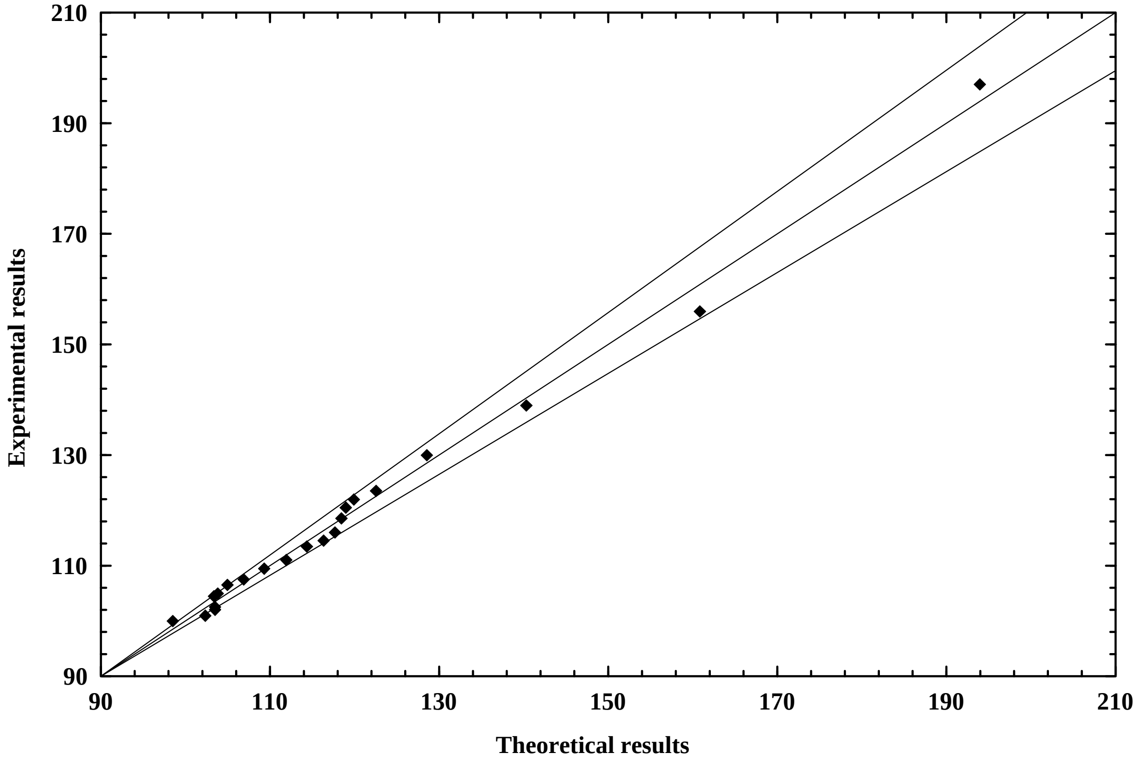

Fig 4.19: Temperature of experimental data vs. temperature of theoretical data

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

From the experimental work the following conclusions are obtained:

1. Addition of Ethylene Glycol to water in percents 0 – 55% leads to decrease gradually in the freezing temperature. Addition of 5% methanol to Ethylene Glycol – Water lead to further decrease gradually of freezing point at different concentrations of ethylene glycol.
2. Addition of 5% methanol to Ethylene Glycol – Water decreases the boiling point at different concentrations of mixture.
3. The minimum freezing point is found at 50% of Ethylene Glycol with 5% methanol where it reads -43°C
4. The boiling point is found at 50% of E.G with 5% methanol where it reads 114.5°C
5. The Leimezs model is found to fairly fit the experimental results then to determine reduced temperature T* from experimental boiling temperature and freezing temperature.

5.2 Recommendations

Further studies could be conducted to:

1. Investigation of the effect of addition of other antifreeze components on the freezing temperature and boiling temperature of water.
2. Investigation of the addition of methanol on corrosion rate of engines and on the physical properties as viscosity and specific gravity of solution.
3. Investigation the effect of environmental conditions such as solution velocity agitation and shear stress on the freezing point.
4. Investigation the parameter a from Redlich-Kwong equation, the enthalpy, and entropy by reduced temperature (T*).

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Appendix A

Table A1: Freezing Temperature of aqueous solution of E.G./water and E.G/Water/Methanol

Wt.%	T(°C) (E.G/WATER)	T(°C) (E.G/WATER/METHAMOL)
0	0	0
5	-1	-3
10	-2.5	-5
15	-4	-8
20	-6	-10
25	-10	-13.5
30	-14	-17
35	-18	-20.5
40	-23	-24.5
45	-29	-32
50	-34.5	-39
55	-40	-43
80	-38	-40
85	-33.5	-35
90	-25.5	-27
95	-21	-18.5
100	-12	-12

Table A2: Boiling Temperature of aqueous solution of E.G./water and E.G/Water/Methanol

Wt%	T(C) (E.G/WATER)	T(C) (E.G/WATER/METHANOL)
0	100	100
5	103	101
10	104.5	102
15	106	102.5
20	107.5	104.5
25	108	105
30	109.5	106.5
35	110.5	107.5
40	112	109.5
45	113.5	111
50	115	113.5
55	116.5	114.5
60	118	116
65	120	118.5
70	122.5	120.5
75	124.5	122
80	127	123.5
85	135	130
90	142	139
95	158	156
100	197	197

Appendix B

Table B1: The Reduced Temperature of E.G, Water, and Mixture at Different Temperature

T(°C)	T(K)	T* (water)	T* (E.G)	**T* (E.G/water)**
290	563.15	1.9216	1.2063	0.496
270	543.15	1.8549	1.1679	0.4555
250	523.15	1.7832	1.1266	0.4119
230	503.15	1.7057	1.0819	0.3648
210	483.15	1.6219	1.0336	0.3139
190	463.15	1.5308	0.9811	0.2585
170	443.15	1.4315	0.9238	0.1981
150	423.15	1.3228	0.8612	0.132
130	403.15	1.2033	0.7923	0.0594
110	383.15	1.0713	0.7163	-0.0209
90	363.15	0.9248	0.6318	-0.1099
70	343.15	0.7612	0.5375	-0.2094
50	323.15	0.5774	0.4316	-0.3211
30	303.15	0.3693	0.3116	-0.4476
10	283.15	0.1318	0.1748	-0.592
-10	263.15	-0.1418	0.0171	-0.7583
-30	243.15	-0.4604	-0.1665	-0.952
-50	223.15	-0.8361	-0.3831	-1.1804
-70	203.15	-1.2858	-0.6423	-1.4537
-90	183.15	-1.8337	-0.958	-1.7868
-110	163.15	-2.5159	-1.3513	-2.2015
-130	143.15	-3.3887	-1.8543	-2.7321

Table B2: The Reduced Temperature of E.G, Water, and Mixture with 5% Methanol at Different Temperature

T(°C)	T(K)	T* (water)	T* (E.G)	T* (E.G/water/5%methanol)
290	563.15	1.9216	1.2063	1.4842
270	543.15	1.8549	1.1679	1.4453
250	523.15	1.7832	1.1266	1.4034
230	503.15	1.7057	1.0819	1.3583
210	483.15	1.6219	1.0336	1.3093
190	463.15	1.5308	0.9811	1.2561
170	443.15	1.4315	0.9238	1.1982
150	423.15	1.3228	0.8612	1.1347
130	403.15	1.2033	0.7923	1.065
110	383.15	1.0713	0.7163	0.988
90	363.15	0.9248	0.6318	0.9025
70	343.15	0.7612	0.5375	0.807
50	323.15	0.5774	0.4316	0.700
30	303.15	0.3693	0.3116	0.5783
10	283.15	0.1318	0.1748	0.4397
-10	263.15	-0.1418	0.0171	0.280
-30	243.15	-0.4604	-0.1665	0.0941
-50	223.15	-0.8361	-0.3831	-0.1252
-70	203.15	-1.2858	-0.6423	-0.3876
-90	183.15	-1.8337	-0.958	-0.7074
-110	163.15	-2.5159	-1.3513	-1.1055
-130	143.15	-3.3887	-1.8543	-1.6149

Table B3: The Reduced Temperature of 2-Propanol, Water, and Mixture at Different Temperature

T(°C)	T(K)	T* **(water)**	T* **(2-propanol)**	**T* (2-propanol/water)**
290	563.15	1.9216	1.3992	1.6582
270	543.15	1.8549	1.374	1.6099
250	523.15	1.7832	1.3469	1.5578
230	503.15	1.7057	1.3177	1.5016
210	483.15	1.6219	1.2861	1.4408
190	463.15	1.5308	1.2517	1.3747
170	443.15	1.4315	1.2142	1.3027
150	423.15	1.3228	1.1732	1.2238
130	403.15	1.2033	1.128	1.1371
110	383.15	1.0713	1.0782	1.0414
90	363.15	0.9248	1.0229	0.9351
70	343.15	0.7612	0.9612	0.8164
50	323.15	0.5774	0.8918	0.6831
30	303.15	0.3693	0.8133	0.5321
10	283.15	0.1318	0.7236	0.3598
-10	263.15	-0.1418	0.6204	0.1614
-30	243.15	-0.4604	0.5001	-0.0697
-50	223.15	-0.8361	0.3583	-0.3422
-70	203.15	-1.2858	0.1886	-0.6685
-90	183.15	-1.8337	-0.0182	-1.065
-110	163.15	-2.5159	-0.2757	-1.5609
-130	143.15	-3.3887	-0.6051	-2.194

Table B4: The Reduced Temperature of Diethylene glycol, Water, and Mixture at Different Temperature

T(°C)	T(K)	T* (water)	T* (Diethylene glycol)	**T* (Diethylene glycol/water)**
290	563.15	1.9216	1.084	1.7
270	543.15	1.8549	1.0485	1.6488
250	523.15	1.7832	1.0104	1.5936
230	503.15	1.7057	0.9692	1.534
210	483.15	1.6219	0.9246	1.4695
190	463.15	1.5308	0.8761	1.3994
170	443.15	1.4315	0.8233	1.323
150	423.15	1.3228	0.7655	1.2394
130	403.15	1.2033	0.702	1.1475
110	383.15	1.0713	0.6318	1.0459
90	363.15	0.9248	0.5539	0.9332
70	343.15	0.7612	0.4669	0.8074
50	323.15	0.5774	0.3692	0.666
30	303.15	0.3693	0.2585	0.506
10	283.15	0.1318	0.1322	0.3232
-10	263.15	-0.1418	-0.0132	-0.1128
-30	243.15	-0.4604	-0.1827	-0.1323
-50	223.15	-0.8361	-0.3824	-0.4213
-70	203.15	-1.2858	-0.6216	-0.7672
-90	183.15	-1.8337	-0.9129	-1.1887
-110	163.15	-2.5159	-1.2757	-1.7135
-130	143.15	-3.3887	-1.7398	-2.3849

Table B5: The Reduced Temperature of Ethanol, Water, and Mixture at Different Temperature

T(°C)	T(K)	T* (water)	T* (Ethanol)	**T*** (Ethanol/water)
290	563.15	1.9216	1.2993	1.8361
270	543.15	1.8549	1.281	1.7849
250	523.15	1.7832	1.2612	1.7299
230	503.15	1.7057	1.24	1.6704
210	483.15	1.6219	1.2169	1.6061
190	463.15	1.5308	1.1919	1.5362
170	443.15	1.4315	1.1646	1.4599
150	423.15	1.3228	1.1348	1.3765
130	403.15	1.2033	1.102	1.2848
110	383.15	1.0713	1.0657	1.1835
90	363.15	0.9248	1.0255	1.0711
70	343.15	0.7612	0.9805	0.9455
50	323.15	0.5774	0.93	0.8044
30	303.15	0.3693	0.8729	0.6447
10	283.15	0.1318	0.8076	0.4624
-10	263.15	-0.1418	0.7325	0.2524
-30	243.15	-0.4604	0.645	0.0008
-50	223.15	-0.8361	0.5418	-0.2804
-70	203.15	-1.2858	0.4183	-0.6255
-90	183.15	-1.8337	0.2678	-1.046
-110	163.15	-2.5159	0.0804	-1.5696
-130	143.15	-3.3887	-0.1593	-2.2396

Table B6: The Reduced Temperature of Glycerol, Water, and Mixture at Different Temperature

T(°C)	T(K)	T* **(water)**	T* **(Glycerol)**	**T* (Glycerol/water)**
290	563.15	1.9216	1	1.6439
270	543.15	1.8549	0.9608	1.5963
250	523.15	1.7832	0.9187	1.5452
230	503.15	1.7057	0.8732	1.4899
210	483.15	1.6219	0.824	1.4301
190	463.15	1.5308	0.7705	1.3652
170	443.15	1.4315	0.7121	1.2943
150	423.15	1.3228	0.6483	1.2168
130	403.15	1.2033	0.6141	1.1316
110	383.15	1.0713	0.5007	1.0375
90	363.15	0.9248	0.4146	0.9374
70	343.15	0.7612	0.3186	0.8164
50	323.15	0.5774	0.2106	0.6853
30	303.15	0.3693	0.0884	0.5369
10	283.15	0.1318	-0.051	0.3675
-10	263.15	-0.1418	-0.2117	0.1724
-30	243.15	-0.4604	-0.3988	-0.0548
-50	223.15	-0.8361	-0.6194	-0.3227
-70	203.15	-1.2858	-0.8834	-0.6434
-90	183.15	-1.8337	-1.2052	-1.0342
-110	163.15	-2.5159	-1.6058	-1.5207
-130	143.15	-3.3887	-2.1183	-2.1431

Table B7: The Reduced Temperature of Methanol, Water, and Mixture at Different Temperature

T(°C)	T(K)	T* (water)	T* (Methanol)	**T* (Methanol/water)**
290	563.15	1.9216	1.4331	1.502
270	543.15	1.8549	1.4093	1.4646
250	523.15	1.7832	1.3836	1.4244
230	503.15	1.7057	1.3558	1.3809
210	483.15	1.6219	1.3258	1.3339
190	463.15	1.5308	1.2931	1.2827
170	443.15	1.4315	1.2575	1.227
150	423.15	1.3228	1.2186	1.166
130	403.15	1.2033	1.1758	1.099
110	383.15	1.0713	1.1285	1.0249
90	363.15	0.9248	1.076	0.9427
70	343.15	0.7612	1.0173	0.8509
50	323.15	0.5774	0.9515	0.7478
30	303.15	0.3693	0.8769	0.631
10	283.15	0.1318	0.7918	0.4977
-10	263.15	-0.1418	0.6938	0.3442
-30	243.15	-0.4604	0.5796	0.1655
-50	223.15	-0.8361	0.445	0.0454
-70	203.15	-1.2858	0.2839	-0.2977
-90	183.15	-1.8337	0.0875	-0.6051
-110	163.15	-2.5159	-0.1569	-0.9879
-130	143.15	-3.3887	-0.4697	-1.4777

Appendix C

Table C1: The Reduced Temperature of Pure Components at Different Temperature

T(K)	T* (Methanol)	T* (Glycerol)	T* (Diethylene glycol))	T* (Ethanol)	T* (2-propanol)	T* (E.G)
563.15	1.4331	1	1.084	1.2993	1.3992	1.2063
543.15	1.4093	0.9608	1.0485	1.281	1.374	1.1679
523.15	1.3836	0.9187	1.0104	1.2612	1.3469	1.1266
503.15	1.3558	0.8732	0.9692	1.24	1.3177	1.0819
483.15	1.3258	0.824	0.9246	1.2169	1.2861	1.0336
463.15	1.2931	0.7705	0.8761	1.1919	1.2517	0.9811
443.15	1.2575	0.7121	0.8233	1.1646	1.2142	0.9238
423.15	1.2186	0.6483	0.7655	1.1348	1.1732	0.8612
403.15	1.1758	0.6141	0.702	1.102	1.128	0.7923
383.15	1.1285	0.5007	0.6318	1.0657	1.0782	0.7163
363.15	1.076	0.4146	0.5539	1.0255	1.0229	0.6318
343.15	1.0173	0.3186	0.4669	0.9805	0.9612	0.5375
323.15	0.9515	0.2106	0.3692	0.93	0.8918	0.4316
303.15	0.8769	0.0884	0.2585	0.8729	0.8133	0.3116
283.15	0.7918	-0.051	0.1322	0.8076	0.7236	0.1748
263.15	0.6938	-0.2117	-0.0132	0.7325	0.6204	0.0171
243.15	0.5796	-0.3988	-0.1827	0.645	0.5001	-0.1665
223.15	0.445	-0.6194	-0.3824	0.5418	0.3583	-0.3831
203.15	0.2839	-0.8834	-0.6216	0.4183	0.1886	-0.6423
183.15	0.0875	-1.2052	-0.9129	0.2678	-0.0182	-0.958
163.15	-0.1569	-1.6058	-1.2757	0.0804	-0.2757	-1.3513
143.15	-0.4697	-2.1183	-1.7398	-0.1593	-0.6051	-1.8543

Table C2: The Reduced Temperature of Solutions at Different Temperature

T(K)	T* (Methanol)	T* (Glycerol)	T* (Diethylene glycol)	T* (Ethanol)	T* (2-propanol)	T* (E.G)	**T* E.G+M**
563.15	**1.502**	**1.6439**	**1.7**	**1.8361**	**1.6582**	**0.496**	**0.4975**
543.15	**1.4646**	**1.5963**	**1.6488**	**1.7849**	**1.6099**	**0.4555**	**0.4575**
523.15	**1.4244**	**1.5452**	**1.5936**	**1.7299**	**1.5578**	**0.4119**	**0.4145**
503.15	**1.3809**	**1.4899**	**1.534**	**1.6704**	**1.5016**	**0.3648**	**0.368**
483.15	**1.3339**	**1.4301**	**1.4695**	**1.6061**	**1.4408**	**0.3139**	**0.3178**
463.15	**1.2827**	**1.3652**	**1.3994**	**1.5362**	**1.3747**	**0.2585**	**0.2631**
443.15	**1.227**	**1.2943**	**1.323**	**1.4599**	**1.3027**	**0.1981**	**0.2036**
423.15	**1.166**	**1.2168**	**1.2394**	**1.3765**	**1.2238**	**0.132**	**0.1384**
403.15	**1.099**	**1.1316**	**1.1475**	**1.2848**	**1.1371**	**0.0594**	**0.0667**
383.15	**1.0249**	**1.0375**	**1.0459**	**1.1835**	**1.0414**	**-0.0209**	**-0.0124**
363.15	**0.9427**	**0.9374**	**0.9332**	**1.0711**	**0.9351**	**-0.1099**	**-0.1003**
343.15	**0.8509**	**0.8164**	**0.8074**	**0.9455**	**0.8164**	**-0.2094**	**-0.1984**
323.15	**0.7478**	**0.6853**	**0.666**	**0.8044**	**0.6831**	**-0.3211**	**-0.3086**
303.15	**0.631**	**0.5369**	**0.506**	**0.6447**	**0.5321**	**-0.4476**	**-0.4334**
283.15	**0.4977**	**0.3675**	**0.3232**	**0.4624**	**0.3598**	**-0.592**	**-0.5759**
263.15	**0.3442**	**0.1724**	**-0.1128**	**0.2524**	**0.1614**	**-0.7583**	**-0.7399**
243.15	**0.1655**	**-0.0548**	**-0.1323**	**0.0008**	**-0.0697**	**-0.952**	**-0.931**
223.15	**0.0454**	**-0.3227**	**-0.4213**	**-0.2804**	**-0.3422**	**-1.1804**	**-1.1563**
203.15	**-0.2977**	**-0.6434**	**-0.7672**	**-0.6255**	**-0.6685**	**-1.4537**	**-1.426**
183.15	**-0.6051**	**-1.0342**	**-1.1887**	**-1.046**	**-1.065**	**-1.7868**	**-1.7545**
163.15	**-0.9879**	**-1.5207**	**-1.7135**	**-1.5696**	**-1.5609**	**-2.2015**	**-2.1637**
143.15	**-1.4777**	**-2.1431**	**-2.3849**	**-2.2396**	**-2.194**	**-2.7321**	**-2.6871**

Appendix D

Table D1: Freezing point of aqueous solution of P.G. – water

Reported by Union Carbide Corp [29]

Wt% (P.G)	T_F(°C)
0.000	**0.000**
10.000	**-3.000**
20.000	**-7.500**
30.000	**-13.000**
40.000	**-22.000**
50.000	**-33.000**
60.000	**-62.000**

Table D2: Boiling point of aqueous solution of P.G. – water

Reported by Union Carbide Corp [29]

Wt% (P.G)	T_B(°C)
0.000	**100.000**
10.000	**100.500**
20.000	**101.500**
30.000	**102.000**
40.000	**104.000**
50.000	**106.500**
60.000	**109.500**
70.000	**113.500**
80.000	**119.000**
90.000	**132.000**
100.000	**187.000**

الخلاصة

يتضمن هذا البحث إيجاد اقل نقطة انجماد يمكن الوصول لها من خلال خلط الماء مع الاثلين كلايكول ولغرض خفض درجة الانجماد أكثر تم إضافة نسبة 5% ميثانول إلى خليط الماء مع الاثلين كلايكول ووجد انه يؤدي الى خفض درجة الانجماد.

التجارب تضمنت ايضا ايجاد درجات الغليان لمحلول اثلين كلايكول مع الماء بنسب مختلفة تتراوح بين (0-100)% مع إضافة 5% الميثانولول إلى المحلول وقد دلت التجارب العملية على ان هذه المواد تؤدي الى خفض درجة الانجماد عن درجة انجماد الماء وهي الصفر المئوي.وقد أجريت التجارب العملية بضغط واحد جو وبدرجة حرارة 20° م.

النتائج اثبتت ان زيادة نسبة الاثلين كلايكول من 0-55% ادى الى زيادة انخفاض درجة الانجماد وفوق 80% درجة الانجماد تبدا بالزيادة. كذلك باضافة الميثانول الى المحلول يؤدي الى انخفاض درجة الانجماد اكثر.

تم تعويض درجات الانجماد ودرجات الغليان المقاسة عمليا في المعادلة الموضحة لإيجاد الحرارة المختزلة:

$$T^* = \frac{\frac{T_F}{T} - 1}{\frac{T_F}{T_B} - 1}$$

وكذلك استخدمت هذه المعادلة لإيجاد الحرارة المختزلة لمواد أخرى عند درجات حرارة تراوحت بين 130- إلى 290°مئوي.

المعادلات التجريبية لحساب درجة الانجماد ودرجة الغليان للمحلول موضحة مع نسبة خطا يتراوح بين 9.9% - 2.25% . النتائج قورينت مع باحثين اخرين استخدموا مواد اخرى.

المعادلة التي تم الحصول عليها نظريا لحساب درجة لانجماد لمحلول اثلين كلايكول مع الماء:

$$TF = -3.06189\times 10\hat{}(-08\times C^{5}) + 3.806444\times 10\hat{}(-05\times C^{4}) + 0.000274\times C^{3}$$
$$-0.0302\times C^{2} + 0.185096\times C - 0.744554$$

ومع اضافة الميثانول الى محلول اثلين كلايكول مع الماء:

$$TF = -5.1\times 10\hat{}^{-10}\times C^{6} + 1.31\times 10\hat{}^{-08}\times C^{5} + 1.69\times 10\hat{}^{-05}\times C^{4} - 0.00173\times C^{3}$$
$$+0.048945\times C^{2} - 0.92848\times C + 0.294131$$

المعادلة التي تم الحصول عليها نظريا لحساب درجة الغليان لمحلول اثلين كلايكول مع الماء:

$$T_B = -12.2722\times 10\hat{}(-09\times C^{6}) + 10.82779\times 10\hat{}(-07\times C^{5}) + 10.82779\times 10\hat{}(-05\times C^{4})$$
$$+0.000359\times C^{3} - 0.044008\times C^{2} + 1.729584\times C + 90.61662$$

ومع اضافة الميثانول الى محلول اثلين كلايكول مع الماء:

$$T_B = 2.17\times 10\hat{}^{-07}\times C^{5} - 4.5\times 10\hat{}^{-05}\times C^{4} + 0.003288\times C^{3} - 0.09532\times C^{2} + 1.160554\times C$$
$$+98.53581$$

شكر و تقدير

أتوجه بالشكر لله على هنيء عطائه ومحمود بلائه وتوالي سبوغ نعمائه الذي مكنني من التغلب على جميع الصعوبات التي واجهتني خلال البحث.

كذلك أود أن اعبر عن امتناني وتقديري إلى أساتذتي الدكتور ضياء الدين محمد والدكتور طالب كشمولة والدكتور باسم عبيد لتوجيهي ومساعدتي ومساندتي طوال فترة البحث.

أود أيضا أن اشكر جميع أساتذة وموظفي قسم الهندسة الكيمياوية في جامعة النهرين لإبدائهم المساعدة اللازمة أثناء البحث.

وأقدم شكري وتقديري إلى منشاة الباسل وخاصة قسم بحوث الكيمياء لأبداهم المساعدة اللازمة لإتمام بحثي.

لا أنسى أن أتوجه بالشكر إلى أحبائي والدي وأخي وأخواتي على دعمهم وتشجيعهم ودعواتهم المستمرة.

شيماء فاضل الزبيدي

2007

دراسة ظاهرة مزج اثلين كلايكول مع الماء لقياس درجة الانجماد

رسالة
مقدمة الى كلية الهندسة في جامعة النهرين وهي جزء من متطلبات نيل
درجة ماجستير علوم في الهندسة الكيمياوية

من قبل
شيماء فاضل مجيد الزبيدي
بكالوريوس علوم في الهندسة الكيمياوية 2004

جمادي الثاني 1428 هـ
حزيران 2007 م