# EFFECT OF ADDITIVES OF LUBRICATING OILS ON FLOW ACTIVATION ENERGY

A Thesis
Submitted to the College of Engineering of
Al-Nahrain University in Partial Fulfillment of the
Requirements for the Degree of Master of Science
in Chemical Engineering

by

**Ramy Mohamed Jebir Al-Alewy**

(B.Sc. in Chemical Engineering 2002)

Rabee el-awal 1426

April 2005

# *CERTIFICATION*

We certify that the preparation of this thesis titled "**Effect of Additives of Lubricating Oils on Flow Activation Energy**" was made by **Ramy Mohamed Jebir Al-Alewy** under our supervision at Al-Nahrain University, College of Engineering, in partial fulfillment of the requirement for the degree of Master of Science in Chemical engineering.

Signature:
Name: **Dr. Talib Kashmoula**
(Supervisor)
Date: / /

Signature:
Name: **Prof. Dr. Qasim J.Slaiman**
Head of Chemical Engineering Department
Date: 22 / 5 / 05

# *CERTIFICATE*

We certify that the preparation of this thesis titled **"Effect of Additives of Lubricating Oils on Flow Activation Energy"** was made by **Ramy Mohamed Jebir Al-Alewy** under our supervision at Al-Nahrain University, College of Engineering, in partial fulfillment of the requirement for the degree of Master of Science in Chemical engineering.

Signature:
Name: **Dr. Talib Kashmoula**
(Supervisor)
Date: / /

Signature:
Name: **Prof. Dr. Qasim J.Slaiman**
(Chairman)
Date: 22/ 5 / 05

Signature:
Name: **Dr. Mohammed N.Latif**
(Member)
Date: 16 / 5 / 05

Signature: N.K.Ibrah
Name:**Ass.Prof. Neran K.Ibrahem**
(Member)
Date: 19/ 5 / 05

Approval of the College of Engineering

Signature:
Name: **Prof. Dr. Fawzi M.Al-Naima**
Dean of the College of Engineering
Date: 8 6 /2005

# ABSTRACT

The dynamic viscosity of lubricating oils, are measured over a temperature range of 298-353 K with and without the additives. The four types of additives were used, Paranox 5263, Paranox 2281, olefin copolymer (OCP) and Polyisoprene 1502.

The flow activation energy of lubricating oils is calculated by using the viscosity measurement data.

This investigation studies the effect of the temperature changes and the concentration (weight percent of additives) on the flow activation energy of different types of mixtures, such as binary mixture and multi – component mixtures.

A method is based upon API gravity of oil, weight percent of additives and API gravity at ١٥,٦ $^0$C of additives is developed to predict the flow activation energy of lubricating oils as follows:

$$\mathbf{Ea = A_1 + A_2 * (WT\ \%) + A_3 * (API_{oil})^{A4}}$$

Where:

A1, A2, A3 and A4 are constant.

Ea= activation energy.

The proposed correlations have been found to fit all experimental data consisting of 294 measurements, with an overall average absolute deviation error 5.92 %

# LIST OF CONTENTS

Subject Page

## Chapter One

## Introduction

## Chapter Two

## Literature Survey

## Chapter Three
## Experimental work

## Chapter Four
## Results & Discussions

## Chapter Five
## Conclusions and Recommendations

## Appendix

# NOMENCLATURE

| | |
|---|---|
| **API** | **American Petroleum Institute** |
| **a** | **Length of jumps ($A^0$)** |
| **E** | **The maximum energy of attraction between two molecules(kJ/mole)** |
| **$E_0$** | **Total activation energy (kJ/mole)** |
| **$E_1$** | **The energy required to form an empty lattice site (hole) ( kJ/mole)** |
| **$E_2$** | **Energy required for the molecule to pass through the intermediate region of higher potential energy, Eq. (2-11)(kJ/mole)** |
| **$E_v$** | **Activation energy at constant volume (kJ/mole)** |
| **H** | **High viscosity index** |
| **h** | **Planck constant ($6.624 \times 10^{-27}$)** |
| **k** | **Frequency of molecule jumps** |
| **K** | **Boltzman constant ($1.380 \times 10^{-16}$)** |
| **$k_{f,}$ $k_b$** | **Frequency of forward jumps, frequency of backward jumps, Eq.(2-3)(Sec.$^{-1}$)** |
| **M** | **Molecular weight, Eq.(2-9)(g mass/g mole)** |
| **N** | **Avogadro number ($6.023 \times 10^{23}$ g/mole)** |
| **No.** | **Number** |
| **R** | **Gas constant (8.314 J/mole.K)** |

| | |
|---|---|
| **Sp.gr.** | **Specific gravity 15°C/15°C** |
| **v** | **The volume of a mole of a liquid, Eq.(2-2)(cm$^3$/mole)** |
| **V** | **Local free volume (cm$^3$/mole)** |
| **$V_0$** | **Critical local free volume, Eq. (2-10)** |
| **$V_f$** | **Eyring and Hirschfelder free volume** |
| **VI** | **Viscosity Index** |
| **$V_{XA}$,$V_{XB}$** | **The net velocity at which the molecules in layer A slip ahead in layer B, Eq.(2-5)(ft/sec)** |
| **Wt** | **Weight percent** |
| **$\Delta E_{vis}$** | **The activation energy for viscous flow, Eq.(2-14)(kJ/mole)** |
| **$\Delta G_0$** | **Free energy of activation Eq.(2-1)(kJ/mole)** |

## ***Abbreviations***

| | |
|---|---|
| **OCP** | **Olefin copolymer** |
| **LOAs** | **Lubricating Oil Additives** |
| **AFAE** | **Apparent flow activation energy** |
| **ASTM** | **American Standard for Testing** |

## ***Greek Letters***

| | |
|---|---|
| **$\mu$** | **Dynamic viscosity(cp)** |
| **$\nu$,$\eta$** | **Kinematics viscosity(cSt)** |
| **$\tau_{xy}$** | **Shear stress (Pascal)** |
| **$\delta$** | **Distance between two layer** |

# *CHAPTER ONE*

# *INTRODUCTION*

## *1-1 Appearance and Composition of Lubricating Oil*

Lubricating oils are composed of paraffins, naphthenes, aromatics and unsaturated compounds. Lubricating oil has a boiling point above 350 $^{o}$C and they are obtained as the main products from vacuum distillation units. The lubricating oils can be classified as animal or vegetable oils mineral oils and synthetic oils {1}.

There are different additives used to improve or modify one or more physical properties of base oils, such as kinematics viscosity, viscosity index, ash content, carbon residue, acid No., pour point, flash point, specific gravity, API, viscosity gravity constant and flow activation energy. The manufactures of these additives, which are controlled by certain companies, give the used additives certain secret name, as the know-how is secret. The additives composition and their structure is highly unknown. The lubricating oil will not be used after certain period of operation in engine. Large amounts of these lubricants are discarded which contain a higher amount of base oil, which is not affected by running in engine.

Reclamation of base oil from used oil is costly and needs a lot of operational costs. The additives in the used automobile lubricating oils are largely destroyed during operation while the base oil is slightly affected during operation. Therefore in order to prolong the life of the lubricating oil, i.e. performance of lubricating oil, it is necessary to adjust the amounts of additives and their types. These additives maintain certain physical and chemical properties of lubricating oil. It is difficult to get one additive to adjust all the physical properties. Therefore different additives were used in order to adjust some of the physical properties but can't adjust all the physical properties as it needs a lot of additives and this is very expensive. There is a limit to the amount of using mixed additives, due to side effects, such as contamination, increase in ash content and carbon residue and metallic deposition which blocks the engine operation and then reduce the performance of the lubricating oil {2}.

The most important property of a lubricating oil is its viscosity, which is a measure of its internal friction or ability to flow, and largely determines its suitability for any particular application {3}.

The viscosity of an oil decreases with rise in temperature but to a varying degree depending on the type of crude oil from which it is derived and the refining treatment to which it has been subjected. The relationship between viscosity and temperature is of significance for lubricating oils since most oils have to operate over a range of temperature.

## *1-2 Apparent Flow Activation Energy*

The theory of the free volume or activation energy of viscous flow has been discussed thoroughly by several researchers such as Eyring and Hirschfelder{4},Ewell and Eyring{5}, Heric and Brewer{6}.

The liquid is assumed to exist as a regular lattice, with momentum transfer resulting from molecules vibrating within the lattice structure, moving into nearby holes, or combinations of these two events; the movement from a lattice site to a hole is considered analogous to an activated chemical reactions{7}.

## *1 - 3 Aim of the Work*

Calculated the dynamic viscosity of lubricating oils, over a temperature range of 298-353 K with and without the additives, The four types of additives were used, Paranox 5263, Paranox 2281, olefin copolymer (OCP) and Polyisoprene 1502.

And study the effect of temperature and concentration of additives on apparent flow activation energy of some types of lubricating oils, also to develop appropriate equations to predict the flow activation energy of the blends at different concentrations and temperatures.

# *CHAPTER TWO*
# *LITERATURE SURVEY*

## *2-1 Lubricants*

There are many types of lubricants with various components used in machines. Some of these lubricants are used in gasoline engine or diesel engine which contain different types of chemical materials known as “additives” used for improving properties of these lubricants and gave the best requirements of operation, i.e. performance, of lubricating oil in engine.

In a lubricated system, where complete separation is attained between two surfaces, the lubricant viscosity becomes the controlling parameter, and the condition is termed hydrodynamic lubrication. Where surfaces interaction continues to exert a significant effect, the term boundary lubrication is used. In the absence of definite contamination, wear is the result of friction and in a simple case is roughly proportional to it. Again, different mechanisms exist due to the adhesion, abrasion, corrosion and fatigue. Even, though the final damage may be the end – product of a combination of these mechanisms {8}.

In brief, the lubrication is the art of minimizing friction and wear by interposing between the rubbing surfaces a film of a further material, known as a lubricant, which may be gaseous, liquid, or solid. Efficient lubrication is achieved as long as, first, a positive separation of the surfaces is achieved under motion and load and, secondly, the shear strength of the lubricant film is lower than that of the material of the surfaces {1}.

## *2-2 Description of Lubricants*

### 2-2-1 Selective Components for Lubricating Oils

Selection the types of lubricants are generally governed by two basic considerations, namely, the requirements of its lubrication functions and the necessity to retain its properties for some time under conditions of operation. The lubrication requirements are estimated for the specific application on the basis of variables, namely, bearing geometry, load, speed, temperature, and oil- flow rate {9}.

So liquid lubricants find the greatest favor in engineering applications because they readily provide separation of surfaces when correctly applied, and have a high cooling ability when circulated through the bearing area {1}.

Lubricating oils from petroleum consist essentially of complex mixtures of hydrocarbon molecules. These generally range from low viscosity oils with molecular weights as low as 250 to very viscous lubricants with molecular weights as high as about 1000. Physical properties, such as viscosity, viscosity-temperature- pressure characteristics, and performance, depend largely on the relative distribution of paraffinic, aromatic, and alicyclic, i.e. naphthenic, components {10, 11}.

The individual refined stock oils from one or more crude sources are blended in various proportions to provide lubricating oils suitable for a wide range of applications. The blending process can be by mechanical or air agitation, and can be either by a batch of a continuous in- line method {12}.

In the majority of cases, chemical additives are used to enhance the properties of base oils to enable specific application requirements to be met. Lubricants frequently contain a number of additives to achieve a balance of properties suitable for the intended application. These must be compatible with the base oil, and with the other additives present. Thus the proper selection of the components for the lubricating oil formulation requires knowledge of the most suitable crude sources for the base oils, the type of refining required, the types of additive necessary and the possible interactions of these components on the properties of the finished lubricating oil {12}.

### 2-2-2 Types of Lubricants

A typical commercially available lubricant is composed of 80 to 90 % of base stock, i.e. base oil, and the rest is the auxiliary materials known as additives. The base oil determines the physical properties and flow characteristics of the lubricant and constitutes its most important component. Base stocks can be classified as biological, mineral and synthetic base oils {13}.

#### 2-2-2-1 Biological Oils

Materials provided the first widely used lubricants, and indeed the derivation of “oil” from “olea”, the olive, is a pointer to this, in the main these products, which result either from “rendering” animal matter or from expression from vegetable matter, practically known as biological oils, such as seeds consist of mixtures of glyceryl esters of various fatty acids. The poor chemical stability of these fatty esters, exemplified by the ease of attack by atmospheric oxygen at slightly elevated temperatures, coupled with their relatively high cost, has lead to their almost complete substitution by alternative materials as major ingredients in lubricants {1}.

Biological oils are mainly used in food and pharmaceutical industry, where non- toxic and minimum contamination risk lubricants are required {13}.

While fatty oils alone find only limited use as lubricants, large quantities are still employed for "compounding" with mineral oils when improved lubricating ability is required. These oils have been commonly used in this way, and thus can be claimed to be some of the earliest lubricating oil additives. The modern use of the word "additives", however, tends to exclude naturally occurring materials {1}.

### 2-2-2-2 Mineral Oils

Lubricating oils with term "mineral oils" generally mean that oils derived from petroleum, which had a suitable viscosity for lubrication. The chemical compounds making up mineral oils are mainly hydrocarbons, which contain only carbon and hydrogen. These are of three basic types. The majority in any lubricating oil is paraffins, in which the carbon atoms are in straight or branched chains, but not rings. The second most common type is naphthenes, in which some of the carbon atoms form rings. Finally there is usually a small proportion, perhaps 2 % of aromatics, in which carbon rings are present. But the proportion of hydrogen is reduced {14}.

If the amount of carbon present in paraffin chains is much higher than the amount in naphthene rings, the oil is called "paraffinic oil" {14}.

Where the straight, long- chain paraffins are wax- like and therefore their concentration must be minimized, especially in these oils for application at low temperatures. On the other hand, branched- chain paraffins can be very desirable constituents in a lubricant because of their good stability and viscosity-temperature characteristics. The longer the side chains in the molecule, the more marked do these attractive features become {1}.

But if the proportion of carbon present in naphthene rings is only a little less than the proportion of carbon in paraffin chains, the oil is called a "naphthenic oil" {14}.

Where naphthenic oils frequently contain a high percentage of asphalt, the number of rings per molecule, in those naphthenes, is low, but the side chains and connecting links are long and paraffinic. With increasing ring condensation and shortening of the paraffinic chains, the viscosity-temperature characteristics of the hydrocarbons progressively worsen in respect of their suitability for the lubricants {1}.

Mineral base oils are the most commonly used lubricants. They are of low cost and satisfactory for general purpose applications, such as for car engines, and common industrial machinery. Because of the extraction of mineral oils from crude oil, they are usually a complex mixture of mostly branched and cyclic hydrocarbons with sizes of 16 to 40 carbon atoms. Mineral oils are categorized, depending on the source of the crude oil, and as mentioned above, into three types – paraffinic, naphthenic, and aromatic. The distinction is based on whether the main portion of carbon atoms is incorporated in paraffinic chains, cyclic parts, or benzene type compounds {13}.

The production of mineral oils from petroleum is done by two steps which are an atmospheric distillation and vacuum distillation. This is followed by decreasing or de – asphalting, as required by the nature of crude oil charge, de – waxing, solvent extraction, finishing which may include filtration, and blending, including mixing various additives with the final lubricating oil {15}.

In Iraq, mineral gasoline engine oils are produced from mixture of base oils 40H, 60H, and 150H which prepared using various percents, and as produced by AL – Durra refinery. The main specifications of these lubricants are similar to the specifications of many types of international equivalent lubricants, i.e.foreign lubricants, such as Shell – Rotella oils, Esso – Essolube HD,etc.{16, 17}.

Finally, mineral oils are generally used as lubricants because they can be drawn between moving parts by hydraulic action; thus they not only keep the parts separated but also act as carriers of heat. Indeed, in many applications, such as highly loaded bearings, and internal – combustion engines, heat removal is just as important as the lubrication function. Secondary properties are also frequently involved, such as prevention of deposit formation, and sealing of close – fitting parts, such as piston rings sliding against cylinder walls {18}.

### 2-2-2-3 Synthetic Lubricants

Synthetic lubricants are abroad ranges of compounds derived from chemical synthesis rather than from petroleum or oils of animal or vegetable origin. Since they are man – made under controllable conditions, synthetic base fluids are usually consisting of pure materials or of mixture of pure materials. Synthetic base fluids are usually compounded with additives in order to improve or modify one or more properties and their performance can be greatly improved.

Synthetic lubricants are problem solvers and are used for special application where petroleum products are inadequate, e.g. extremely high and low temperature, extreme wear conditions or where the lubricants must have special characteristic. A major application for synthetic lubricants is the lubrication of jet engines used in civil and military aircraft {15}.

As mentioned above, synthetic oils are provided properties superior to mineral oils. Some of the available synthetic lubricants include hydrocarbon synthetic lubricants, such as poly – α – olifines, polyisobutylene, and alkylbenzenes, organic esters, such as diesters, and polyol esters, polyglycols, poly ethers, and cyclo aliphatic used as traction fluids. Other types of lubricants include some more “exotic” fluids, which are usually, more expensive and used as specially lubricants. An example is the silicon containing compounds used in very high temperature applications. Another example is the organ halogens known to be stable against oxidation. Many organ halogens are also able to provide boundary lubrication mechanisms, and are used as extreme pressure application lubricants, as hydraulic fluids, and lubricants for computer disks {13}.

## *2-3 Lubricating Oil Additives (LOAs)*

Straight mineral oils, together with compounded oils, were once able to meet all normal lubrication requirements of automotive and industrial practice. As these requirements become more severe with the progressive development of engines and general machinery it becomes necessary firstly to improve the quality of lubricating oils by new methods of refining and eventually to use (additives) either to reinforce existing qualities or to confer additional properties {3}.

In the early days of their use additives were regarded with suspicion - oil that needed an additive was necessarily inferior oil; today additives are an accepted feature of lubricants - as of other petroleum products - and most lubricants now contain one or more additives {19}.

Additives are substances that, in small quantities-from a few parts per million to a few percent-confer specific properties on the lubricant {3}.

The progressive increases in the severity of engine operating conditions for motor oils have made necessary the use of chemical additives. These are employed for the following specific purposes {20}.

- To improve flow properties by: -
Lowering solidification temperature;
decreasing change of viscosity with change of temperature.

- To improve lubricating action by:-
Providing greater oiliness;
decreasing metal wear; furnishing better film strength.

- To provide greater chemical stability by:-
inhibiting oxidation;
neutralizing oxidation promoters;
inhibiting bearing metal corrosion;
preventing sludge and varnish deposition.
- To preserve engine surfaces from rusting and corrosion.
- To prevent oil foaming during use.

Additives are usually called after their particular function, but many additives are multi-functional; it will give some idea of their multiplicity to name the chief functions they fulfill: to improve the viscosity index (VI improvers); to increase oxidation stability (anti-oxidants); to keep contaminants in suspension (dispersants); to prevent wear (anti-wear); to prevent scuffing (extreme-pressure, EP, agents); to depress the pour point (pour point depressant); to prevent rusting (anti-rust); and to prevent foaming (anti-foam){19}.

At last the another effect of additives (polymer additives: OCP & Polyisoprene) was made the oil – stocks bad solvent for Polyisoprene and with increasing temperature the additives made to increased the intrinsic viscosity but at the same time the viscosity of oil – stocks was decreased which compensate the decrease of the viscosity of the oil, so that the viscosity temperature curve have less steepness.

## *2-4 Properties of Mineral Lubricating Oils*

The properties of mineral lubricating oils are to some extent governed by the origin or character of petroleum oil from which they are derived {21}.

Tests on lubricating oil are used in order to evaluate the nature and extent of contamination of gasoline engine oils. Tests are included analysis of viscosity, viscosity index, flash point, pour point, ash content, carbon residue, viscosity gravity constant, specific gravity, API, acid No., etc. {18}.

### *Viscosity*

The viscosity of a liquid can be described as its internal friction,the resistance it offers to motion, either of a foreign body through it or of it against a foreign body. It can be measured by timing the flow of a given volume of the liquid through a properly calibrated tube of capillary size. The result is the kinematics viscosity, expressed in centistokes. If this figure is multiplied by the density of the liquid, the answer comes out in centipoises of absolute viscosity {20}.

Viscosity depends on temperature and decreases as temperature increases; the temperature must therefore always be specified in starting the viscosity of a material {3}.

### *Viscosity Index*

The viscosity index of lubricating oil is the denote of the effects of temperature change on the viscosity of lubricating oil. The higher the viscosity index level, then the smaller the expected viscosity changes. Additives used as VI improvers include oil soluble olefin polymers of average molecular weight in the region of 20,000, methacrylate fatty alcohol / lower alcohol ester copolymers in the range of 20,000 to 250,000 alkyl styrene polymers in the region of 50,000 and vinyl acetate / fumarate fatty alcohol ester copolymers in the region of 100,000. All these materials thus have molecular weights, many times greater than the average molecular weight of the liquids in which they are dissolved {24}.

Small concentrations of such polymers increase the viscosity of an oil blend over the whole operating temperature range, but the increase is proportionally higher at high temperature than at low. The consequent improvement in VI is not linearly proportional to concentration.

### *Ash Content*

A lubricating oil ash is the residue left after all the combustible material has been burnt off. Ash content is mainly used to measure the overall metal content of new formulated oil. It can also be used to assess contamination by solid particles, especially wear metals and external silica. Ash content is also useful in connection with determining additive level in many lubricating oils {23}.

### *Carbon Residue*

Carbon residue test is the measure of the amounts of carbonaceous deposits, which formed in lubricating oil during running in engine. The nature of these deposits varies with the grade of oil used {21}.

### *Flash Point*

The flash point is the lowest temperature at which the vapors produced from lubricating oil will ignite spontaneously, in the presence of a flame under standard conditions. It is measured by using two methods known as open and closed cup methods. The flash point determined in a closed cup is a little lower than that determined in an open cup {23}.

Flash point is used to measure the volatile of oil. A drop in flash point indicates the oil is high volatility and the oil is diluted by contamination {18}.

### *Pour Point*

The pour point is the lowest temperature at which oil continues to flow, when it is cooled without stirring under standard cooling conditions {23}.

The lubricating oil must flow freely, especially during the start-up period, in order to prevent wear occurring in this phase of the operation {18}.

This is achieved by using pour point depressant additives, such as polymethacrylates with 1 % or less, which inhibit the growth of wax crystals in the oil {22}.

### *Specific Gravity*

Specific-gravity values must be known whenever weight and volume factors are of concern. This relates primarily to the shipment and storage of lubricating oils where conversion to either a weight or volume basis is desired at a specific temperature in order to establish a reference point {18}.

### *API*

API test is used to describe the quality of lubricating oils. The higher the API level, then the lower the specific gravity of lubricating oil {18}.

### *Viscosity Gravity Constant*

The VGC calculated is primarily considered to use to recognizing the quality of lubricating oils during the processes of blending lubricants to give the final product with specified characteristics. The **VGC** is of interest because it is also considered to be one of the oldest constants used to characterize the paraffinic nature of a base stock fraction especially. It is calculated from the specific gravity data at 15.6 °C {23}.

### *Acid No*

The acid No. denotes the amount of alkali required neutralizing the acidic products in a specified weight of oil. The neutralization value is normally expressed as the number of milligrams of potassium hydroxide necessary to neutralize the acids contained in one gram of oil. An increase in the acid No. indicates changes in the oil caused by oxidation or exposure to high temperature, since many additives result in raising the acid No. over that of the base oil {23}.

### *Oxidation*

The most important chemical aspects of lubrication are the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can lead to the development of corrosive organic acids and insoluble resinous matter, and a marked increase in viscosity of the lubricant, all of which seriously impair the efficiency of the lubricant, this subject is probably the most thoroughly studied of any relating to lubricating oils {24}.

Oxidation is a markedly exothermic reaction and proceeds by a number of complex steps, the nature of the hydrocarbons in the lubricants having a considerable influence on the nature of the oxidation process.

Since oils are mixture of many hydrocarbons falling in different chemical classes, and covering a rather wide range of molecular weights, each of the main classes should be considered separately. This is possible for paraffins, naphthenes and aromatics, but not so well based for unsaturated compounds of the kinds likely to be produced by cracking of the other three types at engine temperature, reasoning by analogy is at least helpful. It has long been known that after some period of use lubricating oils show greater oiliness, and better protection against rusting than do the same oils when new. These effects are sometimes small, but have been amply confirmed. They are almost certainly produced by polar compounds resembling at least remotely some of the commercial additives used to improve many oils. This gives a hint as to the nature of the compound types produced during the early stages of the oxidation occurring in service, and a laboratory study confirms these surmises. A point of caution should be mentioned here; while the first changes caused by oxidation show beneficial effects, these are only early stages of a deterioration, which quickly becomes harmful, at least motor oils {20}.

With so many operative factors in the process of oxidation, it is not surprising to find that a vast range of materials has been proposed as oxidation inhibitors, functioning by various mechanisms. Some are (chain - breakers) in that they prevent propagation of the chain of reactions by interfering with an intermediate step. Others have a particular ability to react rapidly with hydro-peroxides in a manner that does not produce free radicals, thus removing a source of initiation of the chain reaction. Some compounds can carry out both functions. A less important type acts as anti-oxidants by preventing or reducing the catalytic activity of metals by chelation, to form a non- reactive stable metal complex, or by forming stable films on metal and thus preventing its dissolution into the oil. In practice, most inhibitors are themselves oxidizable and tend to be consumed in the process of inhibition. The inhibitors most used can be divided into two main classes: the first class includes oil-soluble materials containing sulfur or phosphorus, and the second consists of amine or phenolic compounds {24}.

***Corrosion***

Lubricants must be formulated so as to avoid the promotion of corrosion by any of the ingredients or by their degradation products. They must also be able to prevent corrosion in certain sets of adverse circumstances when potentially corrosive contaminants come in to the oil {24}.

The corrosive effect may be minimized in o ways; either the production of harmful peroxides and carboxylic acids can be inhibited, or the reactive metal surfaces can be isolated from the reactive materials with an appropriate film. In practice the oxidation inhibitors, such as zinc dithiophosphate commonly used in internal combustion engine oils, will function in both ways. The inhibitors will also be effective in preventing similar corrosion which might result with some combustion products finding their way past the piston into the crankcase {3}.

Some sulfur compounds will prove very reactive towards certain metals, particularly cuprous and silver alloys, which can be applied as gearing or bearing metals. Objectionable black stains indicate that fatigue life of the metals can also be adversely affected. A copper strip corrosion test is commonly applied to lubricating oils, but although mineral oils contain naturally occurring sulfur compounds capable of producing stains in this type of test, these are largely removed by modem refining processes such as solvent refining, and base lubricating oils almost invariably give negative results. When additives incorporating active sulfur are used in gear and cutting oils, their general corrosive effect on non-ferrous metal can be minimized by metal deactivators, which do not influence the performance of the additives under boundary conditions; mercaptobenzothiazole has been used for this purpose.

Rusting is a special kind of corrosion and both are believed to contribute to wear of moving parts, whereby corrosion products are removed mechanically. Wear caused by friction alone is quite slow where lubrication is adequate. In ordinary automobile use, the wear of cylinder bores and piston rings is usually of the mixed corrosion-wear type; the corrosive action of acidic water in exhaust products explains the fact that bore wear is always greater at the top of ring travel {20}.

## *2-5 Purpose of Lubricating Oil*

The lubricating oil does several jobs in the engine. They are listed as follows {25}.

1. The oil lubricates moving parts to reduce wear: Clearance between moving parts, for example, bearings and rotating shafts, are filled with oil. The parts move on the layers of oil. This reduces power loss in the engine.
2. As the oil moves through the engine, the oil picks up heat: The hot oil drops back down into the cooler oil pan where the oil gives up heat. Some of the heat is dissipated through the pan walls and carried away by the surrounding air the engine may have oil nozzles that spray oil into the undersides of the pistons. This removes heat from the piston heads so the pistons run cooler. In the engine, the lubricating oil serves as a cooling agent.

3. Oil fills the clearances between bearings and rotating journals: When heavy loads are suddenly imposed on the bearings, the oil helps cushion the shock. This reduces bearing wear.
4. The oil helps form a gas-tight seal between piston rings and cylinder walls: the oil reduces blow by in addition to lubricating the piston and rings.
5. The oil acts as a cleaning agent: The circulating oil flushes and cleans the bearings and other engine parts. The oil picks up particles of dirt and grit, carrying them back to the oil pan. Larger particles settle to the bottom of the pan. Smaller particles are filtered out by the oil filter when the oil is sent back through the engine.

## *2-6 Theory of Viscosity of Liquids and Activation Energy*

Our knowledge about the viscosity of liquids is largely empirical, since the kinetic theory of liquids is only partly developed. It is of interest, however, to consider the approximate theory developed by Eyring and Co-workers {26}, which illustrate the mechanisms involved and does permit rough estimation of the viscosity from other physical properties.

In a pure liquid at rest, the individual molecules are constantly in motion; however, because of the close packing, the motion is largely confined to vibration of each molecule within a “cage” formed by its nearest neighbors. This cage is represented by the energy barrier of height ΔGo/N, as shown in figure below:-

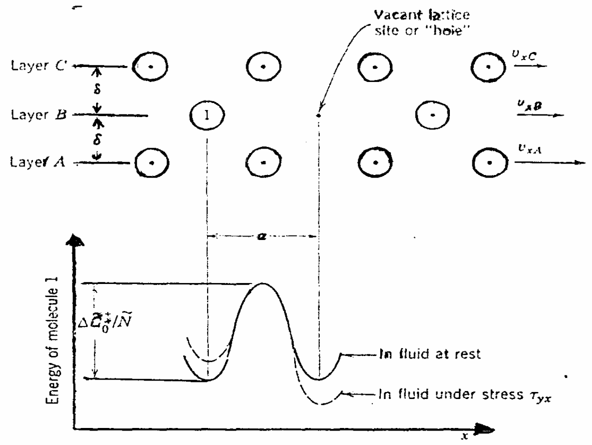

**Figure 2-1:-Illustration of an Ascape Process in Flow of a Liquid. Molecule 1 must Pass Through "Bottleneck" to Reach the Vacant Site.**

Eyring has suggested that a liquid at rest, continually undergoes rearrangement in which one molecule at a time escapes from its" cage" into an adjoining" hole", as shown in figure above, and that the molecules thus move each of the Cartesian coordinate directions in jumps of length (a) at a frequency K per molecule, where K is given by the rate equation:

$$K = \frac{\kappa T}{h} e^{-\Delta G \circ / RT} \qquad 2-1$$

Here: κ and h are the Boltzmann and Planck constants, R is the molar gas constant, and ΔGo is the molar "free energy of activation" in the stationary fluid.

In a fluid that flows in the X-direction with a velocity gradient dvx/dy, the frequency of molecular rearrangements is increased. This effect can be explained by considering the potential energy barrier as distorted under the applied stress $\tau$yx, so that:

$$-\Delta G = -\Delta G \circ \pm (a/\gamma)\left(\frac{\tau_{yx}V}{2}\right) \qquad 2-2$$

Where V is the volume of a mole of a liquid, and ± (a/y)($\tau_{YX}$ V/2) is an approximation to the work done on the molecules as they move to the top of the energy barriers, moving with the applied shear stress (plus sign) or against the applied shear stress (minus sign). Defining $k_f$ as the frequency of forward jumps and $k_b$ as the frequency of backward jumps, one finds from equation 2-1 and 2-2 that:

$$k_f = \frac{\kappa T}{h} e^{-\Delta G \circ / RT} e^{a\tau_{yx}V/2\gamma RT} \qquad 2-3$$

$$k_b = \frac{\kappa T}{h} e^{-\Delta G \circ / RT} e^{-a\tau_{yx}V/2\gamma RT} \qquad 2-4$$

The net velocity at which the molecules in layer A figure 2-1 slip a head of those in layer B is just the distance traveled per jump(a) times the net frequency of forward jumps ($k_f$ -$k_b$); thus:

Considering the velocity profile linear over the very small distance γ between layers A and B, one gets:

$$-\frac{d_{VX}}{d_{Y}}=\frac{a}{\gamma}\left(K_{f}-K_{b}\right) \qquad 2-6$$

by combining equations 2-3, 4, 5, one obtains finally:

$$-\frac{d_{VX}}{d_{Y}}=\frac{a}{\gamma}\left(\frac{\kappa T}{h}e^{-\Delta G\circ/RT}\right)\left(e^{aT_{yx}V/2\gamma RT}-e^{-aT_{yx}V/2\gamma RT}\right)$$

$$2-7$$

$$-\frac{d_{VX}}{d_{Y}}=\frac{a}{\gamma}\left(\frac{\kappa T}{h}e^{-\Delta G\circ/RT}\right)\left(2Sinh\frac{aT_{YX}V}{2\gamma RT}\right)$$

It is interesting to note that equation 2-7 predicts no Newtonian flow for liquids in general; in fact, this equation has the same general form as the Eyring model. If $aT_{yx}V/2\ \gamma\ RT$ is small compared to unity, however, Eq.2-7 becomes consistent with Newtonian law of viscosity, with:

$$\mu=\left(\frac{\gamma}{a}\right)^{2}\frac{Nh}{V}e^{\Delta G\circ/RT} \qquad 2-8$$

In which N is Avogadro's number. In most applications γ/a is taken as unity; this simplification involves no loss of accuracy, since $\Delta G_0$ is determined empirically to make the equation agree with experimental data {27}.

### 2-6-1 Apparent Energy of Activation, Ea, for Viscous Flow:

The apparent energy of activation for melt flow, Ea, is calculated from the slope of straight lines as Ea/R. various approaches have been used to describe the variation of Ea with temperatures. Spencer and Dillon {28} noted that the extrapolated Zero shear viscosity of a high molecular weight fraction (MW=360 000) plotted against l/T gave an essentially constant Ea of 41 Kcal / mole from about 110 to 190 C° and then accidentally change to a lower value of 22 Kcal / mole from 190 to 250 C°.

Working at small but finite rates of shear, Fox and Florry {29} found that Ea in cal / mole was given by Eq.2-9, which gave continuous variation with temperature.

$$Ea = (8.1 \times 10^{17} / T^{5}) \exp(-2530/M) \qquad 2-9$$

They found the value of Ea at Tg to be about 110 Kcal / mole regardless of molecular weight, when the Tg, glass transition temperature {30}.

At present the activation and free volume theories for liquid transport properties seem to represent the most promising approach for a simple method of predicting transport properties in the normal liquid density region. Such theories are analogous to the free volume theories for liquid thermodynamic properties, but the former take account of the possibility of molecules leaving their cells {30}

Features of previous theories due to Eyring {26}, Weymann {31, 32} and Cohen and Turnbull {33} have recently been combined by Macedo and Litoviz. Molecular flow is presumed to occur only if a combination of two criteria is met. Firstly, the molecule must possess energy greater than some critical value $e_v$

termed the activation energy at constant volume, and secondly a fluctuation must occur such that the local free volume is greater than a critical value $V_0$. The viscosity free volume referred to here represent the space unoccupied by molecules, and should not be confused with the quantity termed free volume in thermodynamic theories {34}.

The resulting equation is:

$$\mu = A \exp\left(\frac{V\circ}{V - V\circ}\right) \exp\left(\frac{E_V}{RT}\right) \qquad 2-10$$

Various workers disagree as to the correct form for the pre exponential factor. Most have predicted that A varies with $T^{1/2}$, and such temperature dependence is assumed in this work. Equation 2-1 has been shown to correlate the viscosity data for various liquids including polymeric materials, the parameters Ao,Vo and Ev being treated as adjustable constants for each molecular species. The equation is not very successful when applied in this way to viscosity and self diffusivity data of molecularly simple liquids {34}.

### 2-6-2 Activation Energy of the Eyring Theory of Liquid Viscosity:

In the viscosity theory of Eyring and co-workers {35}, the viscosity coefficient is obtained through a calculation of the shearing rate under an applied stress using the absolute reaction rate theory. The rate process involves the transit of the molecule under the shearing stress from one potential energy minimum in the liquid quasi lattice to an adjoining one. The total activation energy Eo for the process is the sum of the energy $E_2$ required for the molecule to pass through the intermediate region of higher potential energy (the activated complex") and the energy $E_1$ required to form an empty lattice site or "hole" with accompanying expansion of the liquid. The equation for the viscosity coefficient thus obtained is well known and is:

$$\mu = (2\pi mkT)^{1/2}\left(V_f / V\right)\exp(E\circ / kT) \qquad 2-11$$

Where $V_f$ is the Eyring and Hirschfelder free volume [36], V is the volume per molecule, and $E_0=E_1+E_2$. The free volume $V_f$ can be simply expressed in the form:

$$V_f = \frac{4\pi}{3}\gamma^3 V\left[1-(V_\circ / V)^{1/3}\right]^3 \qquad 2-12$$

Where Vo is the incompressible volume of the liquid. The constant $\gamma=a/V^{1/3}$ where "a" is the mean intermolecular distance. Several methods for determining the free volume from independent experimental data have been proposed [37].

The activation energy may be determined by comparing the measured isobaric temperature coefficient of the viscosity with the corresponding derivative of equation 2-11. However, the following relation is ordinarily used and is sufficiently precise for most purposes:

$$\left(\frac{\delta \ln \eta}{\delta T}\right)_P = -\frac{\left(E_{vis}\right)_P}{RT^2} \qquad 2-13$$

Here ($E_{vis}$) = N€$_0$, where N is Avogadro's number to simple liquids, the values of N€0 obtained through the use of equation 2-13 are of the order of 2 to *5* Kcal/mole. Values of the activation energy and of the viscosity calculated according to equation 2-11 and equation 2-12 {38}.

Raw et al. {39, 40, 41} has proposed two approximate relations:

$E/k=0.88C$

And

$\Delta E_{vis}=4.5\ Elk$ cal/mole 2 – 14

Where C is Sutherland's constant (from the temperature dependence of the gas viscosity), $\Delta E_{vis}$ is the activation energy for viscous flow (from the temperature dependence of the liquid viscosity), E is the maximum energy of the attraction between two molecules each of which has an intermolecular force filed described by the Lennard-Jones, and k is Boltzrnann's constant. These two approximations are useful for rough estimates, but are restricted to substances with simple, non polar , symmetrical molecules whose intermolecular potentials are well represented by the Lennard Jones, and which condense to normal liquids {39} .

# *CHAPTER THREE*

# *EXPERIMENTAL WORK*

## *3.1 Oil - Stock*

Three heavy oil-stocks obtained from Al – Daura Refinery, namely 40 stock, 60 stock and 150. stock.40 stock is the lightest one with $^{o}$API gravity 34.97 while 60stock is middle type and 150 stock is heavy one , with $^{o}$API gravity 29.29 and 20.65 respectively .

The main properties of oil stocks (40 stock, 60 stock, and 150stock) were measured in Al – Daura Refinery laboratories according to $^{o}$API and ASTM specification, as listed in table 3-1

**Table 3-1: Properties of oil stocks.**

| Specification | 40 stock | 60 stock | 150 stock |
|---|---|---|---|
| Kin. Viscosity at 40 $^{o}$C, cst | **18.11** | **56.12** | **501.98** |
| Kin. Viscosity at 100 $^{o}$C, cst | **3.14** | **7.69** | **33.38** |
| Viscosity index (VI) | **95** | **95** | **93** |
| Specific gravity at 15.6 $^{o}$C | **0.85** | **0.88** | **0.93** |
| $^{o}$API gravity | **34.97** | **29.29** | **20.65** |
| COC Flash, $^{o}$C | **n.d.** | **200-300** | **290-300** |
| P.M. Flash, $^{o}$C | **160** | **n.d.** | **n.d.** |
| Pour point, $^{o}$C | **-24** | **-6** | **-3** |
| Sulfur content, wt.% | **0.62** | **1.4** | **2** |
| Ran. Res. Wt. % | **0.06** | **0.12** | **0.78** |

n.d.: not determined.

## *3-2 Additives*

Lubricating oil additives (LOAs) impart desirable properties to base stocks to satisfy lubricant standards for high-performance engines. Each additive is selected for its ability to perform one or more specific functions, for example: to restrict oxidation, to modify the viscosity – temperature characteristics, to act as detergents, to depress the pour point, or to inhibit rust and the important specific functions is flow activation energy. Although LOAs are used in petroleum – based lubricants, they themselves are not typical petroleum products; they are considered specialty chemicals.

This study contains four types of additives, the three types of additives which were brought from Al – Daura Refinery. The first one was Paranox 5263 (for gasoline engine), while the second one was Paranox 2281 (for diesel engine), the third one was OCP (olefin copolymer), (for gasoline and diesel engines), and the fourth one was Polyisoprene 1502.

Paranox 5263 and Paranox 2281 are dispersants type (to keep contaminants in suspension and to keep an engine clean); the OCP and Polyisoprene 1502 are VI improver type (to improve the viscosity index VI) {42}.

The main properties of Paranox 5263 and Paranox 2281 brought from Al-Daura Refinery, are listed in table 3-2.

**Table 3-2: Properties of Paranox (5263, 2281)**

| Specifications | Paranox 5263 | Paranox 2281 |
|---|---|---|
| Kin. Viscosity at 40 °C, cst | **3842** | **4600** |
| Kin. Viscosity at100 °C, cst | **167** | **188** |
| API gravity at 15.6 °C | **0.99** | **0.97** |
| Boron Co. wt. % | **0.07** | **0.11** |
| Ca, wt. % | **2.39** | **1.56** |
| Mg, wt. % | **0.16** | **0.36** |
| $N_2$ wt. % | **0.51** | **0.57** |
| P, wt. % | **0.76** | **0.78** |
| Zn, wt. % | **0.84** | **0.86** |
| S, wt. % | **12.56** | **2.39** |
| T.B.N MgKOH/gm oil | **88.5** | **75** |

- T.B.N is Total Base Number.

The main composition of OCP (olefin copolymer) and Polyisoprene 1502 are a polymer and base lube oil-stock. The types of OCP and Polyisoprene 1502 depend on the quantity of polymer and the solubility degree of polymer in a base oil-stock.

## *3-3 Blending*

The composition of each mixture was prepared as volume percentage and then transferred to the weight percent, for more accuracy.

Mixing process was undertaken by shaking; the blended samples required moderate heating (60-80 °C) in a water bath (memmert type).Viscosity measurements were completed immediately, after preparing the mixture to avoid deposit formation or vaporizing the light ends. All the viscosity measurements were carried out at atmospheric pressure.

The following mixtures were prepared in this study:-

### 1-Binar additive

There are four types of binary mixture, as follows:

A. Binary mixtures of each oil-stock type (40 stock, 60 stock and 150 stock) with (0-20 wt. %) of Paranox 5263.
B. Binary mixtures of each oil-stock type (40 stock, 60 stock and 150 stock) with (0-20 wt.%) of Paranox 2281
C. Binary mixtures of each oil-stock type (40 stock, 60 stock and 150 stock) with (0-9 wt. %) of OCP (olefin copolymer).
D. Binary mixtures of each oil-stock type (40 stock, 60 stock and 150 stock) with (0-8 wt. %) of Polyisoprene 1502.

### 2-Multi-component additive

The three types of oil-stocks were mixed to obtain two types of multi-component mixtures at different concentration (wt. %) with (12 wt. %) of each type of two additives (Paranox 5263 and Paranox 2281), as follows:-

1. 40 stock and 60 stock with Paranox 5263.
2. 40 stock and 150 stock with Paranox 5263.
3. 150 stock and 60 stock with Paranox 5263.
4. 40 stock and 60 stock with Paranox 2281.
5. 40 stock and 150 stock with Paranox 2281.
6. 150 stock and 60 stock with Paranox 2281.

## *3-4 Viscosity Measurements*

Viscosities of oil-stocks and mixtures were measured at seven different temperatures, namely 298, 303, 313, 323, 333, 343, and 353 K with a Rheology International Viscometer (Model RI: 1: M, as shown in fig.3-1) and was placed in a water bath (memmert type), which was capable of maintaining the temperature within ± 0.1 $^{o}$C of the selected temperature.

### 3-4-1 Viscometer

The Rheology International Viscometer rotates a sensing element and a fluid and measures the torque necessary to overcome the viscous resistance to the induced movement. This is accomplished by driving the immersed element, which is called a spindle, through a beryllium copper spring via the pivot point assembly. The percentage torque wind-up of the spring due to the viscosity of the fluid is displayed as engineering units, “E”.

The electronic circuitry of the viscometer converts the measured torque into viscosity units, and displays it in cPs, P or KP.

The viscometer is able to measure over a number of ranges since the viscosity is proportional to the torque wind-up of the spring; the torque wind-up is proportional to the spindle speed, and is related to the spindle size and shape. For a material of a given viscosity the drag will be greater as the spindle size and/or rotational speed increases. The minimum viscosity range is obtained by using the largest spindle at the highest speed and the maximum viscosity range by using the smallest spindle at the slowest speed.

AUTOZERO is an important element of preparing the instrument for operation. It is initiated by pressing the AUTOZERO switch on the front panel after power-up, after a spindle changes of when the user requires.It must be completed with a clean spindle attached, and the spindle runs in air.

The AUTOZERO procedure rotates the spindle at 20 RPM, for 20 seconds, noting the mechanical and balance characteristics of the viscometer at that time. The value displayed during this process is not centipoises, etc., but a transducer reading value. The value achieved will be added or subtracted from all subsequent readings (until the next AUTOZERO or power down) to give a correct Centipoises reading. This ensures instrument accuracy over time.

With the spindle immersed in the fluid under test, the instrument will continuously display (as selected) percentage torque wind-up in engineering units (“E”) or viscosity in Cps, P or KP. To freeze the display and hold a reading, press the “Hold” switch. The spindle continues to rotate but the display holds the last reading.

The speeds and spindle selected are displayed at the commencement of rotation, or after a speed/spindle change to allow the user check settings. It is essential that the correct spindle is selected otherwise Centipoises or the engineering unit conversions will be meaningless.

### 3-4-2 Calibration

#### **RI: 1: M**

The RI: 1: M is calibrated to Bureau of standards values on the basis of the Instruments used, with its guard legs attached in a 600 ml low from Griffin Beaker. If the instruments are used in a larger container the ranges over which M1 and M2 spindles measure will be slightly increased, this effect is negligible with spindles M3 to M7.

The readings taken with RI: 1: M spindles in containers other than the type specified above, and / or without guard legs can be used for comparative purposes only.

A condition of turbulent flow may be produced by M1 spindle when rotating above 50 RPM. Below 85 cps a slight degree of non-linearity between indicated and absolute viscosity will be noticed. Above this value the linearity will be observed. For consistent use in fluids below 50 cps the VL Adaptor is recommended.

The M7 spindle has a narrow “neck” on its shaft rather than the groove found on the other spindles. The spindle should be immersed in the fluid so that half of this “neck” is covered.

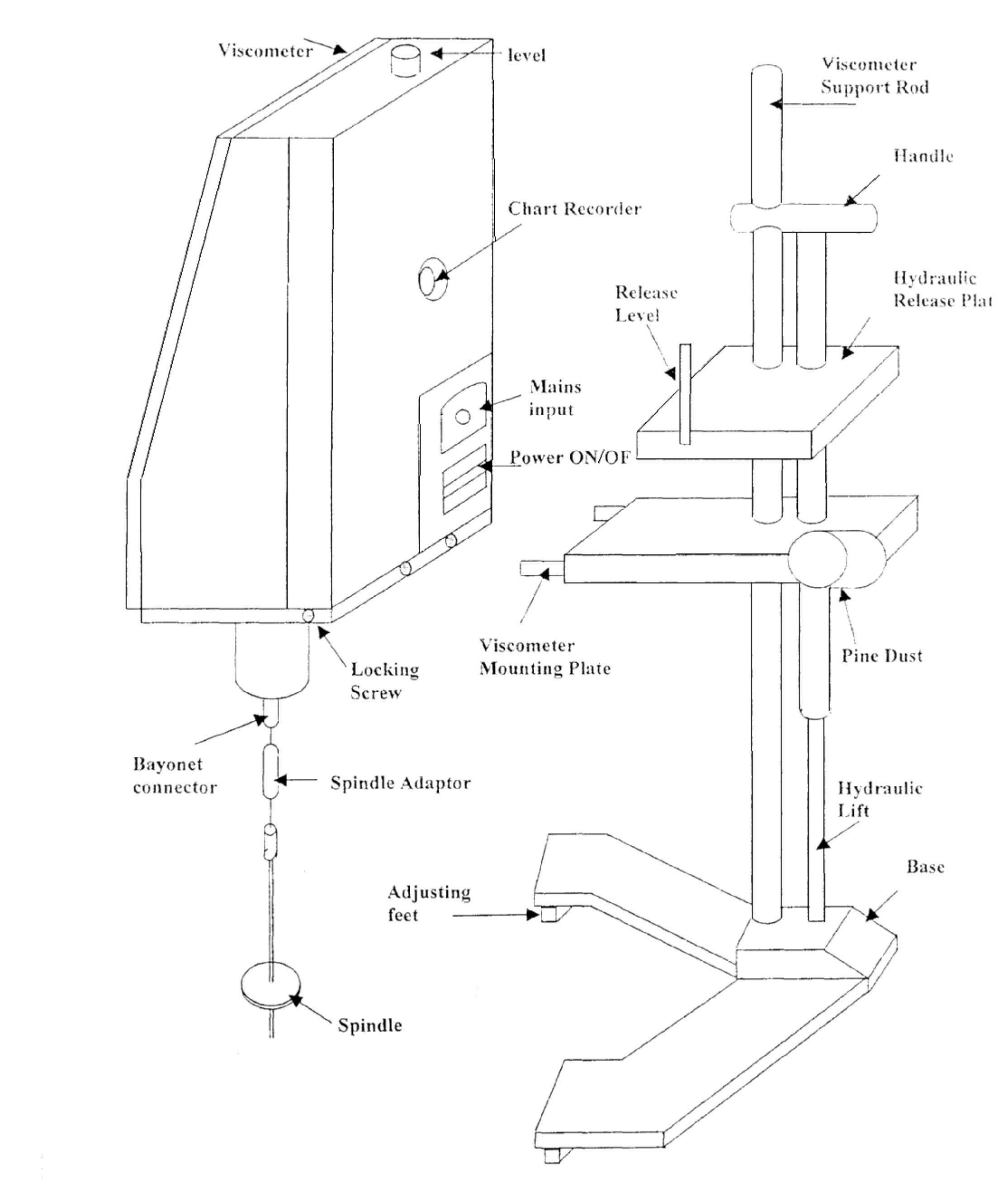

**Fig. 3-1: The Rheology International Viscometer (RI: 1: M) Diagram.**

# *CHAPTRE FOUR*
# *RESULTS AND DISCUSSION*

## *4-1 Viscosity*

### 4-1-1 Introduction

An adequate knowledge of viscosity plays a very important role in a variety of interesting engineering problems involving fluid flow and momentum transfer. This much needed information is scattered throughout the literature, either as data obtained from experimental measurements or as values computed according to one or other theoretical procedure, as may be seen from an examination of the many sources cited for a limited number of materials. The viscosity behavior of lubricating oil is qualitatively similar to that of pure liquids. Oils are known to “thin out” or grow less viscous, as the temperature increases, but no theory has yet been formulated which can precisely predict the variation in viscosity of these liquids with temperature. {43}.

The viscosities of fluids are required in most engineering calculations where fluid flow or mixing is an important factor, such as in the design of reactors, heat exchangers, fractioning towers, and distillation units. For Newtonian fluids, viscosity is defined as the measure of the internal fluid friction which is the constant of proportionality between the shear stress per unit area at any point and velocity gradient. {44}.

### 4-1-2 Lubricating Oil Dynamic Viscosity

Accurate data on lubricating oil dynamic viscosity as a function of temperature are required for reservoir studies, process design or the solution of oil transportation.

The dynamic viscosities of the three types of oil- stocks at atmospheric pressure in the range 298-353 K, are shown in table 4-1 and represented graphically in Fig. 4-1.Clearly, an increase in the temperature of the oil-stock results a decrease in the viscosity (dynamic viscosity). The rate of decrease of the viscosity of the heavy oil – stocks is greater than the rate for the lighter one, i.e. the rate of change to150 stock is greater than the rate of 60 stock and 40 stock.

**Table 4-1: Dynamic viscosity of oil-stocks at different temperatures.**

| Oil – stocks (type) | Viscosity (Cp) at temp., K | | | | | | |
|---|---|---|---|---|---|---|---|
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 40 stock | 46.1 | 40.2 | 33.6 | 27.6 | 23.6 | 20.9 | 18.8 |
| 60 stock | 150.6 | 128.9 | 92.4 | 70.3 | 55.1 | 45.9 | 37 |
| 150 stock | 920.5 | 825.2 | 426.1 | 230.4 | 151.3 | 100.5 | 84.9 |

As shown in table 4-1 and fig. 4-1, heavy oil-stock with low $^{o}$API gravity has a significantly high viscosity. 150 stock of 20.65 $^{o}$API gravity could be considered as heavy oil-stock, which has a viscosity of 920.5 Cp at 298 K, while 40 stock is a typical light oil-stock with °API gravity of 34.97 resulted in a viscosity of 46.1 Cp at 298 K, the other type of oil-stock of °API gravity 29.29 could be classified as middle type with viscosity 150.6 Cp at 298 K.

The rate of viscosity change with temperature depends largely on the nature of oil-stocks, as shown in fig.4-1, and see the change in viscosity is very high above 200 Cp and began slowly change under 200 Cp. These phenomena could be demonstrated for heavy, medium, and light stocks.

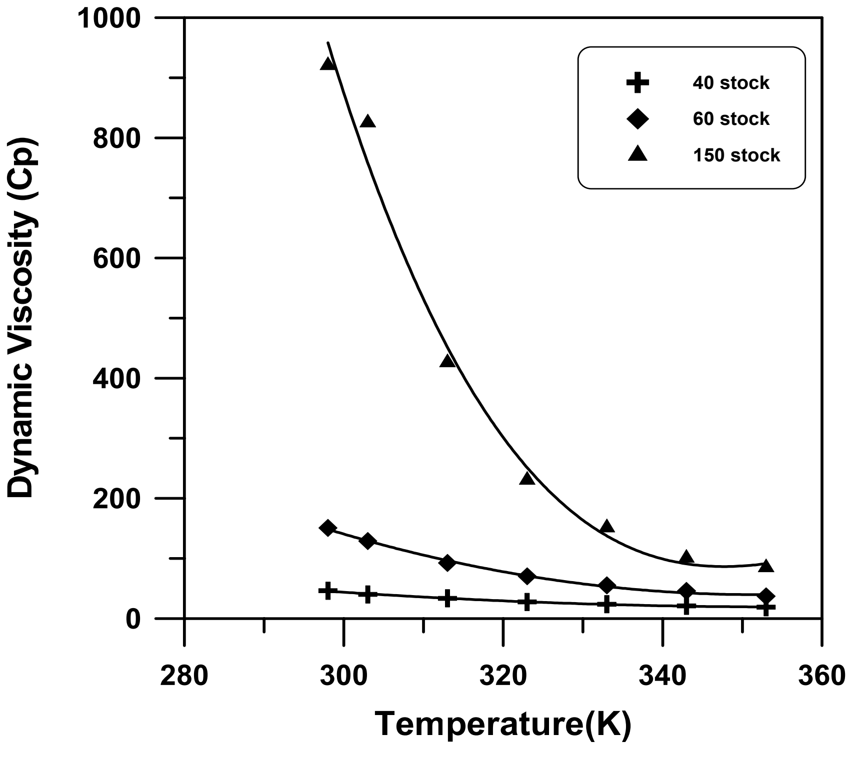

**Fig. 4-1:- effect of temperature on dynamic viscosity of various oil stock.**

## *4-2 Effect of additives on Dynamic Viscosity*

### 4-2-1 Binary Mixtures

#### 4-2-1-1 Blending of oil stocks with Paranox

The three types of oil-stocks of 40 stock, 60 stock, and 150 stock in the range of (20.65 – 34.97) $^{o}$API gravity, are mixing with different concentrations in the range of 0-20 wt.% of Paranox 5263 and Paranox 2281, which have 0.99 and 0.97 $^{o}$API gravity respectively, at different temperatures.

The blending of the three types of oil-stocks with Paranox resulted in a noticeable increase in the viscosity when the weight percent of Paranox increased, because each type of Paranox has higher viscosity than the viscosities of the three types of oil- stocks, Paranox 5263 and Paranox 2281 which have viscosities of 3842 cSt and 4600 cSt at 313 K respectively.

The increase in the viscosity for lighter oil-stock is greater than that of the medium and heavier one, i.e. the effect of Paranox on 40 stock is higher than on 60 and 150 stock respectively, as shown the effects are represented graphically in figs. 4-2 to 4-7

Figs. 4-2 to 4-7 show the effects of increasing temperature on dynamic viscosities of oil-stocks with Paranox. It can be noted that the increase in temperature will decrease the value of dynamic viscosity of oil-stocks for all values of weight percentages of Paranox.

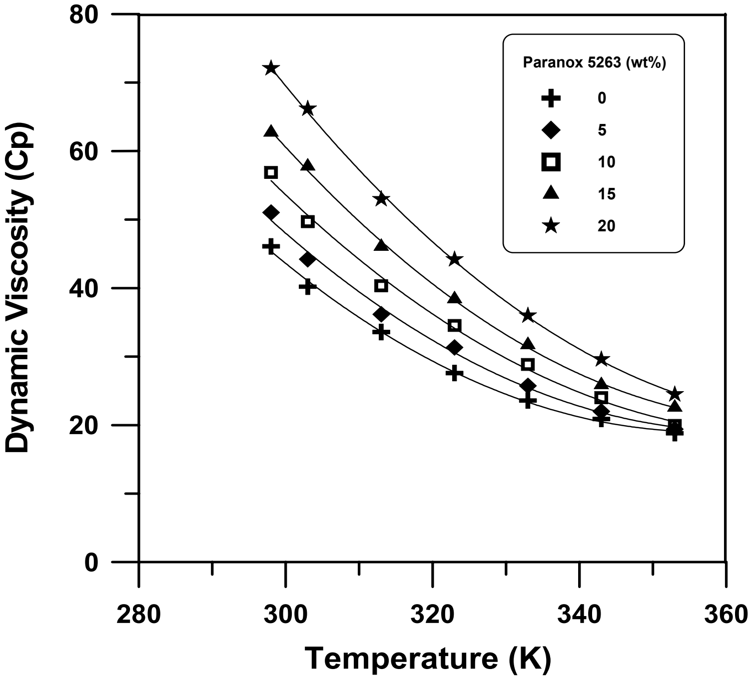

Fig. 4-2:- dynamic viscosity of 40 stock versus temperature at different wt. % of Paranox 5263

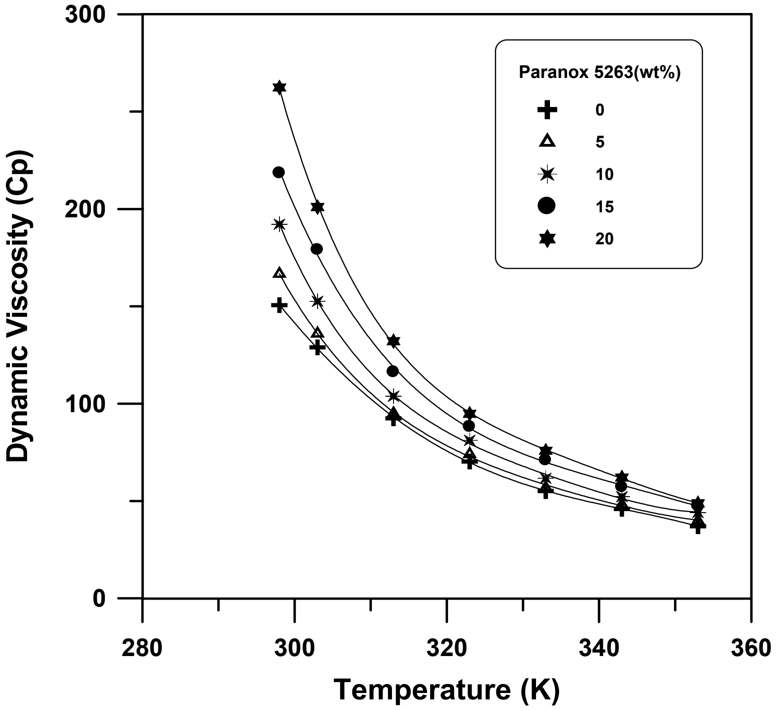

Fig. 4-3:- dynamic viscosity of 60 stock versus temperature at different wt. % of Paranox 5263.

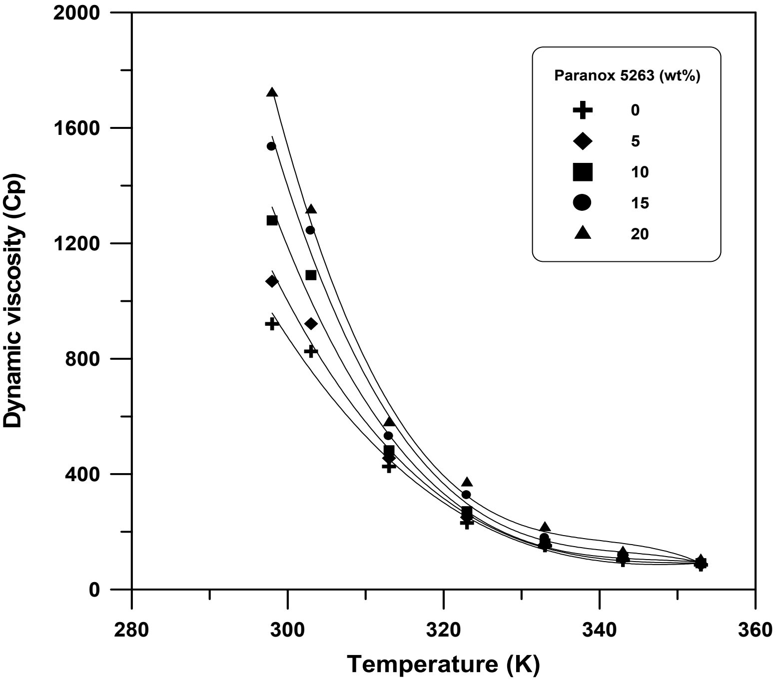

Fig. 4-4:- dynamic viscosity of 150 stock versus temperature at different wt. % of Paranox 5263

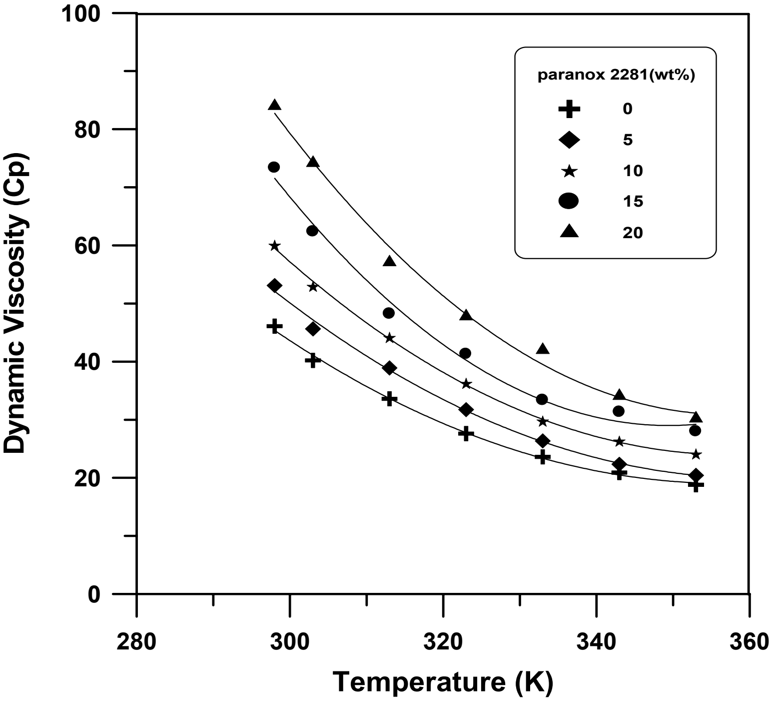

Fig. 4-5:- dynamic viscosity of 40 stock versus temperature at different wt. % of Paranox 2281

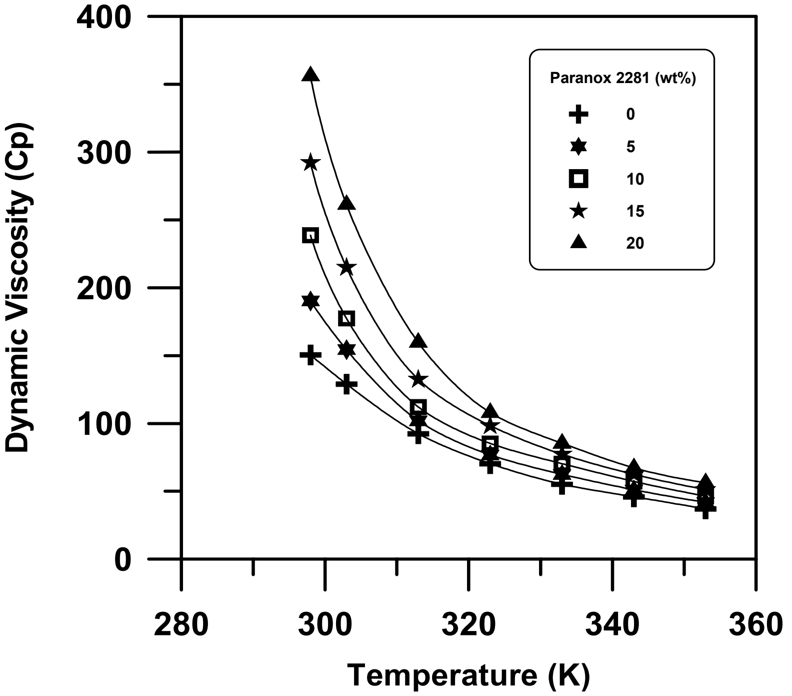

Fig. 4-6:- dynamic viscosity of 60 stock versus temperature at different wt. % of Paranox 2281

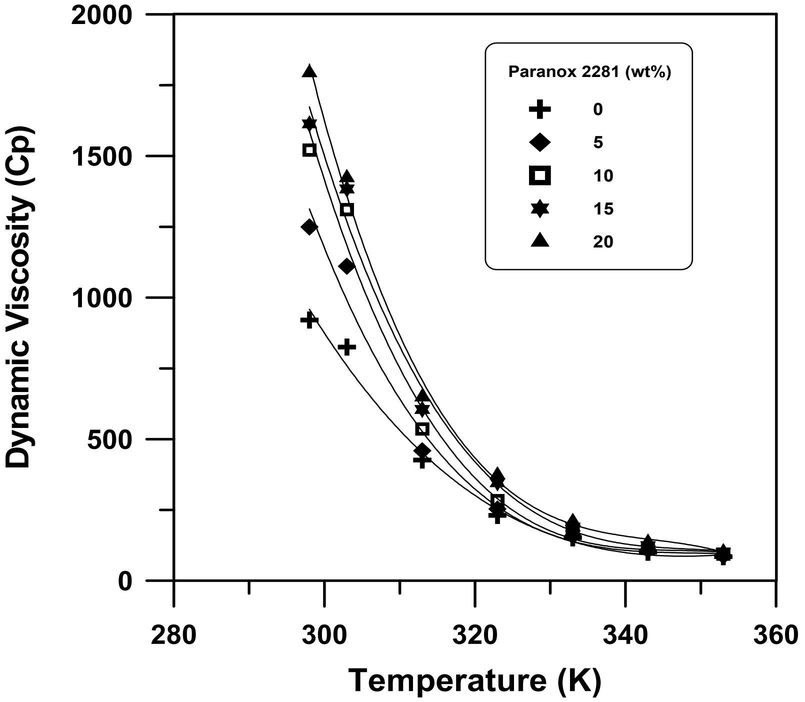

Fig. 4-7:- dynamic viscosity of 150 stock versus temperature at different wt. % of Paranox 2281

Figs. 4-8 to 4-13 illustrate a graphical representation of effects of the temperature and concentration (wt. %) on the dynamic viscosity of oil – stocks. Approximate linear relationship was achieved for the three types of oil – stocks with the two types of Paranox at different temperatures. The rate of the dynamic viscosity depends largely on the nature of oil – stocks and additive type.

It is clear from figs. 4-8 to 4-13 that the effect of temperature in reducing the viscosity of oil – stocks is noticeable at temperature lower than 313 K.

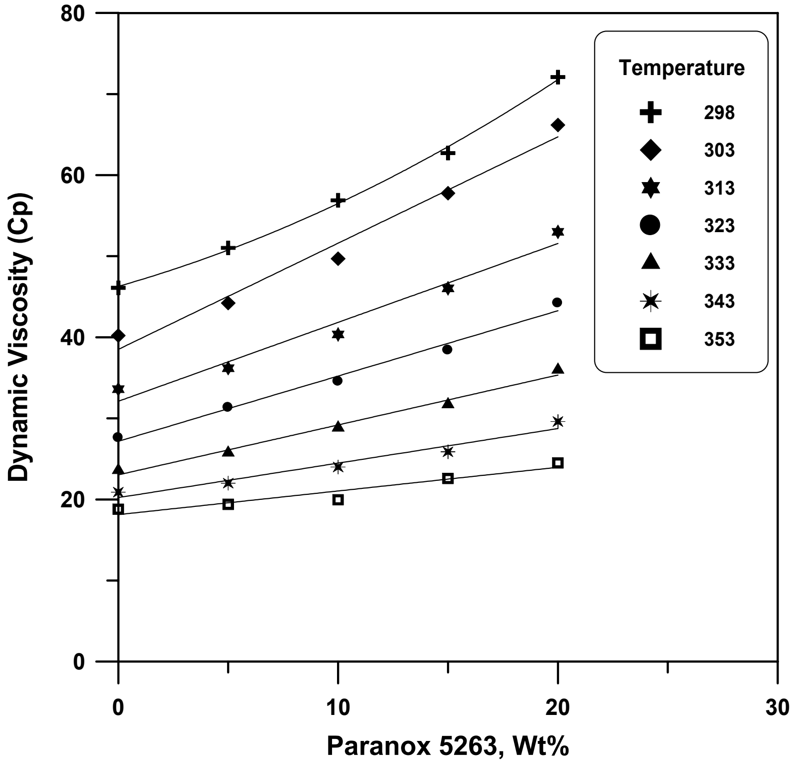

**Fig. 4-8:- dynamic viscosity of 40 stock versus wt% of Paranox 5263 at different temperatures.**

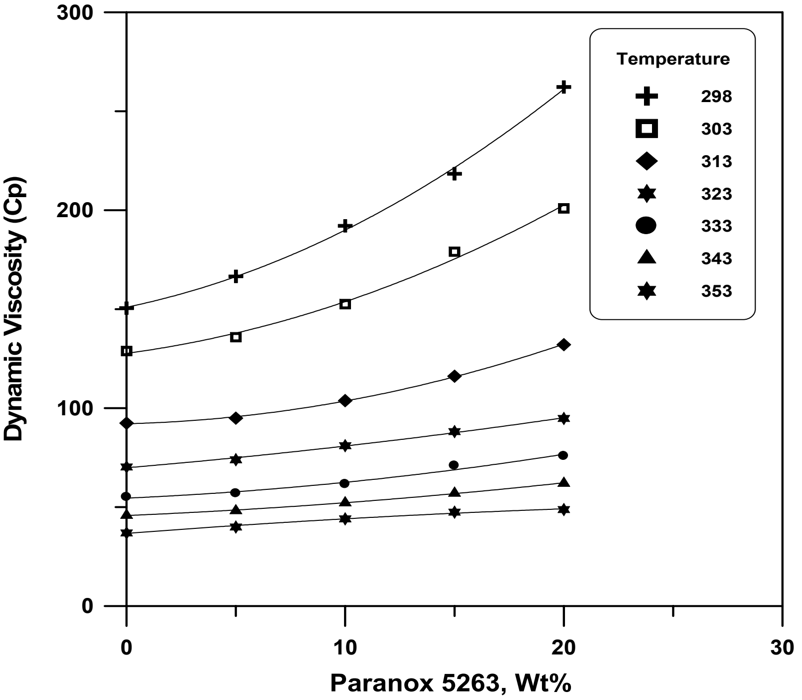

Fig. 4-9:- dynamic viscosity of 60 stock versus wt% of Paranox 5263 at different temperatures.

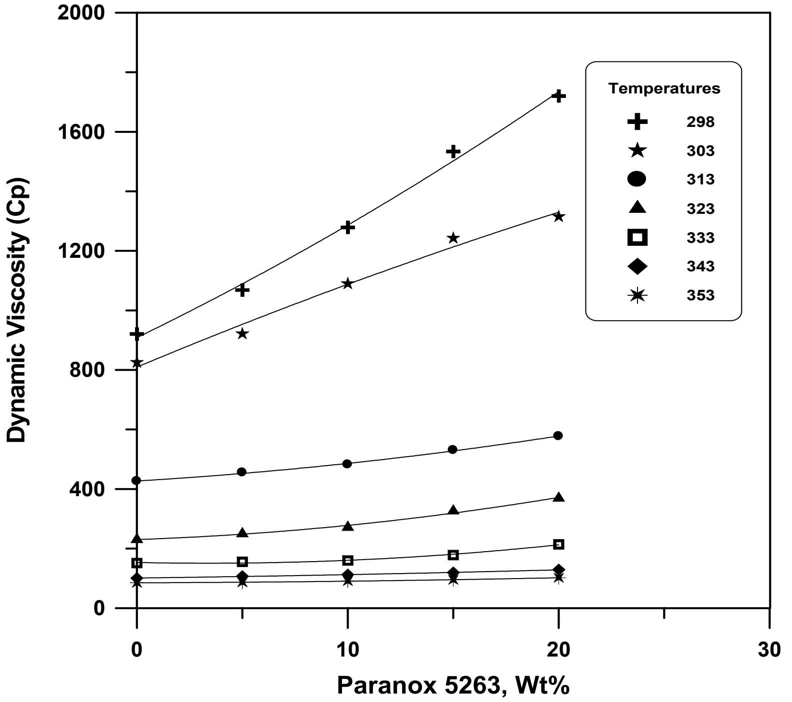

Fig. 4-10:- dynamic viscosity of 150 stock versus wt% of Paranox 5263 at different temperatures.

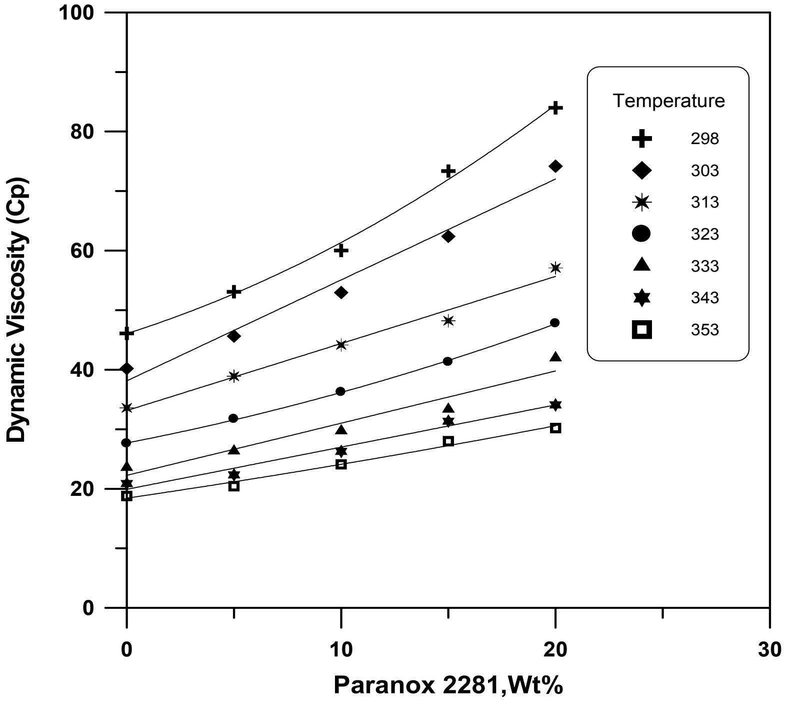

Fig. 4-11:- dynamic viscosity of 40 stock versus wt% of Paranox 2281 at different temperatures.

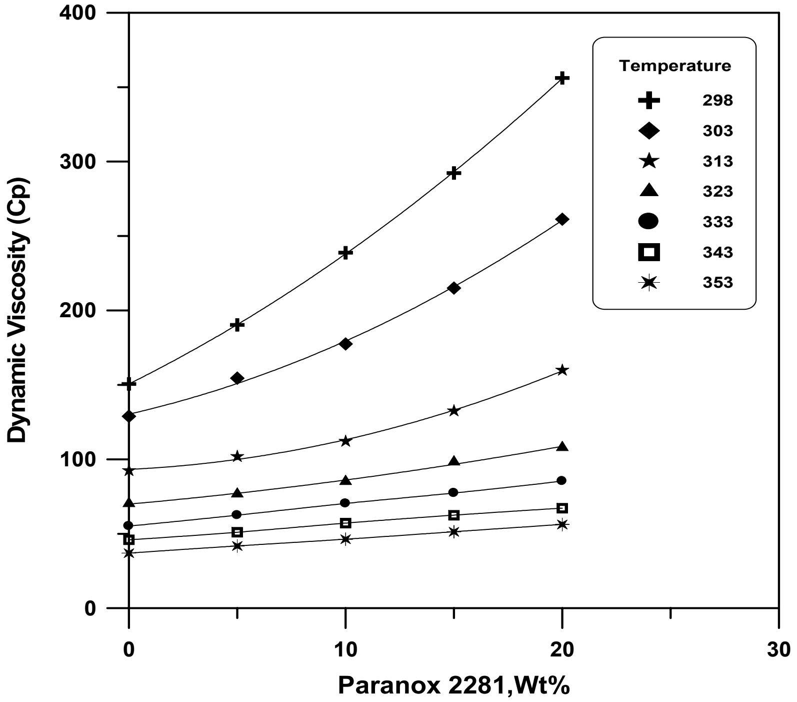

Fig. 4-12:- dynamic viscosity of 60 stock versus wt% of Paranox 2281 at different temperatures.

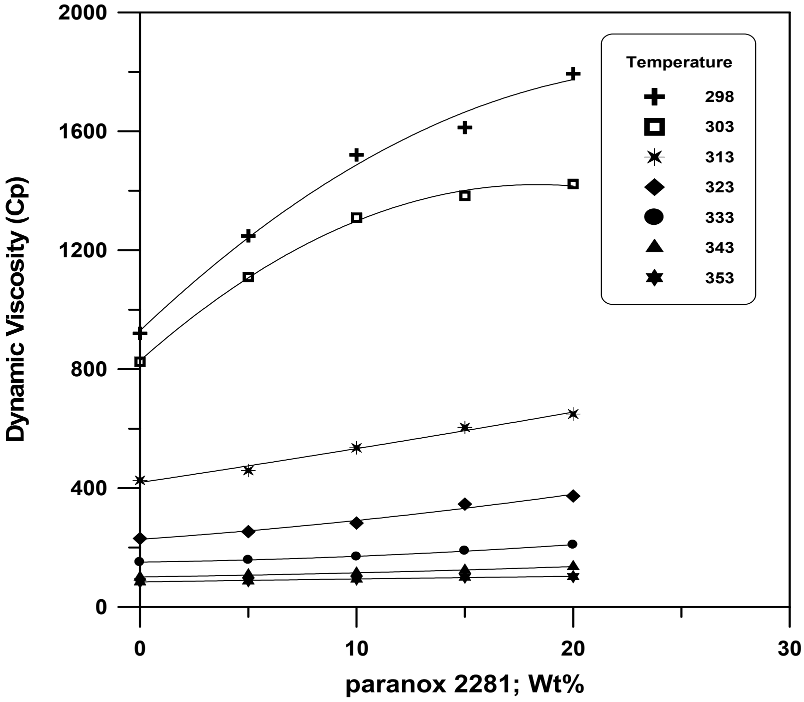

**Fig. 4-13:- dynamic viscosity of 150 stock versus wt% of Paranox 2281 at different temperatures.**

### 4-2-1-2 Blending of oil – stocks with Polyisoprene 1502

The three types of oil-stocks of 40 stock, 60 stock, and 150 stock, are mixing with different concentrations in the range of 0 – 8 wt. % of Polyisoprene 1502.

The blending of the three types of oil-stocks with Polyisoprene 1502 resulted in a noticeable increase in the viscosity when the weight percent of Polyisoprene 1502 increased, because the Polyisoprene 1502 has higher viscosity than the viscosities of the three types of oil- stocks, The increase in the viscosity for lighter oil-stock is greater than that of the medium and heavier one, i.e. the effect of Polyisoprene 1502 on 40 stock is higher than on 60 and 150 stock respectively, as shown the effects are represented graphically in figs. 4-14 to 4-16.

Figs. 4-14 to 4-16 show the effects increasing temperature on dynamic viscosities of oil-stocks with Polyisoprene 1502. It can be noted that the increase in temperature will decrease the value of dynamic viscosity of oil-stocks for all values of weight percentages of Polyisoprene 1502.

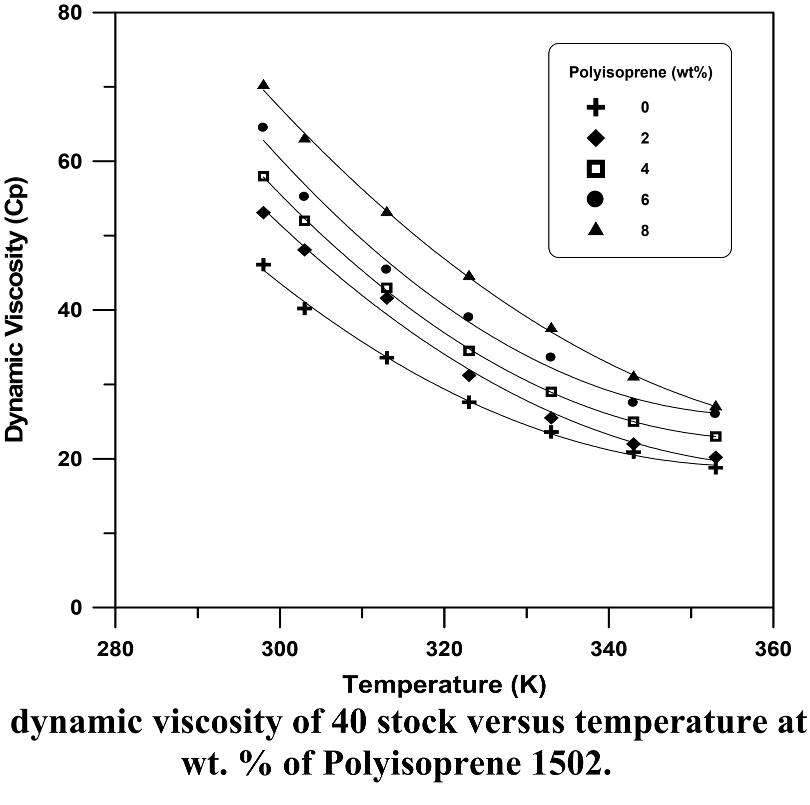

**Fig. 4-14:- dynamic viscosity of 40 stock versus temperature at different wt. % of Polyisoprene 1502.**

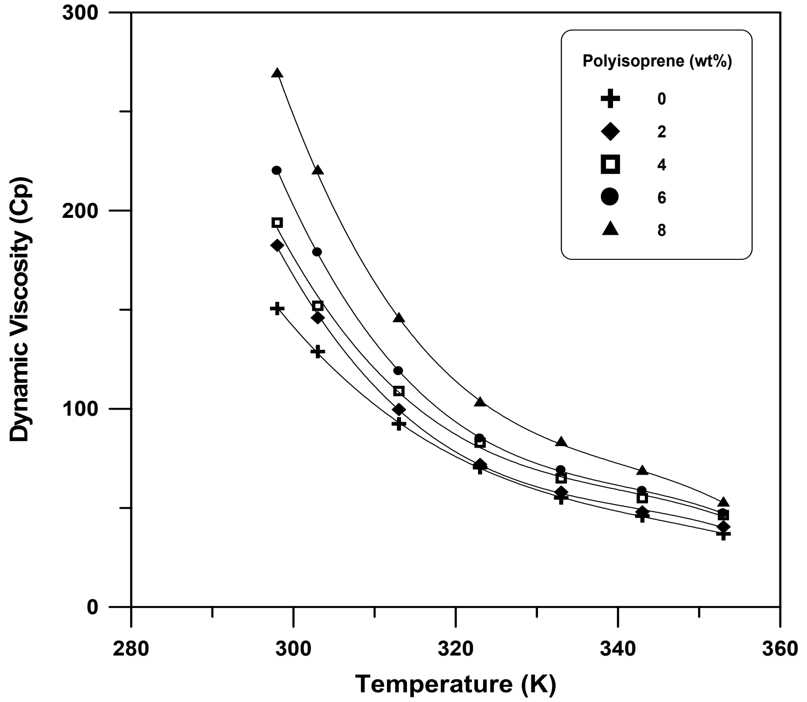

Fig. 4-15:- dynamic viscosity of 60 stock versus temperature at different wt. % of Polyisoprene 1502.

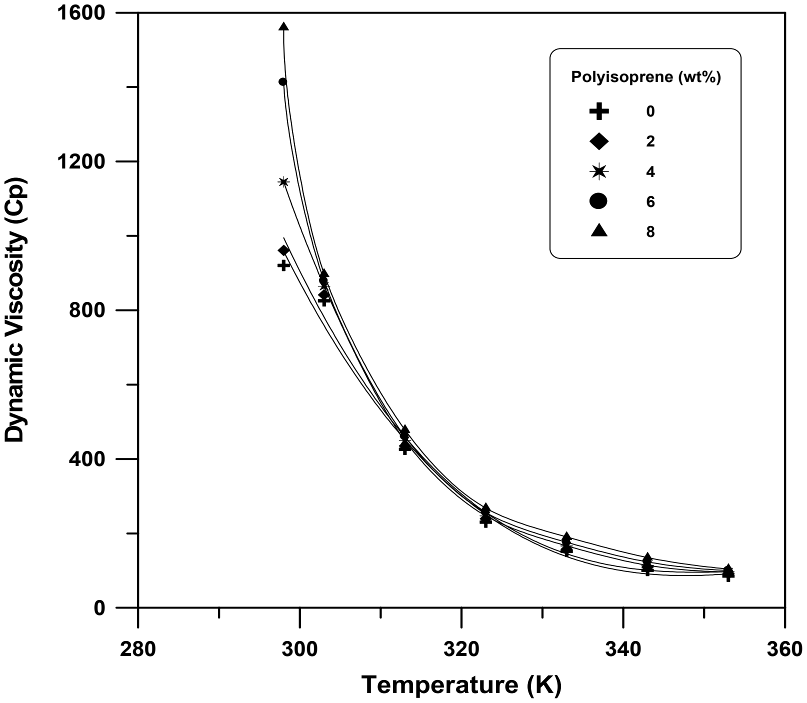

Fig. 4-16:- dynamic viscosity of 150 stock versus temperature at different wt. % of Polyisoprene 1502.

In figures above noted the viscosity change in oil stock without additives is greater than of the oil – stock with additives because the oil – stock is represented as a bad solvent for Polyisoprene and with increasing temperature the viscosity of the base oil decrease in the same time the intrinsic viscosity increased (for bad solvent) which compensate the decrease of the viscosity of the oil, so that the viscosity temperature curve have less steepness {44}.

Figs. 4-17 to 4-19 illustrate a graphical representation of effects of the temperature and concentration (wt. %) on the dynamic viscosity of oil – stocks. Approximate linear relationship was achieved for the three types of oil – stocks with the Polyisoprene 1502 at different temperatures. The rate of the dynamic viscosity depends largely on the nature of oil – stocks and additive type.

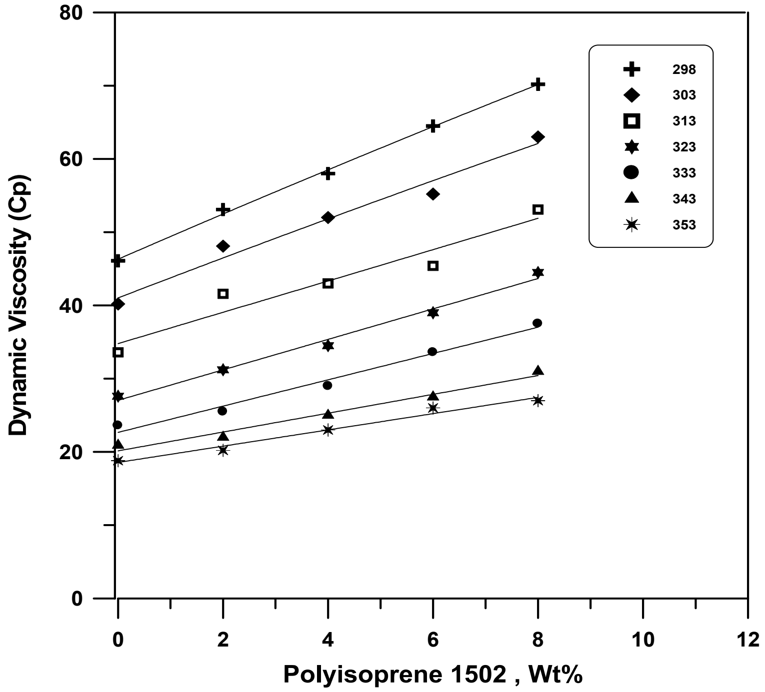

Fig. 4-17:- dynamic viscosity of 40 stock versus wt% of Polyisoprene 1502 at different temperatures.

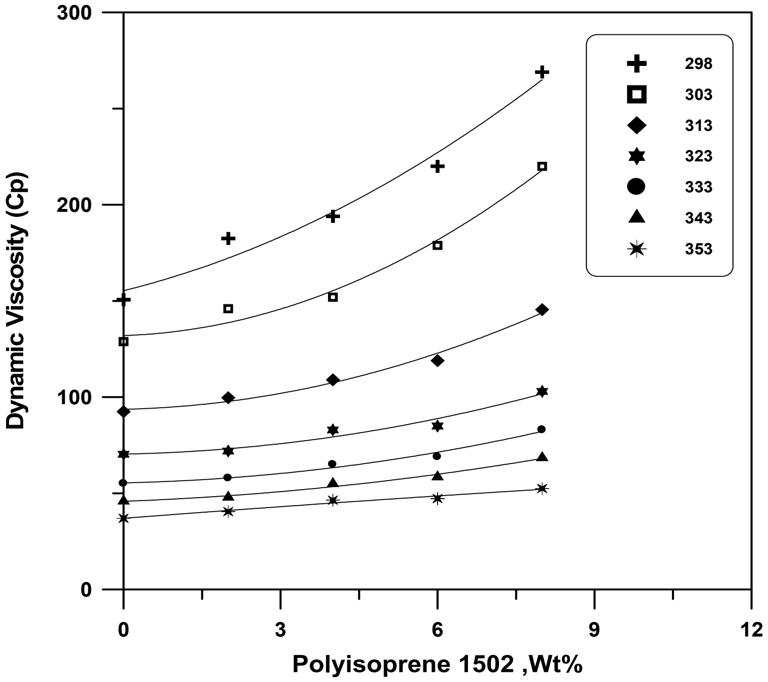

Fig. 4-18:- dynamic viscosity of 60 stock versus wt% of Polyisoprene 1502 at different temperatures.

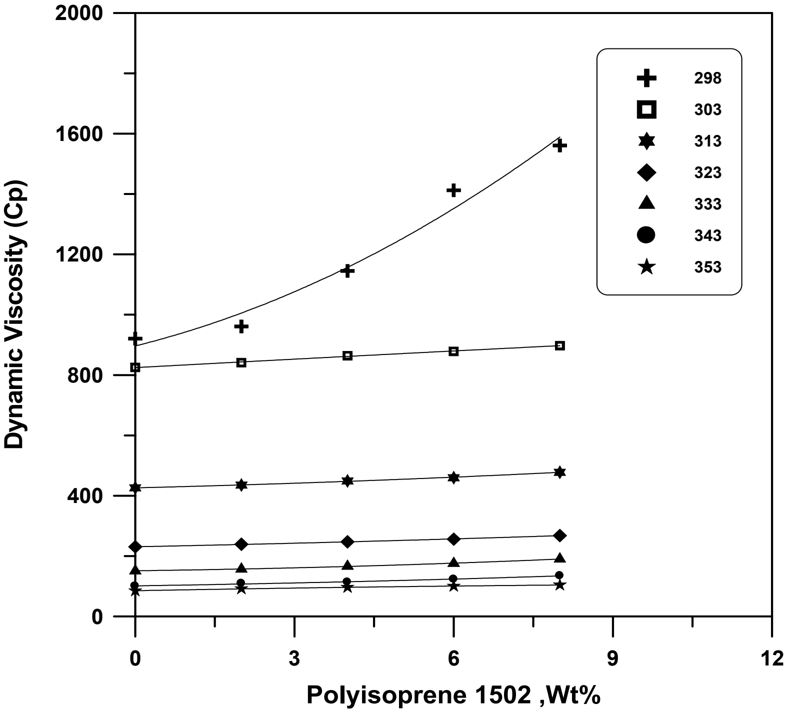

Fig. 4-19:- dynamic viscosity of 150 stock versus wt% of Polyisoprene 1502 at different temperatures.

### 4-2-1-3 Blending of oil – stocks with OCP

Two types of oil – stocks such as 40 stock and 60 stock with $^{o}$API gravity 34.97 and 29.29 respectively were blended with OCP (olefin copolymer) at different temperatures to investigate the temperature effect on the dynamic viscosity. Different OCP concentrations in the range of 0 – 9 wt % were proposed for this study. The results are illustrated in figs. 4- 20 and 4- 21.

It is clear from figs. 4- 20 and 4- 21 that the increase in concentrations affects the increase in the viscosity of each type of oil – stocks, and can be noted that the increase in temperature will decrease the value of dynamic viscosity of oil-stocks for all values of weight percentages of OCP.

From figs. 4- 22 and 4- 23 it obvious that the temperature rise leads to decrease the viscosity. Also it can be noticed at temperatures higher than 303 K the effect of OCP slightly decreases. The figures indicate linear relationships between dynamic weight percent of OCP.

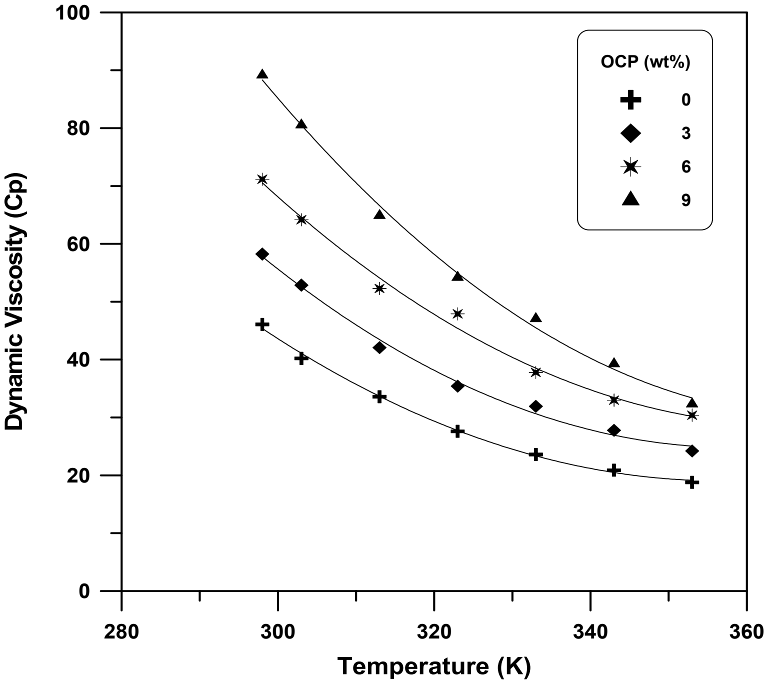

Fig. 4-20:- dynamic viscosity of 40 stock versus temperature at different wt. % of OCP.

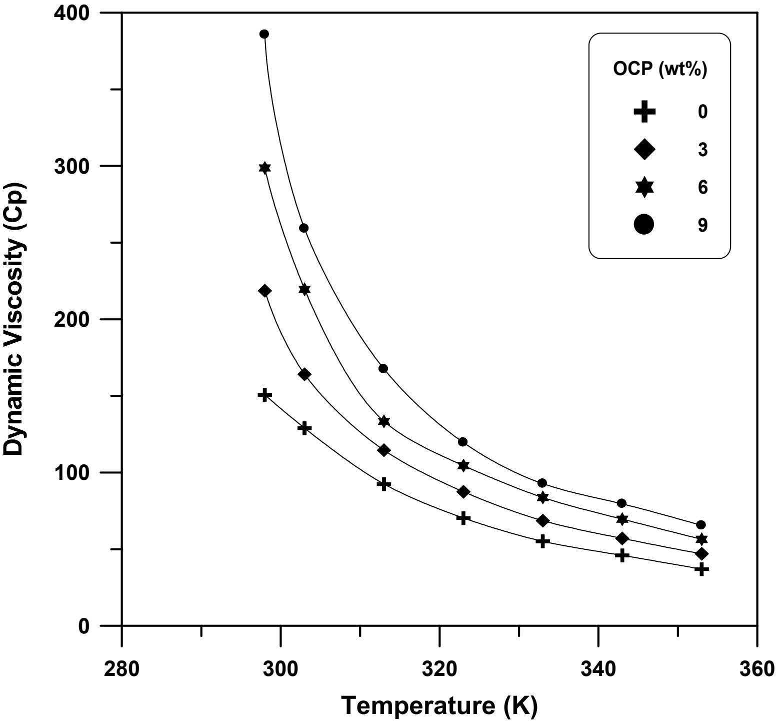

Fig. 4-21:- dynamic viscosity of 60 stock versus temperature at different wt. % of OCP.

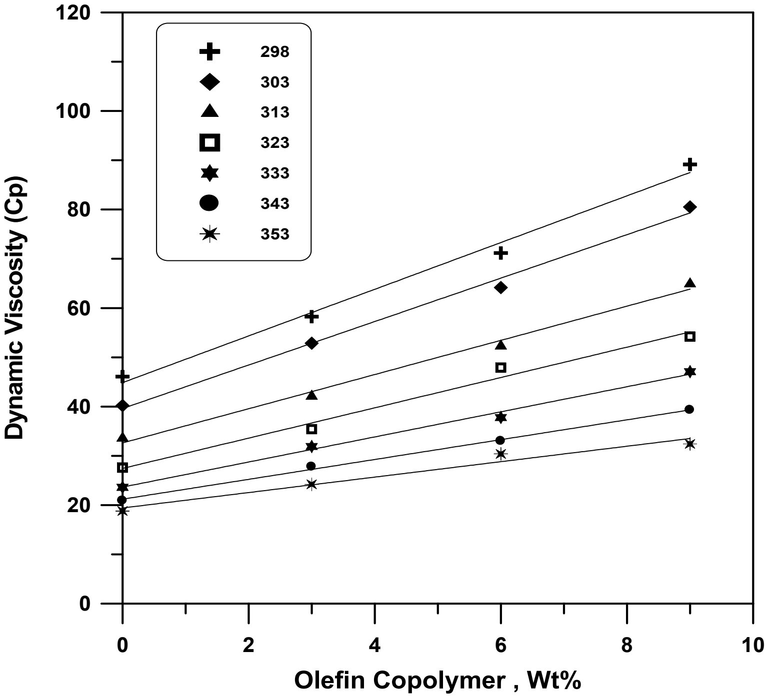

Fig. 4-22:- dynamic viscosity of 40 stock versus wt% of OCP at different temperatures.

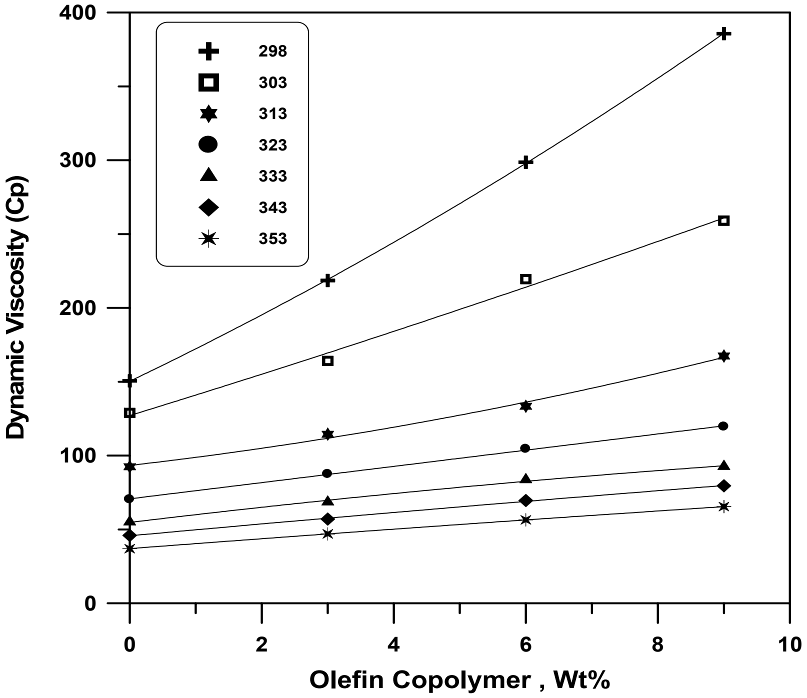

Fig. 4-23:- dynamic viscosity of 60 stock versus wt% of OCP at different temperatures.

### 4-2-2 Multi- Component Mixtures

The standard value of the weight percent of each type of Paranox (Paranox 5263 and Paranox 2281) was chosen as 12 wt % (from Al- Daura Refinery), which was mixed with the three types of oil- stocks of different concentrations (wt %). Different mixtures containing various percentages of oil- stocks were investigated at different temperatures. It is found that the viscosity of blends decreases with the increase in temperature.

As the weight of heavy oil- stocks increases, the reduction in viscosity increases as shown in figs. 4-24 to 4-26.

It is noticeable from figs. 4-24 to 4-26 for a particular mixture the effect on Paranox type 2281 increasing the viscosity is higher than the effect of 5263 for the all investigated range of temperatures. At high temperatures the difference between the effects of these two types of additives (5263 and 2281) decreases.

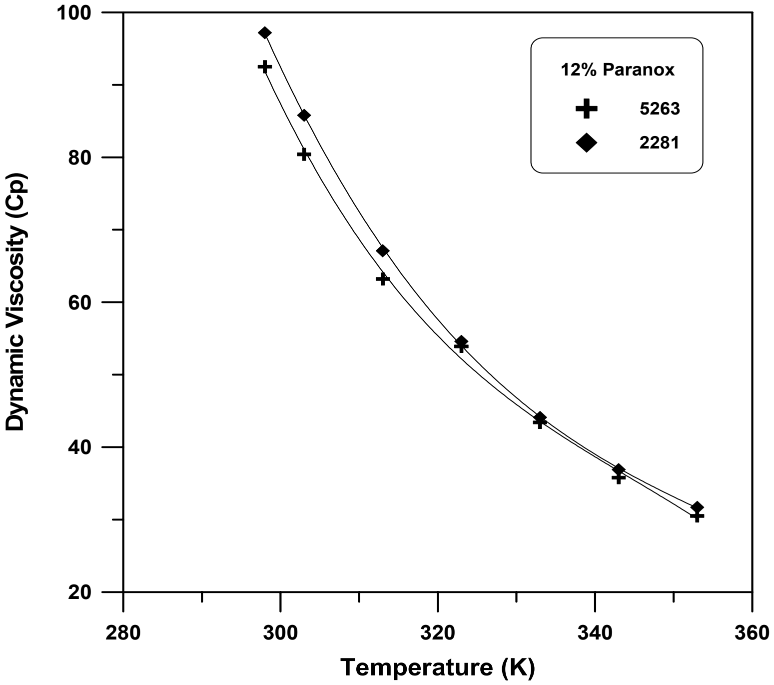

**Fig. 4-24:- dynamic Viscosity of (50% 40 stock + 38% 60 stock) blended with Paranox versus temperature.**

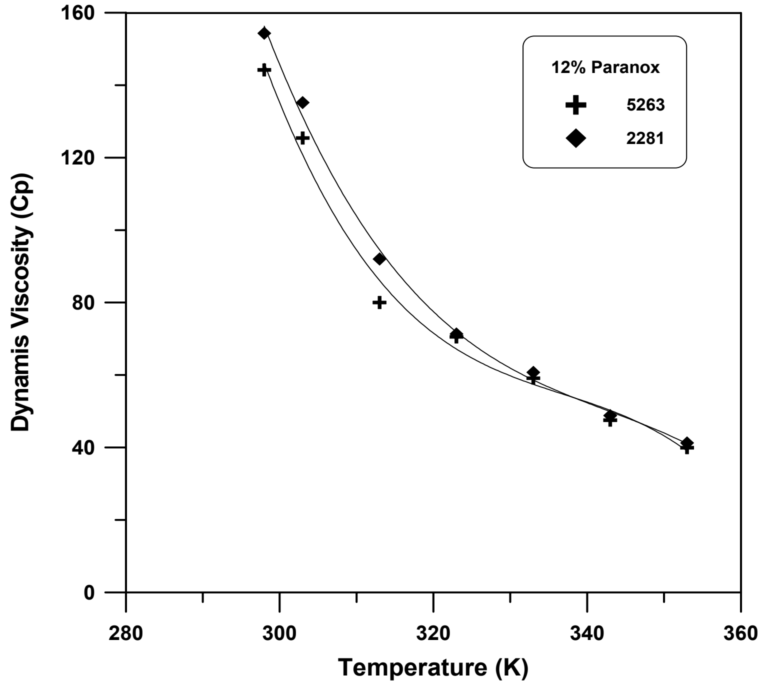

Fig. 4-25:- dynamic Viscosity of (50% 40 stock + 38% 150 stock) blended with Paranox versus temperature.

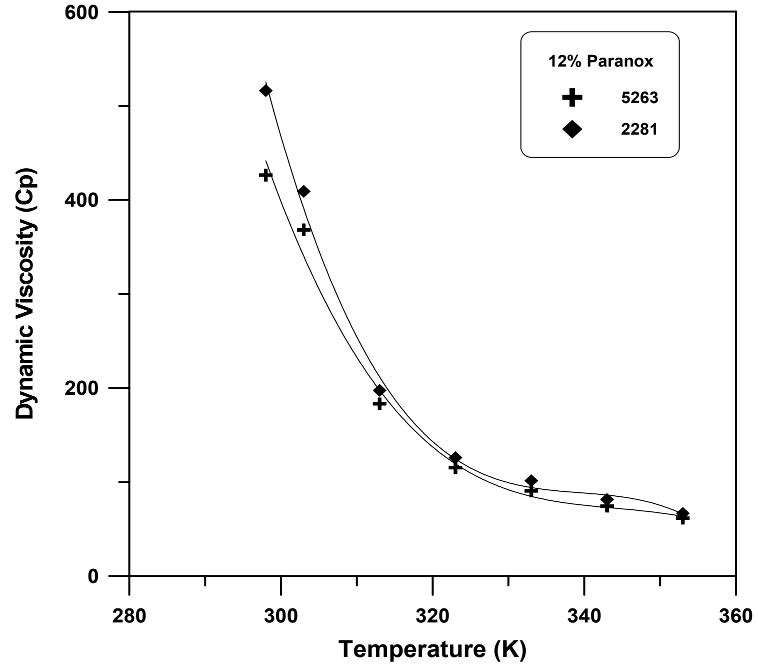

Fig. 4-26:- dynamic Viscosity of (50% 60 stock + 38% 150 stock) blended with Paranox versus temperature.

The measured dynamic viscosities at different temperature and different percent additives of the four types of additives are also presented in tables 4-2 to 4-5 for binary mixture and for multi component mixture is represented in tables 4-6 to 4-7

**Table 4-2: Dynamic viscosity of Oil – stocks with OCP**

| **Dynamic viscosity(Cp) of 40 stock** | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Wt % Addit.** | **Temperature, K** | | | | | | |
| | **298** | **303** | **313** | **323** | **333** | **343** | **353** |
| **3** | **58.3** | **52.9** | **42.1** | **35.4** | **31.9** | **27.8** | **24.2** |
| **6** | **71.2** | **64.2** | **52.3** | **47.9** | **37.8** | **33.1** | **30.4** |
| **9** | **89.2** | **80.6** | **64.9** | **54.2** | **47.1** | **39.3** | **32.4** |

| **Dynamic viscosity(Cp) of 60 stock** | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Wt % Addit.** | **Temperature, K** | | | | | | |
| | **298** | **303** | **313** | **323** | **333** | **343** | **353** |
| **3** | **218.6** | **164.1** | **114.5** | **87.4** | **68.6** | **57.0** | **46.9** |
| **6** | **298.7** | **219.5** | **133.4** | **104.5** | **83.7** | **69.6** | **56.4** |
| **9** | **385.7** | **259.1** | **167.5** | **119.5** | **92.7** | **79.5** | **65.4** |

**Table 4-3: Dynamic viscosity of Oil – stocks with Paranox 5263**

**Dynamic viscosity(Cp) of 40 stock**

| Wt % Addit. | Temperature, K | | | | | | |
|---|---|---|---|---|---|---|---|
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 5 | 51.0 | 44.2 | 36.2 | 31.3 | 25.8 | 22.0 | 19.4 |
| 10 | 56.9 | 49.7 | 40.4 | 34.6 | 28.9 | 24.0 | 20.0 |
| 15 | 62.7 | 57.8 | 46.1 | 38.4 | 31.7 | 25.9 | 22.6 |
| 20 | 72.1 | 66.2 | 53.0 | 44.2 | 36.0 | 29.6 | 24.5 |

**Dynamic viscosity(Cp) of 60 stock**

| Wt % Addit. | Temperature, K | | | | | | |
|---|---|---|---|---|---|---|---|
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 5 | 166.7 | 135.9 | 95.0 | 74.1 | 56.9 | 48.2 | 40.0 |
| 10 | 192.2 | 152.6 | 103.8 | 81.2 | 61.7 | 52.2 | 44.1 |
| 15 | 218.5 | 179.1 | 116.3 | 88.2 | 70.9 | 57.2 | 47.6 |
| 20 | 262.4 | 201.0 | 132.1 | 94.8 | 75.8 | 62.2 | 48.9 |

**Dynamic viscosity(Cp) of 150 stock**

| Wt % Addit. | Temperature, K | | | | | | |
|---|---|---|---|---|---|---|---|
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 5 | 1068.2 | 921.3 | 455.1 | 249.9 | 155.2 | 106.8 | 86.7 |
| 10 | 1278.9 | 1089.4 | 481.7 | 271.2 | 159.4 | 112.1 | 90.7 |
| 15 | 1533.8 | 1242.8 | 530.5 | 326.1 | 178.1 | 119.2 | 94.9 |
| 20 | 1720.1 | 1315.0 | 577.2 | 369.1 | 214.0 | 128.7 | 102.0 |

**Table 4-4: Dynamic viscosity of Oil – stocks with Paranox 2281**

| Dynamic viscosity(Cp) of 40 stock | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wt % Addit. | Temperature, K | | | | | | |
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 5 | 53.1 | 45.6 | 38.9 | 31.7 | 26.4 | 22.3 | 20.4 |
| 10 | 60.1 | 53.0 | 44.2 | 36.3 | 29.8 | 26.3 | 24.1 |
| 15 | 73.4 | 62.4 | 48.2 | 41.3 | 33.4 | 31.4 | 28.0 |
| 20 | 84.0 | 74.2 | 57.1 | 47.8 | 42.0 | 34.1 | 30.2 |

| Dynamic viscosity(Cp) of 60 stock | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wt % Addit. | Temperature, K | | | | | | |
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 5 | 190.4 | 154.5 | 101.9 | 76.7 | 62.4 | 51.0 | 41.8 |
| 10 | 238.8 | 177.5 | 112.1 | 85.2 | 70.3 | 57.1 | 46.3 |
| 15 | 292.4 | 215.1 | 132.5 | 98.3 | 77.3 | 62.4 | 51.3 |
| 20 | 356.2 | 261.4 | 159.8 | 108.0 | 85.3 | 67.2 | 56.2 |

| Dynamic viscosity(Cp) of 150 stock | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wt % Addit. | Temperature, K | | | | | | |
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 5 | 1248.9 | 1110.1 | 459.2 | 253.3 | 158.1 | 108.4 | 88.2 |
| 10 | 1521.1 | 1310.1 | 535.6 | 282.6 | 169.6 | 114.2 | 94.1 |
| 15 | 1613.3 | 1383.4 | 604.7 | 346.1 | 189.2 | 124.2 | 100.4 |
| 20 | 1794.0 | 1423.2 | 649.2 | 373.4 | 209.1 | 136.3 | 102.4 |

**Table 4-5: Dynamic viscosity of Oil – stocks with Polyisoprene 1502**

| Dynamic viscosity(Cp) of 40 stock | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wt % Addit. | Temperature, K | | | | | | |
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 2 | 53.1 | 48.1 | 41.6 | 31.2 | 25.5 | 22.0 | 20.2 |
| 4 | 58.0 | 52.0 | 43.1 | 34.5 | 29.2 | 25.1 | 23.0 |
| 6 | 64.5 | 55.2 | 45.4 | 39.1 | 33.6 | 27.5 | 26.0 |
| 8 | 70.2 | 63.1 | 53.2 | 44.5 | 37.5 | 31.1 | 27.0 |

| Dynamic viscosity(Cp) of 60 stock | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wt % Addit. | Temperature, K | | | | | | |
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 2 | 182.5 | 146.0 | 99.7 | 72.1 | 58.0 | 48.1 | 40.5 |
| 4 | 194.2 | 152.1 | 109.0 | 83.2 | 65.0 | 55.1 | 46.4 |
| 6 | 220.1 | 178.9 | 118.9 | 85.1 | 69.0 | 58.5 | 47.2 |
| 8 | 269.0 | 220.1 | 145.5 | 103.2 | 83.1 | 68.5 | 52.5 |

| Dynamic viscosity(Cp) of 150 stock | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wt % Addit. | Temperature, K | | | | | | |
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 2 | 961.1 | 841.2 | 435.1 | 239.2 | 156.8 | 109.1 | 91.6 |
| 4 | 1145.0 | 864.3 | 449.2 | 247.1 | 166.2 | 114.3 | 96.4 |
| 6 | 1412.5 | 878.4 | 460.0 | 256.0 | 175.8 | 123.1 | 100.2 |
| 8 | 1560.7 | 897.5 | 478.0 | 268.0 | 190.3 | 134.7 | 104.1 |

**Table 4-6: Dynamic viscosity of Oil – stocks mixture with 12 wt % of Paranox 5263**

| Dynamic viscosity(Cp) of mixture | | | | | | | |
|---|---|---|---|---|---|---|---|
| % mixture of Oil stocks | Temperature, K | | | | | | |
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 50% of 40 + 38% of 60 | 92.5 | 80.4 | 63.2 | 53.9 | 43.4 | 35.8 | 30.5 |
| 50% of 40 + 38% of 150 | 144.2 | 125.4 | 80.0 | 70.5 | 59.1 | 47.5 | 39.9 |
| 50% of 60 + 38% of 150 | 426.5 | 368.2 | 183.1 | 115.2 | 90.6 | 74.3 | 61.6 |

**Table 4-7: Dynamic viscosity of Oil – stocks mixture with 12 wt % of Paranox 2281**

| Dynamic viscosity(Cp) of mixture | | | | | | | |
|---|---|---|---|---|---|---|---|
| % mixture of Oil stocks | Temperature, K | | | | | | |
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 |
| 50% of 40 + 38% of 60 | 97.2 | 85.8 | 67.1 | 54.6 | 44.1 | 36.9 | 31.7 |
| 50% of 40 + 38% of 150 | 154.3 | 135.2 | 92.0 | 71.3 | 60.7 | 48.8 | 41.2 |
| 50% of 60 + 38% of 150 | 516.4 | 409.3 | 197.5 | 125.8 | 101.3 | 81.3 | 66.7 |

## *4-3 Apparent Flow Activation Energy (AFAE)*

The activation and free volume theories for liquid transport properties seem to represent the most promising approach for a simple method of predicting transport properties in the normal liquid density region {34}.

Dynamic Viscosity = A EXP (-E/RT)

Ln (Dynamic Viscosity) = Ln (A) + (- E/RT)

Log (Dynamic Viscosity) = Log (A) + (-E/2.303RT)

The apparent flow activation energy is calculated from the slope of straight lines in drawing Log (Dynamic Viscosity) verses 1/Temperature is representing by Figs. 4-27 to 4-40. The slop is equal -Ea/2.303 R where R universal gas constant and equal to 8.314 J / mol. K , and take the absolute value of Ea {45}.

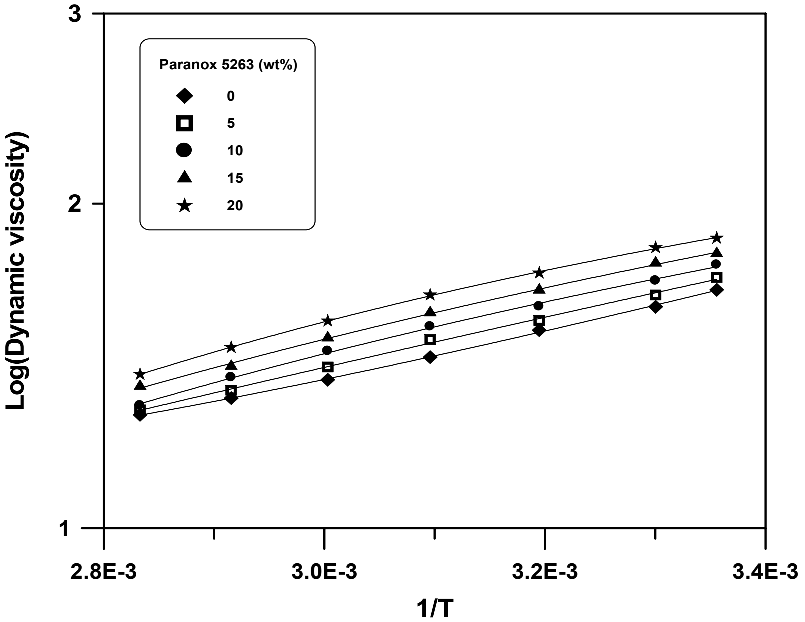

**Fig. 4-27:- Log (dynamic viscosity) of 40 Stock Verses 1/T at Different wt % of Paranox 5263.**

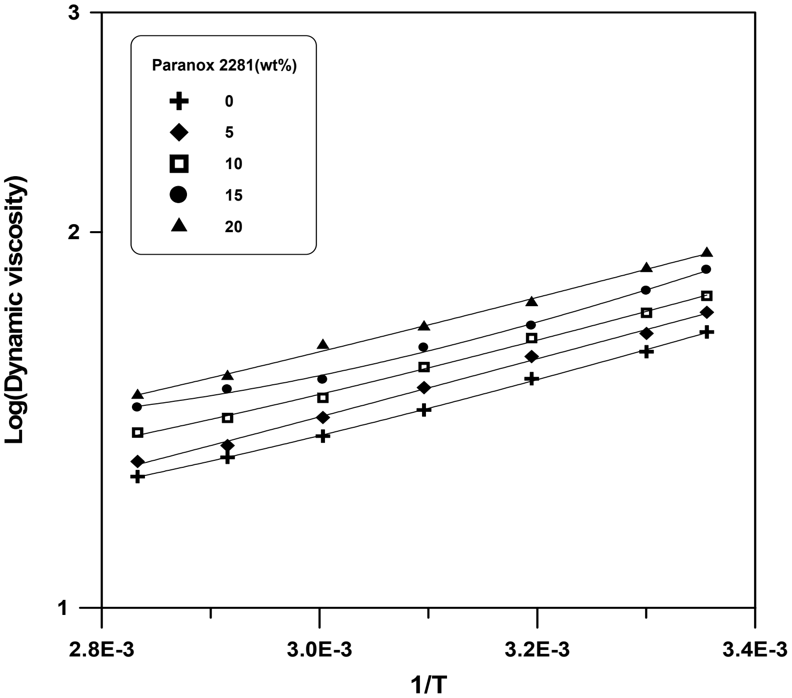

Fig. 4-28:- Log (dynamic viscosity) of 40 stock verses 1/T at different wt % of Paranox 2281.

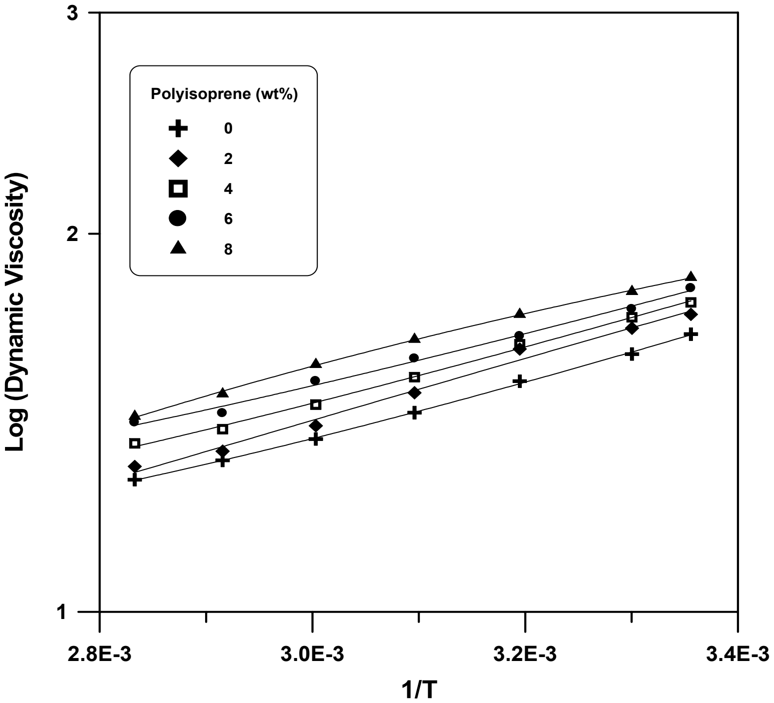

Fig. 4-29:- Log (dynamic viscosity) of 40 stock verses 1/T at different wt % of Polyisoprene 1502.

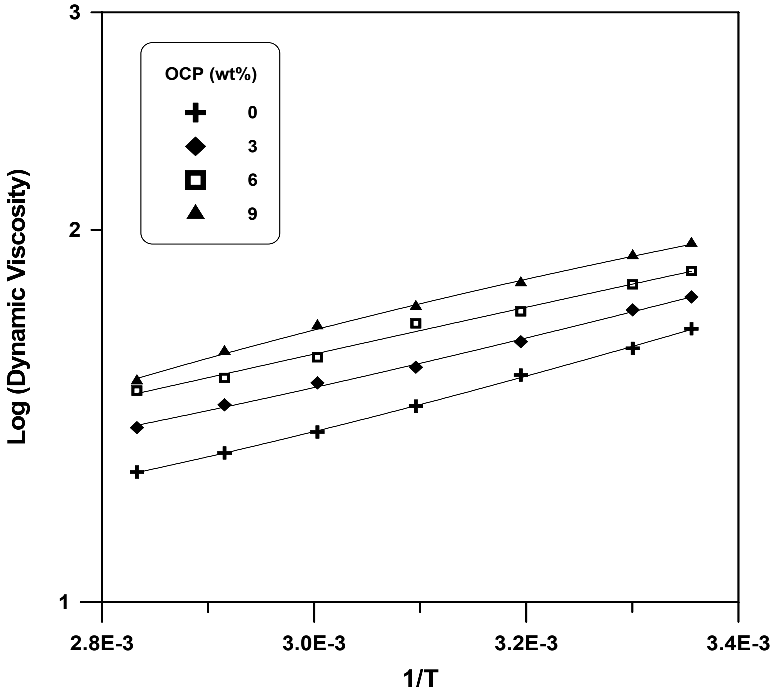

**Fig. 4-30:- Log (dynamic viscosity) of 40 stock verses 1/T at different wt % of OCP.**

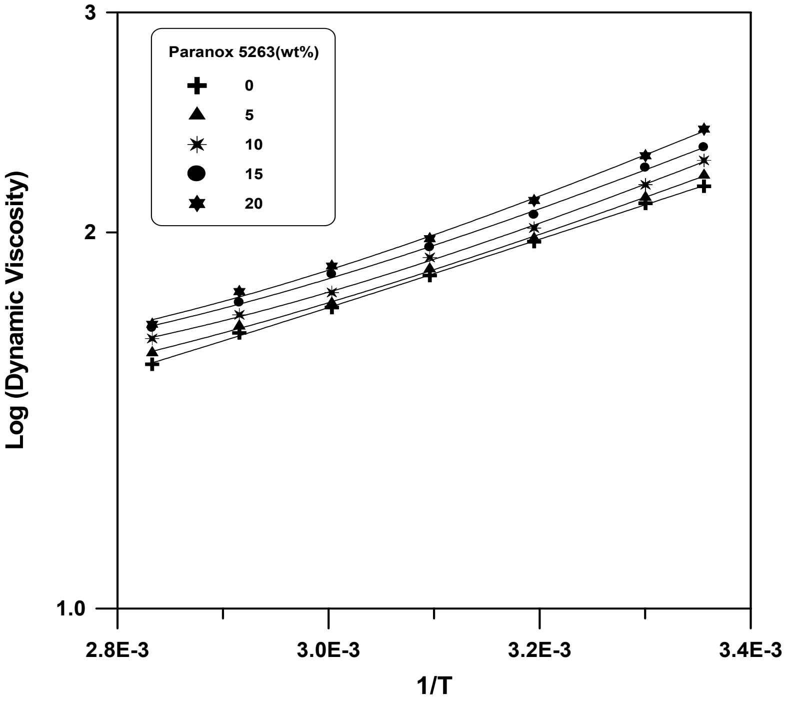

**Fig. 4-31:- Log (dynamic viscosity) of 60 stock verses 1/T at different wt % of Paranox 5263.**

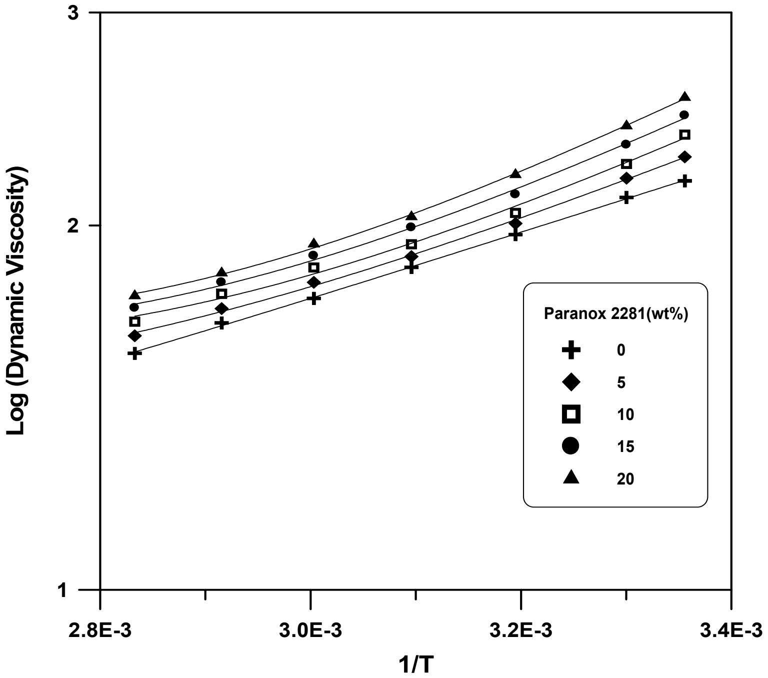

Fig. 4-32:- Log (dynamic viscosity) of 60 stock verses 1/T at different wt % of Paranox 2281.

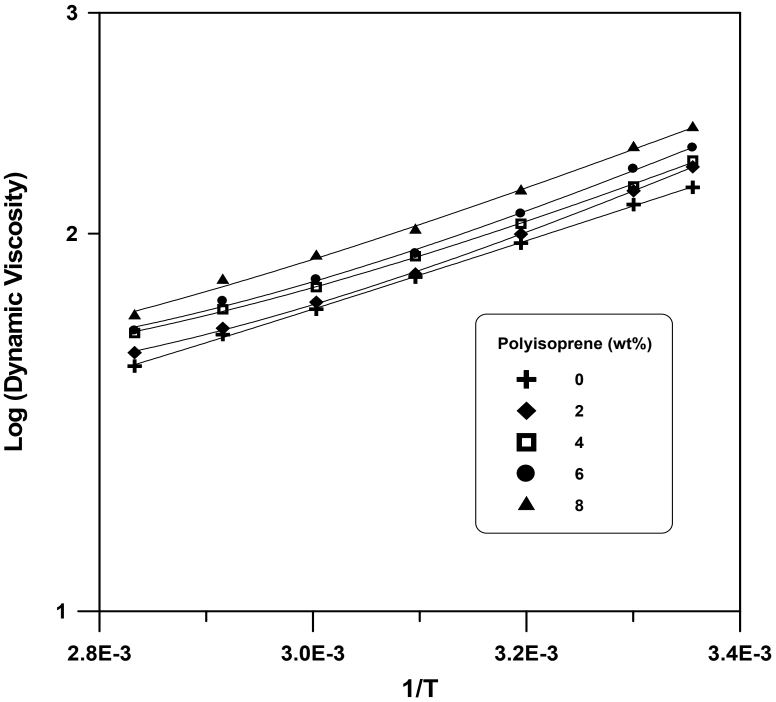

Fig. 4-33:- Log (dynamic viscosity) of 60 stock verses 1/T at different wt % of Polyisoprene 1502.

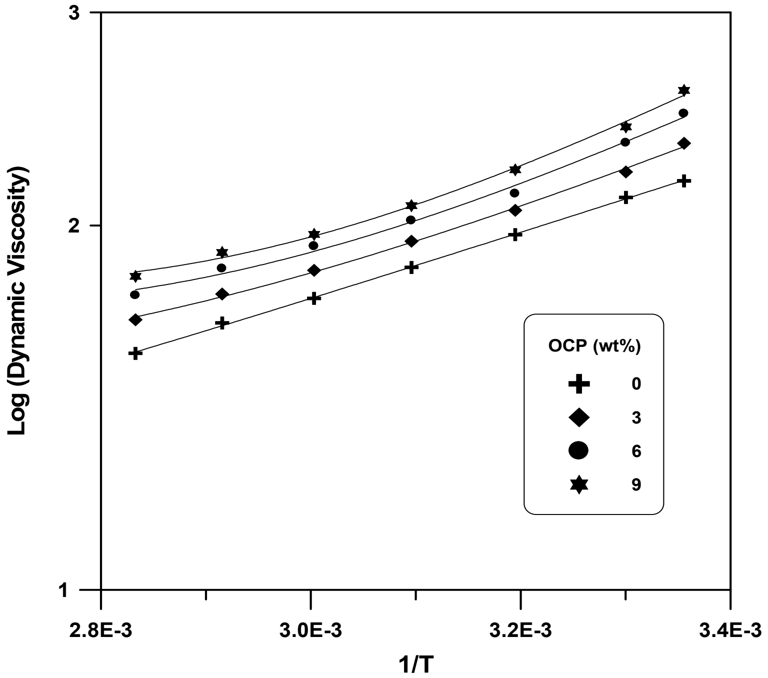

Fig. 4-34:- Log (dynamic viscosity) of 60 stock verses 1/T at different wt % of OCP.

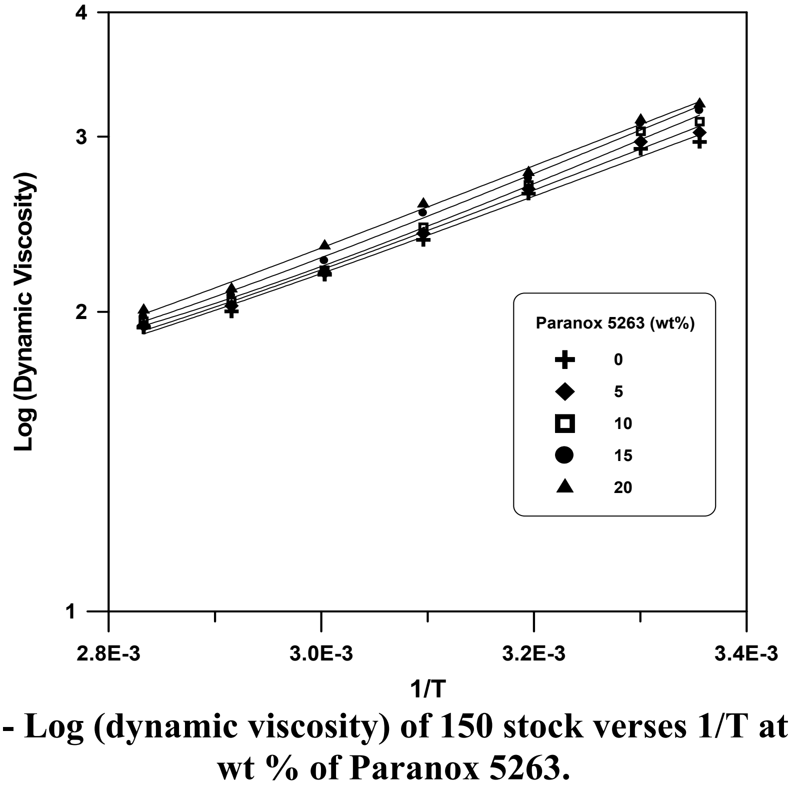

Fig. 4-35:- Log (dynamic viscosity) of 150 stock verses 1/T at different wt % of Paranox 5263.

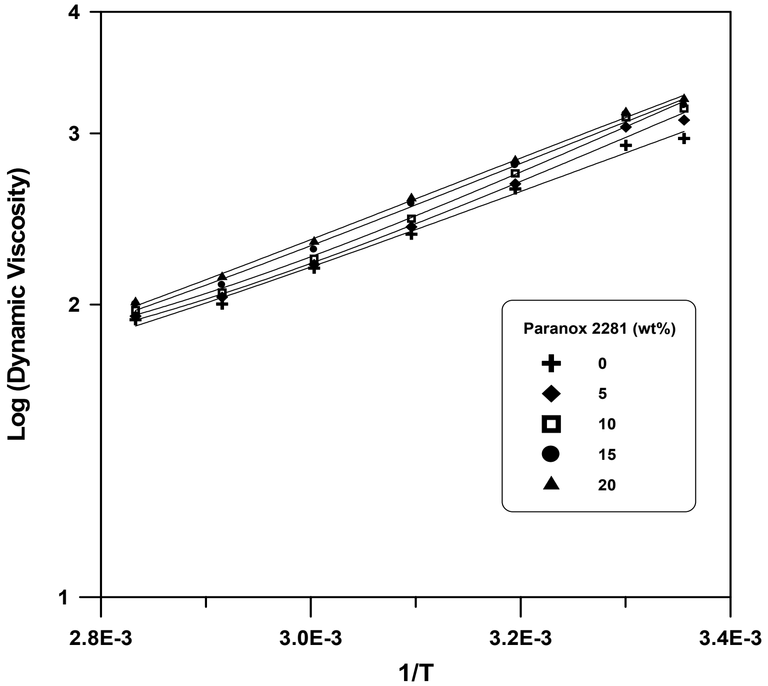

Fig. 4-36:- Log (dynamic viscosity) of 150 stock verses 1/T at different wt % of Paranox 2281.

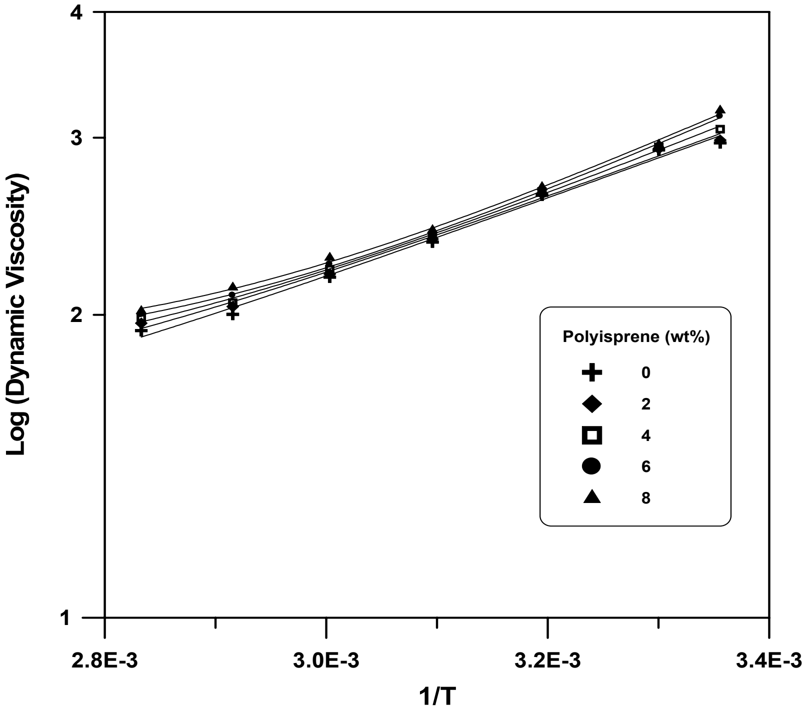

Fig. 4-37:- Log (dynamic viscosity) of 150 stock verses 1/T at different wt % of Polyisoprene 1502.

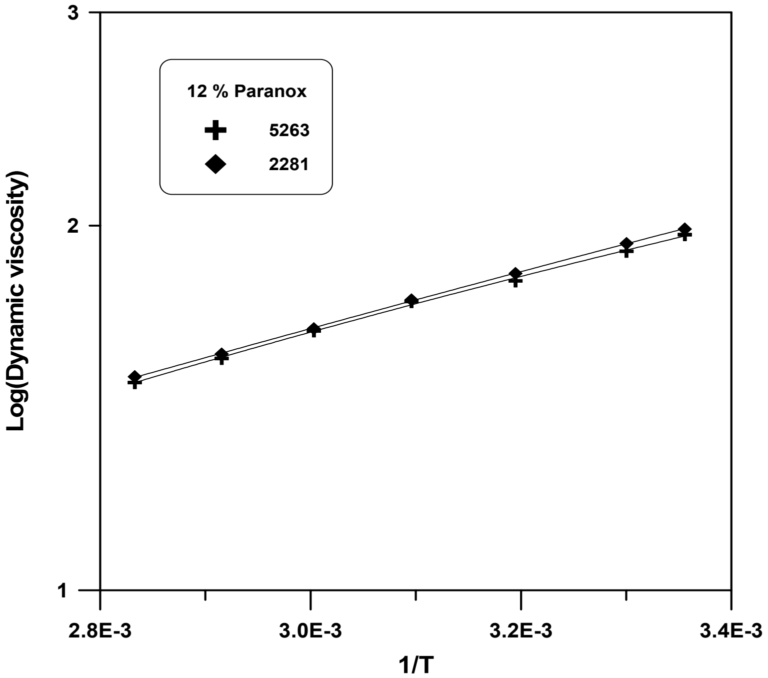

**Fig. 4-38:- Log (dynamic viscosity) of (50% 40 stock + 38% 60 stock) Verses 1/T at 12 wt % of Paranox (5263, 2281)**

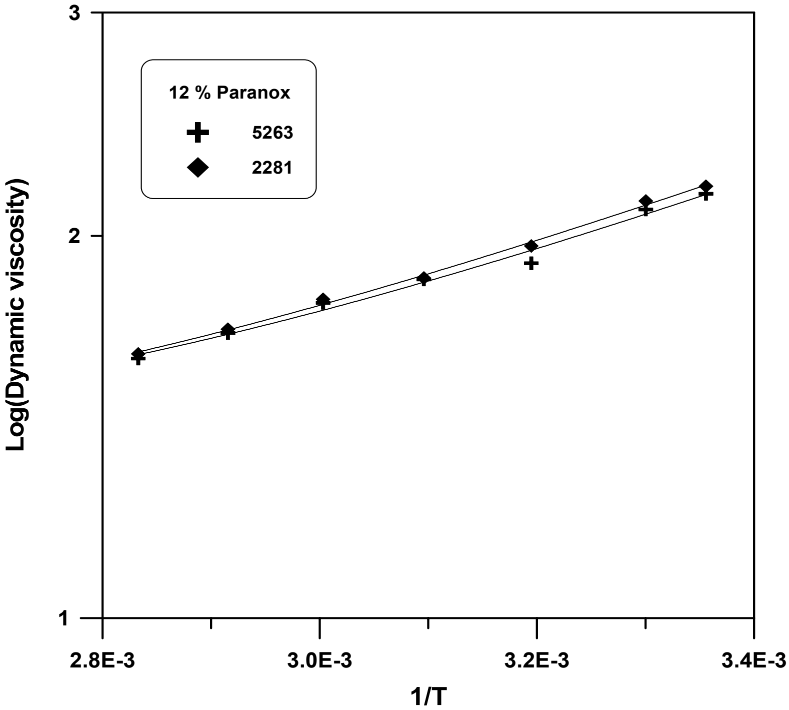

**Fig. 4-39:- Log (dynamic viscosity) of (50% 40 stock + 38% 150 stock) Verses 1/T at 12 wt % of Paranox (5263, 2281)**

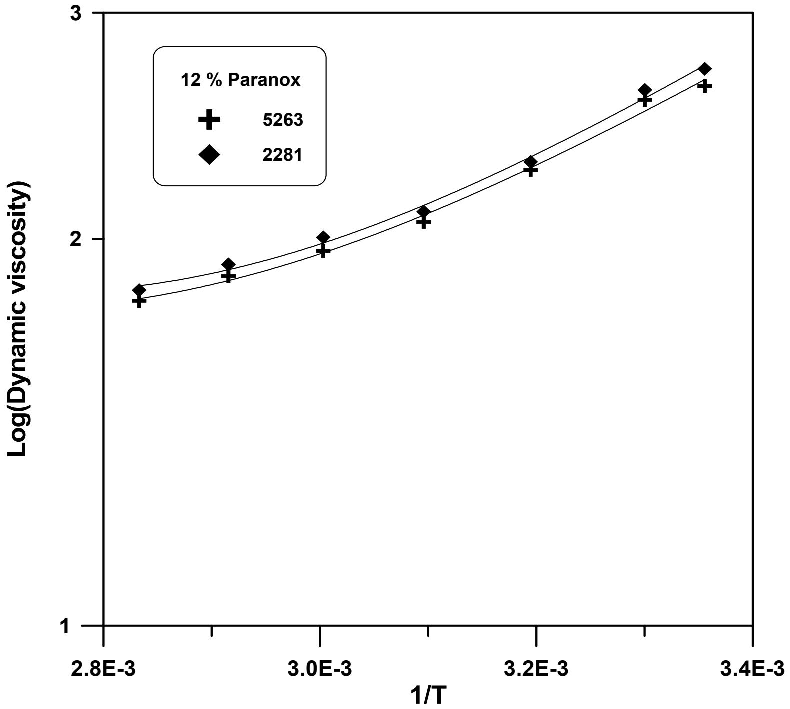

**Fig. 4-40:- Log (dynamic viscosity) of (50% 60 stock + 38% 150 stock) Verses 1/T at 12 wt % of Paranox (5263, 2281)**

In order to determine the influence of Additives concentration on AFAE the results are listed in table 4-8.For the multi- component mixture.

**Table 4-8: summary of calculated activation energy**

| 12 % of Paranox With mixture Oil- Stocks | | |
|---|---|---|
| **% mixture of Oil stocks** | **Ea (KJ/mol) with Paranox 5263** | **Ea (KJ/mol) with Paranox 2281** |
| **50% of 40 + 38% of 60** | **17.6** | **16.1** |
| **50% of 40 + 38% of 150** | **20.6** | **23.9** |
| **50% of 60 + 38% of 150** | **35.0** | **36.4** |

And for binary mixture results are listed in table 4-9.

**Table 4-9: summary of calculated activation energy**

| Paranox 2281 With Oil- Stocks | | | | Paranox 5263 With Oil- Stocks | | | |
|---|---|---|---|---|---|---|---|
| Wt % Addit. | Ea (KJ/mol) 40 stock | Ea (KJ/mol) 60 stock | Ea (KJ/mol) 150 stock | Wt % Addit. | Ea (KJ/mol) 40 stock | Ea (KJ/mol) 60 stock | Ea (KJ/mol) 150 stock |
| 0 | 14.9 | 22.8 | 43.9 | 0 | 14.9 | 22.8 | 43.9 |
| 5 | 16.1 | 24.9 | 48.8 | 5 | 15.5 | 23.6 | 45.7 |
| 10 | 15.8 | 26.4 | 50.6 | 10 | 15.9 | 24.6 | 48.4 |
| 15 | 16.3 | 28.8 | 50.6 | 15 | 16.7 | 25.4 | 48.8 |
| 20 | 16.6 | 31.4 | 50.9 | 20 | 16.9 | 27.2 | 49.1 |

| Polyisoprene With Oil- Stocks | | | | OCP With Oil- Stocks | | | |
|---|---|---|---|---|---|---|---|
| Wt % Addit. | Ea (KJ/mol) 40 stock | Ea (KJ/mol) 60 stock | Ea (KJ/mol) 150 stock | Wt % Addit. | Ea (KJ/mol) 40 stock | Ea (KJ/mol) 60 stock | Ea (KJ/mol) 150 stock |
| 0 | 14.9 | 22.8 | 43.9 | 0 | 14.9 | 22.8 | |
| 2 | 16.2 | 24.4 | 43.2 | 3 | 14.4 | 24.9 | |
| 4 | 16.1 | 25.7 | 44.5 | 6 | 14.6 | 27.0 | |
| 6 | 15.9 | 25.5 | 44.7 | 9 | 15.3 | 29.3 | |
| 8 | 15.7 | 26.3 | 45.3 | | | | |

One of the objectives of the present study was investigate the effect of Additives concentration on AFAE and through the result the value of activation energy ranged from 14.9 for lighter lubricating oil to 43.9 KJ/mole for heavier lubricating oil ,this value is starting value at without additives.

For 40 Stock increasing additives (Paranox 5263, 2281 and OCP) leads to increase value of activation energy, but with additive (Polyisoprene 1502) the value of activation energy is increase at first value and after that small decreased value

For 60 Stock increases the value of all additives the value of activation energy is increasing.

For 150 Stock the value of activation energy is increase at the value of additives (Paranox 5263 and Polyisoprene 1502) are increase, but with Paranox 2281 the value of activation energy is increase between two value of percent additives 0% - 15%, and become approximately constant.

We saw the all values of activation energy in the three types of lubricating oil was increased with the additives because the viscosity of four types of additives is grater than the viscosity of oil – stock and we blending the additives with oil – stock the viscosity of mixture is increased and the value of activation energy is increases because the relation ship between the viscosity and activation energy if the viscosity increased the logarithm of viscosity is increased and the activation energy increased {Log (viscosity) = Log(A) + E/2.303RT}.

This phenomenon is clearly through Fig. 4-41 to 4- 44

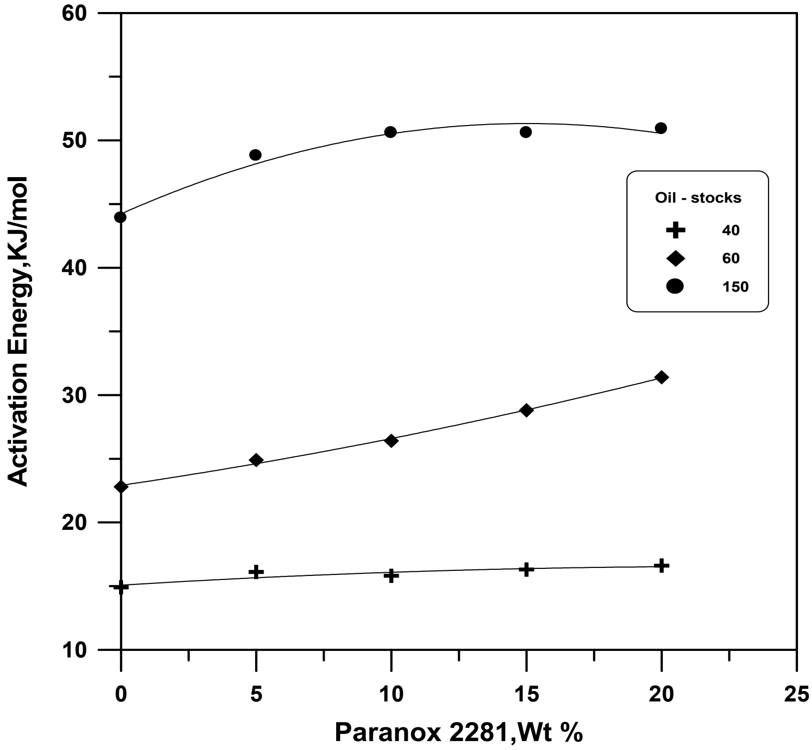

Fig. 4-41:- Activation energy of Oil- stocks verses wt % of Paranox 2281

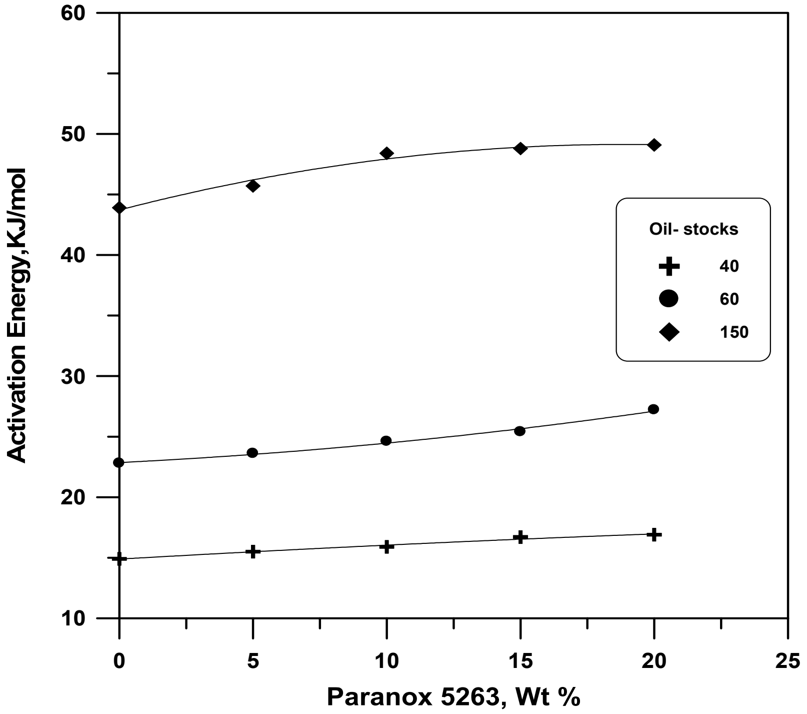

Fig. 4-42:- Activation energy of Oil- stocks verses wt % of Paranox 5263

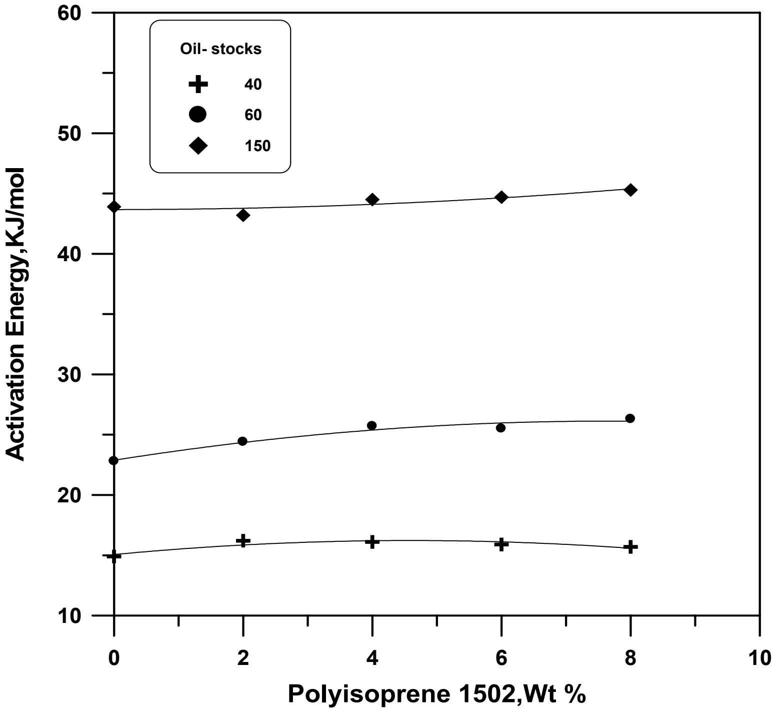

Fig. 4-43:- Activation energy of Oil- stocks verses wt % of Polyisoprene

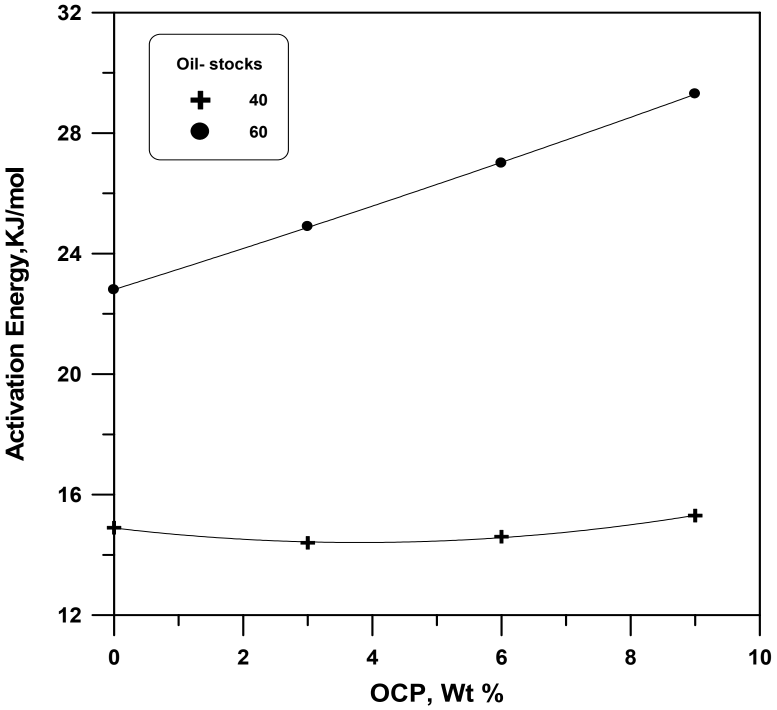

Fig. 4-44:- Activation energy of Oil- stocks verses wt % of OCP

### 4-3-1 Development of a Correlation of AFAE

In order to formulate the values of Ea of Lubricating oil and Lubricating oil mixture with additives were made to relate Ea with typical properties of Lubricating oil like API gravity at 15 C$^{o}$ as well as percent of additives and API gravity of additives.

In order to find a functional relationship between activation energy and various other parameters such as oil API gravity and weight percent of additives.

All statistical concept and multi regression analysis were made using a computer program (statistica). The correlation is

$$\mathbf{Ea = A_1 + A_2 * (WT\ \%) + A_3 * (API_{oil})^{A4}} \qquad .\ 4-1$$

The constants are listed in table 4 – 10.

**Table 4-10: The Constants of Equation 4 – 1**

| $A_1$ | $A_2$ | $A_3$ | $A_4$ |
|---|---|---|---|
| **-159.8196403** | **22.8648424** | **529.4416616** | **-0.313255907** |
| **R<br>Correlation coefficient** | | | |
| **0.993441287** | | | |

Table 4-10 test fit this correlation for lubricating oil and lubricating oil mixtures with additives.

The values of API $_{oil}$ for the three types of oil – stocks are equal 34.97 for 40 stock, 29.29 for 60 stock and 20.65 for 150 stock. And the values of API $_{add}$ for the four types of additives are equal 0.99 for Paranox 5263, 0.97 for Paranox 2281, and for the polymer additives (OCP & Polyisoprene) taken sample value and make this value is references because the properties of OCP & Polyisoprene are depend on the quantity of polymer and the solubility degree of polymer in a base oil – stock; this value is equal 0.789 for Polyisoprene and 0.711 for OCP {42}.

Table 4-11 to 14 listed the predict value of activation energy Ea, the corresponding experimental values and the error involved in the prediction of each data point of these oil and these blends with additives. Table 4-11, 4 -12, 4-13 and 4-14 lists the overall average absolute deviation (OAAD).

**Table 4-11: Activation energy of lubricating oil calculated and experimental values for the oil – stocks with Paranox 2281**

| Paranox 2281 with Oil – Stocks | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 40 stock | | | 60 stock | | | 150 stock | | |
| Wt % Addit. | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error |
| 0 | 14.9 | 14.1 | 5.64 | 22.8 | 23.9 | 5.2 | 43.9 | 45.3 | 3.08 |
| 5 | 16.1 | 15.2 | 5.57 | 24.9 | 25.1 | 0.92 | 48.8 | 46.4 | 4.92 |
| 10 | 15.8 | 16.4 | 3.45 | 26.4 | 26.3 | 0.48 | 50.6 | 47.5 | 6.87 |
| 15 | 16.3 | 17.5 | 7.29 | 28.8 | 27.4 | 4.80 | 50.6 | 48.7 | 3.78 |
| 20 | 16.6 | 18.6 | 12.2 | 31.4 | 28.6 | 9.04 | 50.9 | 49.9 | 1.12 |

**Table 4-12: Activation energy of lubricating oil calculated and experimental values for the oil – stocks with Polyisoprene 1502**

| Polyisoprene 1502 with Oil – Stocks | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 40 stock | | | 60 stock | | | 150 stock | | |
| Wt % Addit. | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error |
| 0 | 14.9 | 13.7 | 7.97 | 22.8 | 23.6 | 3.67 | 43.9 | 44.9 | 2.29 |
| 2 | 16.2 | 14.2 | 15.6 | 24.4 | 24.1 | 2.13 | 43.2 | 45.3 | 5.01 |
| 4 | 16.1 | 14.6 | 9.15 | 25.7 | 24.5 | 1.60 | 44.5 | 45.8 | 2.97 |
| 6 | 15.9 | 15.1 | 2.21 | 25.5 | 25.0 | 1.92 | 44.7 | 46.2 | 2.26 |
| 8 | 15.7 | 15.5 | 1.24 | 26.3 | 25.5 | 3.17 | 45.3 | 46.7 | 3.17 |

**Table 4-13: Activation energy of lubricating oil calculated and experimental values for the oil – stocks with Paranox 5263**

| Paranox 5263 with Oil – Stocks | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 40 stock | | | 60 stock | | | 150 stock | | |
| Wt % Addit. | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error |
| 0 | 14.9 | 14.1 | 5.64 | 22.8 | 23.9 | 5.2 | 43.9 | 45.3 | 3.08 |
| 5 | 15.5 | 15.2 | 1.92 | 23.6 | 25.1 | 6.48 | 45.7 | 46.4 | 1.52 |
| 10 | 15.9 | 16.3 | 2.80 | 24.6 | 26.3 | 6.8 | 48.4 | 47.5 | 1.77 |
| 15 | 16.7 | 17.5 | 4.72 | 25.4 | 27.4 | 7.93 | 48.8 | 48.7 | 0.14 |
| 20 | 16.9 | 18.6 | 10.3 | 27.2 | 28.6 | 4.99 | 49.1 | 49.9 | 1.48 |

**Table 4-14: Activation energy of lubricating oil calculated and experimental values for the oil – stocks with OCP**

| OCP with Oil – Stocks | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 40 stock | | | 60 stock | | | | | |
| Wt % Addit. | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error | Ea,exp KJ/mol | Ea,cal KJ/mol | % Error | | | |
| 0 | 14.9 | 14.1 | 5.64 | 22.8 | 23.9 | 5.2 | | | |
| 3 | 14.4 | 14.7 | 3.32 | 24.9 | 24.7 | 0.92 | | | |
| 6 | 14.6 | 15.4 | 6.16 | 27.0 | 25.4 | 6.08 | | | |
| 9 | 15.3 | 16.1 | 5.34 | 29.3 | 26.1 | 11.11 | | | |

The overall average absolute deviation (OAAD) for tables 4-11, 4-12, 4-13 and 4-14 is equal 5.92 %.

# *CHAPTER FIVE*

# *CONCLUSIONS AND RECOMMENDATIONS*

## *5-1 Conclusions*

From the results of the present work, the following conclusions are obtained:

1. The rate of viscosity change with temperature depends largely on the type of base oil,
2. Blending the three types of oil-stocks with additives (Paranox 5263, Paranox 2281, OCP and Polyisoprene 1502) result a noticeable increase in the viscosity of the mixture.
3. The rate of viscosity change of the heavy oil is greater than the rate of the medium and light oil.
4. The effect of additives on AFAE of lubricating oils was studied. Actual value for the flow activation energy was measured and varied from 14.9KJ/mole for the lighter lubricating oils to 43.9KJ/mole for heavier lubricating oils.
5. Empirical method was developed to predict the AFAE of lubricating oils in the range of API 20.65 to 34.97, weight percent of additives and API gravity of additives with base oil. The correlation gives an overall absolute error of 5.92 % for the three lubricating oils.

$$Ea = A_1 + A_2\,(WT\,\%) + A_3\,(API_{\,oil})^{A4}$$

## *5-2 Recommendations for Future Work*

1. The use of other types of additives (in addition to additive already used) with different concentrations to get new correlations for concentration dependence of the dynamic viscosity and on the AFAE of the oil – stock mixtures.
2. More work to be done on the rheological property of Lubricating oils specially for high shear rate, we believe important rheological property aspects of Lubricating Oils has been reflected to give an explanation of additives effect on AFAE.
3. Studying the effect of the high temperature and concentration on the viscosity change and on the AFAE for types of multi – component mixtures of oil – stock containing various concentrations of the oil - stocks.
4. An attempt can be made to formulate a correlation to predict the AFAE, as a function of Sp.gr and pour point of the mixtures.

# REFERENCE

1. *Hobsen G. D., "***Modern Petroleum Technology***", 5th ed., the Institute of Petroleum, London, Ch. 20 (1984)*
2. *Aries R. S. et al.," ***Petroleum Refiner***", 35, No. 5, P. 235 (1956)*
3. *Brouwer, L. E. J.," ***The Petroleum Handbook***", 5th Ed., P. [116-234] (1966).*
4. *Eyring, H., Hirschfelder, J. "***The theory of the liquid state***" .J.Phys. Chem.41, 249, 1937.*
5. *Ewell, R.H.; Eyring, H."***Theory of Viscosity of liquids as a function of temperature and pressure***". J. Chem. Phys. 5. 726,1937.*
6. *Heric, E. L.; Brewer, J.G. "***Viscosity of some Binary Liquid non electrolyte mixtures***". J. Chem. Eng. Data 12(4), 574, 1967.*
7. *AL- Besharah, J. M.; Akashah, S. A.; Mumford, C. J., Ind. Eng. Chem. res. 28, 213, 1989.*
8. *Evans G. G. and Galyin V. M, "***Lubrication in Practice*** ", Macmillan-Esso Publication, London, P. 7, P. 30 (1972).*
9. *Kirk- Othmer, "***Encyclopedia of Chemical Technology*** ", 1st ed., John Wiley & Sons, Inc., New York, Vol. 8, P. 509 (1952).*
10. *Kirk- Othrner, "***Encyclopedia of Chemical Technology*** ", 2nd ed., John Wiley & Sons, Inc., New York, Vol. 12, P. 564 (1967).*
11. *Kirk- Othrner, "***Encyclopedia of Chemical Technology*** ", 3rd ed., John Wiley & Sons, Inc., New York, Vol. 14, P. 484, P.486 (1967).*
12. *Allinson J. P., "***Criteria for Quality of Petroleum Products*** ", Applied Science Publishers Ltd., London, Ch. 10 (1973).*

13. *Kioupis L. I., "***Molecular Simulations of Hydrocarbon Lubricants, Impact of Molecular Architecture on Performance Properties***", Notre Dame, Indiana, February, P. 4-5 (2000).*

*By Internet:* **http.//www. Nd.. edu/ lkioupis/thesis. Pdf**

14. *Lansdown A. R., "***Lubrication, A Practical Guide to Lubricant Selection***", 1st ed., Pergamon Press Ltd., Ch. 3, Ch. 4 & Ch. 5 (1982).*
15. *Douglas M C., "***Chemical and Process Technology Encyclopedia***", McGraw-Hill Company, New York, P. 701- 705 (1974).*
16. *Marketing Specifications of Iraq Oil Products, "***Gasoline Engines Lubricating Oils***", Ministry of Oil, Iraq, P. 2 7-31 (1995).*
17. *Personal Contact with* ***Laboratories of Lubricating Oils Department,*** *AL-Durra Refinery.*
18. *0'connor J.J., Boyd J. and Avallone E. A., "***Standard Handbook of Lubrication Engineering***", McGraw-Hill, Inc., New York, Ch. 11, Ch 14,Ch. 17, Ch. 26 & Ch. 32(1968).*
19. *Georgi, C.W.,"***Motor Oils and Engine Lubrication***", Reinhold, New York, 1950.*
20. *Gruse, W.A.,"***Motor Oils Performance and Evaluation***", 1967.*
21. *Judge A. W., "***Modern Petrol Engines***", 3rd ed., Chapman & Hall Ltd., London, Ch. 1, Ch. 11 & Ch. 15 (1965).*
22. *Kirk-Othmer, "***Encyclopedia of Chemical Technology***", 4th ed., Technical Information on Viscosity (Lubricating Oil), and Pour-Point Depressants, Vol. 15, April, P. 477, P. 482-483 (2002).*

*Personal Contact with* ***Gulf Organization for Industrial Consulting****.*

23. *Denis J., Briant J. and Hipeaux J. C., "**Lubricant Properties Analysis & Testing** ", Editions Technip, Institut Français Du Pétrole Publications, Paris, France, Ch. 1, Ch. 2 & Ch. 5 (2000).*
24. *Hobson, G.D., "**Modern Petroleum Technology**", Fifth Edition, Applied Science Publishers Ltd., London, 1984.*
25. *Crouse W. H. and Anglin D. L., "**Automotive Engines**", 8th ed., Glencoe Division of Macmillan/McGraw-Hill School Publishing Company, New York, Ch. 7 & Ch. 19 (1995)*
26. *Glasstone, S.; Laidler, K.J.; Eyring, H., **Theory of rate processes**, McGrow Hill, New York, Chapter 9, (1941).*
27. *Bird, R., "**transport phenomena**", 26-28, June (1960).*
28. *Spencer, R.S.; Dillon, R.E.; Colloid Sci... J., Vol. 4, 241, (1949).*
29. *Fox, T.G; P.J. Floory, J. Appl. Phys.21, 581 (1950).*
30. ***Encyclopedia of Polymer Science and Technology** (vol.13), 1970.*
31. *Weymann, H., Kolloide Zeit. , 138, 41(1954).*
32. *Ibid, Vol. 181, 131 (1962).*
33. *Cohen, M.H.; D. Turnbull, J. Chem. Phys., 31, 1164 (1959).*
34. *Keith E. Gubbins; M. J. Tham, "**Free Volume theory for viscosity of simple non polar liquids**", AICHE Journal, page 264, March, 1969.*
35. *Glasstone; Laidler; Eyring; "**theory of rate processes**", (McGraw-Hill Book Company, Inc., New York, 477-580 (1941); Ewell, R.H. and H. Eyring; J. Chem. Phys. 5, 726 (1937).*
36. *Eyring, H.; J.O. Hirschfelder, J. Phys. Chem. 41, 249, (1937). Glasstone, S.; K. J. Laidler; H. Eyring, "**The theory of rate processes** ", Chapt. McGraw-Hill, New York (1941).*

37. *Collins, F.C.; M. H. Navidi, J. Chem. Phys. 22, 1254 (1954); 25,581 (1956).*

38. *Collins, F.C., "**Activation Energy of the Eyring Theory of Liquid Viscosity and Diffusion**", The Journal of Chemical physics vol. 26, no.2, Feb., 398 (1956).*

39. *Raw, C.J.G., "**The Activation Energy for Viscous Flow and Sutherland's Constant** ", J. of Chem. Phys. Vol 22, No.1 P.1946 -1947, 1954.*

40. *Raw, C.J.G., J. S. African Chem. Inst J. of Chem. Phys. Vol 22, No.1 P.1946 -1947, 1954.*

41. *Raw, C.J.G., J. S. Chem. Phys. J. of Chem. Phys. Vol 22, No.1 P.1946 -1947, 1954.*

42. *Al – Taa'ay A.H., M.Sc., Thesis, "**Influence of Polyisoprene additives on the viscosity of base lubricating oils**", Al – Nahrain University, November 2004*

43. *BEG, S.A.; M. B. Amin; I. Hussain, "**Generalized Kinematic Viscosity-Temperature Correlation for undefined petroleum fractions**", the chem. Eng. J. 123-136, 38 (1988).*

44. *Edward Goletz; Dimitrios Tassios, "**An Antoine type equation for liquid viscosity dependency to temperature**", Ind. Eng. Chem. Process Des. Dev., Vol.16, no. 1, 1977.*

45. *Mahmood A.A., M.Sc., Thesis, "**Flow Activation Energy of Iraqi Crude Oils**", Al – Nahrain University, August 2000.*

# *APPENDIX*

## Sample of calculation:

**Example:** Estimate the flow activation energy of a binary mixture which contains (10% of paranox 2281 and 90% of 60 stock) at 1.01325 bar and range of temperature 298 – 353,

Solution:

$$Ea = A_1 + A_2 * (WT\ \%) + A_3 * (API_{\ add})^{A4} + A_5 * (API_{\ oil})^{A6} \qquad \ldots(4-1)$$

The value of the constant:

$A_1 = -159.8196403$

$A_2 = \ \ 22.864842$

$A_3 = \ -1.0037*10^{-7}$

$A_4 = \ -63.535584$

$A_5 = 529.4416616$

$A_6 = -0.31325590$

$API_{\ add} = 0.97$

$API_{\ oil} = 29.29$

$WT\ \% = 10/100$

$$Ea = (-159.81964) + 22.864842 * (10/100) + (-1.0037*10^{-7}) * (0.97)^{-63.535584} + 529.44166 * (29.29)^{-0.3132559}$$

Ea = 26.37851 KJ/mole

# الخـلاصــة

علماً انة تم حساب اللزوجة الديناميكية لزيوت التزييت تحت درجة حرارة تتراوح بين ٢٩٨ ـ ٣٥٣ كلفنْ ، بوجود وعدم وجود الاضافات. والتي هي اربعة انواع من الاضافات وهي:

**(Paranox 5263, Paranox 2281, Olefin copolymer(OCP) & Polyisoprene 1502)**

تم حساب طاقة تنشيط الجريان لزيوت التزييت باستخدام قياسات اللزوجة.

لقد تمت دراسة تأثيرتغيرات درجةالحرارة و التركيز(النسبة الوزنية للمضافات) في طاقة تنشيط الجريان للخلائط المختلفة وهي الخلائط الثنائية و الثلاثية .

وتم التوصل الى طريقةجديده لقياس طاقة تنشيط الجريان لزيوت التزييت تعتمد على (API) لزيت التزييت وعلى النسبة الوزنية للمضافات وعلى (API) في درجة حرارة ١٥,٦ م° للمضافات . وفيما يلي العلاقة التي تم التوصل اليها :

$$\mathbf{Ea = A_1 + A_2\ (WT\ \%) + A_3\ (API_{\ oil})^{A4}}$$

علماً ان:

$A_1,A_2,A_3$ & $A_4$ ثوابت للمعادلة

و Ea = طاقة التنشيط

وخلال المقارنة بين الحسابات الجارية في المختبر والتي اخذت من المعادلة اظهرت ان نسبة الخطأ الكلية للمعادلة ٥,٩٢ % ، تم التوصل الى تلك العلاقة من خلال ٢٩٤ تجربة مختبرية.

# شكر و تقدير

اودُ أن أعبر عن خالص شكري وتقديري وَ امتناني العميق للمشرف الدكتور طالب بهجت كشموله لما بذله من جهد كبير و ارشادات سديدة و قيمة طوال فترة اعداد الرسالة.

أودُ أيضاً أن أشكر موظفي قسم الهندسة الكيماوية لإبدائهم المساعدة اللازمة أثناء فترة البحث.

ولا أنسى أن أتقدم بالشكر و الامتنان إلى من لازمني طوال فترة البحث وخلال أصعب الظروف إلى أعز من في الوجود إلى أبي و أمي و جميع أفراد عائلتي فلهم جزيل الشكر و التقدير.

# تأثير اضافات زيوت التزييت على فعاليت طاقة الجريان

رسالة

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

من قبل

رامي محمد جبر العلوي

بكالوريوس في الهندسة الكيمياوية ٢٠٠٢

ربيع الاول ١٤٢٦

نيسان ٢٠٠٥